New Mechanism of f-f Exchange Interactions Controlled by Fermi Level Position

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Magnetic properties of $Sn_{1-x}Gd_xTe$ semimagnetic semiconductor reveal a strong dependence of antiferromagnetic exchange coupling between Gd spins on the concentration of carriers. We present a model explaining consistently both magnetic and transport properties of SnGdTe as caused by the resonant adjustment of the energy level of Gd $5d^1$ electron states and the Fermi level. [S0031-9007(96)01448-2]

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The mixed crystals of $Sn_{1-x}Gd_xTe$ belong to the family of semimagnetic (diluted magnetic) semiconductors [1,2] and form a diluted magnetic semimetallic system. Our work is devoted to the analysis of correlations between the magnetic and transport properties of SnGdTe. In previous studies of SnGdTe [3–5], Gd was found to substitute Sn^{2+} ions in the rock-salt lattice of SnTe as Gd^{3+} ion being an electrically active (donor) center possessing the $S = 7/2$ well localized magnetic moment due to $4f^7$ electrons. The SnTe matrix is a strongly degenerated *IV-VI* semiconductor with a narrow energy gap. The characteristic property of SnTe is a very high concentration of Sn vacancies. These vacancies are known to be the acceptor centers with zero activation energy [6]. It leads to high, temperature independent, p type conductivity with the conducting hole concentrations (p) of the order of 10^{20}–10^{21} cm^{-3}. There exists a possibility to control the number of Sn vacancies (i.e., the concentration of carriers) by an isothermal annealing. For carrier concentrations $p \geq 2 \times 10^{20}$ cm^{-3}, two valence bands are populated: the band of light holes located at the L point of the Brillouin zone and the band of heavy holes located at the Σ point of the Brillouin zone and shifted down from the top of the L band by about 0.18 eV. The density of states effective mass is about a factor of 20 larger for the Σ band as compared to the L band.

SnTe is diamagnetic even for the highest carrier concentrations encountered, i.e., $p \simeq 2 \times 10^{21}$ cm^{-3}. The crystals of $Sn_{1-x}Gd_xTe$ are Curie-Weiss paramagnets [3–5]. The weak antiferromagnetic f-f exchange coupling was observed with the nearest-neighbors exchange integral of the order of $I_{ff}(R_{nn}) \simeq -0.5$ K. No carrier concentration dependence of magnetic properties was reported. The magnetic properties of $Sn_{1-x}Gd_xTe$ are in drastic contrast to the magnetic properties of related, transition-metal-based, $Sn_{1-x}Mn_xTe$ and $Pb_{1-x-y}Sn_yMn_xTe$ systems. In those crystals the carrier concentration induced ferromagnetic and spin-glass transitions are observed as a result of the Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect exchange interaction via spin polarization of conducting carriers [1,2,7–9].

Our primary motivation for the present work was to verify experimentally whether conducting carriers play a role in the magnetic properties of $Sn_{1-x}Gd_xTe$. We expected that, due to the strong localization of $4f$ orbitals of Gd, the RKKY mechanism involving the free carriers will be much weaker than in the related $Sn_{1-x}Mn_xTe$ crystals, where it is the dominant (*ferromagnetic*) interaction. We will show that, by changing the concentration of carriers, one can change the strength of Gd-Gd *antiferromagnetic* exchange coupling by almost an order of magnitude. This and other experimental findings will be explained based on the new model of Gd ion in SnTe matrix. The theoretical analysis of the f-f exchange interaction performed in the frame of this model shows that the carrier concentration dependence of the magnetic properties of SnGdTe is, most probably, due to the new mechanism proceeding via intraion $4f$-$5d$ exchange interaction followed by the interion $5d$-$5d$ coupling mediated by free carriers or anion orbitals. The enhancement of the interspin coupling is a result of the Fermi level controlled population of $5d^1$ orbital of Gd.

The SnGdTe samples studied by us were grown by the Bridgman method. The crystal structure and the chemical composition were examined by x-ray Debye method and by electron microprobe analysis. The crystals have the rock-salt structure and consist of small monocrystalline blocks. To change the concentration of carriers some of the samples were annealed. The magnetic properties of SnGdTe were studied by SQUID magnetometer (magnetization), by mutual inductance bridge (ac magnetic susceptibility χ), and by electron paramagnetic resonance spectrometer. The Hall effect and the electric conductivity were measured by dc technique.

The typical temperature dependence of $1/\chi$ for SnGdTe is presented in the inset in Fig. 1 (the sample with $p = 5.6 \times 10^{20}$ cm^{-3}). The standard Curie-Weiss behavior is observed as expected for the system of weakly interacting local spins. The negative sign of the paramagnetic Curie temperature (Θ) indicates the presence of antiferromagnetic spin-spin couplings. This type of behavior is observed for all the SnGdTe crystals with $x > 0.05$ as well as for samples with $x < 0.05$ and with

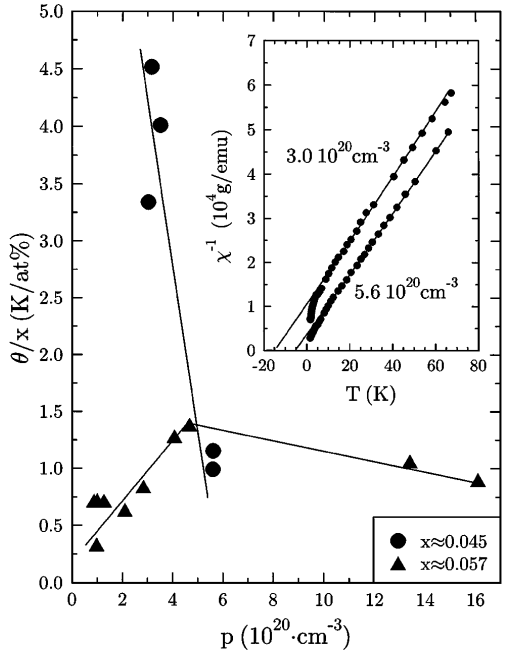

FIG. 1. The carrier concentration dependence of normalized paramagnetic Curie temperature Θ/x. Triangles: the behavior of crystals with $x > 0.05$. Dots: the result for samples with $x < 0.05$. The inset presents the temperature dependence of the inverse magnetic susceptibility of two samples of $Sn_{0.955}Gd_{0.045}Te$ with different carrier concentrations.

large carrier concentrations. For samples with lower Gd content, $x < 0.05$, and $p = (3 \pm 0.5) \times 10^{20}$ cm^{-3} the substantial increase of the absolute value of paramagnetic Curie temperature is observed (see Fig. 1). The pair of samples presented in the inset in Fig. 1 is, in fact, the same sample before and after the annealing during which the concentration of carriers was reduced from $p = 5.6 \times 10^{20}$ cm^{-3} to $p = 3 \times 10^{20}$ cm^{-3}. The Curie constant, measured by the slope of the $\chi^{-1}(T)$ plot, does not depend on the annealing process. It indicates that, most probably, Gd concentration does not change during annealing. The very same technological procedure applied to the crystals with $x > 0.05$ results in a significantly smaller change of Θ.

The dependence of f-f exchange interactions on carrier concentration is presented in Fig. 1 for the parameter Θ/x which is related to the exchange integrals $I_{ff}(R)$ by the expression $k_B\Theta/x = (2/3)S(S + 1)\Sigma z_i I_{ff}(R_i)$, where the sum runs through all the magnetic neighbors z_i. One can notice that the difference in the value of Θ/x for different SnGdTe samples can be as large as a factor of 9. The strong enhancement of the antiferromagnetic interspin coupling is observed for samples with $x < 0.05$ only. The effect for samples with $x > 0.05$ is much less pronounced. The experimental findings mentioned above were verified for about 20 samples of SnGdTe in the Gd concentration range $0.03 \leq x \leq 0.07$. Our experimental results clearly indicate the existence of two different types of behavior. The first one, observed also in early studies of SnGdTe and characterized by quite weak antiferromagnetic interspin interactions, is observed in all samples with $x > 0.05$ and in samples with $x < 0.05$ and $p > 3 \times 10^{20}$ cm^{-3}. The second one, observed for the first time by us and characterized by much stronger antiferromagnetic interactions, is found only in crystals with $x < 0.05$ and $p = (3 \pm 0.5) \times 10^{20}$ cm^{-3}. The presence of relatively strong antiferromagnetic interactions evidenced in our experiments as a large negative value of Θ was confirmed in the measurements of high field magnetization. It is also consistent with the experimental observation of a cusp on the temperature dependence of χ found in the samples with $p = (3 \pm 0.5) \times 10^{20}$ cm^{-3} and $x < 0.05$ at $T = 1.8$ K.

The measurements of transport properties of SnGdTe have also revealed the strong influence of carrier concentration. In the very same samples of SnGdTe in which the large Θ is observed, the carrier mobilities show an increase by a factor of 5 (see Fig. 2). No such increase is observed for samples with $x > 0.05$. Also, despite the presence of up to 9 at. % (i.e., about 1.5×10^{21} cm^{-3}) of assumed donor centers, all the studied samples of SnGdTe show metallic p type conductivity. Moreover, the numerous annealing processes of $Sn_{0.955}Gd_{0.045}Te$ performed in order to reduced the number of acceptorlike Sn vacancies

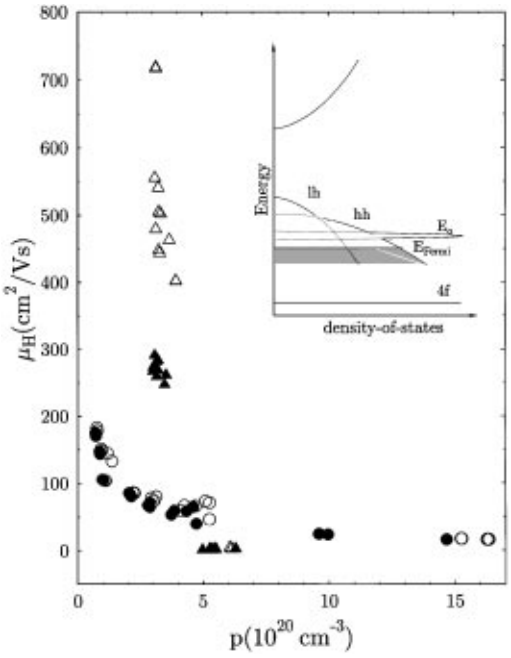

FIG. 2. The carrier concentration dependence of the hole mobility for $Sn_{1-x}Gd_xTe$ with $x = 0.045$ (triangles) and with $x = 0.057$ (circles). The open symbols show the data at $T = 4.2$ K, whereas the full symbols show the data at $T = 77$ K. The inset presents the scheme of the band structure of $Sn_{1-x}Gd_xTe$ with $x < 0.05$. With the increasing Gd content, the E_0 electron level shifts up with respect to the top of the valence band leaving the band of heavy holes for $x \simeq 0.05$.

have resulted in approximately the same hole concentration $p = (3 \pm 0.5) \times 10^{20}\ \mathrm{cm}^{-3}$.

All the experimental results presented above contradict the idea of Gd ions being, in SnTe matrix, always Gd^{3+} donor centers with the f-f superexchange interaction governing the interspin coupling. Our results provide the experimental basis for the new model of Gd ion in SnTe crystal. In our model the $4f^7$ states of Gd are located deep in the valence band, being very well localized and creating the $S = 7/2$ magnetic moment of the Gd ions. All the above mentioned experimental findings can be consistently explained assuming that Gd $5d^1$ electron states are located at the energy level E_0 ($Gd^{2+/3+}$ level) about 0.2 eV below the top of the valence band. It generates a new situation with Gd being in $3+$ or in $2+$ charge state, depending on the relative position of the Fermi level (governed by the concentration of two electrically active centers: Sn vacancies and Gd^{3+} ions) and the E_0 energy level. This assumption has been recently verified by the results of the photoemission experiments [10]. The density of states related to $4f^7$ energy states was found 9.5 eV below the top of the L valence band, whereas the extra (in respect to SnTe) density of states observed just below the top of the valence band was interpreted as related to $5d$ electron states. The scheme of the band structure of SnGdTe is presented in the inset in Fig. 2. The density of states presented in this figure and related to $4f^7$ electrons corresponds to the lower (spin-up) part of the total density of states. The spin-down half of it is located in the conduction band. The density of states assigned in this model to $5d$ electron states represents only the lowest t_{2g} level. This orbital may be empty (corresponding to the usual case of $4f^7 5d^0$, Gd^{3+} configuration) or occupied by just one electron (the case of Gd^{2+} with $4f^7 5d^1$ configuration).

The experimental results presented in this paper have a simple interpretation in the frame of our model. Because of the strong localization of the $4f$ orbitals, the usual superexchange interaction via the orbitals of intervening anions is expected to be weak, as observed in other Gd- and Eu-based semimagnetic semiconductors [3]. Also, the RKKY mechanism due to the p-f exchange coupling between f electrons and conducting holes is quite weak because the p-f exchange integrals are known to be very small due, again, to the very localized character of $4f$ orbitals [11,12]. Furthermore, for the band structure parameters of SnTe, the RKKY interaction is expected to be ferromagnetic, as in $Sn_{1-x}Mn_xTe$. There, however, the other indirect mechanisms may operate, coupling the f spins. They consist of two steps: the intraion $4f$-$5d$ exchange interaction and the interion $5d$-$5d$ coupling which may be of both direct and indirect origin. The first step is known from free ion data, $I_{df} \simeq 0.125$ eV. The second step is also expected to be effective because of the considerably less localized character of $5d$ orbitals. We expect that both direct and superexchange coupling can be effective for pairs of Gd spins located as nearest, as well as next-nearest magnetic neighbors (4.6 Å and 6.3 Å, respectively). No considerable direct overlap between $5d$ orbitals of two Gd ions located at the mean distance (about 10 Å in our samples) is expected. Consequently, our description is based on the idea of Gd $5d$ electron states being somewhat broadened but still local in character with neither $5d$ nor hybrid $5d$-p wide band being formed. One can, alternatively, view this situation as the case of the very narrow $5d$-p band being superimposed on the SnTe valence band states. This idea is supported by the observed very sharp resonantlike behavior of both interspin coupling and carrier mobility dependence on the position of the Fermi level. The idea of the two-stage interspin coupling mechanism for $4f$ spins was developed by Kasuya [13–15] for Eu chalcogenides. In the crystals of SnGdTe a new two-stage mechanism may be effective. In this mechanism the $5d$ spins are coupled by delocalized carriers from the valence band of SnGdTe. The Kasuya model was developed for semi-insulating crystals and involves only local atomiclike p orbitals of anions.

Calculations of the two-stage mechanism with the free carriers mediating the $5d$-$5d$ coupling give the interspin exchange interaction which, in the limit of large interspin distances (R) and the Fermi level below the E_0 level, is described by the formula

$$I_{ff}(R) \sim \frac{m^* V_{pd}^4 k_F}{(E_F - E_0)^2} \frac{\cos(2k_F R)}{R^3}, \qquad (1)$$

where m^* is the effective mass of carriers, k_F is the Fermi wave vector, and V_{pd} describes the hybridization between $5d$ and valence band states. The theory based on the above simple model gives the correct sign of the paramagnetic Curie temperature and qualitatively describes its changes with the shift of the Fermi level, provided that we are not in very resonant conditions. Unfortunately, it fails when $E_F \simeq E_0$. This, probably, is due to the fact that the calculations for the resonant situation require much more precise knowledge of the band structure and the hybridization elements. In our calculations we assumed the simplest model of the parabolic band and $\mathbf{k}$-independent matrix elements V_{pd}.

The composition dependence of interspin exchange interactions in SnGdTe is, in our model, the consequence of the composition evolution of the band structure of SnGdTe. It is known that, in IV-VI semiconductors with Eu and Gd, the energy gap depends on the composition with the rate of about $dE_g/dx \simeq 40$ meV/at.% [11]. Similar dependence is expected for the shift of the top of the valence band with respect to the position of the E_0 level. In such a case, one may expect that, for samples with high enough composition of Gd, the E_0 energy level will be shifted up and located in the L band (above the Σ band). Because of the low density

of states in the L band, the mechanism described above will be strongly reduced. For this mechanism to be fully effective in SnGdTe, one requires the following: The Fermi level must be located very close to the E_0 level being, simultaneously, in the Σ band with high density of states effective mass. The analysis of the electron transport measurements presented below shows that the E_0 level crosses the top of the Σ band at $x \simeq 0.05$. Therefore, the conditions discussed above can be fulfilled only for samples with $x < 0.05$ and with proper carrier concentration. For the samples with $x > 0.05$ we observe the maximum on the Θ/x vs p dependence which is due to the contributions from the heavy and the light hole band. Since the E_0 level is for $x > 0.05$ located above the top of the heavy hole band, the resonance $E_F \simeq E_0$ can be obtained for light holes only producing the much weaker coupling due to the low density of states in this band. The heavy hole contribution is, in this case, nonresonant and switches off for $p < (2 - 3) \times 10^{20}\ \mathrm{cm}^{-3}$. With the Fermi energy approaching from below the E_0 level we expect all three mechanisms for $5d$-$5d$ interaction (i.e., direct, superexchange, and indirect coupling via free carriers) to be resonantly enhanced, as they all depend on the population of the $5d$ orbital. The strong composition dependence of the exchange coupling, which can be explained in terms of the evolution of the band structure of SnGdTe, indicates the relative importance of the band structure sensitive mechanism with the indirect $5d$-$5d$ coupling via free carriers.

The lack of n type conductivity is the consequence of the fact that, for the Fermi level location at or above the E_0 ($\mathrm{Gd}^{2+/3+}$) level, the introduction of extra Gd ions will result in no effect on Fermi level because they all will be in electrically neutral $2+$ charge state. The self-ionization of $\mathrm{Gd}^{2+}(4f^7 5d^1)$ ion to $\mathrm{Gd}^{3+}(4f^7 5d^0)$ would, in such a case, result in the increase of the energy of the system as the lowest available empty electron states are above the Fermi level. The Gd composition dependence of the location of the $5d$ electron level can be determined in an indirect way from the results of transport measurements. For samples annealed in the atmosphere of Sn we observe a certain minimum hole concentration ($p_{\min}$) that can be obtained in such a procedure. It equals $p = 3 \times 10^{20}\ \mathrm{cm}^{-3}$ for crystals with $x = 0.045$ and $p = 5 \times 10^{19}\ \mathrm{cm}^{-3}$ for $x = 0.057$. The value of ($p_{\min}$) is determined by the effect of pinning of the Fermi level at the $\mathrm{Gd}^{2+/3+}$ electron level. In such a case $E_F \simeq E_0$, and one can determine E_0 as the Fermi level position in SnGdTe with $p = p_{\min}$.

To understand the effect of the increase of hole mobility in some samples of SnGdTe, one has to realize that there are two main scattering centers determining the mobility of carriers in SnGdTe at low temperatures. These are Sn vacancies and Gd ions. When comparing the hole mobilities of crystals with $x = 0.045$ and $x = 0.057$ and the same carrier concentration, $p = 3 \times 10^{20}\ \mathrm{cm}^{-3}$, one has to take into account that this situation corresponds to the case of most of Gd ions being in neutral $2+$ charge state for $x = 0.045$ ($E_F \simeq E_0$) and all of them being in electrically active $3+$ state for samples with $x = 0.057$ (E_F below E_0). The Gd^{3+} ions are expected to be much more efficient scattering centers than Gd^{2+} ions for two reasons. First, the electrically active Gd^{3+} ions contribute to the scattering via their Coulomb potential absent for neutral Gd^{2+} ions. Second, the charged ion is expected to influence the local order in the matrix stronger than the neutral one. That results in a larger cross section for the scattering by core potential.

In conclusion, we have presented the experimental evidence and the theoretical analysis of the Fermi level position dependence of the antiferromagnetic f-f exchange interactions in $\mathrm{Sn}_{1-x}\mathrm{Gd}_x\mathrm{Te}$ semimagnetic semiconductor. Our interpretation of this new effect is based on the model of the two-stage indirect f-f coupling via f-d intraion and d-d interion coupling via valence band electrons. Both the strong increase of the spin-spin antiferromagnetic interactions and the unusual transport properties of SnGdTe have been consistently explained based on the new model of the Gd ion in SnTe locating the Gd $5d^1$ electron states close to the Fermi level of SnGdTe. The main mechanism for the observed effects is the Fermi level position controlled population of Gd $5d$ orbitals.

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