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

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The magnetization of In$_{1-x}$Mn$_x$Se 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$_x$Se 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$_x$S and In$_{1-x}$Mn$_x$S).

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 properties.\(^1\)\(^-\)\(^4\) The material that is the subject of this paper (In$_{1-x}$Mn$_x$Se) was recently reported\(^6\) 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$_x$S and In$_{1-x}$Mn$_x$S. The Ga$_{1-x}$Mn$_x$S is a four-atom thick layered bulk crystal, while the In$_{1-x}$Mn$_x$S has a more complicated tetrahedral crystal structure. In this paper, we model the magnetization of a selenium-based III-V DMS compound In$_{1-x}$Mn$_x$Se. It is believed In$_{1-x}$Mn$_x$Se has the same crystal structure as that of Ga$_{1-x}$Mn$_x$S.

In this paper, a singlet model is compared to the experimental data for In$_{1-x}$Mn$_x$Se. 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$_x$S (Refs. 8 and 11) and on In$_{1-x}$Mn$_x$S.\(^9\)\(^,\)\(^10\)

II. EXPERIMENTAL DETAILS

Magnetization measurements were taken in a Quantum Design magnetic property measurement system (MPMS)

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for the valence electrons of Mn consists of the following terms:\(^{11}\) a crystal field potential due to the Coulomb interaction of the 3\(d\) 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 3\(d\) electrons’ interaction with the applied magnetic field.

The Hamiltonian matrix is constructed using the angular momentum basis set\(^{1/20841}H_2^{\text{M}}L_{\text{M}}S_{\text{M}}=H_2^{\text{S}}L_{\text{S}}S_{\text{S}}\), where \(L\) and \(S\) are the total orbital and spin angular momentum quantum numbers of the 3\(d\) 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 \(5 \times 5\). The eigenvalues \(E_i\) of the singlet Hamiltonian are the 3\(d\) electron energy levels.

Parameters used in the construction of the singlet Hamiltonian include the formal oxidation states of In\(^{+2}\) and of Se\(^{−2}\), 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\(^{-1}\))\(^{12}\), and, finally, the spin-spin coupling constant \((\rho = 0.18\) cm\(^{-1}\))\(^{12}\). The general energy level diagram is shown in Fig. 1. Notice, there are 25 total levels. The \(5D\) 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 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\(_x\)S and In\(_{1-x}\)Mn\(_x\)S)\(^{8-11}\). Both of these systems are based on sulfur. Attempts at modeling other III-VI DMS systems have been...
unsuccessful to date. In Ga$_{1-x}$Mn$_x$S and In$_{1-x}$Mn$_x$S, the singlet model has worked well\textsuperscript{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$_x$S or below 140 K in In$_{1-x}$Mn$_x$Se, where the thermal hysteresis effects begin.\textsuperscript{7,13} Unlike the comparatively heavily studied III-V and II-VI DMS,\textsuperscript{14} this class of layered III-VI DMS remains largely unexplored.

### IV. CONCLUSIONS

Agreement was found between the magnetization of In$_{1-x}$Mn$_x$Se 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$_x$Se 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$_x$S and In$_{1-x}$Mn$_x$S). This work on the class of layered III-VI DMS also complements the comparatively heavily studied II-VI and III-V DMS.

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