Physics

Physics Research Publications

Purdue University *Year* 2009

Theoretical model for the experimental magnetization data from the layered III-VI diluted magnetic semiconductor In(1-x)MnxSe (x=0.014 & 0.027)

D. Meda* J. H. Blackburn† L. Maxwell‡
J. Garner** T. M. Pekarek††
I. Miotkowski‡‡ A. K. Ramdas§

*
†
‡
**
††
‡‡
§

Theoretical model for the experimental magnetization data from the layered III-VI diluted magnetic semiconductor $In_{1-x}Mn_xSe$ (x=0.014 & 0.027)

D. Meda,[1] J. H. Blackburn,[1] L. Maxwell,[1] J. Garner,[1] T. M. Pekarek,[1,a)] I. Miotkowski,[2] and A. K. Ramdas[2]

[1]*Department of Chemistry and Physics, University of North Florida, Jacksonville, Florida 32224, USA*
[2]*Department of Physics, Purdue University, West Lafayette, Indiana 47907, USA*

(Presented 13 November 2008; received 17 September 2008; accepted 22 December 2008; published online 26 March 2009)

The magnetization of $In_{1-x}Mn_xSe$ is calculated and measured from 140 to 400 K in magnetic fields up to 7 T for two crystals with concentrations $x=0.014$ and 0.027. The Mn ions enter the InSe bulk crystal substitutionally at the In lattice site and are responsible for the observed magnetization of the sample. A singlet model of isolated Mn ions with a spin-orbit coupling parameter of 38 cm^{-1} fits the experimental data from two different concentration samples for temperatures ranging from 140 to 400 K in fields up to 7 T. This agreement between the experimental magnetization and the theoretical magnetization for $In_{1-x}Mn_xSe$ expands our theoretical understanding of the III-VI diluted magnetic semiconductor (DMS) by adding a Se-based system and complements previous agreement reported for only two other III-VI DMS ($Ga_{1-x}Mn_xS$ and $In_{1-x}Mn_xS$). © *2009 American Institute of Physics*. [DOI: 10.1063/1.3076049]

I. INTRODUCTION

The III-VI diluted magnetic semiconductors (DMSs) consist of a group III element bonded to a group VI element in which some of the group III atoms are replaced by transition metal atoms. The transition metal atoms give rise to the magnetic moments in the sample. The III-VI DMS are of current interest because of their potential for electro-optical applications due to their highly nonlinear optical properties.[1–4] The material that is the subject of this paper ($In_{1-x}Mn_xSe$) was recently reported[5] to have ferromagnetic phases and this raises the possibility of additional applications. Another reason for studying this compound is the unusual hysteresis that has been measured in the magnetization versus temperature plane.[6,7]

The singlet model presented in this paper has been previously used to model the magnetization of two sulfur-based III-VI DMS compounds[8–11] $Ga_{1-x}Mn_xS$ and $In_{1-x}Mn_xS$. The $Ga_{1-x}Mn_xS$ is a four-atom thick layered bulk crystal, while the $In_{1-x}Mn_xS$ has a more complicated tetrahedral crystal structure. In this paper, we model the magnetization of a selenium-based III-VI DMS compound $In_{1-x}Mn_xSe$. It is believed $In_{1-x}Mn_xSe$ has the same crystal structure as that of $Ga_{1-x}Mn_xS$.

In this paper, a singlet model is compared to the experimental data for $In_{1-x}Mn_xSe$. This builds on recent measurements in InSe and expands the exploration of the new class of III-VI DMS into the third III-VI DMS system theoretically modeled to date, complementing previous work on $Ga_{1-x}Mn_xS$ (Refs. 8 and 11) and on $In_{1-x}Mn_xS$.[9,10]

II. EXPERIMENTAL DETAILS

Magnetization measurements were taken in a Quantum Design magnetic property measurement system (MPMS) XL7 superconducting quantum interference device (SQUID) magnetometer at temperatures between 140 and 400 K in fields up to 7 T. A pure InSe crystal was measured to determine the value of the diamagnetic signal due to the semiconductor host. A diamagnetic susceptibility value of -3.2×10^{-7} emu/g G for InSe has been measured and subtracted from the data.

A 0.057 1 g single-crystalline $In_{1-x}Mn_xSe$ sample was taken from a boule grown by the vertical Bridgman method with a nominal concentration of $x=0.10$. A 0.032 0 g sample was taken from a similar boule with nominal concentration of $x=0.01$. The actual concentration was taken to be the value obtained from the theoretical fits to the data, which were found to be $x=0.027$ and 0.014 for the $x=0.10$ and 0.01 nominal concentration samples, respectively. This is within typical variations in concentrations for small samples taken from boules with our nominal concentrations.

III. MAGNETIZATION: MODEL AND MEASUREMENT

The magnetization of the III-VI DMS materials arises from the doping of the III-VI semiconductor with transition metal atoms, which in this paper were Mn. It is assumed that the Mn atoms enter the bulk crystal substituting for a fraction x of the group III elements (In). The substitutional Mn ion has an incomplete 3d shell that gives rise to the magnetization of the samples. If we denote the energy levels of the valence electrons by E_i then in the presence of a magnetic field B the ith level contributes a magnetic dipole moment given by dE_i/dB. The moment is weighted by a Boltzmann factor and, on multiplying by a prefactor that is a function of x, a standard expression[11] for the magnetization $M(T,B)$ is found.

To a first approximation given the smallness of x, one may reasonably assume that the Mn ions do not interact with each other. This is the singlet model. The singlet Hamiltonian

a)Electronic mail: tpekarek@unf.edu.

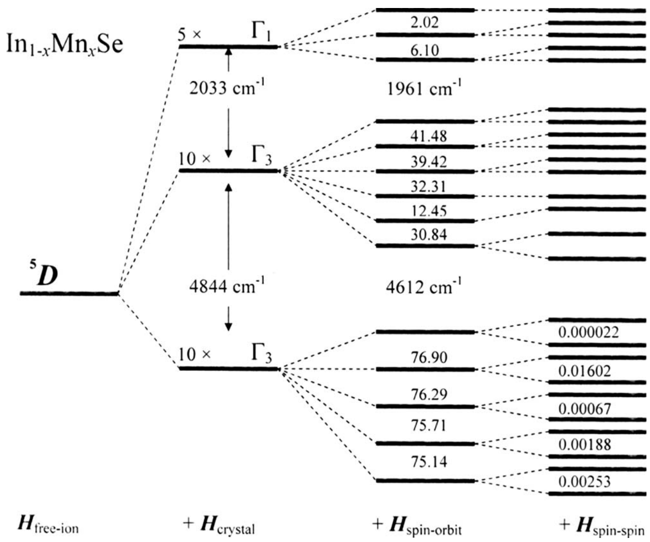

FIG. 1. The overall energy level scheme found from the eigenvalues of the singlet Hamiltonian matrix. The numbers are expressed in inverse centimeter and give the spacing between the levels.

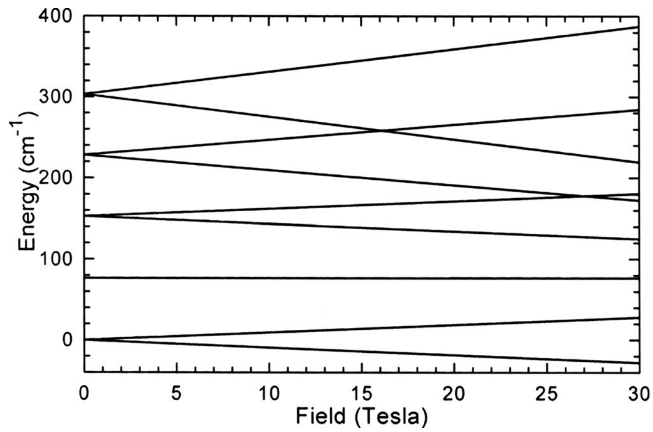

FIG. 2. The dependence of the ten lowest singlet energy levels on magnetic field. All of the levels are twofold degenerate in zero field.

for the valence electrons of Mn consists of the following terms:[11] a crystal field potential due to the Coulomb interaction of the 3d electrons with the nearby semiconductor host atoms, standard spin-orbit and spin-spin terms that are internal to the transition metal ion, and the usual Zeeman term for the 3d electrons' interaction with the applied magnetic field. The Hamiltonian matrix is constructed using the angular momentum basis set $|LM_L\rangle|SM_S\rangle$, where L and S are the total orbital and spin angular momentum quantum numbers of the 3d electrons and M_L and M_S are the associated z-component quantum numbers. With formal oxidation state Mn^{+3}, we have $L=S=2$, giving dimensions of the singlet Hamiltonian matrix $(5\times5)^2=25\times25$. (The choice of Mn^{+3} rather than Mn^{+2} was discussed in an earlier paper.[11]) The eigenvalues E_i of the singlet Hamiltonian are the 3d electron energy levels.

Parameters used in the construction of the singlet Hamiltonian include the formal oxidation states of In($Z=2$) and of Se($Z'=-2$), the In-In bond length ($R=2.802$ Å) and that for In-Se ($R'=2.6418$ Å), the fitted value of the spin-orbit coupling constant ($\lambda=38$ cm^{-1}), and, finally, the spin-spin coupling[12] constant ($\rho=0.18$ cm^{-1}). The general energy level diagram is shown in Fig. 1. Notice, there are 25 total levels. The ^5D is term notation for the ground state of the free Mn ion. The ten lowest singlet energy eigenvalues, which are the most important for calculating the magnetization, are graphed as a function of applied magnetic field in Fig. 2. The slope of these straight lines is the magnetic dipole moment associated with that eigenstate. Evidently, each of the levels is twofold degenerate.

Magnetization versus field data for $In_{0.986}Mn_{0.014}Se$ at 150, 200, 300, and 400 K is shown in Fig. 3(a). The magnetization is clearly linear with field in the entire range from 150 to 400 K. Below 140 K for $In_{1-x}Mn_xSe$ samples, the onset of a thermal hysteresis prevents theoretical modeling at lower temperatures. Magnetization versus temperature data in a 1, 3, 5, and 7 T field is shown in Fig. 3(b). Agreement between theory and experiment is evident over the entire range of temperatures and fields. Additional traces in a 2, 4, and 6 T (not shown) showed similar agreement.

Magnetization versus field data for a sample with double the concentration ($In_{0.973}Mn_{0.027}Se$) at 150, 200, 300, and 400 K is shown in Fig. 4(a). Magnetization versus temperature data in a 1, 3, 5, and 7 T field is shown in Fig. 4(b). Again, the theory and experiment agree over the entire range of temperatures and fields.

Success modeling of other III-VI DMS systems has been reported in only two other systems ($Ga_{1-x}Mn_xS$ and $In_{1-x}Mn_xS$).[8–11] Both of these systems are based on sulfur. Attempts at modeling other III-VI DMS systems have been

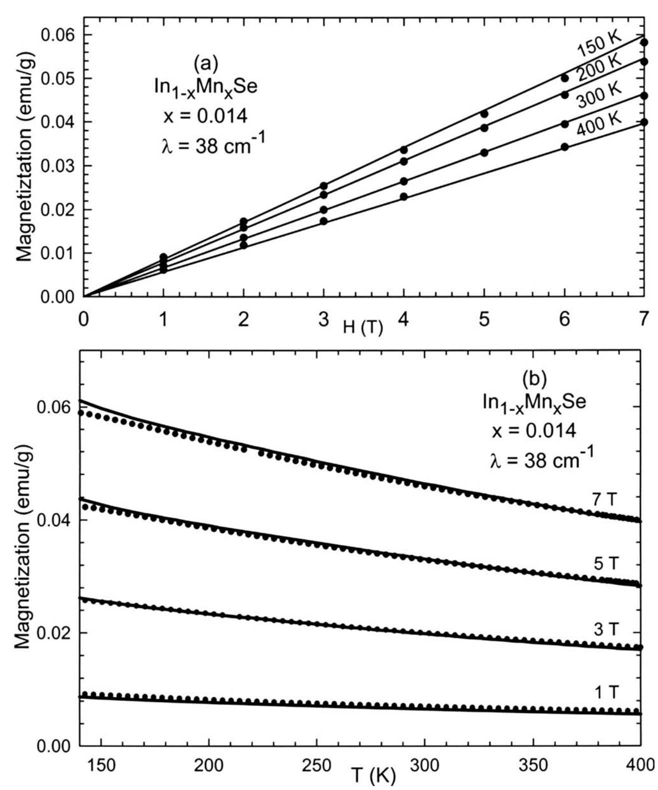

FIG. 3. (a) M vs H data for $In_{1-x}Mn_xSe$ at 150, 200, 300, and 400 K. (b) M vs T data taken in 1, 3, 5, and 7 T. The experimental data are shown by the dots. The lines are a theoretical fit from a model Hamiltonian. The best fit was obtained for $\lambda=38$ cm^{-1} and $x=0.014$.

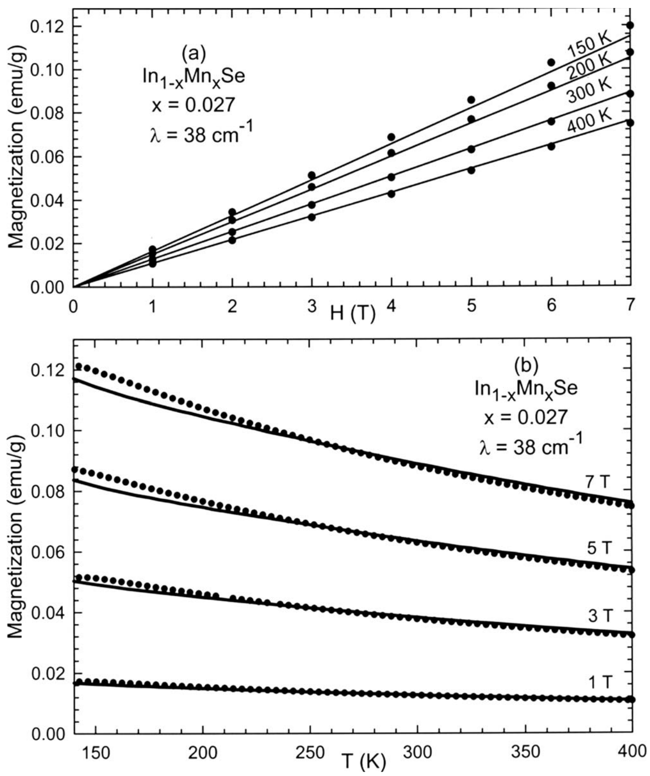

FIG. 4. (a) M vs H data for $In_{1-x}Mn_xSe$ at 150, 200, 300, and 400 K. (b) M vs T data taken in 1, 3, 5, and 7 T. The experimental data are shown by the dots. The lines are a theoretical fit from a model Hamiltonian. The best fit was obtained for $\lambda = 38\ \mathrm{cm}^{-1}$ and $x = 0.027$.

unsuccessful to date. In $Ga_{1-x}Mn_xS$ and $In_{1-x}Mn_xS$, the singlet model has worked well[8–11] in predicting the magnetization over a wide range of fields, temperatures, and concentrations. The theoretical predictions deviate from the data in regimes where additional spin interactions become significant such as near the spin-glass transition in $Ga_{1-x}Mn_xS$ or below 140 K in $In_{1-x}Mn_xSe$, where the thermal hysteresis effects begin.[7,13] Unlike the comparatively heavily studied III-V and II-VI DMS,[14] this class of layered III-VI DMS remains largely unexplored.

IV. CONCLUSIONS

Agreement was found between the magnetization of $In_{1-x}Mn_xSe$ and a theoretical model. The singlet model of isolated Mn ions, substitutionally replacing In in the InSe crystal, with a spin-orbit coupling parameter of 38 cm^{-1} fits the experimental data from $x = 0.014$ and 0.027 samples for temperatures ranging from 140 to 400 K in fields up to 7 T. This agreement between the experimental magnetization and the theoretical magnetization for $In_{1-x}Mn_xSe$ expands our theoretical understanding of the III-VI DMS by adding a Se-based system and complements previous agreement reported for only two other III-VI DMS ($Ga_{1-x}Mn_xS$ and $In_{1-x}Mn_xS$). This work on the class of layered III-VI DMS also complements the comparatively heavily studied II-VI and III-V DMS.

ACKNOWLEDGMENTS

This research was supported by a Purdue Univ. Academic Reinvestment Program under Grant No. ACS-PRF#40209-B5M and by the National Science Foundation (NSF) under Grant Nos. DMR-07-06593 and DMR-04-05082.

[1] D. Errandonea, A. Segura, V. Munoz, and A. Chevy, Phys. Rev. B **60**, 15866 (1999).
[2] K. Watanabe, K. Uchida, and N. Miura, Phys. Rev. B **68**, 155312 (2003).
[3] N. C. Fernelius, Prog. Cryst. Growth Charact. Mater. **28**, 275 (1994).
[4] D. R. Suhre, N. B. Singh, V. Balakrishni, N. C. Fernelius, and F. K. Hopkins, Opt. Lett. **22**, 775 (1997).
[5] V. V. Slyn'ko, A. G. Khandozhko, Z. D. Kovalyuk, V. E. Slyn'ko, A. V. Zaslonkin, M. Arciszewska, and W. Dobrowolski, Phys. Rev. B **71**, 245301 (2005).
[6] T. M. Pekarek, L. H. Ranger, I. Miotkowski, and A. K. Ramdas, J. Appl. Phys. **99**, 08D511 (2006).
[7] T. M. Pekarek, D. J. Arenas, I. Miotkowski, and A. K. Ramdas, J. Appl. Phys. **97**, 10M106 (2005).
[8] J. L. Tracy, R. Mourad, J. Garner, T. M. Pekarek, I. Miotkowski, and A. K. Ramdas, J. Appl. Phys. **99**, 08D507 (2006).
[9] J. L. Tracy, G. Franzese, A. Byrd, J. Garner, T. M. Pekarek, I. Miotkowski, and A. K. Ramdas, Phys. Rev. B **72**, 165201 (2005).
[10] G. Franzese, A. Byrd, J. Tracy, J. Garner, T. M. Pekarek, I. Miotkowski, and A. K. Ramdas, J. Appl. Phys. **97**, 10D308 (2005).
[11] C. Fuller, A. Douglas, J. Garner, T. M. Pekarek, I. Miotkowski, and A. K. Ramdas, Phys. Rev. B **65**, 195211 (2002).
[12] *Electron Paramagnetic Resonance*, edited by A. Abragam and B. B. Bleaney (Oxford University Press, New York, 1971).
[13] T. M. Pekarek, E. M. Watson, J. Garner, P. M. Shand, I. Miotkowski, and A. K. Ramdas, J. Appl. Phys. **101**, 09D511 (2007).
[14] *Semiconductors and Semimetals*, edited by J. K. Furdyna and J. Kossut (Academic, Boston, 1988), Vol. 25.