Thermal hysteresis in the magnetization of the layered III-VI diluted magnetic semiconductor In1-xMnxSe

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Thermal hysteresis in the magnetization of the layered III-VI diluted magnetic semiconductor $In_{1-x}Mn_xSe$

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Magnetic properties of single-crystalline $In_{1-x}Mn_xSe$ (x=0.10) have been measured. A prominent thermal hysteresis in the magnetization is observed between 90 and 290 K. The magnetization is reversible (deviating by only ~0.8%) from 400 down to ~120 K along the upper branch of the hysteresis. In contrast, the lower branch magnetization is irreversible from 5 up to 290 K and deviates by 30% of the 0.010 emu/g hysteresis splitting at 140 K. Magnetic-field hysteresis loops at 200 K between −7 and +7 T demonstrate that changing the magnetic field does not allow movement between the upper and lower branches of the thermal hysteresis. This magnetic behavior is consistent with a charge-density wave. However, the observed ΔT=200 K hysteresis in $In_{1-x}Mn_xSe$ is roughly an order of magnitude larger than other previously reported values of ΔT. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2165924]

I. INTRODUCTION

$In_{1-x}Mn_xSe$ is in the class of layered III-VI diluted magnetic semiconductors (DMS). Only a few III-VI DMS systems have been investigated to date: $Ga_{1-x}Mn_xS$,[1,2] $In_{1-x}Mn_xS$,[3,4] $Ga_{1-x}Mn_xSe$,[5] and $Ga_{1-x}Fe_xSe$.[6] $Ga_{1-x}Mn_xS$ and $In_{1-x}Mn_xS$ are reasonably well understood at this time. In $Ga_{1-x}Mn_xS$ and $In_{1-x}Mn_xS$ the Mn ions go into the lattice substitutionally at the Ga or In lattice site similar to the II-VI DMS.[2,3] However, the $In_{1-x}Mn_xSe$ structure contains two preferred orientations of the In–In bond that are 70° apart.[3] There are no comparable II-VI DMS systems exhibiting this feature. Another behavior in the III-VI DMS with no comparable II-VI DMS system[7] is the large thermal hysteresis between 90 and 290 K recently reported in $In_{1-x}Mn_xSe$.[8] One unusual aspect of this thermal hysteresis is the large ΔT (=200 K).

Other unrelated materials exhibit significantly smaller thermal hysteresis. For example, $CuIr_2S_{4-x}Se_x$ exhibits only a <30 K wide thermal hysteresis around ~200 K.[9] Barium titanate is ferroelectric and has two small 22 K wide thermal hysteresis loops at 193 and 273 K. Another material, 1T-TaS_2, exhibits a charge-density wave hysteresis ~40 K wide near 200 K.[10] In $CuIr_2S_{4-x}Se_x$, barium titanate, or charge-density wave materials, the thermal hysteresis is accompanied by a structural phase transition in conjunction with another phenomenon such as a metal-insulator transition, electric polarization, or charge-density waves.

The III-VI semiconductors GaSe,[5,11–16] InSe,[12,15–21] GaTe,[22] and GaS (Refs. 23–25) have received considerable interest in the last few years because of their remarkable nonlinear optical properties. Recent work on InSe includes studies on polaron energy-level calculations,[15] pressure dependence of phonons and excitons in InSe films,[17] InSe/Si(111) heterojunctions' electronic structure,[16] and solid InSe structural and electronic properties under pressure.[18,21] Suhre *et al.* have shown that adding In to GaSe strengthens the material enough to polish optical faces along arbitrary crystalline directions while enhancing the optical characteristics.[13]

In this work we present magnetic measurements investigating the prominent thermal hysteresis in $In_{1-x}Mn_xSe$. This builds on recent measurements in InSe and expands the exploration of the class of III-VI DMS into the fifth III-VI DMS system investigated to date, complementing previous works on $Ga_{1-x}Mn_xS$,[1,2] $In_{1-x}Mn_xS$,[3,4] $Ga_{1-x}Mn_xSe$,[5] and $Ga_{1-x}Fe_xSe$.[6]

II. EXPERIMENTAL DETAILS

A 0.0571 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 Curie-Weiss fit to the 7 T magnetization data from 150 to 400 K yields x =0.045; however, the actual concentration of this sample is not critical for the discussions in this paper so the nominal value is used. Magnetization measurements were taken in a Quantum Design MPMS XL7 superconducting quantum interference device (SQUID) magnetometer at temperatures between 1.8 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.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Magnetization versus field data for $In_{1-x}Mn_xSe$ at 2, 300, and 400 K is shown in Fig. 1(a). The magnetization is clearly linear with field in the entire range from 2 to 400 K. The magnetization versus temperature data [shown as a plot of

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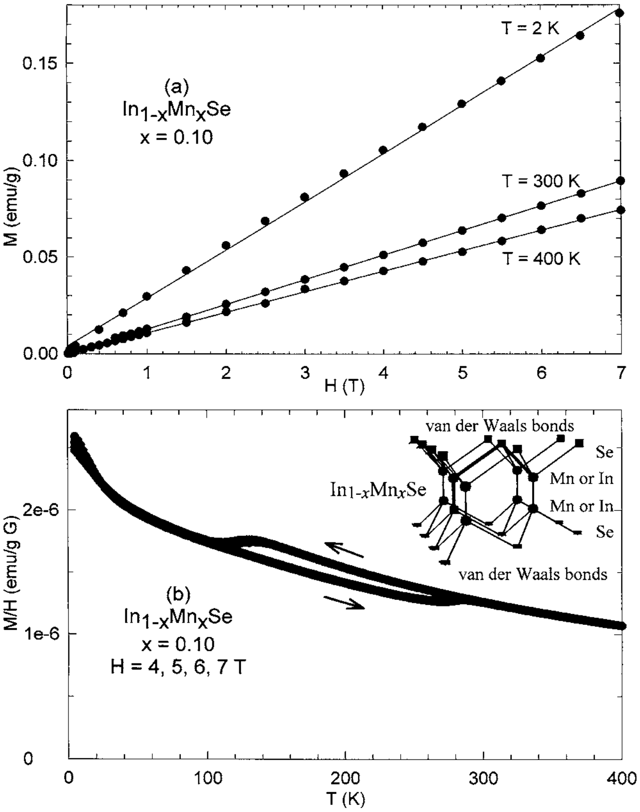

FIG. 1. (a) M vs H data for $In_{1-x}Mn_xSe$ (x=0.10) at 2, 300, and 400 K. The lines are a guide to the eye. (b) M/H vs T data taken in 4, 5, 6, and 7 T. The arrows indicate the warming and cooling traces. Hysteresis is clearly visible between 90 and 290 K. The inset shows a cross section of a single four atom thick layer of $In_{1-x}Mn_xSe$, where the large dots are the In or Mn lattice sites and the small squares are the Se sites. The Mn–Se–Mn pair is shown by the bold solid line. A direct Mn–Mn pair is shown by the bold dotted line.

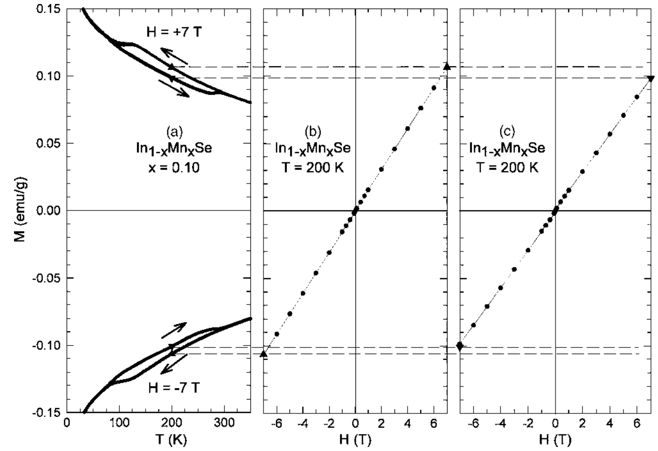

FIG. 2. (a) M vs T data for $In_{1-x}Mn_xSe$ (x=0.10) in +7 and −7 T. The arrows indicate the warming and cooling traces. The magnetization values at 200 K are marked by upright (inverted) triangles on the cooling (warming) branches of each thermal hysteresis for comparison to the M vs H data. The dashed lines are a guide to the eye. (b) M vs H data at 200 K. The sample started at 400 K before cooling to 200 K. (c) M vs H data at 200 K. The sample started at 5 K before warming to 200 K.

M/H vs T in Fig. 1(b)] taken in 4, 5, 6, and 7 T applied fields shows a prominent thermal hysteresis from 90 to 290 K. Despite this prominent thermal hysteresis, the magnetization remains linear with field resulting in the overlap of the 4, 5, 6, and 7 T data when plotted as M/H vs T. Measurements made on pure InSe (not shown) do not exhibit any thermal hysteresis. This thermal hysteresis in $In_{1-x}Mn_xSe$ is unprecedented in the published literature on II-VI and III-VI DMS and has not been previously reported in any other III-VI DMS system.

Magnetization vs temperature data for $In_{1-x}Mn_xSe$ (x=0.10) in +7 and −7 T are shown in Fig. 2(a). The magnetization values at 200 K are marked by upright (inverted) triangles on the cooling (warming) branches of each thermal hysteresis for comparison to the magnetization versus field data. Magnetization versus field loops from +7 to −7 T and back to +7 T at 200 K are shown in Figs. 2(b) and 2(c). No hysteresis is evident in the field hysteresis loops. Prior to taking the field loop in Fig. 2(b), the sample started at 400 K and then was cooled to 200 K. The agreement is excellent (<0.06% difference) between the magnetization at +7 and −7 T with the respective values of the thermal hysteresis shown by the upright triangles. This difference is only 1% of the splitting of the thermal hysteresis at 200 K. This suggests that the system is well behaved in this region with no field history dependence. Prior to taking the field loop in Fig. 2(c), the sample started at 5 K and then was warmed to 200 K. In this case the agreement between the magnetization at +7 and −7 T and the respective values of the thermal hysteresis (shown by the inverted triangles) is less than 3%, but this corresponds to 38% of the thermal hysteresis splitting at 200 K.

Figures 3(a) and 3(b) provide a magnified view of the thermal hysteresis in +7 and −7 T around 290 K. After starting the sample at 400 K and cooling to 290 K, the magnetization was measured as the field was swept from +7 to −7 T and back to +7 T. No hysteresis was observed in the field hysteresis loop. On this expanded scale, only the +7 and −7 T data points are shown in Figs. 3(c) and 3(d), respectively. The agreement is again excellent between the magnetization at +7 and −7 T with the respective values of the

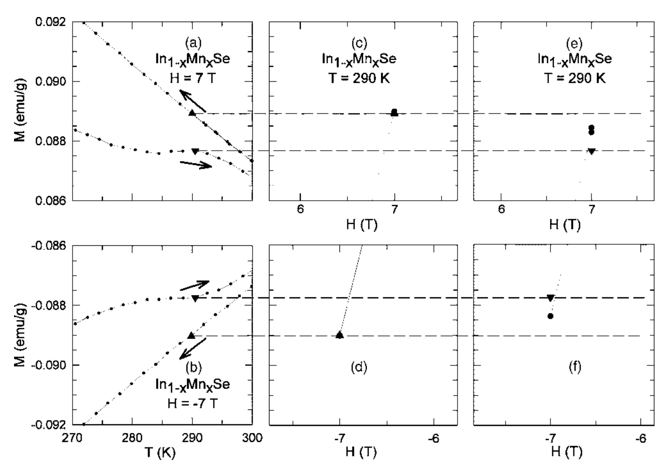

FIG. 3. Magnified view near 290 K and ±7 T. [(a) and (b)] M vs T data for $In_{1-x}Mn_xSe$ (x=0.10) in +7 and −7 T. The arrows indicate the warming and cooling traces. The magnetization values at 290 K are marked by upright (inverted) triangles on the cooling (warming) branches of each thermal hysteresis for comparison to the M vs H data. The dashed lines are a guide to the eye. [(c) and (d)] M vs H data at 290 K. The sample started at 400 K before cooling to 290 K. [(e) and (f)] M vs H data at 290 K. The sample started at 5 K before warming to 290 K.

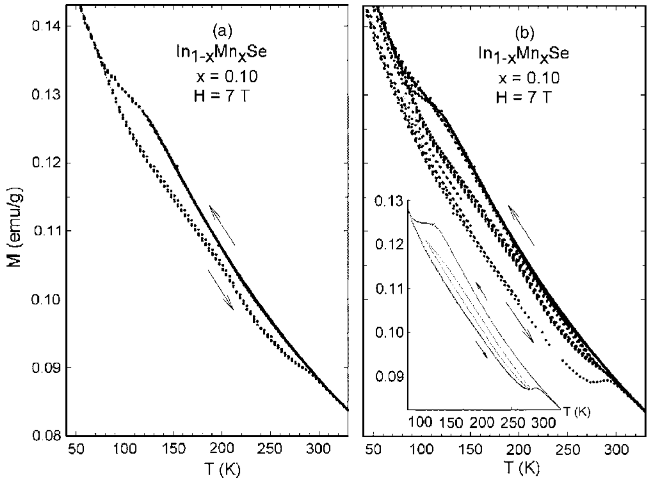

FIG. 4. *M* vs *T* data for $In_{1-x}Mn_xSe$ in a 7 T field. The arrows indicate the warming and cooling traces. (a) several thermal cycles are shown from 350 K down to turning points at 120, 130, 140, and 150 K. Note the magnetization is reversible from 400 down to ~120 K. (b) includes additional thermal cycles from 5 K up to turning points at 140, 150, and 200 K. The inset depicts a minor hysteresis loop beginning at 280 K after warming from 5 K.

thermal hysteresis (upright triangles). After starting the sample at 5 K and warming to 290 K, the magnetization-field loop showed no hysteresis. On this expanded scale, only the +7 and −7 T data points are shown in Figs. 3(e) and 3(f), respectively. As can be seen, the magnetizations at +7 and −7 T are notably different from their respective values of the thermal hysteresis shown by the inverted triangles. However, the difference between the starting and ending data points at 7 T [shown by the two circles in Fig. 3(e)] is not as significant as the difference between these values and the respective value of the thermal hysteresis (inverted triangle). Furthermore, the +7 and −7 T data points from the field hysteresis loop fall systematically in the middle of the thermal hysteresis splitting at 290 K (shown by the dashed lines). This suggests that changing the magnetic field between ±7 T is not the primary cause of this offset from the thermal hysteresis values.

The magnetization versus temperature is shown in Fig. 4(a) for a number of thermal cycles from 350 K down to turning points at 120, 130, 140, and 150 K as well as several full hysteresis loops. The magnetization is reversible (deviating by only ~0.8%) from 400 down to ~120 K along the upper branch of the hysteresis. The magnetization versus temperature plot shown in Fig. 4(b) also includes data from additional thermal cycles from 5 K up to turning points at 140, 150, and 200 K. The inset of Fig. 4(b) depicts a minor hysteresis loop beginning at 280 K after warming from 5 K. In contrast to the reversible upper branch, the magnetization is irreversible along the lower branch from 5 up to 290 K and can deviate by 30% of the 0.010 emu/g hysteresis splitting at 140 K. Consequently, the offset observed in Figs. 3(e) and 3(f) are most likely due to variations in the warming traces illustrated in Fig. 4(b).

While the underlying mechanism causing the pronounced thermal hysteresis in $In_{1-x}Mn_xSe$ is not conclusively known at this time, the magnetic behavior is consistent with a charge-density wave. However, the observed $\Delta T = 200$ K hysteresis in $In_{1-x}Mn_xSe$ is roughly an order of magnitude larger than other previously reported values of ΔT.

ACKNOWLEDGMENTS

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