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Optical and Magneto-Optical Properties of Ferromagnetic InMnAs Thin Films and its Alloys

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Abstract

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The optical and magneto-optical properties of the ferromagnetic semiconductors, InMnAs and its alloy InMnAsP were investigated to determine the band structure and nature of the ferromagnetism in these materials. Alloys were grown by metal-organic vapor phase epitaxy. Infrared absorption of InMnAs was investigated to determine the presence and properties of the Mn related impurity bands. Infrared absorption indicates the formation of shallow and deep impurity bands that result from substitutional Mn and atomic scale cubic MnAs clusters respectively. At room temperature, the shallow Mn acceptors contribute free holes to the valence band while the deep band binds the majority of holes within the clusters. X-ray absorption spectroscopy and magnetic circular dichroism spectra were measured to determine the local environment and electronic state of Mn. By fitting the experimental spectra with calculated atomic spectra, we determined that Mn atoms are substitutional with a d^5 ground state configuration.

An inter-cluster exchange mechanism responsible for global ferromagnetism was proposed and investigated using reflection magnetic circular dichroism over the visible spectral range. A broad featureless transition observed in all samples was tentatively attributed to transitions between an exchange split deep Mn impurity band and conduction band. A fraction of the InMnAs films also exhibit a negative dichroism peak that was ascribed to transitions between spin split valence and conduction bands. Exchange splitting of the deep impurity band and valence band was measured that results in spin polarized bound holes and itinerant holes respectively. Since only the deep impurity band was spin-split in all films, we propose that only bound holes stabilize the global ferromagnetism.

To determine matrix effects on exchange in disordered materials, $In_{1-x}Mn_xAs_{1-y}P_y$ alloys with *x* ranging from 0.01 to 0.04 and *y* ranging from 0.11 to 0.21 were grown. X-ray diffraction established the presence of second phase, hexagonal MnAs clusters, with the fraction of Mn incorporated into MnAs clusters varying between 33-98%. Magnetic properties were measured over the temperature range of 5-350 K. A Curie temperature of 325 K was observed. The Neel model was used to explain the observed irreversibility in the magnetization versus temperature dependence. The room temperature ferromagnetism was attributed to the presence of large clusters with radii greater than 5.5 nm.

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1. Introduction

A new paradigm for electronics has emerged that utilizes not only the electron charge but also its intrinsic spin to transmit information. The use of the spin degree of freedom in spin transport electronics, or spintronics, opens the door for a new generation of devices that integrate standard microelectronics with spin dependent effects.^{1, 2} Two spintronic devices already in use include the spin read head in computer hard drives³ and magnetic random access memory (MRAM).^{4, 5} Both devices consist of metallic ferromagnetic multilayers that operate utilizing giant magneto-resistive (GMR) and tunneling magneto-resistive (TMR) effects.^{6, 7}

Although metal-based spintronic devices are widely used, spintronic devices based upon semiconductors can be easily integrated with existing microelectronic technologies. This may lead to a new class of hybrid devices that combine photonics, electronics, and magnetics including the spin field effect transistor (FET),⁸ spin light emitting diode,⁹ and the spin bipolar junction transistor.¹⁰ The spin-FET in particular, has several advantages over its electronics counterpart: the metal oxide semiconductor field effect transistor (MOSFET). Spin-FETs can change their functionality under software control. As a result of the re-programmable nature of spin-logic devices, full adders can be designed using only 4 spin-logic elements as opposed to 16

MOSFETS. The spintronic version of the full adder would use 85% less power and 75% less space than the current silicon based designs.¹¹

A promising class of materials for semiconductor spintronic applications are the (III,Mn)V ferromagnetic semiconductors, where Mn impurities substitute for a small fraction of group III atoms. (III,Mn)V ferromagnetic semiconductors retain their zinc blende crystal structure upon alloying with Mn and therefore can form high quality interfaces with conventional III-V semiconductors. This allows for easy integration with existing III-V technology.

Two particular (III,Mn)V ferromagnetic semiconductors that have generated a great deal of interest in the scientific community are InMnAs^{12, 13} and GaMnAs.^{14, 15} In molecular beam epitaxy (MBE) grown InMnAs and GaMnAs, extended x-ray absorption fine structure (EXAFS) measurements have demonstrated the majority of Mn are singly substituted.^{16, 17} Moreover, both MBE InMnAs and GaMnAs are ferromagnetic with Curie temperatures (T_c 's) of 90¹³ and 170 K¹⁸ respectively. The nature of the exchange coupling between singly substituted Mn in these two materials remains controversial. In MBE InMnAs, Mn ions form a degenerate impurity band that contributes free holes to the valence band.¹⁹ Munekata *et al.* have proposed that exchange between singly substituted Mn is mediated by itinerant holes in the valence band.^{20, 21} The exchange interaction which couples Mn 3*d* impurity states to the free holes in semiconductor *s*,*p* states is termed *sp-d* exchange. *Sp-d* exchange results in a spin splitting of the valence and conduction bands, resulting in an imbalance of spin carrier populations or spin polarization.²² Therefore, *sp-d* exchange is presumably responsible for both long-range ferromagnetic ordering and a net spin polarization in MBE grown InMnAs.

In MBE GaMnAs, Mn ions form a detached impurity band 110 meV above the valence band maximum.²³⁻²⁵ At cryogenic temperatures where the films are ferromagnetic, the holes freeze out and reside in the impurity band. Consequently, Burch *et al.* proposed that the ferromagnetism in MBE grown GaMnAs must be mediated by delocalized holes in the Mn impurity band.^{26, 27} This mechanism is a variation of Zener double exchange utilized to account for ferromagnetism in manganites.²⁸ In double exchange, the holes in the impurity band hop from one Mn ion to the next, creating a mixture of Mn²⁺ and Mn²⁺ + *h* valence states.²⁹ It is the hopping of holes between neighboring Mn ions that is the origin of the electrical conductivity in this material. Moreover, Zener proposed that these holes will align the local moments of adjacent Mn ions to increase the hopping probability, resulting in ferromagnetic ordering.³⁰

While the strong exchange coupling between Mn ions and conduction holes in MBE InMnAs and GaMnAs results in global ferromagnetism, the T_c of both materials are well below room temperature. Consequently MBE grown InMnAs and GaMnAs are impractical for semiconductor spintronic applications. In contrast, Blattner and coauthors have demonstrated that InMnAs thin films grown by metal organic vapor phase epitaxy (MOVPE) exhibit a T_c of 330 K.³¹⁻³⁴ The room temperature ferromagnetism has been verified by both superconducting quantum interference device (SQUID) and magneto-optic Kerr effect magnetometry methods.^{33, 35} The large disparity in the T_c of MBE grown InMnAs and that grown by MOVPE were previously attributed to the presence of atomic scale Mn clusters observed by extended x-ray absorption fine structure (EXAFS).³⁶ While the Mn in MBE grown InMnAs and GaMnAs are substitutes randomly at In sites, the EXAFS suggests that Mn in MOVPE grown InMnAs preferentially substitutes on nearest neighbor In sites.³⁶ Multiple first principles calculations

demonstrate large intra-cluster exchange energies on the order of 100 meV.^{37, 38} Consequently, the spins within cubic Mn clusters are ferromagnetically aligned at temperatures well above room temperature.³⁷

However, there are several unresolved issues regarding the magnetism in disorderd ferromagnetic semiconductors. First, the inter-cluster exchange mechanism that results in global ferromagnetism is not known. Density functional theory calculations demonstrate that in clustered materials, Mn ions form both shallow and deep Mn impurity bands.³⁹ The shallow band contributes free holes to the valence band while the deep impurity band binds holes within clusters. The presence of multiple impurity bands in disordered ferromagnetic semiconductors results in several potential inter-cluster exchange mechanisms. One mechanism has spin polarized free holes in the valence band mediating the alignment of spins of adjacent clusters via *sp-d* exchange.³⁹ Alternatively, Kaminski and coauthors have proposed that bound holes within the deep impurity band may also mediate magnetism between clusters.^{40, 41} The effect of the alloy host environment on the magnetic properties in clustered ferromagnetic semiconductors is also not well understood. A study of the alloy host environment is significant because varying parameters such as the lattice constant and chemical composition could afford a method of modulating the T_c in clustered materials. For example, the addition of P or Sb into InMnAs alloys could decrease or enhance intra-cluster exchange respectively.⁴²

In the this work we address the nature of inter-cluster exchange in MOVPE InMnAs. To identify the potential inter-cluster exchange mechanisms, we utilized infrared absorption spectroscopy, x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) to determine the presence and properties of Mn impurity bands. Characteristic absorption features due to impurity band to conduction band transitions and valence band to impurity band transitions were measured at energies less than the band gap. The electronic state and local environment of Mn ions in the impurity band(s) were investigated by XAS and XMCD. The ground state configuration, degree of localization of Mn 3d electrons, and the crystal field symmetry of Mn ions in the impurity band(s) were determined from atomic multiplet model fits of the XAS and XMCD spectra. Finally, we examined the spectral dependence of the reflection magnetic circular dichroism (RMCD) to determine whether free holes mediate the ferromagnetic exchange between clusters by *sp-d* exchange. The RMCD spectrum of InMnAs was fit with respect to the dichroism spectrum predicted for transitions between *sp-d* exchange split valence band and conduction bands.

Finally this work focuses on chemical effects in clustered magnetic materials. Specifically, the InMnAs thin films were alloyed with varying concentrations of P. Due to the potential presence of both hexagonal MnAs and MnP clusters, the phase purity of these materials was studied by XRD. The magnetic properties of InMnAsP alloys were measured to determine whether the T_c could be controlled with P concentration.

2. Background and Literature Review

2.1 **Properties of InMnAs grown by MBE and MOVPE**

2.1.1 MBE InMnAs

In the late 1980's Ohno *et al.* utilized a non-equilibrium MBE technique (T_s =250°C) to grow *random substitutional* alloys of In_{1-x}Mn_xAs with 0.01<*x*<0.10.^{12, 43, 44} The non-equilibrium growth technique was required to exceed the equilibrium solubility limit of transition metal ions in a III-V semiconductor (~10¹⁸-10¹⁹ cm⁻³). The substitution of Mn on the cation sites was demonstrated by extended x-ray absorption fine structure (EXAFS) measurements around the Mn *K*-edge.¹⁶ EXAFS measurements indicate that Mn is surrounded by 4 nearest neighbor As, which demonstrates that Mn substitutes for In on a cation site in a zinc-blende lattice. Furthermore, the EXAFS data is best described by a model whereby the Mn is surrounded by 12 second nearest neighbor In atoms. This is consistent with a Mn substituting randomly at cation sites, whereby the majority of Mn are singly substituted at low Mn concentrations (*x*<0.10).⁴⁵

There are three potential electronic states for a substitutional Mn in InMnAs. First, the Mn $(3d^5 4s^2)$ contributes 2 of its $4s^2$ electrons and 1 *d*-electron to covalent bonding. In this case the impurity has a Mn³⁺ valence state and is termed a neutral acceptor (A^0) . In a Mn³⁺ state, each Mn ion has a $3d^4$ electronic configuration and a spin of *S*=2. Second, the Mn provides only 2 of

its $4s^2$ electrons for bonding, to form a Mn²⁺ ion with a $3d^5$ configuration and a localized spin of *S*=2.5. Moreover, due to the missing valence electron, the Mn²⁺ ion acts as an acceptor (*A*⁻), providing itinerant holes in the valence band. Third, a Mn²⁺ ionized acceptor can weakly bind a hole to form a Mn²⁺+*h* ($3d^5+h$) complex. The Mn²⁺+*h* does not provide an itinerant hole in the valence band for conduction. EPR measurements of In_{0.99}Mn_{0.01}As grown by MBE indicate that the dominant Mn impurity is a Mn²⁺ ionized acceptor for *T*>6K.⁴⁶⁻⁴⁸ Since each Mn²⁺ ion will contribute a hole to the valence band, the hole concentration (*p*) should be equal to the concentration of Mn ions (*N*_{Mn}), provided there are not compensating donors.

Hall effect measurements have shown while MBE grown InMnAs is p-type, the hole concentrations range is $1-3x10^{19}$ cm⁻³ for as grown In_{1-x}Mn_xAs with 0.01 < x < 0.16.⁴⁹ The hole concentration is at least an order of magnitude less than the N_{Mn} . The low carrier concentration in MBE InMnAs is attributed to the presence of Mn interstitial double donors, which are compensating defects.¹³ In the case of MBE grown GaMnAs, Mn interstitials have been directly observed by Rutherford backscattering.⁵⁰ The interstitials in GaMnAs are metastable and can be removed by post-growth annealing at 175°C, resulting in an increase in *p* by a factor of 2-3.⁵¹ While the presence of Mn interstitials have not been confirmed for MBE grown InMnAs, annealing at similar temperatures to that of used for MBE GaMnAs (190°C) also resulted in a significant increase in the hole concentration from $1.6x10^{19}$ cm⁻³ to $2.4x10^{20}$ cm⁻³.¹³

InMnAs has been shown to be a ferromagnetic semiconductor from magnetization (M) measurements. Typical M versus T and M versus H plots for an In_{0.93}Mn_{0.07}As sample grown by MBE are given in Figure 2-1a. The M versus H loop exhibits both hysteresis and remanence, which indicates that InMnAs is ferromagnetic. While the particular sample given in Figure 2-1a

has a T_c of ~40 K,²¹ in general the T_c of In_{1-x}Mn_xAs depends on both x and p. Figure 2-1b indicates that the T_c scales linearly with x for x<0.08.⁴⁹ The dependence of the T_c on hole concentration was established by low temperature annealing studies. Schallenberg *et al.* recently demonstrated that annealing a MBE grown In_{0.87}Mn_{0.13}As sample at 190°C increased p by more than order of magnitude from 1.6×10^{19} cm⁻³ to 2.4×10^{20} cm⁻³. ¹³ As suggested previously, the enhancement of the hole concentration is preliminarily attributed to a decrease in the number of compensating Mn interstitials that are unstable at the annealing temperature. The increase in hole concentration was also accompanied by a dramatic increase in the T_c from 20 to 90 K. The low temperature annealing experiment of Schallenberg *et al.* suggests a dependence of the T_c and consequently, the ferromagnetic properties of InMnAs on the hole concentration. However, we emphasize that the increase in T_c with low temperature annealing could also be due to an increase in Mn on substitutional sites where they are ferromagnetic.



Figure 2-1: (a) *M* versus *T* for an $In_{0.93}Mn_{0.07}As/GaSb$ heterostructure with *H*=50 G. Inset shows an *M* versus *H* loop measured at 4 K.²¹ (b) T_c as a function of *x* for $In_{1-x}Mn_xAs$ films grown by MBE on GaSb.⁴⁹

In order to determine the spin polarization and band location of the holes in MBE grown InMnAs, the band structure was determined from optical and magneto-optical spectroscopic measurements. A schematic of the band structure is given in Figure 2-2. In contrast to MBE GaMnAs.^{24, 26} a degenerate impurity band is observed for MBE grown InMnAs. The lack of a discrete impurity band in InMnAs is supported by analysis of the near band edge optical absorption.¹⁹ Neither a reduction of the band gap associated with impurity band to conduction band transitions nor a resonance corresponding to valence band to impurity band transitions was observed in the case of MBE grown InMnAs (see section 2.4.1.1).⁵² Due to the absence of a discrete impurity band, the 10^{19} - 10^{20} cm⁻³ holes are presumably itinerant. Finally, the valence band (VB) and conduction bands (CB) are both spin-split, a conclusion confirmed by reflection magnetic circular dichroism (RMCD) spectroscopy.⁵³ The RMCD spectrum of MBE InMnAs exhibited dichroism enhancement near band structure critical points, which is consistent with spin splitting of the valence and conduction bands (see section 2.4.3). The magnitude of the splitting at the Γ -point was 180 meV at T=5 K.⁵³ This spin splitting indicates that the holes in the valence band are spin polarized, which is essential in the operation of spintronic devices based on FSs.^{1, 8, 54} However, the magnitude of the exchange splitting scales with the magnetization of the material such that the band splitting and spin polarized holes persist only up to the maximum *T_c* of 90 K.



Figure 2-2: Schematic of the spin resolved band structure near the Γ -point for MBE InMnAs at (a) $T < T_c$ (b) $T > T_c$. For simplicity, only the heavy-hole valence band and conduction band are included.

2.1.2 MOVPE InMnAs

The majority of the work on (III,Mn)-V ferromagnetic semiconductors involves random alloys such as MBE grown InMnAs. However, Blattner *et al.* have demonstrated that MOVPE grown InMnAs exhibit distinct structural and magnetic properties from InMnAs grown by MBE. In particular atomic scale substitutional Mn clusters form in MOVPE InMnAs, thereby increasing the disorder in the material.³⁶ Moreover, the T_c of 330 K and its independence on the Mn concentration are both in stark contrast to MBE grown InMnAs.⁵⁵ Therefore, we devote a separate background section to describe the unique properties of MOVPE InMnAs.

The growth of phase pure and epitaxial InMnAs films has been demonstrated previously by x-ray diffraction (XRD) and transmission electron microscopy (TEM). Figure 2-3 gives the θ - 2θ scan for an In_{0.90}Mn_{0.10}As film grown on GaAs at 520°C. Distinct film and substrate (002) and (004) diffraction peaks were resolved due to the large lattice mismatch of ~7%. No other peaks were detected, indicating that the film is nominally phase pure. Similar θ - 2θ patterns were measured for In_{1-x}Mn_xAs films with *x*<0.08 and 480°C<*T_g*<520°C. TEM measurements of ajb 192 (*x*=0.01) corroborated the phase purity of MOVPE grown InMnAs films.³⁴ As shown in the annular dark field TEM images of ajb 192 in Figure 2-4a, the only source of mass–thickness contrast in the TEM image for ajb 192, is due to dislocations in the film. In Figure 2-4b, only the (111) atomic planes are visible in the high-resolution image of the same sample. Furthermore, EDS line profile scans indicate chemical homogeneity down to a spatial resolution of 2.8 nm, with In/As and Mn/As intensity ratios constant at 0.99 and 0.01 respectively. Therefore, TEM and XRD measurements indicate that MOVPE grown InMnAs does not contain hexagonal MnAs precipitates and is therefore phase pure.



Figure 2-3: θ -2 θ XRD scan for an In_{0.90}Mn_{0.10}As/GaAs heterostructure near the InMnAs and GaAs (002) and (004) diffraction peaks. The EDS spectrum for the same sample, given in the inset, demonstrates alloy concentrations of Mn.³¹



Figure 2-4: (a) Cross sectional TEM image of an $In_{0.99}Mn_{0.01}As$ sample grown on GaAs (AJB192) (b) High resolution image with the (111) lattice planes resolved.³⁴

However, in contrast to MBE grown InMnAs, Mn in MOVPE grown InMnAs does not substitute randomly at cation sites. In fact the Mn preferentially substitutes at nearest neighbor cation sites, which causes a significant increase in the number of Mn atomic clusters, including Mn dimers and trimers. The presence of disorder in the cation sublattice or Mn atomic clusters in MOVPE InMnAs has been demonstrated by Mn *K*-edge EXAFS measurements.³⁶ For samples with x<0.08, Mn is surrounded by 4 As nearest neighbors. This is expected for Mn substituting for In in the InAs zinc-blende lattice rather than a two-phase material whereby 6 As nearest neighbors would surround the Mn. Moreover, the second nearest neighbor shell contains approximately 5 Mn atoms and 7 In atoms for an In_{0.97}Mn_{0.03}As sample. This is in contrast to a random alloy whereby the majority of the Mn would have 12 In second nearest neighbors. Consequently, the EXAFS data indicates an increase in Mn clustering or cation lattice disorder in MOVPE in contrast to MBE grown InMnAs thin films.

In addition to the structural properties, striking differences were also observed in the magnetic properties of MOVPE InMnAs relative to MBE grown films. The *M* versus *T* curves for three single phase In_{1-x}Mn_xAs samples with *x* ranging from 0.01 to 0.10 are given in Figure 2-5.³³ The samples were first zero field cooled, and the magnetization was measured upon heating with an applied field of 1T. A similar zero field *M* versus *T* curve was obtained for an applied field of 1 kG. While the saturation magnetization (M_s) scales with *x*, the T_c is 333 K, and essentially independent of the Mn and hole concentrations. This is in contrast to MBE grown InMnAs whereby the T_c scales with x.^{49, 56, 57} In addition, the absolute magnitude of the T_c 's differ by at least 240 K. The dependence of *M* with respect to *H* for an In_{0.90}Mn_{0.10}As is shown in Figure 2-6. The *M* versus *H* loop consists of both paramagnetic and ferromagnetic components. At 5 K, an M_s , M_r , and H_c of 62 emu/cm³ 10 emu/cm³, and 400 G were observed respectively. The hysteresis and remanence persists up to 300 K, indicating that the films are ferromagnetic even at room temperature.



Figure 2-5: *M* versus *T* for $In_{1-x}Mn_xAs/GaAs$ heterostructures for *x*=0.01-0.1. A magnetic field of 1T was applied out of the plane of the film, and the samples were zero field cooled.³³



Figure 2-6: *M* versus *H* at the 5, 150 and 300 K for $In_{0.90}Mn_{0.10}As$ sample grown on GaAs. The full hysteresis loop at 5 K is given in the inset.³³

2.2 Free hole mediated magnetism in MBE grown InMnAs

The mechanism for the stabilization of ferromagnetism in MBE III-V semiconductors remains controversial. The most highly cited theory involving these alloys was proposed by Dietl and coauthors, whereby the spins of singly substituted Mn ions are exchange coupled by free holes in the valence band by *sp-d* exchange.⁵⁶ In this section we first provide evidence of *sp-d* exchange using first principles calculations.⁵⁸ Next, the predictions of the Dietl model for ferromagnetism are compared to the experimental magnetic properties of MBE InMnAs.

2.2.1 First principles calculations and *sp-d* exchange

To determine the exchange interactions that result in ferromagnetism in MBE InMnAs, first principles calculations of the spin resolved density of states and band structure were calculated using a plane wave basis under the local spin density approximation (LSDA).⁵⁸⁻⁶¹ In particular, Jain *et al.* constructed a 32 atom InAs supercell, with an individual Mn impurity

replacing an In atom at the origin of the cell $(In_{0.94}Mn_{0.06}As)$.⁵⁸ The resulting lattice is completely ordered, consisting of periodic singly substituted Mn. Since the majority of Mn in MBE grown InMnAs are singly substituted as measured by EXAFS,¹⁶ the construction of this ordered supercell is a reasonable approximation of a random alloy.

The spin resolved density of states (DOS) calculated by DFT is shown in Figure 2-7a. The spin resolved DOS indicates that InMnAs is half metallic due to a spin-polarized feature that appears just above the Fermi level. In addition, the As 4p DOS closely follows that of the Mn 3d DOS in the orbital resolved DOS shown in Figure 2-7b. This indicates a strong *p*-*d* hybridization or exchange interaction between the As 4p and Mn 3d states. Since As 4p states near E_F are populated by free holes in the valence band, and Mn 3d states originate from Mn single substitutional impurities, *p*-*d* exchange can also be thought of as an exchange interaction that couples the spins of isolated Mn ions and itinerant holes. Analysis of the orbital resolved DOS also demonstrates that a hybridization between the In 5s states and Mn 3d states also occurs in the conduction band that is termed *s*-*d* exchange. In an analogous fashion to *p*-*d* exchange, *s*-*d* exchange is a magnetic interaction coupling the spins of itinerant electrons in the conduction band to Mn ions.



Figure 2-7: Spin resolved (a) total density of states and (b) orbital resolved density of states for $In_{0.94}Mn_{0.06}As$.⁵⁸

The spin resolved band structure of InMnAs calculated by Jain *et al.* is given in Figure 2-8. As shown in Figure 2-8, there is no discrete impurity band observed in the band structure. Moreover, the valence and conduction bands are both spin-split. Jain and coauthors have directly attributed the exchange splitting of the valence and conduction bands to hybridization of Mn 3*d* impurity states with As 4*p* and In 5*s* states respectively, or more succinctly *sp-d* exchange.⁵⁸ Both the absence of the discrete impurity band and the exchange splitting of the valence and conduction bands are consistent with the RMCD spectrum of MBE InMnAs.⁵³ The enhancement of the RMCD near band structure critical points is a signature of *sp-d* exchange splitting was also calculated from the magnitude of the RMCD using a formalism described in section 2.4.3. However, it should be noted that DFT estimates a larger valence band splitting of 400 meV in comparison to the 180 meV the exchange splitting measured by RMCD spectroscopy. The discrepancy is attributed to the LSDA, which is known to overestimate band splitting.⁶³⁻⁶⁵


Figure 2-8: Spin resolved band structure calculated by DFT for $In_{0.94}Mn_{0.06}As$. It should be noted that the band gap in the spin up band structure is less than the that of the spin down band structure by ~0.4 eV due to exchange splitting.⁵⁸

2.2.2 Kinetic exchange and the Dietl model

DFT indicates that the spin split band structure observed in MBE InMnAs can be qualitatively attributed to *sp-d* exchange. However, DFT does not provide analytic relations between the band splitting and magnetization of the material. Moreover, DFT is a ground state calculation valid only at 0 K, and therefore does not predict the dependence of the band splitting and magnetization as a function of temperature. This section summarizes a mean field model used by Dietl *et al.* to calculate the band structure, determine analytic expressions for the valence and conduction band splittings, the *M* versus *T*, and the T_c .^{56, 57} Dietl *et al.* began with a Hamiltonian that explicitly accounts for the *sp-d* exchange observed by DFT.

$$H = H_0 + H_s + H_{sp-d} , 2-1$$

where H_0 is the Hamiltonian of an electron in a periodic potential of a perfect crystal and H_S accounts for the effects of substrate/film strain on a band electron. The third term in equation 2-1

, H_{sp-d} , describes the *sp-d* exchange energy between itinerant carriers and magnetic ions in the exact Heisenberg form:⁶⁶

$$H_{sp-d} = \sum_{n} J(\vec{r} - \vec{R}_{n}) \vec{S}_{n} \cdot \vec{s}$$
 2-2

In equation 2-2, \vec{r} and \vec{s} are the position and spin of the band electron, $\overline{R_n}$ and $\overline{S_n}$ are the position and spin of the n^{th} magnetic ion. The sum occurs over the *n* Mn ions in the system. To simplify the calculation, a mean field approximation (MFA) was made whereby a fraction of the magnetic ion spin equal to *x* is attributed to each cation site. For example, in the case of In_{0.90}Mn_{0.10}As sample where each Mn has *S*=2.5, the MFA assigns a moment of *S*=0.25 to every cation site. The MFA is used to maintain the translational symmetry of a perfect crystal. In mathematical terms, the MFA reduces equation 2-2 to:

$$H_{sp-d} = x < s_z > < S_z > \sum_i J(\vec{r} - \vec{R}_i), \qquad 2-3$$

where spins of the band electrons and magnetic ions are replaced by their thermal averages $\langle s_z \rangle$ and $\langle S_z \rangle$ respectively. Moreover, the sum now occurs over the *i* cation sites in the material. The Hamiltonian in equation 2-1 is solved by a standard $\vec{k} \cdot \vec{p}$ method.⁶⁷ It should be emphasized that the $\vec{k} \cdot \vec{p}$ method is limited in that energy eigenvalues are accurate only near critical points in the band structure. The solution reported by Dietl at the Γ -point indicates a spin split band structure, in agreement with both the experimental results and DFT calculations. However, the Dietl model also quantifies the magnitude of the exchange splitting of the valence (ΔE_V) and conduction bands (ΔE_c) given by the equations:

$$\Delta E_V(0) = E_{hh,\uparrow}(0) - E_{hh,\downarrow}(0) = -\frac{M\beta}{g\mu_B}, \text{ and}$$
 2-4

$$\Delta E_c(0) = E_{c,\uparrow}(0) - E_{c,\downarrow}(0) = \frac{M\alpha}{g\mu_B},$$
2-5

where α and β are the *sp-d* exchange integrals $\langle s | J | s \rangle$ and $\langle p | J | p \rangle$ respectively, *M* is the magnetization, and *g* is the *g*-factor equal to 2.⁶⁸ From equations 2-4 and 2-5, $\Delta E_{\nu}(0)$ and $\Delta E_{c}(0)$ are proportional to the *sp-d* exchange integrals and the magnetization. Therefore this mean field model predicts spin splitting of the valence and conduction bands that is proportional to *M*, in agreement with the experimental band structure (see section 2.1.1). We note that a similar expression relating ΔE and *M* has not been calculated by DFT because an analytical relationship between ΔE and *M* requires a mean field approximation such as that given by equation 2-3.⁶⁰ DFT makes no such mean field approximation.

Dietl *et al.* then assumed that the resulting spin polarized holes in the valence band also mediate long-range ferromagnetic interaction between spins, a mechanism for ferromagnetism termed kinetic exchange. The strength of the kinetic exchange is described by the carrier contribution of the Ginzburg-Landau free energy, F_c . An expression for F_c was determined by integrating over the Fermi volume of the band structure:⁵⁷

$$F_{c} = -\frac{3^{1/3} m^{*} A_{F} p^{1/3} \beta^{2} M^{2}}{4 \pi^{1/3} \hbar^{2} g^{2} \mu_{B}^{2}}.$$
 2-6

In equation 2-6, A_F is the Fermi liquid parameter equal to 1.2,⁶⁹ p is the hole concentration, m^* is valence band hole effective mass, and β is the p-d exchange integral defined previously. As can be seen in equation 2-6, the strength of the kinetic exchange is determined by not only the magnitude of p-d exchange, but also by the hole concentration. M(T) can then be expressed in terms of F_c :

$$M(T) = g\mu_B SN_0 x B_s \left[\frac{g\mu_B}{k_B T} - \frac{\partial F_c}{\partial M}\right] = M(0) B_s \left[\frac{3^{1/3} m^* A_F p^{1/3} \beta^2 M(T)}{4\pi^{1/3} \hbar^2 k_B g \mu_B T}\right] = M(0) B_s(z), \qquad 2-7$$

where $B_s(z)$ is the Brillouin function, and M(T) relates to z by the equation:

$$M(T) = \frac{4\pi^{1/3}\hbar^2 k_B g \mu_B T}{3^{1/3}m^* A_F p^{1/3}\beta^2} z.$$
 2-8

In general, the entire *M* versus *T* dependence can be solved graphically by determining the intersection between the plots of equations 2-7 and 2-8. In the specific case of the T_c , we recall that $T=T_c$ at z=0.⁷⁰ As $z\rightarrow 0$, equation 2-7 simplifies to:

$$M(T) = M(0)\frac{S+1}{3S}z.$$
 2-9

Equating equation 2-8 and 2-9 yields an analytical expression for the T_c :

$$T_c = \frac{3^{1/3} m^* A_F p^{1/3} x N_0 S(S+1) \beta^2}{12\pi^{1/3} \hbar^2 k_B}.$$
 2-10

Using equation 2-10, the absolute magnitude of the T_c can be calculated for MBE grown InMnAs. From section 2.1.1, an MBE grown In_{0.87}Mn_{0.13}As sample with $p=2.4 \times 10^{20}$ cm⁻³ has an experimental T_c of 90 K. Using p and x as input parameters, $A_F = 1.2$, S=2.5 for a Mn²⁺ ion, and $\beta = -6.2 \times 10^{-35}$ erg cm³,⁷¹ equation 2-10 yields a T_c of 95 K, in excellent agreement with the experimental value. The value of β for InMnAs used for the previous calculation was an experimental value determined by ARPES. ⁷¹ In contrast, Dietl assumed a β value equal to that of MBE GaMnAs ($\beta = -8.4 \times 10^{-35}$ erg cm³),⁵⁶ leading to an inaccuracy of the T_c predicted in the paper. We note that the agreement in the absolute value of the T_c maybe coincidental.

Nevertheless, the Dietl model demonstrates several important points. First, the agreement with the experimental magnetic properties and band structure indicates that free holes in the valence band mediate the ferromagnetism in MBE InMnAs through kinetic exchange. Second, the MFA of an average magnetic moment at each cation site is a reasonable approximation of Mn randomly substituting on the cation lattice. Finally, the Dietl model illustrates the important connection between the band structure and the magnetic properties, as the band structure was used directly to calculate the *M* versus *T* dependence and the T_c .

While the predictions of the Dietl model including the proportionality of ΔE_v and ΔE_c to M and the absolute value of the T_c are in agreement with that observed for MBE InMnAs, the model does not correctly predict the measured T_c versus p dependence. Annealing and gating experiments suggest that the T_c of MBE InMnAs increases with increasing hole concentration.^{13,} ⁷² However, the T_c of MBE InMnAs shown in Figure 2-1 increases from 20-60 K without any appreciable change in p.⁴⁹ We emphasize that the linear dependence of the T_c dependence on p observed for MBE grown GaMnAs also contradicts with Dietl's predictions of a T_c with a $p^{1/3}$ dependence.⁵¹

In addition, the Dietl model cannot account for ferromagnetism in materials with low hole concentrations, materials whereby holes conduct in the impurity band, and disordered materials. The Dietl model requires high itinerant hole concentrations >10²⁰ cm⁻³ for room temperature ferromagnetism.⁵⁶ However, ferromagnetism at 298 K was observed in semi-insulating or even n-type GaMnN samples.^{73, 74} The Dietl model also does not consider impurity band mediated ferromagnetism. Due to the large ionization energy of the Mn level in several wide gap III-V materials including GaMnAs²⁴ and GaMnP,⁷⁵ a large fraction of holes are expected to reside in the impurity band at low temperatures at which ferromagnetism is observed. Impurity band formation would be expected for the high concentration of magnetic

ions in ferromagnetic semiconductors. Nevertheless, the Dietl model does not consider exchange mediated by holes in the impurity band and would incorrectly predict that GaMnAs and GaMnP were non-ferromagnetic. Finally, Dietl utilizes a mean field approximation that assumes a uniform distribution of spin moments in the cation sublattice. While this MFA maybe a valid approximation in random alloys such as MBE InMnAs, the MFA fails to properly account for large intra-cluster exchange energies³⁷ (see section 2.3.1). The inapplicability of the MFA in disordered systems leads to a dramatic discrepancy between the experimental magnitude and scaling of the T_c of MOVPE InMnAs³⁴ and that predicted by the Dietl model. Therefore, the Dietl model is extremely limited in its application to random or ordered alloys where itinerant holes in the valence band mediate ferromagnetism.

2.3 Theory of effects of disorder

In order to address the numerous inadequacies of the Dietl model, first principles calculations have been performed that explicitly account for disorder in ferromagnetic semiconductors and their effect on the electronic and magnetic properties of the material. These *ab initio* calculations do not rely on any MFA and are therefore inherently more accurate than the Dietl model. Examples of first principles calculations that consider the role of Mn clustering include those by van Schilfgaarde,³⁷ Timm,⁷⁶ Madahaven,³⁸ Bouzerar,⁷⁷ and Raebiger.^{39, 78} We discuss these simulations because they are crucial in the interpretation of the magnetic properties of disordered ferromagnetic semiconductors, including MOVPE InMnAs. Section 2.3.1 focuses on intra-cluster exchange, or the exchange interactions within a cubic Mn cluster. Next, section 2.3.2 examines the exchange interactions between adjacent clusters, or inter-cluster exchange.

2.3.1 Intra-cluster exchange in disordered materials

Raebiger and coauthors utilized DFT to calculate both the thermodynamic stability and magnitude of the intra-cluster exchange for III-V ferromagnetic semiconductors. First, the energies of four Ga_{0.94}Mn_{0.06}As supercell configurations (30 Ga, 2 Mn, 32 As) with varying distances between the two Mn were determined by the projector augmented-wave method.⁷⁸ As given in Figure 2-9, the ground state corresponds to the Mn dimer configuration, whereby Mn substitutes on nearest neighbor cation sites. The binding energy for the dimer is equivalent to the energy difference between the dimer state and the homogeneous ordered state: +114 meV. The large positive binding energy indicates that the dimerization reaction in GaMnAs is favored thermodynamically by a reduction of enthalpy. In a similar fashion, the binding energies of trimers and tetramers were calculated to be 233 and 271 meV respectively, indicating a further increase in binding energy with increasing cluster size.^{39, 79} A similar trend in cluster binding energies was later reported Mahadevan et al.³⁸ Therefore DFT calculations predict a strong thermodynamic drive towards clustering in all InMnAs alloys, regardless of the growth conditions. Kinetics may limit the formation of clusters, especially at low growth temperatures. However, the kinetics of Mn cluster formation are favored at the growth temperatures for MOVPE growth of InMnAs (480-520°C) over that used for MBE InMnAs (250°C). The difference in the kinetics of cluster formation at varying growth temperatures has been verified by Monte Carlo calculations.⁸⁰



Figure 2-9: Supercells of $Ga_{0.94}Mn_{0.06}As$ at successive stages of clustering. Supercells each contain 30 Ga, 2 Mn, and 32 As atoms. Energies are given with respect to the dimer ground state.⁷⁸

Raebiger *et al.* used the same supercell approach to calculate the intra-cluster exchange energy.⁷⁸ In the case of a dimer in Ga_{0.94}Mn_{0.06}As, the energies corresponding to ferromagnetic and antiferromagnetic states were determined. The energy difference between the two states of 105 meV per Mn is equal to the intra-dimer exchange energy ($J_{cluster}$). Zhao *et al.* obtained a similar intra-dimer exchange energy of 93 meV for In_{0.94}Mn_{0.06}As using the first principles full linearized augmented plane wave method (FLAPW).⁸¹ The large positive exchange energy indicates that the two Mn spins in the dimer are strongly ferromagnetically coupled. The temperature at which the spins within a cluster are no longer coherent, ($T_{c,cluster}$) can also be determined assuming a mean field from the equation:⁸²

$$T_{c,cluster} = 0.447 \frac{J_{cluster}}{k_B},$$
 2-11

where $J_{cluster}$ is in units of eV. From equation 2-11, $T_{c,cluster}$ for Mn dimers, trimers and tetramers in Ga_{0.94}Mn_{0.06}As are 570 K, 637 K and 497 K respectively. For the case of In_{0.94}Mn_{0.06}As, $T_{c,cluster}$ for a Mn dimer is 482 K, which is still well above room temperature. $T_{c,cluster}$ values for higher order clusters could not be calculated for InMnAs, because the $J_{cluster}$ values were only calculated for Mn dimers.⁸¹ We emphasize that while $J_{cluster}$ values do affect the overall T_c of the material, $T_{c,cluster}$ is not equivalent to the T_c for global ferromagnetism. Inter-cluster exchange energies and their corresponding mechanisms must also be considered to determine the T_c .

2.3.2 Inter-cluster exchange in disordered materials

Raebiger *et al.* also utilized DFT to determine the effect of Mn clustering on inter-cluster exchange. In Figure 2-10, the orbital resolved DOS is calculated for $Ga_{0.94}Mn_{0.06}As$ whereby the Mn is uniformly distributed in monomers, dimers, trimers, and tetramers.³⁹ As evident in Figure 2-10a, in the monomer configuration, there is a degenerate spin-polarized impurity band that lies just above the Fermi level. However, as shown in Figure 2-10d, as one progresses from a uniform distribution of monomers to tetramers, the single degenerate impurity band splits into two bands: a shallow band that remains nearly degenerate with the valence band (red arrow) and a second discrete band deeper in the band gap (green arrow). According to Raebiger and coauthors, the fraction of states in the shallow and deep bands are is equal to 1/n and (n-1)/n respectively, where *n* is number Mn atoms per cluster.^{39, 78} The change in band structure with increased disorder is illustrated in Figure 2-11a and Figure 2-11b for the case of a uniform distribution of monomers and tetramers respectively. For the monomer case (n=1) all Mn states

are in the shallow band, and for the tetramer case, only 1/4 of the Mn are in the shallow band. While spin splitting of the valence band (see Figure 2-10) and therefore *p-d* exchange occurs for both the monomer and tetramer case, the deep impurity band formed from Mn clusters enhances the *p-d* exchange. The enhancement in *p-d* exchange is evident not only in the spin resolved DOS, where the As 4p projection in the bump increases relative to the Mn 3d projection, but also by an increase in the exchange splitting of the valence band. To quantify the change in *p-d* exchange interaction, a prescription outlined by Sanvito *et al.* was used to calculate $N_0\beta$ from the exchange splitting for each of the 4 configurations given in Figure 2-9.⁶⁰ Values of $N_0\beta$ increase continuously with Mn clustering, from -5.6 eV in the case of homogeneous distribution to -6.8 eV for the dimer configuration.⁷⁸ The value of $N_0\beta$ calculated by Raebiger *et al.* for a homogeneous distribution closely agrees with the value of -5.5 eV determined by Sanvito *et al.*⁶⁰ However, only Raebiger and coauthors have calculated $N_0\beta$ for the disordered case. Therefore, DFT predicts both the formation of shallow and deep impurity band and a significant enhancement of the *sp-d* constant due to Mn clustering.



Figure 2-10: Majority spin, orbital resolved DOS of $Ga_{0.94}Mn_{0.06}As$ near E_F , calculated for Mn (a) monomer, (b) dimer (c) trimer and (d) tetramer cases.³⁹ Shallow and deep impurity bands marked by red and green arrows respectively.



Figure 2-11: Spin resolved band structure schematic of $Ga_{0.94}Mn_{0.06}As$ for the (a) monomer case (*n*=1) and (b) tetramer case (*n*=5). Note the exchange splitting of the impurity, valence and conduction bands.³⁹

The effect of the formation of both a deep and shallow impurity band on the state of the holes was also studied by DFT. Each shallow impurity band state contributes a hole to the valence band that increases the effective carrier concentration. On the other hand each deep Mn impurity band state localizes holes *within* a cluster, and therefore does not contribute holes to valence band conduction.⁷⁸ This is consistent with the fact that the depth of an impurity level is associated with an increase of the magnitude of the Coulombic potential that binds free carriers in the impurity band.⁶⁸ For n^{th} order clusters, n-1 holes are localized around the center cluster As atom and in the deep Mn impurity band. A cluster of size n contributes only a single shallow impurity band state and potentially a single itinerant valence band hole, regardless of its size.³⁹

Therefore, Mn clustering has multiple and complex effects on inter-cluster exchange. The strength of kinetic exchange depends both upon the hole concentration and sp-d exchange

constants (see equation 2-6). DFT predicts the formation of a deep impurity band that significantly reduces the hole concentration. Furthermore, clustering also increases the *p*-*d* exchange constant. Therefore the net effect of clustering on kinetic exchange is not well understood. Furthermore, the decrease in itinerant carriers in the valence band is also coupled with an increase in bound holes in the deep impurity band. Kaminski *et al.* and Berciu *et al.* have proposed previously that these localized holes can also participate in ferromagnetic exchange.^{40, 41, 83, 84} Consequently, clustering introduces an additional inter-cluster exchange mechanism that must be considered.

2.3.3 The T_c in disordered ferromagnetic semiconductors

While values for $J_{cluster}$ and $T_{c,cluster}$ can be directly determined using the DFT supercell approach, a calculation of the material T_c must also account for a long-range exchange mechanism discussed in the previous section. Three calculations of the T_c starting from first principles that do not utilize the MFA were made by Xu *et al.*⁸⁵, Zunger *et al.*,⁸⁶ and Bouzerar *et al.*⁸⁵ It is important to emphasize that the MFA fails in the case of clustered systems.²² First, Xu *et al.* determined pair-wise exchange energies between any two Mn ions *i* and *j* (J_{ij}) in a supercell using the local density approximation. This included not only exchange energies within a cluster ($J_{cluster}$) but also exchange energies between Mn ions of *different* clusters. An effective Heisenberg Hamiltonian was then defined by the equation:⁸⁷

$$H_{eff} = -\sum_{i,j} J_{ij} \overline{e_i} \cdot \overline{e_j} , \qquad 2-12$$

where $\vec{e_i}$ and $\vec{e_j}$ are unit vectors of the local magnetic moments at sites *i* and *j* respectively. Finally, equation 2-12 was solved by the cluster variation method to obtain the T_c .⁸⁸ Xu *et al.* used the preceding prescription to calculate the T_c corresponding to Ga_{0.92}Mn_{0.08}As supercells with varying degrees of pair correlations function (P_1). In the limits, a value of P_1 =0.66 and P_1 =1 correspond to configurations whereby the Mn in Ga_{0.92}Mn_{0.08}As are randomly substituted or strictly introduced as Mn dimers. As evident from Figure 2-12, the T_c is strongly reduced with an increase of P_1 or clustering. Xu *et al.* attributed the reduction of the T_c to an increase in the average separation between Mn atoms with clustering.



Figure 2-12: Dependence of T_c on the pair correlation function P_1 in Ga_{0.92}Mn_{0.08}As calculated from the DFT supercell method.⁸⁵

Zunger and coauthors performed a similar density functional theory calculation as that made by Xu and coauthors. J_{ij} values were also calculated using the supercell approach under the LDA to determine the Heisenberg Hamiltonian in equation 2-12. However, instead of utilizing the cluster variation method to determine the global T_c from the exchange energies, Zunger *et al.* determined the T_c from Monte Carlo simulations of H_{eff} . The authors utilized Monte Carlo simulation cells 8x8x8 to10x10x10 times the volume of the unit cells used to calculate J_{ij} values. Zunger *et al.* determined that the T_c decreases sharply with increased Mn clustering, in close agreement with the work of Xu *et al.*

The final *ab initio* study of the effect of clustering on the T_c of ferromagnetic semiconductors was reported by Bouzerar *et al.*⁷⁷ However, instead of using the DFT supercell approach to calculate the pair exchange energies (J_{ij}), Bouzerar *et al.* utilized a Green-function method under the coherent potential approximation (CPA). The determination of the T_c from the J_{ij} values also proceeded from Heisenberg Hamiltonian given by equation 2-12. The resulting plot of the T_c of Ga_{0.92}Mn_{0.08}As as a function of the probability of enhanced nearest occupation (P_r) is given in Figure 2-13. We note that P_r differs from the pair-wise correlation function (P_i) used by Xu *et al.* in that random substitutional limit case has $P_r=0$ and the completely clustered case has $P_r=1$. In contrast to the results of the supercell DFT calculation, Bouzerar *et al.* predict an increase in the T_c of 230% from $P_r = 0$ to 1. Therefore, even differing implementations of density functional theory yield conflicting predictions of the effect of disorder on T_c . Furthermore, none of the calculations provides an intuitive mechanism for inter-cluster exchange in clustered system.



Figure 2-13: T_c as a function of P_r for Ga_{0.92}Mn_{0.08}As determined from CPA approach.⁷⁷

2.3.4 Chemical effects on intra- and inter-cluster exchange

In addition to the difficulties in predicting the global T_c , the effect of alloy host environment on inter- and intra cluster exchange in disordered ferromagnetic semiconductors is also not well understood. Calculations of metallic zinc blende MnX (X=N, P, As, and Sb) are of interest because they are an excellent model systems for studying the chemical trends in intracluster exchange. Recently, Hong et al. utilized first principles pseudopotential calculations under the LDA to determine the structural and magnetic properties of zinc-blende MnX binary compounds.⁴² The structural and magnetic properties of zinc-blende MnX binary compounds reasonably approximate the same properties of zinc blende MnX clusters within a semiconductor matrix.⁸⁹ Hong et al. found that the lattice constant increases monotonically from 4.489 to 6.118 Å from zinc-blende MnN to MnSb. The same increase in lattice constant with increasing anion size also occurs for the semiconductor matrix.⁵² It should be noted that the calculated lattice constant for zinc-blende MnAs was smaller by 6% from the extrapolated lattice constants of MBE grown $In_{1-x}Mn_xAs$ (6.01 Å).⁹⁰ While errors in the absolute value of lattice constant using the LDA have been previously reported,⁹¹ DFT calculations yield correct relative values, such that the chemical trend in the lattice constant for MnX compounds determined by Hong et al. is still accurate.

As given in Figure 2-14, the effect of increasing the atomic number (and radius) of X from N to Sb is an increase in the magnetic moment per Mn and the difference between the energies of the antiferromagnetic (E_{AFM}) and ferromagnetic (E_{FM}) states. In section 2.3.1, the same energy difference was used to calculate the intra-cluster exchange energy. It should be noted that the intra-cluster exchange energy per Mn for a cubic Mn dimer in GaAs (0.105 eV)⁷⁸

agrees with the E_{AFM} - E_{FM} per Mn for zinc blende MnAs (95 meV). The agreement is presumably more than coincidental and therefore supports the use of zinc blende MnX compounds to model intra-cluster exchange energies of zinc blende clusters in ferromagnetic semiconductors. Therefore, since E_{AFM} - E_{FM} increases with increasing anion size, we may also conclude that the intra-cluster exchange energy, $J_{cluster}$ also increases from N to Sb. If the overall T_c is dominated by the intra-cluster exchange energy, we would also predict a decrease in T_c by alloying P with InMnAs (smaller $J_{cluster}$ for smaller anions).



Figure 2-14: Exchange energies and magnetic moment per Mn calculated for zinc blende MnN, MnP, MnAs and MnSb.⁴²

It was demonstrated in the previous section that the addition of P into InMnAs would decrease the intra-cluster exchange interaction. However, if kinetic exchange mediates the ferromagnetism between clusters, the addition of P will also have a significant effect on the strength of the inter-cluster exchange as well. Huang and Wessels established that the depth of the "shallow" Mn impurity level increases with P concentration (*y*) in InMnAs_{1-y}P_y.^{92, 93} In Figure 2-15, the Mn acceptor level in InMnAs_{1-y}P_y is degenerate for *y*<0.2, but increases with *y*

to an acceptor energy of 287 meV at y=1. Dietl *et al.* and Bhattacharjee *et al.* have both shown that increase in acceptor energy corresponds to an increase in *sp-d* exchange constant.^{94, 95} Finally, as given by equation 2-6, the magnitude of the kinetic exchange interaction is also proportional the nominal cation concentration, N_0 . Since N_0 is inversely proportional to the cube of the lattice constant (a_0), a decrease in a_0 due to an increase in P concentration would increase N_0 and hence the magnitude of the *sp-d* exchange coupling. Therefore the addition of P enhances kinetic exchange, a potential inter-cluster exchange mechanism.



Figure 2-15: Position of the valence band maximum (E_v) , conduction band minimum (E_c) , and the Mn acceptor level (E_A) with respect to the vacuum level for InMnAs_{1-y}P_y.⁹³

An increase in the P concentration in InMnAsP alloys has opposite effects on the intra and inter-cluster exchange. Consequently, without a more precise theory, it is difficult to predict the net effect of P addition on the magnetic properties and the T_c of the quaternary alloy. Therefore, an experimental investigation of the structural, electronic, and magnetic properties of InMnAs₁- $_{y}P_{y}$ as function of *y*, is necessary to elucidate the nature of the effect of alloy host environment on clustered ferromagnetic semiconductors.

2.4 Experimental methods of probing the band structure

The purpose of this thesis is to address two open questions regarding magnetism in disordered ferromagnetic semiconductors. First, the effect of alloy host environment on the magnetic properties of clustered ferromagnetic semiconductors is unknown. These effects were investigated by measuring the structural and magnetic properties of InMnAs films alloyed with P. Since the techniques associated with this study have been well described previously,⁵⁵ we do not devote a separate background section to describe those methods.

Second, a strong inter-cluster exchange mechanism necessary for the observed global ferromagnetism in the MOVPE InMnAs has not been identified. DFT suggests that shallow and deep Mn impurity bands form upon clustering.³⁹ Holes that are strongly bound to clusters reside in the deep impurity band, and may mediate magnetism between clusters.^{40, 41} While the Dietl model predicts a T_c far less than 330 K for a material in which valence band holes mediate ferromagnetism by kinetic exchange,⁵⁶ DFT calculations indicate that the *sp-d* exchange constants used as a parameter in the Dietl model, may be underestimated in clustered materials.⁷⁸ Therefore, kinetic exchange could still act as an inter-cluster exchange mechanism above room temperature due to a cluster-induced enhancement of the *sp-d* exchange constants. The following sections outline the specific spectroscopic methods used to elucidate the nature of inter-cluster exchange in MOVPE InMnAs.

2.4.1 Infrared absorption spectroscopy

As discussed previously, the potential formation of deep and shallow Mn impurity bands in clustered ferromagnetic semiconductors can have significant effects on inter-cluster exchange. Therefore in this section, we describe how infrared spectroscopy can be used to determine the presence and properties of impurity bands. The effects of impurity band formation on the itinerant hole concentration can also be determined from the free carrier absorption.

2.4.1.1 Impurity band absorption

One of the important applications of infrared absorption spectroscopy (IAS) is for the determination of electronic impurity states in the band gap. Absorption associated with either impurity band to conduction band or valence band to conduction band transitions result in characteristic absorption from which the depth of the impurity band can be calculated. In particular, for an acceptor impurity, there are two types of optical transitions involving the impurity band. First, as shown in Figure 2-16a, a photon with energy equal to the activation energy (E_A) excites an electron from the valence band to a neutral acceptor, $A^{0.52}$ For an effective mass-like impurity, valence band to impurity band transitions lead to a peak in the absorption, with the maximum of the absorption at E_A .⁹⁶ An example of valence band to impurity band absorption in the case of boron-doped silicon is given in Figure 2-16b. A broad maximum at 0.052 eV is observed, in good agreement with the activation energy determined by Hall effect of 0.045 eV.⁹⁷

In the second transition type, an electron is excited from an ionized acceptor (A^{-}) into the conduction band. As evident in Figure 2-16c, this transition occurs at photon energies greater than E_g - E_A . Since the activation energy is of the order 100 meV or less, the high-energy side of

the resonance corresponding these transitions is typically obscured by the direct band to band transitions. An example of absorption related to bound to free transitions is given in the case of Ge doped InSb in Figure 2-16d, where a distinct shoulder was observed 7.9 meV below the band edge.⁹⁸ However, for p-type InAs doped with Zn, a distinctive edge due to a shallow impurity band was not distinguished from the background absorption due band tailing.^{99, 100} Instead, a reduction of the band gap from 0.41 eV for undoped InAs to 0.37 eV for p-type InAs was observed.⁹⁸ The difference in band gaps was attributed to the formation of an impurity level, 40 meV above the valence band maximum.

Optical absorption has been measured at and below the band edge for MBE grown $In_{0.99}Mn_{0.01}As.^{19}$ Absorption corresponding to free to bound transitions was not observed. Furthermore, neither a shoulder at the low energy side of the band edge nor a significant reduction of the band gap to indicate ionized acceptor (Mn^{2+}) to conduction band transitions was observed. At *T*=298 K, the band gap of $In_{0.99}Mn_{0.01}As$ was measured at 0.355 eV,¹⁹ in close agreement with the literature value of undoped InAs of 0.354 eV.¹⁰¹ Therefore the optical absorption indicates an absence of a discrete impurity level or band in MBE InMnAs.



Figure 2-16: (a) Schematic band diagram for free to bound transitions and (b) corresponding absorption spectrum for boron doped silicon at T=4K.¹⁰² (c) Schematic band diagram for bound to free transitions and (d) corresponding absorption spectrum in the case of germanium doped InSb at T=10 K.⁹⁸

2.4.1.2 Free carrier absorption

Optical absorption can also be used to determine the properties of free carriers in the valence and conduction bands by measuring the free carrier absorption. Free carrier absorption takes place when photons excite electrons or holes to a higher energy state within the same band.¹⁰³ In a p-type semiconductor, holes are excited from the top of the valence band to a deeper state in the band. Free carrier absorption in semiconductors is best treated using the Drude model, due to its simplicity. In the Drude model, free carriers are treated as free particles in a gas, subject to an electric field, \overline{E} . The free holes also have a mean scattering time, τ , which

causes the drift velocity of the electron to relax to zero upon removal of the electric field. The effect of the crystal on the free electrons is to change the electron mass (m_e) to an effective mass (m^*) . The result of the Drude model for a p-type semiconductor is given by the equation:^{104, 105}

$$\alpha_{drude}(E) = \frac{2}{Y + Y_0} \sigma_1(E) = \frac{2}{Y + Y_0} \frac{p e^2 \tau}{m^* (1 + (E/\hbar)^2 \tau^2)},$$
 2-13

where p is the hole concentration, m^* is the hole effective mass, and Y and Y_0 are the admittances of the substrate and free space respectively. A plot of the equation 2-13 indicates that the defining characteristic of free carrier absorption is a Drude absorption edge that appears at energies less than the plasma energy, $E_p = 4\pi \hbar e^2 p / m^*$. As shown in Figure 2-17a, MBE grown $In_{0.99}Mn_{0.01}As$ exhibits a classic Drude-edge at T=300 K, where E_p occurs in the IR spectral region at 0.15 eV. The corresponding fit of the Drude-edge for MBE In_{0.99}Mn_{0.01}As with respect to equation 2-13 is given in Figure 2-17b. The best fit occurs for a $p=2.1 \times 10^{19}$ cm⁻³ and $\tau=9$ fs, in excellent agreement with room temperature Hall effect measurements. A similar close fit was obtained for the 10 K absorption spectrum. In all Drude fits, an effective mass equal to the heavy hole mass of undoped InAs (0.33 m_e) was used.⁵² From the Drude model fitting, several conclusions can be made. In general, the free carrier absorption can be fit to obtain important parameters including the free hole concentration and scattering time (proportional to the mobility). Next, the excellent fit with respect to the Drude model indicates that the holes in MBE InMnAs are delocalized in the valence band between 10-300 K. This is again consistent with the absence of a non-degenerate Mn impurity band.



Figure 2-17: (a) α versus *E* of In_{0.99}Mn_{0.01}As grown by MBE at *T*=300 K. Box highlights the Drude edge. (b) α versus *E* between 0-0.2 eV at *T*=300 K. Red line corresponds to the Drude model fit.¹⁹

2.4.2 X-ray absorption and magnetic circular dichroism

2.4.2.1 Spectroscopic specificity

In contrast to IAS, whereby impurity band absorption must be distinguished from other sources of absorption, x-ray absorption spectroscopy (XAS) can be used as both an elemental and orbital specific probe of the Mn 3*d* states.^{106, 107} XAS measures the absorption corresponding to dipole selection rule allowed transitions between a core state and an unoccupied valence state $(E>E_F)$. In addition, XAS utilizes the strong dependence of the absorption edge energy on atomic number to determine the electronic structure of *each* alloy component. The dipole-allowed transitions studied in this thesis are the Mn L_2 and L_3 edge, corresponding to transitions between Mn $2p_{1/2}$ and $2p_{3/2}$ core states and the Mn 3*d* band states respectively. A band structure schematic of these transitions is given in Figure 2-18. Therefore, XAS allows for an specific study of the Mn 3*d* related band, by measuring the Mn $L_{2,3}$ edge absorption.



Figure 2-18: Schematic of the absorption of right and left circularly polarized x-rays resulting in the transition of spin polarized photoelectrons from Mn core $2p_{3/2}$ and $2p_{1/2}$ levels to a spin-split Mn 3*d* band.¹⁰⁶

X-ray magnetic circular dichroism (XMCD) measurements involving the Mn $L_{2,3}$ edge add an additional level of specificity over XAS, because only ferromagnetically active (spin polarized) Mn will contribute to the XMCD spectra. The XMCD relative intensity is given by:

$$XMCD = \frac{\alpha_{+} - \alpha_{-}}{\alpha_{+} + \alpha_{-}} = \frac{\alpha_{+} - \alpha_{-}}{\alpha} \quad .$$

From equation 2-14, the XMCD is defined as the difference in the absorption coefficient of right (α_{+}) and left (α_{-}) circularly polarized light, normalized by the total absorption (α) . It should be noted that the absorption coefficients depend on energy. As given in Figure 2-18, the spin dependent absorption of circularly polarized light can be visualized as a two-step process.¹⁰⁶ First, a right circularly polarized (RCP)/left circularly polarized (LCP) photon preferentially excites a spin up/spin down electron from a core level. In the second step, the spin up/spin down photoelectron must be captured by an unoccupied state above E_F . This unoccupied state must be

spin up/spin down in order to satisfy the spin selection rule, which dictates that the change in spin angular momentum (ΔS) following dipole absorption equals 0. In this two-step formalism, Fermi's golden rule can be used to obtain an expression for the absorption of LCP and RCP light in terms of the spin resolved DOS:¹⁰⁶

$$\alpha_{\pm}(E) = \phi |M(E)|^2 [p_{\pm}(\uparrow)g_{\uparrow}(E) + p_{\pm}(\downarrow)g_{\downarrow}(E)], \qquad 2-15$$

where ϕ is an energy dependent constant, M(E) is the transition matrix element, $p_{\pm}(\uparrow,\downarrow)$ are the relative weights for spin-up/down photoelectron polarization from RCP and LCP, and $g_{\uparrow,\downarrow}(E)$ are the spin up and spin down DOS. Substituting equation 2-15 into 2-14 we obtain:

$$XMCD = \frac{\alpha_{+} - \alpha_{-}}{\alpha_{+} + \alpha_{-}} = \left(\frac{p_{\uparrow} - p_{\downarrow}}{p_{\uparrow} + p_{\downarrow}}\right) \frac{g_{\uparrow}(E) - g_{\downarrow}(E)}{g_{\uparrow}(E) + g_{\downarrow}(E)} = P_{e} \frac{g_{\uparrow}(E) - g_{\downarrow}(E)}{g(E)}.$$
 2-16

Note that in the simplification of equation 2-16, the terms ϕ and M(E) normalize out. Since the photoelectron polarization P_e is independent of energy, the XMCD spectrum is therefore proportional to the difference of the spin up and down DOS. For ferromagnetically active Mn, there is an exchange splitting of the Mn 3*d* spin up and spin down valence band states that results in a nonzero difference $g_{\uparrow}(E)$ and $g_{\downarrow}(E)$.¹⁰⁸ Given that the difference in $g_{\uparrow}(E)$ and $g_{\downarrow}(E)$ for the Mn 3*d* bands is proportional to the magnetization, we may also conclude that the XMCD will be proportional to M.¹⁰⁸ By contrast, the DOS of a nonferromagnetic (either paramagnetic or antiferromagnetic) Mn are spin symmetric at low fields $(g_{\uparrow}(E) - g_{\downarrow}(E) = 0)$, and therefore do not contribute to the XMCD spectrum.

2.4.2.2 Electronic and local environment effects

The importance of measuring the Mn $L_{2,3}$ edge XAS and XMCD transitions is that the Mn 3d DOS is highly sensitive to the electronic state (ground state configuration, degree of localization of 3d electrons, and crystal field) of Mn¹⁰⁹⁻¹¹¹ and its local environment (symmetry and atoms in the first nearest neighbor shell).¹¹² To determine the electronic state of the Mn 3d orbitals, the XAS and XMCD spectra are most often fit with respect to theoretical spectra generated by an atomic multiplet model.^{107, 113, 114} The atomic model assumes a single isolated Mn ion in vacuum, and then subjects the ion to a crystal field and spin orbit interactions. In the atomic model, the *d*-electrons are highly localized around the Mn ion. The Mn $L_{2,3}$ XAS and XMCD spectra of a Mn ion with a d^4 configuration under tetrahedral crystal fields (T_d) of 0 and 1 eV calculated by this model are given in Figure 2-19a.¹¹⁵ Figure 2-19b gives the spectra for the d^4 , d^5 , and d^6 configurations without the application of a crystal field, where the groups of peaks marked by the red and green arrows correspond to Mn $2p_{3/2}$ to Mn 3d and Mn $2p_{1/2}$ to Mn 3d transitions respectively.^{115, 116} The clear differences in the spectra in Figure 2-19 emphasize the effect of crystal field and valence on the Mn 3d DOS and hence the Mn $L_{2,3}$ edge XAS and XMCD transition lineshape. While an atomic mulitplet model of an isolated Mn ion does not accurately represent a ferromagnetic semiconductor lattice, the model is assumed frequently due to its simplicity and excellent agreement with experimental XAS and XMCD spectra.^{110, 111} An example of atomic model fit to the XMCD data for an MBE grown Ga_{0.98}Mn_{0.02}As sample is given in Figure 2-20.¹⁰⁹ An excellent fit to the experimental dichroism spectrum is obtained for a linear combination of d^5 (80%) and d^6 (20%) atomic spectra, with $T_d=0$ eV.¹⁰⁹ It should be noted

that there are no corresponding atomic fits for MBE grown InMnAs, as the XAS/XMCD spectra of this material have not been measured.



Figure 2-19: XAS and XMCD spectra generated by the atomic multiplet model (a) for a d^4 configuration with $T_d=0$ and 1 eV. (b) for Mn d^4 , d^5 , and d^6 configurations.¹¹⁵ Features highlighted by the red and green arrows correspond to Mn $2p_{3/2}$ to Mn 3*d* and Mn $2p_{1/2}$ to Mn 3*d* transitions respectively



Figure 2-20: Comparison between experimental XMCD spectrum of an MBE grown $Ga_{0.98}Mn_{0.02}As$ sample measured at 15 K and that calculated by the atomic model. A linear combination of d^4 and d^5 ground state configurations was assumed.¹⁰⁹

The effect of the local environment on the XAS and XMCD spectral lineshape is not well accounted for by the atomic model. Rather, local environment effects are better illustrated by a qualitative comparison of the dichroism spectra. For example the XMCD spectra of a Ga_{0.97}Mn_{0.03}As random alloy grown by MBE, a GaAs/Mn digital alloy (10 monolayers/0.5 monolayers), and a hexagonal MnAs thin film are given in Figure 2-21.¹¹² The significant differences in XMCD spectra between the GaMnAs and MnAs are attributed to differences in the coordination number between the two materials. Mn in GaMnAs and MnAs have 4 and 6 nearest neighbor As atoms respectively. However, the XMCD spectrum of the GaAs/Mn digital alloys are similar to GaMnAs random alloys because both have Mn tetrahedrally bonded to 4 nearest neighbor As, the number of second nearest neighbor Mn in digital alloys is greater than in random alloys. The similarity between in Mn $L_{2.3}$ XAS/XMCD spectra of GaAs/Mn digital alloys and GaMnAs

random alloys indicates that XAS/XMCD spectral lineshapes are only sensitive to differences in the first nearest neighbor shell.



Figure 2-21: Comparison of the *T*=5K XMCD spectra of a $Ga_{0.97}Mn_{0.03}As$ random alloy, Mn/GaAs digital alloy, and hexagonal MnAs film grown by MBE.¹¹²

2.4.3 Reflection magnetic circular dichroism

In this section, we discuss the final magneto-optical spectroscopic method utilized in this thesis: reflection magnetic circular dichroism (RMCD). RMCD is a particularly important technique because dichroism is proportional to the exchange splitting (ΔE) of the bands of a ferromagnetic semiconductor. Moreover, the RMCD spectral lineshape can be used to identify the ferromagnetic exchange mechanism that results in the spin splitting of the bands.

In order to determine the expression that relates the RMCD to the exchange splitting, we begin with a definition of the RMCD. As discussed in greater detail in section 3.6, the RMCD

(ϕ) describes the change in the ellipticity of the polarization state upon reflection off a magnetic material ($M \neq 0$):

$$\phi = \frac{R_+ - R_-}{R}, \qquad 2-17$$

where R_{\pm} are the reflectivities of RCP and LCP light respectively. We then assume that the application of a magnetic field shifts the reflectivity spectrum for RCP and LCP light by $+\Delta E/2$ and $-\Delta E/2$ respectively, but *does not change the overall spectral lineshape*.^{62, 117} This approximation is supported by visible range reflectivity measurements of ZnMnTe using circularly polarized light.¹¹⁸ Therefore, R_{\pm} can be expressed in terms of ΔE by the equation:

$$R_{\pm}(E) = R(E \pm \frac{\Delta E}{2}).$$
 2-18

Upon Taylor-expansion of the right side of equation 2-18:

$$R_{\pm}(E) = R(E \pm \frac{\Delta E}{2}) = R(E) \pm \frac{\Delta E}{2} \frac{dR}{dE} + O(\Delta E^2) + \dots$$
 2-19

In equation 2-19 terms of order ΔE^2 and higher are ignored. Since the RMCD spectra in this thesis are measured at photon energies much greater than ΔE , the omission of these higher order terms is an excellent approximation. Substituting equation 2-19 into equation 2-17 yields the desired expression for ϕ in terms of ΔE :

$$\phi = \frac{1}{R} \frac{dR}{dE} \Delta E .$$
 2-20

From equation 2-20, the RMCD, in units of radians, is proportional to the differential reflectivity $(\frac{1}{R}\frac{dR}{dE})$ and ΔE , which depends on energy. Therefore a determination of the spectral dependence of the differential reflectivity and RMCD yields the complete spectral dependence of

the exchange splitting. We also note that a similar expression for transmission MCD (ϕ_F) (Faraday effect) in units of radians can be derived using a similar formalism:

$$\phi_F = \frac{\alpha_+ - \alpha_-}{\alpha} = \frac{1}{\alpha} \frac{d\alpha}{dE} \Delta E, \qquad 2-21$$

where α_{\pm} are the absorption coefficient of RCP and LCP light and α is the total absorption. Similar to the case of RMCD, the main approximation in this derivation is that α_{+} and α_{-} differ only by a constant energy shift, ΔE . This assumption has been validated *in the visible range* by Szczytko and coauthors for MBE grown GaMnAs.⁶⁴

Dichroism in ferromagnetic semiconductors, including MBE grown InMnAs,⁵³ has typically been attributed to transitions between *sp-d* exchange split valence and conduction bands (see section 2.2.1).^{53, 62, 117, 119} Therefore, for MBE InMnAs, *1/R dR/dE* and ΔE in equation 2-20 specifically correspond to the differential reflectivity due to VB to CB transitions and exchange splitting of the VB and CB respectively.

To explain the RMCD spectra due to *sp-d* exchange, we first provide background regarding the spectral dependence of $1/R \ dR/dE$ associated with VB to CB transitions. We approximate the differential reflectivity spectrum of MBE InMnAs with a simulated $1/R \ dR/dE$ of undoped InAs calculated by a nonlocal pseudpotential method.¹²⁰ We note that while differential reflectivity of MBE InMnAs has not been reported, Mn doping typically results in only subtle shifts in the $1/R \ dR/dE$ on the order of 10 meV.¹²¹⁻¹²³ As shown in Figure 2-22, between 0-3.1 eV, there are four major peaks in the differential reflectivity spectrum. By definition, band structure critical points (CPs) occur where $d^2R/dE^2=0$ or the extrema in the differential reflectivity spectrum.¹²¹⁻¹²³ In particular, the positive peak in $1/R \ dR/dE$ at 0.35 eV

corresponds to the E_0 critical point (CP). As shown in Figure 2-23b, the E_0 critical point is attributed to transitions between the heavy hole (hh) valence band and conduction band at the Γ point. The negative peak at 0.72 eV in the differential reflectivity spectrum corresponds to Γ point transitions between the split off valence band and conduction band ($E_0+\Delta_0$ CP). The two peaks at 2.61 (E_1 CP) and 2.88 eV ($E_1+\Delta_1$ CP) are associated with heavy hole VB to CB and light hole VB to CB transitions at the *L*-point, respectively. Finally, we emphasize that the magnitude of the differential reflectivity is greater near band structure CPs than that away from CPs. For example, using Figure 2-22, the magnitude of the peak associated with the E_1 critical point (2.61 eV) has a magnitude of 0.26 eV⁻¹. However, at 1.6 eV, an energy well separated from any CPs has $1/R dR/dE=0.16 \text{ eV}^{-1}$. The enhancement of the differential reflectivity near band structure CPs has important ramifications on the spectral lineshape of the dichroism.



Figure 2-22: Differential reflectivity spectrum of undoped InAs calculated by the non-local pseudpotential method.¹²⁰ Features in the $1/R \ dR/dE$ spectrum corresponding to band structure CPs are marked by solid lines.



Figure 2-23: (a) Full band structure of undoped InAs calculated using the nonlocal pseudopotential method. (b) Zoom-in view of the valence and conduction bands. Critical point transitions that result in peaks in the differential reflectivity between 0-3.1 eV are marked by arrows.¹²⁰

Next, as evident from equation 2-20, the energy dependence of the VB and CB spin splitting can also affect the spectral lineshape of the dichroism. We emphasize the *sp-d* exchange splitting of the VB and CB *also depends strongly on energy*. As discussed in section 2.2.2, an expression for the *sp-d* exchange splitting of the VB and CB can be accurately determined by the $\vec{k} \cdot \vec{p}$ method *only at band structure critical points* (CPs). In particular, the expressions for the spin splitting of the CB (ΔE_c) and VB (ΔE_v) evaluated at the Γ -point (E_0) are given by equations 2-4 and 2-5 respectively. The exchange splitting at E_0 ($\Delta E(E_0)$) is then simply the sum of $\Delta E_c(E_0)$ and $\Delta E_v(E_0)$:

$$\Delta E(E_0) = \Delta E_c(E_0) + \Delta E_v(E_0) = \frac{M(\alpha - \beta)}{g\mu_B}, \qquad 2-22$$

where α and β are the *sp-d* integrals previously defined in section 2.2.2. As evident in equation 2-22, $\Delta E(E_0)$ is proportional to the magnetization and the difference between the *s-d* and *p-d* exchange integrals.

Analytical expressions for the *sp-d* exchange splittings at the E_0 , $E_0 + \Delta_0$, E_1 , and $E_1 + \Delta_1$ critical points (CPs) were also derived using a similar formalism as that given in section 2.2.2.^{22,} ¹²⁴ These analytical expressions for ΔE at the 4 CPs are given in Table 2-1.¹²⁵ As can be seen in Table 2-1, the sign of ΔE changes for the 4 critical points, demonstrating that ΔE depends on energy. It should also be noted that the magnitude of the splittings due to *sp-d* exchange are significantly larger as compared to the Zeeman splitting ($g\mu_BH$). For example, the *sp-d* exchange splitting of Ga_{0.96}Mn_{0.04}As at the Γ -point is 170 meV at applied fields as low as 0.1 T.¹²⁵ These values are much larger in magnitude than typical Zeeman splitting in undoped semiconductors that are of the order 10⁻² meV at 0.1 T.

Table 2-1: *Sp-d* exchange splittings at the E_0 , $E_0 + \Delta_0$, E_1 , and $E_1 + \Delta_1$ CPs. In the expression for $\Delta E(E_1)$ and $\Delta E(E_1 + \Delta_1)$.

Critical Energy	Transition	Critical Point	ΔE expression
E_0	hh VB-CB	Г-point	$M(\alpha-\beta)/g\mu_{B}$
$E_0 + \Delta_0$	Split-off VB-CB	Г-point	$M(-3\alpha+\beta)/3g\mu_B$
E_1	hh VB-CB	L-point	$\frac{1}{2}M(\alpha - \frac{1}{4}\beta)/g\mu_B$
$E_1 + \Delta_1$	lh VB-CB	L-point	$-\frac{1}{2}M(\alpha-\frac{1}{4}\beta)/g\mu_B$

Using the spectral dependence of the differential reflectivity shown in Figure 2-22 and the *sp-d* exchange energies shown in Table 2-1, we can explain the RMCD spectrum of MBE InMnAs measured between 1.6-3.1 eV. In this spectral range, there are two critical point transitions: E_1 (2.61 eV) and $E_1 + \Delta_1$ (2.88 eV). In Figure 2-22, the critical point transitions correspond to peaks in the differential reflectivity. Correspondingly, there is a large negative peak at 2.61 eV and another subtle positive peak at 2.88 eV in the dichroism spectrum of MBE InMnAs shown in Figure 2-24. Since the peaks in the dichroism correspond to peaks in the differential reflectivity, enhancement of the RMCD near CPs has been attributed to the spectral dependence of 1/R dR/dE.¹²⁶ For example, the dichroism at E_1 =2.61 eV is -73 mdeg as compared to that away from the E_1 CP ($\phi(1.6 \text{ eV}) = -29 \text{ mdeg}$). The relative increase in $\phi(E_1)$ relative to that at ϕ (1.6 eV) is consistent with the increase in 1/R dR/dE at E_1 compared to that at 1.6 eV. The enhancement of the dichroism at band structure CPs in MBE InMnAs is also consistent with the experimental RMCD spectra due to *sp-d* exchange for a number of different ferromagnetic semiconductors including MBE grown GaMnAs, CdMnTe, and ZnCrTe.^{62, 117, 119} Therefore the signature of *sp-d* exchange in the dichroism spectrum is the *enhancement of RMCD near band* structure CPs relative to that away from CPs.



Figure 2-24: RMCD spectrum MBE grown In_{0.88}Mn_{0.12}As, measured at T= 5K and H=0.2 T.⁵³ Lines mark the $E_I, E_I+\Delta_I$ CPs.

Moreover, the change in sign of the E_I and $E_I + \Delta_I$ RMCD of MBE InMnAs can be explained in terms of a change in sign of the exchange energy (ΔE). As seen in Figure 2-22, the differential reflectivity is negative for both *L*-critical points. However, according to Table 2-1, the exchange splitting is positive at E_I , resulting in a negative RMCD at E_I . Similarly, the exchange splitting is negative at $E_I + \Delta_I$, resulting in a positive dichroism at that energy. The predicted signs of the dichroism are consistent with that observed in Figure 2-24. Finally, as given in Figure 2-24, the measured dichroism magnitude at E_I is greater than that at $E_I + \Delta_I$ CPs. This contradicts mean field theory which predicts equal and opposite peaks at E_I and $E_I + \Delta_I$.^{22,} ¹²⁴ On the other hand, it is consistent with the experimental RMCD spectra of other ferromagnetic semiconductors which only observe a single dominant peak at the *L*-point.^{119, 127}
Therefore the occurrence of a single dominant dichroism peak at 2.61 eV is a *specific fingerprint* of *sp-d* exchange in InMnAs.⁵³

In conclusion, RMCD spectroscopy is an integral technique for this thesis because RMCD can be used to determine the presence and magnitude of sp-d exchange in ferromagnetic semiconductors. The signature of sp-d exchange is the enhancement of RMCD at band structure CPs relative to that away from CPs. The magnitudes of the peaks at the critical points are associated with the magnitude of the sp-d exchange. In the specific case of InMnAs, a single resonance at 2.61 eV is predicted in the visible light range, associated with sp-d exchange of the valence and conduction bands at the L-point.

3. Experimental Techniques

3.1 InMnAs and InMnAsP film growth

3.1.1 MOVPE system design and precursors

InMnAs and InMnAsP thin films were grown by atmospheric pressure metal organic vapor phase epitaxy in a horizontal cold wall reactor. A schematic of the system is given in Figure 3-1. The growth apparatus shown in Figure 3-1 has been previously described in detail by Blattner⁵⁵ and Han¹²⁸. No further modifications to the growth system have been implemented for the growth of the InMnAs and InMnAsP thin films described in this thesis.

The precursors utilized for this work include a phosphine/hydrogen balance (5% PH₃; Matheson Trigas), an arsine/hydrogen balance (0.3% AsH₃; Matheson Trigas), trimethylindium (TMIn) (Morton International 99.999% purity), and tri-carbonyl manganese (TCMn) (Oryza Laboratories, Chelmsford, MA, 99.999% purity). Hydrogen was used as both a push gas and carrier gas for the precursors. The hydrogen was supplied from a hydrogen generator (Teledyne Energy Systems, Hunt Valley, MD, HS100) and subsequently purified by a palladium purifier (Johnson Matthey, London, United Kingdom, HP-10).



Figure 3-1: Schematic of the MOVPE deposition system used for this work.

3.1.2 Reactor/substrate preparation

The following section outlines the preparation of the substrate and reactor prior to growth. Both InAs (001) and GaAs (001) epi-ready substrates were used for MOVPE growth of InMnAs and InMnAsP. The semi-insulating GaAs substrates (M/A Com) were double sided polished, 3" in diameter, and 635 μ m thick. In contrast, n-type InAs (Bayville Chemical) were single sided polished, 2" in diameter, and 400 μ m thick. The carrier concentration of the InAs wafers was $3x10^{16}$ cm⁻³. Prior to growth, the GaAs and InAs wafers were diced using a SiC scribe to a sample size of 1x1cm² and 1x0.5 cm² respectively. The diced substrates were then

ultrasonically cleaned for five minutes in acetone (JT Baker 9005-5) and 5 minutes in methanol (JT Baker 9073-5). Next the substrates were dried using UHP nitrogen and loaded on to a graphite susceptor (Poco Graphite NWU-01AJN).

In order to remove growth deposits from the quartz reactor walls, the reactors were immersed in an *aqua regia* (3:1 HCI:HNO₃) for at least 1 hour. Following the acid clean, the reactors were flushed in DI water for 7 minutes. The reactor was then rinsed thoroughly in acetone and methanol and dried in UHP N_2 . The reactor was assembled with the substrates/susceptor on the endcap, and connected to the manifold. The reactor was leak checked using a standard bubble test procedure,⁵⁵ and purged initially in 240 sccm/min of N_2 to eliminate the majority of the air in the reactor. Finally, the reactor was purged in 1000 sccm H_2 for at least 2 hours in the reactor side to remove any residual oxygen and water in the reactor.

3.1.3 InMnAs growth procedure

InMnAs films were grown on GaAs substrates for infrared absorption and electronic transport measurements. Prior to the start of InMnAs/GaAs growths, precursor conditions were set according to that specified in Table 3-1. Precursor flows were sent to the vent side of the manifold. It should be noted that the same flow rates in Table 3-1 were also used for the substrate anneals, buffer layer growth and InMnAs main layer growths. A 1000 sccm H₂ served as the carrier gas for growth. The substrate temperature was then ramped at a rate of 25°C/min to an ultimate temperature of 600°C. During the ramping, AsH₃ was passed over the substrate for temperatures greater than 300°C to prevent decomposition at the substrate surface. The GaAs substrate was annealed in H₂ (1000 sccm) and AsH₃ (50 sccm) at 600°C for 10 minutes to remove any oxides on the surface. Following the substrate anneal, the temperature was lowered

to 400°C, and allowed to stabilize for 1 minute. The TMIn was then switched from the vent to the reactor to start the growth of a low temperature buffer layer. After 5 minutes, the TMIn was switched back to the vent to terminate the buffer layer growth. The temperature was then increased to 480°C for the main growth of InMnAs. The temperature was again stabilized for 1 minute prior to switching TMIn to the reactor. After an additional 5 seconds, the Mn-bypass was opened to the reactor to introduce TCMn metalorganic. The main growth then typically proceeded for 1 hour. To terminate the main growth, the TCMn pneumatic was switched to the vent, and after 5 seconds, the TMIn solenoid was also switched to the vent. The temperature was then rapidly ramped down by manually turning down the current to the heater lamps. The rapid quenching helped to prevent the formation of MnAs precipitates. At 300° C AsH₃ was switched to the vent, and the system was allowed to purge in H₂ for 30 minutes prior to sample removal.

Material	Gas Temperature (°C)	Bubbler Temperature (°C)	Flow Rate (sccm)
H ₂	25	-	1000
AsH ₃	25	-	50
TMIn	-	10	25.5
TCMn	-	55	1.3-7.5

Table 3-1: Typical precursor conditions used for InMnAs growths.

InMnAs was also grown on InAs substrates to improve the surface morphology of the InMnAs films. The superior surface morphology of InMnAs grown on InAs relative to films grown on GaAs is attributed a large reduction in lattice mismatch from 7.2% to 0.6%. The resulting decrease in surface roughness is particularly important for spectroscopic measurements in the reflection geometry, including MOKE. There were two differences between InMnAs growths on InAs and those on GaAs. First, to minimize decomposition, the optimum substrate anneal for InAs occurred at 510°C.¹²⁹ Second, due to the excellent lattice matching between InMnAs and InAs, a buffer layer growth at 400°C was unnecessary. Otherwise the growth procedure and precursor flows are identical to that described in the previous paragraph.

3.1.4 InMnAsP growth procedure

InMnAsP films were grown on InAs substrates to investigate the effect of P addition on the magnetic properties. Prior to growth of InMnAsP, precursors conditions were set according to that specified in Table 3-2. The temperature was then increased at a rate of 25°C/min to an ultimate temperature of 510°C. During the ramp, AsH₃ was switched from vent to reactor side flow at 300°C. The InAs substrate was annealed in H₂ and AsH₃ at 510°C for 10 minutes. The temperature was reduced to 480°C for the main growth, where the temperature was again stabilized for 1 minute. PH_3 was switched to the reactor for 1 minute, to allow the group V gases to mix in the manifold. Then TMIn was introduced to the reactor to begin a 1 minute InAsP buffer layer growth. Finally, the TCMn-bypass was opened to the reactor start the growth of InMnAsP. The main growth then proceeded for 1 hour. To terminate the main growth, the TCMn pneumatic was switched to the vent, and after 5 seconds, the TMIn solenoid was also switched to the vent. The temperature was then rapidly ramped down by manually turning down the current to the heater lamps. At 300°C, $A_{s}H_{3}$ and PH_{3} were switched to the vent, and the system was allowed to purge in N₂ for 30 minutes prior to sample removal. It is important to emphasize that post-growth purge occurred in N₂ instead of H₂. One of the byproducts of the InMnAsP growth is white phosphorous. As white phosphorous is self-igniting, it is therefore important to purge out any potentially flammable gases including H₂.

Material	Gas Temperature (°C)	Bubbler Temperature (°C)	Flow Rate (sccm)
H ₂	25	-	1000
AsH ₃	25	-	50
PH_3	25	-	10-50
TMIn	-	10	25.5
TCMn	-	55	1.3-7.5

Table 3-2: Typical precursor conditions used for InMnAsP growths.

3.2 Structural and compositional characterization

X-ray diffraction (XRD) was used to investigate the crystalline quality, composition and phase purity of the InMnAs thin films. XRD measurements were performed on a diffractometer (Rigaku 12 kW double crystal) equipped with Cu-K_{α 1} radiation, located in the Materials Research Center Diffraction Facility. θ -2 θ scans were measured to determine the phase composition of ternary and quaternary films. Film peaks were indexed with respect to substrate peaks. Rocking curves around the primary film peaks were performed to measure the variation of the out of plane crystal grain tilt. A rocking curve was measured by maintaining the detector (2 θ) at a constant angle while rotating the sample position (θ) around a strong Bragg reflection. Narrower rocking curves correspond to better out of plane alignment and film quality. For films doped with manganese, the presence of MnAs and MnP phases was also investigated.^{130, 131} We emphasize that XRD is a well established technique used to detect nanometer scale magnetic precipitates in nonmagnetic matrices.¹³²⁻¹³⁵ In one specific case, well resolved by θ -2 θ scans around the Fe₃O₄ impurity diffraction peaks were attributed to precipitates 1.8 nm in radius.¹³⁵

The Mn concentration of InMnAs and InMnAsP films was determined by energy dispersive x-ray spectroscopy (EDS). The EDS spectra were measured in a scanning electron

microscope (Hitachi S-3500) with a Ge x-ray detector (Princeton Gamma Tech) at the Electron Probe Instrumentation Center (EPIC). The sample was mounted on an aluminum stage using double sided copper tape and placed inside the SEM. A Faraday cup was placed adjacent to the sample for the purpose of measuring the beam current. Following pump down of the SEM chamber, the accelerating voltage was set at 20 kV. The electron beam was focused into the Faraday cup and a nanoammeter (Keithley Nanoammeter 480) was attached to the sample stage. The beam current was then set to maintain a 1.12 nA beam current. Therefore, use of the Faraday cup guaranteed a consistent beam current for all EDS runs. EDS spectra were measured at 3-9 locations on the sample at a magnification of 150X and an integration time of 120 seconds. The conversion of the x-ray fluorescence peaks to atomic percent was based upon standard EDS spectra generated from a pure Mn sample and an InAs substrate. The conditions for measuring the spectra of the standards, including beam voltage and beam current, were identical to that used for all thin film samples. Consistency in the conditions for standards and samples is necessary for accurate quantitative analysis. However, even with standard based analysis, EDS is sensitive to elemental concentrations of only 0.5%. It should also be noted that the beam voltage of 20 kV used in EDS measurements has a 1-2 µm interaction depth, such that a significant fraction of spectrum was due to the substrate. Therefore, only films grown on GaAs yielded an accurate measurement of the relative Mn to In concentration. Films grown on InAs have a large In background signal, making it difficult to measure the relative In:Mn concentration.

The surface morphology of the thin films was characterized by an atomic force microscope (AFM Jeol 5200) at EPIC. AFM scans ranging from 5x5 μ m to 9x9 μ m were measured with a Si₃N₄ tips at a rate 6 Hz. Scan artifacts were then removed using the

accompanying instrument software (WinSPM DPS v2.02). The RMS roughness was calculated directly from the microscopy images using the same software.

In general, the film thickness and growth rate were determined by profilemetry. InMnAs and InAs thin films grown on GaAs were coated with photoresist (Shipley AZ 1518), hard baked at 90°C for 1 minute, exposed under UV light for 30 s (Quintel Q2000), and then developed (Shipley AZ 400K) for an additional minute. The resulting patterned sample was then etched in a 1:1:1 solution of citric acid:H₂O₂ etch:H₂0. The etch has a 10:1 selectivity between InMnAs, InAs and GaAs, which prevents overetching and thickness measurement errors.¹³⁶ Each etch was terminated when the resistance across the masked and etched portion increased above 1 MΩ. Finally, a surface profiler (Tencor P-10) was used to measure the resulting step edge. It should be noted that the same procedure cannot be used for InMnAs films grown on InAs. The citric acid etch selectivity between the InMnAs and InAs is insufficient to prevent significant unintentional etching of the substrate.

3.3 Optical spectroscopy

3.3.1 Infrared absorption spectroscopy

The infrared transmission spectra of the InMnAs films grown on GaAs (001) substrates were measured using a Bio-Rad FTS-60 FTIR located in the Chemical Analysis Laboratory. The transmission spectra were determined at room temperature between 0.05-0.55 eV. In order to convert the transmission into an absorption coefficient, $\alpha(E)$, the following equation was used:

$$\alpha(E) = \ln(\frac{T_{GaAs}(E)}{T_{InMnAs}(E)}) / d, \qquad 3-1$$

where *d* is the thickness of the InMnAs thin film and T_{InMnAs} and T_{GaAs} are the transmittances of film and substrate respectively. It should be noted that equation 3-1 assumes that the reflectivity between 0.05-0.55 is negligible.⁵² For the case of InAs, reflectivity in the IR is weak in magnitude (0.07) and weakly energy dependent.¹²⁰ The absorption coefficient can also be related to the real part of the optical conductivity, $\sigma_l(E)$ by the formula:¹⁰⁴

$$\sigma_1(E) = \frac{Y + Y_0}{2} \alpha(E), \qquad 3-2$$

where $Y(9.19 \times 10^{-3} \Omega^{-1})$ and $Y_0(2.65 \times 10^{-3} \Omega^{-1})$ are the admittances of the GaAs substrate and free space, respectively.

3.3.2 Visible light reflectance

The reflectivity was measured using a Cary 500 UV/Vis spectrometer coupled with a Varian diffuse reflectance accessory at the Keck I Bio-Physics Facility. Reflectivity spectra were determined over a spectral range of 1.6-3.5 eV at room temperature. The diffuse reflectance accessory consists of a 110 mm integrating sphere coated with a polytrifluorothylene (PTFE). The PTFE integrating sphere is highly efficient for both the collection of diffuse and specular reflectance due to the high reflectivity for PTFE of >98% throughout the visible light range. The reflectance of InMnAs was collected and normalized with respect to that of a PTFE reference plate. The ratio of the reflectance of the InMnAs to the PTFE was then corrected with tabulated data for PTFE in order to obtain the absolute reflectivity (R).

3.4 Magnetic characterization

The field and temperature dependencies of the magnetization (M) were measured in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, model

MPMS) located in the MRC Low Temperature Magnet Facility. The magnetometer consists of a liquid helium dewar for the superconducting magnet coils, SQUID probe, all of which are electronically controlled with a computer. The SQUID is capable of temperature control between 4-400 K, and magnetic fields as large as 5 T. The sensitivity of the SQUID probe is approximately 10⁻⁸ emu.

 M_{total} versus *H* hysteresis loops were measured from -2T to 2T at room temperature. M_{total} , or the measured magnetization is defined by the equation:

$$M_{total}(T,H) = M_{film}(T,H) + M_{substrate}(H) = M_{film}(T,H) + \chi_d H.$$
 3-3

As given in equation 3-3, M_{total} contains contributions from magnetizations of the ferromagnetic thin film (M_{film}) and that of the diamagnetic substrate ($M_{substrate}$). In order to remove the substrate component to obtain an M_{film} versus H loop, a value for the absolute substrate susceptibility (χ_d) must be determined. χ_d was calculated for each sample by first measuring the sample mass using a balance with 10⁻⁴ g precision (Mettler AE 163). Although this measures the mass of both substrate and film, the total mass is an excellent approximation of only the substrate mass (<1% error) given the relative thickness of the substrate (400-635 µm) to the film (<2 µm). The volume of the substrate was then obtained by normalizing with respect to the mass of the density of the substrate. The mass densities used for InAs and GaAs substrates were 5.68 g/cm³ and 5.32 g/cm³ respectively. Determination of the substrate volume by a mass measurement avoids errors in direct volume measurements including substrate thickness variation, poor dicing quality, and inaccurate measurements of substrate size. The substrate volume was then multiplied with respect to the volume susceptibility (κ) with units of emu/cm³G to obtain the absolute susceptibility (χ_d) of the substrate in units of emu/G.⁵⁵ The values of κ used in this study for InAs and GaAs substrates were -1.66x10⁻⁶ emu/cm³G and -1.22x10⁻⁶ emu/cm³G respectively.¹³⁷ The contribution of substrate diamagnetism is then subtracted from the M_{total} versus H loop according to equation 3-3 to obtain the desired M_{film} versus H loop. It should be noted that this can be a major source of error. The resulting film susceptibilities ranged from 1x10⁻⁷ emu/cm³G to 1x10⁻⁸ emu/cm³G, or 1 to 2 orders of magnitude less than the substrate susceptibility.

 M_{total} versus T curves were measured from 5-375 K. For the measurement of InMnAs samples, an applied field of 1 T was used. For InMnAsP samples, field cooled and zero field cooled M versus T curves were measured using a smaller field of 500 G. The substrate background was removed by multiplying the χ_d value obtained by the mass measurement method described above with the applied magnetic field. The resulting $M_{substrate}$ is then subtracted from every M_{total} value for desired the M_{film} versus T curve. This procedure utilizes the fact that χ_d is independent of temperature. It is important to note that M_{total} values were corrected to M_{film} values in any subsequent chapters.

3.5 X-ray absorption spectroscopy/magnetic circular dichroism

X-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) measurements were performed using the soft x-ray beam line (4-ID-C) of the Advance Photon Source. As seen in Figure 3-2a, the instrumentation consists of a circular polarized undulator to provide >96% right (RCP) and left circular polarization (LCP) x-rays.¹³⁸ The circularly polarized x-rays then passes through a spherical grating monochromator that yields high intensity and high energy resolution (~0.3 eV) x-ray radiation between 0.5-3 keV. Following the monochromator, the beam has a diameter of 1mm^2 . Since InMnAs samples measured by XAS and XMCD had

dimensions greater than 0.5 cm^2 , the beam-spot size is far less than the sample size. As given in Figure 3-2b, the sample is placed within a high field chamber at an angle of 45° with respect to the x-ray radiation. The high field chamber applies a variable magnetic field between -7 to +7 T parallel to the incident beam and uses an integrated liquid helium cryostat to vary the temperature between 5 and 300 K.



Figure 3-2: (a) X-ray beam path and the major optical components of sector 4-ID-C. (b) Detailed schematic of the high field chamber.

X-ray absorption of the sample was measured in the high field chamber in both total fluorescence yield (TFY) and total electron yield (TEY). In TFY, the fluorescent photons are detected down to a probe depth of 100 nm using a liquid nitrogen cooled detector (Canberra GUI01105). While TFY has the advantage of being a bulk sensitive technique, it is also susceptible to self-absorption, whereby fluorescent photons are reabsorbed by the sample prior to reaching the photon detector. Self-absorption can significantly reduce the number of detected photons and thereby depress the overall signal to noise of the measurement. TEY monitors the photoelectron emission following x-ray excitation. An ammeter (Stanford Research Systems SR570) measures the drain current necessary to maintain the sample at ground potential. This drain current is equivalent to the photoelectron emission current. It should be noted that the primary mechanism responsible for the creation of these photoelectrons is attributed to Auger emission.¹⁰⁶ In contrast to fluorescent photons, Auger electrons have an escape depth of approximately 5 nm, making TEY a highly surface sensitive measurement.

The total x-ray absorption of a sample was measured with right circularly polarized xrays. The TEY and TFY were then monitored as a function of the photon energy. For XMCD spectra, a 2T magnetic field was applied in order to saturate the magnetization of the sample. The circularly polarized undulator then modulated the polarization between RCP and LCP to sequentially obtain values of TEY_{+}/TFY_{+} and TEY_{-}/TFY_{-} at each photon energy. The XMCD intensity is then defined by the equation below:

$$XMCD = \frac{\alpha_{+} - \alpha_{-}}{\alpha_{+} + \alpha_{-}} = \frac{TEY_{+} - TEY_{-}}{TEY_{+} + TEY_{-}} = \frac{TFY_{+} - TFY_{-}}{TFY_{+} + TFY_{-}},$$
3-4

where α_{\pm} , TEY_±, and TFY_± are the absorption coefficient, TEY, and TFY of left and right circularly polarized x-rays respectively.

3.6 Magneto-optic Kerr effect

Magneto-optical Kerr effect (MOKE) spectroscopy was the primary characterization tool utilized in this thesis. Prior to a discussion of the setups used to measure MOKE spectra in the longitudinal and polar geometries, we introduce some of the formalism of MOKE for the purpose of background. MOKE describes the change in the polarization light state following a reflection off a material with $M \neq 0$. To illustrate the magneto-optic Kerr effect, we begin with the simple case of light polarized along the *y*-axis, and propagating along the *z*-axis. As given in Figure 3-3, the light polarized along the *y*-axis can be resolved into RCP and LCP light waves, each with equal amplitude.¹³⁹ The reflection of light off a sample is given simply in terms of the Fresnel coefficients for RCP and LCP light (\hat{r}_{\pm}):

$$\hat{r}_{\pm} = r_{\pm} e^{i\theta_{\pm}}$$
, 3-5

where r_{\pm} and θ_{\pm} are the amplitudes and phase of the reflected RCP/LCP modes. Graphically, r_{+} and r_{-} correspond to the radii of the red and blue circles in Figure 3-3 respectively. θ_{+} and θ_{-} are the angle between the polarization vector of RCP and LCP and the *y*-axis. In the case of a nonmagnetic sample, where $\theta_{+} = \theta_{-}$ and $r_{+} = r_{-}$, the polarization of the reflected light remains linearly polarized along the *y*-axis. For a reflection off a magnetic sample, there are three potential cases. Some magnetic samples have $\theta_{+} \neq \theta_{-}$ and $r_{+} = r_{-}$. In this case, the reflected beam is also linearly polarized, but the plane of polarization rotates by an angle termed the Kerr rotation (θ_{K}). The Kerr rotation in units of radians is related to the Fresnel phases of RCP and LCP by the equation:

$$\theta_{K} = \frac{\theta_{+} - \theta_{-}}{2}.$$
3-6

Other magnetic samples have $\theta_+ = \theta_-$ and $r_+ \neq r_-$, such that the reflected beam is now elliptically polarized, but the plane of polarization remains parallel to the *y*-axis. The ellipticity of the reflected light is defined by the reflection magnetic circular dichroism (ϕ):

$$\phi = \frac{2(r_{+}^{2} - r_{-}^{2})}{(r_{+}^{2} + r_{-}^{2})} = \frac{R_{+} - R_{-}}{R},$$
3-7

where $R_{\pm} = r_{\pm}^2$ are the reflectivities of RCP and LCP light, and the total reflectivity is defined by:

$$R = \frac{1}{2}(r_{+}^{2} + r_{-}^{2}).$$
3-8

As given in equation 3-7, ϕ is equal to the difference in reflectivities of RCP and LCP normalized by the total reflectivity. From a graphical perspective, ϕ is twice the difference of the squares of the semi-major and semi-minor axes of the reflected ellipse normalized by their sum. In general, magnetic samples have both $\theta_{+} \neq \theta_{-}$ and $r_{+} \neq r_{-}$ yielding an elliptically polarized beam with the semi-major axis rotated by θ_{K} with respect to the *y*-axis and an ellipticity defined by ϕ .¹⁴⁰



Figure 3-3: Input and reflected polarization states at $t = t_0$ and $t = t_0 + \delta$. The reflected polarization state is given for a (a) nonmagnetic sample (b) magnetic sample inducing a pure θ_K (c) magnetic sample inducing a pure ϕ (d) magnetic sample both θ_K and ϕ . Red and blue arrows give the RCP and LCP components of the polarization vector. Black is the resultant. Green line gives the plane of polarization.

3.6.1 Longitudinal MOKE

The longitudinal MOKE apparatus described in the following sections was primarily designed to measure θ_K as a function of the in-plane magnetic field. Since this MOKE apparatus was custom built for this project at Northwestern University, its design and operation will be extensively discussed.

3.6.1.1 Optical layout of the longitudinal MOKE setup

A schematic of the longitudinal MOKE setup is given in Figure 3-4, that is modeled after an apparatus described by Qui *et al.*¹⁴¹ A picture of the setup is shown in Figure 3-5. The light source is a stabilized 1.95 eV, 1 mW He-Ne laser (JDSU 1100) modulated at approximately 330 Hz by an optical chopper (Scitec 300C). The incident light is polarized along the x-axis using a Glan-Thompson polarizer (Thorlabs GTH-10) mounted in a precision rotation mount (Thorlabs PRM05). The rotation mount uses a micrometer dial for precise changes in the polarization angle down to a resolution 0.02°. The light then reflects off the sample at an angle of 20°, which corresponds to the maximum angle incidence prior to clipping the light by the magnet coils. The maximum angle of incidence is used because the longitudinal Kerr effect increases linearly with respect to the angle of incidence from $0-60^{\circ}$.¹⁴² A magnetic field is applied parallel to the sample surface and plane of incidence as defined by the longitudinal MOKE geometry. The sample is mounted on a combination rotation/kinematic mount using a double-sided adhesive tab (SPI Supplies 05095-AB). The rotation part of the mount allows for changes in the azimuthal angle with a minimum resolution of 15°. Upon reflection, the light passes through an aperture that indicates the optimal alignment for the reflected beam. The light transmits through an analyzer (Thorlabs GTH-10) with its polarization at an angle $+\delta$ from the y-axis. The light is then focused into a photomultiplier tube (Hamamatsu R928) using a 12.5 cm focal length lens (Thorlabs LA1384). The photomultiplier (PMT) utilized in the setup is sensitive between 1.5-6.7 eV.



Figure 3-4: (a) Schematic of the setup used for longitudinal MOKE measurements. (b) Polarization geometry of the optics used. The *x*-axis is parallel to the plane of incidence and the applied field.



Figure 3-5: Photograph of the longitudinal MOKE setup. Major optical components are labeled in white.

An expression for the light intensity detected by the PMT (I_{Kerr}) for the longitudinal MOKE setup shown in Figure 3-4 is as follows:

$$I_{Kerr} = I_0 (1 + \frac{2\theta_K}{\delta}), \qquad 3-9$$

where θ_K is the Kerr rotation and δ is the offset angle of the analyzer polarizer. The derivation of equation 3-9 using the Jones matrix formalism is given in Appendix A.1. From equation 3-9, it is evident that I_{Kerr} for the given setup is linearly proportional to θ_K , but independent of the RMCD (ϕ).

3.6.1.2 Electronic configuration of the longitudinal MOKE setup

To illustrate the detection and the subsequent signal processing of the Kerr intensity, a schematic diagram for the longitudinal MOKE setup is given in Figure 3-6. The Kerr response, I_{Kerr} , is first converted to a photocurrent using a PMT driven by a 1.25 kV DC power supply (Stanford Research Systems PS 310). The output of the PMT is connected to the lock-in amplifier in parallel with a 300 k Ω load resistor (Princeton Applied Research 5208). The 300 k Ω load resistor reduces signal attenuation due to poor impedance matching between load and driving circuits. The lock-in amplifier is referenced to a 330 Hz TTL signal from the chopper controller box. Typical settings for the lock-in amplifier are given in Table 3-3. Finally, the analog voltage output of the lock-in amplifier is measured by a personal computer via a D/A card (National Instruments 6014). The voltage output from the lock-in amplifier, termed the Kerr voltage (V_{Kerr}), is proportional to the Kerr intensity by a gain factor g such that:

$$V_{Kerr} = gI_{Kerr} = gI_0(1 + \frac{2\theta_K}{\delta}) = V_0(1 + \frac{2\theta_K}{\delta}).$$
3-10

In order to determine the desired hysteresis loops, V_{Kerr} is measured as a function of the applied magnetic field. The parameters V_0 and the offset angle δ can be measured using a method described in the next section. A personal computer with the D/A card interface is used to control and measure the magnetic field. The analog output of the D/A card outputs a 0-10 V signal that connects directly to a signal control port on the magnetic field, is directly proportional to the 0-10 V signal. The magnetic field is measured using a gaussmeter (FW Bell 5080). The analog output of the gaussmeter outputs 0.1 V/kG, and is interfaced with the computer via the D/A card.

Table 3-3: Typical settings for the PAR 5208 lock-in amplifier during longitudinal MOKE magnetometry scans.

Lock in Amplifier Setting		PAR 5208 Value	PAR 5208 Value		
Measurement Mode		Volts Channel A	Volts Channel A		
(Chassis	Grounded	Grounded		
	Sensitivity	300 µV	300 µV		
Filter		Band Pass-Track	Band Pass-Track		
Refe	rence Input	330 Hz TTL	330 Hz TTL		
Reference Phase		200°	200°		
Display	Time Constant	100 ms	100 ms		
DC Power Supply (SRS PS 310)	PMT (HM R928)	Lock In Amplifier (PAR 5208) (FW Be	ssmeter ell 5080)		
50 Ω BN		Ω BNC Ref. Out: Banana Jack 100 kΩ Ioad	Analog Input 0,1 (NI 6014)		
Magnet Power Supply (Varian V2900)	Optical Chopper (Scitec 300C)	Chopper Controller (Scitec 300C)	sonal nputer ium III)		
	4 pi Bana	in DIN	Analog Output 1 (NI 6014)		

Figure 3-6: Wiring diagram for electronics used in the longitudinal MOKE setup.

3.6.1.3 Longitudinal MOKE measurement procedure

The following section outlines the procedure used to measure longitudinal θ_{K} versus *H* hysteresis loops utilizing the setup described in sections 3.6.1.1 and 3.6.1.2. For the measurement, the sample was glued to the rotation/kinematic mount with a double-sided adhesive tab (SPI Supplies 05095-AB). The kinematic portion of the mount was used to compensate for variability in the adhesive tabs and align the reflected beam through the alignment aperture. The voltage output of the lock-in amplifier was minimized using the micrometer dial on the analyzer polarizer. The gain of the PMT was set such that the lock-in amplifier detects a 15-30 μ V signal at the extinction condition. The extinction condition is defined by minimum lock-in amplifier signal with respect to the analyzer angle. The analyzer micrometer dial was then rotated counterclockwise to increase the lock-in amplifier output by an additional 30 μ V. The offset angle δ specified in equation 3-10 equals the difference in the analyzer dial angle before and after the analyzer rotation.

 V_{Kerr} was then measured as a function of the applied magnetic field. The measurement was automated using the Labview program named "KerrHystersis11.vi" The program measures the number of loops specified, and signal averages the V_{Kerr} and H field values in real time. With the stabilized He-Ne laser, as many as a hundred signal-averaged loops were required to resolve a θ_K value of 0.1 mdeg. For θ_K values greater than 1 mdeg, approximately 20 loops yielded V_{Kerr} versusH plots with sufficient signal to noise ratios. For an easy axis measurement, H was scanned out to a maximum field of 0.3 T, as this field was sufficient to saturate the magnetization of InMnAs. In contrast, larger saturation fields along the hard axis of InMnAs required a maximum field of 0.6 T. The field step size was varied to maintain a constant number of field steps for each measurement. Finally, the dwell time at each magnetic field was set to a low value of 100 ms to minimize the effects of long-term drift of laser intensity or PMT response. The output of "KerrHysteresis11.vi" is a V_{Kerr} versus H plot similar to that given in Figure 3-7. In order to convert the V_{Kerr} versus H to a θ_K versus H plot, a value for V_0 was obtained by determining the average V_{Kerr} at positive and negative saturation fields $(\pm H_s)$. With V_0 and δ as known parameters, equation 3-10 can be used to convert V_{Kerr} at each magnetic field, yielding the desired θ_K versus H plot.



Figure 3-7: Example V_{Kerr} versus H plot. V_{Kerr} at positive and negative saturation fields and V_0 are labeled on the right hand side of the plot.

3.6.2 Polar MOKE

There are two important distinctions between the longitudinal MOKE instrument described in section 3.6.1 and the polar MOKE setup described in the following section. The first is that polar MOKE measures the change in polarization upon reflection with the field applied

perpendicular to the sample plane. The primary advantage of polar MOKE is that the magnitude of the Kerr rotation and RMCD measured in the polar geometry are approximately 10 times greater than that measured in the longitudinal geometry.¹⁴² The order of magnitude increase in signal is especially significant in spectroscopic MOKE measurements whereby a tungsten halogen lamp is used instead of a laser. The increase in signal gained by changing the measurement geometry helps to offset the loss in signal to noise resulting from the use of a tungsten halogen lamp rather than a laser. The second difference between the two MOKE setups is that the polar MOKE apparatus utilizes a photoelastic modulator (PEM). By modulating the polarization, the PEM allows for a *simultaneous* measurement of both θ_{K} and ϕ . The measurement of the spectroscopic dependence of ϕ is particularly important given that the RMCD spectrum is used as a measure of the presence and magnitude of *sp-d* exchange (see section 2.4.3). As is evident in equation 3-10, the longitudinal MOKE setup described in section 3.6.1 does not measure the RMCD.

3.6.2.1 Polar MOKE setup

The polar Kerr effect was measured in a setup similar to that described by Sato *et al.*¹⁴³ A schematic and photograph of the apparatus are shown in Figure 3-9 and 3-10 respectively. For spectroscopic measurements, a 150 W tungsten halogen lamp (Stocker Yale 300 C) coupled with a monochromator (Jobin Yvon H-20) is used. The spectral range of the monochromator and lamp is limited to measurements between 1.6-3.0 eV. For temperature and field dependence measurements, a broadband source is not necessary. Therefore a 1 mW He-Ne laser (JDSU 1100) or a 100 mW Krypton-Argon (Spectra-Physics 245 exciter) are utilized. The use of the two lasers allows for high signal to noise measurements of the polar MOKE at discrete photon

energies including 1.95, 2.40, 2.54, and 2.68 eV. The light intensity is modulated using the chopper (Scitec 300C). As given in Figure 3-8, a 15 cm focal length lens focuses the light onto the sample. The light transmits through a polarizer oriented 45° from the y-axis, and then the photoelastic modulator with its fast axis parallel to the x-axis (Hinds PEM-80). The incident light passes through a 1.25" hole drilled through the center axis of one of the magnet pole faces. The light reflects off the sample at an angle of incidence of 3°. This small angle of incidence balances the need to spatially separate the input and reflected optical components, while simultaneously maximizing the polar Kerr effect. For room temperature measurements, the sample is placed in either optical mount identical to that described in section 3.6.1.1. A discussion of modifications to the setup necessary for measurements between 13-400 K is described in section 3.6.2.3. Upon reflection from the sample, the light reflects at an angle approximately 45° from the sample normal using a 1" silver mirror (Thorlabs PF10-03-P01). The large size of polarizers and PEM necessitates the use of a mirror to provide further separation between the reflection and input optics. The light then transmits through the analyzer oriented along the x-axis and an aperture used to define the optimum reflected beam path. Finally the light is focused into the PMT (Hamamatsu R928) using a 12.5 cm focal length lens. The PMT used has a sensitivity range of 1.5-6.7 eV.



Figure 3-8: (a) Schematic of the setup used for polar MOKE. (b) Geometry of the polarizing optics used with their respective Jones matrices. The *x*-axis is parallel to the plane of incidence.



Figure 3-9: Picture of the polar MOKE setup. The major optical components are highlighted in white. The 12.5 cm focal length lens is obscured from view by the analyzer.

The Kerr intensity measured by the PMT (I_{Kerr}) for the polar MOKE setup given in Figure 3-8 is given by the expression:

$$I_{Kerr} = I(0) + I(\omega)\sin\omega t + I(2\omega)\sin 2\omega t .$$
3-11

In equation 3-11, I(0), $I(\omega)$, and $I(2\omega)$ are defined by the equations.

$$I(0) = I_0 + J_0(\Gamma_0)\theta_K \approx I_0,$$
 3-12

$$I(\omega) = 2I_0 \phi J_{\perp}(\Gamma_0) \qquad , \qquad 3-13$$

$$I(2\omega) = 2I_0 \theta_{\kappa} J_2(\Gamma_0), \qquad 3-14$$

where $J_n(\Gamma_0)$ is the n^{th} order Bessel function evaluated at the phase oscillation amplitude of the PEM (Γ_0), ϕ is the RMCD and θ_K is the Kerr rotation. Equations 3-11 to 3-14 are derived by the Jones matrix method in Appendix A-2. The output intensity measured by the detector therefore consists of three applicable components: a dc component, a component at the frequency of the PEM (ω), and a component at 2ω Assuming that $\theta_K << I_0$, a measurement of the dc component will yield an accurate measurement of I_0 . It should also be noted that $I(\omega)$ and $I(2\omega)$ are proportional to the RMCD and Kerr rotation respectively.

3.6.2.2 Electronic configuration of the polar MOKE setup

The electronics used for the signal processing of I_{Kerr} given by equation 3-11 are drawn schematically in Figure 3-10. A PMT (Hamamatsu R928) driven by a 1.25 kV DC power supply (Stanford Research Systems PS 310) converts I_{Kerr} to a photocurrent. The PMT current output is connected in parallel with a 10 k Ω load resistor and a low noise voltage preamplifier (EG&G 500) with a gain of 10³. In order to detect signals at ω (42 kHz) and 2 ω (84 kHz), a 10 k Ω resistor is necessary to eliminate RC time constant attenuation. The 10 k Ω resistor provides a voltage to current gain of 10^5 V/A. The use of the preamplifier increases the total voltage to current gain to 10^8 V/A. Next the output of the preamplifier is split and connected to three separate lock-in amplifiers to simultaneously measure the DC, ω , and 2ω components of the Kerr intensity. The first lock-in amplifier (Princeton Applied Research 5208) is referenced to the frequency of the chopper (330 Hz) and therefore detects the magnitude of I(0). The second (Princeton Applied Research 5209) and third (Princeton Applied Research 5210) lock in amplifiers are referenced at ω and 2ω to detect the magnitude of $I(\omega)$ and $I(2\omega)$ respectively. Typical settings for the three lock-in amplifiers are given in Table 3-4.

Table 3-4: Typical settings for the three lock-in amplifiers used for polar MOKE measurements.

Lock-in Setting	PAR 5208 Value	PAR 5210 Value	PAR 5210 Value
Measurement Mode	Volts Channel A	Volts Channel A	Volts Channel A
Chassis	Grounded	Grounded	Grounded
Sensitivity	5 V	10 mV	30 mV
Filter	Band Pass-Track	Band Pass-Track	Band Pass-Track
Reference Input	330 Hz TTL	42 kHz TTL	84 kHz TTL
Reference Signal	200°	-118°	-120°
Display Time Constant	100 ms-3s	100 ms-3s	100 ms-3s



Figure 3-10: Wiring diagram for electronics used in the polar MOKE setup.

The voltage outputs of the lock-in amplifiers can be expressed as follows in terms of equations 3-12-3-14:

$$V(0) = g_1 I(0) = g_1 I_0, \qquad 3-15$$

$$V(\omega) = g_2 I(\omega) = 2g_2 I_0 \phi J_1(\Gamma_0), \text{ and}$$
3-16

$$V(2\omega) = g_3 I(2\omega) = 2g_3 I_0 \theta_{\kappa} J_2(\Gamma_0).$$
 3-17

where g_1 , g_2 , and g_3 are the respective gain factors for the lock-in amplifiers referenced to the chopper, ω , and 2ω . Each of the three lock-in voltages is transmitted to the computer through the D/A card. However, in order to convert the lock-in voltages to values for θ_K and ϕ , additional data processing within the Labview software interface is required. First $V(\omega)$ and $V(2\omega)$ in equations 3-16 and 3-17 are normalized by V(0) from equation 3-15 to yield:

$$V(\omega)/V(0) = 2\frac{g_2}{g_1}J_1(\Gamma_0)\phi = AJ_1(\Gamma_0)\phi$$
, and 3-18

$$V(2\omega)/V(0) = 2\frac{g_3}{g_1}J_2(\Gamma_0)\theta_K = BJ_2(\Gamma_0)\theta_K.$$
3-19

The normalization of $V(\omega)$ and $V(2\omega)$ by V(0) is particularly important because the ratios of $V(\omega)/V(0)$ and $V(2\omega)/V(0)$ are independent of I_0 . Since I_0 , defined by equation 3-12 is a function of output lamp intensity and monochromator sensitivity, the normalization procedure corrects for the spectroscopic dependence of the lamp and monochromator. Next, the constants A, B, $J_1(\Gamma_0)$ and $J_2(\Gamma_0)$ must be determined. The gain factors A and B were 1.125 and 1.538 respectively using a calibration procedure described previously.¹⁴³ The amplitude of the retardation (Γ_0) was kept constant at 2.629 throughout the visible light range by supplying a wavelength proportional voltage to the input of the PEM controller (Hinds PEM 80). Therefore, Labview uses the equations below to calculate the desired Kerr rotation and RMCD in terms of the voltage ratios given in equations 3-18 and 3-19:

$$\phi = \frac{1}{1.125J_1(2.629)} \frac{V(\omega)}{V(0)} = 1.922 \frac{V(\omega)}{V(0)} \text{ and}$$
 3-20

$$\theta_{\kappa} = \frac{1}{1.538J_2(2.69)} \frac{V(2\omega)}{V(0)} = 1.406 \frac{V(2\omega)}{V(0)}.$$
3-21

The Labview interface also controls the photon energy for spectroscopic measurements through a parallel port connection between the computer and the monochromator. The magnetic field is controlled and measured in an identical manner to that described in section 3.6.1.2. Software control of the temperature is described in the next section.

3.6.2.3 Temperature dependent MOKE setup modifications

A closed cycle optical cryostat connected to a helium compressor (Displex DE202) is used to vary the sample temperature between 13-400 K. The temperature of the sample is stabilized using a temperature controller (Lakeshore 330) interfaced with a calibrated silicon diode (Lakeshore DT-470-SD-13) and Ni-Cr (Lakeshore NC-32) resistive wire. A diffusion pump (Leybold Diffusion 170) is used to pump the cryostat to a base pressure of 5×10^{-5} torr prior to activation of the compressor for sample cooling.

In order to integrate the cryostat with the polar MOKE setup, a custom aluminum table was built on top of the magnet-yolk. A hole in the table allows for a top-down mounting of the cryostat with the sample cold finger centered between the magnetic pole faces. A schematic of the cryostat integrated with the magnet is given in Figure 3-11a. However, without any additional modifications to the cryostat, the quartz window on the cryostat vacuum shroud that allows for optical probing is not only in between the polarizer and analyzer, but also between the magnet pole faces. Therefore the Faraday effect from the quartz window will be measured in the configuration given in Figure 3-11a. The equations for the Faraday effect are given as follows:

$$\eta_F = V_{n,F} l H , \qquad 3-22$$

$$\theta_F = V_{\theta,F} l H , \qquad 3-23$$

where η_F and θ_F are the Faraday dichroism and rotation, $V_{\eta,F}$ and $V_{\theta,F}$ are the dichroism and rotation Verdet constants, and *l* is the thickness of the material. It is important to emphasize that the PEM setup used to measure polar MOKE will measure the Faraday dichroism and rotation as spurious RMCD and Kerr rotation signals respectively.¹⁴⁰ Moreover, since the applied magnetic field on the sample is equal to that of the window, the Faraday effect from the window cannot be subtracted from a MOKE spectrum by measuring spectra in both positive and negative fields. In fact, the MOKE spectrum would be a combination of the Faraday spectrum of the window and the MOKE spectrum of the sample. In the case of hysteresis loops, the Faraday effect of the window would result in a hysteresis loop on top of a linear background. Both the linear background and contribution to the spectrum due the Faraday effect of the window will be large in comparison to the MOKE due to the sample. To demonstrate this point, the Faraday dichroism and rotation of a quartz window at 1.95 eV are 11 mdeg/T and 375 mdeg/T respectively. The typical magnitude of the θ_K and ϕ from an InMnAs sample ranges between 1-10 mdeg.



Figure 3-11: Side view of the cryostat integrated with the MOKE magnet, (a) before and (b) after the addition of the vacuum tube.

In order to eliminate the spurious Faraday effect, the window was epoxied to the end of a brass vacuum tube. The vacuum tube extends through the hole in the magnet pole face. A leak tight connection between the cryostat and the vacuum tube was made by a standard quick connect flange (Kurt Lesker B125-KM). The male portion of the quick connect flange was hard-soldered directly on the vacuum shroud while the female portion slips over the brass vacuum tube. The flange allows for a straightforward removal of the vacuum tube for sample changes, while providing a high vacuum seal. Following the addition of the vacuum tube, the maximum applied field on the window reaches 50 G as opposed to 0.5 T. As shown in Figure 3-12, this leads to a reduction in the window Faraday effect by two orders of magnitude.



Figure 3-12: θ_K versus *H* measured for a Si substrate at 1.95 eV with and without use of the vacuum tube.

The final modification to the MOKE cryostat was the addition of a temperature controller (Lakeshore 320) to regulate the temperature of the brass vacuum tube. The 0-80 A of current inside the magnet poles generates enough heat to significantly change the temperature of the

brass tube and the quartz window. Differences in the thermal expansion coefficients of the window and vacuum tube are sufficient to create a strain on the window, which in turn generates another spurious dichroism signal that affects the measured RMCD. The strain-induced dichroism is extremely sensitive to small changes in the brass tube temperature. A 1°C change in the brass tube corresponds to a 10 mdeg change in the strain induced dichroism. Since the temperature of the tube can increase over 5°C over the course of a MOKE spectrum measurement, the strain-induced dichroism can also overshadow any sample RMCD. The spurious signal caused by strain-induced dichroism can be eliminated by regulating the temperature of the vacuum tube. A resistive wire (Lakeshore NC-32) and a Si diode sensor (Lakeshore DT-470-SD-13) were wrapped around the tube and then coated in a layer of varnish to improve the thermal contact. The temperature of the vacuum tube was set slightly above room temperature at 300 K. In this way, any changes in temperature due to the magnet coil heating could be compensated with a drop in heater current. Using this temperature control system, the vacuum tube temperature was regulated to within 0.1 K for over two hours. A schematic and picture of the cryostat setup following the addition of a temperature-regulated vacuum tube are given in Figure 3-11b and Figure 3-13 respectively. The effect of the temperature controller on the RMCD spectrum of undoped Si is shown in Figure 3-14. While the desired null spectrum is obtained with a temperature regulator, a large spurious RMCD spectrum was measured without the temperature regulator.



Figure 3-13: Photograph of the polar MOKE cryostat following the addition of a temperature regulated vacuum tube.



Figure 3-14: ϕ versus *E* for a Si substrate with the sample temperature at 100 K, with and without temperature regulation of the quartz window.

3.6.2.4 Polar MOKE measurement procedure

This section outlines the procedure for measuring polar MOKE hysteresis loops, temperature dependence, and spectra using the setup outlined in sections 3.6.2.1, 3.6.2.2, and 3.6.2.3. As before, samples were first mounted using adhesive tabs (SPI supplies 05095-AB) on the azimuthal/kinematic mount for room temperature measurements. For low temperature measurements, the samples were mounted to the cryostat cold finger using varnish (Lakeshore 7031). The reflected beam was then aligned with respect to the output aperture.

Spectroscopic measurements were automated by the Labview program, "KerrSpec4.vi." The program first applied a +0.5 T magnetic field perpendicular to the plane of the sample. The program started at a photon energy of 1.6 eV and increments the photon energy up to 3.0 eV. At each energy ϕ and θ_K were measured automatically according to equation 3-20. The dwell time at each energy was set to 3s. A large dwell time is necessary due to the low output intensity of the tungsten halogen lamp. The energy step size is limited by the monochromator slit width. For all MOKE spectra, a 2 mm slit width, corresponding to an 8 nm resolution was used. The program then reversed the field to apply a field of -0.5 T, and measured another spectrum. "KerrSpec4.vi" output individual files for the spectra determined in positive and negative fields. The spectra at ± 0.5 T were both necessary because the polar MOKE setup measures the changes in polarization due to all optical components between the polarizer and analyzer. This includes not only the sample, but also the PEM, 1" silver mirror, and quartz window in the case of low temperature measurements. However, if the two spectra at ± 0.5 T are subtracted and normalized by 2, the background is removed because the magnetic field near the mirror, PEM, and quartz window is approximately 0. In contrast, the sample is directly in a ± 0.5 T magnetic field. Successive MOKE spectra were measured to improve the signal to noise of the final spectrum.

Polar MOKE hysteresis loops were also determined automatically using the program "KerrHysteresis14.vi." The scan parameters for polar hysteresis loops were similar to that described in section 3.6.1.3. However, the out of plane axis of InMnAs is the hard axis due to shape anisotropy. Therefore, loops were measured out to a maximum field between 0.5-0.6 T with a field step size between 50-60 G respectively. The dwell time at each field was set at 100 ms to minimize drift. Since, the polar Kerr effects are typically larger than longitudinal Kerr effects, only 10-20 loops were required to obtain loops with high signal to noise. The output of the "KerrHysteresis14.vi" was a single file containing the field, Kerr rotation and RMCD data. While ϕ and θ_K were in real units of mdeg, the polarization artifacts from the PEM, mirror, and quartz window results in a simple shift along the *y*-axis. The magnitude of the shift is the average
of ϕ ($\pm H_s$) and θ_K ($\pm H_s$). These shifts were subtracted out of the respective ϕ versus *H* and θ_K versus *H* plots to obtain symmetric loops about the *x*-axis.

Finally, the temperature dependent measurements were made automatically using the program "TemperatureScan2.vi" The program prompts the user for a temperature range and step size. The scan began at the maximum temperature and decreased the temperature incrementally. Each temperature was allowed to stabilize for 5 minutes, after which ϕ and θ_K were measured in both positive and negative 0.5 T for 1 s. The program subtracted the values and normalized by 2 automatically to subtract out the spurious polarization artifacts.

4. **Results: Mn related electronic states**

Infrared absorption (IAS), x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) spectroscopies are utilized to determine the presence and electronic state of Mn related impurity bands in MOVPE InMnAs. First principles calculations have *predicted* that atomic scale clusters in InMnAs observed by EXAFS³⁶ result in the formation of a shallow and deep Mn impurity band near midgap.^{39, 78} Raebiger *et al.* assert that the deep Mn impurity band tightly binds holes within clusters while the shallow band contributes itinerant holes to the valence band at room temperature.^{39, 78} Since both itinerant and bound holes can participate in long-range exchange interactions, ^{40, 41} the properties of the Mn impurity bands corresponding to the two distinct hole species are of particular importance for understanding ferromagnetism in MOVPE InMnAs. Therefore, the electronic properties of shallow and deep impurity bands and their effect on holes were characterized by IAS and XAS/XMCD.

In the first half of the chapter, the results from the IAS spectra are presented. First, transitions from ionized Mn states in a shallow impurity band to the conduction band are observed near the band gap of MOVPE InMnAs. Moreover, from the free carrier absorption in the far IR range of the spectrum, we may infer the existence of two hole species at room temperature: itinerant holes in the valence band from ionized acceptors in the shallow impurity

band, and tightly bound holes that reside in a deeper impurity band. A Drude model fit of the free carrier absorption is utilized to quantitatively determine the room temperature concentrations of the two types of holes in MOVPE InMnAs.

In the second half of the chapter, XAS and XMCD are used as element and orbital specific spectroscopic probes of the electronic state of both the shallow and deep Mn 3*d* impurity band states. More specifically, an atomic multiplet model of the XAS spectrum is utilized to determine the ground state configuration of Mn and the itinerancy of the 3*d* electrons. The XMCD demonstrates that the Mn 3*d* impurity states associated with Mn clusters are spin split at room temperature. Finally, the temperature dependence of the XMCD indicates the presence of two ferromagnetic species, which are attributed to large and small of cubic Mn clusters.

4.1 Infrared absorption spectroscopy

4.1.1 Shallow impurity band absorption

Shallow Mn acceptor states in MOVPE InMnAs are particularly significant because they contribute free holes that potentially mediate exchange between clusters. In order to determine the properties of a shallow Mn acceptor, the infrared absorption spectrum near the band gap (0.25-0.4 eV) was studied for an undoped InAs film and 5 In_{1-x}Mn_xAs films grown on GaAs. A reduction of the band gap from undoped to doped films has been previously attributed to the formation of a shallow impurity band in the band gap.⁹⁸ Table 4-1 summarizes the composition, thickness, and optical properties of the films used in this study. Plots of the absorption coefficient squared (α^2) as a function of energy at *T*=298 K for the undoped InAs film (ajb 145) and three In_{1-x}Mn_xAs films with *x*=0.002 (ajb 059), 0.01 (ajb 156) and 0.03 (ajb 191) are shown in Figure 4-1. For ease of comparison, the α^2 values corresponding to each of the three samples

were normalized by their respective values at 0.4 eV. The importance of an α^2 versus *E* dependence is that the resulting plot yields the band gap (*E*₀) for a direct gap semiconductor. As given by following equation:⁵²

$$\alpha(E) \propto (E - E_0)^{1/2}, \qquad 4-1$$

transitions between parabolic valence and conduction bands of a direct gap semiconductor yield a linear α^2 versus *E* plot for $E > E_0$, where the *x*-intercept equals the band gap. The InAs film, ajb 145, exhibits a classic linear dependence that is characteristic of a direct gap semiconductor. An extrapolation of the α^2 versus *E* for ajb 145 to the *x*-axis given by the red dotted line in Figure 4-1 yields a value of 0.357 eV for the bandgap of InAs. This agrees well with previous room temperature measurements of the bandgap (0.354 eV) for undoped InAs.¹⁰¹



Figure 4-1: Plot of normalized α^2 versus photon energy for InAs (ajb 145), In_{1-x}Mn_xAs with x<0.01 (ajb 059) and 0.03 (ajb 191) at *T*=298 K. All α^2 values are normalized with respect to $\alpha^2(0.4 \text{ eV})$.

Sample #	x	Thickness (nm)	$E_{\theta}(\mathrm{eV})$	E _{URB} (meV)
ajb 145	0	2800	0.357	27
ajb 059	0.002	900	0.335	67
ajb 156	0.010	970	0.333	77
ajb 191	0.034	490	0.334	82
ajb 190	0.070	420	0.333	93
ajb 197	0.085	350	0.334	98

Table 4-1: Structural and room temperature optical properties of $In_{1-x}Mn_xAs$ thin films grown on GaAs investigated in section 4.1.

In contrast, the plots of α^2 as a function of energy for the InMnAs films are nonlinear near the band edge, presumably due band tailing. The nature of band tailing in InMnAs will be discussed later in this section. To account for nonlinearities in the α^2 versus *E* dependence due to band tailing, the maximum E_0 was determined from a linear fit of α^2 versus *E* plot between 0.36-0.40 eV in Figure 4-1. In this spectral range, the absorption is not significantly affected by band tailing such that α^2 retains a linear dependence on energy for InMnAs samples. It should be noted that linear fits over a wider spectral range yielded smaller values for E_0 . The linear fit between 0.36-0.4 eV for InMnAs, given by the black dotted line in Figure 4-1, resulted in a maximum E_0 of 0.334 eV for the lightly doped sample with *x*=0.002. The same procedure was utilized to determine the maximum E_0 for the other 4 samples. The corresponding dependence of the maximum E_0 with respect to *x* is shown in Figure 4-2. In Figure 4-2, there is an abrupt reduction of the band gap from InAs to lightly doped In_{1-x}Mn_xAs (*x*=0.002) by 23 meV. For 0.002<*x*<0.09, E_0 nearly remains constant at 0.334 eV.



Figure 4-2: Maximum room temperature band gap versus x in $In_{1-x}Mn_xAs$ films grown on GaAs substrates. Solid line is a guide to the eye.

The rapid decrease in the band gap from undoped InAs to lightly doped InMnAs is attributed to the formation of a Mn related impurity level, 23 meV above the valence band maximum. This implies that the observed absorption that leads to the reduction in E_0 corresponds to transitions between the impurity level and the conduction band. Such impurity band to conduction band transitions are indicated by the orange arrow in Figure 4-3a. We note that in the case of MBE grown InMnAs, the Mn impurity band is degenerate with the valence band. Consequently, E_0 of InMnAs grown by MBE is nearly identical to that of undoped InAs at 0.355 eV.¹⁹ However, we emphasize that studies of Zn doped InAs films exhibited a similar reduction in band gap between undoped and doped films that was assigned to the formation of a Zn impurity band 40 meV above the valence band maximum.⁹⁸ In addition, the depth of the Mn impurity level in MOVPE InMnAs measured by optical absorption is consistent with effective

mass theory and electronic transport measurements. Effective mass theory predicts an E_A of 29 meV assuming a hole effective mass of 0.33 m_e and a dielectric constant of 12.5 equal to that of undoped InAs.⁹⁹ A hole ionization energy of 21 meV was also measured by May and coauthors using variable temperature Hall effect.¹⁴⁴

The independence of the maximum band gap on the Mn concentration is also consistent with electronic transport measurements.¹⁴⁵ As *x* increases, the number of Mn states in the gap increases, which then broadens the Mn impurity level into an impurity band.¹⁴⁵ Since E_0 corresponds to transitions from the top of the Mn impurity band (E_T) to the conduction band, the effect of impurity band broadening alone should result in a decrease E_0 with increasing *x*. However, Hall effect measurements in MOVPE InMnAs and other doped semiconductors also indicate a decrease in the activation energy, E_A , with an increase in impurity concentration.^{145, 146} As given in Figure 4-3b, in the case of an impurity band, E_A corresponds to the energy difference between the VBM and the center of the impurity band. The near edge absorption measurements of alloyed samples indicate that an increase in *x* leads to both an increase in E_T and a decrease in E_A . The two effects balance to yield an invariant E_0 with *x*.



Figure 4-3: Schematic energy level diagram for MOVPE $In_{1-x}Mn_xAs$ films. E_T-E_A corresponds to the half width of the impurity band. Orange, green, and purple correspond to shallow impurity band to conduction band absorption, intervalence band absorption, and free carrier absorption respectively. Exchange splitting of the bands are omitted from this schematic for simplicity.

Finally we provide the rationale for previously ascribing the nonlinearity in the α^2 versus E plots to band tailing. Band tailing refers to the formation of conduction band and valence band tail states extending into the band gap, caused by the incorporation of ionized impurities such as Mn.¹⁴⁷⁻¹⁴⁹ The attribution of nonlinearities in the α^2 versus E plots to band tailing is supported by the Urbach-Martienssen rule, which states that the absorption corresponding to transitions between band tails is given by the equation:¹⁰⁰

$$\alpha(E) = \alpha_0 \exp(E/E_{URB}), \qquad 4-2$$

where E_{URB} is an empirical parameter known as the Urbach energy that describes the width of the band tails. From equation 4-2, it is evident that the absorption due to transitions between band

tails increases exponentially with energy. Furthermore, a plot of $ln(\alpha)$ versus *E* is linear, with the slope equal to $1/E_{URB}$. Figure 4-4 shows the linear dependence of $ln(\alpha)$ on energy for the 5 InMnAs samples listed in Table 4-1. As given in Figure 4-5, the Urbach energy determined from the plot in Figure 4-4, increases linearly from *x*=0.002 to *x*=0.08. Therefore, the magnitude of the band tailing increases with the impurity concentration, a result that is consistent with previous work involving heavily doped direct gap semiconductors.^{150, 151}



Figure 4-4: $ln(\alpha)$ as a function of E for In_{1-x}Mn_xAs samples with x<0.01, x=0.01, x=0.03, x=0.07, and x=0.08.



Figure 4-5: Urbach energy versus x for $In_{1-x}Mn_xAs$ films from x=0.002 to x=0.08.

4.1.2 Free carrier absorption

Near band-edge absorption measurements indicated the presence of a shallow impurity band 23 meV above the VBM. In order to determine the number of states in this shallow band, the free carrier absorption at 298 K was analyzed to determine the concentration of itinerant holes in MOVPE InMnAs films. Assuming negligible compensation¹⁴⁵ and that deeper states Mn states do not contribute any holes the valence band, each shallow acceptor will be ionized at 298 K such that the number of free holes is equal to the number of shallow acceptors. As discussed previously in section 2.4.1.2, the itinerant hole concentration, and therefore the number of shallow band states can be determined from the free carrier absorption corresponding to intravalence band transitions (purple arrow in Figure 4-3). The equation relating the Drude absorption (α_{Drude}) to the hole concentration (*p*) is given by the following: ^{104, 105}

$$\alpha_{Drude}(E) = \frac{2}{Y + Y_0} \frac{p e^2 \tau}{m^* (1 + (E/\hbar)^2 \tau^2)}.$$
4-3

As shown in Figure 4-6, the free carrier absorption of MBE grown $In_{0.99}Mn_{0.01}As$ results in a Drude edge in the absorption spectrum from 0.05 to 0.2 eV. A fit of the experimental data using equation 4-3 yields a $p=2.1\times10^{19}$ cm⁻³ and $\tau=9$ fs, ¹⁹ in excellent agreement with room temperature Hall effect measurements ($p=2-3\times10^{19}$ cm⁻³).^{19, 49} This demonstrates that a *well-defined* Drude edge can be fit to determine both the hole scattering time (τ) and the hole concentration, p. However, as given in Figure 4-6, in contrast to MBE InMnAs, a distinct Drude edge was not observed in the T=298 K absorption of MOVPE grown films. The absence of the Drude edge in the case of MOVPE InMnAs (ajb 191) was attributed to the low carrier concentration of 1.4×10^{18} cm⁻³ that was also determined by Drude model fitting. In comparison to the p_{Drude} values in Table 4-4, the MBE grown sample has a hole concentration 15 times greater than that of MOVPE grown films. Since α_{Drude} scales with p (see equation 4-3),^{104, 105} the Drude absorption of MBE InMnAs is predicted to be 15 times greater than that of MOVPE films. This appears to be the case as shown in Figure 4-6.



Figure 4-6: Comparison of the free carrier absorption of MOVPE $In_{0.97}Mn_{0.03}As$ ($p=1.4x10^{18}$ cm⁻³) and MBE grown $In_{0.99}Mn_{0.01}As$ films ($p=2.1x10^{19}$ cm⁻³).

Here we describe the method used to determine the hole concentration in MOVPE InMnAs, even in the absence of a well defined Drude edge. While the lack of a prominent Drude edge prevents a simultaneous determination of τ and p, if a value for τ is known, the maximum free hole concentration can still be obtained from the absorption data. In the following Drude model analysis, m^* for InMnAs is assumed to be equivalent to the effective heavy hole mass in undoped InAs (0.33 m_e).⁵² In addition, a value of τ for each sample was determined from the measured room temperature hole mobilities (μ) using equation 4-5. Several α_{Drude} versus E plots were then calculated using equation 4-3, with the itinerant hole concentration as a floating parameter. A comparison of the computed spectral dependence of α_{Drude} for several p values ranging from 7.5×10^{17} cm⁻³ to 3.0×10^{18} cm⁻³ and the experimental absorption spectrum of ajb 197 (x=0.09) is given in Figure 4-7. The magnitude of the predicted Drude absorption increases with increasing p. However, for free hole concentrations greater than 1.5×10^{18} cm⁻³, the calculated Drude absorption exceeds the total measured absorption. Therefore, we conclude a maximum itinerant hole concentration of 1.5×10^{18} cm⁻³ obtained by Drude fitting (p_{Drude}) is still consistent with the measured T=298 K absorption spectrum of ajb 197. The same procedure was applied to the other 4 InMnAs samples in Table 4-1. Table 4-2 summarizes the calculated 298 K p_{Drude} values, which vary between 1.5×10^{18} cm⁻³ to 3.0×10^{18} cm⁻³.



Figure 4-7: $\alpha(E)$ for an In_{0.92}Mn_{0.08}As thin film (ajb197) measured at *T*=298 K. Blue, green, and red lines are the predicted Drude contributions to the absorption for *p*=7.5x10¹⁷ cm⁻³, 1.6x10¹⁸ cm⁻³ and 3.0x10¹⁸ cm⁻³ respectively.

Table 4-2: Room temperature free hole concentrations of $In_{1-x}Mn_xAs/GaAs$ heterostructures measured by Hall effect ($p_{Hall Effect}$) and Drude model fitting of the free carrier absorption (p_{Drude}).

Sample #	x	Thickness (nm)	$p_{Hall \ Effect} \ (10^{18} \ \mathrm{cm}^{-3})$	<i>p</i> _{Drude} (10 ¹⁸ cm ⁻³)
ajb 059	0.002	900	2.5	2.2
ajb 156	0.01	970	3.0	3.0
ajb 191	0.03	490	1.2	1.4
ajb 190	0.07	420	1.9	1.6
ajb 197	0.08	350	1.3	1.5

We now assert that the maximum free hole concentration at 0.07 eV obtained by the Drude model corresponds to the actual free hole concentration. In order to evaluate the validity of this conclusion, p_{Drude} values were compared with the itinerant hole concentrations measured by Hall effect ($p_{Hall Effect}$) at T=298 K.¹⁴⁴ Room temperature $p_{Hall Effect}$ values for the five In_{1-x}Mn_xAs samples are summarized in Table 4-2. A plot of p_{Drude} as a function of $p_{Hall Effect}$ is shown in Figure 4-8. In the case of perfect agreement between the two methods of measuring the free

hole concentration, the experimental data points would coincide with the plot of $p_{Drude} = p_{Hall Effect}$ given by the red line in Figure 4-8. Within the error of the measurement, the data points do in fact agree with the linear fit. Therefore, Drude model fitting of the free carrier absorption yields accurate itinerant hole concentrations between 1.3×10^{18} and 3.0×10^{18} cm⁻³, even in the absence of a distinct Drude-edge lineshape described by equation 4-3. The hole concentrations indicate that there are only 1.3 to 3.0×10^{18} cm⁻³ uncompensated shallow acceptors in MOVPE InMnAs. We emphasize that number of shallow acceptors and room temperature hole concentrations are approximately 60-100 times less than the nominal Mn concentration. We will address the origin of the low hole concentration/number of shallow acceptors in section 4.1.4.



Figure 4-8: p_{Drude} as function of $p_{Hall Effect}$. Red line corresponds to the function $p_{Drude} = p_{Hall Effect}$.

4.1.3 Deep impurity band absorption

In addition to the shallow Mn impurity band, first principles calculations predict the formation of a deep Mn related impurity band in disordered ferromagnetic semiconductors.^{39, 78} The deep impurity band binds holes within clusters, thereby reducing the itinerant hole concentration. However, it has been proposed that these bound holes can also mediate exchange between clusters.^{40, 41} Therefore, the sub-band gap absorption was measured between 0.07 to 0.25 eV at T=298 K to determine whether or not Mn also forms a deep level impurity band. While a shallow band with $E_A=23$ meV was already observed by near-edge optical measurements, free to bound transitions involving the *deep* Mn impurity band can result in an additional resonance in the sub-band gap absorption (0.07-0.25 eV). Free to bound transitions correspond to the excitation of an electron in the valence band to a deep Mn acceptor.⁵² However, according to Fermi's golden rule for optical transitions, the magnitude of the absorption due to free to bound transitions is proportional to the number of Nn clusters $(N_{cluster})$.⁵² The number of clusters is equal to the N_{Mn} normalized by the number of Mn per cluster (n). Therefore by Fermi's golden rule, we may express the absorption due to valence band to deep impurity band transitions (α_{vb-ib}) by the following equation:⁵²

$$\alpha_{vb-ib} = N_{cluster} \cdot \sigma_{vb-ib}(E) = \frac{N_{Mn}}{n} \cdot \sigma_{vb-ib}(E), \qquad 4-4$$

where $\sigma_{vb-ib}(E)$ is the optical cross section for free to bound transitions.

The sub-band gap absorption for the undoped InAs sample (ajb 145) and two $In_{1-x}Mn_xAs$ samples with *x*=0.03 (ajb 191) and 0.08 (ajb 197) are given in Figure 4-9. In order to selectively study the absorption due to free to bound transitions, the Drude contribution to the absorption

was removed in Figure 4-9. Following subtraction of the free carrier absorption, the absorption increases sharply from E=0.07 to 0.15 eV, and then is essentially constant at α -1000 cm⁻¹ from E=0.15 eV to 0.25 eV. This is in contrast to the InAs sample where α oscillates around 330 cm⁻¹. Oscillations in the absorption of ajb 145 are attributed to Fabry-Perot thickness fringes. Therefore, the sub-band gap absorption of InMnAs samples is more than three times higher than that of undoped samples. In order to determine if the enhanced sub-band gap absorption is dominated by free to bound transitions involving the deep Mn impurity band, the magnitude of the sub-band absorption at 0.15 eV ($\alpha_{sub-band}$) observed for InMnAs samples was plotted with respect to N_{Mn} . We note that the sub-band absorption was quantified by the absorption magnitude at 0.15 eV because the absorption effects of Urbach tails are negligible at this energy. However, as evident in Figure 4-10, $\alpha_{sub-band}$ does not scale with the nominal Mn concentration. In fact, $\alpha_{sub-band}$ decreases with increasing nominal Mn concentration between $N_{Mn}=1.8\times10^{20}$ cm⁻³ to 5.4×10^{20} cm⁻³. Consequently, the enhanced sub-band gap absorption in MOVPE InMnAs cannot be *solely* attributed to free to bound transitions involving a deep Mn impurity band.



Figure 4-9: α versus *E* for InAs (ajb 145), In_{0.97}Mn_{0.03}As (ajb 191), and In_{0.92}Mn_{0.08}As (ajb 197) measured at *T*=298 K.



Figure 4-10: (a) $\alpha_{sub-band}$ as function of N_{Mn} for MOVPE grown $In_{1-x}Mn_xAs$ films. $\alpha_{sub-band}$ is the equal to the absorption at 0.15 eV.

We attribute the absence of a clear $\alpha_{sub-band}$ versus N_{Mn} dependence to the fact that $\alpha_{sub-band}$ is dominated by intervalence band transitions. As illustrated by the green arrow in Figure 4-3, inter-valence band transitions occur in p-type materials such as MOVPE grown InMnAs, between the heavy hole (hh), light hole (lh) valence bands.¹⁵² We note that the lh and hh hole valence bands are not split at the Γ -point. In InMnAs, the Mn acceptors in the shallow impurity band (E_A =23 meV) will be ionized at room temperature and therefore populate the hh and lh bands with free holes.¹⁴⁵ The introduction of free holes or empty states in the lh and hh bands allows for transitions between the lh and hh bands. The lh-hh absorption (α_{lh-hh}) depends upon the number of empty states or the hole concentration (p):^{153, 154}

$$\alpha_{lh-hh} = p\sigma_{lh-hh}, \qquad 4-5$$

where σ_{lh-hh} is the optical cross section for lh-hh transitions. It is important to note that in equation 4-5, the α_{lh-hh} should decrease to 0 as the hole concentration goes to 0.

While $\alpha_{sub-band}$ increases with increasing free hole concentration in Figure 4-11, the free hole concentration does not extrapolate back to 0 absorption as *p* approaches 0. In fact a linear fit (dotted line) that assumes that sub-band absorption solely due to lh-hh transitions has a low R^2 value of 0.075. Instead the sub-band absorption is better described by an equation that assumes that the absorption is due to both lh-hh transitions (α_{lh-hh}) and free to bound transitions involving the deep impurity band (α_{vb-ib}):

$$\alpha_{sub-band} = \alpha_{lh-hh} + \alpha_{vb-ib} = p\sigma_{lh-hh} + N_{Mn}\sigma_{vb-ib} .$$

$$4-6$$

The red line in Figure 4-11 corresponds to the fit of the $\alpha_{sub-band}$ versus *p* curve using equation 4-6. As evident in Figure 4-11, the fit using equation 4-6 results in a significant improvement in

the quality fit with an associated R^2 value of 0.98 relative to the fit using equation 4-5 (R^2 =0.075). The slope of the red line corresponds to the optical cross section for lh-hh transitions, which equals 2.1x10⁻¹⁶ cm⁻². This agrees well with the previously measured values of σ_{lh-hh} of 5x10⁻¹⁶ cm⁻² in p-type InAs doped with Zn.¹⁵⁵ The *y*-intercept obtained from the fit in Figure 4-11 is 590 cm⁻¹. Recalling that the baseline absorption of InAs was 330 cm⁻¹, we attributed 260 cm⁻¹ of the total sub-band gap absorption to transitions between the valence band and deep impurity band. Normalizing α_{vb-ib} =260 cm⁻¹ by the N_{Mn} , we obtained values for σ_{vb-ib} ranging from 2.7x10⁻¹⁷ cm⁻² to 2.4x10⁻¹⁸ cm⁻² that are 1-2 orders of magnitude less than σ_{ih-hh} . The calculation of σ_{vb-ib} assumes that n=14.³⁶ We emphasize that while σ_{vb-ib} values are low relative to σ_{lh-hh} values, free to bound optical cross sections in this range have been previously observed.^{156, 157}



Figure 4-11: $\alpha_{sub-band}$ as a function of p for In_{1-x}Mn_xAs thin films. Dotted line gives a linear fit of the data assuming only lh-hh transitions. Red line fit assumes both lh-hh and free to bound transitions.

Therefore, both intervalence band transitions and free to bound transitions contribute to the sub-band gap absorption. However, the low optical cross section associated with valence band to deep impurity band transitions relative to lh-hh transitions results in sub-band absorption that does not clearly scale with N_{Mn} . Inter-valence band absorption simply overwhelms subtle absorption features related to a deep Mn impurity band. It is also important to emphasize that strong intervalence band absorption also prevents the observation of a clear resonance in the subband absorption and therefore an accurate measure of the E_A of the deep impurity band.

4.1.4 Deep impurity band and bound holes

The itinerant hole concentration measured by Drude model fitting and its dependence on *x* provides additional evidence of a deep impurity band in InMnAs. Both the magnitude of *p* and its scaling with *x* contradicts that expected in the case where all Mn are in the shallow impurity band with $E_A=23$ meV.⁶⁸ A plot of $p_{Drude}(298 \text{ K})$ as a function of *x* is given in Figure 4-12. For comparison, the corresponding room temperature hole concentrations of MBE grown InMnAs are plotted in the same figure.⁴⁹ The hole concentrations of MBE InMnAs were measured by Hall Effect and range from $2x10^{19}$ to $3x10^{19}$ cm⁻³, independent of *x*. We note that $p_{Hall Effect}$ values are used in Figure 4-12 for the case of MBE InMnAs because p_{Drude} values were only measured for a single MBE grown sample. According to Figure 4-12, the hole concentrations in MOVPE films are a factor of 7-25 less at $1.2x10^{18}$ to $3.0x10^{18}$ cm⁻³, but are also essentially independent of *x*. However, in the case of where all the substitutional Mn in the film act as a shallow acceptor, each Mn impurity ion will contribute a single hole at 298 K. Therefore, hole concentrations for alloyed films should be of the order 10^{20} cm⁻³ and scale with *x*.



Figure 4-12: Room temperature free hole concentration versus *x*. Free hole concentrations for MOVPE and MBE InMnAs were determined from the free carrier absorption and Hall effect respectively.⁴⁹

In order to determine the origin of low hole concentrations in MOVPE InMnAs, we first examined the possibility of compensation from large donor concentrations. Mn interstitials are double donor defects that form readily in MBE InMnAs as a result of the low temperature growth process.^{12, 43, 49} However Mn interstitial defects in InMnAs are only stable up to temperatures of 190°C.¹³ Due to the high temperatures utilized in the growth of InMnAs by MOVPE (480-520°C), the concentrations of this defect will be negligible. This conclusion is supported by electronic transport measurements, which indicate that the donor concentrations are approximately $5x10^{17}$ cm⁻³.¹⁴⁵ Consequently, Mn interstitials or other donor defects cannot account for the ~1x10¹⁸ cm⁻³ free holes observed in MOVPE InMnAs. Rather, donor defect concentrations on the order of $1x10^{20}$ cm⁻³ would be required to account for the low hole concentrations in MOVPE InMnAs.

Instead, recent density functional calculations emphasize the importance of Mn clustering in determining the free hole concentration.^{39, 78} Raebiger *et al.* predicts that in GaMnAs, Mn clustering splits a single shallow Mn impurity band into two bands: a shallow one and a deep Mn one (near midgap). We emphasize that both the shallow and deep impurity bands are associated with Mn cluster states. For a cluster containing *n* substitutional Mn atoms, *n-1* holes are bound within the cluster and reside in the deep Mn impurity band. Due to the larger E_A of the deep impurity band, the *n-1* holes do not contribute to conduction at room temperature. The remaining holes reside in a shallow impurity band at cryogenic temperatures. At room temperature, there is sufficient energy to ionize the shallow Mn acceptor to yield a free hole in the valence band. This free hole can be measured by Hall effect and contributes to the free carrier absorption. Again each cluster contributes only a single hole regardless of its size *n*.

In order to estimate the number of holes bound in the deep impurity band that do not contribute to conduction, the average size of the Mn atomic clusters must be determined. EXAFS measurements made by Soo *et al.* on MOVPE InMnAs not only indicate the presence of clusters, but also provide information regarding the average number of atoms in a cluster.³⁶ EXAFS measurements indicate that for MOVPE In_{1-x}Mn_xAs samples with 0.03 < x < 0.05, the average number of second nearest neighbors Mn is 5±2 out of a possible 12. This corresponds to an average cluster that contains 14 substitutional Mn and a diameter of 0.9 nm.³⁶ In the case of an In_{0.97}Mn_{0.03}As sample containing substitutional Mn clusters with *n*=14, clustering results in a calculated free hole concentration to 4.1×10^{19} cm⁻³. However, accounting for Mn clustering still yields an itinerant hole concentration over an order of magnitude larger than the measured hole concentration. It should be emphasized that Raebiger *et al.* only demonstrated that each cluster

contributes a single free hole to the valence band for a maximum cluster size with 5 Mn. Some of the larger cubic Mn clusters ($n \ge 14$ Mn) in MOVPE InMnAs observed by EXAFS, could bind all the holes within the cluster and thereby further reduce the free hole concentration. Alternatively, these shallow holes may be involved in stabilizing the ferromagnetic state.

The better agreement between hole concentrations predicted from the average Mn cluster size and the measured room temperature p_{Drude} values suggests the presence of two species of holes residing in two distinct impurity bands: itinerant holes in a shallow band and bound holes in a deep band. First, there are $\sim 1 \times 10^{18}$ cm⁻³ itinerant holes in the valence band at room temperature, resulting from the ionization of $\sim 1 \times 10^{18}$ shallow Mn acceptor states 23 meV above the VBM. According to the Raebiger model, Mn clusters will contribute a small fraction of their Mn 3d states towards the formation of the shallow Mn impurity band. Second, the majority of the remaining holes ($\sim 1 \times 10^{20}$ cm⁻³) are localized within Mn clusters. According to DFT calculations these bound holes form a deep Mn impurity band near the middle of the band gap in clustered ferromagnetic semiconductors.^{39, 78} While the sub-band absorption measurements indicated the presence of deep impurity band absorption, the large background absorption due to inter-valence band transitions also did not allow for a precise determination of the E_A of this band. Therefore we inferred the presence of approximately 1×10^{20} cm⁻³ deep impurity states near the middle of the gap ($E_A \sim 0.12$ eV) that bind the majority of holes in MOVPE InMnAs. A schematic illustrating the bound and free holes within the InMnAs lattice is shown in Figure 4-13. In accordance with the Raebiger calculations, each cluster contributes a single free hole, drawn as a red arrows in Figure 4-13. The itinerant holes are free to travel throughout the lattice. We note that at low temperatures, there would be insufficient energy to ionize the shallow Mn acceptor

states, leading to a reduction of free holes. The bound holes, given by the black arrows are localized around the center As atom.



Figure 4-13: Schematic of bound and free holes in a clustered InMnAs alloy. Clusters outlined by dotted red lines. The Bohr radii of the bound and free holes are not included in this diagram. Wavefunctions of the two hole species will be addressed in the following chapter.

In summary, from the near edge absorption, we have demonstrated the existence of a shallow Mn impurity band (E_A =23 meV). A reduction in the band gap was observed that was attributed to shallow impurity band to conduction band transitions. Next the low hole concentrations of the order 1x10¹⁸ cm⁻³ determined from the free carrier absorption were ascribed the presence of a deep Mn impurity band. The deep impurity band binds the majority of holes in clusters that limit the free carrier absorption.

4.2 XAS/XMCD

In order to characterize the ground state configuration, *d*-electron localization, and crystal field symmetry of Mn 3*d* states in the shallow and deep impurity bands, XAS and XMCD spectra associated with the Mn $L_{2,3}$ edge were measured. The importance of measuring the Mn $L_{2,3}$ edge is that the Mn 3*d* DOS and therefore the XAS spectral lineshape is sensitive to the electronic state of Mn (configuration, *d*-electron localization) and its local environment (crystal field). The Mn $L_{2,3}$ edge XAS specifically results from transitions from the Mn 2*p* core levels to Mn 3*d* states above E_F .¹⁵⁸ While XAS can be used to determine electron state parameters including the ground state configuration of Mn, the poor energy resolution of XAS (0.3 eV)¹³⁸ prevents an accurate measurement of the depth Mn impurity bands predicted by Raebiger.³⁹ The Mn $L_{2,3}$ edge XMCD adds an additional level of specificity over the XAS because the dichroism spectral lineshape is specific to the electronic state of ferromagnetically ordered Mn ions. Only ferromagnetically active Mn will have exchange split Mn 3*d* impurity band states that result in a net XMCD.¹⁰⁶

4.2.1 Mn L_{2,3} XAS

We begin with an analysis of the Mn $L_{2,3}$ XAS spectrum to determine the electronic state and local environment of the Mn 3*d* orbitals. The Mn *L*-edge XAS measured by the total electron yield (TEY) method at 50 K for two In_{1-x}Mn_xAs samples described by Table 4-3, are given in Figure 4-14a. TEY measures the total number of photoelectrons that escape the sample by Auger emission following photoexcitation. The number of Auger electrons is proportional to the XAS intensity.¹⁰⁶ It should be noted that the XAS spectra of ptc 015 (*x*=0.02) and ajb 214 (*x*=0.05) measured between 5-300 K are nearly identical to the 50 K XAS spectra shown in Figure 4-14a. Both XAS spectra are comprised of a triplet structure (peaks A-C) split apart from a doublet (peaks D-E) structure by 10.4 eV. In addition both groups of peaks are on top of a broad step-like background. We note that the rich XAS lineshape including the triplet and doublet features for the L_3 and L_2 edges respectively is similar to the spectrum of MBE grown GaMnAs.^{29, 159, 160} A comparison of the XAS spectra of MOVPE InMnAs with MBE InMnAs is not possible as the spectrum for the MBE grown material has not been measured.

We attribute the step-like background in the XAS spectrum to transitions between the Mn 2p core states and the vacuum. These transitions that do not probe the 3d states are typically subtracted out prior to analysis of the XAS spectrum. As shown in Figure 4-14b, the triplet and doublet peak structures correspond to transitions from the $2p_{3/2}$ (L_3 edge) and $2p_{1/2}$ (L_2 edge) core level states to *unoccupied* 3d band states respectively. These transitions *are the focus* of this Mn $L_{2,3}$ edge XAS study. The 10.4 eV splitting between the L_3 and L_2 edge peaks is due to the characteristic spin orbit splitting of the $2p_{3/2}$ and $2p_{1/2}$ core level states.¹⁰⁶ Since the magnitude of Mn 2p spin orbit splitting is a universal property,^{109, 161-163} we emphasize that *all known Mn compounds* exhibit Mn *L*-edge XAS comprised of two groups of peaks separated by 10.4 eV.

Table 4-3: Structural properties of InMnAs and hexagonal MnAs films discussed in section 4.2. MnAs film was grown in the Ketterson laboratory at Northwestern University by MBE.¹⁶⁴

Sample #	Film	Substrate	Thickness (nm)
ptc 015	In _{0.98} Mn _{0.02} As	GaAs	240
ajb 214	In _{0.95} Mn _{0.05} As	GaAs	800
jhs 110	MnAs	Si	100



Figure 4-14: (a) Mn $L_{2,3}$ XAS measured by TEY at 50 K for $In_{1-x}Mn_xAs$ with x=0.02 (ptc 015) and x=0.05 (ajb 214). (b) Schematic of the Mn $L_{2,3}$ edge transitions in the absence of a magnetic field. Green and red arrows mark the L_3 and L_2 edge transitions respectively. It should be noted that transitions between the $2p_{3/2}$ level to features D, E do not occur because they are disallowed by selection rules. The same is true for transitions between the $2p_{1/2}$ to the features A, B, C.

While spin orbit splitting of the L_3 and L_2 edges is universal to all Mn XAS spectra, the splitting *within* the L_3 and L_2 edge varies with respect to the electronic state of the Mn 3*d* orbitals. In particular, the splitting and lineshape *within* the L_3 and L_2 edges is attributed to intraion *d* electron repulsion and spin orbit splitting of the 3*d* density of states (see Figure 4-14b).¹⁶⁵ The splitting due to intra-ion *d* repulsion and spin orbit coupling are highly sensitive to the ground state configuration and occur even in the absence of local environment effects such as the crystal field.^{115, 116} However, an external crystal field can induce additional broadening, shifting, or even splitting of the peaks in the L_3 and L_2 edges. The change in lineshape due to the crystal field depends upon both the crystal field symmetry and magnitude. It is important to note that for Mn d^4 , d^5 , and d^6 ground state configurations, crystal field magnitudes 10 Dq>1.0 eV are required to observe crystal field splitting of the L_3 and L_2 edge.¹¹⁶ For 10 Dq<1.0 eV, crystal field interactions result in more subtle broadening and shifting of the L_3 and L_2 edge peak structures.¹¹⁶

To determine the electronic state of the Mn 3d orbitals, the specific peak structures within the L_3 and L_2 edges measured in the experimental XAS were fit with respect to a theoretical spectrum generated by an atomic multiplet model obtained from van Veenendaal.¹⁶⁶ As shown in Figure 4-15, the atomic model only considers contributions to the XAS from transitions between occupied Mn 2p and unoccupied 3d states. Consequently, the contribution to the XAS spectrum from transitions from the 2p core level to the vacuum was removed according to a method similar to that described by Shirley et al.¹⁶⁷ The background-subtracted spectra were subsequently fit with respect to simulated spectra based upon linear combinations of Mn atomic spectra using a least squares fitting program. The fitting parameters include the relative percentages of d^4 , d^5 , d^6 configurations, varying crystal field symmetries and magnitudes. The fitting parameters and resultant R^2 values are summarized in Table 4-4. As evident in Table 4-4, the highest R^2 value was obtained using a **pure** $3d^5$ ground state configuration with a weak tetrahedral crystal field strength of 10 Dq=0.5 eV. In Figure 4-16a and Figure 4-16b, the observed peak positions and lineshape in the experimental spectrum of ptc 015 and ajb 214 respectively are also well reproduced using a $3d^5$ configuration (or a Mn²⁺ valence state) and a tetrahedral crystal field of 10 Dq=0.5 eV.



Figure 4-15: XAS spectrum of an $In_{0.98}Mn_{0.02}As$ sample (ptc 015) measured at *T*=50 K before and after the removal of the step background absorption.¹⁶⁷



Figure 4-16: Comparison of experimental XAS spectra of (a) ptc 015 and (b) ajb 214, with theoretical spectral calculated assuming a d^5 configuration and 10 Dq=0.5 eV. The experimental spectra were measured at T=298 K.

Sample #	% <i>d</i> ⁴	$\% d^5$	10 Dq (eV)	R^2
ptc 015	10	90	0	0.962
ptc 015	0	100	0	0.975
ptc 015	0	100	0.5	0.985
ajb 214	0	100	0	0.974
ajb 214	0	100	0.5	0.982

Table 4-4: Summary of the parameters used in atomic model fits of the experimental XAS and the resulting R^2 values. Fit parameters yielding the highest R^2 values are shaded in gray.

The excellent fit of the experimental XAS assuming a 100% d^5 configuration and a tetrahedral crystal field with 10 Dq=0.5 eV yields several important conclusions. First, all Mn are in the high spin configuration with an associated spin moment of 5 μ_B . As shown in Table 4-4, the introduction of a nonzero percentage of d^4 Mn ions (neutral acceptors) results in a significant decrease in the R^2 value. Second, the 5d electrons associated with each Mn ion are highly localized. As discussed in section 2.4.2.2, the simulated spectra calculated by the atomic multiplet model assumes isolated Mn atoms 3d electrons. Third, the low tetrahedral crystal field magnitude of 10 Dq=0.5 eV indicates that splitting within the L_3 and L_2 edges are primarily due to intra-ion d-d electron repulsion and spin orbit coupling. In fact, the triplet and doublet structures in the $L_{3,2}$ edges appear in the theoretical d^5 atomic spectra even for 10 Dq=0.¹¹⁶ However, the atomic fit was nonetheless improved using a weak tetrahedral crystal field. Qualitatively, the predicted broadening of the L_3 and L_2 edge features better match the experimental spectrum using a nonzero tetrahedral crystal field. Quantitatively, an increase in the R^2 value of the atomic fit of the experimental XAS of ptc 015 from 0.975 to 0.985 was observed by increasing the tetrahedral crystal field magnitude from 10 Dq=0 to 0.5 eV. As shown in Table

4-4, a similar increase in the R^2 value was also observed for ajb 214. The significance of the fit improvement using a tetrahedral crystal field is that the symmetry of the crystal field is consistent with substitutional Mn in InMnAs, where Mn are tetrahedrally bonded to 4 As atoms.¹⁶ Therefore the XAS spectrum confirms EXAFS measurements, which also indicate that Mn substitutes coherently for In in MOVPE InMnAs.³⁶

While the atomic multiplet model considers crystal field perturbations, we emphasize that the model ignores changes in the local environment around Mn ions due to the hybridization of s,p states with the Mn 3d states, or sp-d exchange.¹¹⁶ The excellence of the atomic fit indicates that perturbations to the local environment due to sp-d exchange are difficult to detect. This is consistent with XAS measurements of MBE GaMnAs, whereby evidence of sp-d exchange was not observed at the Mn *L*-edge.^{109, 159, 160} Visible MCD measurements were required to observe the sp-d exchange in interaction in MBE GaMnAs.^{168, 169} Therefore, RMCD, a technique that is more sensitive to sp-d exchange than XAS will be reported in the following chapter.¹⁷⁰

We now combine the conclusions of the XAS atomic model fitting with that made from optical absorption measurements in section 4.1.4 to provide a more complete description of the electronic state of Mn in the deep and shallow impurity bands. Hole concentrations measured from the free carrier absorption indicate the presence of $\sim 1 \times 10^{18}$ cm⁻³ ionized acceptors, which is much lower than the Mn concentration. The other remaining $\sim 1 \times 10^{20}$ cm⁻³ holes were inferred to be bound by $\sim 1 \times 10^{20}$ cm⁻³ Mn acceptor states deep impurity band. From the atomic fitting of the room temperature XAS spectrum, we now conclude Mn impurities in the shallow and deep impurity bands have a d^5 and d^5+h configurations respectively at *T*=298K. The *h* for the electronic state of the deep impurity band refers to a bound hole. On the other hand, holes in the

shallow band fully are ionized at room temperature and consequently have a simple d^5 ground state configuration.

Finally, many of the conclusions in this section were based upon the d^5 ground state configuration determined from fitting of the XAS measured by TEY. However, it is important to note that TEY is a highly surface sensitive technique with a probe depth of only 5 nm. Edmonds and coauthors have demonstrated that a layer of antiferromagnetic MnO forms at the surface of GaMnAs films grown by MBE.¹¹¹ In addition, it was shown that Mn in the MnO surface layer exhibits a highly localized d^5 XAS spectrum similar to that observed for MOVPE grown InMnAs.¹⁷¹ One could then argue that the Mn in MnO dominates the XAS spectrum measured by TEY rather than the Mn in InMnAs, due to the surface sensitivity of the TEY method. Therefore, as a positive control, the Mn $L_{2,3}$ edge XAS of InMnAs was also measured by the total fluorescence yield (TFY) method, a bulk sensitive technique with a probe depth of approximately 100 nm. As given in Figure 4-17, the XAS of ptc 015 as measured by TFY has a similar lineshape as that measured by TEY. The TFY spectrum of ptc 015 also exhibits of the signature of an atomic d^5 XAS with weak crystal field interaction. The only difference between the two spectra is the relative magnitudes of the L_3 and L_2 peaks. This discrepancy is attributed to self-absorption process that preferentially quenches the L_3 resonance in TFY spectrum.¹⁷²⁻¹⁷⁴ Therefore, due to the bulk sensitivity of TFY, we may conclude that an atomic d^5 spectral lineshape is still consistent with the electronic state of Mn in InMnAs. Contributions of a potential surface oxide to the XAS measured by TFY are negligible.



Figure 4-17: Mn $L_{2,3}$ edge XAS of In_{0.98}Mn_{0.02}As (ptc 015) as measured by TFY at T=100 K compared with that measured by TEY at T=50 K. Both the TFY And TEY spectra are normalized by their respective values at 638.7 eV for the purpose of comparison.

4.2.2 Mn *L*_{2.3} edge XMCD

XMCD measures the asymmetry or exchange splitting of the Mn 3*d* states. Since only *ferromagnetically active Mn* in the material contribute to the exchange splitting of the 3*d* DOS, XMCD adds an additional level specificity over XAS. XAS measures *all* Mn 3*d* states in the material. Furthermore, we can determine whether the exchange splitting of the Mn 3*d* states persists up to the T_c of 330 K from the XMCD versus *T* curve. Therefore, we now present the XMCD spectra of MOVPE InMnAs measured at the Mn $L_{2,3}$ edge. The XMCD intensity is defined by the ratio:

$$XMCD = \frac{\alpha_{+} - \alpha_{-}}{\alpha_{+} + \alpha_{-}} = \frac{\alpha_{+} - \alpha_{-}}{\alpha},$$
4-7

where α_{\pm} is the XAS measured by TEY for RCP and LCP x-rays respectively. For the XMCD spectral measurements, an applied field of *H*=2T was applied to saturate the magnetization in the material. While the XMCD spectrum was also measured in TFY, the lineshape of the TFY XMCD is severely distorted due to self-absorption and has a lower signal to noise than the TEY. Therefore, the following dichroism analysis focuses on XMCD spectra measured by TEY.

The α_+ and α_- spectra for ptc 015 (In_{0.98}Mn_{0.02}As) and ajb 214 (In_{0.95}Mn_{0.05}As) at *T*=5 K are given in the top panel of Figure 4-18a and Figure 4-18b respectively. We emphasize that there is *no observable shift* in the position of the peaks for the α_+ and α_- spectra. The primary differences between the absorption in RCP and LCP x-rays occur in the *magnitudes* of peaks A-E. For example, in the case of peak A, the absorption in LCP is greater than that observed in RCP. Therefore, equation 4-7 predicts that feature A in the XMCD will have a negative sign. This is consistent with the measured XMCD spectra of ptc 015 and ajb 214 in the bottom panels of Figure 4-18a and Figure 4-18b. Furthermore, since there is no shift in the peak positions in RCP and LCP, the negative peak A in the XMCD has the same energy as peak A in the XAS (638.7 eV). Using a similar argument, peaks B-E in the XMCD spectra occur at the same energies than that observed in XAS. This is demonstrated by the reference lines in Figure 4-18.



Figure 4-18: Mn $L_{2,3}$ edge TEY XAS measured T=50 K and TEY XMCD measured at T=5 and 50 K for (a) ptc 015 and (b) ajb 214. An applied field of H=2T was used for the XMCD spectra.

It is important to emphasize that the sign of peak A in the XMCD yields important information regarding the spin resolved 3*d* DOS. For the L_3 edge, RCP *x*-rays preferentially excite *spin up* electrons from the $2p_{3/2}$ core state to unoccupied spin up 3*d* states (vice versa for LCP x-rays). We note that by definition, the magnetic field is applied in the *up direction*. Since feature A in the XMCD is negative, spin down transitions dominate over spin up transitions at 638.7 eV. As illustrated in Figure 4-19a, spin down transitions dominate because there are more available 3*d* states in the spin down density of states 638.7 eV above the $2p_{3/2}$ core level. Similarly, peaks B, C in the L_3 edge are positive because there are more unoccupied *spin up* 3*d* states than spin down states 640 and 642 eV above the $2p_{3/2}$ core level state respectively. However, for the L_2 edge peaks (D, E), the sign of the spin orbit coupling is opposite that of the L_3 edge,^{106, 158} such that RCP and LCP excite spin down and spin up electrons from the $2p_{1/2}$ core state, respectively (see Figure 4-19b). Due to the opposite sign of the spin orbit coupling, the positive peaks in the L_2 edge demonstrate that there are more unoccupied spin down states than spin up states 649 and 651 eV above the $2p_{1/2}$ core level respectively. Since it is clear from the magnitudes of the XMCD peaks that the dominant asymmetry in the 3*d* DOS occurs at the energy corresponding to peak A, overall there are more unoccupied spin down states than spin up states. It follows then that there are more occupied 3*d* states in the spin up DOS relative to the spin down DOS. Since spin up electrons are aligned with the applied magnetic field (up direction), this results in a net magnetization that parallel to *H*.



Figure 4-19: Schematic of the spin resolved Mn (a) L_3 edge (b) L_2 edge transitions. The applied magnetic field is in the up direction. Note that RCP x-rays excite spin down electrons for L_2 edge transitions.
While a clear XMCD spectrum resolved for both ptc 015 and ajb 214 is indicative of exchange splitting of the Mn 3*d* states, the exchange splitting cannot be quantified by a single parameter (ΔE). In section 2.4.3, we demonstrated in the limit that $\alpha_+(E)$ and $\alpha_-(E)$ differ only by a shift defined as ΔE , the XMCD may be expressed by the equation:

$$XMCD = \frac{1}{\alpha} \frac{d\alpha}{dE} \Delta E, \qquad 4-8$$

where α is the XAS. While this approximation has been validated in the case of visible and infrared spectral range,^{62, 64} as shown in the top panels of Figure 4-18, $\alpha_+(E)$ and $\alpha_-(E)$ are not shifted from one another. Presumably the assumption of shifted RCP and LCP absorption spectra breaks down for the large energy ranges utilized in XMCD spectroscopy. Therefore, we could not determine ΔE from the XMCD spectra. However, we note that exchange splitting energy of the Mn impurity bands will be reported in the next chapter.

As shown in Figure 4-18, a clearly resolved dichroism spectra was observed at 5 and 50 K, indicating that exchange splitting of the Mn bands occurs at these temperatures. The dichroism spectra at the two temperatures have the nearly identical spectral lineshapes, exhibiting features closely related to the XAS. While the XMCD spectral *lineshape* measured at 5 K is nearly identical to that measured at 50 K, the main difference between the dichroism spectra is the *magnitude* of features A-E. At T=5K and E=638.7 eV, XMCD magnitudes of 0.15 and 0.17 were calculated using equation 4-7 for ptc 015 and ajb 214 respectively. As the *T* is increased to 50 K, the XMCD at 638.7 eV decreases to 0.07 and 0.08. A series of XMCD spectra near the 638.7 eV resonance were measured between 5-300 K for ptc 015 to determine the full dependence of the XMCD magnitude as a function of *T*. The full XMCD versus *T* dependence of

ajb 214 was not measured. As shown in Figure 4-20, peak A (638.7 eV) decreases with increasing temperature. However, it is important to emphasize that even at room temperature, peak A is still clearly resolved in the XMCD spectrum. Therefore, the exchange splitting of the Mn impurity bands persists to at least room temperature for ptc 015. The absence of the subtle peak at 640 eV (peak B) for T>100K was attributed to a decrease in signal to noise of the XMCD spectra at high temperatures.



Figure 4-20: XMCD spectra of ptc 015 measured from 5-300 K with an applied field of 2T. The spectral range is limited to the peaks in the A and B in the L_3 edge.

A plot of the XMCD magnitude at 638.7 eV as a function of *T* using the XMCD curves in Figure 4-20 is shown in Figure 4-21. For the sake of comparison, the *M* versus *T* dependence is also given in the same figure. In Figure 4-21 there is a slow linear decrease in the XMCD with respect to temperature from 30 to 300 K, in excellent agreement with the observed *M* versus *T* curve. The monotonic dependence of the XMCD as function of *T* from 30-300 K is consistent with dichroism due to a single ferromagnetic species with a T_c of 330 K. However, for T < 30 K, there is a sharp increase in the XMCD that is reproduced in the *M* versus *T* plot. We emphasize that this characteristic increase in the XMCD and magnetization at low temperatures is in direct contrast to the Dietl model. As *T* decreases from 30 to 5 K, the itinerant hole concentration decreases by more than order of magnitude in MOVPE InMnAs.¹⁴⁵ According to the Dietl model the reduction in free holes should result a sharp *decrease* in *M* and XMCD for *T*<30 K. Therefore the temperature dependence of the XMCD illustrates the inapplicability of the Dietl model to MOVPE InMnAs. Rather, the abrupt increase in the XMCD is presumably the result of a second ferromagnetic species contributing to the dichroism with a transition temperature of approximately 30 K. It is important to note that the observed low temperature increase in the magnetization is not unique to ptc 015. Several InMnAs films grown MOVPE, including those that will be discussed in the next chapter, also exhibit two component *M* versus *T* curves that are also presumably due to two distinct ferromagnetic species. The high temperature species has the standard *T_c* of ~330 K while the low temperature species has a *T_c* ranging from 15-40 K.



Figure 4-21: XMCD at 638.7 eV versus temperature for an $In_{0.98}Mn_{0.02}As$ sample (ptc 015). *M* versus *T* for the same sample is given as a reference.

To determine the identity of the ferromagnetic species with transition temperatures of approximately 30 and 330 K, the XMCD spectra at 5 and 50 K were then fit with respect to linear combinations of dichroism spectra generated by the atomic multiplet model. The 5 K and 50 K XMCD correspond to the ferromagnetic species with T_c 's of 30 and 330 K respectively. The results of the atomic fitting of the 5 K XMCD spectra are summarized in Table 4-5. As evident in Table 4-5, the best fit occurs using the same d^5 configuration and tetrahedral crystal field of 10 Dq=0.5 eV as determined in the XAS fitting. A comparison of the atomic spectra using the optimum fitting parameters and the corresponding experimental 5 K spectra of ptc 015 and ajb 214 are given in Figure 4-22a and Figure 4-22b, respectively. From Figure 4-22, it is evident that the sign, magnitude and positions of XMCD peaks A-E are in agreement with that predicted by the atomic multiplet model. A similar high quality fit was obtained for the dichroism spectra measured at 50 K. The excellent fit indicates that the *ferromagnetically* ordered Mn in MOVPE InMnAs also have a highly atomic-like d^5 configuration at both 5 and 50 K. Moreover, the improvement of the fit using a tetrahedral crystal field of 10 Dq=0.5 eV (see Table 4-5) also indicates that the low and high temperature ferromagnetic species both contain substitutional Mn with tetrahedral symmetry. This precludes an ascription of the two ferromagnetic components to hexagonal MnAs precipitates where Mn are in a hexagonal crystal field. Instead, potential ferromagnetic species that match this criterion include singly substituted Mn and MnAs clusters having tetrahedral symmetry.

Table 4-5: Summary of the parameters used in atomic model fits of the experimental XMCD and the resulting R^2 values. Fit parameters yielding the highest R^2 values are shaded in gray.

Sample #	% <i>d</i> ⁴	$\% d^5$	10 Dq (eV)	R^2
ptc 015	10	90	0	0.850
ptc 015	0	100	0	0.911
ptc 015	0	100	0.5	0.926
ajb 214	0	100	0	0.953
ajb 214	0	100	0.5	0.962



Figure 4-22: Comparison of the 5K experimental XMCD spectra for (a) ptc 015 and (b) ajb 214 and the theoretical spectral calculated assuming a d^5 configuration and 10 Dq=0.5 eV.

The attribution of the low and high temperature dichroism to ferromagnetic species composed of substitutional Mn rather than hexagonal MnAs precipitates is supported by a comparison of the experimental XMCD spectra of MOVPE InMnAs and that of hexagonal MnAs. We note here that an experimental hexagonal MnAs spectrum is used for this comparison due to the difficulties associated with the calculation of a theoretical Mn *L*-edge XMCD of hexagonal MnAs.¹⁷⁵ While the atomic multiplet model was used successfully in the case of

MOVPE InMnAs, the model does not yield accurate XMCD spectra for MnAs because it assumes localized 3*d* electrons. For metals such as hexagonal MnAs, 3*d* electrons participate in conduction and therefore are delocalized.⁹¹ Consequently, more sophisticated configuration interaction^{176, 177} or density functional theory^{178, 179} calculations are required to accurately model the XMCD spectrum hexagonal MnAs.

As evident in Figure 4-23, there are three main points of contrast between the experimental XMCD spectra of ptc 015 associated with the low temperature ferromagnetic species and the experimental dichroism spectrum of hexagonal MnAs thin film (see Table 4-3). First, feature A in the XMCD is a sharp negative peak in the case of the MnAs film, while only a subtle shoulder for the InMnAs samples. Second, the positive peak corresponding to feature B for ptc 015 is absent for MnAs. Finally, the L_2 dichroism peaks of MnAs are broadened and red shifted by 1 eV relative to the InMnAs L_2 (features C and D). Similar points of contrast are evident in a comparison of the *T*=50 K dichroism spectra of ptc 015, corresponding to the high temperature ferromagnetic species, and the MnAs XMCD spectrum. Therefore, the significant differences in Mn $L_{2,3}$ dichroic lineshapes indicate that both the low and high temperature ferromagnetic species in the InMnAs films cannot be attributed to hexagonal MnAs precipitates but rather singly substituted Mn or cubic Mn clusters. This is consistent with not only previous atomic multiplet fits but also XRD,³¹ TEM,³⁴ and EXAFS³⁶ measurements which all excluded the possibility of hexagonal MnAs precipitates in MOVPE InMnAs.



Figure 4-23: Comparison of the XMCD of $In_{0.98}Mn_{0.02}As$ (ptc 015) and MnAs (jhs 110). The dichroism spectrum of InMnAs was measured at *T*=5 K with *H*=2T. The dichroism spectrum of MnAs was taken at 300 K in remanence.

Despite the agreement of the T_c of MBE grown InMnAs⁴⁹ alloys containing primarily singly substituted Mn,¹⁶ and the T_c of the low temperature ferromagnetic species in MOVPE InMnAs, the low temperature component cannot be attributed to simple substitutional Mn. The magnitude of the contribution of the low temperature species to the XMCD intensity relative to the high temperature species precludes such an assignment. Between 50 and 5 K, the XMCD intensity and magnetization of ptc 015 nearly double, from 0.08 to 0.15 and 10 emu/cm³ to 16 emu/cm³ respectively. In the case where the low temperature enhancement of the XMCD was due to singly substituted Mn, we conclude from the XMCD and magnetization versus *T* plots that 37 to 47% of the Mn are singly substituted. Since each simple substitutional Mn contributes a single free hole to the valence band, then ptc 015 (*x*=0.02) should have a room temperature free hole concentration of 1.5×10^{20} cm⁻³ to 1.7×10^{20} cm⁻³. This is in sharp contrast to the measured itinerant hole concentration at *T*=298 K of 1.6×10^{18} cm⁻³. Therefore, attributing the low temperature enhancement in the XMCD to singly substituted Mn directly contradicts the observed hole concentration.

Instead, we attribute the low and high temperature ferromagnetic components to large and small cubic Mn clusters respectively. Berciu *et al.* predicted a similar increase in the magnetization at low temperatures due to an inhomogeneous distribution of Mn based upon a numerical mean field model.^{83, 84} In volumes with small clusters, the distances between clusters will be also small such that even a weak inter-cluster exchange mechanism will ferromagnetically align the spins of different clusters up to the transition temperature of 330 K. On the other hand, in volumes with large clusters, the cubic clusters are spatially separated such that the same inter-cluster exchange interaction only aligns the spins between clusters up to a T_c of approximately 30 K. While the nature of the inter-cluster exchange interaction is explicitly omitted from this discussion, the mechanism by which clusters align with respect to each other will be proposed in the next chapter.

The similarity in the XMCD spectral lineshape at 5 K and 50 K is also consistent with the assignment of the low and high temperature ferromagnetic components in MOVPE InMnAs to regions of high and low concentrations of cubic Mn clusters respectively. Unlike techniques such as EXAFS, XMCD is only sensitive to differences in the chemical environment of the first nearest neighbor shell¹¹² (see section 2.4.2.2). Therefore, singly substituted Mn, low and high concentrations of cubic Mn clusters, and even zinc blende MnAs will all exhibit matching XMCD spectra because each Mn specie has Mn tetrahedrally coordinated with four As atoms in

the nearest neighbor shell. For example, as given in Figure 4-24, the XMCD spectrum of MBE Ga_{0.98}Mn_{0.02}As,¹⁰⁹ composed primarily of singly substituted Mn, matches that of MOVPE InMnAs. Discrepancies in the local environment between Mn clusters and simple substitutional Mn occur in the 2nd nearest neighbor shell. In the case of low and high concentrations of Mn clusters, differences in the chemical environment occur at distances greater than the 2nd nearest neighbor shell. Therefore, the two ferromagnetic species attributed to high and low concentrations of Mn clusters also exhibit matching XMCD spectra. Finally, Mn in hexagonal MnAs films, are coordinated with 6 nearest neighbor As atoms respectively. Due to the differences in the chemical environment within the nearest neighbor shell between InMnAs and MnAs, the two materials have contrasting XMCD spectra.



Figure 4-24: Comparison of the XMCD lineshape of MOVPE grown $In_{0.98}Mn_{0.02}As$ and MBE grown $Ga_{0.98}Mn_{0.02}As$.¹⁰⁹ The spectra were measured at *T*=5K with *H*=2T and *T*=15K and *H*=0.55 T respectively.

Finally, in Figure 4-25, we use the IAS, XAS and XMCD spectra to propose an energy level diagram for MOVPE InMnAs. In section 4.1.4, the optical absorption data demonstrated the formation of both shallow ($E_A=23$ meV) and deep (near midgap) Mn impurity bands. These shallow and deep impurity centers are drawn in Figure 4-25. According to Raebiger et al., both deep and shallow impurity bands in GaMnAs are composed of Mn 3d cluster states.^{39, 78} Modeling of the XAS and XMCD spectra indicates that Mn formed deep and shallow impurity centers have a d^5 configuration. However in the case of the deep impurity center, each d^5 Mn ion also binds a hole (h), resulting in a d^5+h configuration. In contrast, the Mn shallow acceptor is ionized at 298 K and consequently has a d^5 ground state configuration. Therefore, the shallow and deep impurity bands are labeled with their respective ground state configurations in Figure 4-25 as d^5 and d^5+h , respectively. We note that at low temperature the configuration of the shallow impurity band becomes d^4 (neutral acceptor).¹⁴⁵ Finally, the XMCD as a function of temperature indicates that the spin splitting of the Mn impurity bands persists up to 298 K. Mn $L_{2,3}$ edge XMCD measures the exchange splitting of the Mn 3d states, including the Mn impurity bands. The exchange splitting of both the shallow and deep impurity bands is also illustrated in Figure 4-25. We emphasize that exchange splitting of the deep and shallow impurity bands in clustered ferromagnetic semiconductors was also predicted by Raebiger and coauthors (see section 2.3.2).³⁹ We also note that in Figure 4-25, the exchange splitting of the valence and conduction band is explicitly omitted. The spin splitting of these bands will be addressed in the following chapter.



Figure 4-25: Room temperature energy level diagram that includes the ground state configuration and exchange splitting of the Mn impurity bands. While the exchange splitting of the valence and conduction bands is omitted from this figure, it will be addressed in the next chapter.

4.3 Summary and conclusions

In this chapter, infrared absorption spectroscopy and XAS/XMCD were used to determine the presence and properties of Mn impurity levels in MOVPE grown InMnAs films. From the near band-edge infrared absorption, a shallow impurity band 23 meV above the valence band maximum was observed. However, Drude-model fitting of the free carrier absorption indicates that the itinerant hole concentrations are approximately two orders of magnitude less than that expected in the case where the Mn predominantly act as simple acceptors with an E_A of 23 meV. Therefore, the formation of an additional deep Mn impurity center near midgap due to Mn clustering was proposed. This deep impurity band tightly binds the majority of the holes

within Mn clusters with tetrahedral symmetry and an average diameter of 0.9 nm. This formation results in the low itinerant hole concentrations determined from the free carrier absorption. The formation of a deep impurity band due to Mn clustering, that reduces hole concentration has also been predicted by first principles calculations.⁷⁸

The ground state configuration, *d*-electron localization, and crystal field symmetry of Mn 3d states were measured by XAS and XMCD spectroscopy. Using atomic multiplet model fits of the XAS spectra and its temperature dependence, we determined that the Mn *d*-electrons in the MOVPE grown InMnAs are highly localized with a d^5 configuration. Moreover, the atomic model fit indicated a tetrahedral crystal field symmetry around the Mn. This consistent with substitutional Mn. A strong XMCD was observed from 5 to 300 K. The XMCD spectra were well-fit using a theoretical atomic d^5 spectra. The observation of dichroism at 300 K indicates that spin splitting of the Mn impurity bands persists up to room temperature. The temperature dependence of the XMCD intensity indicated the presence of two ferromagnetic species. One species contributes to the dichroism to room temperature, while a second low temperature species adds to the dichroism to 30 K. The dichroism data is consistent with an attribution of the low and high temperature ferromagnetic components large and small cubic clusters respectively.

5. Results: Inter-cluster and *sp-d* exchange

Reflectance magnetic circular dichroism (RMCD) spectroscopy was utilized to determine the long-range exchange mechanism in MOVPE InMnAs. In disordered ferromagnetic semiconductors, there are two potential mechanisms for inter-cluster exchange that must be considered. First, free holes in the valence band can mediate spins of adjacent clusters by *sp-d* exchange. Second, DFT predicts the presence of a second hole species in clustered materials: bound holes in a deep impurity band.^{39, 78} Kaminski *et al.* and Berciu *et al.* have proposed that these localized holes can also participate in ferromagnetic exchange.^{40, 41, 83, 84} While previous optical absorption, XAS/XMCD spectra are consistent with the presence of free and bound holes in MOVPE InMnAs, these techniques do not specifically identify which of the two hole species is responsible for the exchange between Mn clusters. Therefore, RMCD spectroscopy was used to elucidate the nature of inter-cluster exchange in MOVPE InMnAs. The technique is particularly useful because *sp-d* exchange (one of the potential inter-cluster exchange mechanisms) results in a specific enhancement in the RMCD near band structure critical points

In this chapter, we first establish two types of InMnAs samples based upon their respective room temperature RMCD spectral responses. One type exhibits a broad negative response, while the other exhibits both the broad background and a prominent negative peak

centered near the E_1 band structure critical point. The broad transition in the first type of films is attributed to spin dependent transitions between a spin-split deep impurity band and the spin symmetric conduction band. The two spectral features observed in the second type correspond to two distinct RMCD transitions: a broad background attributed to Mn impurity to conduction band transitions and a negative peak due to transitions between an *sp-d* exchange split valence band and the conduction band.

In the final part of the chapter, we emphasize the important insights that RMCD spectroscopy yields regarding the room temperature ferromagnetism in MOVPE InMnAs. While both types of InMnAs films exhibit evidence of a spin split deep impurity band, spin splitting of the valence band is only observed in the second type of films. Consequently, exchange between clusters that leads to macroscopic ferromagnetism in MOVPE InMnAs is not mediated by free holes in the valence band, but rather by spin polarized bound holes associated with Mn acceptors that form a deep impurity band.

5.1 Above gap critical points of InMnAs

The differential reflectivity spectra of MOVPE InMnAs films were measured due to their importance in the interpretation of the dichroism spectrum of MOVPE InMnAs. As discussed in section 2.4.3, RMCD due to transitions between *sp-d* exchange split valence and conduction bands is proportional to the differential reflectivity ($1/R \ dR/dE$). While the CPs and lineshape of the differential reflectivity spectrum of undoped InAs have been previously reported,¹⁸⁰ Mn doping can significantly effect the spectra of III-V and II-VI semiconductors.^{121, 122, 181} First, the peaks in the $1/R \ dR/dE$ spectrum can be broadened due to disorder. Furthermore the extrema of

the differential reflectivity spectrum, which correspond to band structure CPs potentially can be shifted by Mn doping. Therefore the differential reflectivity spectra of MOVPE InMnAs were studied as a function of Mn concentration.

A summary of the In_{1-x}Mn_xAs samples used for this study is given in Table 5-1. Room temperature reflectance spectra were measured from 1.6-3.1 eV for an undoped InAs film (ajb 145) and two $In_{1-x}Mn_xAs$ films with x=0.034 (ptc 121) and x=0.085 (ajb 197). The spectra are shown in Figure 5-1a. For the purpose of comparison, the reflectance for each of the three samples was normalized with respect to their respective R values at 2.55 eV. The reflectance spectra were then numerically differentiated with respect to energy and normalized by R to yield a differential reflectivity spectrum. I/R dR/dE versus E plots for a b 145, ptc 121 and a b 197 are shown in Figure 5-1b. We emphasize that the plots of 1/R dR/dE versus E for both undoped and Mn doped films are similar. The differential reflectivity remains constant from 1.6-2.4 eV for all three samples. In addition, two sharp negative peaks, marked by red arrows in Figure 5-1b were observed at approximately 2.6 and 2.9 eV. The two minima correspond to the E_1 and $E_1 + \Delta_1$ CPs. As shown in the schematic band structure in Figure 5-2, the E_1 and $E_1+\Delta_1$ CPs are due to transitions between the heavy hole VB to the CB (E_l) and light hole VB to the CB ($E_l + \Delta_l$). It is important to emphasize that the magnitude of the E_I peak (0.6 eV⁻¹) in the differential reflectivity spectrum is greater than that observed away from the $E_I \text{ CP} (0.25-0.30 \text{ eV}^{-1})$ for both Mn doped and undoped films. Therefore undoped and Mn doped InMnAs films exhibit similar differential reflectivity spectra including negative peaks at the E_1 and $E_1+\Delta_1$ CPs and a significant enhancement in 1/R dR/dE at CPs.



Figure 5-1: Plot of (a) normalized *R* versus *E* (b) and 1/R dR/dE versus *E* for InAs (ajb 145), In_{0.966}Mn_{0.034}As (ptc 121), and In_{0.915}Mn_{0.085}As (ajb 197) thin films. *E*₁ and *E*₁+ Δ_1 CPs are indicated by the red arrows in part (b) of the figure.



Figure 5-2: Schematic band structure of InMnAs thin films with *L*-point critical transitions indicated. Impurity bands omitted for simplicity.

Sample #	x	$E_{I}(\mathbf{eV})$	$E_{l}+\Delta_{l}(\mathrm{eV})$
ajb 145	0	2.58	2.90
ptc 121	0.034	2.57	2.88
ptc 209	0.063	2.56	2.88
ajb 190	0.070	2.56	2.88
ajb 197	0.085	2.56	2.87
ajb 189	0.12	2.55	2.86

Table 5-1: Room temperature *L*-critical point energies of In_{1-x}Mn_xAs thin films.

The primary difference in the I/R dR/dE versus E of undoped versus Mn doped films is a red shift in the E_1 and $E_1+\Delta_1$ CPs that increases with Mn concentration. The E_1 and $E_1+\Delta_1$ CPs are defined as the energy where $I/R d^2R/dE^2=0$.¹²¹⁻¹²³ In the case of ajb 145 (x=0), the E_1 and $E_1+\Delta_1$ CPs are 2.58 and 2.90 eV, in good agreement with previously measured values for undoped InAs (2.60 and 2.88 eV).¹⁸² In contrast, the E_1 and $E_1+\Delta_1$ CPs of ptc 121 (x=0.034) are 12 and 16 meV less than that observed for undoped InAs (ajb 145), respectively. Therefore, Mn doping induces a subtle red-shift of higher lying *L*-point critical transitions. The E_1 and $E_1+\Delta_1$ CPs for the remaining InMnAs samples are summarized in the Table 5-1. As shown in Table 5-1 and Figure 5-3, the red shift magnitude of the E_1 and $E_1+\Delta_1$ CPs are reduced by 27 meV and 34 meV relative to undoped InAs respectively.



Figure 5-3: The dependence of room temperature E_I CP on x for $In_{1-x}Mn_xAs$ samples, with x ranging from 0 to 0.12. Linear fit of the experimental data is given by the red line.

We attribute the red shift in the E_1 and $E_1 + \Delta_1$ CPs with x in MOVPE InMnAs to a Coulombic potential perturbation arising from ionized Mn impurities in the sample. Similar linear red shifts of *L*-critical points in heavily doped Si,¹⁸³ Ge,¹⁸⁴ and GaAs¹²³ were also assigned to this effect. We emphasize that the Coulombic potential perturbation is electrostatic in nature and also occurs in semiconductors with *nonmagnetic dopants*.

In contrast, alternative mechanisms for the red-shifts observed at the *L*-point, including, sp-d exchange and Mn impurity band to conduction band transitions (see section 4.1.1), are inconsistent with experimental results. First, Burch *et al.* demonstrated that in the absence of a magnetic field, sp-d exchange induces a *blue-shift* of the *L*-critical points of MBE grown GaMnAs.¹²¹ The *sp-d* exchange interaction drives the Mn impurity level deeper into the gap and the valence band to lower energies. This increases the energy gap between the valence and conduction bands at the *L*-point and results in the observed blue-shift. We note that spectroscopic

studies of the above gap critical points in MBE grown InMnAs have not been previously reported. Second, transitions from the deep ($E_A \approx 0.12 \text{ eV}$) and shallow ($E_A \approx 23 \text{ meV}$) impurity bands would not result in a simple red-shift at E_I , but rather resonances in the reflectivity spectrum at 1.38 and 1.48 eV respectively as given by Figure 5-4.¹²⁰ The calculation of the red-shift magnitudes assumes that the energy dependence of the two Mn impurity bands are independent of the wavevector, \vec{k} .²⁵ Since both transitions are outside the measured spectral range, these resonances would not be observed in the visible light reflectivity spectrum.



Figure 5-4:Schematic band structure of InMnAs near the critical point whereby transitions between the deep and shallow Mn impurity bands are highlighted in red and green respectively.¹²⁰

5.2 Visible range polar RMCD spectroscopy

Reflectance magnetic circular dichroism (RMCD) measured in the polar geometry from 1.6-3.1 meV was utilized to study the effect of *sp-d* exchange splitting of the band structure near

the *L*-critical points of MOVPE InMnAs. *Sp-d* exchange has a particular signature in the dichroism spectrum: enhancement of the RMCD near band structure CPs relative to that away from CPs. The enhancement of the RMCD (ϕ) near CPs can be explained in terms of the equation derived in section 2.4.3 that relates ϕ in units of degrees to the exchange splitting of the bands (ΔE): ¹¹⁷

$$\phi = \frac{45}{\pi} \frac{1}{R} \frac{dR}{dE} \Delta E \,. \tag{5-1}$$

The enhancement of the RMCD in ferromagnetic semiconductors is attributed to an enhancement in *1/R dR/dE* near CPs relative to *1/R dR/dE* away from CPs. According to equation 5-1, it is also evident that the dichroism peaks at CPs will be positive or negative because *both* the differential reflectivity and exchange splitting can change sign. In the specific case of MBE grown InMnAs, a single RMCD negative peak at 2.61 eV was attributed to strong *sp-d* exchange at the *L*-point.⁵³ Gaj *et al.* predicted two equal and opposite RMCD peaks associated with the *E*₁ (2.52 eV) and $E_1+\Delta_1$ (2.79 eV) CPs due to a change in sign of ΔE at E_1 and $E_1+\Delta_1$ (*1/R dR/dE*<0 at E_1 and $E_1+\Delta_1$)^{22, 124} However a single peak has been detected at the *L*-point for InMnAs and several other materials.^{119, 127} Therefore the occurrence of a single dichroism peak between the 2.52 and 2.79 eV is a specific fingerprint of *sp-d* exchange in InMnAs.

Table 5-2 summarizes the composition, magnetic, and transport properties of the ten $In_{1-x}Mn_xAs$ films utilized in the RMCD study. As is evident from Table 5-2, the InMnAs films investigated by RMCD spectroscopy have T_c 's near 330 K. The T_c does not scale with Mn concentration. Moreover, the room temperature itinerant hole concentrations range between

 6.1×10^{17} cm⁻³ to 1.61×10^{18} cm⁻³. Both the magnetic properties³³ and transport properties¹⁴⁴ of the samples in Table 5-2 are highly consistent with that reported previously by Blattner *et al.*

Sample #	x	Туре	<i>T_c</i> (K)	<i>p</i> (300K) (x10 ¹⁸ cm ⁻³)
ptc 112	0.033	1	336	0.61
ptc 118	0.037	1	-	-
ptc 146	0.040	1	333	1.02
ptc 147	0.045	1	-	0.57
ptc 015	0.020	2	325	1.61
ptc 121	0.034	2	333	-
ptc 208	0.026	2	-	-
ptc 210	0.045	2	334	-
ptc 211	0.057	2	-	-
ptc 209	0.063	2	-	-

Table 5-2: Type 1 and Type 2 $In_{1-x}Mn_xAs$ thin films and their magnetic/transport properties. The T_c and hole concentrations were measured by SQUID and Hall effect respectively.

The samples in Table 5-2 were divided into two types based upon their respective room temperature dichroism spectra. The *T*=298 K RMCD spectra of ptc 118 (*x*=0.037) and ptc 147 (*x*=0.045), two of the four samples designated as Type 1 films, are given in Figure 5-5. The RMCD spectra were measured with a 0.5 T applied field to saturate the magnetization of the samples. As shown in Figure 5-5, ptc 118 and 147 exhibit a broad, *negative* RMCD lineshape that extends from 1.6 to 3.1 eV. No peaks near the E_1 and $E_1+\Delta_1$ CPs were observed. Similar featureless spectra were also observed for the other two Type 1 films: ptc 112 and 146. However a different room temperature spectral lineshape was measured for the six remaining films, termed Type 2 films. As shown in Figure 5-6, two of the Type 2 films, ptc 015 (*x*=0.02) and ptc 121 (*x*=0.034) exhibit two salient spectral features. First, a broad negative dichroism response similar to that measured for Type 1 films was observed. Second, a single negative peak centered at 2.68 eV and 2.60 eV was measured for samples ptc 015 and ptc 121, respectively. However it is

important to emphasize that the magnitude of this peak is only 1/3 to 1/2 the magnitude of the broad negative response.



Figure 5-5: Room temperature RMCD spectra of ptc 118 (x=0.037) and ptc 147 (x=0.045). ptc 118 and 147 are examples of Type 1 In_{1-x}Mn_xAs films.



Figure 5-6: RMCD as a function of photon energy at T=298 K and H=0.5 T for (a) ptc 015 (x=0.020) and (b) ptc 121 (x=0.034). Both ptc 015 and 121 are Type 2 In_{1-x}Mn_xAs films.

In order to determine whether the dichroism spectra of Type 1 and Type 2 films can be *exclusively* attributed to transitions between *sp-d* exchange split valence and conduction bands, the RMCD spectra in Figure 5-5 and Figure 5-6 were compared to that of MBE InMnAs. As discussed in section 2.4.3, the dichroism spectrum of MBE InMnAs has been attributed to transitions between *sp-d* exchange split VB and CB.⁵³ First, we fit the dichroism spectrum of the Type 1 film, ptc 118 (x=0.037) to that of MBE InMnAs. For the purpose of comparison, the spectrum of MBE InMnAs was scaled such that ϕ (1.6 eV) was equal to that of ptc 118. As evident from Figure 5-7a, the fit of the dichroism spectrum of ptc 118 with respect to that predicted for RMCD due *sp-d* exchange is extremely poor for two principle reasons. First, the relative magnitudes of the dichroism at 1.6 and 2.6 eV do not agree. In the case of MBE InMnAs, the dichroism is 2.5 times stronger at 2.6 eV (-26 mdeg) relative to that at 1.6 eV (-10 mdeg). The enhancement of the dichroism in MBE InMnAs at the E_1 CP is a classic signature of *sp-d* exchange. However, in the case of ptc 118, no peak above the noise threshold (~0.7 mdeg) was even observed at 2.6 eV. Consequently, the dichroism at 2.6 eV (-9.5 mdeg) is less than that observed at 1.6 eV (-10 mdeg). Second, the shape of the broad background from 1.6-2.2 eV observed for ptc 118 also does not agree with that of MBE InMnAs. For MBE InMnAs, ϕ increases from -10 to +8.8 mdeg between 1.6-2.2 eV. In contrast, ϕ for ptc 118 increases slightly from -10 to -7.4 mdeg, but does not change sign. Therefore, the absence of any relative enhancement of the RMCD at the E_1 CP and lineshape of the background from 1.6-2.22 eV indicate that the dichroism in Type 1 films cannot be attributed to sp-d exchange splitting of the VB and CB.



Figure 5-7: Fit of the RMCD spectrum MBE InMnAs⁵³ with respect to (a) the Type 1 film, ptc 118 (x=0.037) and (b) the Type 2 film, ptc 121 (x=0.034). Dichroism spectrum of MBE InMnAs was scaled such that $\phi(1.6 \text{ eV})$ for each of the two spectra were equal.

Next we fit the dichroism spectrum of a Type 2 film, ptc 121, with respect to that of MBE InMnAs. The spectrum of MBE InMnAs was scaled such that $\phi(1.6 \text{ eV})$ was equal for the two spectra. Similar to the case of Type 1 films, the fit shown in Figure 5-7b is also poor. While a peak near 2.6 eV was observed in all Type 2 films, the magnitude of this peak relative to that of the background does not agree with the relative magnitudes observed for MBE InMnAs. For example, in the case of ptc 121, the broad background is nearly constant -26 mdeg, while the magnitude of the negative peak is only -8 mdeg (see Figure 5-6b). Therefore, the magnitude negative peak is *only 1/3* the magnitude of the background at 1.6 eV (-29 mdeg). Therefore, the differences in the relative magnitude of the peak as compared to the background (factor of 8.4) indicates that the RMCD spectrum of Type 2 films.

However, if the broad background and negative peak features in Type 2 films are due to *two distinct transitions* (between different sets of bands), then the negative peak feature could still be a signature of *sp-d* exchange splitting at the *L*-point. Following subtraction of the broad background feature, we fit dichroism spectrum of ptc 121 with respect to that of MBE InMnAs. The spectrum of MBE InMnAs was scaled by a factor 0.11 for the purpose of comparison. As evident in Figure 5-8, we find excellent agreement between the peak shape and peak position of the *background subtracted spectrum* of ptc 121 and that of MBE InMnAs. The lineshape is also consistent in the relative magnitudes of the background and peak. In contrast, *since there is no observable peak in Type 1 films*, even a background subtracted spectrum does not agree with that of MBE InMnAs.



Figure 5-8: Comparison of the RMCD spectra of ptc 121 (x=0.034) and that of MBE grown InMnAs. The dichroism spectrum of the MBE InMnAs is scaled by a factor 0.11.

Therefore, the RMCD spectra shown in Figure 5-5 and Figure 5-6 of Type 1 and Type 2 InMnAs thin films, respectively, yield several important questions:

- 1. What is the origin of the broad negative RMCD response observed in Type 1 films?
- 2. Are the two spectral features observed in Type 2 films related to two distinct optical transitions such that the negative peak transition can be attributed to *sp-d* exchange?

The two questions will be addressed in sections 5.2.1 and 5.2.2 respectively.

5.2.1 Nature of the RMCD transitions in Type 1 films

In this section, we address the origin of the broad negative RMCD response in Type 1 films. We attributed this response to spin dependent transitions between ionized Mn acceptors in the Mn related *deep* impurity band to the conduction band (CB) as illustrated in Figure 5-9. The transitions can also be represented by the expressions:

$$\begin{array}{c} \text{RCP} \\ (\text{Mn}^{2+}+h)\uparrow \to (\text{Mn}^{3+}+h)\uparrow + e\uparrow^{-}(\text{CB}) \\ \text{5-2} \end{array}$$

$$(\mathrm{Mn}^{2+}+h)\downarrow \to (\mathrm{Mn}^{3+}+h)\downarrow + e\downarrow^{-}(\mathrm{CB})$$
5-3

In equations 5-2 and 5-3, the initial electronic state of Mn acceptors in the deep impurity band prior to photoexcitation is $(Mn^{2+}+h)\uparrow$ or $(Mn^{2+}+h)\downarrow$ according to section 4.2.1. Following the absorption of an RCP or LCP photon, a spin up $(e\uparrow)$ or spin down electron $(e\downarrow)$ is promoted into the CB. This results in the formation of either a $(Mn^{3+}+h)\uparrow$ or $(Mn^{3+}+h)\downarrow$ excited state, respectively. Although similar transitions between the shallow Mn impurity band to the CB are allowed in principle, these transitions are not considered because there are presumably 100 times more Mn in the deep impurity as opposed to the shallow impurity band. Therefore, we assume that deep impurity band to CB transitions dominate over interband transitions involving the shallow impurity band.



Figure 5-9: Schematic illustrating spin dependent transitions between the deep Mn impurity band and the conduction band.

In order to calculate an RMCD spectrum associated with these bound to free transitions shown in Figure 5-9, we begin with the general expression that relates ϕ to ΔE given by equation 5-1. Since we are modeling dichroism due to deep impurity band to CB transitions (ϕ_{ib-cb}), we may change the general reflectivity (R) in equation 5-1 to reflectivity specifically due to deep impurity band to CB transitions (R_{ib-cb}). While the exchange splitting (ΔE) generally would involve the splitting of both the deep impurity band (ΔE_{ib}) and conduction bands (ΔE_{cb}), *this model only considers the exchange splitting of the deep impurity band*. This is a reasonable assumption as conduction band splitting in ferromagnetic semiconductors is extremely weak and therefore often omitted.⁶² The significance of this supposition is that due to the strong E versus \vec{k} dependence for the conduction bands,^{58, 81} ΔE_{cb} depends strongly on energy (see section 2.4.3). The exchange energy depends upon the density of states, which is turn proportional to $d\vec{k}/dE$.⁵² On the other hand, Mn impurity bands typically have weak energy dependences with \vec{k} such that ΔE_{ib} will be nearly independent of energy.²⁵ Using these assumptions, ϕ_{ib-cb} in units of degrees is given by the following:

$$\phi_{ib-cb} = -\frac{45}{\pi} \frac{1}{R_{ib-cb}} \frac{dR_{ib-cb}}{dE} \Delta E_{ib} .$$
5-4

We emphasize the simplicity of equation 5-4. Since this model assumes that ΔE_{ib} does not depend on *E*, the spectral dependence of ϕ_{ib-cb} will be proportional to $1/R_{ib-cb} dR_{ib-cb}/dE$. Consequently, we reduced the simulation of $\phi_{ib-cb}(E)$ to a *spin independent* calculation $R_{ib-cb}(E)$. The spin dependence of $\phi_{ib-cb}(E)$ can be accounted for by multiplying $1/R_{ib-cb} dR_{ib-cb}/dE$ by a single constant, ΔE_{ib} .

The energy dependence of the reflectivity (R_{ib-cb}) due to bound to free transitions can be determined using the Lucovsky model for optical transitions.¹⁸⁵ According to the Lucovsky model, the spectral dependence of the imaginary index of refraction (k) for a defect level is given by the equation:

$$k(E) = \frac{8N\pi e^2 \hbar^2 E_i^{1/2}}{3m^*} \frac{(E - E_i)^{3/2}}{E^4} = A \frac{(E - E_i)^{3/2}}{E^4},$$
5-5

where *N* in this case is the nominal concentration of Mn deep level impurities, E_i is the difference in energy between the conduction band minimum (E_c) and E_A of the deep impurity band, and m^* is the effective mass of an electron in the deep impurity band. For simplicity, these constants were grouped into a single term, *A*, in equation 5-5.

While the Lucovsky model provides an expression for the spectral dependence of k, the determination of R_{ib-cb} also requires the real part of the index of refraction (n) as demonstrated by the following equation: ¹⁰³

$$R_{ib-cb}(E) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}.$$
 5-6

Therefore, n(E) was calculated through a Kramers-Kronig (KK) transformation:¹⁸⁶

$$n(E) = 1 + A \frac{64(E - E_i)^2 + 160(E - E_i) + 20}{256(E - E_i)^2 + 256(E - E_i)^3 + 96(E - E_i)^2 + 16(E - E_i) + 1}.$$
5-7

An explicit derivation of equation 5-7 utilizing a KK transformation is given in Appendix B. The real and imaginary index of refraction terms were then substituted into equation 5-6 to obtain R_{ib} .

In order to obtain real values for R_{ib-cb} , specific values for N, E_b and m^* must also be determined (see equation 5-5). For this we assumed a Mn concentration equal to that of ptc 147 (x=0.047) such that N=8.5x10²⁰ cm⁻³. An activation energy (E_A) of 0.12 eV was chosen that is consistent with the IR absorption measurements and first principles calculations.³⁹ We emphasize that the activation energy 0.12 eV was inferred because inter-valence band transitions prevented a direct measurement of the deep impurity band E_A . The ionization energy, E_i is then difference between E_c and E_A (0.23 eV). Furthermore, the effective mass of a deep impurity band hole (m^*) can be estimated from E_A using the equation:⁶⁸

$$m^* = E_A \frac{m_e \varepsilon^2}{13.6 eV},$$
 5-8

where ε is the dielectric constant of InMnAs equal to 12.5 and m_e is the mass of the an electron. From equation 5-8, we calculated $m^*=1.4m_e=1.3 \times 10^{-27}$ g. The reflectivity spectrum predicted by the Lucovsky model was then calculated and is shown in Figure 5-10a. The calculated reflectivity has a sharp maximum with R=0.20 at the $E=E_i=0.23$ eV. However, from 0.23 eV to 1 eV, the reflectivity decreases rapidly from its maximum of R=0.20 to R=8.4x10⁻⁴. In the visible light range between 1.6-3.1 eV, the reflectivity *decreases* slowly with increasing energy from 8.4x10⁻⁵ to 3.5x10⁻⁶. The R_{ib-cb} versus Edependence was then numerically differentiated to determine the $1/R_{ib-cb} dR_{ib-cb}/dE$ spectrum. As given in Figure 5-10b, the differential reflectivity changes sign from positive to negative at the ionization energy. However, we emphasize that in the visible spectral range $1/R_{ib-cb} dR_{ib-cb}/dE$ is *broad and negative*.



Figure 5-10: (a) R_{ib-cb} versus *E* and (b) $1/R_{ib-cb} dR_{ib-cb}/dE$ versus *E* for an In_{0.953}Mn_{0.047}As film calculated from the Lucovsky model.

According to equation 5-4 and the assumption that ΔE_{ib} is independent of energy, the differential reflectivity spectrum can be converted into a ϕ_{ib-cb} spectrum by multiplying the $1/R_{ib-cb}/dE$ by ΔE_{ib} . Moreover, we can fit the experimental RMCD spectrum using equation 5-4

with ΔE_{ib} as a fitting parameter. The quality of the fit determines whether the model assumptions described previously are justified. Since ΔE_{ib} is a fitting parameter, the Lucovsky fit will also yield a measure of the exchange splitting of the deep impurity band.

A comparison of the Lucovsky model dichroism spectrum and the experimental spectrum of ptc 147 is shown in Figure 5-11. We emphasize that the RMCD spectral lineshape predicted by the Lucovsky model is consistent with the nearly featureless transitions observed in Figure 5-5. Both spectra are also well described by a linear fit. Similar high quality fits were observed for the other Type 1 films. The quality of the fit shown in Figure 5-11 indicates the broad negative dichroic response observed for Type 1 films can be attributed to transitions between the spin split deep Mn impurity band and spin symmetric conduction band. In contrast, the fit of Type 1 films assuming transitions between the VB and CB yielded an extremely poor fit. As discussed previously, the Lucovsky model used to fit the experimental spectrum *neglects spin* splitting of the conduction band. Therefore the model indicates that the deep impurity band is spin split, in agreement with the XMCD results (see section 4.2.2). As shown in Table 5-3, the magnitude of the exchange splitting, ΔE_{ib} , ranges from 1.2 to 2.9 meV for the four Type 1 films. We emphasize that the positive sign of the ΔE_{ib} values indicates that the negative RMCD results from the specific energy dependence of the differential reflectivity $(1/R_{ib-cb}/dE < 0)$. However, we caution that there is a large uncertainty in the absolute values of ΔE_{ib} in Table 5-3 because $1/R_{ib-cb} dR_{ib-cb}/dE$ was modeled and not directly measured.



Figure 5-11: Comparison of the linear, Lucovsky fits of the experimental RMCD spectrum of ptc 147 (x=0.045).

Table 5-3: Summary of the deep impurity band exchange splitting in $In_{1-x}Mn_xAs$ films determined from Lucovsky model fits of the experimental dichroism spectra.

Sample #	x	ΔE _{ib} (meV)
ptc 112	0.033	1.2
ptc 118	0.037	2.9
ptc 146	0.040	2.4
ptc 147	0.045	1.6

Finally we note that attribution of broad background dichroism in Type 1 films to transitions between a spin split deep impurity band and spin symmetric CB can be corroborated with infrared dichroism measurements. As shown in Figure 5-10b, the Lucovsky model predicts that the dichroism changes sign from positive to negative at the ionization energy. Moreover,

since this RMCD sign change occurs at E_i , the IR RMCD spectrum provides a method for precisely measuring the activation energy of the deep impurity band. The energy at which ϕ_{ib} . $_{cb}=0$ is equal to E_i , and E_A is then the difference between E_0 and E_i . However, such IR dichroism measurements are beyond the scope of this thesis.

5.2.2 Nature of the RMCD transitions in Type 2 films

In order to establish the origin of the transitions observed in the RMCD spectra of Type 2 InMnAs films, we measured the temperature and field dependence of the spectra at 1.95 eV and 2.54 eV. Since the broad background transition dominates the RMCD at 1.95 eV and both the negative peak and background contribute at 2.54 eV, measuring the RMCD as a function of Tand H at the two energies allows for selective characterization of each feature. There are two reasons for measuring RMCD versus T and H at 1.95 and 2.54 eV. First, RMCD due to a ferromagnetic component in the material will exhibit classic signs of hysteresis and remanence in the field dependence. Second, if distinct differences were observed in either the temperature dependence at these two energies, the two RMCD spectral features could be attributed to two distinct transition types,¹⁶⁸ where one transition is due to *sp-d* exchange.

5.2.2.1 RMCD field dependence

In order to establish whether the two transitions observed in Type 2 films are due to ferromagnetic component(s) in the material, the RMCD hysteresis loops were measured at 1.95 eV and 2.54 eV. The dependence of the polar RMCD on *H* for ptc 015 (x=0.020) at the two specified energies is given in Figure 5-12. The dichroism field dependence was measured out of plane from -0.4 T to 0.4 T at room temperature. As is evident in Figure 5-12, aside from the differences in magnitude, the RMCD versus *H* at 1.95 eV and 2.54 eV are nearly identical. Both

have a coercive field (H_c) of 290 G and a remanent RMCD (ϕ_r) that is 11% of the saturation RMCD (ϕ_s) . Since hysteresis and remanence are both signatures of ferromagnetism, we assert that the broad background and negative peak transitions observed for ptc 015 can both be attributed to ferromagnetic specie(s) in this particular sample.



Figure 5-12: Room temperature RMCD hysteresis loops measured with E=1.95 and 2.54 eV for ptc 015 (x=0.020).

Although the RMCD field dependence of ptc 015 exhibits classic evidence of ferromagnetism, the hysteresis loops of Type 2 samples vary significantly. In fact as the sample magnetization increases, the shape of the out of plane hysteresis loops changes systematically. As shown in Table 5-4, the room temperature saturation magnetizations (M_s) of Type 2 samples increases from ptc 210, to ptc 015, to ptc 121. The polar RMCD field dependences corresponding to each of the three samples are given in Figure 5-13. From both Table 5-4 and Figure 5-13, it is clear that both the out of plane H_c and ϕ_r decrease with increasing M_s . The

sample with the smallest M_s (3.0 emu/cm³), ptc 210, exhibits clear evidence of hysteresis (H_c =420 G) and remanence (ϕ_r =36%). However, the sample with the largest M_s (17 emu/cm³), ptc 121, has a nearly reversible, superparamagnetic-like polar hysteresis loop.



Figure 5-13: Polar hysteresis loops of (a) ptc 210 (x=0.045), (b) ptc 015 (x=0.020), and (c) ptc 121 (x=0.034).

Table 5-4: Room temperature M_s , H_c , ϕ_r values of InMnAs films. M_s was measured by SQUID magnetometry. H_c and ϕ_r were measured by RMCD magnetometry in the polar geometry. Samples are ordered with respect to the magnitude of their M_s values.

Sample #	x	$\frac{M_s}{(\text{emu/cm}^3)}$	<i>H</i> _c (G)	ϕ_r (% ϕ_s)
ptc 210	0.045	3.0	420	36
ptc 015	0.020	3.8	290	11
ptc 121	0.034	17	~10	1.3

In order to determine if the decrease in polar dichroism hysteresis can be attributed to an increase in the fraction of Mn incorporated into superparamagnetic particles, ϕ versus *H* loops were also measured along the [110] direction. The signature of superparamagnetic particles in the dichroism field dependence is a completely reversible ϕ versus *H* loop (no remanence and hysteresis), regardless of the direction of the applied field.⁷⁰ Plots of the room temperature inplane RMCD hysteresis loops with the field along the [110] and [001] for ptc 121 (*x*=0.034) are given in Figure 5-14. Although the polar ϕ versus *H* loop is nearly reversible, the in-plane [110] RMCD field dependence is strongly hysteretic (*H_c*=1210 G) and nearly fully remanent (ϕ =99%). Hysteresis loops for the field in the [110] direction of ptc 015 and ptc 121 have a similar shape. ^{35, 187} The observation of strong hysteresis in the [110] ϕ versus *H* loops directly contradicts the predicted reversibility in the case of superparamagnetic precipitates. Therefore the observed RMCD is not the result of an increase of a superparamagnetic second phase in the material.


Figure 5-14: ϕ versus *H* for ptc 121 (*x*=0.034) measured at *T*=298 K along the [110] (in plane) and [001] (out-of plane) directions. ϕ versus *H* loop measured along the [110] direction was scaled by a factor 45 for the purpose of comparison.

Instead, the reversibility observed in the polar hysteresis is attributed to an increase in shape anisotropy with increasing sample saturation magnetization. Aligning the magnetization perpendicular to the plane requires larger applied fields than that required in plane due to a relative increase in energies associated with demagnetization fields for the two geometries.⁷⁰ Therefore, shape anisotropy of a thin film results in the easy axis being in the plane of the film.¹⁸⁸⁻¹⁹⁰ According to Thompson and Tait, the shape anisotropy magnitude of a thin film is proportional to $4\pi M_s$.¹⁹¹ The effect of large shape anisotropy is square in-plane hysteresis loops with low saturation fields, and out of plane loops that have increasing saturation fields and reversibility with increasing M_s .⁷⁰ This is consistent with the experimental out-of plane RMCD field dependence of MOVPE InMnAs.⁷⁰

5.2.2.2 RMCD Temperature Dependence

Prior to the assignment of the two RMCD spectral features observed in Type 2 InMnAs films, we measured the temperature dependence of the dichroism to determine whether the two features correspond to one or two distinct transitions. Since the negative peak could be attributed to *L*-point *sp-d* exchange for an RMCD spectrum due to *two distinct transitions* (see section 5.2), differentiating between a one or two component spectrum is particularly significant. In the case where the spectrum is due to two distinct transitions, the magnitude of the RMCD at each photon energy could have unique temperature dependences.¹⁶⁸ This also implies that if the dichroism spectra measured at different temperatures are normalized by the RMCD at a given photon energy, the spectra would differ. Conversely if the two features are associated with a single transition, then their temperature dependences will be identical and the spectra measured at varying temperatures will normalize to a single curve.²²

In order to determine if the two broad background and negative peak are due to two distinct transitions, a series of dichroism spectra were measured between 13-330 K. The temperature dependent spectra for ptc 015 and ptc 210 are shown in the top panels of Figure 5-15a and Figure 5-15b respectively. The dichroism spectra at various temperatures were then normalized to their respective values at 1.95 eV. The results following normalization for ptc 015 and ptc 210 are shown in the bottom panels of Figure 5-15b respectively. The curves measured at T>200 K approximately scales to a single spectrum. In contrast, at $T\leq200$ K, the magnitude of the negative peak feature observed for ptc 015 is significantly enhanced relative to the broad negative feature. As shown in Figure 5-15b, similar conclusions can be drawn from the temperature dependent spectra measured for ptc 210. While, the spectra of ptc 210 normalize

to a single similar curve for T>150 K, there is also a large relative increase in the magnitude of the peak over the background for $T\le150$ K.



Figure 5-15: RMCD spectra of (a) ptc 015 and (b) ptc 210 with H=0.4 T and T between 13-333 K. In the top panels the spectra are not normalized. In the bottom panels the spectra are normalized with respect to their respective RMCD values at E=1.95 eV.

To better compare the temperature dependence of the two dichroic responses, we plot the magnitude of the broad background and negative peak as a function of *T* for ptc 015 (x=0.020) and ptc 210 (x=0.045). We first present the results for ptc 015. The magnitude of the negative peak and background versus *T* curves were determined by evaluating each spectrum shown in

Figure 5-15a at 1.95 eV and 2.71 eV respectively. The resultant plots of the RMCD response at 1.95 and 2.71 eV, along with the magnetization as a function of temperature are given in Figure 5-16a. For the purpose of comparison, the magnitudes of ϕ and M in Figure 5-16a are all normalized with respect to their values at 298 K. The temperature dependence of ϕ at 2.71 eV, ϕ at 1.95 eV, and M for ptc 015 all exhibit similar behavior near the T_c of 325 K. However, at temperatures less than 200 K, there are significant deviations in the magnitude of the peak and broad background responsivities. In the case of ptc 015, the negative peak increases by a factor of 2.2 from T=250 K to 25 K. The increase is similar to the increase in the magnetization at low temperatures. On the other hand, the magnitude of the broad transition is nearly constant over the same temperature range. For ptc 210, the normalized peak and background spectral magnitudes were determined from the spectra given in Figure 5-15b at 1.95 and 2.59 eV, respectively. The change in probe energy for the negative peak is due to the fact that the peak observed for ptc 210 is red-shifted relative to that of ptc 015. As evident from Figure 5-16b, the dependence of the magnetization and RMCD response are similar for temperatures greater than 250 K. Between T=250 to 13 K, the magnitude of the negative peak increases dramatically by a factor of 1.8, which roughly agrees with the enhancement in the magnetization by a factor of 2.0. In contrast, the broad background magnitude is again independent of temperature for T < 250 K.



Figure 5-16: Plot of ϕ of the background, negative peak and magnetization as a function of *T* for (a) ptc 015 (*x*=0.020) and (b) ptc 210 (*x*=0.045). The ϕ magnitudes and *M* values are all normalized with respect to their values at *T*=298 K.

By measuring with improved temperature resolution (~3 K), subtle differences in the RMCD response at 1.95 and 2.54 eV versus *T* curves between *T*=273 to 350 K were resolved. The high resolution ϕ versus *T* plots for Type 2 samples, ptc 015 (*x*=0.020) and ptc 121 (*x*=0.034) are shown in the top panels of Figure 5-17a and Figure 5-17b respectively. It should be noted that in Figure 5-17, the RMCD response is normalized by its value at 275 K ($|\phi_n|$) for ease of comparison. For both samples, the largest point of contrast between the temperature dependence of $|\phi_n|$ at 1.95 eV and 2.54 eV occurs near the *T_c*, between 330-350 K. Between 330 K and 350 K, the values of $|\phi_n|$ at 1.95 eV decreases and approaches 0. However, $|\phi_n|$ at 2.54 eV exhibits a persistent nonzero tail over the same temperature range.



Figure 5-17: High temperature resolution plots of the ϕ magnitudes of the background (1.95 eV) and negative peak (2.54 eV) as a function of *T* for (a) ptc 015 (*x*=0.020) and (b) ptc 121 (*x*=0.034). All ϕ magnitudes are normalized with respect to their values at *T*=273 K. ϕ_n and $1/\phi_n$ versus *T* plots are given in the top and bottom panels respectively. Curie Weiss fits are shown in the bottom panels as dotted lines.

In addition, the T_c and Curie constant values calculated from the $|\phi_n|$ temperature dependence between 275-350 K differ significantly from 1.95 eV to 2.54 eV. The Curie temperature and Curie constant can be determined from Curie-Weiss mean field theory, which states that for $T>T_c$:¹⁰³

$$\frac{1}{|\phi_n|} = \frac{1}{C'H} (T - T_c),$$
 5-9

where *H* is the applied field and *C'* is the Curie constant. Equation 5-9 indicates that the slope and *x*-intercept from the $1/|\phi_n|$ as a function *T* plot correspond to the Curie constant and *T_c* respectively. It is important to note that utilization of $1/|\phi_n|$ versus *T* plots and equation 5-9 yields highly accurate values of *T_c* and *C'*. Although large errors in the measurement of *T_c* and *C'* from *M* versus *T* plots can occur due to an imprecise subtraction of the substrate susceptibility, the substrate does not contribute to the dichroism. Plots of $1/|\phi_n|$ versus *T* for ptc 015 and ptc 121 are given in the bottom panels of Figure 5-17a and Figure 5-17b respectively. The values of *T_c* and *C'* constants are summarized for both samples in Table 5-5. The *C'* constants measured at 2.54 eV (0.65 to 0.74 T/K) are within a factor of 3 to that measured by Blattner et al. (1.4 T/K).³⁴ However, as seen in Table 5-5, Curie constants measured at 1.95 eV are 8-10 times greater than that measured at 2.54 eV.

		1.95 eV	RMCD	2.54 eV RMCD	
Sample #	x	С' (Т/К)	T_c (K)	С' (Т/К)	T_c (K)
ptc 015	0.020	9.1×10^{-2}	337	7.4×10^{-1}	327
ptc 121	0.034	7.4×10^{-2}	339	6.5×10^{-1}	326

Table 5-5: Type 2 In_{1-x}Mn_xAs samples and the associated constants derived from the $1/|\phi_n|$ versus *T* plots.

As discussed previously, dichroism due to a single distinct transition should have identical temperature dependence *at each photon energy*. However, we observed clear differences in the dichroism temperature dependence of the negative peak and background both near the T_c and T<200 K. Therefore we attributed the negative peak and broad background features to *two distinct transitions*. The transitions are unique in that they occur between different bands. Therefore for Type 2 films, we related the RMCD response to the exchange energy by the following sum:¹⁶⁸

$$\phi_{total} = \sum_{i=1}^{2} \phi_{i} = -\frac{45}{\pi} \left(\frac{1}{R_{1}} \frac{dR_{1}}{dE} \Delta E_{1} + \frac{1}{R_{2}} \frac{dR_{2}}{dE} \Delta E_{2} \right).$$
 5-10

where R_i and ΔE_i are the reflectance and exchange energies associated with i^{th} transition type. Since each of the two transition types are unique, they can also have different associated ferromagnetic exchange interactions, such that $\Delta E_1(T) \neq \Delta E_2(T)$.¹⁶⁸ The differences in the temperature dependence of ΔE_1 and ΔE_2 would result in the differences in the RMCD versus *T* curves of the negative peak and broad background.¹⁶⁸

Although dichroism spectra of ferromagnetic semiconductors are typically attributed to a single transition type,^{53, 62, 119, 127} the two component RMCD formalism described by equation 5-10 is corroborated by the dichroism spectrum observed for MBE grown GaMnAs.¹⁶⁸ The dichroism spectrum of GaMnAs consists of both a broad positive background from 1.4-2.4 eV and a sharp negative peak centered at 1.6 eV. Similar to MOVPE InMnAs, the two spectral features were attributed to two distinct transitions due to the temperature dependence of the MCD spectra. As shown in Figure 5-18a, the MCD spectra do not normalize to a single curve as predicted for the case where the dichroism spectra is due to a single transition type. Moreover, MCD magnitudes measured at the center of negative peak (1.6 eV) and maximum of the positive background (1.87 eV) have different temperature dependences. The origin of the transitions was determined from the lineshape of the two spectral features. From the peak position and shape, Beschoten *et al.* attributed the negative peak to *sp-d* exchange splitting of the valence and conduction bands at the *F*-point. In contrast, Beschoten and coauthors assigned the broad

positive background to transitions between the Mn impurity band with an E_A =0.1 eV to higher lying impurity bands above the conduction band. Moreover, the authors accounted for the disparities in the MCD versus *T* to differences in the exchange splitting. In particular the exchange splitting of the valence and conduction bands as a function of *T* differs from the exchange splitting of the Mn impurity band versus *T*.¹⁶⁸



Figure 5-18: (a) MCD spectrum of MBE grown GaMnAs measured at T=5 K and T=100K. Both spectra were normalized by their respective values at 1.87 eV. Arrows mark the negative peak center (1.6 eV) and broad positive background maximum (1.87 eV). (b) Normalized MCD (ϕ_n) versus *T* measured at 1.6 and 1.87 eV, with a 1T applied magnetic field.¹⁶⁸

Following a similar methodology, we now identify two distinct transitions on the basis of their respective dichroic spectral lineshapes.¹⁶⁸ Due to the similarity in the lineshape of the broad transition in Type 2 films to the overall RMCD lineshape observed in Type 1 films, we also attribute the broad negative feature in Type 2 films to transitions involving a spin-split deep Mn impurity band to the conduction band (bound to free transitions). Next, this contribution was subtracted from the total RMCD spectra of Type 2 films. The subtraction is justified as the

Lucovsky model generates a nearly linear RMCD spectrum from 1.6 to 3.1 eV (see Figure 5-11). As shown in Figure 5-8 and discussed in section 5.2, following background subtraction, the spectrum of ptc 121 (x=0.034) agrees with that observed for MBE InMnAs. The background subtracted spectrum MOVPE InMnAs and the spectrum of MBE InMnAs both exhibit a single prominent negative peak that is consistent in its peak position and shape. Moreover, the magnitude of the dichroism of ptc 121 at the E_1 CP relative to that observed away from the CP also agrees with MBE InMnAs. As previously discussed in section 2.4.3, the negative RMCD peak at 2.6 eV of MBE grown InMnAs was attributed to *sp-d* exchange at the *L*-critical point. In a similar fashion, we assigned the negative peak observed in Type 2 InMnAs films to transitions between an *sp-d* exchange split valence band to the conduction band near the *L*-point of the band structure. The major difference between the two materials is that *sp-d* exchange in MOVPE InMnAs.

A schematic of these spin-dependent transitions is shown in Figure 5-19. It should be noted that in Figure 5-19, only the valence band is spin split near the *L*-point. Although the conduction band can also be spin split by *sp-d* exchange, the splitting of the conduction band is typically 20 times less than of the valence band.⁶² A typical value for the exchange splitting of the conduction band at the *L*-point is 0.1 meV.⁶² Conduction band splitting is negligible due to symmetry. Mn 3*d* orbitals are orthogonal to *s* states in the CB and consequently do not hybridize.^{29, 62} There are no such constraints with the hybridization of the Mn 3*d* and *p* states in the valence band.⁶² Therefore, *sp-d* exchange splitting of the conduction band is neglected in Figure 5-19 and in the rest of this chapter.



Figure 5-19: Schematic of the spin dependent transitions around the *L*-critical point of MOVPE InMnAs that results in the negative peak the RMCD spectrum. For simplicity, the Mn impurity bands and light valence band are omitted from this figure.

Utilizing the assignments of the two spectral features, the general expression relating the RMCD in Type 2 films to the exchange splitting given by equation 5-10 can be revised to the following:

$$\phi_{total} = \phi_{sp-d} + \phi_{ib-cb} = \frac{45}{\pi} \frac{1}{R_{cb-vb}} \frac{dR_{cb-vb}}{dE} \Delta E_{sp-d} + \frac{45}{\pi} \frac{1}{R_{ib-cb}} \frac{dR_{ib-cb}}{dE} \Delta E_{ib}.$$
 5-11

The first and second terms of the equation 5-11 refer to dichroism due to transitions between *spd* exchange split valence and conduction bands (ϕ_{sp-d}), and RMCD due to impurity band to conduction band transitions (ϕ_{tb-cb}) respectively. It should be noted that the measured reflectivity in section 5.1 is dominated by the reflectivity due to transitions between the valence and conduction band (R_{vb-cb}). From Figure 5-10, the contribution of R_{ib-cb} to the total reflectivity is small in the visible range (~1x10⁻⁵) and therefore difficult to resolve from the measured reflectivity. We now contrast the dichroism spectrum observed for MOVPE InMnAs and several MBE grown ferromagnetic semiconductors. For MBE grown InMnAs,⁵³ CdMnTe,⁶² and ZnCrTe,¹¹⁹ the RMCD spectrum is only composed of transitions between valence and conduction band that are spin split by *sp-d* exchange (ϕ_{sp-d} term in equation 5-11). However, the similarities between the dichroism spectrum of MBE grown GaMnAs and that of MOVPE InMnAs are striking. Both have a spectral component due to *sp-d* exchange and a second component involving transitions from a Mn impurity band in the band gap.

5.2.2.3 Magnitude of the *sp-d* exchange splitting

The magnitude of the *sp-d* exchange splitting (ΔE_{sp-d}) is of particular importance in ferromagnetic semiconductor based spintronic devices. *Sp-d* exchange splitting of the valence band results in spin polarized itinerant holes utilized in spin-based devices.⁵⁴ Moreover, the magnitude of the *sp-d* exchange determines the spin polarization of the itinerant carriers at a given temperature.¹⁹² Consequently, we utilized equation 5-11 to quantify the magnitude of the *sp-d* exchange energy of the valence band in InMnAs. First, the $\phi_{ib-cb}(E)$ contribution was subtracted to yield a $\phi_{sp-d}(E)$ curve. Next, the expression relating $\phi_{sp-d}(E)$ to ΔE_{sp-d} is given by the equation:

$$\phi_{sp-d} = \frac{45}{\pi} \frac{1}{R_{vb-cb}} \frac{dR_{vb-cb}}{dE} \Delta E_{sp-d} \,.$$
 5-12

Therefore, ϕ_{sp-d} was normalized by the differential reflectivity associated with valence to conduction band transitions $(1/R_{cb-vb} dR_{cb-vb}/dE)$ to yield a value for ΔE_{sp-d} .

The resultant values for ΔE_{sp-d} evaluated at the E_1 critical point (2.56 eV) are summarized in Table 5-6 for Type 2 samples, ptc 015 (x=0.020), ptc 121 (x=0.034), and ptc 210 (x=0.045). The energy of the E_1 CP (2.56 eV) and the corresponding differential reflectivity ($1/R_{cb-vb} dR_{cb-vb}/dE = -0.24$) were determined from polar reflectivity measurements (see section 5.1) At room temperature, $\Delta E_{sp-d}(E_1)$ values for ptc 015, ptc 121, and ptc 210 are 1.8 meV, 2.2 meV, and 1.9 meV respectively. The values of $\Delta E_{sp-d}(E_1)$ ptc 015, ptc 121 and ptc 210 at 13 K are significantly higher at 3.5 meV, 4.0 meV, and 5.1 meV respectively.

Table 5-6: *Sp-d* exchange splittings observed at the E_1 critical point for MOVPE InMnAs thin films. ΔE_{sp-d} was determined at T=13 and 298 K.

Sample #	x	$\frac{M(13 \text{ K})}{(\text{emu/cm}^3)}$	$\Delta E_{sp-d}(E_1, 298 \text{ K})$ (meV)	$\frac{\Delta E_{sp-d}(E_{I}, 13 \text{ K})}{(\text{meV})}$
ptc 015	0.020	13	1.8	3.5
ptc 121	0.034	31	2.2	4.0
ptc 210	0.045	6.2	1.9	5.1

We emphasize that $\Delta E_{sp-d}(E_I)$ values shown in Table 5-6 are large as compared to the spin splitting caused by the Zeeman effect. In the absence of *sp-d* exchange, the primary mechanism for exchange splitting of the VB is by Zeeman splitting, which occurs in all materials. An equation relating Zeeman splitting, ΔE_{Zeeman} , to the applied field is given by:⁷⁰

$$\Delta E_{Zeeman} = g \mu_B (H_{appl} + 4\pi M), \qquad 5-13$$

where H_{appl} is the applied field and M is the net magnetization of the material. In equation 5-13 the magnetization supplements the applied field, resulting in an enhancement in the Zeeman splitting. To calculate ΔE_{Zeeman} at E_I =2.56 eV, for ptc 015, ptc 121 and ptc 210, we used M values shown in Table 5-6, H_{appl} =5000 G, and g(2.56 eV)=5.1.⁵³ The applied field of 5000 G utilized in this calculation is the same field used for the dichroism measurements. The g-factor at the E_I critical point was determined from previous dichroism measurements of undoped InAs.⁵³ Using equation 5-13, we calculate that $\Delta E_{Zeeman} = 0.15$ meV for ptc 015, ptc 121 and ptc 210. We note that the differences of the *M* values for the three samples do not significantly affect the ΔE_{Zeeman} values because $H_{appl} >> 4\pi M$. According to Table 5-6, the spin splitting due to the Zeeman effect is 23-35 times *less than* the *sp-d* exchange splitting at 13 K. The large difference in the magnitude of ΔE_{sp-d} as compared to ΔE_{Zeeman} indicates that *sp-d* hybridization of the Mn 3*d* states with semiconductor band states *is required* to account for the magnitude of exchange splittings in Table 5-6.

The magnitude of the *sp-d* exchange at E_I observed for MOVPE InMnAs was also compared to that observed for MBE InMnAs⁵³ and that calculated by Freeman *et al.* using DFT.⁸¹ Although we can directly compare $\Delta E_{sp-d}(E_I)$ values, *sp-d* exchange splitting is also proportional to M,⁶² which then depends on *x*, *H* and *T*. Therefore, it is preferable to compare *sp-d* exchange integrals α and β , because α and β are independent of *M*. As previously discussed in section 2.4.3, the *sp-d* exchange splitting at the E_I CP is given by the expression:¹²⁴

$$\Delta E_{sp-d}(E_1) = \frac{\frac{1}{2}M(\alpha - \frac{1}{4}\beta)}{g\mu_B} .$$
 5-14

where g=2 for Mn²⁺ ions.¹⁷⁰ Furthermore, since we have assumed that that the exchange splitting of the conduction band is negligible in this material, α is equal to 0 (see equation 2-5). The resulting values for β can be used to estimate the *sp-d* exchange splitting at the band gap CP ($\Delta E_{sp-d}(E_0)$) using the equation:⁶²

$$\Delta E_{sp-d}(E_0) = \frac{M(\alpha - \beta)}{g\mu_B}$$
5-15

The exchange splitting at the band gap is particularly relevant to devices because the itinerant holes reside in the valence band at the Γ -point.

The resulting values for β and $\Delta E_{sp-d}(E_0)$ for the three MOVPE InMnAs are summarized in Table 5-7. As shown in Table 5-7, the exchange splitting at the Γ -point is 8 times larger relative to that observed at the *L*-point, ranging from 28-41 meV at 13 K. The β values of MOVPE InMnAs films vary between -3.1×10^{-35} to -1.9×10^{-34} erg cm³ ($N_0\beta$ = -0.35 to -2.1 eV). By comparison, β values measured for MBE InMnAs⁵³ and determined by DFT⁵⁸ are -5.2×10^{-35} erg cm³ and -2.4×10^{-34} erg cm³ respectively. We first note that β calculated by DFT is within 20% of that measured for ptc 210. On the other hand, the β values of ptc 015 and ptc 121 better match that of MBE InMnAs. The *p-d* exchange integral of ptc 015 and ptc 121 are 23% greater and 40% less than that of MBE InMnAs.

Table 5-7: Summary of β and $\Delta E_{sp-d}(E_0)$ values calculated from equations 5-14 and 5-15 respectively. $\Delta E_{sp-d}(E_1)$ and $\Delta E_{sp-d}(E_0)$ were determined at T=13 K. Exchange splitting and magnetizations for MBE InMnAs and that calculated by DFT were obtained from references 53 and 58 respectively.

Sample #	x	$\frac{M(13 \text{ K})}{(\text{emu/cm}^3)}$	$\frac{\Delta E_{sp-d}(E_I)}{(\text{meV})}$	$\frac{\boldsymbol{\beta}}{(10^{-35}\mathrm{erg}\mathrm{cm}^3)}$	$\frac{\Delta E_{sp-d}(E_{\theta})}{(\text{meV})}$
ptc 015	0.020	13	3.5	-6.4	28
ptc 121	0.034	31	4.0	-3.1	32
ptc 210	0.045	6.2	5.1	-19	41
MBE InMnAs	0.13	100	22	-5.2	180
DFT	0.063	52	-	-24	442

It is important to emphasize the large variability of the β values for MOVPE InMnAs samples. The *p*-*d* exchange integral for ptc 210 is 6 times greater than that observed for ptc 121. Moreover, Type 1 samples do not even exhibit any evidence of *sp*-*d* exchange splitting and

therefore have β ~0. Since all samples were grown using the same technique and have similar magnetic properties (T_c ~330 K), the origin of the differences in the magnitude of *sp-d* exchange splitting in MOVPE InMnAs films is presently unknown.

5.2.3 Ferromagnetic species associated with RMCD

In order to determine the identity of the ferromagnetic species responsible for the spin splitting of the impurity, valence, and conduction bands, the dependence of the RMCD on composition was investigated. For Mn-doped III-V and II-VI random alloys, where the majority of Mn are singly substituted,^{16, 17} mean field theory predicts that the magnitude of RMCD depends linearly on x (see section 2.4.3).²² On the other hand, if the room temperature RMCD is dependent on the concentration of clusters rather than that of singly substituted Mn, a superlinear composition dependence would be observed. For example, the concentration of dimers (*D*) depends on x^2 and not x. Similarly for dimers, the RMCD would have an x^2 dependence. Therefore, by fitting the dichroism with respect to x, we can elucidate the role of Mn atomic clusters and short range ordering on the observed room temperature RMCD.

The dependence of the RMCD spectra of Type 2 $In_{1-x}Mn_xAs$ films with respect to *x* is shown in Figure 5-20a. In Figure 5-20b, the contribution of the broad transition was subtracted from the RMCD spectrum to accentuate the evolution of the negative peak with *x*. As evident in Figure 5-20a, the shape of the broad background is also nearly independent of *x*. Moreover from Figure 5-20b, there are no systematic changes in shape or center of the negative peak with increasing *x*. It should be noted that the subtle red-shifts in the *L*-critical points discussed in section 5.1 would not be observed due to the low energy resolution (30-50 meV) of the RMCD



Figure 5-20: RMCD as a function of *E* for Type 2 $In_{1-x}Mn_xAs$ samples with *x* ranging between 0.020 to 0.063 (a) including the spectral contribution of the broad background transition (b) with the background transition linearly subtracted. All spectra were measured at 298 K with an applied field of 0.5 T.

In order to quantify the magnitudes of the background $(|\phi_b|)$ and negative peak $(|\phi_p|)$ dichroism, the RMCD was evaluated at 1.95 eV in Figure 5-20a and 2.73 eV in Figure 5-20b respectively. The values are summarized in Table 5-8. As indicated in Table 5-8, the magnitudes of the two dichroism components increase from 5.6 to 41 mdeg and 2.5 to 19 mdeg respectively between *x*=0.020 and 0.063.

Table 5-8: $In_{1-x}Mn_xAs$ samples used for this study and the magnitude of peak and background dichroism at T=298 K.

Sample	x	\$\phi_b (1.95 eV) (mdeg)	\phi_p (2.73 eV) (mdeg)
ptc 015	0.020	5.6	2.5
ptc 208	0.026	6.8	3.1
ptc 210	0.045	17	7.3
ptc 211	0.057	34	11
ptc 209	0.063	41	19

Next, the composition dependence of $|\phi_b|$ and $|\phi_p|$ as a function of x shown in Table 5-8 was fit with respect to four different models. The models assume that the dichroism is proportional to the concentration of *either* singly substituted Mn (S), dimers (D), trimers (T), or tetramers (T') in the material:

$$\phi_{\sin gle} = A_1 S = A_1 [N_0 x (1-x)^{12}], \qquad 5-16$$

$$\phi_{\dim er} = A_2 D = A_2 [12N_0 x^2 (1-x)^{18}], \qquad 5-17$$

$$\phi_{trimer} = A_3 T = A_3 [24N_0 x^3 (1-x)^{22}], \text{ and}$$
 5-18

$$\phi_{tetramer} = A_4 T' = A_4 [48N_0 x^4 (1-x)^{26}]$$
5-19

where A_n is the proportionality constant relating of concentration of n^{th} order clusters to the magnitude of the dichroism (units of mdeg cm³) and N_0 is the nominal cation concentration. The

expressions for *S*, *D*, *T*, and *T'* given in brackets in equations 5-16 to equation 5-19 were previously determined by Behringer *et al.*⁴⁵ It is important to note that the equations for *S*, *D*, *T*, and *T'* do not consider the effect of negative binding energies or the thermodynamic tendency to form clusters.^{37, 38, 79} Consequently the magnitudes of the *D*, *T*, and *T'* predicted by equations 5-17 to 5-19 will be less than the actual concentration. Conversely, the predicted values for *S* will be greater than the actual concentration of singly substituted Mn. However, we emphasize that negative binding energies would not affect the *lineshape* of the cluster concentration versus *x* plot. For example, Reiss and coauthors demonstrated that the concentration of dimers has an x^2 dependence, regardless of the magnitude of the binding energy for dimers.^{34, 193, 194} Therefore, the fits of the dichroism composition dependence using the previous expressions for *S*, *D*, *T*, and *T'* will still be valid because binding energies do not effect the shape of the ϕ versus *x* plots.

Plots of the measured $|\phi_b|$ and $|\phi_p|$ versus *x* dependence and the corresponding fits using equations 5-16 to 5-19 are shown in Figure 5-21a and Figure 5-21b, respectively. A_n was used as fitting parameter. The A_n fitting parameters and resultant R^2 values are summarized in Table 5-9. As shown in Figure 5-21a and Figure 5-21b, the fit of the experimental composition dependence improves with increasing cluster size, *n*. In particular, the model that attributes the dichroism to tetramers (*n*=4) reproduces the superlinear dependence of $|\phi_b|$ and $|\phi_p|$ with *x* at high Mn concentrations. In contrast, the model that attributes the dichroism to singly substituted Mn significantly underestimates the magnitude of the dichroism at high Mn concentrations. The improvement of the fit of the composition dependence with increasing cluster size is also evident from the R^2 values in Table 5-9. The singly substituted Mn model fit of $|\phi_b|$ versus *x* has an R^2 value of 0.63. The R^2 values increase to 0.89 for the dimer model fit and to 0.97 for the trimer

model fit. The fit with the highest R^2 value corresponds to the tetramer model fit (0.99). A similar increase in R^2 values from 0.60 to 0.92 with increasing cluster size were observed in the fits of the $|\phi_p|$ versus *x* dependence. Therefore, the compositional dependence of the RMCD suggests that both the broad transition and negative peak are related to Mn clusters, a result consistent with earlier EXAFS work.³⁶



Figure 5-21: Dependence of (a) $|\phi_b|$ (1.95 eV) (b) $|\phi_p|$ (2.73 eV) on *x*. Single substitutional model (single), dimer model, trimer model, and tetramer model fits are given as the red, blue, green, and black curves respectively.

Table 5-9: Summary of parameters used to fit the composition dependence of $|\phi_b|$ and $|\phi_p|$ and the resulting R^2 values. Four models for the composition dependence were used including the single substitutional model (single), dimer model, trimer model, and tetramer model.

	ø ₀ Fi	t	∅ ₀ Fit		
Model	A_n	R^2	A_n	R^2	
	(mdeg cm ³)		(mdeg cm ³)		
Single	$A_1 = 5.4 \times 10^{20}$	0.63	$A_1 = 5.3 \times 10^{20}$	0.60	
Dimer	$A_2=1.3 \times 10^{-19}$	0.89	$A_2=2.2 \times 10^{-19}$	0.84	
Trimer	$A_3=1.5 \times 10^{-18}$	0.97	$A_3 = 6.1 \times 10^{-19}$	0.90	
Tetramer	$A_4=1.7 \times 10^{-17}$	0.99	$A_4 = 6.7 \times 10^{-18}$	0.92	

We note that above models only account for changes in the dichroism composition dependence due cluster sizes of $n \le 4$. However, the EXAFS data indicated that an average Mn cluster size contains 14 atoms.³⁶ The effect of size n=14 on the dichroism composition dependence was not considered because Behringer does not provide a general analytical expressions for an concentration of n^{th} order clusters on x.⁴⁵ Nevertheless, we emphasize that the presence of clusters is still required to explain the measured superlinear $|\phi_b|$ and $|\phi_p|$ versus x dependence.

The cluster model fitting of the RMCD as a function of x indicates that the Mn states in the deep impurity band that give rise to the broad background, specifically correspond to Mn cluster *d*-states. Furthermore, in Type 2 samples, the Mn cluster *d*-states in the impurity band couple with the states in the valence band. The exchange between the 3*d* states *from Mn clusters* with semiconductor band states results in a *sp-d* exchange splitting that persists past room temperature. In contrast, hybridization of singly substituted Mn 3*d* states (i.e. MBE InMnAs) results in *sp-d* exchange splitting up to 90 K.¹³ Therefore, Mn cluster states are also necessary for *sp-d* exchange splitting of the valence band to persist up to room temperature. These conclusions support first principles calculations performed by Raebiger *et al.* who predicted that the deep impurity band and the valence band are composed of Mn 3*d* cluster states.^{39, 78} Moreover, the same calculation also predicted an enhancement in the strength of *sp-d* exchange with increased Mn clustering.⁷⁸

5.3 Broader implications of the RMCD spectroscopy

Here, we utilize the visible RMCD spectroscopic results to determine the inter-cluster exchange mechanism that results in a ferromagnetic material with a T_c of 330 K. From the visible RMCD data, we can supplement the energy level diagram shown in Figure 4-25 to that shown in Figure 5-22. Type 1 films exhibit only a negative and featureless transition in their T=298 K RMCD spectra, corresponding to transitions between a spin split deep Mn impurity band and the conduction band. Therefore the deep impurity band in Figure 5-22a is exchange split, creating a net spin polarization of bound holes. As given in Table 5-3, the magnitude of the deep impurity band splitting is 1.2-2.9 meV. Although the splitting of the shallow impurity band was not measured directly, we assume in Figure 5-22a that the shallow impurity band is also spin split. On the other hand, Type 2 films exhibit both a negative peak and broad background in the room temperature dichroism spectra. As shown in Figure 5-22b, this is indicative of room temperature spin splitting of not only the deep Mn impurity band, but also sp-d exchange splitting of the valence band. The magnitudes of the room temperature splitting of the deep impurity band (1.2-2.9 meV) and valence band at the L-point (1.8-2.2 meV) are indicated in Figure 5-22b. The absolute values of the deep impurity band and valence band exchange splitting were calculated in section 5.2.1 and 5.2.2.3 respectively. We note that the exchange splittings of the deep impurity

band and valence band are both less than k_BT at 298 K (25 meV). However, the exchange splitting of the valence band at the Γ -point in Type 2 films is considerably larger at 14-18 meV. In addition, the spin splitting of the deep impurity band maybe underestimated because l/R_{ib-cb} dR_{ib-cb}/dE was predicted and not measured (see section 5.2.1).



Figure 5-22: Room temperature energy level diagram of (a) Type 1 and (b) Type 2 MOVPE InMnAs thin films. The band structure considers exchange splitting of both the Mn impurity bands, but also the valence and conduction bands in the case of Type 2 films.

We now compare the final energy level diagrams of MOVPE InMnAs with that predicted for clustered films by first principles calculations. The DOS and corresponding energy level diagram calculated by Raebiger *et al.* for a clustered ferromagnetic semiconductor for a uniform distribution of tetramers is shown in Figure 5-23.³⁹ From Figure 5-23, it is evident that the spin splitting of the deep impurity band observed for all InMnAs (broad background dichroism feature) qualitatively agrees with the Raebiger model. Furthermore, the *sp-d* exchange splitting of the valence band determined for Type 2 films also agrees with DFT. The difference between the energy level diagrams shown in Figure 5-22 and Figure 5-23, is that the predicted magnitude of the exchange splitting of the deep impurity and valence bands is much greater than the measured value. In particular, the predicted exchange splitting of the deep impurity band is sufficiently large such that the spin down deep impurity band is degenerate with the valence band. In contrast, the spin splitting of the deep impurity states are still detached from the valence band. However, we reiterate that the difference in exchange splitting magnitude is a common artifact of the local density approximation used in DFT calculations. Wei and coauthors have attributed the large exchange splitting predicted by DFT to an overestimation of the p-d exchange integral.⁶⁵



Figure 5-23: (a) Spin up density states for $Ga_{0.94}Mn_{0.06}As$ sample calculated assuming a uniform distribution of tetramers. Shallow and deep impurity bands are marked by red and green arrows respectively.³⁹ (b) Associated spin resolved energy level diagram.

One potential inter-cluster exchange mechanism identified at the start of this chapter has $\sim 10^{18}$ cm⁻³ free holes in the valence band mediating long-range ferromagnetic interaction between clusters through sp-d exchange. While sp-d exchange at T=298 K has been observed, we assert that *sp-d* kinetic exchange cannot be the inter-cluster exchange mechanism responsible for global ferromagnetism in MOVPE InMnAs. The rationale for this conclusion is that sp-dexchange splitting of the valence band was only observed in Type 2 films. The Type 1 films, which constitute four out of the ten InMnAs films studied, exhibit no evidence of sp-d exchange at room temperature. If free holes mediate room temperature ferromagnetism between clusters, Type 1 and Type 2 films should exhibit T_c 's << 298 K and T_c 's >298 K respectively. However, as shown in Table 5-2, both Type 1 and Type 2 films exhibit the same T_c of approximately 330 K. Furthermore, at low temperatures (T < 150 K), the free hole concentration in some InMnAs samples decreases by an order of magnitude, without a corresponding change in the magnetization. May and Wessels have asserted that the absence a correlation between M and palso indicates that the exchange between clusters is not mediated by itinerant valence band holes through *sp-d* exchange.¹⁴⁵ This conclusion is in agreement with the RMCD spectroscopic results.

Instead, we propose that the room temperature ferromagnetism in MOVPE InMnAs is mediated by bound holes in the deep impurity band. Although a full analytical model has not been published, a bound hole inter-cluster exchange mechanism has been proposed previously for ferromagnetic semiconductors.^{40, 41} As predicted by Raebiger *et al.*, a deep impurity band composed of Mn cluster 3*d* states forms in disordered III-V ferromagnetic semiconductors (see section 2.3.2).³⁹ The deep impurity band strongly localizes holes within clusters due its large

activation energy (~0.12 eV), even at room temperature. Consequently, in contrast to itinerant holes in the valence band, these bound holes are not observed in Hall effect measurements.

The proposed bound hole mediated inter-cluster exchange mechanism is supported not only by the energy level diagrams in Figure 5-22 but also a simple model that considers wavefunction overlap of the bound holes. First, as evident from Figure 5-22, the common feature of Type 1 and Type 2 band structures is the spin splitting of the deep Mn impurity band. Just as *sp-d* exchange splitting of the valence band implies a magnetic interaction between Mn ions and free holes (see section 2.2.1), the spin splitting of the deep Mn impurity band implies an exchange interaction between the ~10²⁰ cm⁻³ bound holes and Mn cluster states in the deep impurity band. The exchange splitting of the deep impurity band indicates that Mn clusters align the spins of the bound holes, such that the bound holes are spin polarized (see Figure 5-22). Since exchange interactions are reciprocal, this also implies that bound holes can align the spins of Mn clusters. Therefore, the spin splitting of the deep impurity band common to all InMnAs samples indicates that *bound holes* in clusters mediate exchange between adjacent Mn clusters.

Moreover, we can utilize EXAFS to demonstrate that the wavefunctions of holes localized with in clusters overlap to mediate coupling between Mn moments in neighboring clusters. In the case where the distance between the outermost Mn atoms of adjacent clusters ($d_{critical}$) is less than twice the Bohr radius (a_B) of the bound holes, bound holes can mediate exchange between clusters and therefore give rise to ferromagnetism in MOVPE InMnAs. The average distance between clusters can be determined from the EXAFS measurements. According to EXAFS, the average cluster size in an In_{0.96}Mn_{0.04}As sample contains approximately 14 Mn atoms. The number clusters with size n=14 clusters ($N_{cluster}$) is given by the equation:

$$N_{cluster} = \frac{xN_0}{n},$$
 5-20

where N_0 is the nominal cation concentration equal to 1.8×10^{22} cm⁻³. Substituting for *x*=0.04 and *n*=14, we obtain $N_{cluster}$ =5.1×10¹⁹ cm⁻³.³⁶ Assuming spherical shaped clusters, the average distance between clusters is given by the equation:

$$d_{critical} = \frac{1}{(4\pi N_{cluster} / 3)^{1/3}} - 2r_{cluster}$$
 5-21

where $r_{cluster}$ is the average radius of a cluster. According measurements made by Soo *et al.*, a cluster with n=14 will have a radius, $r_{cluster}=0.45$ nm. Substituting for $r_{cluster}$ and $N_{cluster}$, we calculate $d_{critical}=0.77$ nm.

Next, the value for $d_{critical}$ was compared to the Bohr radius (a_B) of a bound hole in the deep impurity band. Assuming a spherical Bohr orbital, a_B is given by the equation:⁶⁸

$$a_B = \frac{\varepsilon \hbar^2}{m^* e^2},$$
 5-22

where ε is the dielectric constant and m^* is the effective mass of a hole in the deep impurity band. For the calculation of a_B of a bound hole, an ε value equal to that of InAs was used (12.5). Similar to the method discussed in section 5.2.1, an approximate effective mass was calculated from the inferred activation energy of the deep impurity band (~0.12 eV). Using equation 5-8, we obtain an approximate $m^*=1.3 \times 10^{-27}$ g. Substituting for m^* and ε into equation 5-22 yields a bound hole Bohr radius equal to 0.46 nm. Since $2a_B=0.92$ nm is greater than $d_{critical}=0.77$ nm, there is significant bound hole wavefunction overlap between adjacent clusters. A real-space schematic illustrating the wavefunction overlap of bound holes and the resulting ferromagnetic alignment of Mn cluster spins is shown in Figure 5-24. We note that the minimum Mn concentration (x_{min}) required for bound hole wavefunction overlap can also be calculated by setting set $2a_B=d_{critical}$ and solving for x. Using the same values for a_B , $r_{cluster}$, and N_0 , we obtain a value of $x_{min}=0.03$. While InMnAs films with x<0.03 exhibit ferromagnetism, we note that calculated value for x_{min} may be inaccurate due to the Bohr radius used. It should be emphasized that first principles calculations suggest that the Bohr radius of a localized hole is approximately 1 nm.⁷⁹ Using $a_B=1$ nm results in a decrease in x_{min} from 0.03 to 0.007, which is consistent with the magnetic properties of MOVPE InMnAs.³⁴



Figure 5-24: Schematic of the wavefunction overlap between bound holes in adjacent Mn clusters. Hole wavefunctions given as gray circles. Spins of bound holes and Mn are antiferromagnetically aligned.^{40, 41}

Finally, it is important to emphasize that while free holes do not mediate exchange between clusters via sp-d exchange, the observation of room temperature sp-d exchange in Type

2 InMnAs films is nonetheless significant. *Sp-d* exchange in ferromagnetic semiconductors results in spin splitting of the valence band, leading to spin polarized itinerant holes. Spin polarized holes are necessary in semiconductor based spintronic devices. For example, the spin light emitting diode⁹ and spin field effect transistor¹⁹⁵ utilize ferromagnetic semiconductors as a source of spin polarized carriers. Furthermore, the spin bipolar junction transistor,¹⁰ which acts as a spin amplifier, requires spin splitting of the valence band. Ferromagnetic semiconductors including MBE grown GaMnAs and InMnAs have demonstrated the presence of spin splitting of the valence band by *sp-d* exchange,^{53, 168} and the resulting spin polarization of free holes.¹⁹² However, MBE grown InMnAs and GaMnAs are not useful spintronic materials because the spin splitting and spin polarization only persist up to temperatures of 90 K¹³ and 170 K¹⁸ respectively. In contrast, MOVPE grown InMnAs is a promising candidate for *practical* semiconductor based spintronic devices, due to the demonstration of room temperature *sp-d* exchange by RMCD spectroscopy.

5.4 Summary and conclusions

In this chapter, visible reflection magnetic circular dichroism (RMCD) spectroscopy was utilized to determine the nature of the inter-cluster exchange mechanism in MOVPE InMnAs. Two types of InMnAs samples were observed from the T=298 K RMCD spectra: Type 1 films that exhibit a broad negative response over the entire spectral range, and Type 2 that exhibit both the broad response and a negative peak between 2.6-2.73 eV. The broad spectral response observed in the RMCD spectra of Type 1 films was assigned to transitions between the exchange split deep Mn impurity band and the conduction band. A simulated RMCD spectrum using the

Lucovsky model for bound to free transitions indicated a broad transition in agreement with the experimental data.

For Type 2 InMnAs films, the RMCD and temperature dependence indicated that the two observed transitions have distinct origins. Prominent differences in the temperature dependence of the two components were observed near T_c and for T<200 K respectively. The differences in the temperature dependence indicates the presence of two distinct RMCD spectral transitions that occurs between two unique sets of bands. Similar to Type 1 films, the broad dichroic response was attributed to transitions between the deep Mn impurity band and conduction band. The negative peak was attributed transitions between an *sp-d* exchange split valence band and conduction band near the *L*-critical point due to the agreement in the spectral lineshape of the negative peak feature and the dichroism spectrum of MBE grown InMnAs. The *p-d* exchange integral, β was calculated from the magnitude the negative peak. β values ranged from -3.1x10⁻³⁵ to -1.9x10⁻³⁴ erg cm³ ($N_0\beta$ =-0.35 to -2.1 eV), in good agreement with that observed previously for MBE InMnAs.

The spin splitting of valence and impurity bands in MOVPE InMnAs at room temperature are in sharp contrast to MBE grown InMnAs and GaMnAs, which exhibit spin splitting for temperatures between 90¹³ and 170 K¹⁸, respectively. We attributed the differences in the temperature dependence of the exchange splitting of the three materials to the presence of Mn clusters in MOVPE InMnAs. The observed superlinear composition dependence of the two transitions on composition indicates that Mn does not randomly substitute, but forms atomic clusters.

While Mn clustering induces room temperature *sp-d* exchange splitting of the valence band in Type 2 films, free holes do not mediate magnetism between Mn clusters via *sp-d* exchange. Type 1 films, which have nearly identical T_c 's as compared to Type 2 films, did not show evidence of room temperature *sp-d* exchange. In contrast, all films exhibited room temperature spin splitting of the deep impurity band, indicating an exchange interaction between bound holes in that band and the Mn clusters. Furthermore, we demonstrated that wavefunctions of bound holes overlap sufficiently to align the spins of Mn clusters with respect to one another. For *n*=14 size clusters, the distance between the outermost Mn atoms in two neighboring clusters is 0.77 nm. In comparison, twice the Bohr radius of bound hole (*a_B*), which describes the spatial extent of bound hole wavefunction, is 0.92 nm. Since $2a_B$ is greater than the distance between clusters, we concluded that bound holes mediate exchange between clusters.

6. Results: Chemical effects on cluster exchange

The relative importance of inter versus intra-cluster exchange in disordered ferromagnetic InMnAs was investigated by alloying it with phosphorous. The high T_c of 330 K observed in MOVPE InMnAs has been previously attributed to strong intra-cluster exchange in Mn dimers in the material^{32-34, 55} that persists above 298 K.³⁷ In the previous chapter, we proposed that bound holes mediate exchange between neighboring clusters. However, the exchange mechanism (inter or intra-cluster exchange) that determines the global ferromagnetism is not understood One approach to studying the relative importance of inter-cluster or intra-cluster exchange is to alloy InMnAs with P and measure its magnetic properties as a function of P concentration. In the case where intra-cluster exchange dominates, a decrease in T_c is predicted with phosphorous addition by both experiment and theory. DFT predicts a decrease in the intra-cluster exchange from cubic MnAs clusters to MnP clusters.⁴² In contrast, alloying with P also decreases the lattice constant, thereby reducing the relative distance between clusters. This should enhance bound-hole mediated ferromagnetism by increasing the wavefunction overlap between localized holes in adjacent clusters. Consequently, if inter-cluster exchange dominates, P addition is predicted to increase the T_c .

In this chapter, we first discuss the structural properties of $In_{1-x}MnAs_{1-y}P_y$ thin films with *x* ranging from 0.01 to 0.04 and *y* from 0.11 and 0.20. These quaternary alloys have excellent structural properties with rocking curve widths less than 0.14°. The film morphology and RMS roughnesses are also comparable to those observed for InMnAs. The XRD indicates the presence of *hexagonal* MnAs clusters in InMnAsP films. Direct comparison model analysis of the XRD data indicates that between 33-98% of Mn is incorporated in MnAs clusters. In contrast, InMnAs films are phase pure XRD for *x*<0.08.³⁴

The magnetic properties of InMnAsP thin films are subsequently presented. The field cooled (FC) and zero field cooled (ZFC) M versus T curves are highly irreversible. The irreversibility and shape of the ZFC/FC M versus T curves is explained utilizing the Neel model of non-interacting hexagonal MnAs clusters.¹⁹⁶ Moreover, the Neel model yields the size distribution of the clusters from the ZFC curve. Next, room temperature ferromagnetism in the InMnAsP films is attributed to hexagonal MnAs clusters that are sufficiently large to exhibit ferromagnetism even as single domain particles. Therefore, the structural and magnetic properties both indicate the formation of two-phase InMnAsP:MnAs rather than single phase InMnAsP.

6.1 Deposition of InAsP thin films

Prior to the work on Mn doped InAsP films, the deposition parameters of undoped InAsP thin films and their properties were investigated. While MOVPE deposition of InMnAsP thin films have been reported,⁹³ the growth conditions of these films were restricted to growth temperatures (T_g) of 600°C. Since optimal Mn doping using the metalorganic precursor tri-

carbonyl manganese (TCMn) occurs at 480° C,^{197, 198} Mn containing alloys are difficult to achieve using T_g =600°C. Therefore, the primary purpose of the undoped InAsP film study was to determine the optimal growth conditions for InMnAsP alloy formation at 480°C.

The composition for a series of five $InAs_{1-y}P_y$ films grown on InAs substrates was controlled by the relative partial pressure of group V precursors: phosphine (PH₃) and arsine (AsH₃). Table 6-1 summarizes the InAsP films utilized for this study and their corresponding phosphine to total group V flow ratios (PH₃/V). High PH₃/V flow ratios were required to compensate for the low pyrolysis efficiency of PH₃ relative to AsH₃¹⁹⁹ and thereby obtain alloy concentrations of P in InAsP at the growth temperature of 480°C.

Table 6-1: Composition and structural properties of $InAs_{1-y}P_y$ thin films grown on InAs substrates. Samples are organized according to their respective P concentrations. All films were grown at 480°C.

Sample #	PH ₃ /V	у	(°)	<i>RMS roughness</i> (nm)
ndp 014	0.971	0.11	0.07	-
ptc 235	0.980	0.16	0.07	2.51
ptc 234	0.985	0.20	0.07	3.52
ptc 233	0.988	0.24	0.07	3.35
ndp 013	0.990	0.25	0.06	-

The P concentrations (y) for the five $InAs_{1-y}P_y$ samples were determined from x-ray diffraction (XRD). The θ - 2θ x-ray diffraction scans around the InAs (004) and InAsP (004) substrate and film diffraction peaks for ptc 233 (y=0.24) and ptc 235 (y=0.16) are given in Figure 6-1a. We note that all x-ray intensities in this chapter have been normalized with respect to the intensity of the straight through beam. For both samples, a distinct InAsP film peak was resolved at higher 2θ values and therefore smaller lattice constants relative to the InAs substrate. This is consistent with the incorporation of P into InAs, since InP (5.869 Å) has a smaller lattice

constant than InAs (6.0584 Å).⁹⁹ The P atomic fraction was determined from the film lattice constant (a_{film}) in units of Å using the following equation:²⁰⁰

$$y = 32.0 - 5.28a_{film} \,. \tag{6-1}$$

The *y* values ranged from 0.11 to 0.25 as summarized in Table 6-1. Next, we plot the dependence of the P concentration measured by XRD on the PH₃/V flow ratio. As shown in Figure 6-1b, the plot of *y* versus PH₃/V flow ratio curve is highly linear with R^2 =0.97. This indicates that the P concentration in InAsP films can be precisely controlled by varying the flow ratio of group V precursors.



Figure 6-1: (a) θ -2 θ x-ray diffraction pattern of ptc 233 (InAs_{0.76}P_{0.24}) and ptc 235 (InAs_{0.84}P_{0.16}). Arrows mark both the InAsP (004) film peak and InAs (004) substrate peaks. (b) Dependence of the P concentration on PH₃/V precursor flow ratio.

The relative crystalline quality of the InAsP films was determined from their rocking curve widths and surface morphology. In particular, the FWHM of the rocking curve measures the out-of plane epitaxial alignment in a film. The surface morphology was used to determine the RMS roughness in addition to providing an indication of the growth mechanism. The XRD rocking curves for samples ptc 233 (y=0.24) and ptc 235 (y=0.16) are given in Figure 6-2. As shown in Figure 6-2, aside from the differences in the peak center due to the difference in lattice constants, the rocking curves of the two films are nearly identical. The FWHM of the rocking curves ($\omega_{InAsP,(004)}$)are both 0.07°, which is slightly above the angular resolution limit of the diffractometer (~0.06°). As shown in Table 6-1, $\omega_{InAsP,(004)}$ values for the other three InAsP samples are similar to that observed for ptc 233 and ptc 235. The small rocking curve widths indicate excellent out of plane epitaxial alignment between the film and substrate.



Figure 6-2: Rocking-curve XRD scans for ptc 233 (y=0.24) and ptc 235 (y=0.16).

The surface morphology of the $InAs_{1-y}P_y$ film, ptc 233 (y=0.24) is shown in Figure 6-3a. The thickness of ptc 233 is 2.5 µm. As given in Figure 6-3a, the morphology is composed of a series of long columns 6-8 µm in width oriented along the [110] direction. A surface profile across the width of columns shown in Figure 6-3b demonstrates that they are separated by a series of lines that are 10 nm in depth. A similar morphology was observed in $InAsP^{93}$ and
InGaAsP²⁰¹ films grown on InP substrates. These lines were previously attributed to misfit dislocation arrays that relax the mismatch strain between the film and substrate. The main source of the measured RMS roughness of 3.4 nm for ptc 233 originates from these dislocations. We also assert that $InAs_{1-y}P_y$ samples ptc 234 and ptc 235 exhibit similar morphologies and RMS roughnesses (see Table 6-1) to that shown for ptc 233. The low RMS roughness values and the XRD data indicate that the InAsP films exhibit excellent structural properties.



Figure 6-3: (a) $30x30 \ \mu\text{m}^2$ AFM micrograph of ptc 233 (y=0.24). The dotted line indicates the region used to measure the surface profile. (b) Surface profile showing the columnar morphology of ptc 233.

6.2 Deposition of InMnAsP thin films

A series of $In_{1-x}Mn_xAs_{1-y}P_y$ films with P concentrations ranging from *y*=0.11 to 0.21 and Mn concentrations from *x*=0.01 to 0.04 were subsequently grown. The structural and magnetic properties of these quaternary alloys were then compared with respect to that of ternary InMnAs alloys (*y*=0).

Deposition of $In_{1-x}Mn_xAs_{1-y}P_y$ films requires simultaneous control of both TCMn to total group III (TCMn/III) and PH₃ to total group V (PH₃/V) flow ratios. Two series of $In_{1-x}Mn_xAs_{1-x}P_y$

_yP_y films with *y* ranging from 0.11 to 0.21 were grown with PH₃/V flow ratios of 0.971 and 0.988. The Mn concentration in the two series of alloys was determined by energy dispersive spectroscopy (EDS). A typical EDS spectrum of an InMnAsP sample, ptc 238, is shown in Figure 6-4a. As evident from Figure 6-4a, clear P and Mn fluorescence peaks were resolved. We note that P concentrations cannot be determined by EDS due to the GaAs or InAs substrate contribution to the As fluorescence. However, the absence of a substrate contribution to the In fluorescence for InMnAsP films grown on GaAs allows for a calculation of *x* using a standard based fitting routine (see section 3.2). The resulting *x* values summarized in Table 6-2, are also plotted with respect to the TCMn/III flow ratio. As shown in Figure 6-4b, it is evident that *x* is nearly proportional to the TCMn/III flow ratio (R^2 =0.91), demonstrating that the Mn concentration in InMnAsP alloys can be systematically controlled. We also note that in Figure 6-4b, all InMnAsP samples are plotted, regardless of the PH₃/V flow ratios. The linear fit of the data indicates that Mn incorporation is relatively independent of the PH₃/V flow ratio.



Figure 6-4: (a) EDS spectrum for the $In_{1-x}Mn_xAs_{1-y}P_y$ film, ptc 238. The corresponding *x* calculated from the EDS spectrum was 0.043. (b) Plot of Mn concentration versus TCMn/III flow ratio.

Sample #	у	x	@nMnAsP,(004) (°)	RMS roughness (nm)	Thickness (µm)
ptc 239	0.11	0.022	0.07	28	2.4
ptc 240	0.12	0.035	0.07	8.7	2.3
ptc 241	0.12	0.039	0.08	39	2.3
ndp 019	0.20	0.009	0.13	-	-
ndp 015	0.20	0.020	0.14	4.9	-
ndp016	0.21	0.040	0.13	4.0	-
ptc 238	0.21	0.043	0.15	7.5	1.9

Table 6-2: Composition and structural properties of $In_{1-x}Mn_xAs_{1-y}P_y$ thin films. Samples with *y*~0.11 and *y*~0.20 are shaded and unshaded respectively.

Since the P concentration in InMnAsP cannot be directly measured from the EDS spectrum, we have calculated *y* from the $\theta - 2\theta$ XRD scans. The $\theta - 2\theta$ scans for ptc 238 (*x*=0.043) and ptc 241 (*x*=0.039), two In_{1-x}Mn_xAs_{1-y}P_y samples deposited with PH₃/V flow ratios of 0.988 and 0.971 respectively, are given in Figure 6-5. In Figure 6-5, an InMnAsP (004) diffraction peak is clearly resolved from the InAs (004) substrate peak. Furthermore, the InMnAsP (004) film shifts to higher 2θ values or lower lattice constants with increasing PH₃/V flow ratios. Similar to InAsP thin films, the decrease in lattice constant is consistent with an increase in P incorporation in InMnAsP samples. However, it is important to emphasize that a direct measurement of *y* from a_{film} values may be inaccurate due to the fact that Mn incorporation can also affect the film lattice constant. In fact, the Mn concentration in MBE grown InMnAs and GaMnAs are measured from the lattice constant.



Figure 6-5: θ -2 θ XRD pattern for In_{1-x}Mn_xAs_{1-y}P_y films ptc 238 (*x*=0.043) and ptc 241 (*x*=0.039). ptc 238 and ptc 241 were grown with PH₃/V flow ratios of 0.988 and 0.971 respectively.

To account for the potential changes of the film lattice constant due to Mn incorporation, we measured the a_{film} as a function of x for the In_{1-x}Mn_xAs_{1-y}P_y film series grown with PH₃/V flow ratios of 0.971 and 0.988. As given in Figure 6-6, there is no significant change in the InMnAsP lattice constant from x=0 to x=0.039 for films grown with a PH₃/V flow ratio of 0.971. We note that a similar independence of a_{film} on x was also observed for MOVPE InMnAs samples grown on InAs and GaAs substrates.⁵⁵ In the case of In_{1-x}Mn_xAs_{1-y}P_y films grown with a PH₃/V flow ratio of 0.988, an abrupt increase in a_{film} was observed for the films with x=0 (6.013 Å) and x=0.009 (6.021 Å). However, for x=0.009 to x=0.043, the lattice constant is nearly independent of the Mn concentration. The absence of a linear dependence of a_{film} on x indicates that for both series InMnAsP films, Mn incorporation does result in a significant change in lattice constant. Since evidence of Mn incorporation was not observed in the XRD scans, we may infer that the observed decrease in lattice constant with increasing PH₃/V flow ratios is strictly due to P incorporation. This allows for a direct determination of *y* from a_{film} values utilizing equation 6-1. As given in Table 6-2, the In_{1-x}Mn_xAs_{1-y}P_y films grown with PH₃/V of 0.971 and 0.988 correspond to *y* values of 0.11-0.12 and 0.20-0.21, respectively.



Figure 6-6: a_{film} versus x for two series of $In_{1-x}Mn_xAs_{1-y}P_y$ films grown with PH₃/V flow ratios of 0.971 and 0.988.

Finally, we provide a potential mechanism for the abrupt change in a_{film} between x=0 to x=0.009 for the In_{1-x}Mn_xAs_{1-y}P_y samples grown with a PH₃ flow ratio of 0.988. We propose that the decrease occurs due to a parasitic reaction between PH₃ and TCMn that occurs upstream from the substrate. Although a specific parasitic pre-reaction between PH₃ and TCMn has not been reported, analogous reactions have been observed between PH₃ and TEIn or TEGa.^{202, 203} It is also suggested that a similar decrease is not observed for the InMnAsP films grown with the lower PH₃/V ratio of 0.971 because changes in PH₃ incorporation due to TCMn may only become evident at high PH₃/V flow ratios.

The rocking curve around the InMnAsP (004) film peak for ptc 241 238 (y=0.12; x=0.039) and ptc 238 (y=0.21; x=0.043) are given in Figure 6-7. As shown in Figure 6-7, the FWHM around the InMnAsP (004) peaking ($\omega_{n,MnAsP,(004)}$) for ptc 238 (0.15°) is significantly higher than that of ptc 241 (0.08°). Table 6-2 summarizes the rocking curve widths for the remaining InMnAsP films. As evident from Table 6-2, the $\omega_{ln,MnAsP,(004)}$ values for In_{1-x}Mn_xAs₁. _yP_y with y=0.20-0.21 are all nearly double that of the undoped InAsP films with comparable P concentrations. The increase $\omega_{ln,MnAsP,(004)}$ values between In_{1-x}Mn_xAs_{1-y}P_y films with y=0.11-0.12 and those with y=0.20-0.21 is attributed to an increase in lattice mismatch between the two film series. Both strain and the resulting dislocations can significantly broaden XRD rocking cures.²⁰⁴ Nevertheless, we note that the $\omega_{ln,MnAsP,(004)}$ values exhibited by all InMnAsP films in Table 6-2 are low as compared those observed for other heteroepitaxial systems such as InMnAs grown on GaAs ($\omega_{ln,MnAsP,(004)}$ >0.25°).³¹ Therefore the rocking curves indicate the high crystalline quality of these quaternary alloys.



Figure 6-7: XRD rocking curves of $In_{1-x}Mn_xAs_{1-y}P_y$ films, ptc 241 (y=0.12; x=0.039) and ptc 238 (y=0.21, x=0.043). The film thickness of the ptc 241 and 238 are 2.3 and 1.8 µm.

In order to determine the effect of Mn doping on surface morphology, AFM was performed for a series InMnAsP samples. The AFM image for the $In_{1-x}Mn_xAs_{1-y}P_y$ film, ptc 239 (*y*=0.11, *x*=0.022) is shown in Figure 6-8a. As evident from Figure 6-8a, the morphology changes from a columnar-type structure measured for undoped films to a morphology dominated by pitting features for Mn doped films. The pitted surface morphology observed for InMnAsP films has also been observed previously in MOVPE grown InMnAs films.⁵⁵ From the surface profile in Figure 6-8b, the pits range in depth from 10-50 nm in height. The resulting RMS roughness for ptc 239 is 28 nm. The RMS roughnesses for the remaining InMnAsP films are summarized in Table 6-2. The pit density (4.8-9.3 pits/ μ m²) and pit depth (10-160 nm) vary for different films, resulting in a range in RMS roughness (4.0 nm-39 nm) that are comparable to RMS roughnesses observed for InMnAs films grown on InAs.



Figure 6-8: (a) $9x9 \ \mu\text{m}^2$ of AFM micrograph of the $\text{In}_{1-x}\text{Mn}_x\text{As}_{1-y}\text{P}_y$ film, ptc 239 (y=0.11; x=0.022). Red line indicates the region along which the surface profile was measured. (b) Line scan showing the width and depth of pitting features.

 θ -2 θ XRD scans measured from 2θ =30°-50° were utilized to detect the presence of impurity phases in InMnAsP thin films. In the case of InMnAs thin films grown by MOVPE, diffraction peaks at 2θ =31.8° and 42.2° have been observed previously in two-phase samples. The peaks were attributed to the formation of hexagonal α -MnAs precipitates in an InMnAs matrix. While hexagonal MnAs precipitates are the primary impurity phase in MOVPE InMnAs, the possibility of an additional orthorhombic MnP phase in InMnAsP thin films must also be considered.^{205, 206} In the angular range used for this study, XRD diffraction peaks associated with MnP phases are at 2θ =30.2°, 34.1°, 37.5°, 46.2°, 49.4° for Cu-K_{\alphal} radiation.²⁰⁵

 θ -2 θ survey scans for two In_{1-x}Mn_xAs_{1-y}P_y films, ptc 241 (y=0.12, x=0.039) and ndp 016 (y=0.21, x=0.040) are given in Figure 6-9a and Figure 6-9b respectively. Both InMnAsP samples exhibit two diffraction peaks labeled at 2θ =31.8° and 42.2° as features A and B respectively. We

emphasize that this XRD pattern is common to all InMnAsP samples, regardless of P or Mn concentration. Similar to the assignment made by Blattner and coauthors, we attribute these two diffraction peaks to the presence of *hexagonal* α-MnAs clusters in InMnAsP. The A and B peaks correspond to two orientations of hexagonal MnAs clusters with respect to the InMnAsP matrix: one with the (101) MnAs planes parallel to the InMnAsP (001) matrix and the other with the (102) precipitate planes oriented along the (001) matrix planes, respectively. Moreover, from Figure 6-9, the intensity of the (101) diffraction peak is 1-2 orders of magnitude greater than that of the (102) peak. This suggests that the preferred orientation of the hexagonal MnAs clusters is with the (101) cluster planes parallel (001) matrix planes. All observed impurity peaks are associated with the MnAs phase. No orthorhombic MnP phase was resolved.



Figure 6-9: θ -2 θ XRD patterns of In_{1-x}Mn_xAs_{1-y}P_y samples, (a) ptc 241 (y=0.12, x=0.039) and (b) ndp 016 (y=0.21, x=0.040). Peaks A and B correspond to the hexagonal MnAs (101) and (102) diffraction peaks respectively.

We assert that the formation of the second phase hexagonal MnAs in InMnAsP thin films is in stark contrast to InMnAs films. Impurity diffraction peaks A and B were observed in *all* In $In_{1-x}Mn_xAs_{1-y}P_y$ samples with x ranging from 0.01 to 0.043. On the other hand, no hexagonal MnAs XRD peaks were resolved in $In_{1-x}Mn_xAs$ samples for x<0.08.⁵⁵ The evolution of the MnAs diffraction peak with respect to P concentration shown in Figure 6-10 underscores the differences in the phase purity of InMnAs and InMnAsP films. In Figure 6-10, θ -2 θ scans of samples ptc 121 (y=0, x=0.034), ptc 241 (y=0.12, x=0.039), and ptc 238 (y=0.21, x=0.043) are centered on the dominant (101) MnAs peak and the InMnAsP (004) film peak. While the InMnAs sample ptc 121 exhibits no resolvable peak above the noise, a clear peak labeled feature A was measured for both InMnAsP samples. We can quantitatively compare the integrated intensities of the MnAs (101) peak ($I_{MnAs(101)}$) for three films. $I_{MnAs(101)}$ values for ptc 238 and 241 are 1.5×10^{-6} and 1.7×10^{-6} . In contrast the InMnAs film has an $I_{MnAs(101)}$ value that is at least a factor thirty (<3.1x10⁻⁸) less than those observed for the InMnAsP films. Integrated intensities for the remaining InMnAsP films given in Table 6-3 range from 3.7×10^{-7} to 1.7×10^{-6} , which are all at least an order of magnitude greater than that observed for ptc 121. Therefore the composition range in which phase pure InMnAsP can be grown is narrower than that of InMnAs.

Sample #	у	x	$I_{MnAs,(101)} \\ (1x10^{-7})$	$\begin{array}{c} I_{InMnAsP,(004)} \\ (1x10^{-3}) \end{array}$	<i>W</i> _{MnAs,(101)} (°)	W InMnAsP,(004) (°)
ptc 239	0.11	0.022	6.6	1.4	0.65	0.07
ptc 240	0.12	0.035	18	2.0	0.68	0.07
ptc 241	0.12	0.039	15	1.1	0.53	0.08
ndp 019	0.20	0.009	3.7	5.3	0.44	0.13
ndp 015	0.20	0.020	4.2	4.6	0.60	0.14
ptc 238	0.21	0.043	17	5.9	0.86	0.15

Table 6-3: Integrated intensities and rocking curve widths of the MnAs (101) and InMnAsP (004) diffraction peaks.



Figure 6-10: θ -2 θ scans around the MnAs (101) (peak A), InAs (004) (peak B), and InMnAsP (004) (peak C) peaks for (a) ptc 121 (y=0, x=0.034) (b) ptc 241 (y=0.12, x=0.040) and (c) ptc 238 (y=0.20, x=0.043).

The rocking curves around the MnAs (101) diffraction peak were also measured to determine the magnitude of the deviation of hexagonal MnAs clusters from the main orientation defined previously. The MnAs (101) rocking curves for $In_{1-x}Mn_xAs_{1-y}P_y$ samples ptc 241 (y=0.12, x=0.039) and ptc 238 (y=0.21, x=0.043) are given in Figure 6-11a and Figure 6-11b respectively. The rocking curves around the InMnAsP (004) film peak are concurrently plotted for the purpose of comparison. Table 6-3 summarizes the widths determined from the rocking

curves in Figure 6-11. As shown in Table 6-3, the rocking curve widths around the MnAs (101) $(\omega_{MnAs,(101)})$ are broad, ranging from 0.44°-0.86°. This indicates that a significant fraction of MnAs clusters have their (101) planes misaligned with respect to the (001) planes of InMnAsP by as much as 0.86°. In contrast, both Table 6-3 and Figure 6-11 demonstrate a comparatively small out of plane crystal tilt of the InMnAsP matrix grains that varies between 0.07°-0.15°. Therefore, we emphasize the significant difference in rocking curve widths of the two phases. At the minimum, in the case of ndp 019, $\omega_{MnAs,(101)}$ is 3.4 times larger than $\omega_{lnMAsP,(004)}$. The maximum difference occurs for ptc 241 whereby an increase in width by a factor of 9.7 was measured.



Figure 6-11: InMnAsP (004) and MnAs (101) rocking curves for $In_{1-x}Mn_xAs_{1-y}P_y$ thin films (a) ptc 241 (y=0.12, x=0.039) and (b) ptc 238 (y=0.21, x=0.043). The x-axis is the difference between θ and angle corresponding to the center of the rocking curve (θ_c)

XRD qualitatively indicates the presence of a hexagonal MnAs second phase in InMnAsP films. However, the XRD must also be analyzed quantitatively to determine the extent of the phase segregation or equivalently, the volume fraction (c_{MnAs}) of MnAs in the quaternary alloy.

To determine c_{MnAs} , the direct comparison model described by Cullity was utilized.²⁰⁷ In this particular implementation, the intensity of the MnAs (101) and InMnAsP (004) diffraction peaks *integrated in three reciprocal space dimensions* were related to the volume fraction of those hexagonal α -MnAs and InMnAsP matrix phases. This 3-D approach is particularly critical in the case of significant deviations of rocking curve widths for the two phases.^{208, 209} From Table 6-3 and Figure 6-11, it is evident that 3-D integrated intensities of the MnAs (101) ($Q_{MnAs,(101)}$)and InMnAsP (004) ($Q_{InMnAsP,(004)}$) diffraction peaks are required. An expression for $Q_{MnAs,(101)}$ is given simply as:²¹⁰

$$Q_{MnAs,(101)} = \omega_{MnAs,(101)}^{2} I_{MnAs,(101)}, \qquad 6-2$$

where $\omega_{MnAs(101)}$ and $I_{MnAs,(101)}$ are the MnAs (101) rocking curve width in degrees and **1-D** integrated intensity of the MnAs (101) θ -2 θ peak respectively. In equation 6-2 we have assumed that the misalignment of the MnAs clusters is isotropic, a conclusion that has been demonstrated by previously by Moreno and coauthors for the GaMnAs:MnAs two phase system.²¹¹ An analogous expression for $Q_{InMnAsP,(004)}$ is shown below:²¹⁰

$$Q_{InMnAsP,(004)} = \omega_{InMnAsP,(004)}^{2} I_{InMnAsP,(004)}$$
 6-3

Next, according to the direct comparison model, the expression relating the 3-D integrated intensities to c_{MnAs} is given by:²⁰⁷

$$c_{MnAs} = \frac{R_{InMnAsP,(004)}Q_{MnAs,(101)}}{R_{MnAs,(101)}Q_{InMnAsP,(004)} + R_{InMnAsP,(004)}Q_{MnAs,(101)}}$$
6-4

In equation 6-4, the terms $R_{MnAs,(101)}$ and $R_{InMnAsP,(004)}$ are described by the following expressions:

$$R_{MnAs,(101)} = \frac{S_{MnAs,(101)}^2}{v_{MnAs}^2} \frac{1 + \cos^2 2\theta_{(101)}}{\sin 2\theta_{(101)}} \text{ and}$$
 6-5

$$R_{InMnAsP,(004)} = \frac{S_{InMnAsP,(004)}^2}{v_{InMnAsP}^2} \frac{1 + \cos^2 2\theta_{(004)}}{\sin 2\theta_{(004)}}, \qquad 6-6$$

where *S* is the structure factor, *v* is the volume unit cell (Å³), and θ is the Bragg angle (radians). Using structure factors from Warren and coauthors,²¹² $R_{MnAs,(101)}$ and $R_{InMnAsP,(004)}$ are 1.85 and 0.75 respectively. As evident from equations 6-5 and 6-6, the direct comparison model also normalizes out disparities in the structure factor, unit cell volume, and polarization factors

The c_{MnAs} values calculated from equation 6-4 are summarized in Table 6-4. The volume fractions range from 3.3×10^{-3} to 3.8×10^{-2} . The fraction (F_{MnAs}) of Mn incorporated in hexagonal MnAs clusters can also be calculated simply from c_{MnAs} values using the expression:

$$F_{MnAs} = \frac{c_{MnAs}}{x} \cdot 100\%$$

 F_{MnAs} for the InMnAsP thin films are also given in Table 6-4. As shown in Table 6-4, the direct comparison model predicts that a significant fraction of Mn in InMnAsP thin films are incorporated into MnAs clusters. F_{MnAs} values range from 33% for the case of ndp 019 to 98% in ptc 240 where nearly all Mn are incorporated into the MnAs second phase. We contrast the F_{MnAs} values observed for InMnAsP to that of InMnAs. In InMnAs samples, the fraction of Mn in MnAs precipitates determined by XRD is 0 for *x*<0.08.⁵⁵ A plot of F_{MnAs} with respect to *x* given in Figure 6-12 indicates that F_{MnAs} increase with *x*. This suggests that second phase formation can be suppressed by growing InMnAsP films with lower Mn concentrations. However, we emphasize that decreasing *x* below 0.01 in In_{1-x}Mn_xAs_{1-y}P_y will yield films with magnetizations that are difficult to resolve, even by SQUID magnetometry.

Sample #	у	x	$\begin{array}{c} c_{MnAs} \\ (1 \times 10^{-2}) \end{array}$	F _{MnAs} (%)
ptc 239	0.11	0.022	1.6	74
ptc 240	0.12	0.035	3.3	98
ptc 241	0.12	0.039	2.3	60
ndp 019	0.20	0.009	0.33	33
ndp 015	0.20	0.020	0.66	33
ptc 238	0.21	0.043	3.8	88

Table 6-4: c_{MnAs} and F_{MnAs} values of $In_{1-x}Mn_xAs_{1-y}P_y$ thin films determined from direct comparison model analysis of the XRD data.



Figure 6-12: Plot of F_{MnAs} as a function of x for $In_{1-x}Mn_xAs_{1-y}P_y$ samples.

It should also be noted that the F_{MnAs} and c_{MnAs} values given in Table 6-3 and Figure 6-11 are only lower bound estimates. The direct comparison model only assumes the presence of a α phase hexagonal MnAs. While α -phase is the stable crystalline phase of MnAs at room temperature, strain can also stabilize orthorhombic β -phase in epitaxial films.²¹³ Blattner *et. al* have measured impurity diffraction peaks attributed to β -phase MnAs in InMnAs.⁵⁵ Therefore, the assumption a single impurity phase in InMnAsP may be inaccurate. Further, MnAs (102) peaks are also observed by XRD. The contribution of hexagonal MnAs clusters with this crystallographic orientation has not been taken into account in the above calculations.

6.3 Magnetic properties

In the previous section, we used XRD to demonstrate that InMnAsP is a two-phase material that contains a significant volume fraction of hexagonal α -MnAs. The magnetization dependence on temperature and field were measured to determine the effect these hexagonal MnAs clusters on the magnetic properties of InMnAsP. In particular, there are two signatures of hexagonal MnAs impurities on the *M* versus *T* curves. First, if MnAs clusters dominate the magnetic properties, a T_c near that of bulk MnAs (317 K)²¹⁴ is expected that does not vary with P concentration. On the other hand, we predict either an increase or decrease in the T_c of *single phase* InMnAsP relative to that of InMnAs (330 K) in the case where inter or intra-cluster exchange dominates the overall T_c .

Second, the Neel model for a two phase material containing hexagonal MnAs clusters predicts a characteristic irreversibility in the field cooled (FC) and zero-field (ZFC) cooled Mversus T curves.¹⁹⁶ Here we explain the origin of the M versus T irreversibility for the case of an ensemble of isolated single domain hexagonal MnAs clusters with a radius, r = 5.0 nm. MnAs clusters are uniaxially anisotropic with easy axes of magnetization in the spin \uparrow and \downarrow direction and an associated volume anisotropy constant, K_V equal 1.4×10^6 erg/cm³.²¹⁵ A FC curve is measured by applying a magnetic field at 298 K, and cooling the sample to 5 K. Following the sample cool down there is a pause of 1.0×10^2 s prior to the first magnetization measurement. This pause allows for the spins in the material to equilibrate with respect to the applied field and is termed the measurement time (τ_{meas}). Finally, the *M* versus *T* curve is measured as the temperature increases. The spin dynamics of the r = 5.0 nm MnAs clusters for the FC measurement are best illustrated with an energy landscape diagram shown in Figure 6-13a. As shown in Figure 6-13a, prior to the application of the field, there are as many clusters in the spin \uparrow state and as spin \downarrow . The spins states are separated by an anisotropy energy barrier equal to $K_V V$, where *V* is the volume of the MnAs cluster. As shown in Figure 6-13b, upon application of a field of H=500 G in the \uparrow direction, the clusters with a spin \uparrow state have lower energy than those in the spin \downarrow state. In order to minimize the energy of the system, the Mn clusters with spin \downarrow must flip to the spin \uparrow state by traversing over an energy barrier equal to $(K_V - mH)V$, where in the *m* is the magnetization of bulk MnAs. The time required for the spin flip (τ) by thermal excitation over this energy barrier given by standard Arrhenius equation:⁷⁰

$$\tau = \tau_0 \exp[\frac{(K_V - mH)V}{k_B T}] = \tau_0 \exp[\frac{(K_V - mH)(\frac{4}{3}\pi r^3)}{k_B T}],$$
6-8

where $1/\tau_0$ is the time period between attempts for a cluster to change its spin (experimentally determined to be 1×10^{-10} s)¹⁹⁶ and *m* is equal to 550 emu/cm³ at 298 K.²¹⁶ Using equation 6-8, τ for a MnAs cluster with r = 5.0 nm is 1.6×10^{-4} s. Since $\tau << \tau_{meas}$, all clusters will be aligned \uparrow (see Figure 6-13c) and *M* will be at a maximum when the measurement begins at T = 5 K. The magnetization will then decrease with increasing *T* as the spins *within* each cluster become unaligned. The temperature at which the *M* approaches 0 in the FC *M* versus *T* curve corresponds to the intra-cluster T_c .²¹⁷



Figure 6-13: Energy landscape diagrams of uniaxial hexagonal MnAs clusters during a FC M versus T measurement.

The ZFC curve in a two-phase system has a contrasting lineshape to the FC curve due to a difference in the temperature at which the magnetic field is applied for two cases. In the case of a ZFC *M* versus *T*, the sample is cooled from 298 K to 5 K, at which point a magnetic field of 500 G is applied. After a pause of $\tau_{meas}=1.0 \times 10^2$ s, the *M* versus *T* curve is measured with increasing *T*. We emphasize that the major point of contrast between the ZFC and FC measurements is that the *field is applied at 5 K and 298 K respectively*. The effect of this change in temperature on the spin dynamics of the same ensemble of *r* =5.0 nm MnAs clusters can be explained using an energy landscape diagram shown in Figure 6-14 and equation 6-8. As shown in Figure 6-14a, the sample is cooled to 5 K without an applied field such that spin state remains at equilibrium (equal spin \uparrow and spin \downarrow). A field of *H*=500 G in the \uparrow direction is then applied at 5 K. However, from equation 6-8, τ to align with the field becomes infinite at 5 K. For all practical time scales, the *r* = 5.0 nm clusters with spin \downarrow do not have sufficient thermal energy to jump to the spin \uparrow state (see Figure 6-14b). Therefore, as given in Figure 6-14c, at the start of the ZFC measurement, there are still equal numbers of clusters with spin \uparrow and spin \downarrow , yielding an initial net magnetization of 0. As the temperature is increased, the magnetization will remain at 0 until there is sufficient thermal energy for the spins of the clusters to align with the field in less than 100 s. A net magnetization will be measured only if the clusters align in time less than τ_{meas} =100 s. This temperature required to flip the spin state in $\tau < \tau_{meas}$ is defined as the blocking temperature (T_b). T_b is related to the size of a spherical cluster by the equation:²¹⁸

$$T_b = \frac{K_V}{25k_B} (\frac{4}{3}\pi r^3) \,. \tag{6-9}$$

Using a equation 6-9, a single MnAs cluster size of r = 5.0 nm will have a T_b at 193 K. Consequently, at 193 K the clusters will have a sufficient thermal energy to overcome the anisotropy barrier and align with respect to the field in a time τ that is less than τ_{meas} . The ZFC *M* versus *T* will therefore exhibit a single sharp increase up at $T_b=193$ K. At temperatures greater than 193 K, the magnetization will decrease as the spins *within* each cluster become randomized due to entropy. Since the ZFC lineshape is in stark contrast to the FC, the Neel model accounts for the irreversibility in the FC/ZFC curves.



Figure 6-14: Energy landscape diagrams of uniaxial hexagonal MnAs clusters during a ZFC M versus T measurement.

It is important to contrast the FC/ZFC *M* versus *T* dependence of a two-phase system described by the Neel model to the case of a homogeneous ferromagnet. For a homogeneous ferromagnet, the magnetization will saturate in the time scale of domain dynamics (~10⁻⁹ s), regardless of the temperature at which the field is applied.²¹⁹⁻²²¹ Therefore, the domains will align with respect to the field prior to the start of either a FC or ZFC *M* versus *T* curves. This results in identical or completely reversible *M* versus *T* curves for homogeneous ferromagnets.

The FC and ZFC *M* versus *T* curves with *H*=500 G for the In_{1-x}Mn_xAs_{1-y}P_y sample, ptc 238 (y=0.21, x=0.043) are given in Figure 6-15. The FC curve exhibits a Brillouin-like dependence,⁷⁰ whereby the magnetization decreases rapidly with increasing temperature near T_c . A value for the T_c of InMnAsP was determined from a Curie-Weiss fit of the inverse FC susceptibility ($1/\chi_{FC}$). For $T>T_c$, the expression relating $1/\chi_{FC}$ to the Curie temperature is:⁷⁰

$$\frac{1}{\chi_{FC}} = \frac{H}{M_{FC}} = \frac{1}{C} (T - T_c), \qquad 6-10$$

where *C* is the Curie constant. A plot of $1/\chi_{FC}$ as a function of *T* and the corresponding Curie Weiss fit is shown in Figure 6-16. The T_c corresponds to the *x*-intercept of the linear fit. It is important to emphasize that the field cooled curve exhibits a single T_c at 325±5 K. This T_c is close to that observed for bulk MnAs (318 K) and single phase InMnAs (330 K).²²² In addition, there were no other sharp increases in the $1/\chi_{FC}$ versus *T* plots to indicate the presence of any ferromagnetic components with T_c 's other than 325 K. As stated previously, the signature of single-phase InMnAsP would be a significant increase or decrease in the global T_c with increasing P concentration. On the other hand, in the case where the second phase observed by XRD dominates the magnetic properties, a T_c near that of bulk MnAs would be observed. Therefore, the absence of a significant change in the T_c of InMnAsP suggests that the magnetic properties of InMnAsP are dominated hexagonal by the MnAs second phase.



Figure 6-15: Field cooled and zero field cooled *M* versus *T* curves for ptc 238 (y=0.21, x=0.043). An applied field of 500 G was used for both measurements.



Figure 6-16: $1/\chi_{FC}$ versus *T* for ptc 238 (y=0.21, x=0.043). Red line corresponds to the Curie-Weiss fit the inverse susceptibility data.

In Figure 6-15, the ZFC *M* versus *T* curve also exhibits significant differences from the FC plot that is consistent the presence of non-interacting hexagonal MnAs clusters. While M decreases continuously with increasing T from 5-350 K in the FC curve, the ZFC magnetization increases gradually with temperature from 5 K to a maximum temperature of 65 K. At temperatures greater than 65 K, the ZFC magnetization decreases with increasing temperature. At temperature greater than 300 K, the ZFC and FC curves coincide. The observed irreversibility of the ZFC and FC M versus T curves between 5-300 K agrees with the Neel model noninteracting magnetic clusters. As discussed previously, the Neel model predicts an irreversibility in the ZFC/FC curves due to the differences in τ for a field applied at 298 K (FC case) and τ for a field applied at 5 K (ZFC case). The irreversibility in the magnetization temperature dependence is in stark contrast that predicted for homogeneous ferromagnets. Due to the nanosecond time scales associated with domain wall motion, ZFC and FC curves of homogeneous ferromagnets are identical and hence reversible.²¹⁹⁻²²¹ Therefore, the disparity in the ZFC and FC curves indicates that InMnAsP is not a homogeneous ferromagnet, but rather a material containing hexagonal MnAs clusters described by the Neel model. We note here that while the Neel model accounts the irreversibility in the ZFC and FC curves, data that cannot be explained by the Neel model, including the magnitude of H_c and $\langle S_z \rangle$ will be indicated later in this chapter.

The ZFC and FC *M* versus *T* curves can be utilized for more than a qualitative determination of phase purity in InMnAsP. In particular, the size distribution of hexagonal MnAs clusters in the material can be determined from the shape of the ZFC *M* versus *T* curve. First, the relative magnitudes of the ZFC curve and FC curve at *T*=5K yields a measure of the fraction of hexagonal MnAs clusters with a $T_b \le 5$ K. As discussed previously, only clusters with $T_b \le 5$ K

will align with respect to an applied field in a time $\tau < \tau_{meas}$, and thus contribute to the ZFC *M*. On the other hand, all clusters will contribute to the FC curve at 5 K. Therefore the fraction of MnAs clusters with $T_b \le 5$ K is given by the ratio of the ZFC *M* over the FC *M*. Furthermore, in the specific case of hexagonal MnAs clusters, we can use equation 6-9 calculate the radius MnAs cluster corresponding to a T_b of 5 K. Substituting for $K_V=1.4\times10^6$ erg/cm³, we obtain an r = 1.4nm. Therefore we may infer that clusters with a $r \le 1.4$ nm will contribute to the measured ZFC magnetization at 5 K. Applying this formalism to the case of ptc 238, we calculate that 44% of the hexagonal MnAs clusters have $r \le 1.4$ nm from the ZFC and FC curves in Figure 6-15. We emphasize that the large ZFC magnetization relative to FC magnetization is due to the large fraction of MnAs clusters in ptc 238 that have $r \le 1.4$. In contrast, the fictitious ensemble of r =5.0 nm clusters discussed previously has zero ZFC M at 5 K because none of the clusters in the ensemble have $r \le 1.4$.

Moreover, the specific lineshape of the ZFC *M* versus *T* between 5-350 K can be used to determine the size distribution of MnAs clusters with r>1.4 nm using a procedure described by Laiho and coauthors to analyze a ZnMnAs₂:MnAs two phase system.²¹⁷ In order to calculate the size distribution, we first determine $F(T_b)$. $F(T_b)$ describes the number of MnAs clusters with a blocking temperature, T_b , and is given by the equation:

$$F(T_b) = \frac{1}{\gamma} \frac{d}{dT} \left[\frac{T \chi_{ZFC}(T)}{m(T)} \right], \tag{6-11}$$

where m(T) is the dependence of the saturation magnetization of bulk MnAs as a function T.²¹⁶ The constant γ can be determined by normalizing $F(T_b)$ to unity.¹⁴⁰ The γ value determined by normalization was 2.7x10⁻⁸. $F(T_b)$ can then be converted to F(r) using equation 6-9. The resulting normalized size distribution of MnAs precipitates in ptc 238 calculated from the ZFC *M* versus *T* curve is shown in Figure 6-17. As evident in Figure 6-17, a wide distribution of hexagonal MnAs cluster sizes is present in ptc 238 ranging from at least 1.4-6.0 nm in radius. From equation 6-11, the broadness of the ZFC curve in Figure 6-15, results in the wide F(r) size distribution function. The most prevalent radius (r_p) at 4.1% occurs for a radius of 3.0. We note that F(r) decreases slowly from r = 3.0 to r = 1.4 nm, such that a significant fraction of clusters r = 1.4 nm (2.5%). Assuming a similarly slow decrease in F(r) from r = 1.4 to r = 0, we would predict from the size distribution in Figure 6-17 that large fraction of MnAs clusters would have $r \leq 1.4$ nm. This is consistent with previous calculation of fraction of clusters with $r \leq 1.4$ nm based on the ratio of the ZFC magnetization over the FC magnetization. Finally, we emphasize that the size of the MnAs clusters is consistent with XRD measurements, which also indicates the presence of hexagonal MnAs second phase in InMnAsP. XRD is routinely used to detect nanometer scale clusters.¹³²⁻¹³⁵



Figure 6-17: Distribution function of the MnAs cluster radius for ptc 238 (y=0.21, x=0.043).

Although the wide size distribution of the MnAs clusters was *inferred* from the broad ZFC curve, we assert that for the GaMnAs:MnAs granular system, a broad ZFC curve also corresponds to a wide distribution of clusters *measured directly* by TEM. The ZFC and FC curves for a GaMnAs:MnAs granular system containing 8% Mn are shown in Figure 6-18a.²²³. In Figure 6-18a, there is strong irreversibility in the ZFC and FC curves, in accordance with that predicted by the Neel model for a two phase system. Moreover, a broadly peaked ZFC curve with a maximum at 210 K was measured.²²³ The corresponding TEM image for the same GaMnAs:MnAs sample is given in Figure 6-18b. As evident in Figure 6-18b, a wide range clusters ranging from r = 3 nm to r = 25 nm were observed directly by TEM. Therefore, Moreno and coauthors also attributed the broad ZFC curve lineshape to the wide distribution of MnAs clusters observed by TEM.



Figure 6-18: (a) TEM and FC/ZFC *M* versus *T* curves measured with an applied field of 100 G for a GaAs:MnAs samples that contains 8% Mn.²²³

We have previously demonstrated that the Neel model accounts for the irreversibility and shape of the ZFC and FC *M* versus *T* curves. Next, the predictions of the Neel model regarding the field dependence of the magnetization were compared with respect to the measured *M* versus *H* loops. The room temperature hysteresis loop measured with the magnetic field applied out of the plane for ptc 238 (y=0.21, x=0.043), is shown in Figure 6-19. As evident in Figure 6-19, the *M* versus *H* plot measured at *T*=298 K exhibits a coercive field (H_c) of 140 G and a remanent magnetization (M_r) equal to 24% of the saturation magnetization (M_s). The out-of plane *M* versus *H* dependence measured at 5 K is also given in Figure 6-19. As the temperature decreases from 298 to 5 K, M_s increases significantly to 5.20 emu/cm³. The average magnetic moment per Mn ($\langle S_z \rangle$) corresponding to an M_s =5.20 emu/cm³ is equal to 0.36 using the equation:

$$\langle S_z \rangle = \frac{M_s}{N_{M_n} g \mu_B}, \qquad 6-12$$

where a *g*-factor of 2 was used in the previous calculation. In contrast, the $\langle S_z \rangle$ value corresponding to bulk MnAs is 1.6.²¹⁶ The low $\langle S_z \rangle$ value is tentatively attributed to regions in the material that are anti-ferromagnetic due to the presence of MnP based clusters. Previous first principles calculations indicated that both zinc blende and hexagonal MnP clusters are anti-ferromagnetic.⁴² Therefore, a Neel model that only considers the presence of hexagonal MnAs clusters does not *completely* describe the magnetic properties of InMnAsP. In addition, the hysteresis increases from 298 to 5 K as evident from the enhancement in both H_c and M_r to 380 G and 32% M_s respectively. The relevant constants measured from the out of plane field M versus H plots are summarized in Table 6-5. We emphasize that since the M versus H loops measured at 5 and 298 K both exhibit coercivity and remanence, InMnAsP is also ferromagnetic at those temperatures.



Figure 6-19: Out of plane *M* versus *H* loops measured at 5 and 298 K for PTC 238 (y=0.25, x=0.043).

Table 6-5: Out of plane coercive field and remanent magnetization for ptc 238 (y=0.21, x=0.043). Both H_c and M_r were measured by SQUID.

Т (К)	M_s (emu/cm ³)	<i>H</i> _c (G)	M_r (% M_s)
5	5.20	380	32
295	3.14	140	24

Here we utilize the size distribution of hexagonal MnAs clusters in Figure 6-17 and the Neel model to account for the observed *M* versus *H* dependence in InMnAsP thin films. In order to explain the appearance of hysteresis in isolated single domain particles, it is necessary to consider the time response of the MnAs cluster spin during an *M* versus *H* measurement. In a magnetic hysteresis measurement, a large magnetic field on the order of 1×10^4 G is first applied in the \uparrow direction. As shown in Figure 6-20, the field is sufficiently large to align all MnAs clusters in the spin \uparrow state instantly, regardless of their size. Since, $mH > K_V$ with $H=1 \times 10^4$ G,

according to equation 6-8, τ =0 regardless of the cluster size. We note that this is in contrast to ZFC/FC measurements whereby the time required to align clusters in a field depended strongly on *r* because a much smaller field of 500 G was applied (*mH*<<*K*_V in this case).

The next step in the measurement of an *M* versus *H* loop is to reduce the field to 0. In the absence of a magnetic field, the cluster spins will relax back to an equilibrium state with equal numbers of clusters in the spin \uparrow state as spin \uparrow . However, it is important to emphasize that this spin relaxation time (τ) is again dependent upon the cluster size:⁷⁰

$$\tau = \tau_0 \exp[\frac{K_V V}{k_B T}] = \tau_0 \exp[\frac{K_V (\frac{4}{3}\pi r^3)}{k_B T}].$$
6-13

For example, we consider two discrete sizes of MnAs clusters, with $r_1 = 3.0$ nm and $r_2 = 5.5$ nm at room temperature. Using equation 6-13, we calculate $\tau(r_1)=8.8 \times 10^{-6}$ s and $\tau(r_2)=1.1 \times 10^2$ s. Therefore a change in cluster radius of 2.5 nm results in nearly an 8 order of magnitude difference in τ . The key to the determination of whether a cluster with size r will behave as a superparamagnet ($H_c = M_r = 0$) or as a ferromagnet ($H_c \neq 0$; $M_r \neq 0$) is to compare τ to the time between magnetization measurements during a field sweep ($\tau_{meas}=1\times10^2$ s). Clusters with $\tau >$ τ_{meas} will remain aligned with respect to the field, exhibit a net remanent magnetization, and thus be ferromagnetic. On the other hand, clusters with $\tau < \tau_{meas}$, will relax to the equilibrium state, exhibit an $M_r = 0$, and therefore be superparamagnetic.²²⁴ Therefore, since clusters with $\tau(r_1) <$ τ_{meas} , clusters with r = 3.0 nm will be superparamagnetic (see Figure 6-20a). In contrast, clusters with $r_2 = 5.5$ will be ferromagnetic because $\tau(r_1) > \tau_{meas}$ (see Figure 6-20b). We also emphasize that according to equation 6-13, any MnAs cluster with r<5.5 nm will have $\tau < \tau_{meas}$ and be superparagmagnetic. Therefore, according to the Neel model, only hexagonal MnAs clusters with $r \ge 5.5$ nm will be ferromagnetic at room temperature.



Figure 6-20: Energy landscape diagram of (a) r = 3.0 nm sized MnAs clusters (b) r = 5.5 nm clusters with an applied field of 1×10^4 and after removing the field. Schematic is drawn at room temperature.

From the plot of F(r) versus r shown in Figure 6-17, it is evident that a fraction MnAs clusters at the upper end of the size distribution have $r \ge 5.5$. As demonstrated previously using the Neel model, at 298 K, these large single domain clusters exhibit coercivity (nonzero loop width), remanence (nonzero loop height at H=0) and net magnetization (nonzero loop height at the saturation field). We emphasize that this analysis is consistent with Moreno *et al.*, who found

that precipitates with sizes ranging from r = 5 - 7.5 nm exhibit hysteresis in the *M* versus *H* loops.²²³ However, the majority of the MnAs clusters (r < 5.5 nm) will be superparamagnetic at 298 K. These clusters will therefore contribute to the measured saturization magnetization but not to the coercivity and remanence. Since only a small fraction of MnAs clusters have $r \ge 5.5$ (0.043) in Figure 6-17, the average of the *M* versus *H* loops contributed by all clusters (which are predominantly superparamagnetic) will yield only weak hysteresis at room temperature. This is evident from Table 6-5, whereby only a $H_c=140$ G and $M_r=0.24$ M_s was measured.

However, as the temperature decreases to 5 K, the fraction of clusters that are ferromagnetic and contribute to H_c and M_r increases significantly. Using equation 6-13, we find that clusters with r = 1.4 nm have a $\tau = 1.2 \times 10^2$ s. Since $\tau \sim \tau_{meas}$, clusters with $r \ge 1.4$ nm will be ferromagnetic. Therefore, the critical radius for ferromagnetism decreases significantly from 298 to 5 K such that clusters with r ranging from 1.4 to 5.5 nm contribute to the coercivity and remanence at 5 K. Moreover, according to Figure 6-17, a large fraction of clusters have r>1.4 nm. In fact the most prevalent cluster radius was 3.0 nm. Therefore we attribute the factor of 2.7 increase in H_c from 298 K to 5 K to the large increase in the fraction of ferromagnetic MnAs clusters over the same temperature range. We note a similar increase in H_c at 298 K (100 G) to that at 5 K (330 G) has also been observed in an 8% GaAs:MnAs film shown in Figure 6-18.

One other discrepancy (besides the low $\langle S_z \rangle$ value) between the magnetic properties predicted by the Neel model and that measured experimentally for the InMnAsP:MnAs two phase system is the magnitude of the coercive field. A quantitative expression for H_c was derived in a calculation by Pfeiffer:²²⁵

$$H_c = \frac{0.96K_V}{m(T)} \left[1 - \frac{T}{T_b}\right]^{0.77}$$
6-14

where m(T) is again the magnetization of bulk MnAs. Utilizing equation 6-14, we calculated H_c at T = 5 K to be equal to 1380 G. For this calculation, we used a K_V =1.4x10⁶ erg/cm³, m=910 emu/cm³, and a T_b (47 K) corresponding to the most prevalent MnAs cluster size (r = 3.0 nm). The absolute magnitude of the H_c predicted by the Neel model is therefore a factor 3.6 greater than the measured value of 380 G. A similar reduction in the measured coercive field to that predicted by Neel model has been previously attributed to a breakdown of the Neel model approximation of *completely* isolated clusters.^{215, 226-228} In the case where there is a weak intercluster exchange mechanism, the MnAs clusters cannot be strictly treated as a single domains. Rather a weak inter-cluster exchange mechanism could mediate exchange between several clusters to form a multidomain.²²⁸ Since the coercive fields of multidomains are typically less than that of a single domain clusters, the introduction of inter-cluster exchange will decrease the measured H_c .²²⁸

A partial breakdown in the Neel model assumption of isolated magnetic particles is not unexpected in the case of InMnAsP. As shown previously, there is large fraction (~0.44) of MnAs clusters with r < 1.4 nm. The presence of small clusters indicates that the spatial separation between clusters is not large such that a weak inter-cluster exchange could still mediate spins between neighboring hexagonal MnAs clusters. However, the exact inter-cluster exchange mechanism in InMnAsP is not known and consequently requires further study.

6.3.1 Comparison to the magnetic properties of InMnAs

Here we compare and contrast the magnetic properties of MOVPE InMnAsP to a closely related system, MOVPE InMnAs. First, the ZFC and FC *M* versus *T* curves in InMnAsP are highly irreversible. This agrees with the Neel model for non-interacting hexagonal MnAs clusters, which also predicts an irreversibility in the ZFC and FC curves.¹⁹⁶ In contrast, Blattner *et al.* observed identical ZFC and FC curves for InMnAs using an applied field of 1000 G.³³ Reversibility in the ZFC and FC curves is a signature of a homogeneous ferromagnet.²¹⁹⁻²²¹ Therefore, the *M* versus *T* dependence indicates that MOVPE InMnAs is a homogeneous ferromagnet while MOVPE InMnAsP is not.

Second, as evident from the *M* versus *H* loops, InMnAsP and InMnAs grown by MOVPE both exhibit room temperature ferromagnetism. However, in the case of two phase InMnAsP:MnAs, we used the Neel model to demonstrate that some of the hexagonal MnAs clusters (with r>5.5 nm) are large enough to exhibit ferromagnetism as single domain particles. On the other hand, the cubic Mn clusters in single phase InMnAs are much smaller than the hexagonal MnAs clusters in InMnAsP:MnAs. According to EXAFS, the average radius of cubic Mn cluster in MOVPE InMnAs is only 0.45 nm.³⁶ From equation 6-13, the spin relaxation time of a cubic cluster with r = 0.45 will be $1.0x10^{-10}$ s. Since, $\tau <<\tau_{meas}$, each cubic Mn cluster will behave as a superparamagnet in the absence of an inter-cluster exchange mechanism. Therefore, an inter-cluster exchange mechanism such as the bound hole mediated mechanism proposed in the previous chapter is required to *qualitatively* account for the observation of hysteresis in MOVPE InMnAs. We emphasize that an inter-cluster exchange mechanism is not necessary to *qualitatively* explain the hysteresis in InMnAsP, due to the presence of large hexagonal MnAs clusters in the material.

6.3.2 Mechanism for increased phase segregation

The structural and magnetic properties indicate an increase in the formation of hexagonal MnAs precipitates in InMnAsP relative to InMnAs thin films. In this section, we use nucleation theory to provide a mechanism for the enhanced phase segregation in InMnAsP films.^{229, 230} The formation of hexagonal MnAs precipitates in a zinc blende (ZB) semiconductor matrix can be reduced to a two step process. First, coherent zinc blende MnAs clusters nucleate in the ZB matrix²³¹ due to a significant reduction in enthalpy with Mn clustering.^{37, 79} Second, the ZB MnAs clusters undergo a phase transformation to form hexagonal α -MnAs precipitates, accompanied by the formation of dislocations at the interface of the precipitate to account for the misregistry between the ZB and HCP lattices. We propose that the concentration of MnAs clusters.

Here we utilize nucleation theory to determine the effect of an increase in P concentration in InMnAsP on the concentration of ZB MnAs nuclei (N_c) and the corresponding critical nucleus radius (r_c). We emphasize that this model primarily accounts for the effect of P concentration via a change in the coherency strain between the ZB MnAs clusters and semiconductor matrix (matrix lattice constant changes with y). An expression for N_c is given directly by nucleation theory:²³⁰

$$N_c = N_{Mn} \exp(-\frac{\Delta F^*}{k_B T}), \qquad 6-15$$

where N_{Mn} is the total Mn atoms per unit volume, and ΔF^* is the critical energy for the formation of stable ZB MnAs clusters. As evident from the Arrhenius form of equation 6-15, ΔF^* can be regarded as an activation energy for ZB MnAs cluster nucleation. In the case of a perfect coherent interface between cluster and matrix, ΔF^* can be expressed as:

$$\Delta F^* = \frac{16\pi\sigma^3}{3(\Delta F_{\nu,c} + \Delta F_{\nu,strain})^2},$$
6-16

where σ is the chemical interfacial free energy. There is no contribution to the interfacial free energy due to dislocations because ZB MnAs clusters/nuclei are coherent with respect to the InMnAsP matrix. The term $\Delta F_{v,c.}$, is a chemical volume free energy associated with enthalpic differences in bond free energies between the homogeneous phase versus a two phase system. $\Delta F_{v,c}$ is negative in the case of InMnAs and InMnAsP, which reflects the tendency towards phase segregation.²³⁰ The $\Delta F_{v,strain}$ term is related to strain energy per unit volume due to a difference in lattice constant between the ZB MnAs and semiconductor matrix. Assuming that the entire mismatch is accommodated by straining the ZB MnAs cluster, $\Delta F_{v,strain}$ is related to the lattice constants of the two phases by the equation:²³²

$$\Delta F_{v,strain} = \frac{Y}{1 - v} \left(\frac{a_{matrix} - a_{cluster}}{a_{cluster}}\right)^2,$$
6-17

where *Y* and v are Young's modulus and Poisson's ratio of ZB InMnAsP respectively. a_{matrix} and $a_{cluster}$ are the equilibrium lattice constant of the host and ZB MnAs respectively. Finally the critical nucleation radius (r_c) of ZB MnAs clusters is also given by nucleation theory in terms of σ , $\Delta F_{v,c}$, and $\Delta F_{v,strain}$:²³⁰

$$r_c = -\frac{2\sigma}{\Delta F_{v,c} + \Delta F_{v,strain}}$$
6-18

The critical nucleation radius is significant because, ZB MnAs clusters with $r > r_c$ will be stable while those with $r < r_c$ will dissociate due to entropy.

Using equations 6-15 and 6-18, we then calculated absolute values of N_c and r_c for both an In_{0.96}Mn_{0.04}As film and an In_{0.96}Mn_{0.04}As_{0.80}P_{0.20} film. The primary effect of the increase in P concentration is a change in the $\Delta F_{v,strain}$ term. Substituting for the lattice constant of In_{0.96}Mn_{0.04}As_{0.80}P_{0.20} (6.02 Å), ZB MnAs (6.01 Å),⁹⁰ Y=5.14x10¹¹ erg/cm³,²³³ and v=0.35²³³ yields an $\Delta F_{v,strain} = 1.8x10^6$ erg/cm³. Here we have assumed that we used the Young's modulus and Poisson's ratio of InMnAsP is similar to that of InAs. In a similar fashion, we calculated that $\Delta F_{v,strain}$ for InMnAs to be 5.0x10⁷ erg/cm³. Therefore there is a significant decrease in $\Delta F_{v,strain}$ by a factor 28 as the P concentration increases from 0 to 0.20. We note that N_{Mn} only increases slightly from 7.2x10²⁰ cm⁻³ to 7.3x10²⁰ cm⁻³ over the same P concentration range.

However, a determination of N_c and r_c also requires values for $\Delta F_{v,c}$ and σ . $\Delta F_{v,c}$ has been calculated previously by first principles calculations to be -3.0×10^9 erg/cm³.⁷⁸ Moreover a typical interfacial free energy for a coherent cluster is 30 erg/cm².²³⁴ Substituting the values $\Delta F_{v,strain}$, N_{Mn} , ΔF_{v} , and σ into equation 6-15, we determined that the concentration of ZB MnAs clusters in InMnAs and InMnAsP to be 1.7×10^{18} cm⁻³ and 1.8×10^{18} cm⁻³ respectively. Therefore the factor of 27 decrease in $\Delta F_{v,strain}$ with y increasing from 0 to 0.20 does not result in a significant difference in N_c . Substituting $\Delta F_{v,strain}$, ΔF_{v} , and σ into equation 6-18, we also find that r_c remains constant at 0.20 nm as the P concentration increases from 0 to 0.20. Therefore we have used nucleation theory to rule out the possibility that a change in the coherency strain between the ZB MnAs clusters and semiconductor results in the increased phase segregation in InMnAsP. Instead, we preliminarily assign the enhanced phase segregation to a chemical effect, whereby the P catalyzes the formation of a MnAs second phase. However, an analytical model of P catalyzed precipitation in InMnAsP is beyond the scope of this thesis.

6.4 Summary and conclusions

The structural and magnetic properties of InMnAsP films grown on InAs substrates were characterized to determine the effect of alloy host environment on the ferromagnetism of clustered ferromagnetic semiconductors. At the optimum deposition temperature of 480°C, In₁. ${}_xMn_xAs_{1-y}P_y$ films with *x* ranging from 0.01 to 0.04 and *y* ranging from 0.11 to 0.21 exhibited narrow rocking curve widths near the diffractometer resolution limit. Periodic pitting features dominated the surface morphology of these quaternary alloys resulting in RMS roughnesses ranging from 4.0-39 nm. Both the magnitude of the roughness and the measured morphology of InMnAsP films were comparable to that observed for InMnAs films.

While the XRD rocking curves and surface morphology confirmed the growth of high crystalline quality InMnAsP films, XRD θ -2 θ scans also indicated the presence of hexagonal α -MnAs impurities. MnAs impurities were predominantly oriented with the (101) precipitate planes parallel to the (001) planes of InAs. In contrast, MnAs (101) impurity peaks were not observed in In_{1-x}Mn_xAs films with the same *x*. The direct comparison model analysis of the XRD data indicated a significant fraction of Mn in MnAs (F_{MnAs}) in InMnAsP films that varies from 33% to 98%.
The effect of the hexagonal MnAs precipitates on the ferromagnetic properties of InMnAsP:MnAs two phase films was determined using temperature and field dependent measurements of the magnetization. The field cooled (FC) and zero field cooled (ZFC) M versus T curves measured with an applied field of 500 G exhibited significant irreversibility for T < 300K. The irreversibility of the ZFC and FC curves was explained using the Neel model for a twophase material containing non-interacting hexagonal MnAs clusters. Using the Neel model, a wide size distribution of the MnAs clusters ranging from r = 1.4-6.0 nm was calculated from the ZFC curve. The *M* versus *H* dependence indicated that InMnAsP films are ferromagnetic at 5 and 298 K. At 298 K, the weak hysteresis (H_c =140 G) was attributed to hexagonal MnAs clusters with $r \ge 5.5$ nm. According to the Neel model, MnAs clusters with $r \ge 5.5$ nm are ferromagnetic as single domains even at room temperature. However at 5 K, the coercive field increases significantly to 380 G due to an increase in the fraction of MnAs single domain particles that are ferromagnetic. At 5 K, MnAs cluster with $r \ge 1.4$ nm are ferromagnetic as single domain particles. Although the Neel model accurately predicts irreversibility in the ZFC and FC curves and qualitatively explains the room temperature hysteresis in InMnAsP, the magnitude of the coercive field is not consistent with Neel model. This discrepancy indicates that a weak intercluster exchange interaction must exist in InMnAsP.

7. Summary and Conclusions

In this study, the inter-cluster exchange mechanism in MOVPE grown InMnAs thin films was investigated in detail. Due to the important correlation between band structure and magnetic exchange in ferromagnetic semiconductors, we probed the band structure of clustered InMnAs thin films using optical and magneto-optical spectroscopy. The band structures were then utilized to deduce the nature of inter-cluster exchange in MOVPE InMnAs. The effect of alloy host environment on inter- and intra-cluster exchange in clustered ferromagnetic semiconductors was also investigated by alloying InMnAs films with P. The introduction of P in InMnAsP alloys has important ramifications on the local environment around cubic Mn clusters, including changes in lattice constant and chemical composition.

Infrared absorption (IAS), x-ray absorption (XAS), x-ray magnetic circular dichroism (XMCD), and reflection magnetic circular dichroism (RMCD) spectroscopies were used to identify the inter-cluster exchange mechanism in MOVPE InMnAs. The infrared absorption spectra indicate the presence of two distinct Mn impurity bands. One is a shallow impurity band contributing on the order of 1×10^{18} cm⁻³ free holes to the valence band at room temperature. A deep impurity band that forms due to Mn clustering was inferred from the free carrier absorption. The majority of the holes are localized in the deep impurity states, a conclusion corroborated by

recent density functional theory calculations.³⁹ The XAS spectra yield the ground state configuration, *d*-electron localization, and crystal field symmetry of Mn in the deep impurity band. In particular we find that there are five tightly bound *d*-electrons (d^5 configuration) associated with each Mn ion in the deep impurity band. The XAS spectra indicate a tetrahedral crystal field symmetry around Mn. This is consistent with substitutional Mn. In addition, XMCD observed at room temperature indicates that the deep impurity band is spin split at 298 K.

In order to determine whether the free holes from the shallow impurity band or the bound holes in the deep impurity band mediate exchange between clusters, we measured the visible range RMCD spectra of InMnAs. The spin splitting of the deep impurity band measured by XMCD was confirmed as a property common to all InMnAs samples by RMCD spectroscopy. A negative and featureless transition was observed in the visible range that is attributed to transitions between an exchange-split deep impurity band and the conduction band. In addition, a fraction of the InMnAs thin films exhibit not only the broad transition but also a negative peak feature associated with *sp-d* exchange and spin polarized free holes in the valence band. Although spin polarized itinerant holes in the valence band can mediate magnetism between clusters by *sp-d* exchange, *sp-d* exchange was not observed in all InMnAs samples. On the other hand, the deep impurity band is spin-split in all films at room temperature, indicating a strong exchange interaction between bound holes and Mn clusters. Therefore, we proposed an intercluster exchange mechanism whereby wavefunction overlap between bound holes in clusters stabilizes long range ferromagnetic ordering between clusters.

InMnAsP quaternary alloys with alloy concentrations of P and Mn were deposited and characterized to determine the chemical and matrix effects on inter- and intra cluster exchange.

X-ray diffraction indicates that InMnAsP films are not single-phase. Strong impurity diffraction peaks observed in the x-ray diffraction (XRD) were attributed to the presence of hexagonal MnAs nanoclusters. Quantitative analysis of the intensities of the film and MnAs impurity XRD peaks yielded a measure of the fraction of Mn in MnAs clusters, which varied from 33-98%, The shape and irreversibility of the *M* versus *T* curves were explained using the Neel model for two-phase materials. A broad size distribution of hexagonal MnAs clusters with radii between 1.4 and 6.0 nm was also determined from the temperature dependence of the magnetization.

The specific findings of this research were as follows:

- 1. Drude model fitting of the free carrier absorption yielded itinerant hole concentrations between 1.4×10^{18} cm⁻³ to 3.0×10^{18} cm⁻³. The presence of a deep impurity band near midgap that forms due to Mn clustering was proposed to account for the low itinerant hole concentrations. The majority of holes are localized in the deep level or within Mn clusters.
- 2. The near band edge absorption indicated the presence of a second shallow impurity band 23 meV above the valence band maximum. The shallow impurity band contributes the $\sim 1 \times 10^{18}$ cm⁻³ free holes observed by the free carrier absorption. The presence of both deep and shallow impurity bands induced by Mn clustering has been predicted by first principles calculations. ³⁹
- 3. The valence state, *d*-electron localization, and crystal field environment of Mn states in the deep impurity band were investigated by XAS. Atomic model fits of the XAS spectra indicated that the Mn acceptors have a d^5+h configuration. The atomic fit also

demonstrated that the Mn are surrounded by a tetrahedral crystal field. The symmetry of the crystal field is consistent with substitutional Mn.

- 4. Strong XMCD from 5-300 K demonstrated that the Mn states are exchange split. Moreover, the observation of dichroism at 300 K indicated that spin splitting of the Mn impurity band persists up to room temperature.
- 5. Two types of responses for InMnAs thin films were observed by RMCD spectroscopy: Type 1 films that exhibit only a broad negative transition between 1.6-3.1 eV, and Type 2 films that exhibit both the broad negative response and a negative peak between 2.6-2.7 eV.
- 6. The broad transition for both types of films was attributed to transitions between a spin split deep impurity band and the conduction band. The lineshape of the broad transition was consistent with a Lucovsky model that describes these spin dependent transitions.¹⁸⁵
- 7. In Type 2 films, we utilized temperature dependent RMCD measurements to demonstrate that the transitions associated with the negative peak are distinct from those that result in the broad background. At T<150 K, the negative peak increased by factor of 2 while the broad background was nearly constant in the same temperature range. In addition, Curie-Weiss fits of the RMCD temperature dependence of the two features also yielded different T_c 's and Curie constants.
- 8. The negative peak feature in Type 2 films was attributed to transitions between a spin split valence band and conduction band near the *L*-point of the band structure. The assignment was based upon a comparison of the RMCD spectral lineshape of MBE grown InMnAs, whereby a similar peak was also attributed to *sp-d* exchange. We

emphasize that this is the first observation of room temperature sp-d exchange in (III,Mn)V ferromagnetic semiconductors. Room temperature sp-d exchange results in spin polarization of itinerant holes required in semiconductor spintronic devices.

- 9. The magnitude of the exchange splitting of the valence band varied between 1.8 to 2.2 meV at room temperature. The spin splitting magnitude increases to 3.5 to 5.1 meV at 13 K. The *p*-*d* exchange integral β was calculated from the exchange splitting of the valence band. β varied from -3.1x10⁻³⁵ to -1.9x10⁻³⁴ erg cm³ ($N_0\beta$ = -0.35 to -2.1 eV) for Type 2 samples. The sign and magnitude of β are consistent with that observed previously for MBE InMnAs.
- 10. The absence of the *L*-point *sp-d* exchange at 298 K in a fraction of samples and universality of deep impurity band exchange splitting indicated that bound holes rather than free holes mediate exchange between adjacent clusters. From previously published EXAFS data, the wavefunctions of holes localized within clusters overlap with bound holes in neighboring clusters.
- 11. The nature of the ferromagnetic species responsible for the RMCD observed in InMnAs samples was investigated by measuring dichroism as function of composition. The superlinear RMCD versus *x* dependence indicates that Mn clusters are necessary to account for room temperature splitting of the valence band and deep Mn impurity band.
- In_{1-x}Mn_xAs_{1-y}P_y thin films were grown on InAs (001) substrates to determine the effect of alloy host environment on the ferromagnetism. Trimethylindium (TMIn), arsine (AsH₃), phosphine (PH₃), and tricarbonyl manganese (TCMn) were used as reactants.

- 13. Mn and P concentrations in InMnAsP alloys were determined by EDX and θ -2 θ XRD scans respectively. Alloy concentrations of both Mn and P were obtained in In_{1-x}Mn_xAs_{1-y}P_y films with *x* ranging from 0.01 to 0.04 and *y* varying from 0.11 to 0.21. The films exhibit excellent structural properties including RMS roughness comparable to that observed for InMnAs/InAs heterostructures and narrow rocking curve widths between 0.07-0.14°.
- 14. A dominant impurity diffraction peak associated with hexagonal α -MnAs was observed in the θ -2 θ scans. Hexagonal MnAs clusters were predominantly oriented with the (101) cluster planes aligned with the (001) planes of InMnAsP matrix. Rocking curves around the MnAs (101) peak indicated a misalignment of the cluster (101) planes with respect to the InMnAsP (001) planes between 0.44-0.86°.
- 15. Direct comparison model analysis was utilized to determine the fraction (F_{MnAs}) of Mn in MnAs clusters. F_{MnAs} values varied from 33-98%, demonstrating that InMnAsP films are phase segregated.
- 16. The field cooled (FC) and zero field cooled (ZFC) *M* versus *T* curves were highly irreversible. The irreversibility of the ZFC and FC curves was described by the Neel model for MnAs clusters in a nonmagnetic matrix.
- 17. The distribution of hexagonal MnAs cluster sizes was determined from the ZFC curve. MnAs precipitates ranging from 1.4 to 6.0 nm in radius were observed, with the most prevalent radius at 3.0 nm.

- 18. Weak coercivity and remanence observed in the *M* versus *H* loops at room temperature were attributed to hexagonal MnAs clusters precipitates with blocking temperatures greater than or equal to 298 K. This corresponded to clusters with radii >5.5 nm.
- 19. While the Neel model accounts for the qualitative observation of hysteresis in InMnAsP, the model underestimates the magnitude of H_c . This indicates the presence of a weak inter-cluster exchange mechanism in InMnAsP.

8. Suggestions for future work

In this chapter, we specify three research areas that would complement and build upon the work described in this thesis. The areas include further study of bound hole ferromagnetism, measurement of infrared dichroism spectrum InMnAs, and the growth/characterization of InMnAs_{1-y}Sb_y thin films.

The mediation of exchange between clusters by bound holes proposed in this thesis can be further elucidated from two additional experiments. First, the distances between clusters and number of bound holes in MOVPE InMnAs are two critical parameters used to determine the degree of bound hole wavefunction overlap. In this thesis, overlap was calculated assuming an average cluster size and separation determined by EXAFS. However, a more precise calculation of the overlap requires knowledge of the size and spatial *distribution* of the clusters. We propose that physical structure of the clusters should be measured by the local electrode atom probe (LEAP). LEAP is capable of measuring the spatial coordinates of In, Mn and As atoms with atomic level resolution and will therefore yield both size and spatial cluster distributions. Second, in the bound hole magnetism model, itinerant holes do not participate in inter-cluster exchange. In order to test this prediction, InMnAs should be doped with a compensating donor defect such as Si. The resulting reduction of hole concentration or a change from *p*-type to *n*-type conduction should not effect on the T_c if the bound hole magnetism model is valid. However one can also decrease the number of bound holes by compensation.

Another potential topic of future research is the measurement of the RMCD spectrum in the infrared range. The *sp-d* exchange constants were calculated at the E_I critical point using a formula determined by group theory calculations. However, the accuracy of the expression relating the E_I critical point *sp-d* exchange splitting to α and β is controversial. In contrast, at the band gap (0.35 eV), the splitting is simply proportional to the difference of α and β . Therefore, the magnitude of the RMCD at the band gap will allow for a direct calculation of α and β . Furthermore, measurement of the IR RMCD can also be used to corroborate an important conclusion in thesis. We concluded that a deep Mn impurity band forms in InMnAs due Mn clustering. IR RMCD would be useful because a characteristic change in sign of the dichroism is predicted for spin dependent transitions between a deep impurity band and the conduction band. The energy at which the dichroism changes sign corresponds to the ionization energy of the deep Mn impurity band.

The final suggestion for future work is the deposition and magnetic characterization of InMnAs_{1-y}Sb_y films. Hong and coauthors demonstrated that cubic MnSb clusters exhibit larger intra-cluster exchange energies than cubic MnAs clusters. In the case where intra-cluster exchange dominates the global T_c , alloying InMnAs with Sb could provide method to increase the T_c above 330 K.

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A. Appendix: Kerr intensity derivations

A.1 Longitudinal Kerr Intensity

An expression for the Kerr intensity for the longitudinal Kerr effect setup shown in Figure 3-3, can be obtained from the Jones matrix formalism. The incident light is represented by the matrix $[M_0]$, in the *x*-*y* basis:²³⁵

where E_x is the initial electric field strength of the laser. The polarizer oriented along the *x*-axis, is represented by the matrix $[M_I]$:

$$[M_1] = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}.$$
 A-2

In section 2.4.3, it was stated that the magneto-optic Kerr effect is given in terms of the Fresnel coefficients for right and left circularly polarized light (\hat{r}_{\pm}) :

$$\hat{r}_{\pm} = r_{\pm} e^{i\theta_{\pm}} , \qquad \text{A-3}$$

where r_{\pm} and θ_{\pm} are the amplitudes and phase of the reflected RCP/LCP modes. MOKE can also in matrix form in the **RCP/LCP basis** as follows:

$$[M_2]' = \begin{pmatrix} \hat{r}_+ & 0\\ 0 & \hat{r}_- \end{pmatrix}.$$
 A-4

However, since the initial light polarization is defined in the *x*-*y* basis, we need to transform $[M_2]'$ from the RCP/LCP to the *x*-*y* basis. In the *x*-*y* basis, MOKE is given the matrix $[M_2]$:

$$[M_{2}] = \frac{1}{2} \begin{pmatrix} \hat{r}_{+} + \hat{r}_{-} & i(\hat{r}_{-} - \hat{r}_{+}) \\ i(\hat{r}_{+} - \hat{r}_{-}) & \hat{r}_{+} + \hat{r}_{-} \end{pmatrix}.$$
 A-5

Since $\hat{r}_+ \neq \hat{r}_-$ in magnetic samples, the off-diagonal elements in the matrix will be nonzero. These off-diagonal elements in matrix $[M_2]$ indicate that the magneto-optic Kerr effect will induce a small electric field component along the *y*-axis upon reflection off a magnetic sample.

The final optical component is an analyzer oriented at a small angle δ from the *y*-axis that varies from 0-0.5°. The analyzer is represented by the Jones matrix, [*M*₃]:

$$\begin{bmatrix} M_3 \end{bmatrix} = \begin{bmatrix} \sin \delta & 0 \\ 0 & \cos \delta \end{bmatrix}.$$
 A-6

The electric field transmitted through the analyzer (E_{out}) can be simplified by matrix multiplication of the matrices $[M_0]$, $[M_1]$, $[M_2]$, and $[M_4]$:

$$E_{out} = [M_3] \cdot [M_1] \cdot [M_0] = \frac{1}{2} E_x \begin{pmatrix} \sin \delta(\hat{r}_+ + \hat{r}_-) \\ \cos \delta(\hat{r}_+ - \hat{r}_-) \end{pmatrix},$$
 A-7

where a small angle approximation was used to simplify the trigonometric terms. The Kerr intensity (I_{Kerr}) detected by the PMT is then:

$$I_{Kerr} = E_{out} \cdot E_{out}^* \cdot A-8$$

If we substitute equations A-3 and A-7 into equation A-8, we obtain the following expression for the Kerr intensity for the longitudinal MOKE setup:

$$I_{Kerr} = |E_x|^2 |\delta(\hat{r}_+ + \hat{r}_-) + i(\hat{r}_+ - \hat{r}_-)|^2 \approx R |E_x|^2 \delta^2 (1 + \frac{2\theta_K}{\delta}) = I_0 (1 + \frac{2\theta_K}{\delta})$$
A-9

A.2 Polar Kerr Intensity

Similar to section A.1, the Jones Matrix formalism can also be used to derive an expression for the intensity observed by the polar MOKE setup shown in Figure 3-6. We will begin with light polarized along the *x*-axis, which can be represented by the matrix $[M_0]$ in the *x*-y basis:

$$[M_0] = E_x \begin{bmatrix} 1\\ 0 \end{bmatrix}, \qquad A-10$$

where E_x is the initial electric field of the incident light. According to b, the light is then polarized at an angle 45° with respect to the y-axis, represented by the matrix $[M_1]$:

$$[M_1] = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1\\ 1 & 1 \end{bmatrix}.$$
 A-11

Following the initial polarizer, the light passes through the PEM with its retardation and fast axes parallel to the x and y-axes respectively. A PEM consists of quartz plate attached to a piezoelectric transducer that stresses the quartz along the y-axis sinusoidally with respect to time. The stress in turn, induces a time dependent change in the phase of the light (Γ), polarized along the y-axis. An expression for Γ as function of time is given by the equation:

$$\Gamma = \Gamma_0 \sin(2\pi ft) = \Gamma_0 \sin \omega t , \qquad A-12$$

where Γ_0 and *f* are the magnitude and frequency of the phase oscillations respectively. The frequency of the PEM is 42 kHz, corresponding to the resonant frequency of quartz. In contrast

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to the y-axis, the phase of the light polarized along the x-axis is unaffected by the PEM. Therefore the Jones Matrix that corresponds to the PEM is given by $[M_2]$:

$$[M_2] = \begin{bmatrix} 1 & 0 \\ 0 & e^{i\Gamma} \end{bmatrix}.$$
 A-13

Following the PEM, the light beam reflects off the sample. The magneto-optic Kerr effect is represented by the same Jones matrix as given by equation A-5:

$$[M_{2}] = \frac{1}{2} \begin{pmatrix} \hat{r}_{+} + \hat{r}_{-} & i(\hat{r}_{-} - \hat{r}_{+}) \\ i(\hat{r}_{+} - \hat{r}_{-}) & \hat{r}_{+} + \hat{r}_{-} \end{pmatrix}.$$
 A-14

The final optical element in the polar MOKE setup is an analyzer polarized along the *x*-axis. The matrix corresponding to the analyzer is given by the equation:

$$[M_4] = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}.$$
 A-15

An expression for the electric field transmitted (E_{out}) through the polarizer can be derived by matrix multiplication of $[M_0]$ to $[M_4]$. The detected intensity (I_{Kerr}) is then the product of E_{out} and its complex conjugate as given by the equation:

$$I_{Kerr} = R |E_x|^2 (1 + \phi \sin \Gamma + \theta_K \cos \Gamma) = I_0 (1 + \phi \sin \Gamma + \theta_K \cos \Gamma).$$
 A-16

In the simplification of equation A-16, the equations 2-20 to 2-22 are used once again. Next, the terms $cos \Gamma$ and $sin \Gamma$ in equation A-16 may be expanded out in terms of Bessel functions using the following formulae:

$$\sin \Gamma = \sin(\Gamma_0 \sin \omega t) = 2J_1(\Gamma_0) \sin \omega t + \dots$$
 and A-17

$$\cos\Gamma = \cos(\Gamma_0 \sin \omega t) = J_0(\Gamma_0) + 2J_2(\Gamma_0) \sin 2\omega t + \dots$$
 A-18

Substituting equations A-17 and A-18 into equation A-16, we obtain the following expression for the Kerr intensity corresponding to the polar MOKE setup.

$$I_{Kerr} = I(0) + I(\omega)\sin\omega t + I(2\omega)\sin 2\omega t .$$
 A-19

In equation A-19, I(0), $I(\omega)$, and $I(2\omega)$ are defined by the equations:

$$I(0) = I_0 + J_0(\Gamma_0)\theta_K \approx I_0, \qquad A-20$$

$$I(\omega) = 2I_0 \phi J_1(\Gamma_0) \quad , \qquad \qquad \text{A-21}$$

$$I(2\omega) = 2I_0 \theta_K J_2(\Gamma_0), \qquad A-22$$

B. Appendix: Lucovsky model formalism

This section outlines a precise calculation of the reflectivity due to transitions between an impurity band to the conduction band in a heavily doped semiconductor. We begin with the Lucovsky model, which provides an expression for the imaginary part of the index refraction, (k), associated with transitions between the impurity and conduction bands.¹⁸⁵

$$k(E) = \frac{8N_{impurity}\pi e^2\hbar^2 E_i^{1/2}}{3m^*} \frac{(E-E_i)^{3/2}}{E^4} = A\frac{(E-E_i)^{3/2}}{E^4} \qquad \text{for } E > E_i \text{ and} \qquad B-1$$

$$k(E) = 0 \text{ for } E < E_i,$$
B-2

where $N_{impurity}$ is the nominal concentration of impurities, E_i is the energy difference between the conduction band and the impurity band, and m^* is the effective mass of the impurity band. For simplicity, all the constants in equation B-1 have been grouped together into a single constant denoted A. However an expression for k(E) alone is insufficient to determine the spectral dependence of the reflectivity, as R(E) is dependent upon both the real (n) and imaginary parts of the index of refraction:

$$R(E) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}.$$
 B-3

In order to obtain an expression for n(E), a Kramers Kronig (KK) transformation was utilized. A KK relation allows one to calculate the real portion of the complex variable if the imaginary

portion is known and vice versa. The specific KK relation for relating the real to imaginary index of refraction is given by:¹⁸⁶

$$n(E) = 1 + \frac{2}{\pi} \wp_0^{\infty} \frac{E'k(E')}{E'^2 - E^2} dE'.$$
 B-4

In equation B-4, \wp is defined as the Cauchy principle value of the integral, whereby contributions to the integral at singularities are omitted. We then substitute equations B-1 and B-2 into B-4 to obtain the expression:

$$n(E) = 1 + \frac{2A}{\pi} \bigotimes_{E_i}^{\infty} \frac{(E' - E_i)^{3/2}}{E'^3 (E'^2 - E^2)} dE'.$$
 B-5

Note that the integration limits are now from E_i to ∞ , due to the fact that k(E) is 0 for $E < E_i$. In order to simplify the limits of integration, the following substitutions were made in equation B-5:

$$x^2 = E' - E_i$$
 and B-6

$$y^2 = E - E_i,$$
 B-7

to yield the equation:

$$n(E) = 1 + \frac{2A}{\pi} \wp \int_{0}^{\infty} \frac{2x^4 dx}{(x^2 - y^2)(x^2 + y^2 + 2E_i)(x^2 + E_i)^3} = 1 + \frac{2A}{\pi} \wp \int_{0}^{\infty} f(x, y, E_i) dx.$$
 B-8

For $E > E_i$, a singularity occurs at x = y in the equation B-8. In order to exclude this singularity, we integrate from x = 0 to $x = y - \delta$ and then from $x = y + \delta$ to $x = \infty$, in the limit as δ approaches 0. This precise definition of the Cauchy principle integral in the case of an individual singularity at x = y, leads directly to the equation:

$$n(E) = 1 + \frac{2A}{\pi} \lim_{\delta \to 0} \left[\int_{0}^{y-\delta} f(x, y, E_i) dx + \int_{y+\delta}^{\infty} f(x, y, E_i) dx \right].$$
 B-9

The two integrals in equation B-9 were solved analytically using a Maple program. The expression for n(E) for $E > E_i$ is given by:

$$n(E) = 1 + A \frac{64(E - E_i)^2 + 160(E - E_i) + 20}{256(E - E_i)^2 + 256(E - E_i)^3 + 96(E - E_i)^2 + 16(E - E_i) + 1}$$
B-10

Therefore, we have closed form analytical formulas for both the real and imaginary parts of the index of refraction for $E > E_i$. If we substitute equations B-9 (n(E)) and B-1 (k(E)) into equation B-3, the desired expression for R(E) can be obtained. Due to the complexity of the expression for R(E), the equation for R(E) is not given here.

Thus far, the previous derivation applies to the optical properties of any heavily doped semiconductor with an impurity band. However, to plot the lineshape of n(E), k(E) and R(E) in the case of MOVPE InMnAs, specific values for E_i , $N_{impurity}$, and m^* must be determined (see equation B-1 and B-10). Two impurity bands were proposed in section 4.1.3: a shallow impurity band (E_A =23 meV) ²³⁶ and a deep impurity band near midgap (E_A ~0.12 eV). Since there are roughly 100 times more Mn states in the deep as opposed to the shallow impurity band we focus on spin dependent transitions from the deep impurity band to the conduction band. We again assume that the deep impurity level is near midgap with $E_i = 0.23$ eV. For an In_{1-x}Mn_xAs sample with *x*=0.047, $N_{impurity}$ or the concentration of Mn impurities is 8.5×10^{20} cm⁻³. Finally we assume an effective mass for the hole deep impurity band that is given by the equation:⁶⁸

$$m^* = E_A \frac{m_e \varepsilon^2}{13.6eV}$$
B-11

Using an $E_A=0.12$ eV, we calculate a value for $m^*=1.4m_e=1.3 \times 10^{-27}$ g. Unfortunately, this final assumption has no solid experimental basis. Inaccuracies in m^* will effect the magnitudes of n(E), k(E) and R(E), but not the lineshape. Therefore while interpretations of the three spectra
based on *lineshape alone are justified*, we caution that any calculations based on the *absolute magnitudes* of n(E), k(E) and R(E) will have large associated errors. The plots of n(E), k(E) and R(E) for InMnAs are given in Figure B-1, Figure B-2 and Figure B-3 respectively.



Figure B-1: Spectral dependence of k(E) related to Mn impurity band to conduction band transitions for an In_{0.97}Mn_{0.03}As film. An expression for k(E) was obtained directly from the Lucovksy model for optical transitions.¹⁸⁵



Figure B-2: Spectral dependence of *n* related to Mn impurity band to conduction band transitions for an $In_{0.97}Mn_{0.03}As$ film, calculated by a Kramers Kronig transformation of k(E).



Figure B-3: Reflectivity due to deep Mn impurity band to conduction band transitions for an $In_{0.97}Mn_{0.03}As$ film. R(E) was calculated using the imaginary and real components of the index of refraction.

The imaginary index of refraction increases from 0 at $E=E_i=0.23$ eV, reaches a maximum at $2E_i=0.46$ eV, and then decreases approximately as $E^{-3/2}$ for E>>0.46 eV. The magnitude of k is small at less than 0.08 throughout the spectral range. A similar lineshape is observed for n versus E and R versus E. In contrast to k, n and R reach a maximum at the ionization energy equal to 0.23 eV. The real component of the index rapidly approaches 1 for E>>0.23 eV. Similarly, R decreases rapidly to 0 for energies greater than the ionization energy. In the visible light range (1.6-3.1 eV), the reflectivity gradually decreases from 8.4×10^{-5} to 3.5×10^{-6} .