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Magnetic and electrical transport properties of Gd_2CoGe_6 and Tb_2CoGe_6 germanides

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ABSTRACT

The low-temperature physical properties of two intermetallics, Gd_2CoGe_6 and Tb_2CoGe_6, crystallizing with the orthorhombic Ce_2CuGe_6-type structure, have been studied by means of magnetization and electrical resistivity measurements. The magnetic behavior of these compounds involves the presence of magnetic moments on the rare earth and cobalt atoms sites. Both phases have been found to order antiferromagnetically below 20 and 22 K, respectively. In each case, complex behavior of the magnetic susceptibility in the ordered state hints at some changes in the magnetic structure on decreasing the temperature. The two compounds exhibit metallic-type electrical conductivity.

1. Introduction

Homologous series of rare-earth (R) intermetallics with the general composition R_2TGe_6 have been reported to form with various d-electron transition metals T = Cu, Ag, Au, Pd, Pt [1], Ni [2], and Co [3]. These phases crystallize with an orthorhombic crystal structure of the Ce_2CuGe_6-type (space group *Amm2*), which can be described as an ordered stacking of the AlB_2-, $BaAl_4$-, αPu-, and $ZrSi_2$-type slabs [4]. Isotypic ternary germanide Ce_2MnGe_6 was found in the Ce–Mn–Ge system [5], and recently the crystal structure and magnetic properties investigations were reported for La_2MnGe_6 [6]. Most of the hitherto studied R_2TGe_6 compounds order antiferromagnetically at low temperatures [2,7–13]. Sometimes they show fairly complex magnetic behavior, possibly related to the presence of two crystallographically inequivalent sublattices of magnetic R atoms.

In this paper we report for the first time on the physical behavior of two isotypic compounds, namely Gd_2CoGe_6 and Tb_2CoGe_6.

2. Experimental details

Polycrystalline samples of Gd_2CoGe_6 and Tb_2CoGe_6 were synthesized by arc-melting the elemental constituents (nominal purities: Gd, Tb – 99.9 wt.%, Co – 99.99 wt.%, Ge – 99.999 wt.%) on a water-cooled copper hearth in titanium-gettered argon atmosphere. The ingots were turned over and re-melted a few times to ensure good homogeneity. Subsequently, the buttons were sealed in evacuated quartz tubes and annealed at 600 °C for two months. Finally the products were quenched in cold water.

The sample quality was examined by X-ray powder diffraction at room temperature on a DRON-2.0 m powder diffractometer using Fe K_α radiation. The phase analysis was carried out and the lattice parameters were determined using the CSD software package [14].

Magnetic measurements were performed in the temperature range 1.72–400 K and in external fields up to 5 T using a Quantum Design MPMS-5 SQUID magnetometer. The electrical resistivity was measured over the temperature interval 4.2–300 K employing the standard dc four-probe technique.

3. Results

The X-ray powder diffraction measurements revealed that the two compounds investigated crystallize with orthorhombic unit cells of the space group *Amm2*. The lattice parameters derived from the X-ray pattern of Gd_2CoGe_6 are $a = 0.3956(4)$ nm, $b = 0.4016(4)$ nm and $c = 2.1495(2)$ nm, while those refined for Tb_2CoGe_6 are $a = 0.3938(1)$ nm, $b = 0.4006(1)$ nm and $c = 2.1408(4)$ nm. No foreign Bragg peaks were observed, hence indicating single-phase character of the obtained samples.

The magnetic properties of Gd_2CoGe_6 and Tb_2CoGe_6 are displayed in Fig. 1. Above 20 K, the inverse magnetic susceptibility of the former compound exhibits a straight-line behavior that can be well described by the Curie–Weiss (CW) formula, $\chi_m(T) = C/(T - \theta_p)$, where C is the Curie constant, and θ_p is the paramagnetic Curie temperature. The least-squares fitting to the experimental data yielded $C = 17.47$ (emu K)/mol and $\theta_p = -8.0$ K. Similar approximation of the $\chi_m(T)$ curve of Tb_2CoGe_6 is possible only above about 100 K, and the so-derived parameters are $C = 25.03$ (emu K)/mol and $\theta_p = -13.8$ K. The limited applicability of the CW law to the latter compound likely arises from crystalline electric field (CEF) interactions, which cause splitting of the 13-fold degenerated $^7F_6$ ground

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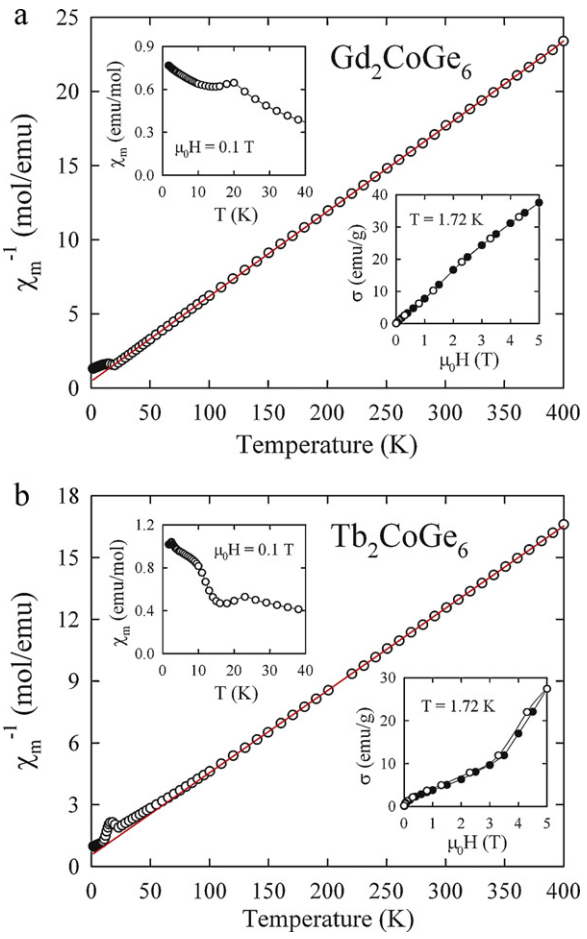

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility of (a) Gd_2CoGe_6 and (b) Tb_2CoGe_6. The solid lines represent the Curie–Weiss fits described in the text. The upper insets show the magnetic susceptibility at low temperatures. The lower insets present the field dependence of the magnetization taken at 1.72 K with increasing (full circles) and decreasing (open circles) magnetic field strength.

multiplet of Tb^{3+} ions in the electrostatic potential due to neighboring atoms. Such an effect is not observed for Gd_2CoGe_6 because trivalent gadolinium ions have the angular momentum $L = 0$ (the ground multiplet $^8S_{7/2}$ can be split in magnetic field only).

For both compounds, the derived Curie constant C is distinctly larger than the respective value calculated with the Russell–Saunders L–S coupling scenario for free Gd^{3+} and Tb^{3+} ions. This finding signals that the magnetic properties of Gd_2CoGe_6 and Tb_2CoGe_6 are probably governed not only by the magnetic moments carried on the rare-earth ions but also by the magnetic moments of cobalt. Setting $C = (1/8)[2(\mu_{eff}^{R})^2 + (\mu_{eff}^{Co})^2]$ and assuming that the rare-earth contributions (the first term) are equal to the theoretical L–S values, i.e. $\mu_{eff}^{Gd} = 7.94\,\mu_B$ and $\mu_{eff}^{Tb} = 9.72\,\mu_B$, one obtains the effective magnetic moment due to cobalt (the second term) to be $3.70\,\mu_B$ in Gd_2CoGe_6 and $3.36\,\mu_B$ in Tb_2CoGe_6. These values can be compared with the spin-only effective moment of Co^{2+} ion ($\mu_{eff}^{Co} = 3.87\,\mu_B$) with the electronic ground state $^4F_{9/2}$. Though the experimental values of μ_{eff}^{Co} are somewhat smaller than the theoretical one, the contributions due to cobalt to the magnetic susceptibility of the two ternaries are instantly recognizable.

The negative values of the paramagnetic Curie temperatures in Gd_2CoGe_6 and Tb_2CoGe_6 hint at significant antiferromagnetic correlations that eventually may give rise to long-range magnetic ordering. Indeed, as demonstrated in the upper insets to Fig. 1a and b, respectively, for both compounds, the magnetic susceptibility $\chi_m(T)$ shows a maximum that signals the onset of antiferromagnetic state. The so-defined Neel temperatures T_N are 20 K and 22 K for Gd_2CoGe_6 and Tb_2CoGe_6, respectively. In the ordered state, the magnetic susceptibility does not decrease with decreasing temperature, as would be expected for a simple antiferromagnet. Instead, below a shallow minimum near 15 K, the $\chi_m(T)$ variation of Gd_2CoGe_6 exhibits a monotonic upturn, while that of Tb_2CoGe_6 shows a kink at 10 K (the little feature seen near 2 K is probably due to tiny admixture of Tb_2O_3 [15]). This fairly complex behavior seen for each compound may suggest some changes in their magnetic structures occurring on decreasing the temperature.

The antiferromagnetic nature of the ordered state in Gd_2CoGe_6 and Tb_2CoGe_6 is reflected in characteristic shapes of the magnetization isotherms taken at 1.72 K (see the lower insets to Fig. 1). In weak magnetic fields, the $\sigma(H)$ curve of the Gd-based material exhibits a straight-line behavior up to about 1.5 T, at which field a spin-flop transition takes place, i.e. the antiparallel magnetic moments reorient perpendicular to the applied field. Similar effect, yet much better pronounced, is observed for Tb_2CoGe_6 near $\mu_0H = 3.2$ T. Another feature revealed for the latter phase is some small spontaneous magnetization seen in weak fields and little hysteresis in $\sigma(H)$ noticeable in strong fields. Both effects hint at the presence of tiny ferromagnetic contribution to the magnetization at 1.72 K. Attributing this weak ferromagnetic signal to an intrinsic behavior of Tb_2CoGe_6 it might be considered as an evidence for canted or non-collinear antiferromagnetic arrangement of the terbium magnetic moments at this temperature. Another possible explanation involves some small ferri- or ferromagnetic component due to the cobalt sublattice.

Fig. 2 shows the temperature dependencies of the electrical resistivity of Gd_2CoGe_6 and Tb_2CoGe_6. Both compounds exhibit metallic character of the electronic transport, reflected in the magnitudes of the resistivity measured at room temperature and the overall shapes of the $\rho(T)$ curves. In the paramagnetic region, the resistivity data of Gd_2CoGe_6 can be well approximated by the Bloch–Grüneissen–Mott (BGM) formula [16]

$$\rho(T) = (\rho_0 + \rho_0^{\infty}) + 4RT\left(\frac{T}{\Theta_R}\right)^4 \int_0^{\Theta_R/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} - KT^3$$

where the first term represents the scattering of conduction electrons on static defects in the crystal lattice (residual resistivity ρ_0) and on disordered magnetic moments (spin-disorder resistivity ρ_0^{∞}), the second term describes the phonon contribution to the total resistivity (the parameter Θ_R is considered as a measure of the Debye temperature Θ_D), and the third one accounts for Mott-type interband scattering processes. The least-squares fitting of the above equation to the experimental data of yielded the parameters: $\rho_0 + \rho_0^{\infty} = 101.7\,\mu\Omega$ cm, $R = 0.595\,\mu\Omega$ cm/K, $\Theta_R = 254.1$ K and $K = -7.5 \times 10^{-7}\,\mu\Omega$ cm/K^3.

As the BGM approach neglects crystalline electric field interactions, essentially it is applicable to magnetic systems solely in the temperature range, in which the CEF effect is negligible (i.e. the spin-disorder resistivity can be assumed independent of temperature). In the case of Tb_2CoGe_6, the magnetic susceptibility data suggested that the entire $^7F_6$ multiplet is thermally well populated above about 100 K. Consequently, the BGM expression was fitted to the experimental data in this high temperature region only (see the solid line in Fig. 2b). The so-derived values of the parameters are as follows: $\rho_0 + \rho_0^{\infty} = 163.0\,\mu\Omega$ cm, $R = 1.118\,\mu\Omega$ cm/K, $\Theta_R = 234.1$ K and $K = -22.1 \times 10^{-7}\,\mu\Omega$ cm/K^3. Worth noting is that the value of Θ_R is fairly similar to that estimated for Gd_2CoGe_6, as expected for isostructural systems, thus proving correctness of the analysis performed.

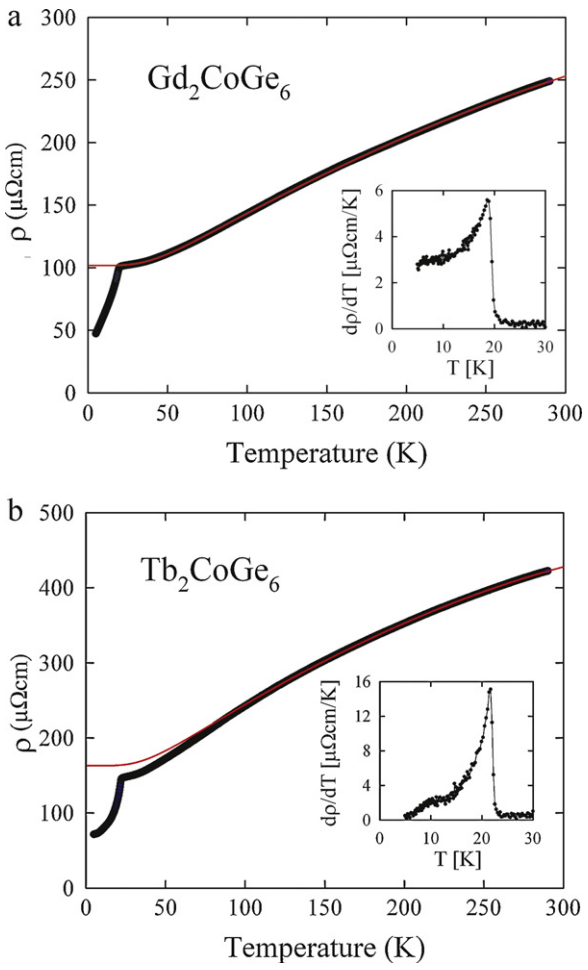

Fig. 2. Temperature dependence of the electrical resistivity of (a) Gd_2CoGe_6 and (b) Tb_2CoGe_6. The solid lines are the Bloch–Grüneisen–Mott fits described in the text. The insets display for each compound the temperature derivative of the electrical resistivity in the vicinity of the antiferromagnetic phase transition.

The onsets of the antiferromagnetic ordering in Gd_2CoGe_6 and Tb_2CoGe_6 manifest themselves as distinct kinks on the $\rho(T)$ variations at $T_N = 20$ and 22 K, respectively, which give rise to sharp lambda-like maxima in the temperature derivative of the resistivity (see the insets to Fig. 2). For the Tb-based compound, an additional anomaly in $d\rho/dT(T)$ is visible near 10 K, and this finding supports the hypothesis on the order–order transition anticipated from the magnetic susceptibility data (see above). In turn, the resistivity of Gd_2CoGe_6 rapidly decreases down to the lowest temperatures available in the performed experiment (note large magnitude of $d\rho/dT$), hence subsequent magnetic transition in the ordered state beyond the studied temperature range seems also likely.

4. Conclusions

The two compounds studied in the present work, i.e. Gd_2CoGe_6 and Tb_2CoGe_6, were found to order antiferromagnetically at $T_N = 20$ and 22 K, respectively. Moreover, both phases likely exhibit subsequent magnetic transitions at $T_t < 1.72$ K for the Gd-based germanide and $T_t \approx 10$ K for the Tb-based one. Regarding this behavior they are quite similar to their Cu-containing counterparts Gd_2CuGe_6 ($T_N = 20.6$ K, $T_t < 1.72$ K) and Tb_2CuGe_6 ($T_N = 33.1$ K, $T_t = 8.5$ K) [7]. However, in relation to the latter ternaries, the magnetic structures in Gd_2CoGe_6 and Tb_2CoGe_6 may be even more complex because of the anticipated contribution due to the magnetic Co-sublattice. Neutron diffraction experiments are required to determine the magnetic structures in both compounds.

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