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Magnetic Specific Heat of $Pb_{1-x}Eu_xTe$

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The temperature dependence of the magnetic specific heat was studied experimentally and theoretically in the semimagnetic semiconductor $Pb_{1-x}Eu_xTe$ for $x = 0.027$ and $x = 0.073$, over the temperature range from 0.5 K to 15 K, in magnetic fields up to 2 T. In zero magnetic field at about 2 K there was a broad maximum in the magnetic specific heat, which was much higher than that predicted by the model of superexchange interaction between nearest neighbors; the maximum values increased with magnetic field. The experimental data were analyzed in the framework of a model which takes into account the spin splitting of the ground state of a single Eu^{2+} ion in the presence of local lattice distortions in the $Pb_{1-x}Eu_xTe$ mixed crystal. The model describes well the experimental data, especially for lower x-values, where the contribution from singlets dominates.

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1. Introduction

There have been a few studies of magnetic properties of IV–VI semimagnetic semiconductors (SMSC) doped with rare-earth ions such as Eu and Gd [1–3]. Magnetization and magnetic susceptibility measurements have shown that in general the rare-earth-ion doped SMSC have a much weaker exchange interaction than that found in Mn-doped II–VI SMSC or IV–VI SMSC. A more complete understanding of magnetic properties of SMSC may be reached by taking into account the results of specific heat studies together with the complementary results of magnetization and magnetic susceptibility measurements.

Up to now, no experimental data on the magnetic contribution to the specific heat of rare-earth-doped SMSC have been available. Therefore, in this work we present preliminary data on the temperature and magnetic field dependence of the magnetic specific heat of two samples of $Pb_{1-x}Eu_xTe$ with different Eu content.

2. Experiment

The $Pb_{1-x}Eu_xTe$ samples were prepared by the Bridgman technique and the Eu concentration was estimated from the amounts of the components introduced into the growth chamber and measured by the energy-dispersive X-ray analysis (EDAX). The nominal x-values were 0.03 and 0.06 with uncertainty of about 20%. The samples were p-type with carrier concentrations of about 1×10^{18} cm^{-3}, as determined from the Hall measurements. Our results concerning magnetic susceptibility and high field magnetization were reported previously [1]. By fitting the susceptibility data to the Curie–Weiss law we obtained the average Eu content in our samples and very small Curie–Weiss temperatures indicating an antiferromagnetic exchange between Eu ions, $J/k_B = -0.38$ K and –0.27 K for $x_{av} = 0.027$ and 0.073, respectively.

The heat capacity was measured in a cryostat using a ^{3}He or ^{4}He system, over the temperature range 0.5–15 K, in magnetic fields 0, 0.5, 1, and 2 T. We used the standard adiabatic heat-pulse method. The experimental details have been described elsewhere [4]. Errors in the heat capacity values were about 5%.

The magnetic contribution to the specific heat was determined by the subtraction of the PbTe lattice specific heat from the total specific heat of $Pb_{1-x}Eu_xTe$, both determined experimentally in the same system. This subtraction was only an approximation because the specific heat of PbTe is a little greater than that of $Pb_{1-x}Eu_xTe$ due to the lattice contribution. That is, the replacement of Pb with an atomic mass of 207.2 by Eu with an atomic mass of 151.97 leads to a decrease in heat capacity, even for small values of x. Therefore, we emphasize in the present work the data at temperatures below 5 K, where the lattice specific heat is much smaller than the total specific heat. In the interesting region, below 2 K, the specific heat of PbTe was more than 3 orders of magnitude smaller than that of $Pb_{1-x}Eu_xTe$.

The magnetic specific heat data for $Pb_{1-x}Eu_xTe$ are shown in Fig. 1. At zero magnetic field we see a broad maximum, several times higher than that predicted by the model of superexchange interaction between nearest neighbors (see Fig. 2). We have observed similar results in $Pb_{1-x}Mn_xTe$ [4]. However, at higher magnetic fields in $Pb_{1-x}Eu_xTe$ the value of specific heat at the maximum increased, while in $Pb_{1-x}Mn_xTe$ the maximum did not increase much in value but shifted towards higher temperatures.

3. Results and discussion

In the literature there are two approaches to the description of zero magnetic field magnetic specific heat (ZMFMSH) in SMSC. The first one takes into account the exchange interaction between two magnetic ions. This interaction may be of short [5, 6] or of long range [7]. In either case it removes the degeneracy of the ground state of the magnetic ion and results in nonzero magnetic specific heat in

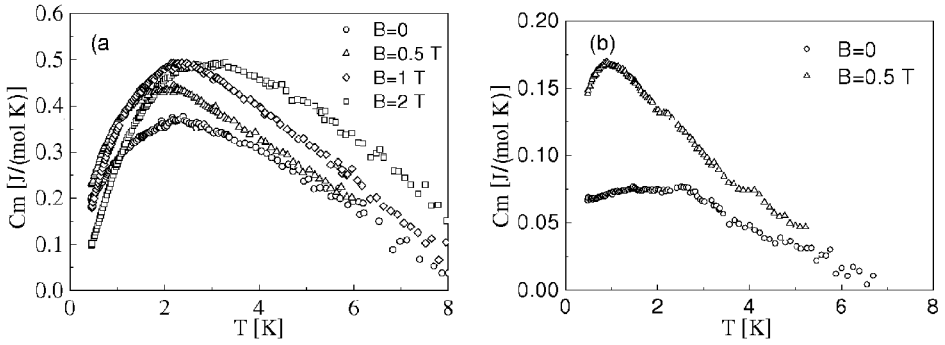

Fig. 1. Magnetic specific heat of $Pb_{1-x}Eu_xTe$ in various magnetic fields. (a) $x = 0.073$, (b) $x = 0.027$. Experimental data.

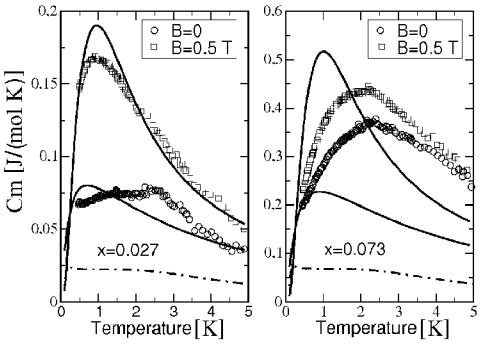

Fig. 2. Magnetic specific heat of $Pb_{1-x}Eu_xTe$. Markers — experimental data, continuous lines — theoretical predictions of our model, broken lines — calculated specific heat due to the interactions between Eu nearest neighbors.

zero external magnetic field. In the second approach the interaction between the magnetic ion and the free carriers is taken into account [4]. It also leads to nonzero ZMFMSH.

In the case of $Pb_{1-x}Eu_xTe$ both approaches fail. The exchange integrals between two Eu ions are too small to be responsible for the broad maxima observed in the experiment. Also, the exchange integrals between magnetic ions and carriers, $J_{pf} = 26$ meV, $J_{sf} = 5$ meV, are much smaller in $Pb_{1-x}Eu_xTe$ than in $Pb_{1-x}Mn_xTe$ and II–VI SMSC [8].

On the other hand, electron paramagnetic resonance (EPR) measurements [9, 10] reveal a much stronger spin lattice interaction for an Eu ion in lead chalcogenides than for an Mn ion. This is rather surprising because one would suspect that due to small interaction of $4f$ electrons (shielded by $5s$ and $5p$) with the crystal potential the effect should be the opposite. However, the ratio of the spin splittings for Eu and Mn in PbTe in a perfect octahedral environment is of an order of 10 [9, 11]. For the Mn ion, in a strained epitaxial PbTe layer grown on

a KCl substrate, the spin splitting is approximately equal to 7×10^{-2} K [12] for axial strain of the order of 0.5% [13]. That is why we expect the spin splitting of the Eu ion to be of the order of a few K since the deformations are larger.

In a series of magnetooptical experiments, Krenn et al. measured the dependence of the fundamental absorption gap energy on Eu concentration, x, in $Pb_{1-x}Eu_xTe$ [14]. From that reference we know that the transfer energy of an electron from the $4f$ level to the conduction band depends on x, and for x-values that are of interest to the present experiment is less than 0.5 eV.

Let us notice that since the conduction band wave functions in PbTe at the L point of the Brillouin zone are of odd parity, the transitions from the $4f$ level (also odd parity) are possible only if the bottom of conduction band wave functions in $Pb_{1-x}Eu_xTe$ contain an admixture of wave functions of even parity.

We assume that this admixture comes from the $5d$ level of europium. The $5d$ level is the lowest energy level above the $4f$ level and it is known that the conduction band in EuTe is built from these functions [15]; thus the local replacement of $6p$ Pb orbitals by $5d$ Eu orbitals seems plausible. In our model we replace this $5d$ level, distributed among the band states, by a single $5d$ level placed about $\epsilon_0 = 1$ eV above the $4f$ level.

There are two important ingredients in our model. First is a local deformation around Eu atom. The distances $d_{\mathrm{Eu-Te}} = 3.3$ Å and $d_{\mathrm{Pb-Te}} = 3.2$ Å are different. Random distribution of Eu ions in the crystal results in random deformations of Eu ions surroundings. Zero temperature Monte Carlo simulations performed for a lattice containing $40 \times 40 \times 40$ unit cells with atoms connected with springs enabled us to calculate, in the simple six-point charge model, the coefficients of the crystal potential $V_{\mathrm{cr}} = \sum_{lm} V_{lm} Y_l^m(\theta, \varphi)$ for each Eu atom. The crystal potential contains terms with odd l, which results in a nonzero reduced matrix element $\langle \phi_{4f} || V_{\mathrm{cr}} || \phi_{5d} \rangle$. The nonzero value of this matrix element enables $4f^7 \rightarrow 4f^6 5d^1$ virtual transitions. The second ingredient of the model is the spin–orbit coupling in the $4f^6$ configuration. We model it by a term $\lambda \boldsymbol{L} \cdot \boldsymbol{S} + \lambda_1 (\boldsymbol{L} \cdot \boldsymbol{S})^2$ with $\lambda = 0.0276$ eV and $\lambda_1 = -0.0006$ eV to describe the energy scheme of the ${}^7F_J$ multiplet of the $4f^6$ configuration [16]. In addition, we take into account an energy 10 Dq = 1 eV for the $5d_t$–$5d_e$ splitting, but the final results do not depend significantly on this value. The same is true for the $5d$–$4f$ spin–spin exchange interaction and for the spin–orbit interaction on the $5d$ shell and that is why we neglect them in our model.

In the standard second-order perturbation theory with respect to V_{cr} we obtain the effective spin Hamiltonian for the $4f^7$ configuration for an atom. Its diagonalization enables us to calculate the contribution of that atom to the magnetic specific heat.

The physical mechanism of the ground state splitting of the Eu^{2+} ion is the following [17]: first, the crystal field potential transfers an electron, let us say with spin $+1/2$, from the $4f$ level to the $5d$ state leaving an Eu atom in the $4f^6$

configuration with the z component of the spin $S^z = M - 1/2$, where M is the initial z component of the spin in the $4f^7$ configuration. The spin–orbit coupling $\lambda \boldsymbol{L} \cdot \boldsymbol{S}$ produces, with certain probability amplitudes, states with spin $S^z, S^z \pm 1$. Thus, after completion of the process, i.e. after return of the electron from the $5d$ level we find the $4f^7$ level, with certain probability amplitudes, in states $M, M \pm 1$. This leads to a splitting of the initially degenerate state.

In Fig. 2 we show some results of our model predictions. The trends for both experiment and theory are similar although the magnitudes of the peaks are different and the theoretical peak positions are at somewhat lower temperatures than are found experimentally.

In conclusion, we have measured the magnetic contribution to the specific heat of semimagnetic semiconductor $Pb_{1-x}Eu_xTe$ with $x = 0.073$ and $x = 0.027$. We have proposed a mechanism that leads to the ground state Eu^{2+} ion splitting and results in nonzero magnetic specific heat calculated in zero external magnetic field. The mechanism is a combined effect of configuration mixing $4f^7 \rightarrow 4f^6 5d^1$ and the spin–orbit coupling in $4f^6$ europium state in the presence of lattice deformations caused by a random Eu distribution. This mechanism leads to the splitting energy corresponding to a few K. The theory describes quite well the experimental results for lower Eu concentration. For higher concentration the agreement is worse. This is probably due to the fact that for larger Eu concentrations the simple spring-atom model should be replaced by a more sophisticated one. In addition, for higher Eu concentrations one expects a growing role for the $5d$ states as the band states and for Eu–Eu exchange interactions; these are not taken into account in our model.

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