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Magnetic and related properties of the solid solution $CeCu_xGa_{4-x}$

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ABSTRACT

Physical properties of polycrystalline samples of $CeCu_xGa_{4-x}$ ($x = 0.2$–1.4), crystallizing in the tetragonal $BaAl_4$-type structure (space group I 4/mmm), were studied by means of X-ray powder diffraction, magnetization, specific heat, electrical resistivity and magnetoresistivity measurements in wide temperature and magnetic fields ranges. The unit-cell volume of the system was found to decrease with increasing x (in total by about 4%) but the magnetic moments of Ce^{3+} ions remain localized in the whole x-range studied. The alloys exhibit ferromagnetic order at low temperatures, which manifests itself as distinct and relatively sharp anomalies in all the temperature characteristics measured. The ordering temperature decreases with increasing the Cu content from 5.5(1) K for $x = 0.2$ down to 1.35 (5) K for $x = 1.4$, and the electrical transport properties of the system show some features characteristic of Kondo lattices.

1. Introduction

The exchange-interaction integral, which describes the strength of hybridization between localized (d or f) and delocalized (conduction) electrons, is believed to be the main factor governing magnetic ground states in Ce-based intermetallics [1]. It is commonly known that its value can be modified by applying hydrostatic pressure or external magnetic field, or by changing chemical composition. In the latter case, atoms of one chemical element are partly substituted in the crystal structure with atoms of another element of similar chemical character. In most cases, such studies are limited to dilution of a magnetic sublattice or electron/hole doping into a nonmagnetic sublattice aimed at tuning unit cell volume. In turn, swapping p-electron atoms with d-electron ones, which might imply distinct modifications in the strength of f-(p,d)-hybridization, has so far been rather rarely applied.

The system $CeCu_xGa_{4-x}$ is an ideal candidate to perform $p \rightarrow d$ substitutions. It forms with the tetragonal $BaAl_4$-type structure (space group $I4/mmm$, no. 139) [2], in which Ce atoms form a body-centered unit cell and the Cu and Ga randomly occupy two crystallographic sites within three adjacent atomic layers, i.e. Ce–Cu/Ga(1)–Cu/Ga(2)–Cu/Ga(1)–Ce (see Fig. 1). For $x = 1.0$ this atomic disorder can be entirely removed by formation of an ordered noncentrosymmetric $BaNiSn_3$-type structure (space group $I4/mm$, no. 107), in which the sequence of layers is Ce–Ga(1)–Ga(2)–Cu(1)–Ce–Ga(1)–Ga(2)–Cu(1)–Ce [3,4].

Previously, the physical properties of $CeCu_xGa_{4-x}$ have been studied for few concentrations and only at temperatures higher than the boiling point of liquid ^{4}He. In this temperature range, a long-range ferromagnetic order was evidenced for the alloys with x ranging from 0.5 (T_C=6 K) to 0.8 (T_C=4.8 K) [2,5,6]. Moreover, some ferromagnetic-like features were found in the specific heat and electrical resistivity data of specimens with higher Cu content (up to x= 1.5) [5,7]. In parallel, distinct Kondo-like behavior in the electrical resistivity was observed [5,7,8]. Interestingly, for x= 1.0 (i.e. $CeCuGa_3$) several different magnetic ground states have been proposed: paramagnetic behavior down to 0.4 K [9], antiferromagnetic order at 1.9 K [10], incommensurate magnetic structure below 1.25 K [3] and ferromagnetic order at 4.0 K [4], signalling non-trivial properties of the system.

In this paper we present the results of our systematic re-investigation of the solid solution $CeCu_xGa_{4-x}$ by means of X-ray powder diffraction, magnetization, specific heat, electrical resistivity and magnetoresistivity, extended for selected compositions down to about 0.4 K.

2. Material and methods

Polycrystalline $CeCu_xGa_{4-x}$ alloys with the nominal composition x= 0–2 were prepared by conventional arc-melting the stoichiometric amounts of constituents (with purity at least 99.5%) under protective purified-argon atmosphere. Products were subsequently wrapped with tantalum foil, sealed in evacuated silica tubes and homogenized at 800 °C for 2 weeks. Quality of samples was verified by means of X-ray powder diffraction

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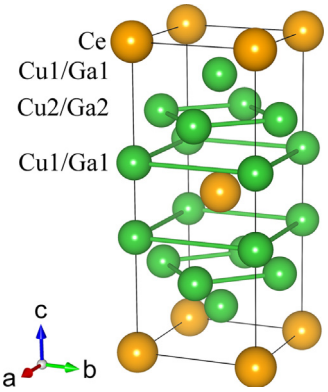

Fig. 1. Crystal structure of $CeCu_xGa_{4-x}$. For details see Section 3.1 and Ref. [2].

(Xpert Pro PANalytical diffractometer with Cu Kα radiation). The obtained patterns were analyzed using the Rietveld refinement implemented into the Fullprof software [11].

Magnetization was measured using a commercial SQUID (Superconducting Quantum Interference Device) magnetometer at temperatures 1.7–300 K and in magnetic fields up to 5 T. Specific heat and electrical resistivity of bar-shaped samples were measured in a Quantum Design PPMS (Physical Property Measurement System) platform at temperatures down to 0.35 K and in magnetic fields up to 9 T. Thermoelectric power was studied by static differential method using a home-made device, from 5 K to room temperature, with a temperature gradient of 2 K.

3. Results and discussion

3.1. Crystal structure

The analysis of X-ray powder diffraction patterns confirmed that the solid solution $CeCu_xGa_{4-x}$ exists only in a limited composition range [2]. In particular, only the samples with $0.2 \le x \le 1.4$ were found to be single-phase and their patterns were easily described within the tetragonal $BaAl_4$-type structure (space group $I4/mmm$, no. 139) [2]. All other compositions appeared to be multiphase.

As can be inferred from Fig. 2, partial substitution of Ga by Cu atoms in $CeCu_xGa_{4-x}$ results in a monotonic decrease of the lattice parameters a and c, and hence also in the monotonic compression of the unit-cell volume V. The total change in V between the two terminal compositions ($x=$ 0.2 and 1.4) is of about 4%. Nearly constant c/a ratio shows that the shape of the unit cell of the system is not deformed. Our observations are in agreement with the previous reports [2,7].

3.2. Magnetic properties

Fig. 3(a) shows the temperature variation of the inverse magnetic susceptibility χ_m^{-1} for selected compositions of $CeCu_xGa_{4-x}$ (the other ones are omitted for clarity). At elevated temperatures the $\chi_m^{-1}(T)$ curves show a linear behavior and above $\approx$ 100 K can be described using a Curie–Weiss law with the effective magnetic moment μ_{eff} of about $2.4-2.5\ \mu_B$ and positive paramagnetic Curie temperature θ_p of the order of a few kelvins (see the solid lines in Fig. 3(a)). The obtained values of μ_{eff} are close to that expected for a free Ce^{3+} ion (i.e. $2.54\ \mu_B$) and imply the presence of well localized magnetic moments. The positive values of θ_p suggest a ferromagnetic character of the exchange interactions between the magnetic moments. In line with this observation, distinct Brillouin-like anomalies visible in temperature dependence of the magnetization

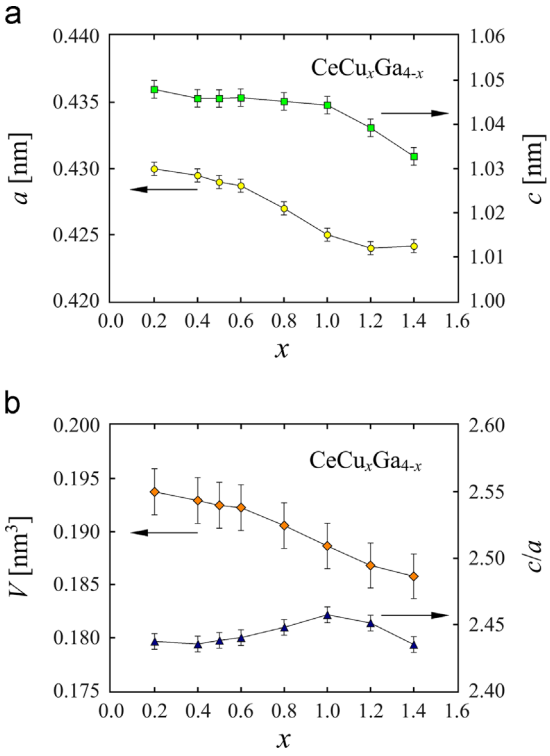

Fig. 2. (a) Lattice parameters a and c, and (b) unit–cell volume V and c/a ratio of $CeCu_xGa_{4-x}$ as a function of Cu-concentration x. Solid lines serves as guides for the eye.

M of the solid solution with $x \le 0.8$ (Fig. 3(b)) clearly manifest ferromagnetic phase transitions. For $x \ge 1.0$ (not shown here) no similar anomaly in $M(T)$ was observed down to 1.7 K.

3.3. Specific heat

The ferromagnetic phase transitions in $CeCu_xGa_{4-x}$ with $x=$ 0.4–0.8 (Fig. 3(b)) manifest themselves as sharp lambda-shaped anomalies in $C_p(T)/T$ (see Fig. 4(a)). Remarkably, very similar specific heat anomalies are seen also for $x \ge 1.0$. Presumably, the latter features are also due to bulk long-range ferromagnetic orderings, which set in below the lowest accessible temperature in the performed magnetization studies.

Fig. 4(b) displays the 4*f*-derived specific heat of a few $CeCu_xGa_{4-x}$ alloys obtained by subtracting from the total specific heat the phonon and conduction-band electron contribution represented by $C_p(T)$ of their isostructural non-*f*-electron counterpart $LaCuGa_3$ (cf. Fig. 4(a)). The composition $x = 1$ of the phonon analogue was chosen arbitrary assuming that the phonon spectra of the other references, $LaCu_xGa_{4-x}$, do not differ significantly from each other. In the paramagnetic region, the so-obtained $\Delta C_p(T)/T$ curves show broad humps located at $T_{max} \approx 20$–30 K, which probably originate from Schottky effect. Generally, the crystalline electric field contribution to the specific heat can be represented by the formula:

$$C_{Sch}(T) = R\frac{\sum_i e^{-E_i/T}\sum_i E_i^2 e^{-E_i/T} - \left(\sum_i E_i e^{-E_i/T}\right)^2}{T^2\left(\sum_i e^{-E_i/T}\right)^2}, \quad (1)$$

where R is the gas constant and E_i is the energy of the i'th level of the m-level system ($i = 1, 2, \ldots m$) expressed in kelvins [12]. In the case of Ce^{3+} ions placed in a non-cubic environment, the number of levels is reduced to three doublets with relative energies $E_1 \equiv 0$, E_2 and E_3. As for $CeCu_xGa_{4-x}$ the Schottky peak in $\Delta C_p(T)/T$ is located in the proximity of the magnetic phase transition, in which the presence of short-range correlations must be taken into account. As can be noticed