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Magnetic and Electronic Properties in Series of GdT_xGa_{4-x} Solid Solutions (T = Ni or Cu)

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We present results of extensive measurements of magnetic susceptibility, electrical resistance, specific heat and thermoelectric power of two series of solid solutions $GdNi_xGa_{4-x}$ and $GdCu_xGa_{4-x}$, for ranges of doping x from 0.6 to 1 and from 1 to 1.5, respectively. All studied phases display the Curie–Weiss behaviour of magnetic susceptibility and antiferromagnetic ordering at temperatures below 23 K. Substitution of gallium with transition metal atoms has strong influence on Néel temperatures of all studied phases, shifting them by few K, depending on x. Metamagnetic-like anomalies are observed for some compositions. Behaviour of the electrical resistivity reveals metallic nature of all samples. Their magnetic ordering is reflected in low-temperature anomalies of the resistivity and the heat capacity.

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1. Introduction

Solid solutions RT_xGa_{4-x} with $BaAl_4$-type crystal structure have been studied for many combinations of R and T (denoting rare-earth and transition metal, respectively) and often for wide ranges of doping x [1–7]. However, those based on gadolinium seem almost neglected, since crystallographic data and magnetic properties have been reported only for $GdNiGa_3$ [3] and $GdCu_{1.25}Ga_{2.75}$ [4]. Both alloys adopt the $BaAl_4$-type crystal structure and are paramagnetic above 80 K with the Curie–Weiss magnetic susceptibility characterized by the effective magnetic moments very close to the free Gd^{3+} ion value. At low temperatures, $GdNiGa_3$ and $GdCu_{1.25}Ga_{2.75}$ order antiferromagnetically with Néel temperatures of 15 and 10 K, respectively [3, 4]. Studies of Gd-based solutions are important since they can provide valuable background information for examination of analogous compositions with rare-earth possessing unstable $4f$-electronic states.

Here, we present a more extended study of the physical properties of two series of solid solutions: $GdNi_xGa_{4-x}$ and $GdCu_xGa_{4-x}$, with x ranging from 0.6 to 1 and from 1 to 1.5, respectively.

2. Experimental details

Polycrystalline samples of $GdNi_xGa_{4-x}$ and $GdCu_xGa_{4-x}$ solid solutions were synthesized from high purity elements by electric arc melting. X-ray powder diffraction analysis confirmed isotypism of all compositions, with the expected $BaAl_4$-type crystal structure. Derived lattice parameters were similar to those reported before [3, 4], and their variation with changing composition parameter, x, never exceeded 1%.

Magnetic susceptibility measurements were carried out in the temperature range 1.72–400 K and in magnetic fields up to 5 T using a Quantum Design SQUID magnetometer. Resistivity and heat capacity measurements were performed in the temperature interval from 0.4 K to 300 K with a Quantum Design Physical Property Measurement System (PPMS). The thermoelectric power was studied from 5 K to room temperature by static-differential method using a home-made setup (with uncertainty of about 0.2 μV/K).

3. Results and discussion

The magnetic properties of the $GdNi_xGa_{4-x}$ and $GdCu_xGa_{4-x}$ series are summarized in Fig. 1. All the studied alloys exhibit the Curie–Weiss behaviour at temperatures above 40 K. The experimental effective magnetic moments, μ_{eff}, are very close to the free Gd^{3+} ion value. At low temperatures, the magnetic susceptibility curves $\chi(T)$ show distinct anomalies (maxima or kinks), which signal antiferromagnetic ordering (upper-left insets). The Néel temperatures, T_{N}, were derived from these anomalies, using Fisher's criterion (as corresponding to maxima in $\mathrm{d}(\chi(T)T)/\mathrm{d}T$) [8]. In the ordered state, some upturns in the magnetic susceptibility are observed, which hint at complex spin arrangement in the background state. Characteristic parameters derived from the magnetic susceptibility data are given in Table.

Field dependences of the magnetization, σ, recorded at $T = 1.72$ K are shown in bottom-right insets in Fig. 1. They are linear in weak magnetic fields, as expected for antiferromagnets, and show moderate changes in slope in fields above 1 T. The latter anomalies probably arise due to metamagnetic-like reorientation of magnetic moments. The $\sigma(H)$ isotherm measured for $GdNi_{0.6}Ga_{3.4}$ has a slightly convex shape, with a tendency to saturation in strong magnetic fields. This feature, together with a distinct upturn in $\chi(T)$, hints at more complex spin arrangement in the magnetic ground state.

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TABLE

Parameters characterizing the magnetic properties of $GdNi_xGa_{4-x}$ and $GdCu_xGa_{4-x}$ solutions: effective moment, $\mu_{\rm eff}$, Curie-Weiss temperature, θ, and Néel temperature, $T_{\rm N}$ (derived by method described in Ref. [8].

Formula	$\mu_{\rm eff}$ [$\mu_{\rm B}$]	θ [K]	$T_{\rm N}$ [K]
$GdNi_{0.6}Ga_{3.4}$	7.94	–17.6	9.5
$GdNi_{0.8}Ga_{3.2}$	8.09	–20.7	13
$GdNiGa_3$	8.16	–14.4	13
$GdCuGa_3$	7.99	–11.8	8.7
$GdCu_{1.2}Ga_{2.8}$	7.87	–12.3	8.2
$GdCu_{1.4}Ga_{2.6}$	8.07	–11.3	15.5
$GdCu_{1.5}Ga_{2.5}$	8.03	–2.2	19.5

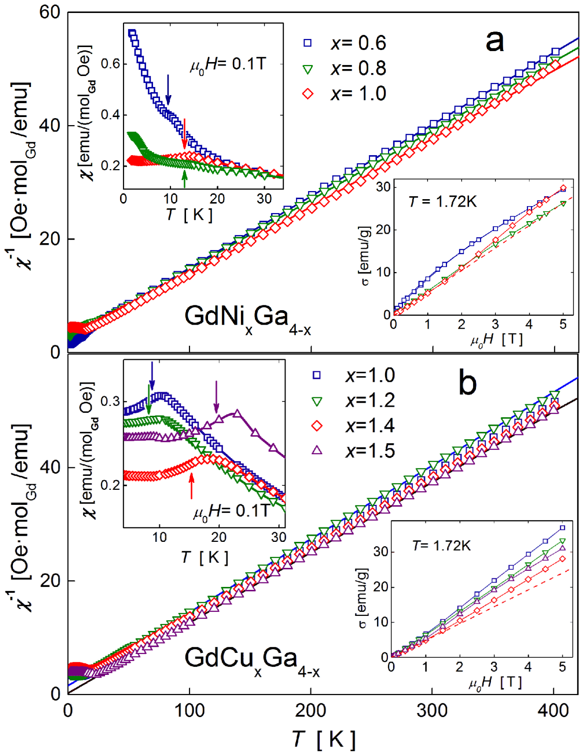

Fig. 1. Temperature variations of the inverse magnetic susceptibility of (a) $GdNi_xGa_{4-x}$ and (b) $GdCu_xGa_{4-x}$ series (straight lines represent fitted Curie-Weiss functions). Upper-left insets: low-temperature dependences of magnetic susceptibility (arrows indicate Néel temperatures). Bottom-right insets: field dependences of magnetization at $T = 1.72$ K. Dashed lines emphasize metamagnetic-like anomalies in two compositions.

The electrical resistivity of all the $GdNi_xGa_{4-x}$ and $GdCu_xGa_{4-x}$ samples studied had very similar magnitude at room temperature (between 85 and 105 $\mu\Omega$ cm), so for the clarity it is presented in Fig. 2 in normalized units. All the alloys show metallic-like behaviour with fairly large residual resistivity values, which reflect strong atomic disorder resulting from inherent random occupation of atomic sites by Ga and Ni or Cu. At low temperatures, the resistivity curves display distinct anomalies, which correspond to the occurrence of the magnetic ordering below the Néel temperatures derived from the magnetic data.

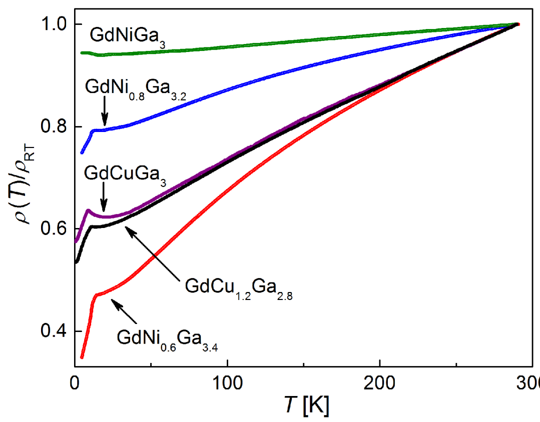

Fig. 2. Temperature variations of the electrical resistivity of $GdNi_xGa_{4-x}$ and $GdCu_xGa_{4-x}$ alloys, normalized to room temperature values.

The specific heat, C_p, was measured for $GdNi_{0.8}Ga_{3.2}$ and three $GdCu_xGa_{4-x}$ alloys (see Fig. 3). For all these samples the data taken above 40 K are nearly identical (for clarity a single curve is shown). In this temperature range, $C_p(T)$ could be very well fitted with the standard formula that takes into account the electronic (γT) and the phonon (combined Debye and Einstein modes) contributions. Fitted number of atoms obeying the Debye mode was 4 and that of the Einstein modes was 2. This may indicate that heavier Gd atoms behave like the Einstein oscillators with two degrees of freedom, related to intrinsic anisotropy of tetragonal crystal structure, whereas Ga and Cu or Ni obey the Debye regime.

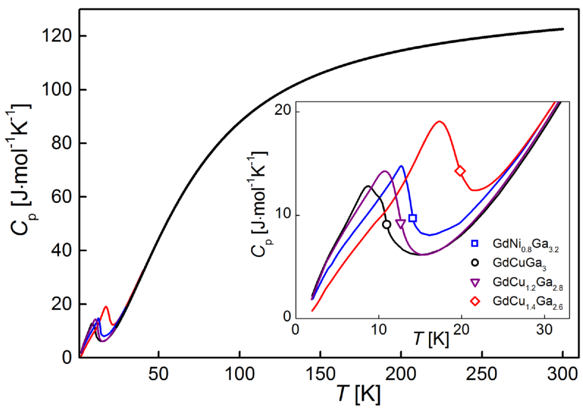

Fig. 3. Temperature variation of the specific heat of $GdNi_{0.8}Ga_{3.2}$ and $GdCuNi_xGa_{4-x}$. Inset shows behaviour at lower temperatures, reflecting the magnetic ordering.

Characteristic temperatures obtained from these fits are: $\theta_D = 287(\pm 2)$ K (Debye) and $\theta_E = 80(\pm 5)$ K (Einstein). Sommerfeld coefficients, γ, are almost identical for all four alloys with values of about 40 mJ mol^{-1} K^{-2} (see Fig. 4).

At lower temperatures, close to T_{N} values determined from the magnetic data, prominent lambda-shaped maxima in $C_p(T)$ reflect the transitions to the antiferromagnetically ordered states (inset to Fig. 3). At a few K below T_{N} there appear hump-like anomalies, which can be more clearly observed in the C_p/T versus T dependences shown in Fig. 4 separately for each sample. These features can be attributed to a removal of the eightfold degeneracy of the $^8\mathrm{S}_{7/2}$ multiplet of the Gd^{3+} ions exposed to internal magnetic exchange field.

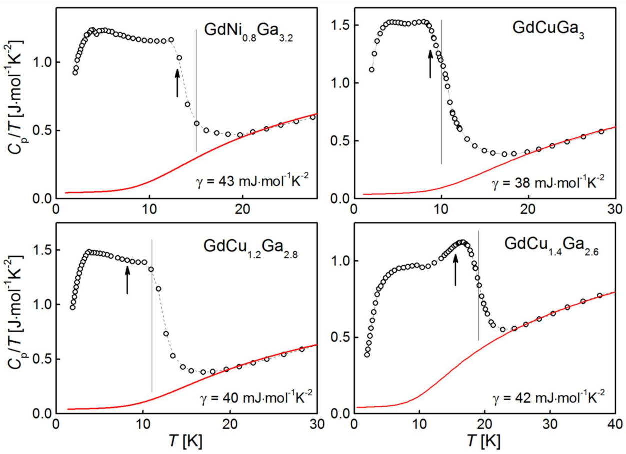

Fig. 4. Low-temperature specific heat of $\mathrm{GdNi_{0.8}Ga_{3.2}}$ and $\mathrm{GdCuNi}_x\mathrm{Ga}_{4-x}$. Solid lines represent least-squares fits of the sums of the electronic and phonon contributions (see text). Values of the Sommerfeld coefficient γ derived from the fits are given for each sample. Arrows mark T_{N} collected in Table, vertical lines — positions of maxima in $\chi(T)$.

The temperature dependences of the thermoelectric power, S, of $\mathrm{GdNi_{0.6}Ga_{3.4}}$ and $\mathrm{GdNiGa_3}$ are presented in Fig. 5.

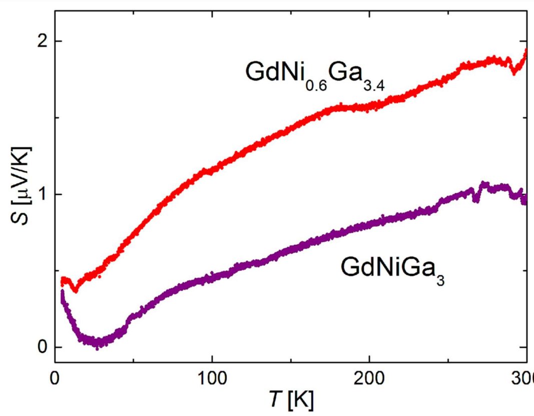

Fig. 5. Temperature variations of the thermoelectric power of $\mathrm{GdNi_{0.6}Ga_{3.4}}$ and $\mathrm{GdNiGa_3}$.

For both samples, the Seebeck coefficient is positive and its magnitude does not exceed 2 μV/K in the whole temperature range from 5 to 300 K. No obvious anomalies are observed in $S(T)$ at the magnetic phase transitions.

4. Conclusions

The solid solutions belonging to the $\mathrm{GdNi}_x\mathrm{Ga}_{4-x}$ and $\mathrm{GdCu}_x\mathrm{Ga}_{4-x}$ series are all metals with high residual electrical resistivity, resulting from atomic disorder of Ni or Cu randomly occupying its sites together with Ga atoms. The paramagnetic state is characterized by the localized magnetic moments of Gd^{3+} ions and negative paramagnetic Curie temperatures due to antiferromagnetic interactions. At temperatures below 23 K, there are anomalies observed in the temperature dependences of the electrical resistivity, the magnetic susceptibility and the specific heat, which correspond to the occurrence of antiferromagnetic ordering. Substitution of gallium with transition metal atoms has strong influence on Néel temperatures of all studied phases, shifting them by few K, depending on x. Since the electronic state at lowest temperatures does not change significantly (as γ values are almost independent of x), most likely the effects on θ, T_{N} and low temperature spin arrangements originate from changing strength of the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction caused by varying concentration of conduction electrons.

Acknowledgments

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