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Magnetic properties of $Pb_{1-x}Eu_xTe$ grown by molecular-beam epitaxy

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We have measured the magnetization and magnetic susceptibility of molecular-beam-epitaxy grown $Pb_{1-x}Eu_xTe$ with $x = 0.042$, 0.096, 0.316, and 1.00, in the temperature range $2\text{ K} < T < 300$ K and for fields $0 < H < 4$ T. The magnetic susceptibility follows a Curie-Weiss behavior: $\chi \sim N_{\text{Eu}}/(T-\Theta)$. For all the concentrations studied, Θ is negative indicating that the Eu-Eu interaction is predominantly antiferromagnetic. However, the absolute values of Θ are 1 or 2 orders of magnitude smaller than those observed in (II,M_n)-VI diluted magnetic semiconductors. The magnetization can be described by a modified Brillouin function: $M \sim N^*_{\text{Eu}} B[(T-T_0)^{-1}]$ in which, for each sample, the number of Eu atoms N^*_{Eu} and the parameter T_0 are nearly the same as N_{Eu} and Θ respectively, obtained from the susceptibility measurement. The results of the present study indicate that Eu-Eu exchange effects in $Pb_{1-x}Eu_xTe$ are much weaker than Mn-Mn interactions in (II,M_n)-VI compounds.

INTRODUCTION

Diluted magnetic semiconductors (DMS's) are usually II-VI semiconducting compounds such as CdTe and ZnSe in which a fraction of the metallic ions (Cd,Zn) are replaced by transition-metal magnetic ions, commonly Mn.[1] $Pb_{1-x}Eu_xTe$ has a structure analogous to that of the DMS's in which Pb atoms are replaced by magnetic Eu ions. Thus it could be expected that this material would show magnetic, magneto-optic and magnetotransport phenomena similar to those exhibited by the conventional DMS's. However, there are some differences between PbEuTe and the traditional DMS's. While the latter materials usually crystallize in the zinc-blende structure, PbEuTe has the rocksalt structure. This difference in crystalline structure implies, in turn, differences in bonding characteristics and in the energy-band structure. In the (II,Mn)-VI compounds, the Mn $3d$ electrons, which give rise to the magnetic moments responsible for the unique properties of DMS's, are less localized than the analogous $4f$ electrons of Eu. The Eu $4f$ electrons are, therefore, less likely to interact with neighboring atoms. Whether these structural differences influence the physical properties of PbEuTe, making PbEuTe different from the traditional DMS's, could be of fundamental importance in the understanding of the physical properties of DMS's.

Some studies of the magnetic, magneto-optical, and magnetotransport properties of PbMnTe (Refs. 2–5) and PbMnSe (Ref. 6) have previously been made. These Mn-Pb chalcogenide compounds, which also crystallize in the rocksalt structure, indeed exhibit semimagnetic properties but the magnetic exchange interactions which give rise to these effects are also much weaker than in the case of the (II,Mn)-VI alloys. In an investigation of the magnetic susceptibility in very dilute $Pb_{1-x}Eu_xTe$ samples ($0.001 < x < 0.018$), Andrianov *et al.*[7] found rather large values of the Curie-Weiss temperature (i.e., $\Theta = \sim 20$ K for $x \simeq 0.01$) which would indicate a strong exchange interaction between Eu atoms. Different conclusions were drawn by Goltsos *et al.*[8] who performed optical and magneto-optical measurements on (MBE) molecular-beam-epitaxy-grown PbEuTe epilayers, similar to those used in the present study. These authors conclude that Eu-ion spin-exchange effects are rather weak in this material.

In this communication we present magnetization and magnetic susceptibility measurements on $Pb_{1-x}Eu_xTe$ epilayers grown by MBE with $x = 0.042$, 0.096, 0.316, and 1. Our results indicate that the magnetic exchange interactions in PbEuTe are much weaker than in the (II,Mn)-VI DMS's, in agreement with Ref. 8.

EXPERIMENTAL RESULTS

Single crystals of $Pb_{1-x}Eu_xTe$, having large Eu concentrations x, could not be achieved by conventional growth methods. The use of the technique of molecular-beam epitaxy to grow the samples has made possible the synthesis of large defect-free single-crystal epilayers, whose Eu concentrations span the entire range $0 \le x \le 1$. Details of the growth and characterization of the films can be found in Ref. 9.

The samples used in the present study were grown by molecular-beam epitaxy on $\langle 111 \rangle$ oriented BaF_2 substrates.[9] The thickness of the films was varied from 0.8 to 30 μm in such a way that each sample contains the same total number of magnetic ions per unit area, $\sim 10^{17}$ cm^{-2} Eu atoms. Because of nonstoichiometric growth, the films are lightly p-type with room-temperature carrier concentrations of $\simeq 10^{17}$ cm^{-3}. The dc magnetic susceptibility and magnetization measurements were carried out in the temperature range 2 K $< T <$ 300 K and for fields $0 < H < 4$ T using a S.H.E. Corporation SQUID (superconducting quantum interference device) magnetometer at the F. Bitter National Magnet Laboratory.

To evaluate the diamagnetic contributions to the measured susceptibilities, arising from the lattice and from the BaF$_2$ substrate (which is considerably thicker than the films), we measured the magnetic susceptibility of a sample of PbTe grown by MBE in the same way as the PbEuTe samples. We found almost no temperature dependence in the susceptibility of the PbTe samples. We therefore analyzed our data assuming two contributions to the magnetic susceptibility χ, a constant term χ_d which takes into account all diamagnetic effects (film and substrate) and a Curie-Weiss term due to the Eu spins. Then

$$\chi = \chi_d + C/(T - \Theta) , \tag{1}$$

where C is the Curie constant

$$C = N_{\mathrm{Eu}} g^2 \mu_B^2 S(S+1)/3k_B . \tag{2}$$

N_{Eu} is the density of Eu atoms, Θ is the Curie-Weiss temperature, $g=2$, and $S=\frac{7}{2}$, while χ_d, C, and Θ were used as parameters in a least-squares fitting of the experimental data.

Figure 1 shows the temperature dependence of the susceptibility χ (open circles) and inverse susceptibility $1/(\chi-\chi_d)$ (dots) of the MBE-grown EuTe sample ($x=1.00$). The peak in the susceptibility at 10.5 K corresponds to the transition to an antiferromagnetic phase below T_N, previously observed in bulk material, although in the latter case $T_N = 9.6$ K.[10] Extrapolation of the linear part of the inverse susceptibility, to the negative temperature axis gives a Curie-Weiss temperature of $\Theta = -4.0 \pm 0.5$ K, in good agreement with the value reported for bulk EuTe where $\Theta = -4.0$ K.[10] The small change in T_N could be due to strain induced in these epilayers by the small lattice mismatch with the BaF$_2$ substrate.

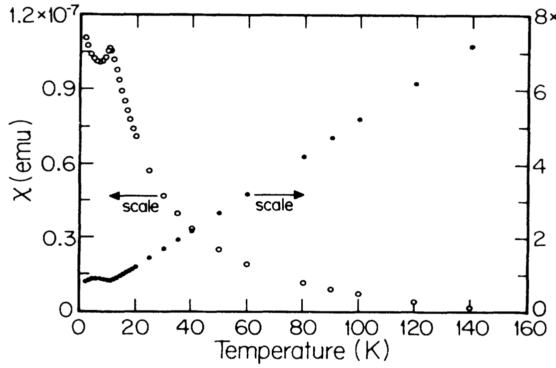

FIG. 1. Magnetic susceptibility (○, open circles) and inverse susceptibility (●, dots), corrected for diamagnetic contributions, for a sample of EuTe grown by MBE on a BaF$_2$ substrate. The cusp in χ and the discontinuity in the slope of $1/(\chi-\chi_d)$ correspond to the transition to an antiferromagnetic phase previously observed in bulk EuTe (Ref. 10).

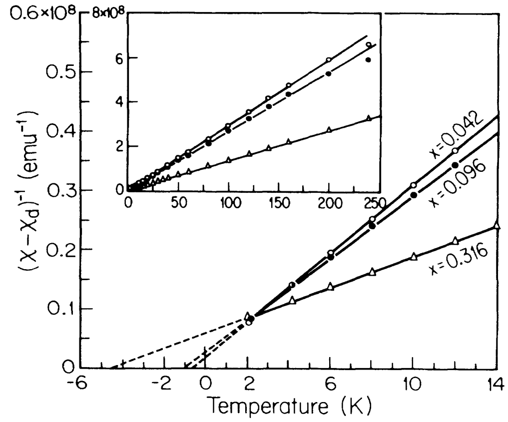

FIG. 2. Inverse susceptibilities (corrected for diamagnetic contributions) for the samples of Pb$_{1-x}$Eu$_x$Te, grown by MBE, with $x=0.042$, 0.096, and 0.316, extrapolated to the negative temperature axis. The solid curves are fittings to the experimental data using Eq. (1). The inset shows the inverse susceptibilities in the temperature range 2 K $< T <$ 250 K.

The inverse susceptibilities, corrected for the diamagnetic component, are presented in Fig. 2 for the samples of Pb$_{1-x}$Eu$_x$Te with $x=0.042$, 0.096, and 0.316, along with their fittings based on Eq. (1). As seen in the inset to Fig. 2, the Curie-Weiss law is obeyed by all three samples from 2 to 200 K. Above about 220 K the signal was too weak to produce accurate results and this is probably the cause of the deviations from the straight-line dependence observed above 200 K. The extrapolations of these straight lines intersect the negative temperature axis, indicating that the exchange interaction between the Eu ions in PbEuTe is predominantly antiferromagnetic. The absolute value of the Curie-Weiss temperature, for each concentration x, is much smaller than the corresponding temperature observed in the (II,Mn)-IV DMS's for the same

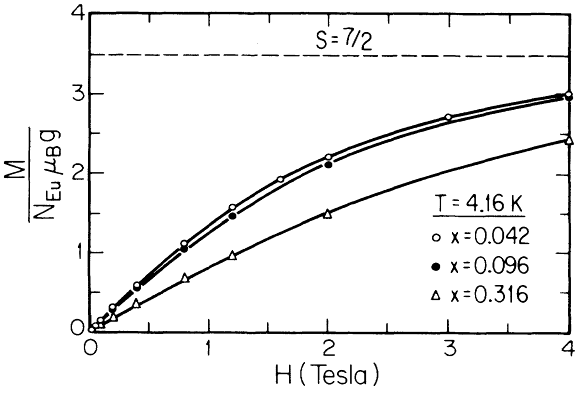

FIG. 3. Magnetization versus field curves for MBE-grown Pb$_{1-x}$Eu$_x$Te with $x=0.042$, 0.096, and 0.316, measured at 4.16 K. The solid curves are fittings to the experimental data using the modified Brillouin function described in Eqs. (3) and (4). Note that N_{Eu} in the ordinate refers to N_{Eu}^{*} in the text.

TABLE I. Results of the fits to the magnetic susceptibility and magnetization measurements for the $Pb_{1-x}Eu_xTe$ epilayers grown by MBE.

x	Density Eu atoms[a] (cm^{-3}) (±5%)	N_{Eu}[b] (cm^{-3}) (±5%)	N^*_{Eu}[c] (cm^{-3}) (±5%)	Θ[b] (K) (±10%)	T_0^b (K) (±10%)
0.042	6.19×10^{20}	5.44×10^{20}	5.27×10^{20}	−0.6	−0.7
0.096	1.40×10^{21}	1.12×10^{21}	1.08×10^{21}	−1.0	−1.1
0.316	4.54×10^{21}	4.66×10^{21}	4.16×10^{21}	−4.6	−4.2
1.0	1.40×10^{22}	1.43×10^{22}		−4.0±0.5	

[a] From weight and dimensions.

[b] From susceptibility measurements [using Eqs. (1) and (2)].

[c] From magnetization measurements [using Eqs. (3) and (4)].

x. The values of Θ and N_{Eu} deduced from the fitting to Eq. (1) are summarized in Table I.

The results of the magnetization studies are shown in Fig. 3, in which the points represent the experimental data and the solid curves are the results of least-squares fittings. To fit the experimental data it was necessary to use a modified Brillouin function much in the same way as is done in the traditional DMS's,[1] expressing the magnetization as

$$M = N^*_{Eu} g\mu_B S B_S(y) , \tag{3}$$

with

$$y = (g\mu_B/k_B)\frac{H}{(T-T_0)} , \tag{4}$$

where N^*_{Eu} is the density of Eu atoms and T_0 is a phenomenological parameter arising from the Eu-Eu antiferromagnetic interactions. N^*_{Eu} and T_0 were used as fitting parameters to yield the solid curves in Fig. 3, and their values, for each Eu fractional concentration, are summarized in Table I.

DISCUSSION

Table I shows that for each sample the density of Eu atoms N^*_{Eu} and the parameter T_0 obtained from the magnetization measurements are nearly the same as N_{Eu} and Θ, respectively, obtained from susceptibility measurements. A similar result was reported also for $Pb_{1-x}Mn_xTe$.[2] The densities of Eu atoms deduced from the magnetic measurements are slightly smaller than the densities of Eu atoms deduced from the reported compositions and measured weights. This difference could be due to inaccuracy in the determination of the stoichiometric composition. Clustering effects are probably not responsible for the apparent reduction in the density of isolated Eu ions because of the relatively high temperatures used in the present study and the very weak exchange interactions we observe.

The Curie-Weiss temperatures are plotted as a function of composition in Fig. 4. For low Eu concentrations ($x < 0.4$) we observe a monotonic increase in the negative magnitude of Θ with increasing concentration; this increase in Θ would extrapolate to a value of $\Theta = -15$ K for EuTe, larger by about a factor of 4 than the experimentally determined $\Theta_{EuTe} = -4.0 \pm 0.5$ K. But when we compare the values of Θ measured on PbEuTe with the values of Θ reported for (II,Mn)-VI DMS's (Ref. 11) having similar concentrations of magnetic ions, we find that the Curie-Weiss temperatures in the traditional DMS's are one or two orders of magnitude larger than in the Eu-lead chalcogenides alloys. This behavior indicates that the Eu-Eu exchange effects influence the magnetic properties of PbEuTe but the strength of this interaction is much smaller than in the (II,Mn)-VI DMS's. We also observe in Fig. 4 that the Curie-Weiss temperatures reported for PbMnTe samples, in Ref. 2, follow nearly the same Θ versus concentration dependence as the PbEuTe samples measured in the present study, indicating that the Mn-Mn exchange interaction in PbMnTe is of similar strength as the Eu-Eu interaction in PbEuTe.

We can only suggest a qualitative explanation for the observed relative magnitude of the exchange interactions. There is increasing evidence that the large exchange interaction between pairs of Mn ions and between the Mn d and the band electrons in the (II,Mn)-VI DMS's is strongly correlated with a large $3d$-$5p$ hybridization due to the near degeneracy of the Mn $3d$ and Te $5p$ atomic levels observed in these compounds.[12–14] Such a strong hybridization is not likely to occur in PbEuTe, in which, by analogy to the present model for the electronic structure of EuTe,[10] the Eu $4f$ electron states are expected to be highly

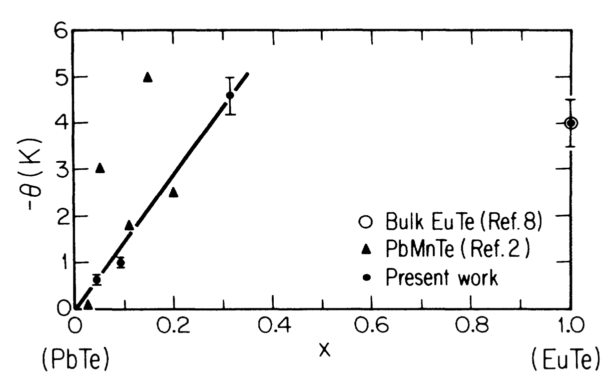

FIG. 4. Curie-Weiss temperature Θ as a function of concentration x, in MBE-grown $Pb_{1-x}Eu_xTe$. Curie-Weiss temperatures for bulk EuTe (Ref. 10) (○, open circle) and for $Pb_{1-x}Mn_xTe$ (Ref. 12) (Δ, triangles) are also shown for comparison. The solid line is a guide to the eye.

localized and not mixed with the Te *p* states. Consequently, exchange effects are expected to be weak in the Eu-lead chalcogenides. The experimental results reported in Ref. 2 suggest that the admixture of Mn *d* states and Te *p* states in PbMnTe is also small. This could be attributed to the rather complicated band structure of this compound where the direct band gap occurs at the *L* points of the Brillouin zone and secondary maxima of the same valence band are located along the Σ axis, and the relative positions of the two valence-band maxima depend on temperature and Mn concentration. Further studies would be very desirable to understand the bonding characteristics of Eu and Mn in the lead chalcogenides and their relation to the magnetic exchange effects.

In summary, we have studied the magnetic properties of epilayers of $Pb_{1-x}Eu_xTe$ grown by MBE. For all the concentrations studied ($x=0.042$, 0.096, 0.316, and 1.00), the Eu-Eu interaction is predominantly antiferromagnetic. Eu-Eu exchange effects in PbEuTe are found to be much weaker than the Mn-Mn interaction in (II,Mn)-VI DMS's. This difference is attributed to the strong localization of the Eu $4f$ electrons in PbEuTe, in contrast to the large admixture with anion *p* levels and inherent delocalization of the Mn *d* levels in the (II,Mn)-VI compounds.

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[1] J. K. Furdyna, J. Appl. Phys. **53**, 7637 (1982).
[2] M. Escorne, A. Mauger, J. L. Tholence, and R. Triboulet, Phys. Rev. B **29**, 6306 (1984).
[3] H. Pasher, E. J. Fantner, G. Bauer, W. Zawadzki, and M. V. Ortenberg, Solid State Commun. **48**, 461 (1983).
[4] J. R. Anderson and M. Gorska, Solid State Commun. **52**, 601 (1984).
[5] M. Bartkowski, A. H. Reddoch, D. F. Williams, G. Lamarche, and Z. Korczak, Solid State Commun. **57**, 185 (1986).
[6] G. Karczewski and L. Kowalczyk, Solid State Commun. **48**, 653 (1983).
[7] D. G. Andrianov, S. A. Belokon, A. A. Burdakin, V. M. Lakeenkov, and S. M. Yakubenya, Fiz. Tekh. Poluprovodn. **19**, 1257 (1985) [Sov. Phys.—Semicond. **19**, 770 (1985)].
[8] W. C. Goltsos, A. V. Nurmikko, and D. L. Partin, Bull. Am. Phys. Soc. **31**, 251 (1986).
[9] D. L. Partin, J. Elec. Mater. **13**, 493 (1984).
[10] E. G. P. Wachter, Crit. Rev. Solid State Sci. **3**, 189 (1972).
[11] S. B. Oseroff, Phys. Rev. B **25**, 6584 (1982).
[12] B. E. Larson, K. C. Hass, H. Ehrenreich, and A. E. Carlsson, Solid State Commun. **56**, 347 (1985).
[13] M. Taniguchi, L. Ley, R. L. Johnson, J. Ghijsen, and M. Cardona, Phys. Rev. B **33**, 1206 (1986).
[14] J. Spalek, A. Lewicki, Z. Tarnawski, J. K. Furdyna, R. R. Galazka, and Z. Obuszko, Phys. Rev. B **33**, 3407 (1986).