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Influence of pair-exchange interaction on the magnetization of IV-VI-compound diluted magnetic semiconductors

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The magnetization of IV-VI-compound diluted magnetic semiconductor systems has been measured at 4.2 K with use of the sample-extraction method in steady magnetic fields up to 30 T. The results have been fitted by an expression containing a Brillouin function, representing isolated magnetic ions, plus a term representing pair interactions. The fitting parameters are $\bar{x}_1$, the effective occupation probability of a cation site by a Mn ion; T_0, representing the exchange interaction between Mn^{2+} ions; $\bar{x}_2$, representing the number of Mn^{2+} ions in pairs; and J_P, a pair-exchange parameter. Reasonable agreement of these high-field parameters with parameters obtained from the low-field susceptibility was obtained. Fits including the nearest-neighbor-pair–exchange function confirm the importance of nearest-neighbor pairs in the antiferromagnetic exchange interaction.

I. INTRODUCTION

Single crystals of IV-VI chalcogenides containing Mn or rare-earth ions, substitutionally replacing some of the cations, have been grown by the Bridgman technique. Measurements have shown the strong influence of a magnetic field on the physical properties of these diluted-magnetic-semiconducting (DMS) materials. Previously we examined the high-temperature susceptibility of the ternary alloys $Pb_{1-x}Mn_xTe$, $Pb_{1-x}Mn_xSe$, and $Pb_{1-x}Gd_xTe$ and compared the exchange values with those of II-VI-compound DMS systems.[1] The magnitude of the exchange in II-VI systems was found to be significantly larger than the exchange in IV-VI systems; these results are consistent with a model based upon superexchange mediated by the group-VI anions. Thus the exchange interaction is extremely sensitive to the cation-anion separation.

In the present study we have extended our magnetization measurements to high fields in order to study the pair-exchange interaction more completely. We will show that the high-field, low-temperature magnetization and exchange interactions are consistent with the low-field, high-temperature measurements. Some preliminary results have been reported previously.[2] In addition to the ternary DMS systems listed above, we have investigated the quaternary materials $Pb_{1-x-y}Sn_yMn_xSe$ with x values up to 0.02. The values of x and y were chosen to keep the energy gap constant at approximately the value for PbSe (0.145 eV at 4.2 K).[3] These crystals were p type with carrier concentrations ranging from 5×10^{18} to 10^{19} cm^{-3}.

II. EXPERIMENTAL TECHNIQUE

The concentrations of the magnetic ions in our single-crystal samples were determined by electron microprobe and x-ray fluorescence with an accuracy of about 20%. There was less than a 5% variation in magnetic ion concentration throughout each sample. The samples studied with their x values are listed in Table I.

The high-field experiments were carried out in the High-Field Laboratory for Superconducting Materials of Tohoku University. Both water-cooled copper magnets, which produced magnetic fields to 15 T, and hybrid magnets, which were composed of a superconducting magnet outside a water-cooled magnet and produced fields up to 31 T, were used. The magnetic field was determined by the currents through the magnets. Calibrations had been done previously by means of Hall probes and pickup coils. The magnetic field was determined with an accuracy of 2%.

The magnetization was measured in steady fields by the

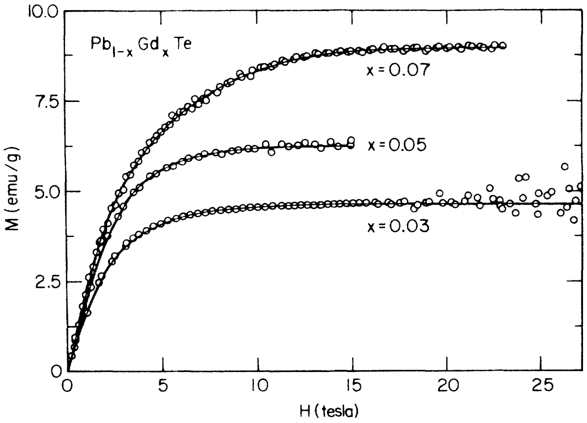

FIG. 1. Magnetization of $Pb_{1-x}Gd_xTe$ at 4.2 K. The circles represent the data and the solid lines were obtained from three-parameter fits (see Table I).

TABLE I. Singles and pairs fitting parameters.

Compound	x	y	$\bar{x}_1$[a]	T_0[a] (K)	$\bar{x}_1$[b]	$\bar{x}_2$[b]	J_P/k_B[b] (K)
$Pb_{1-x}Gd_xTe$	0.035		0.040	1.6	0.026	0.014	−0.39
	0.055		0.054	2.0	0.023	0.031	−0.27
	0.07		0.074	4.4	0.037	0.036	−0.69
$Pb_{1-x}Mn_xTe$	0.01[c]		0.013	1.9[c]	0.009	0.004[c]	−1.97[c]
	0.022		0.026	1.2	0.019	0.006	−0.88
	0.04		0.033	1.7	0.022	0.010	−0.82
$Pb_{1-x}Mn_xSe$	0.03		0.038	2.6	0.022	0.015	−0.93
	0.07		0.057	4.0	0.027	0.028	−1.03
$Pb_{1-x-y}Sn_yMn_xSe$	0.007	0.02	0.0071	0.8	0.006	0.001	−1.21
	0.015	0.03	0.014	1.2	0.011	0.003	−0.89
	0.017	0.05	0.015	1.06	0.012	0.003	−0.81

[a] Modified Brillouin function: two-parameter fit.
[b] Brillouin function plus pairs: three-parameter fit.
[c] Large experimental errors; fit unreliable.

sample-extraction method; that is, the sample was inserted into a pickup coil concentric with the magnet and quickly extracted. Five samples, moved by pistons driven by compressed air, could be studied sequentially during one field sweep. The magnetization was obtained from the voltage obtained in a pickup coil and the calibration was obtained from measurements on a nickel sphere. A computer was used to control the sequential movements of the pistons and to integrate the pickup voltage to obtain the magnetization. All the steady-field measurements reported here were carried out at 4.2 K with the samples immersed in liquid helium. The errors in magnetization were typically 5%, as indicated by the scatter in the data (Figs. 1–4).

III. RESULTS

Figures 1–4 show the magnetization versus magnetic field H for $Pb_{1-x}Gd_xTe$, $Pb_{1-x}Mn_xTe$, and $Pb_{1-x}Mn_xSe$, and $Pb_{1-x-y}Sn_yMn_xSe$, respectively, for different concentrations of the magnetic ions. At the measurement temperature, 4.2 K, the magnetization is nearly saturated at fields above 15 T. In many of our experimental runs, excess noise was observed above 20 T, apparently due to mechanical vibrations, but the experimental values were consistent with the results at lower fields. The solid lines in Figs. 1–4 are fits of the data to Eq. (1), which has three terms: The first, M_S, is a modified Brillouin function; the second, M_P, represents the pair exchange; the third is a term linear in magnetic field, $\chi_0 H$, that represents the diamagnetic contribution of the PbTe or PbSe matrix. Thus the magnetization was fitted to the expression

$$M = M_S + M_P + \chi_0 H \ , \tag{1}$$

where

$$M_S = M_0 S \bar{x}_1 B_S(\zeta) \ , \tag{2}$$

$$M_0 = g_M \mu_B N_0 \ . \tag{3}$$

$B_S(\zeta)$ is a modified Brillouin function,

$$B_S(\zeta) = \frac{2S+1}{2S} \coth\left[\frac{2S+1}{2S}\zeta\right] - \frac{1}{2S}\coth\left[\frac{\zeta}{2S}\right] \ , \tag{4}$$

and

$$\zeta = \frac{S g_M \mu_B H}{k_B (T+T_0)} \ . \tag{5}$$

The expression for M_P is

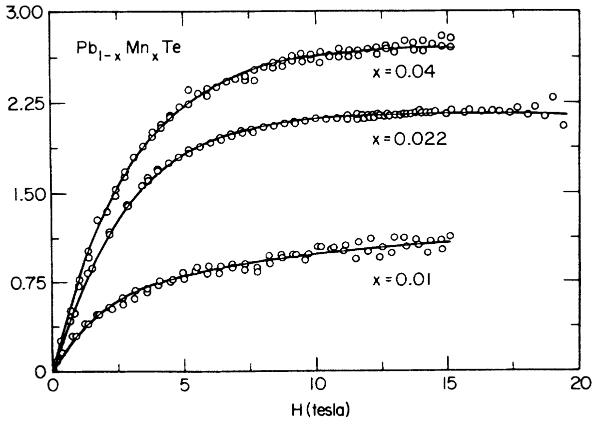

FIG. 2. Magnetization of $Pb_{1-x}Mn_xTe$ at 4.2 K. The circles represent the data and the solid lines were obtained from three-parameter fits (see Table I).

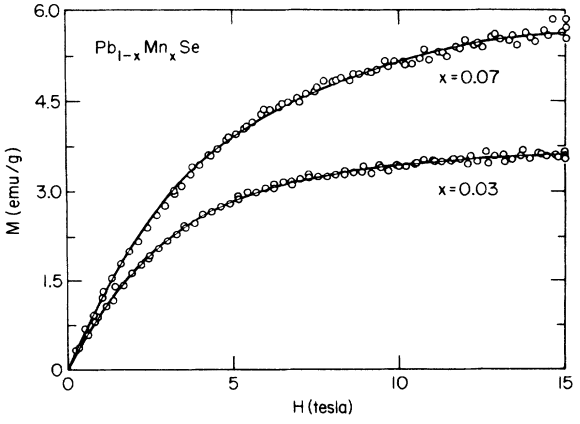

FIG. 3. Magnetization of $Pb_{1-x}Mn_xSe$ at 4.2 K. The circles represent the data and the solid lines were obtained from three-parameter fits (see Table I).

$$M_P=\tfrac{1}{2}M_0\bar{x}_2\frac{\displaystyle\sum_{s=0}^{S_{\max}}\exp\left[\frac{J_P}{k_BT}s(s+1)\right]s\left[\sinh\left[\frac{2s+1}{2s}\xi_P\right]\right]B_s(\xi_P)}{\displaystyle\sum_{s=0}^{S_{\max}}\exp\left[\frac{J_P}{k_BT}s(s+1)\right]\sinh\left[\frac{2s+1}{2s}\xi_P\right]}\,, \tag{6}$$

where $\xi_P=sg_M\mu_BH/k_BT$ and $S_{\max}=2S$. This equation for M_P is essentially the same as that given by Bastard and Lewiner.[4]

The magnetization is given in emu/g, S is $\frac{5}{2}$ for Mn and $\frac{7}{2}$ for Gd, g_M $(=2)$ is the g factor of the magnetic ion, μ_B is the Bohr magneton, N_0 is the number of cation sites per gram, k_B is the Boltzmann constant, and T is the temperature.

The two fitting parameters, T_0 and $\bar{x}_1$, represent an exchange interaction and the effective occupation of a cation site by an isolated Mn^{2+} ion, respectively. If M_P is omitted, T_0 represents primarily pair-exchange interactions. The diamagnetic susceptibility, χ_0, is about -3×10^{-7} emu/g for PbTe and -3.6×10^{-7} emu/g for PbSe at temperatures greater than 10 K.[5] Although χ_0 decreased somewhat in magnitude at lower temperatures, we used the values given above for our fits. The two fitting parameters in M_P are $\bar{x}_2$, representing the effective number of Mn^{2+} ions in pairs, and J_P, representing the pair exchange.

The term M_P gives steps or plateaus at magnetic fields $H_i=2iJ_P/g_M\mu_B$, $i=1,2,\ldots,S_{\max}$, but the steps should be visible only for $J_P>k_BT$. Since in our sample-extraction experiments $J_P<k_BT$, we do not expect the steps to be apparent in the data. If, however, one looks carefully at some of the most noise-free data, for example, $\mathrm{Pb}_{0.93}\mathrm{Gd}_{0.07}\mathrm{Te}$ (Fig. 1), there appears to be some structure at roughly 6 T. Although it is possible that this structure is related to the last plateau in the pair function, the fact that $J_P<k_BT$ would make observation of this step unlikely. We should also mention that, in $\mathrm{Pb}_{1-x-y}\mathrm{Sn}_y\mathrm{Mn}_x\mathrm{Se}$, a small, rather abrupt increase in the measured magnetization appears between 15 and 17 T. The shift is too small to be evident to the eye in Fig. 4 and may be only an artifact of the method of sweeping the magnetic field. This effect will be examined more carefully during future measurements.

The pair function in the limit in which $J_P/k_BT\ll1$ is a Brillouin function and therefore is identical in form to the first term in Eq. (1) with $T_0=0$. Consequently, obtaining the pair contribution directly by including the second term in Eq. (1) is difficult, unless the measurements are carried out at magnetic fields high enough and temperatures low enough that the magnetization nearly saturates. Since this is the case for most of our data, we have fixed T_0 at zero and carried out three-parameter fits to the data, by allowing only $\bar{x}_1$, J_P, and $\bar{x}_2$ to vary.

In order to exhibit the improvement obtained by including the second term in Eq. (1), we show in Fig. 5, on an expanded scale, magnetization data for $\mathrm{Pb}_{1-x-y}\mathrm{Sn}_y\mathrm{Mn}_x\mathrm{Se}$ with $x=0.007$ and $y=0.02$. These data have been fitted to the modified Brillouin function plus a diamagnetic term, using two fitting parameters $\bar{x}_1$ and T_0, and to the full Eq. (1) with $T_0=0$ and three fitting parameters $\bar{x}_1$, $\bar{x}_2$, and J_P/k_B. At fields below 5 T, both fits seem to be equally good; however, at fields above 7 T the expression taking pairs directly into account fits the experimental data noticeably better than

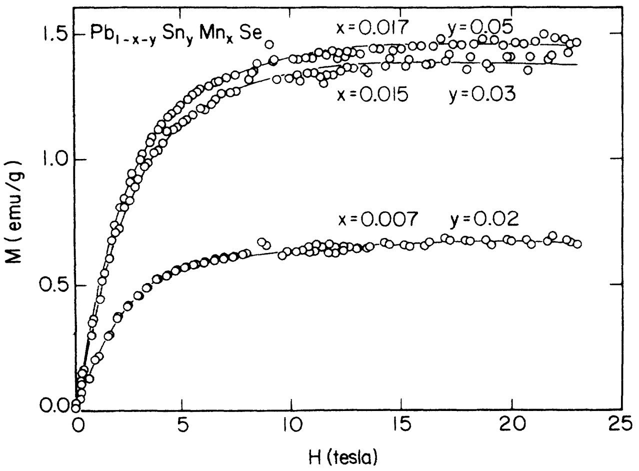

FIG. 4. Magnetization of $\mathrm{Pb}_{1-x-y}\mathrm{Sn}_y\mathrm{Mn}_x\mathrm{Se}$ at 4.2 K. The circles represent the data and the solid lines were obtained from three-parameter fits (see Table I).

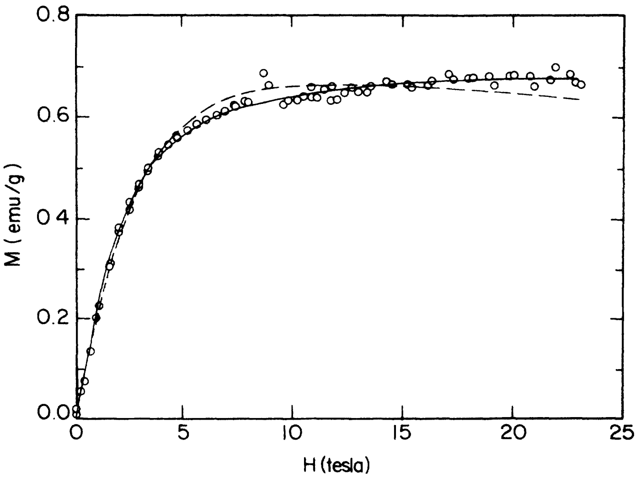

FIG. 5. Comparison of fit using the modified Brillouin function alone (dashed line) with that in which the pair-interaction function is included explicitly (solid line). The data are for $\mathrm{Pb}_{0.973}\mathrm{Sn}_{0.02}\mathrm{Mn}_{0.007}\mathrm{Se}$ and the fits were carried out to 23 T.

the modified Brillouin function. Although steps are not apparent in the data, there is a positive slope in the magnetization in the high-field region which is described well when the pair-interaction function is included. The two-parameter, modified-Brillouin-function fit saturates too soon and then declines due to the negative diamagnetic contribution of the host lattice. Similar results were observed in all the IV-VI systems that we investigated. Therefore, we see that even when the steps are not explicitly visible, the pair-exchange interaction has a strong influence on the magnetization of IV-VI-compound DMS materials and should be taken directly into account. The indirect approach, i.e., inclusion as T_0 in the modified Brillouin function, is reasonably good at fields below 5 T, but not adequate for description of the magnetization up to high magnetic fields.

A summary of the fitting parameters for the samples investigated in given in Table I. For comparison, all parameter values presented in Table I were obtained from fits carried out to 15 T. However, in samples in which experimental data at fields above 15 T were available, we also calculated fits up to higher fields. The results are shown as solid lines in Figs. 1–4. The errors, estimated from the scatter in the experimental data and from the uncertainties in the fitting, are ±20% for $\bar{x}_1$, ±25%, for T_0, ±30% for J_P/k_B, and ±30% for $\bar{x}_2$. From the modified-Brillouin-function fits only [the first and third terms in Eq. (1)] we obtain values of T_0 that are in reasonable agreement with the results from the low-temperature susceptibility measurements. In all fits the values of χ_0 are fixed as described above. The other parameters are quite insensitive to the values chosen for χ_0. The values of $\bar{x}_1$ from the two-parameter fit are, within experimental error, equal to or less than x as expected, since x is small.

We look at the values of J_P/k_B obtained from the three-parameter fits. Since T_0 has been set equal to zero, J_P/k_B should represent the pair contribution to the exchange. Taking into account the large uncertainties in the fitting parameters, we assume J_P/k_B is independent of x and take the average for each different system. Then we see that J_P/k_B for the system containing the rare-earth ion is less than $\frac{1}{2}$ of the values for the Mn-containing systems. In addition, we note that the value for $\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ is approximately the same as that for the quaternary, $\mathrm{Pb}_{1-y-x}\mathrm{Sn}_y\mathrm{Mn}_x\mathrm{Se}$, and is larger than the value for $\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Te}$. The trends noted here for J_P/k_B agree with results from high-temperature susceptibility measurements.[1]

In Table I we also show the parameters from the three-parameter fit, $\bar{x}_1$ and $\bar{x}_2$, which, in principle, represent the number of individual Mn^{2+} ions and the number of Mn^{2+} ions in pairs, respectively. We do not consider the values of $\bar{x}_1$ and $\bar{x}_2$ very reliable because these two parameters may be strongly correlated. Therefore, the sum, $\bar{x}_1+\bar{x}_2$, sometimes is greater than x, although it lies within the experimental uncertainty of x. Moreover, it is not possible to correlate the ratio $\bar{x}_2/\bar{x}_1$ with the ratio of probabilities of pairs to singles in order to compare with a random distribution of magnetic ions. In spite of this, the variation of this ratio with x follows the trend expected for a random distribution.

For data that were sufficiently noise-free and a maximum field sufficiently high, we were able to allow T_0 to vary and obtain fits with all four parameters, $\bar{x}_1$, T_0, J_P/k_B, and $\bar{x}_2$. In this case T_0 should represent the contribution to exchange from clusters other than pairs. The resulting parameters were compatible with three-parameters fits and the exchange estimated from T_0 from the four-parameter fit was considerably smaller than J_P/k_B.

IV. CONCLUSIONS

Fits with the modified Brillouin function alone, two-parameter fits using only M_S in Eq. (1), were significantly poorer than fits that included the pair term M_P. This shows the strong influence of pairs in the exchange for our low-concentration DMS alloys. The values of J_P/k_B are largest for $\mathrm{Pb}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ and smallest for $\mathrm{Pb}_{1-x}\mathrm{Gd}_x\mathrm{Te}$, in agreement with the results for the Curie-Weiss parameter Θ from the high-temperature susceptibility. We expect the exchange interaction to be smaller in DMS systems containing rare-earth ions, since the magnetic properties of rare-earth ions depend on their f-shell electrons, which are shielded and bound more closely to the nucleus than the d-shell electrons in Mn. We have found that reliable three- and four-parameter fits can be obtained only if the maximum field is high enough that saturation is nearly attained. This was especially apparent when we studied II-VI-compound DMS systems, which have an exchange interaction at least 10 times that for IV-VI-compound DMS materials. For example, we were not even able to obtain good three-parameter fits for $\mathrm{Hg}_{0.9}\mathrm{Mn}_{0.1}\mathrm{Te}$ with fields limited to a maximum of 24 T.[6]

The temperature was too high in our steady-field experiments to observe explicitly steps in the magnetization caused by nearest-neighbor Mn pairs. Some pulsed-field measurements at 1.5 K at fields up to 45 T are in progress in order to search for steps. If there is, however, a long-range contribution to the exchange, such as that predicted by de Jonge *et al.*,[7] the steps might not be explicitly apparent even at low temperatures.

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