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Hole density and composition dependence of ferromagnetic ordering in Pb-Sn-Mn-Te

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The influence of the concentration of charge carriers on the ferromagnetic phase transition of the semimagnetic semiconductor $Pb_{1-x-y}Sn_yMn_xTe$ for various compositions is reported. A critical density of carriers above which a ferromagnetic transition can take place, is observed. A simple modified Ruderman-Kittel-Kasuya-Yosida mechanism for semiconductors is proposed in which carriers from two valence bands located in different regions of the Brillouin zone contribute and a finite mean free path is implemented. An excellent quantitative agreement with the data is obtained.

Diluted magnetic or semimagnetic semiconductors —i.e., semiconducting alloys with substituted magnetic ions—exhibit a variety of interesting transport, magneto-optical, and magnetic properties.[1] Recently Story, Gałązka, Frankel, and Wolff[2] reported the observation of a carrier-concentration-induced ferromagnetic transition $Pb_{0.25}Sn_{0.72}Mn_{0.03}Te$ above a critical carrier concentration p_{crit}. This can be considered as a demonstration of the strong effect of carrier concentration on the magnetic properties of diluted magnetic semiconductors, resulting in a magnetic phase diagram which includes the carrier concentration as a parameter.

Application of pressure on the system in the ferromagnetic regime yielded a shift in the transition temperature (T_c) which, according to Suski, Igalson, and Story,[3] could be *qualitatively* understood on the basis of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction mechanism.[4] It was pointed out, however, that a redistribution of carriers due to the pressure dependence of the specific band structure should be taken into account. A RKKY interaction between localized moments, resulting from intraband scattering of the charge carriers by the magnetic moments, seems to be the only interaction that is strong enough and sufficiently long ranged to explain the magnitude of the observed critical temperature well above the critical carrier concentration. The abrupt change in T_c at the critical hole density p_{crit}, however, cannot be understood by the RKKY model, originally modeled for free (parabolic) electrons. In this Rapid Communication, we will present new experimental data on the phase diagram of Pb-Sn-Mn-Te. A model will be presented which explains *quantitatively* the typical carrier concentration dependence of the Curie-Weiss (CW) temperature Θ and T_c. In particular, we will show that the steplike increase of Θ at a critical hole density can be understood on the basis of the modified RKKY interaction mechanism extended with a more realistic two-valence-band approximation and a finite mean free path for the carriers. With this modification, a new extension for the applicability of the RKKY interaction in the diluted magnetic semiconductors is suggested.

$Pb_{1-x-y}Sn_yMn_xTe$ (PSMT) is a quaternary alloy with a rocksalt fcc lattice in which the Mn ions are randomly distributed. The samples were grown by a Bridgman method. The composition and homogeneity were characterized by x-ray diffraction and microprobe measurements. All investigated samples were single phased ($0.005 < x < 0.09$ and $0.47 < y < 0.72$). The carrier concentration of PSMT can be controlled by isothermal annealing in a Te- or Sn-rich atmosphere from below 10^{20} cm^{-3} to above 10^{21} cm^{-3}. Such carrier densities are much larger than those found in Pb-Mn-Te and vary over a much wider range than in Sn-Mn-Te and Ge-Mn-Te. The carrier density in PSMT is temperature independent below 100 K and the values for the carrier concentration quoted in this Rapid Communication were measured at $T = 79$ K.

ac susceptibility and specific-heat measurements have been performed in the temperature range 0.4–50 K. Above the critical carrier concentration $p_{crit} \simeq 3 \times 10^{20}$ cm^{-3}, a magnetic phase transition was observed. An illustration of the low-temperature behavior is shown in Fig. 1(a). Magnetization and dc susceptibility confirmed the ferromagnetic nature of the transition. The high-temperature part of χ_{ac}, corrected for the diamagnetic contribution of the host material, obeys a Curie-Weiss law at temperatures above roughly 10 K, as shown in Fig. 1(b). The Curie-Weiss temperature Θ, which is proportional to the average exchange interaction between the Mn ions, matches T_c within a few tenths of a degree and is proportional to x as expected for a random system with long-range interactions [see inset, Fig. 1(b)]. Figure 2 shows the carrier concentration dependence of Θ for several compositions, supplemented with the earlier re-

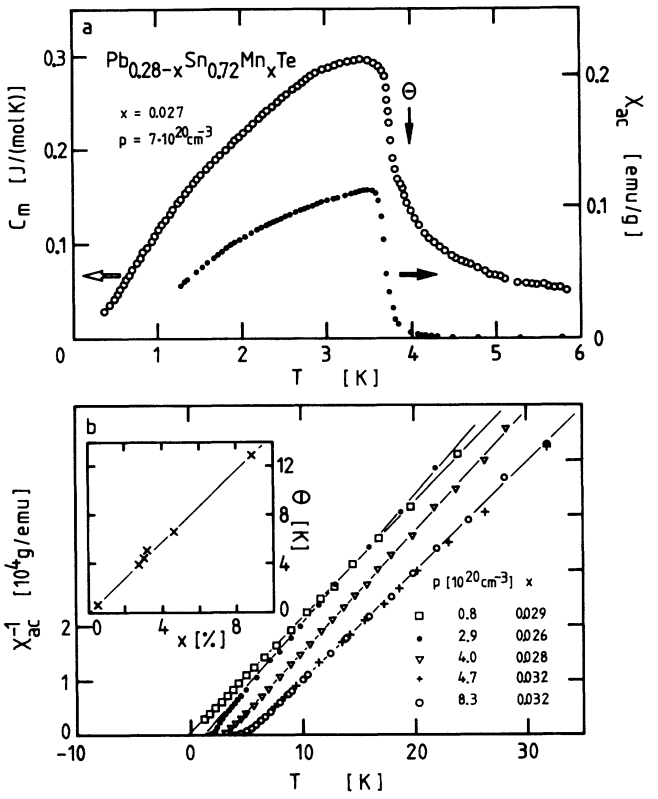

FIG. 1. (a) Low-temperature magnetic specific heat (C_m) and ac susceptibility (χ_{ac}) of $Pb_{0.28-x}Sn_{0.72}Mn_xTe$, $x=0.027$ and $p=7\times10^{20}$ cm^{-3}, showing the transition to a ferromagnetic state; (b) inverse ac susceptibility (χ_{ac}^{-1}) for $x\simeq0.03$ and several carrier concentrations (p); the Curie-Weiss temperature (Θ) as a function of the Mn concentration (x), in the ferromagnetic regime, is inserted.

sults of Story *et al.*[2] Above p_{crit} an abrupt, almost steplike increase of Θ from approximately zero to large positive values is observed, indicating a net ferromagnetic interaction. The data in Fig. 2 suggest a rather universal dependence on the carrier concentration, only slightly dependent on the composition. However, we like to note that in $Pb_{0.50}Sn_{0.47}Mn_{0.03}Te$ a reduction of p_{crit} ($\simeq1\times10^{20}$ cm^{-3}), with respect to the systems with $y=0.72$ is suggested, although a larger set of samples is necessary to obtain more pertinent conclusions.

To explain the abrupt transition to a ferromagnetic phase as the hole density exceeds a critical density, we will introduce a simple model. We consider a system of localized magnetic moments, the Mn ions in the Pb-Sn-Te matrix, interacting with the free holes. The following assumptions will be made: (i) intraband RKKY interaction between the magnetic moments; (ii) mean-field approximation for the spin system; (iii) a finite mean free path for the free holes; (iv) representation of the complicated band structure of PSMT by a set of two parabolic valence bands with different effective masses, as shown in Fig. 3. The first assumption includes the use of second-order perturbation theory, although for PSMT the exchange constant J might well be of the same order of magnitude as the Fermi energy (E_F) of the free holes (see, however, the

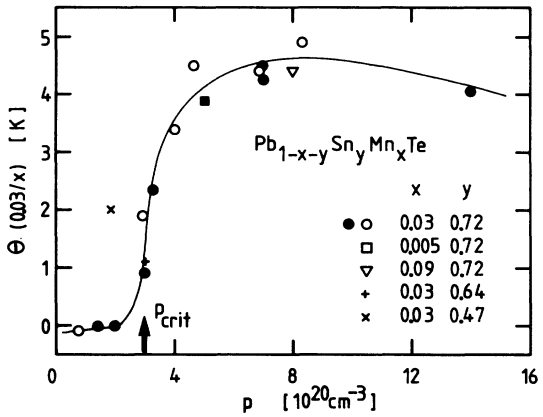

FIG. 2. Curie-Weiss temperature, scaled on $x=0.03$ [$\Theta(0.03/x)$] of $Pb_{1-x-y}Sn_yMn_xTe$ as a function of the carrier concentration (p); the dark circles are data obtained from Story *et al.* (Ref. 2); the solid line is a guide to the eye.

discussion of Mauger and Godart in Ref. 5). The mean-field approximation completely neglects the dynamics of the spin system. The RKKY interaction was originally modeled for metals, i.e., for free electrons with parabolic bands. The application to semiconductors requires at least two essential modifications, which are expressed in the third and fourth assumption. First, the mean free path of free carriers cannot be taken to be infinite. Second, the detailed band structure of a semiconductor might play a decisive role. We used the band structure of $Pb_{1-x}Sn_xTe$ as a reference model for the band structure of PSMT. It is assumed that the presence of Mn ions does not significantly alter the band structure (see Ref. 1). We take into account only the highest two valence bands according to different band-structure calculations[6-9] for SnTe and $Pb_{1-x}Sn_xTe$ with $x>0.4$. Although the assumptions listed above are rather crude, we believe that this simple model contains the relevant characteristics of the magnetic subsystem as well as the hole subsystem. Within this model, the Curie-Weiss temperature is given by

$$\Theta=\frac{2S(S+1)x}{3k_B}\sum_{i=1}^{2}\sum_{j\geq1}J_i^{\text{eff}}(R_j)\ , \tag{1a}$$

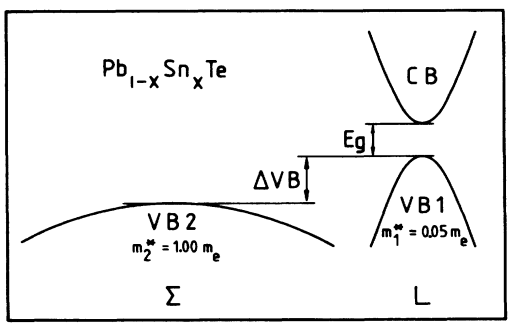

FIG. 3. Schematic illustration of the band structure of $Pb_{1-x}Sn_xTe$ used in the model calculations as described in the text.

where $J_i^{\text{eff}}(R_j)$ is the exchange integral

$$J_i^{\text{eff}}(R_j) = \left(\frac{m_i^*}{m_e} J_i^2\right) \frac{m_e}{128\pi^3\hbar^2} \left(\frac{a_0^2}{j^2}\right) e^{-R_j/\lambda} F(z_j^i) \ , \tag{1b}$$

with

$$F(z_j^i) = [\sin(z_j^i) - z_j^i \cos(z_j^i)] \ , \tag{1c}$$

and with $z_j^i = 2k_F^i R_j$, where k_F^i is the Fermi wave number for the ith band. R_j is the distance between two lattice points in the fcc lattice ($R_0 = 0$ and R_1 is the nearest-neighbor distance). S is the magnitude of the spin ($S = \frac{5}{2}$ for Mn^{2+}), J_i the exchange constant for VBi, and a_0 is the lattice parameter. The effect of a finite mean free path (λ) is incorporated along the lines proposed by de Gennes,[10] by inclusion of an exponential term in $J_i^{\text{eff}}(R_j)$.

Next, some results of our model calculation for $Pb_{0.25}Sn_{0.72}Mn_{0.03}Te$ will be presented. We would like to stress that the parameters are not obtained from a fit to the experimental data. The lattice parameter $a_0 = 6.347$ Å was estimated from the Pb-Mn-Te and Sn-Mn-Te data[11,12] by linear Vegard-type interpolation. For the exchange constants, it was assumed that $J_1 = J_2 = 0.3$ eV, from a linear interpolation between the experimental values[13] for Pb-Mn-Te (0.07 eV) and for Sn-Mn-Te (0.40 eV). However, it is *a priori* not excluded that the exchange integrals differ for both valence bands.[14] For the effective masses we take the values from Ocio[15] for $Pb_{0.53}Sn_{0.47}Te$: $m_1^* = 0.05m_e$ and $m_2^* = 1.00m_e$. Figure 4(a) shows the Curie-Weiss temperature as a function of hole density, as calculated from Eq. (1) with contributions from both valence bands. Also, the theoretical curves corresponding to the case that only VB1 or VB2 is filled are inserted, for an infinite mean free path. The difference between these contributions is mainly caused by the considerable difference between the effective masses m_1^* and m_2^*; see Eq. (1b). In Fig. 4(b) the model calculations are compared with the experimental data. The different curves correspond to different values of the mean free path λ of the holes. It is clear from this plot that the effect of λ can be large. We used realistic values for λ, i.e., 7 and 13 Å, corresponding to the experimentally observed mobilities ($\mu = 2e\lambda^2/\hbar$) in the range 15–50 cm^2/Vs. The critical hole concentration in Figs. 4(a) and 4(b), $p_{\text{crit}} \simeq 2.4\times10^{20}$ cm^{-3}, has been determined from a two-band Kane model,[15] with as additional parameters[16] $E_g = 0.15$ eV and $\Delta E_{VB} = 0.6$ eV (see Fig. 3). Experimental values for p_{crit},[15,17] deduced from the temperature dependence of the Hall factor, vary roughly between 2 and 3×10^{20} cm^{-3}, which is consistent with the Kane approximation.

The excellent agreement between the calculations and the data shown in Fig. 4(b) is obvious. The observed steplike increase of Θ to positive (ferromagnetic) values at a critical carrier density as well as the magnitude of Θ above and below that critical concentration are correctly predicted. At this point, however, it should be noted that the *quantitative* agreement may be somewhat fortuitous since it depends also on the value for J_1 and J_2, the p-d exchange constants, which in a first approximation we have assumed to be equal to 0.3 eV by linear interpolation. A further verification of the validity of the model can possibly be found in an extension of the composition range (Pb-Sn) which would yield a slight shift in p_{crit} brought about by the variation in ΔE_{VB}. The observed quasiuniversal behavior of $\Theta(p)$ in the restricted composition range studied so far is in accordance with the existing data on ΔE_{VB} in that range.[15,17]

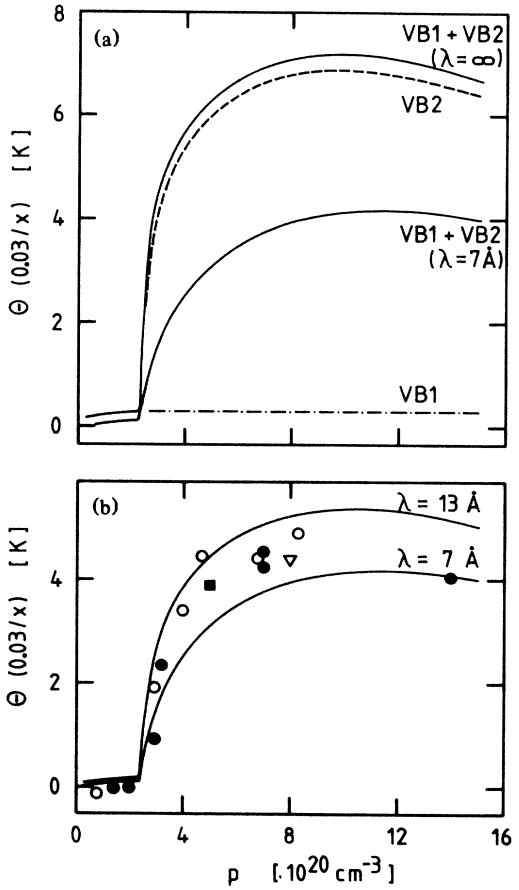

FIG. 4. (a) Curie-Weiss temperature scaled on $x = 0.03$ [$\Theta(0.03/x)$] as a function of the carrier concentration (p), as calculated from Eq. (1). The full lines correspond to contribution from both valence bands, for $\lambda = \infty$ and $\lambda = 7$ Å, whereas the dashed-dotted and dashed line represent the contribution of VB1 and VB2, respectively, for $\lambda = \infty$; (b) $\Theta(0.03/x)$ as a function of p, for $\lambda = 7$ Å and $\lambda = 13$ Å, in combination with the experimental data for $Pb_{1-x-y}Sn_yMn_xTe$; see Fig. 2 for the description of the symbols.

It is worthwhile to note that on the basis of the present model the contrasting magnetic behavior of Sn-Mn-Te and Pb-Mn-Te can be explained by the difference in carrier concentration. Ferromagnetism was found in Sn-Mn-Te (Ref. 18) (with $p \simeq 5\times10^{20}$ cm^{-3}) while Pb-Mn-Te ($p < 10^{20}$ cm^{-3}) is paramagnetic down to very low temperatures where recently a spin-glass transition was observed.[19] The reported antiferromagnetic (AF) sign of the interactions in Pb-Mn-Te is probably due to the increasing relevance of other than intraband mechanisms which might be AF for low carrier concentrations. In

fact, one might conjecture that also in PSMT for low concentrations a spin-glass transition at very low temperatures would occur.

Finally, we would like to add that one of the essential results of the present study, i.e., the first indication of separate contributions from carriers in different regions of the Brillouin zone might also be relevant for calculations of *inter*band interaction mechanisms which have been proposed for diluted magnetic semiconductors.

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[1]N. B. Brandt and V. V. Moshchalkov, Adv. Phys. **33**, 193 (1984); J. K. Furdyna and N. Samarth, J. Appl. Phys. **61**, 3526 (1987); R. R. Gałązka, *Proceedings of the Third International Conference on Physics of Magnetic Materials, Szczyrk-Biła, Poland, 1986,* edited by W. Gorzkowski, H. K. Lachowicz, and H. Szymczak (World Scientific, Singapore, 1987), p. 26.

[2]T. Story, R. R. Gałązka, R. B. Frankel, and P. A. Wolff, Phys. Rev. Lett. **56**, 777 (1986).

[3]T. Suski, J. Igalson, and T. Story, *Proceedings of the Eighteenth International Conference on the Physics of Semiconductors, Stockholm, 1986,* edited by Olof Engström (World Scientific, Singapore, 1987), p. 1747; J. Magn. Magn. Mater. **66**, 325 (1987).

[4]M. Rudermann and C. Kittel, Phys. Rev. **96**, 99 (1954); T. Kasuya, Prog. Theor. Phys. **16**, 45 (1956); K. Yoshida, Phys. Rev. **106**, 893 (1957).

[5]A. Mauger and C. Godart, Phys. Rep. **141**, 51 (1986).

[6]Y. Ota and S. Rabii, in *The Physics of Semimetals and Narrow Gap Semiconductors,* edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1971), p. 343.

[7]J. O. Dimmock, in *The Physics of Semimetals and Narrow Gap Semiconductors,* edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1971), p. 319.

[8]G. Martinez, M. Schluter, and M. L. Cohen, Phys. Rev. B **11**, 651 (1976).

[9]Y. W. Tung and M. L. Cohen, Phys. Rev. **180**, 823 (1969).

[10]P. J. de Gennes, J. Phys. Radium **23**, 630 (1962).

[11]V. G. Vanyarkho, V. P. Zlomanov, and A. V. Novoselova, Izv. Akad. Nauk, SSSR Neorg. Mater. **6**, 1534 (1970).

[12]U. Sondermann, J. Magn. Magn. Mater. **2**, 216 (1976).

[13]*Landolt-Börnstein: Physics of Group IV Elements and III-V Compounds,* edited by O. Madelung, H. Schultz, and H. Weiss (Springer, Berlin, 1982), Vol. 17, Pt. a.

[14]J. Ginter, J. A. Gaj, and Le Si Dang, Solid State Commun. **48**, 849 (1983).

[15]M. Ocio, Phys. Rev. B **10**, 4274 (1974).

[16]G. Nimtz, B. Schlicht, and R. Dornhaus, *Narrow Gap Semiconductors* (Springer, Berlin, 1983).

[17]A. Aladgadgyan and A. Toneva, Phys. Status Solidi (b) **85**, K131 (1978).

[18]A. Mauger and M. Escorne, Phys. Rev. B **35**, 1902 (1987).

[19]M. Escorne, A. Mauger, J. L. Tholence, and R. Triboulet, Phys. Rev. B **29**, 6306 (1984).