Concentration dependence of the exchange interaction in Pb$_{1-x}$Eu$_x$Te

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From low-field measurements of the susceptibility at temperatures up to 385 K, fitted to the Curie-Weiss expression, the exchange constant J/k_B of Pb$_{1-x}$Eu$_x$Te has been obtained for different values of x. It has been observed that J/k_B decreases with increasing x. Reasons for this decrease are proposed. Measurements of the low-temperature magnetization at fields up to 23 T yield a value of the pair exchange constant J_p/k_B, which is somewhat larger than the values from the susceptibility measurements and is nearly independent of x. This result seems to be due to the clustering of Eu atoms. [S0163-1829(97)08807-3]

I. INTRODUCTION

There have been a few studies of the exchange in IV-VI chalcogenides doped with rare-earth atoms, Eu and Gd, which indicate that the nearest-neighbor exchange interaction is small.[1–4] However, there have been no systematic investigations with sufficient precision to determine whether there is a dependence upon the concentration of the rare-earth ions.

Our previous experiments on high-temperature susceptibility of Pb$_{1-x}$Eu$_x$Te for $x=0.03$ and 0.06 indicated a small antiferromagnetic nearest-neighbor interaction J/k_B of about -0.3 K, which was assumed consistent, within experimental uncertainty, with our high-field, low-temperature results for the pair exchange ($J_p/k_B \sim -0.5$ K).[1] (Here k_B is Boltzmann's constant.) At the same time we noted smaller values of J/k_B, -0.116 K presented by Braunstein *et al.*[2] for a thin film with $x=0.32$ and a positive value, $+0.043$, given by Wachter[3] for EuTe ($x=1$). We did not attempt to compare these values with our results except to note that the samples were quite different from ours. Our new measurements for $x=0.1$ appear to be consistent with all the measurements if one assumes that the nearest-neighbor exchange interaction decreases with increasing x.

II. EXPERIMENT

The diluted magnetic semiconductor (DMS) samples of Pb$_{1-x}$Eu$_x$Te were prepared by the Bridgman technique and the Eu concentration was measured by energy-dispersive x-ray analysis (EDAX) and estimated from the amounts of the components introduced into the growth chamber. The uncertainty in the x values is about 20%. The crystals were cut in the shape of Hall bars with typical dimensions 1.5 $\times 2 \times 6$ mm^3. The samples with $x=0.03$ and 0.06 were p type with carrier concentrations, from Hall measurements, of about 1×10^{18} cm^{-3}, but for $x=0.1$ the sample was n type with a concentration of about 5×10^{17} cm^{-3}. With increasing x, the hole concentration decreased and the mobility increased.

The susceptibility measurements at fields H up to 0.1 T and temperatures T from about 4 K to a maximum of 385 K ($x=0.1$) were carried out in a SQUID magnetometer system. Results for $x=0.03$ and 0.06 were reported previously.[1] The susceptibility at each temperature was determined from a least-squares fit to the magnetization at three or more magnetic fields. During measurement at each fixed temperature, the temperature varied by less than 0.02 K for $T<30$ K and by less than 0.1 K for $T>30$ K. The magnetization at fields up to 5.5 T was measured in the same SQUID system.
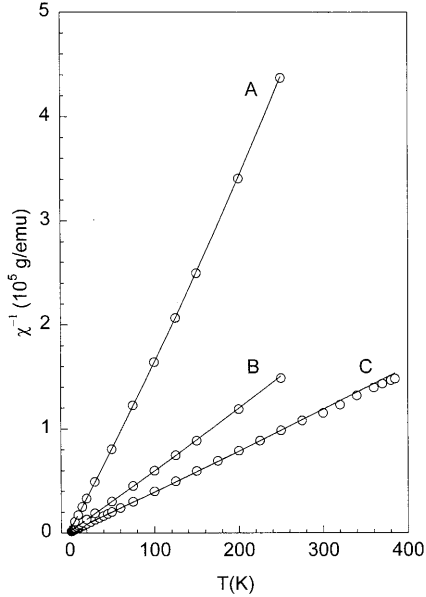
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FIG. 1. Inverse susceptibility vs temperature. A: $x=0.03$; B: $x=0.06$; C: $x=0.1$. The open circles represent the data and the solid lines were obtained from fits to the Curie-Weiss law, Eq. (1).

High-field magnetization experiments were carried out by the sample extraction method at the High-Field Laboratory for Superconducting Materials of Tohoku University. Fields up to 23 T, produced by hybrid magnets consisting of an outer superconducting magnet and an inner water-cooled polyhelix copper magnet, were used in these studies. The magnetic field was accurate to 2% and the uncertainty in the magnetization was about 3%.

III. RESULTS

Figure 1 shows the inverse susceptibility χ^{-1} versus T for three samples of $Pb_{1-x}Eu_xTe$: $A-x=0.03$; $B-x=0.06$; and $C-x=0.1$. One can see that χ^{-1} varies almost linearly with temperature and χ is larger for larger x as expected. The data above 20 K have been fitted to a Curie-Weiss expression of the form

$$\chi=P_1/(T+\theta)+\chi_0, \tag{1}$$

where P_1 and θ are fitting parameters. The parameter P_1 represents the effective number of magnetic ion spins, x_{av}, where

$$x_{av}=(m_A+m_B)/\{S(S+1)(g_{Eu}\mu_B)^2N_A/(3k_BP_1)$$

$$+m_A-m_{Eu}\}. \tag{2}$$

Here m_A, m_B, and m_{Eu} are the atomic masses of the cation, anion, and Eu, respectively, N_A is Avagadro's number, μ_B is the Bohr magneton, and g_{Eu} is the Eu g factor, assumed to be 2.0, S is the spin of the Eu ($S=7/2$ for Eu^{2+}).

The quantity θ represents the Curie-Weiss temperature. Since our experimental results show that $\theta \ll T$, we can use θ to estimate the exchange interaction, which we have assumed to be the nearest-neighbor exchange, from the relation

$$J/k_B=-\frac{3\theta}{2x_{av}S(S+1)z}, \tag{3}$$

TABLE I. $Pb_{1-x}Eu_xTe$ susceptibility parameters.

x	x_{av}	θ	J/k_B (Expt) (K)	J/k_B (Calc)[a] (K)
0.03	0.027	1.30	−0.38	−0.38[b]
0.06	0.073	2.48	−0.27	−0.33
0.10	0.110	2.69	−0.19	−0.27
0.32[c]	0.316	4.60	−0.116	−0.19
1.00[d]	1.0	4.00	+0.043	

[a]Equation (13).
[b]Fitted at this value.
[c]Reference 2.
[d]Reference 3.

where z is the number of nearest-neighbor cation sites, 12 for the NaCl structure.[5] The nearest cations to the cation site $(0,0,0)$ lie at $\{0.5,0.5,0\}$ sites, i.e., on the faces of the cation face centered cubic lattice. The angle between the two cation-anion bonds is 90° and the cation-cation separation is $a/\sqrt{2}$, where a is the lattice constant. There are six next-nearest-neighbor cations with the same cation-anion separation, but the bond angle is 180° instead of 90°, and the cation-cation separation is a. We have shown previously that a semiquantitative description of the exchange interaction can be obtained by taking into account only the cation-anion separation, which is the same for nearest-neighbor and next-nearest-neighbor cations in the NaCl structure.[4] Therefore, although we have taken z as 12 in estimating the exchange, 18 is also a possible choice. For our purpose, where we are comparing the same system, changing only the x value, this difference in z is not very important.

The susceptibility χ_0 is the diamagnetic susceptibility of the host lattice, -3×10^{-7} emu/g from our previous studies of PbTe.[6]

In Table I the values of the exchange, estimated from χ, and the values of x_{av} are presented for our $Pb_{1-x}Eu_xTe$ samples along with the results given by Braunstein et al.[2]
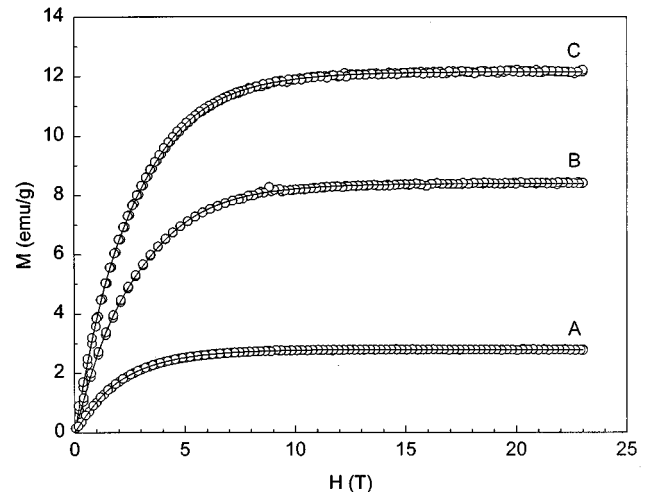

FIG. 2. High-field magnetization vs magnetic field at 4.2 K. A: $x=0.03$; B: $x=0.06$; C: $x=0.1$. The open circles represent the data and the solid lines are obtained from fits to Eq. (4).

and Wachter[3] for larger values of x. We observe in Table I that J/k_B is negative, its magnitude decreasing with increasing x, and is actually ferromagnetic (positive) for EuTe. (It is claimed that the next-nearest-neighbor interaction, which is antiferromagnetic, is dominant in EuTe.[3,7]) This decrease in exchange now seems to be a real effect, which we will discuss in Sec. IV.

In Fig. 2 the high-field magnetization M versus field H is presented for the same three samples. The saturation value of M is larger for larger values of x as anticipated. Field values were high enough that clear saturation was obtained for all the samples and therefore we were able to fit the data to an expression containing explicitly the magnetization for isolated ions M_s and pairs M_p.[8,9] For completeness we repeat this expression below:

$$M = M_s + M_p + \chi_0 H, \tag{4}$$

where

$$M_s = M_0 S x_1 B_s(\zeta), \tag{5}$$

$$M_0 = g_{\mathrm{Eu}} \mu_B N_0, \tag{6}$$

and $B_s(\zeta)$ is the modified Brillouin function:

$$B_s(\zeta) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S}\zeta\right) - \frac{1}{2S}\coth\left(\frac{\zeta}{2S}\right) \tag{7}$$

where

$$\zeta = \frac{S g_{\mathrm{Eu}} \mu_B H}{k_B(T+T_0)}. \tag{8}$$

The pair exchange term M_p is given by

$$M_p = 0.5 M_0 x_2 \frac{\sum_{s=0}^{S_{\max}} e^{J_p s(s+1)/(k_B T)} s (\sinh\{[(2s+1)/2s]\zeta_p\}) B_s(\zeta_p)}{\sum_{s=0}^{S_{\max}} e^{J_p s(s+1)/k_B T}\sinh\{[(2s+1)/2s]\zeta_p\}}, \tag{9}$$

where

$$\zeta_p = \frac{s g_{\mathrm{Eu}} \mu_B H}{k_B T}, \tag{10}$$

and $S_{\max} = 2S$.

The diamagnetic contribution is $\chi_0 H$. For Eu we have assumed that $S = 7/2$. The parameters x_2 and J_p represent the number of paired magnetic ions and the pair exchange, respectively.

The solid lines in Fig. 2 are fits to the expression given above; it is clear that very good fits are obtained. The fitting parameters, x_2 and J_p/k_B, are given in Table II. The parameter χ_0 is the same as in Eq. (1). The sum of x_1 and x_2 agrees well with x_{av} obtained from the high-temperature susceptibility. The values of J_p/k_B, however, are somewhat larger than the values of J/k_B, from the susceptibility, and are independent of x within our experimental uncertainty.

IV. DISCUSSION

We have shown that the values of the exchange, J/k_B, decrease significantly with increasing x. Now we will discuss this result on the basis of our model of superexchange between Eu ions moderated by the anion Te.[4,5] In Ref. 4 we have shown that the f-f superexchange calculated from the

TABLE II. Magnetization parameters.

x	x_1	x_2	J_p/k_B (K)
0.03	0.019	0.0056	-0.43
0.06	0.04	0.032	-0.50
0.10	0.06	0.043	-0.48

direct interaction between Eu f and Te p levels is too small to give the measured values of the antiferromagnetic exchange interaction. Therefore, in the present work we accept the approach of Kasuya, in which the exchange takes place via an f-d exchange on the Eu ion, a d-p exchange between cations and the Te anions, followed by the f-d exchange on the other Eu cation.[10] Thus the expression for the exchange interaction J becomes

$$J = -2 V_{pd\sigma}^4 I_{fd}^2 / \Delta E^5, \tag{11}$$

where I_{fd} represents the intra-atomic f-d exchange, which we assume is independent of the change of Eu concentration, and $\Delta E = E_d - E_v$, which is the energy difference between the $5d$ levels and the top of the valence band. The quantity $V_{pd\sigma}$ represents a matrix element linking p levels of the valence band with d levels of the magnetic ion, taking into account only the σ bond.[10] (In general there could be a combination of matrix elements, $V_{pl\alpha}$, where $l = f$ or d, and α refers to either a σ or π bond.[4]) Then following Harrison's approach,[11] we express

$$V_{pf\alpha} \propto (r_p r_f^5)^{1/2}/d(x)^5, \quad V_{pd\alpha} \propto (r_p r_d^3)^{1/2}/d(x)^4, \tag{12}$$

where $d(x)$ is the cation-anion separation, which depends on x, and r_p, r_d, and r_f are the atomic radii for the p, d and f levels, respectively.

In Kasuya's model there is a dependence of J/k_B on ΔE^{-5}, instead of ΔE^{-2} as in our earlier model. We believe that, due to the energy gap variation with x, this fifth-power dependence may cause the variation of J with x in Eu-doped DMS.

We will use expressions (11) and (12) to estimate the variation in the exchange interaction with x, after making
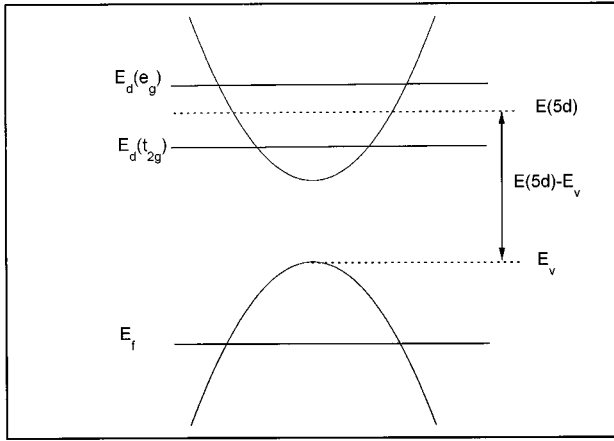
FIG. 3. Schematic (not to scale) of the energy bands in $Pb_{1-x}Eu_xTe$. E_f represents the $4f$ levels, E_v is the top of the valence band, and $E(5d)$ is the weighted average of the $5d$ levels, $E_d(t_{2g})$ and $E_d(e_g)$.

several assumptions: (1) $\Delta E = E(5d) - E_v$, where $E(5d)$ is the energy of the weighted average of the $5d$ levels of the Eu^{2+} ion and E_v is the energy of the top of the valence band; (2) the band offsets are related by $\Delta E_v(x) = \Delta E_c(x)$, where $\Delta E_v(x) + \Delta E_c(x) + E_g^0 = E_g(x)$, where E_g^0 is the band gap for $x=0$ (there seem to be no reliable values for the band offsets in the literature, but we accept the results suggested by Partin et al.[12,13]); (3) the values of $E_g(x)$, obtained from Iida et al.,[14] can be fitted to a convenient phenomenological expression, although it has no theoretical basis, of the form $E_g(x) = E_g^0 + A \tanh(\beta x)$, with $A=0.6$ and $\beta=6.0$, at least up to $x=0.35$. The energy gap increases from 0.19 eV at $x=0$ to approximately 1 eV at $x=0.32$. (4) as a consequence, $\Delta E(x) = E(5d) - [E_v(x=0) - 0.5A \tanh(\beta x)]$. The value of $\Delta E(x)$ increases with increasing x.

We also use the values given by Wachter[3] to find the energy levels in EuTe, measured from the average of the $4f$ levels, viz. $E(5d\ t_{2g}) = +2.6$ eV and $E(5d\ e_g) = +4.15$ eV. We assume that $E(5d)$ is the weighted average of the $5d\ t_{2g}$ and $5d\ e_g$, i.e., 3.22 eV, and make two additional assumptions: (5) the separation between the occupied $4f^7$ and the 5-d levels does not vary with x; (6) the occupied $4f^7$ lies approximately 1.5 eV below the top of the valence band[14] and moves up relative to the valence band with increasing x.

If we set the zero of energy as the top of the valence band for $x=0$, then we obtain the energy diagram shown in Fig. 3. At $x=0$, the lowest unoccupied d levels are situated at $E(5d\ t_{2g}) = 1.1$ eV and $E(5d\ e_g) = 2.65$ eV, with $E(4f^7) = -1.5$ eV and $E(5d) = 1.72$ eV. Using these assumptions and estimates, we express the exchange interaction as

$$\frac{J(x)}{k_B} = \frac{J(0)}{k_B} \left(\frac{d(0)}{d(x)}\right)^{16} \left(\frac{\Delta E(0)}{\Delta E(x)}\right)^5, \qquad (13)$$

with $\Delta E(x)$ given by assumption (4) above. The cation-anion separation $d(x)$ is proportional to the lattice constant, which increases from 6.462 Å for PbTe to 6.598 Å for EuTe. Even though $d(x)$ occurs to the 16th power in Eq. (13), its contribution to the variation of J/k_B with x is much smaller than that of $\Delta E(x)$.

The values of $J(x)/k_B$, adjusted to agree with the experimental results for $x=0.03$, are presented in Table I. The trend of decreasing exchange with increasing x is clearly represented by Eq. (13) and, in view of the assumptions and uncertainties in the estimates of the parameters, the model appears to be qualitatively reasonable. Therefore, we believe that the variation with x of the cation-anion distance and of the separation between the valence band and the unoccupied lowest d bands can account for a significant part of the x dependence of the exchange. This model assumes complete transfer of two electrons from Eu to Te and therefore implies ionic bonding. Perhaps partial covalent bonding could contribute to the decreasing value of the exchange with x.

Next we consider the high-field magnetization results. The parameters are shown in Table II and represent the fit to single ions, pairs, and the diamagnetic host, from Eq. (4). The temperature of measurement, 4.2 K, is too large compared to the exchange interaction to observe magnetization steps such as those reported by Bindilatti et al.[15] for $Pb_{1-x}Eu_xSe$. As we noted in Sec. III, the exchange term J_p/k_B is larger in magnitude than the value from the susceptibility and is essentially independent of x. We believe this result can be explained by the presence of clusters of ions larger than pairs, with the number of these clusters increasing with x. In our fits such larger clusters are taken into account only in a mean-field approximation with T_0, but we were unable to obtain a reliable fit with T_0 as a fitting parameter. Therefore, we fixed T_0 equal to zero.

In our fits, the exchange times the magnetic moment is treated as a unit. We cannot distinguish between the exchange of a pair, J_p, times the moment of a pair, m_p, and the exchange of a higher cluster, J_{clus}, times the moment of the cluster, m_{clus}, which is proportional to the number of ions in the cluster, n. Therefore, if we assume we are observing pairs and actually there is a contribution from clusters with $n>2$, then the exchange will appear to be larger than it actually is. The assumption that we take only pairs into account is quite good for $x<0.05$, the value corresponding to maximum pair probability, but larger clusters become important for larger values of x. We believe this is the reason that the exchange from high-field measurements is larger than the values from susceptibility for $x \geq 0.06$, at which point the influence of higher clusters becomes significant.

We have carried out some calculations fitting the high-field data to singles plus triplets (instead of pairs). The fits are just as good as for the pair fits, but the exchange J_t is much smaller. These results also confirm our conclusion that there is a significant contribution to the high-field data from clusters with $n>2$.

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