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Study of the magnetic properties of the $La_{1-x}Gd_xTe$ solid solution

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Abstract

We present a study of the physical properties of the $La_{1-x}Gd_xTe$ solid solution. Although both LaTe and GdTe crystallize in the fcc structure and are metallic, two domains in the x-dependence of the lattice parameters of their solid solution can be distinguished. At the critical concentration, no anomalies in the magnetic susceptibility or the electrical resistivity can be detected. Both the Néel and paramagnetic Curie temperatures are linearly x-dependent, at $x \geq 0.5$, with opposite slopes. The results are discussed within a molecular field treatment of the RKKY exchange interaction in which the disorder generated by spin dilution is averaged out.

1. Introduction

For many years, much effort has been devoted to the study of diluted magnetic systems. To address this problem, a new class of materials has been generated, the so-called semimagnetic compounds. Among them, the semimagnetic semiconductors, in which the magnetic interactions are short range, have been studied extensively [1]. In this paper we are concerned with semimagnetic metals that differ from their semiconductor counterparts, since the Ruderman–Kittel–Kasuya–Yosida (RKKY) magnetic interaction [2] mediated via the free carriers is long range.

The rare-earth monotellurides form a series of compounds that crystallize in the fcc structure. Depending on the nature and valence of the rare-earth ion, they can be magnetic or non-magnetic, with metallic or semiconducting characteristics. Thus, by mixing together appropriate rare-earth monotellurides, different kinds of solid solutions can be generated. In some cases, the dilution of magnetism is accompanied by a metal–insulator transition [3], and in others, the semiconducting phase is retained [4,5]. A different situation is found in $La_{1-x}Gd_xTe$, since the substitution of Gd^{3+} by La^{3+} generates a metallic solid solution in which the dilution of magnetism occurs without any modification of the free carrier concentration. GdTe is a type II antiferromagnetic metal. As Gd^{3+} carries a magnetic moment of 7 μ_B when La^{3+} is not magnetic, this solid solution is an archetype for the investigation of the magnetic dilution effects in metallic fcc systems with constant free carrier concentrations. The present paper reports on the physical properties of these materials.

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2. Experimental

The samples were obtained by direct reaction of required amounts of the elements in molybdenum crucibles, arc welded under argon. Rapid heating to 2000°C followed by a slow cooling at a rate of 4–10°C/h leads to single crystals typically $1 \times 1 \times 2$ mm in size. Electron microprobe analysis revealed that the single crystals were homogeneous, with a final composition very close to the initial one. The lattice parameters were determined from powder X-ray diffraction patterns by Rietveld refinement. The magnetic susceptibilities were measured in a Faraday balance in magnetic fields up to 3 kOe. The thermal variation of the electrical resistance was measured in an ac configuration. The absolute values of the resistivity were deduced from Van der Pauw measurements at room temperature. Electrical contacts were made by ultrasound diffusion of indium.

3. Results

The x-dependence of the lattice parameter a is reported in Fig. 1. Vegard's law is not obeyed. Two composition domains can be distinguished, $x \leq 0.80$ and $x > 0.80$, in which a varies linearly with x. From X-ray observations, this feature cannot be associated with any overstructure or change in the fcc structure of the solid solution. It is worth noting that this anomaly is associated with drastic changes in the colour of the samples: for $x \leq 0.80$ the single crystals are wine red, the colour of undoped LaTe, and for $x > 0.80$, they are blue, the colour of the GdTe compound.

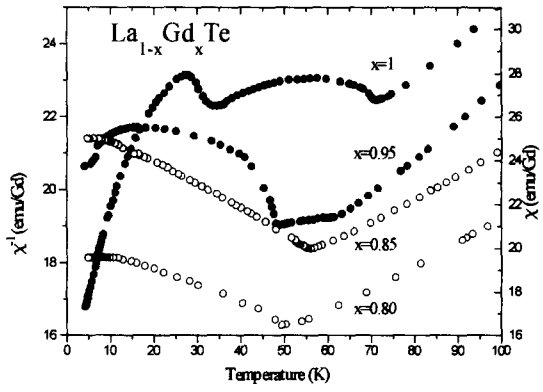

Fig. 2. Thermal variation of the inverse magnetic susceptibility of $La_{1-x}Gd_xTe$, for $x = 1$, 0.9, 0.85 and 0.80. Solid circles: left y-axis; open circles: right y-axis.

At high temperatures, $T \geq 150$ K, the Curie–Weiss law is obeyed, from which we can deduce an effective magnetic moment close to the theoretical value for the free Gd^{3+} ion ($\mu_{eff} = 7.94\ \mu_B$). The extrapolated paramagnetic Curie temperatures are negative, indicating a predominance of antiferromagnetic interactions. The low-temperature part of the thermal variation of the inverse magnetic susceptibility, χ^{-1}, is shown in Fig. 2 for $x = 1$, 0.95, 0.85 and 0.80, and in Fig. 3 for $x = 0.7$, 0.6, 0.5 and 0.4. For $x > 0.50$, a cusp in $\chi^{-1}(T)$ is observed, associated with the appearance of an antiferromagnetic ordering, which allows us to define the Néel temperature,

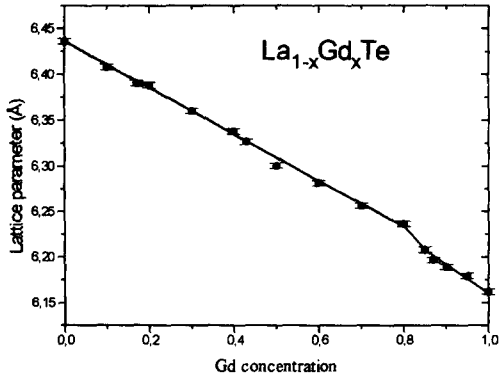

Fig. 1. x-dependence of the lattice parameter a in the $La_{1-x}Gd_xTe$ solid solutions.

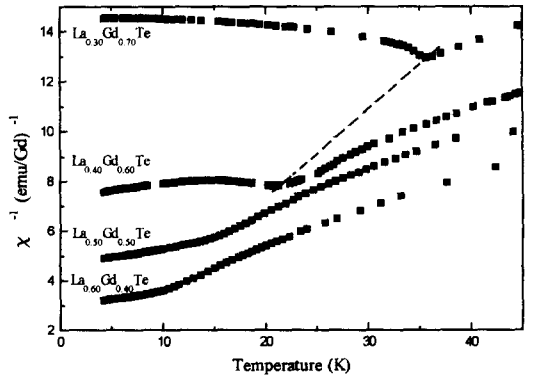

Fig. 3. Thermal variation of the inverse magnetic susceptibility of $La_{1-x}Gd_xTe$, for $x = 0.7$, 0.6, 0.5 and 0.4.

T_N. For $x \leq 0.5$, the cusp is smeared out, so that it is no longer possible to define an ordering temperature from the thermal variation of the magnetic susceptibility. Actually, the systems enters a spin glass regime in the vicinity of $x = 0.5$. This is confirmed by the onset of irreversibility determined from field-cooled and zero-field-cooled magnetic susceptibility measurements.

Prior works indicate that GdTe undergoes a structural transition at $T_1 = 56$ K, which creates a second minimum in $\chi^{-1}(T)$ [6]. This structural transition is associated with a modification of the orientation of the Gd^{3+} magnetic moments; they switch from the [111] direction above T_1 to the [110] direction at lower temperature. This anomaly is observed in our GdTe compound (Fig. 2) even though the characteristic temperature is 18 K lower than expected (from Ref. [6]). This difference comes from the fact that T_1 depends strongly on the departure from stoichiometry in GdTe. In particular, a Gd deficiency implies an increase in T_1. This result may be correlated with the fact that T_1 increases when going from $x = 1$ to 0.95, as can be seen in Fig. 2. Meanwhile, T_N decreases, so that $T_1 = T_N$ for $x = 0.85$, a composition close to the x value for the change in colour and the anomaly in the x-dependence of the lattice parameter.

The thermal variations of the electrical resistivity ρ of $La_{1-x}Gd_xTe$ are illustrated in Fig. 4 and Fig. 5 for several values of x. At high temperature, ρ increases linearly with T. On the one hand, this is expected for a metallic compound, due to the diffusion of the free carriers by phonons, but on the other, the linear T-dependence of ρ extends to very low temperatures, especially for $x = 0.5$. In terms of the Grüneisen–Bloch law, this would mean a vanishing Debye temperature, which is non-physical. This result suggests that the diffusion of free carriers by spin fluctuations contributes to the low-temperature part of $\rho(T)$ at this composition, which is the critical concentration for the onset of long-range magnetic ordering. Indeed, for high Gd concentrations ($x \geq 0.6$), an anomalous behaviour of the resistivity is found at T_N. This anomaly in $\rho(T)$ is not observed at lower Gd concentrations. Therefore, this anomalous behaviour of $\rho(T)$ could be related to the critical scattering of the free carriers by spin fluctuations at the onset of long-range magnetic ordering

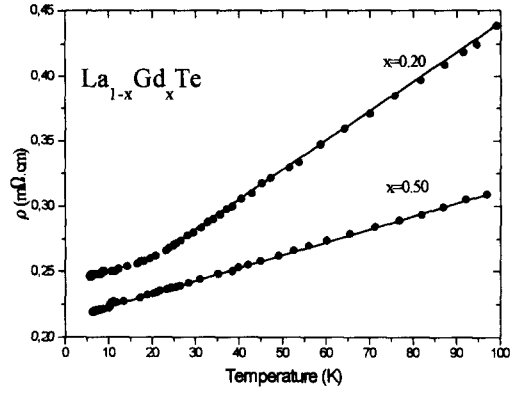

Fig. 5. Thermal variation of the electrical resistivity of $La_{1-x}Gd_xTe$, for $x = 0.5$ and 0.2.

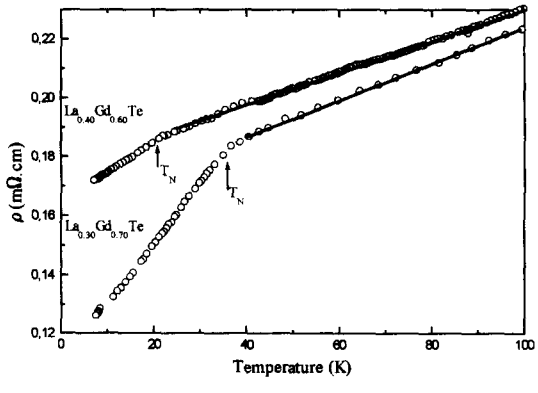

Fig. 4. Thermal variation of the electrical resistivity of $La_{1-x}Gd_xTe$ for $x = 0.7$ and 0.6.

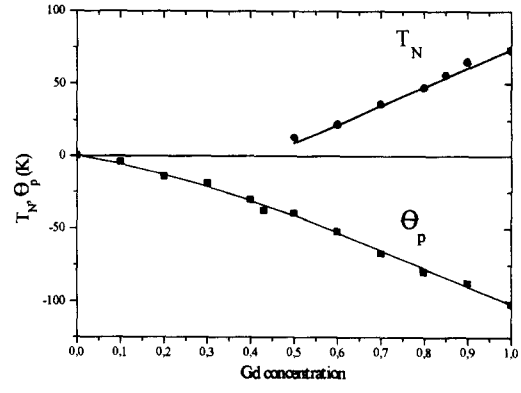

Fig. 6. x-dependence of T_N and Θ_p. Solid lines: linear fits of T_N and Θ_p; dotted line: x^2 fit of Θ_p at low Gd concentrations.

[7]. It also corroborates that long-range ordering exists in this material only above a critical concentration $x_c \approx 0.5$. At lower concentrations, the dilution plus frustration effects force the system to freeze in a spin glass rather than antiferromagnetic ordering.

The x-dependences of both the paramagnetic Curie temperature and the Néel temperature are almost linear, at least for $x > 0.4$, as can be seen in Fig. 6. In this domain, the slopes of the $T_N(x)$ and $\Theta_p(x)$ curves have almost the same absolute value.

4. Discussion

According to the RKKY exchange model, the Hamiltonian is

$$H = -\frac{1}{2}\sum_{i,j} J_{\text{eff}}(\boldsymbol{R}_{ij})\boldsymbol{S}_i\boldsymbol{S}_j, \tag{1}$$

with the exchange coupling between spins S_i and S_j at sites R_i and R_j, respectively, given by

$$J_{\text{eff}}(\boldsymbol{R}_{ij}) = \left(\frac{J}{N_0}\right)^2 \sum_{\boldsymbol{k},\boldsymbol{k}'} \frac{n_{\boldsymbol{k}}}{E(\boldsymbol{k}) - E(\boldsymbol{k}')} e^{i(\boldsymbol{k}-\boldsymbol{k}')\boldsymbol{R}_{ij}}, \tag{2}$$

where $n_{\boldsymbol{k}}$ is the occupation number of a free carrier with wave vector $\boldsymbol{k}$ and energy $E(k)$, and N_0 is the number of unit cells. For the dispersion relation $E(k) \propto k^2$ appropriate to free carriers, this exchange constant can be written in the form

$$J_{\text{eff}}(R_{ij}) = \frac{3N_e}{8E_F}\left(\frac{J}{N_0}\right)^2 \sum_q H(q)\, e^{i\boldsymbol{q}\boldsymbol{R}_{ij}}, \tag{3}$$

where N_e is the number of free carriers, and $H(q)$ is the Lindhart function,

$$H(q) = 1 + \frac{4k_F^2 - q^2}{4k_F q}\log\left|\frac{(q+2k_F)}{(q-2k_F)}\right|, \tag{4}$$

k_F is the wavevector at the Fermi energy E_F. The paramagnetic Curie temperature within the molecular field approximation (MFA) is defined by

$$\Theta_p = \frac{2S(S+1)}{3k_B}\sum_j J_{\text{eff}}(R_{ij}). \tag{5}$$

Since $H(q=0) = 2$ (from Eq. (4)), Eqs. (3) and (5) lead to

$$\Theta_p = \frac{S(S+1)}{8k_B}\frac{J^2\Omega}{E_F}nx, \tag{6}$$

where Ω is the volume of the unit cell, and n is the free carrier concentration. In our material, where n does not depend on x, Eq. (6) predicts that $\Theta_p \propto x$. At the low Gd concentration $x \leq 0.5$, an x^2 dependence can be deduced from the data in Fig. 6. This deviation from the mean field approximation (MFA) is not surprising, since the MFA is not valid at such low Gd concentrations where the material freezes in a spin glass state. The surprise comes from the linear behaviour of Θ_p at $x \geq 0.5$, in agreement with the prediction of Eq. (6). Indeed, Eqs. (1)–(6) can be found in many books, but they are questionable, since the derivation of Eq. (6) from Eq. (5) requires not only that the MFA is valid, but also that the summation over j in Eq. (5) is substituted by an integral. As a consequence, Eq. (6) lacks any resemblance to the periodicity in the spatial arrangement of the magnetic ions diluted on a lattice. A simple geometric argument would predict a loss of spatial ordering effects for a dilution rate such that the average distance between magnetic ions becomes large compared with the lattice parameter, say $x < 0.5$. In the absence of dilution ($x = 1$), the discrete character of the summation in Eq. (5) on a periodic lattice results in the well-known RKKY oscillations of Θ_p as a function of n, averaged out in the derivation of Eq. (6). In the same way, one might have expected an oscillation of Θ_p as a function of x at large x. The linear variation of Θ_p as a function of x in Fig. 6, up to x close to unity is therefore evidence that the spatial disorder associated with the dilution of the magnetic ions is very efficient in destroying the coherence between the Friedel oscillations of the local magnetization of the electron gas. Note also that this linear variation suggests that the magnetic properties are not sensitive to the deformation of the electron density of states. Such an effect is often observed in ferromagnets, as a result of the partial decoupling of the spin up–spin down subbands [8]. In the present case, however, the partial decoupling effects associated with fluctuations in the staggered magnetization occur at a wave vector in

the Brillouin zone equal to the vector $\boldsymbol{Q}$ associated with the magnetic structure, which is large in the case of an antiferromagnet. Unless one is close to a resonant condition $\boldsymbol{k}_F = \boldsymbol{Q}$, with k_F the wave vector of the electrons at the Fermi level, the perturbation of spin fluctuations on the density of electron states near E_F is very small, inasmuch as the resonant condition can be fulfilled only at discrete points on the Fermi surface.

Θ_p is a mean field parameter, so that it vanishes at $x = 0$. On the other hand, T_N does not have to extrapolate to zero at $x = 0$, but instead should vanish at some effective magnetic percolation threshold. To understand the behaviour of the Néel temperature, one should first remember that GdTe is a type II antiferromagnet. In this particular magnetic order, the nearest-neighbour magnetic interaction J_1 between Gd atoms is of no importance. The magnetic ordering is ruled by the next-nearest-neighbour (nnn) exchange interaction J_2. Indeed, if we neglect magnetic interactions between more remote magnetic ions (we show later in this paper that they are not relevant), T_N is given by

$$T_N = -6\frac{2S(S+1)}{3k_B}J_2 \qquad (7)$$

within the MFA, and is therefore independent of J_1. According to this feature, the magnetic percolation threshold for type II antiferromagnetic ordering upon the dilution of the magnetic ions is of the order of magnitude of the site percolation threshold for the lattice built by nnn magnetic sites, namely, the simple cubic lattice, which is $p_c = 0.3$ [9]. Indeed, this compares with the experimental value $x_c \approx 0.5$ we have determined here in $La_{1-x}Gd_xTe$. Qualitatively, the difference between p_c and x_c arises mainly from the fact that the percolation argument omits the concept of frustration. The type II antiferromagnet is not frustrated when it is not diluted (note that T_N in Eq. (7) is not reduced by any frustration effect). However, the type II ordering implies that $J_2 < 0$, and frustration of the nnn antiferromagnetic interactions takes place upon dilution. This frustration hinders the magnetic ordering, and hence $x_c > p_c$. The hypothesis that purely geometrical arguments alone (percolation and frustration) are responsible for the onset of the spin glass phase at x_c is supported by the fact that the numerical value of $x_c = 0.5$ is characteristic of diluted type II antiferromagnets. For instance, this is the value of x_c found in various metals such as $La_{1-x}Gd_xTe$ metal (present work), where the magnetic interactions are long range, and in insulators such as $Eu_xSr_{1-x}Te$ [4] and $Eu_xYb_{1-x}Te$ [5], where the exchange interactions are short range. Therefore, x_c is not sensitive to the range of the magnetic interaction. This provides evidence that the next-nearest-neighbour antiferromagnetic interaction only is the relevant parameter in type II antiferromagnets. It also does not matter whether the matrix is antiferromagnetic (like EuTe in the cases just mentioned) or ferromagnetic such as EuS. For instance, the same value of x_c is observed in $Eu_xSr_{1-x}S$ [4]. In EuTe, the antiferromagnetism comes from the dominant antiferromagnetic interactions J_2. The ferromagnetism in EuS is due to ferromagnetic interactions J_1 between nearest neighbours, although the nnn interactions are antiferromagnetic, as J_1 is larger than J_2 in absolute value. But the spin glass ordering upon diluting magnetic Eu^{2+} ions by non-magnetic Sr ions still comes from the frustration associated with the antiferromagnetic nnn interactions. Note also that the value of x_c is the same in $Eu_xSr_{1-x}S$ or $Eu_xSr_{1-x}Te$, which are insulators, as in $Eu_xLa_{1-x}S$ [10], which is metallic. Therefore, neither the range of the magnetic interactions, nor the carrier concentration plays a significant role in the determination of x_c. That purely geometrical effects (dilution of nnn antiferromagnetic interactions and the related frustration effects in an fcc lattice) play dominant roles is also supported by the fact that x_c is indeed sensitive to the geometry. For instance, spin dilution in rare earths which crystallize in a hexagonal structure and order in a spiral magnetic structure have quite different x_c. In this case, Child et al. found that the long-range magnetic ordering temperature scales with the magnetic energy in the MFA, so that $x_c \approx 0$, which is indeed very far from 0.5 [11]. Monte Carlo simulations are now in progress to explore these frustration effects on a more quantitative basis.

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