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Suppression of ferromagnetism in solid solution $CePd_xGa_{4-x}$

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ABSTRACT

In order to extend our knowledge on effects of substitution of gallium by transition metal in solid solutions of gallides with the tetragonal $BaAl_4$-type crystal structure we studied physical properties of polycrystalline samples of $CePd_xGa_{4-x}$ ($x = 0.2–0.8$). X-ray diffraction confirmed that the unit-cell volume of the system changes in a non-monotonic way with a maximum around $x^* = 0.6$. We performed magnetization, specific heat, electrical resistivity and thermoelectric power measurements in wide temperature and magnetic field ranges. Magnetic moments of Ce^{3+} ions are very close to the value corresponding to the localized 4*f*-state in the whole *x*-range covered, yet their variation with *x* coincides with that of lattice parameters, with a minimum close to x^*. The alloys order ferromagnetically at low temperatures, which causes distinct anomalies of the measured properties. The ordering temperature decreases with increasing the Pd content from 3.7 K for $x = 0.2$ down to 1.3 K for $x = 0.8$. The results suggest that no quantum critical transition can be approached within the solid solution existence range.

1. Introduction

Changing chemical composition while preserving the crystal symmetry, is an effective method to modify the strength of hybridization between localized (*d* or *f*) and delocalized (conduction) electrons, which is considered as the main factor governing magnetic ground state in Ce-based intermetallics [1]. However, partial substitution of a chemical element with another one is usually 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 for *d*-electron ones, which might imply distinct modifications in the strength of *f*-(*p*,*d*)-hybridization, has so far been rather rarely applied.

An example of such a study is recent investigation of the $CeCu_xGa_{4-x}$ system [2], in which suppression of the ferromagnetic order is conventional only up to $x \approx 0.8$, where an inflection in the phase boundary line $T_C(x)$, followed by a saturation of the Curie temperature at higher *x*, is clearly seen. The unconventional shape of the phase boundary line in that system has been provisionally ascribed to a disorder-driven smearing of the critical point (for a review see Ref. [3]).

In the present paper we report on another $p \rightarrow d$ substitution in a similar system, namely $CePd_xGa_{4-x}$. Since Pd is a larger atom than Cu, we expected different effect of substitution, not only on crystallographic parameters (already shown in Refs. [4–6]) but also on magnetic and electronic properties. The alloys crystallize with the tetragonal $BaAl_4$-type structure (space group *I*4/*mmm*, no. 139), in which Ce atoms form a body-centered unit cell, while Pd and Ga atoms randomly occupy 4*e* (0,0,*z* ≈ 0.38) and 4*d* (0,½,¼) crystallographic sites (forming three adjacent atomic layers) [4], although the former site is preferentially occupied by palladium [5]. Some magnetic properties on these materials were presented before in Ref. [4], and for $CePd_{0.3}Ga_{3.7}$ a more detailed report on its ferromagnetic behavior is available in Ref. [7]. Here, we present the results of our systematic investigation of the solid solution $CePd_xGa_{4-x}$ by means of x-ray powder diffraction, magnetization, specific heat, electrical resistivity and thermoelectric power measurements.

2. Materials and methods

Polycrystalline samples of the solid solution $CePd_xGa_{4-x}$ with the nominal compositions $x = 0.1–0.9$ were prepared by conventional arc-melting stoichiometric amounts of the elemental constituents (with purity at least 99.5%) under protective purified-argon atmosphere. The products were subsequently wrapped with tantalum foil, sealed in evacuated silica tubes and homogenized at 600 °C for one month. Quality of the samples was verified by means of X-ray powder diffraction (X'pert Pro PANalytical diffractometer with Cu–Kα radiation). The obtained X-ray patterns

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were analyzed by the Rietveld method implemented into the Fullprof software [8].

The magnetic properties were studied at temperatures from 0.5 to 300 K and in magnetic fields up to 5 T using an SQUID magnetometer (Quantum Design MPMS-XL) equipped with an iQuantum ^{3}He refrigerator. The specific heat and the electrical resistivity of bar-shaped samples were measured over the temperature intervals 0.4–10 K and 0.4–300 K, respectively, employing a commercial equipment (Quantum Design PPMS-9). Thermoelectric power measurements were conducted from 6 to 300 K, with a temperature gradient of 2 K, by static differential method implemented in a home-made setup.

3. Results and discussion

3.1. Crystal structure

The X-ray powder diffraction patterns indicated that the $CePd_xGa_{4-x}$ alloys form a continuous solid solution with the tetragonal $BaAl_4$-type structure (space group $I4/mmm$, no. 139). The established homogeneity range $0.2 \le x \le 0.8$ is close to the previously reported data ($0.2 \le x \le 0.9$ [4]). The samples with $x = 0.1$ and 0.9 contained unidentified foreign phase (or phases) and hence were excluded from further studies. In this context it is worth noting that for the composition $CePdGa_3$ (i.e. $x = 1$) a different (orthorhombic) crystal structure was found [9], contrary to the $CeCuGa_3$ case, where random occupation disappears and a closely related, but noncentrosymmetric, ordered tetragonal $BaNiSn_3$-type structure is adopted. The latter structure has also been considered for Pd-rich $CePd_{0.875}Ga_{3.125}$ single crystal but $BaAl_4$-type was favored due to its higher symmetry [5]. Our structure refinement on powder diffractograms was very weakly sensitive to occupation parameters of 4*e* and 4*d* sites and finally we fixed *x* at nominal values, assumed homogenous distribution of Pd and Cu on both sites and refined lattice parameters. We believe that for a decisive, precise description of crystal structure of $CePd_xGa_{4-x}$ solution a detailed study on single crystals would be necessary, far beyond the scope of this work.

As can be inferred from Fig. 1, the refined lattice parameters of the alloys are in very good agreement with those derived in Ref. [4], which confirms that the nominal composition of our samples is close to the actual one. The partial substitution of Ga by Pd atoms in $CePd_xGa_{4-x}$ results in non-monotonic changes in the lattice parameters *a* and *c*. Their extrema visible around $x = 0.5$–0.6 corroborate the previous result [4]. It is worth noting that the homogeneity range of the $CePd_xGa_{4-x}$ system is narrower than that of $CeCu_xGa_{4-x}$ ($0.2 \le x \le 1.4$) [6,2], and the lattice parameters of the solid solution with Pd evolve with *x* in an opposite way than observed for $CeCu_xGa_{4-x}$.

3.2. Thermodynamic properties

The temperature variations of the inverse magnetic susceptibility χ_m^{-1} of $CePd_xGa_{4-x}$ are shown in Fig. 2. Above about 100 K, the $\chi_m^{-1}(T)$ data show a linear behavior and can be described by the Curie–Weiss law (represented by solid lines in Fig. 2a) with the effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_p being fitting parameters. The so-obtained values of μ_{eff} (see Fig. 2b) are close to that expected for a free Ce^{3+} ion (i.e. $2.54\,\mu_B$), which signals the presence of well localized magnetic moments. However, they vary slightly with *x*, showing a minimum value around $x = 0.5$, associated with a similar evolution of the values of θ_p: it changes from negative to positive and back to negative (see Fig. 2c). Remarkably, these features coincide with the

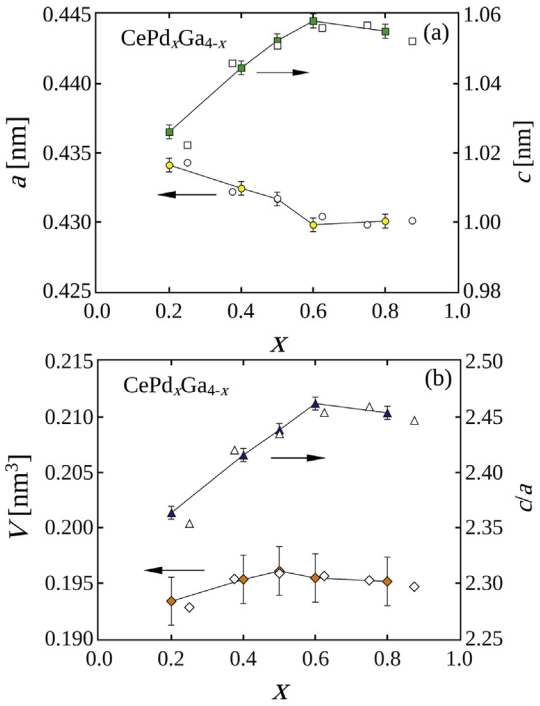

Fig. 1. (a) Lattice parameters *a* and *c*, and (b) unit–cell volume *V* and *c*/*a*-ratio of $CePd_xGa_{4-x}$ (tetragonal $BaAl_4$-type structure) as function of a nominal Pd-concentration *x*. Solid lines serve as guides for the eye; open symbols represent the data taken from Ref. [4].

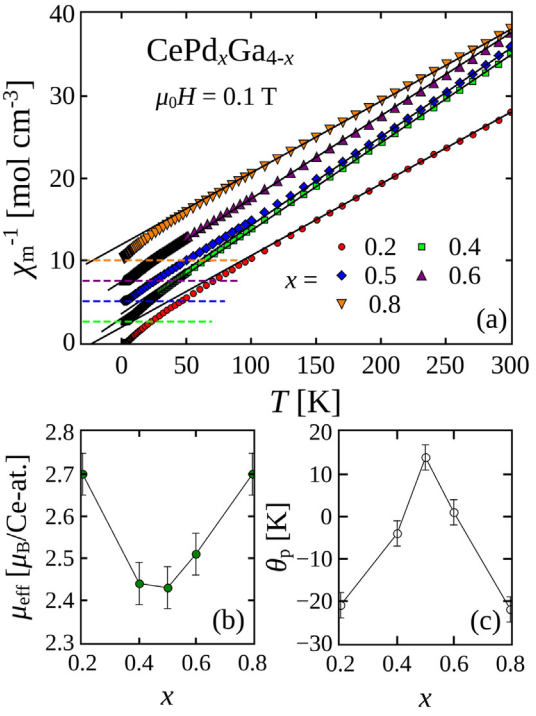

Fig. 2. (a) Inverse molar magnetic susceptibility χ_m^{-1} of $CePd_xGa_{4-x}$ as a function of temperature *T*; datapoints for $x = 0.4$, 0.5, 0.6 and 0.8 are offset by 2.5, 5, 7.5 and 10 mol/cm^{-3}, respectively; dashed lines indicate zero-baseline positions. Straight solid lines are fits of the Curie–Weiss law to the experimental data (for details see Sec. 3.2). Lower panels show *x*-dependence of the fitting parameters: μ_{eff} (b) and θ_p (c); solid lines serve as guides for the eye.