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Magnetic measurements on Ga$_{1-x}$Mn$_x$S in high fields using the cantilever technique

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Abstract

High field magnetic measurements have been taken on the III-VI Diluted Magnetic Semiconductor Ga$_{1-x}$Mn$_x$S at the National High Magnetic Field Laboratory. This paper discusses the calibration of magnetic measurements made using the cantilever technique. It has been discovered that efficiency of cantilevers may decline over time, signaled by the onset of an oscillatory effect in the cantilever data. (Feb. 2001)

Introduction

III-VI Diluted Magnetic Semiconductor

Background

The new layered III-VI Diluted Magnetic Semiconductors (DMS) are 2-D systems containing transition metal ions (e.g. Mn, Fe, Co, etc.) in a III-VI semiconducting host (e.g. GaSe, GaS, etc.). The III-VI DMS Ga$_{1-x}$Mn$_x$Se exhibits a strong red emission at 1.804 eV attributed to the Mn ions. The III-VI semiconductors are known for their remarkable nonlinear optical properties and are promising materials for photoelectronic applications. This work also complements the enormous progress in the II-VI DMS and the more recent efforts in the Mn doped III-V DMS systems.

Pekerak et al presented magnetization data on the III-VI DMS Ga$_{1-x}$Mn$_x$Se that is strikingly different from any of the II-VI DMS data. A key feature is a broad peak in the magnetization versus temperature data between 120 and 195 K that is ascribed to direct Mn-Mn pairs. This is a fundamentally different behavior that that observed in the heavily studied II-VI DMS. Except for this single publication, no previous magnetic or calorimetric measurements on III-VI DMS have been reported.

Since this presentation more recent work on the magnetic measurement on Ga$_{1-x}$Mn$_x$S has been conducted. Its magnetic behavior was remarkably different from Ga$_{1-x}$Mn$_x$Se and II-VI DMS. The prominent broad peak between 120 and 195 K in the magnetization of Ga$_{1-x}$Mn$_x$Se, ascribed to direct Mn-Mn pairs, is absent in the Ga$_{1-x}$Mn$_x$S data. This suggests that there are no direct Mn-Mn pairs in the GaS system. However, the magnetization of Ga$_{1-x}$Mn$_x$S does show a sharp cusp at 11.3 K (an order of magnitude higher than the spin-glass transition in Cd$_{1-x}$Mn$_x$S) suggesting that a similar mechanism with Mn-Se-Mn pairs may be present in Ga$_{1-x}$Mn$_x$S. The exchange interactions in Ga$_{1-x}$Mn$_x$Se and Ga$_{1-x}$Mn$_x$S (with lower symmetry than the II-VI and III-V DMS) are more complex and exhibit significantly different magnetic properties. The magnetic and calorimetric measurements will provide key information for unraveling some of the observed novel magnetic effects.

The III-VI semiconductors GaSe, InSe, GaTe, and GaS have generated considerable interest in the last few years because they have remarkable nonlinear optical properties and are promising materials for photoelectronic applications in the visible range (the band gap for GaSe is 2.0 eV). Furthermore, Shigetomi et al. and Lee et al. studied Mn-doped GaSe samples and report a strong red emission at 1.804 eV (Fig. 1), which is important for compatibility with commercial lasers. They attribute this emission line to the Mn ions’ acceptor level. This makes Ga$_{1-x}$Mn$_x$S particularly interesting to study. Since the magnetic behavior is a measure of the field and temperature dependence of the Mn ion energy levels, the results of this work will lead to an increased understanding of this important emission line.
To understand the Ga$_{1-x}$Mn$_x$S and other III-VI DMS completely enough to predict the behavior of these systems within a wide range of experimental conditions, it is essential to first know how the Mn ions behave individually as well as cooperatively throughout the crystal. Calorimetric and magnetic studies are well suited for this task.

Further investigation into the magnetic properties of Ga$_{1-x}$Mn$_x$S are needed to determine the electronic levels of the individual Mn ions, the interactions of various nearest neighbor configurations (e.g. Mn-Mn, Mn-Se-Mn, Mn-Ga-Se-Mn, etc.), and the longer-range cooperative effects in the bulk crystal. This will directly provide information about how the temperature and field affect the electronic levels, in particular the levels giving rise to the 1.804 eV emission line in Ga$_{1-x}$Mn$_x$Se (Fig.1).
The work of Shigetomi et al. in 1994 confirms the results of Lee et al. and provides Hall effect and deep-level transient spectroscopy measurements confirming the 0.34 eV acceptor level. The results of the proposed magnetic and calorimetric investigations should provide additional insight into the published data reported in these papers.

**Published Magnetic Measurements on Ga$_{1-x}$Mn$_x$Se**

A key feature of Ga$_{1-x}$Mn$_x$Se is its two-dimensional crystal structure. Each Ga$_{1-x}$Mn$_x$Se layer is comprised of a top two-dimensional layer of Se ions, two middle layers of Ga ions, and a bottom layer of Se ions (Fig. 2). Within each four atom thick layer the bonding is covalent. Layers are weakly coupled through van der Waals bonding similar to mica, which further enhances the two-dimensional nature of this crystal. This is therefore an excellent system to investigate 2-D magnetism as well as the dimensional crossover between the 2-D and 3-D regimes.

**Magnetic Measurements on Ga$_{1-x}$Mn$_x$S**

We have already conducted initial magnetic measurements on single crystalline Ga$_{1-x}$Mn$_x$S. Magnetic versus temperature measurements taken in a 0.0050 and 0.1 T field are shown in figure 3. The prominent broad peak from 119 to 195 K in the magnetization of Ga$_{1-x}$Mn$_x$Se, ascribed to direct Mn-Mn pairs, is absent in our Ga$_{1-x}$Mn$_x$S data. This suggests there are no direct Mn-Mn pairs in the GaS system.

We see a prominent cusp at 11.3 K in figure 4. While the presence of a cusp of this sort can arise from several different mechanisms including a spin-glass transition or cluster locking, many of the II-VI DMS also display similar cusps at low temperature due (in the case of the II-VI DMS) to a spin-glass transition. However, a more sophisticated analysis is needed before any specific conclusions can be drawn from the presence of the cusp in our Ga$_{1-x}$Mn$_x$S data. Nonetheless, the presence of the cusp provides additional evidence to the Curie-Weiss behavior that there are Mn-Se-Mn (and/or perhaps Mn-Se-Ga-Mn) pairs in Ga$_{1-x}$Mn$_x$S.

The absence of the peak in figure 3, the Curie-Weiss behavior (not shown), and now the cusp in figure 4 all are reminiscent of the II-VI DMS in stark contrast to the dramatically different behavior of Ga$_{1-x}$Mn$_x$Se. Still there are some features of the Ga$_{1-x}$Mn$_x$S data that distinguish
Ga$_{1-x}$Mn$_x$S from the II-VI DMS. For one, the cusp we observe at 11.3 K is more than an order of magnitude higher than the spin-glass transition in Cd$_{0.934}$Mn$_{0.066}$S, which occurs at $\sim$0.08 K.

The singlet behavior of isolated Mn ions in Ga$_{1-x}$Mn$_x$S is also somewhat unusual compared with the II-VI DMS. At $10\,\text{K}$ in a $6\,\text{T}$ field (not shown), the magnetization for an $x = 0.066$ sample has reached $\sim$10% of the expected saturation magnetization for $S = 5/2$ and remains roughly linear with field where $M/H = 2 \times 10^{-5}\,\text{emu/g G}$. This linear response is dramatically different from the behavior of V, Cr, Co, and Mn-based II-VI DMS, which all show definite signs of saturation by $6\,\text{T}$ at $10\,\text{K}$. However, Fe-based II-VI DMS exhibit Van Vleck paramagnetism with an initially weak linear response. It is still too soon to conclude that singlet Mn ions in Ga$_{1-x}$Mn$_x$S and Ga$_{1-x}$Mn$_x$Se are Van Vleck paramagnets. The difference between the Ga$_{1-x}$Mn$_x$Se and Ga$_{1-x}$Mn$_x$S systems may provide a good opportunity to investigate the difference in exchange channels between Mn-Mn versus Mn-Se-Mn pairs and the different magnetic behavior each consequently exhibits.

Cantilever Magnetometry

Magnetization measurements were conducted at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, FL. The NHMFL is one of only nine such facilities in the world and is the largest and high-powered magnet laboratory of it's kind. Magnetization measurements were performed using a newly developed cantilever technique. This process involves mounting a $\sim$0.0010g sample on the cantilever device at the end of a probe (Figure 5). The cantilever device consists of a cantilever beam; where the sample is attached, placed into the helium-3 cryostat, and cooled. The probe was then lowered into a NHMFL 30 Tesla resistive magnet.

Cantilever magnetometry is based on the principle that a magnetic sample secured to the flexible beam will encounter a torque and a force when placed in an external magnetic field. Magnetization $M$ is the magnetic dipole moment per unit volume of the sample. Magnetic moments experience a torque

$$t = M \times B$$

in the presence of a uniform magnetic field $B$. This allows us to find the component of magnetization perpendicular to the applied field. A force

$$F = M \cdot dB/dz$$

is exerted on a magnetic moment in a field gradient. This force allows us to measure to the magnetization component parallel to the applied field. The cantilever beam responds by a deflection proportional to the torque or force on the sample. The deflection of the cantilever beam is measured by a change in capacitance between the fixed base plate and the flexible cantilever beam, which holds the sample (Fig.1). Measurement of the capacitance is made with a 1616 General Radio capacitance bridge and a lock-in amplifier used to drive the bridge and detect the imbalance signal. Theoretically, it is possible to obtain calibrated magnetization curves from this technique. Relative measurements are easily obtained. In the case of Ga$_{1-x}$Mn$_x$S, the perpendicular signal was small compared to the parallel magnetization. Therefore, we will focus on the parallel magnetization of Ga$_{1-x}$Mn$_x$S.

Calibration

Our most recent magnet time at the NHMFL has provided a chance to improve the calibration techniques for cantilever magnetometry. Measurements taken at NHMFL give the raw data for magnetization measurements in terms of voltage $V$ versus applied field $H$. The following section is devoted to describing the calibration method used to convert the raw voltage data into calibrated magnetization (emu/g) data.
A small wire loop attached to the surface of our cantilever. By setting a current in this loop, we generate a known magnetic dipole moment. In a magnetic field gradient, this magnetic dipole produces a force on the cantilever. The force deflects the cantilever and changes the capacitance. By supplying a known current to the loop of known area we can calculate the current loops magnetic dipole moment, the force exerted on the cantilever beam, and the corresponding change in capacitance for such a force. From this we may determine a relationship between the voltages given in the data file and the magnetization of the sample. The following is a detailed description of the calibration process.

To begin the calibration procedure, place the probe above the magnet center where it will be in the maximum field gradient when the magnetic field $B_{\text{SetCal}}$ is set. Set the temperature and wait for it to stabilize. The area of the current loop should be recorded. The setting of the capacitance bridge should be recorded as well as the lock-in signal in zero field.

Set the current $I_{\text{Loop}}$ and record both the values of the set current and the resulting change in capacitance $\Delta C$ from the zero current value.

The raw data files record a voltage data point $V_{\text{Data}}$. This voltage comes from the lock-in amplifier that is used to drive the capacitance bridge and detect the imbalance signal. For the calibration, the relationship between a change in capacitance and a change in voltage must be established. This is done at the NHMFL by making changes in the capacitance bridge by hand and noting the change in voltage from the lock-in. Each cell containing a magnet at the NHMFL has its own Magnet Profile from which the value of the field and field gradient may be found for any position inside the magnet core. The value of the applied field at 8 cm up from center is found with the following equation.

Recall from $F = M \cdot \frac{\Delta C}{\delta}$ that the force $F_{\text{Loop}}$ exerted on the loop is given by:

$$F_{\text{Loop}} = M_{\text{Loop}} \cdot \left( \frac{\Delta C}{\delta} \right)_{\text{Cal}}$$

$$F_{\text{Loop}} = (A_{\text{Loop}} I_{\text{Loop}}) \cdot \left( \frac{\Delta C}{\delta} \right)_{\text{Cal}}$$

(4)

where $(\frac{\Delta C}{\delta})_{\text{Cal}}$ is the field gradient when the constant applied field is set during the calibration procedure itself. The sample on the cantilever also produces a force

$$F_{\text{Sample}} = M_{\text{II}} \cdot \left( \frac{\Delta C}{\delta} \right)_{\text{Data}}$$

(5)

where $(\frac{\Delta C}{\delta})_{\text{Data}}$ is the constantly changing field gradient during a normal data sweep.

Using the change in capacitance $\Delta C$ found when a current is supplied in the loop, the conversion coefficient $\frac{\Delta C}{\delta}$, and the voltage data point $V_{\text{Data}}$, we get:

$$F_{\text{Sample}} = (V_{\text{Data}}) \cdot \left( \frac{\Delta C}{\delta} \right)_{\text{Data}} ((F_{\text{Loop}})/(\Delta C))$$

(6)

$M_{\text{II}}$ is the final value we seek so, solving for $M_{\text{II}}$ in (5) and substituting (6) for $F_{\text{Sample}}$

$$M_{\text{II}} = \left[ (V_{\text{Data}}) \left( \frac{\Delta C}{\delta} \right)_{\text{Data}} ((F_{\text{Loop}})/(\Delta C)) \right] / \left( \frac{\Delta C}{\delta} \right)_{\text{Data}}$$

(7)

$$M_{\text{II}} = \left[ (V_{\text{Data}}) \left( \frac{\Delta C}{\delta} \right)_{\text{Data}} ((A_{\text{Loop}} I_{\text{Loop}} (\frac{\Delta C}{\delta})_{\text{Cal}})/(\Delta C)) \right] / \left( \frac{\Delta C}{\delta} \right)_{\text{Data}}$$

(8)

We now must determine the values of the two different field gradients in the numerator and denominator. Each cell containing a magnet at the NHMFL has its own Magnet Profile from which the value of the field and field gradient may be found for any position inside the magnet core. The value of the applied field at 8 cm up from center is found with the following equation.

$$B_{\text{8 cm up}} = B_{\text{set}} \left( \frac{B_{\text{max 8 cm up}}}{B_{\text{max center}}} \right)$$

(9)

$B_{\text{max 8 cm up}} / B_{\text{max center}}$ is given in the magnet profile. The maximum field gradient of the 30 T magnet in Cell 9 is found at 8 cm up from center. This point may differ with the
use of different magnets in different cells at the NHMFL. The field gradient can also be found using the Magnet Profile. The following equation gives the value of the field gradient.

\[
\frac{\Delta B}{\Delta z} = B_{\text{set}} \left[ \left( \frac{B_{\text{max}} \text{up}}{B_{\text{max}} \text{center}} \right) - \left( \frac{B_{\text{max}} \text{center}}{B_{\text{max}} \text{up}} \right) \right]
\]

Note that the difference between the field gradients in equation 8 lies in the value of \( B_{\text{set}} \) in equation 10. The field gradient \( \left( \frac{\Delta B}{\Delta z} \right)_{\text{Cal}} \) in the numerator comes from the calibration procedure where \( B_{\text{set,Cal}} \) is a constant value. On the other hand, the field gradient \( \left( \frac{\Delta B}{\Delta z} \right)_{\text{Data}} \) in the denominator is found by using the ever changing value of \( B_{\text{set}} \) as the magnetic field is ramped up and down through the data run. Use \( B_{\text{Data}} \) to represent the changing applied field of the data runs, the second term of equation 10 cancels out in equation 8 and we are left with:

\[
M_H = \left[ \frac{V_{\text{Data}}}{B_{\text{Data}}} \right] \left[ \frac{\left( \frac{\Delta V}{\Delta W} \right) \left( A_{\text{Loop}} I_{\text{Loop}} \right) B_{\text{set,Cal}}}{\left( \frac{\Delta C}{\Delta W} \right)} \right]
\]

All values in the second term are known. We may set this term equal to a calibration constant \( C_{\text{Cantilever}} \).

\[
M_H = \left[ \frac{V_{\text{Data}}}{B_{\text{Data}}} \right] C_{\text{Cantilever}}; \quad C_{\text{Cantilever}} = \left[ \frac{\left( \frac{\Delta V}{\Delta W} \right) \left( A_{\text{Loop}} I_{\text{Loop}} B_{\text{set,Cal}} \right)}{\left( \frac{\Delta C}{\Delta W} \right)} \right]
\]

Both \( V_{\text{Data}} \) and \( B_{\text{Data}} \) are extracted from the raw data files.

Note that this \( M_H \) value is given in units of J/T or Am². We seek a final value with the units of emu/g. 1 J/T is equivalent to 10⁻³ emu. Simple of use this conversion and dividing by the mass of the sample we arrive at units of emu/g.

**Cantilever effect**

Recent measurements made using the cantilever method at the National High Magnetic Field Laboratory have shown an oscillatory and hysteretical effect in the magnetization as a function of field (Figure 6). Preliminary analysis suggested that these oscillations may have been due to the de Haas-van Alphen effect. The oscillations are observed at very low temperatures and high magnetic fields. The oscillations in our Ga₁₋ₓMnₓS sample occur in the temperature range of 1.3K - 1.7K and field range of 8T - 18T.

After several attempts to identify the source of these oscillations, it has been found that the mechanical properties of the...
cantilever declines over time. The decline of a cantilever’s usefulness is signaled by the onset of an oscillatory and hysteresis effect in the cantilever data. Our research group has played an important role in identifying this effect. This information will aid future NHMFL magnet users to quickly identify the source of faulty data; saving both time and money.

Calibrated results for magnetic measurement on Ga$_{1-x}$Mn$_x$S in high magnetic fields using the cantilever technique

The following pages show our results for the calibrated magnetization measurements on Ga$_{1-x}$Mn$_x$S. Current theoretical work is in the final stages and will be submitted for publication along with this data in an appropriate peer-reviewed journal.

Appendix A

The following is an example of a SigmaPlot transform used to calibrate raw cantilever data from the NHMFL.

```plaintext
;P1252ML4b_001

;PARAMETERS

  cell(11,1) = “sample mass (g )=”
  cell(12,1) = mass
  mass = 0.0023

  cell(11,2) = “L_Loop (A )=”
  cell(12,2) = L_Loop
  L_Loop = 10e-3

  cell(11,3) = “A_Loop (m*m)=”
  cell(12,3) = A_Loop
  A_Loop = 1.295907e-5

  cell(11,4) = “deltaC/deltaV (F/V)=”
  cell(12,4) = CV
  CV = 6.2696e-10

  cell(11,5) = “deltaC_5K (F)=”
  cell(12,5) = deltaC
  deltaC = 0.000365e-12

  cell(11,6) = “B/B_o =”
  cell(12,6) = BB_o
  BB_o = .79

  ; correct B_set to B at the sample 8cm up
  col(13) = col(1) * BB_o

  ;calibrate data
  cell(11,7) = “cal const , K=”
  cell(12,7) = K
  K = (CV * ((L_Loop * A_Loop * 5)/deltaC)) * 1e3
  col(14) = Mag_II
  Mag_II = -(col(3)/col(1) * K)/mass
```

Appendix B

$\Delta C$ = change in capacitance when a current is placed in the loop

$A_{Loop}$ = area of the loop

$I_{Loop}$ = current in the loop

$B_{Set, Cal}$ = applied field value while performing the initial calibration procedures

$\%v$ = conversion coefficient used to convert the raw voltage data to a capacitance

$M_{Loop}$ = magnetic dipole moment of the loop

$(\%a)_{Cal}$ = field gradient value while performing the initial calibration procedures

$F_{Loop}$ = force on the loop in a field gradient

$F_{Sample}$ = force on the sample in a field gradient

$M_{II}$ = magnetization of the sample

$(\%a)_{Data}$ = changing field gradient value during data sweeps

$V_{Data}$ = raw voltage data point value

$F_{Sample} = (V_{Data} ((\%v) ((F_{Loop})/(\Delta C))))$ (6)

$B_{8cm up}$ = actual field value at maximum field gradient

$B_{set}$ = set field value
The following is a step by step example of the calibration of a single raw data point. After following the calibration procedure at the NHMFL as described above, the following values are given.

Data from the initial calibration steps would appear as follows.

<table>
<thead>
<tr>
<th>Capacitance Bridge Value</th>
<th>Lock-in Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3 mV</td>
<td>9845 pF</td>
</tr>
<tr>
<td>24.30 mV</td>
<td>9955 pF</td>
</tr>
<tr>
<td>38.30 mV</td>
<td>9555 pF</td>
</tr>
</tbody>
</table>

Using the calibration data at 5T, the following values are found:

\[ \Delta C = 0.000365 \times 10^{-12} \text{ F} \]

\[ A_{\text{Loop}} = 6.25 \times 10^{-6} \text{ m}^2 \]

\[ I_{\text{Loop}} = 10^{-3} \text{ A} \]

\[ B_{\text{setcal}} = 5 \text{ T} \]

\[ \frac{\Delta B}{\Delta V} = 6.2695925 \times 10^{-10} \text{ F/V} \]

mass = 0.0023 g

The calibration coefficient can be found using equation 12

\[ C_{\text{cantilever}} = 0.53678 \text{ J/T} \]

or in units of emu/g

\[ C_{\text{cantilever}} = 233382 \text{ emu/g} \]

This value can then be used as the calibration coefficient in a math transform similar to that shown in Appendix A.

Work Cited


7 Donavan Hall, Magnetic Measurements with Metal Film Cantilevers: A user’s Guide (1999)