Intermetallics 32 (2013) 219–224

Contents lists available at SciVerse ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Electronic and magnetic properties of CeCoGa

Jerzy Goraus*, Andrzej Ślebarski, Marcin Fijałkowski

Institute of Physics, University of Silesia, 40-007 Katowice, Poland

ARTICLE INFO

Article history:
Received 12 June 2012
Accepted 15 August 2012
Available online 9 October 2012

Keywords:
A. Rare-earth intermetallics
B. Magnetic properties
B. Electronic structure of metals and alloys
B. Thermal properties
E. Ab-initio calculations

ABSTRACT

We report the magnetic and electronic transport properties of CeCoGa, using magnetic susceptibility, magnetization, specific heat and electrical resistivity investigations. We also present X-ray photoemission valence band spectra (VB-XPS) as well as ab-initio band structure calculations for the ferromagnetic and antiferromagnetic ordering. The *dc* and *ac* magnetic susceptibility data reveal a magnetic phase transition at $T_N = 4.3$ K. For $T < T_N$ magnetization M vs. magnetic field B isoterms have two metamagnetic transitions. Above T_N susceptibility shows evidence of spin-glass like behavior. The magnetic entropy is strongly reduced at T_N due to the on-site Kondo coupling. For CeCoGa the Kondo temperature is ~20 K, much larger than the temperature of the magnetic ordering. Our calculations show that within bare local spin density approximation (LSDA) the ground state of CeCoGa is weakly magnetic, however, the 4*f* correlations when they are included within LSDA + U approach lead to stable antiferromagnetic ground state. Calculations for moderate U parameter indicate that magnetic ordering is present not only at the Ce sublattice, but also for the Co sites, moreover small induced magnetic moment is also present at the Ga sites. All sublattices exhibit antiferromagnetic ordering with different values of local magnetic moments what explains the ferrimagnetic behavior of CeCoGa. The magnetization M vs. magnetic field B shows at $T = 2$ K two metamagnetic features at $B = 0.1$ T and $B = 5$ T, which well correlates with the calculated magnetic moments of Co and Ga. The first transition can be attributed to spin–flop within the magnetic moments induced in Ga sublattice, whereas the anomaly at $B = 5$ T is related to the spin–flop within the Co sublattice.

1. Introduction

Cerium intermetallic compounds exhibit several interesting physical phenomena such as complex magnetic structure, valence fluctuation, heavy fermion (HF) behavior, unconventional superconductivity, non-Fermi liquid (NFL) behavior and quantum criticality, resulting from the competition of the RKKY and Kondo interactions. The first effect leads to long range magnetic order of the localized Ce-moments, while the latter one suppresses the Ce 4*f* magnetic moments and may lead to the Abrikosov-Suhl resonance manifesting itself in the narrow peak in the quasi-particle density of states (DOS) at the Fermi level. The first model, which qualitatively explained the role of this competition was proposed by Doniach [1]. However, the complexity of the phase diagram of various magnetic/non-magnetic Ce-based Kondo lattices can be better understand within a single theoretical framework such as Anderson- [2] or Kondo-lattice models [3]. It also has been shown [4], that the stability of the magnetic ground state in the Kondo-lattice limit is first of all strongly dependent on the on-site hybridization V_{cf} between conduction and *f*-electron states and the number of valence electrons n_e. The theoretical phase diagram on the V_{cf}–n_e plane has been shown to provide a qualitative account for experimental results on the series of Ce-ternary intermetallics [5].

Many of cerium HF compounds order antiferromagnetically, nonetheless, there is known a group of ferromagnetic heavy fermions [6–9] or Ce-based Kondo lattices where atomic disorder leads to existence of a spin-glass-like state [10]. Since the coupling constant J_{cf} between the 4f spins and the conduction spins as well as the hybridization energy V_{cf} determine the ground state properties and simultaneously the exchange integrals are strongly dependent on the Ce–Ce distance and local symmetry of Ce ion, we have started to investigate the physical properties of the ternary CeTX compounds, where T is the transition metal and X is Sb, Sn, Ga or Al element. Studies of CeTX provide an opportunity to investigate the effect of variation of J_{cf} on magnetic properties of the ground state by selection of the T or X element. For the series of elements X: Sb, Sn, Ga, and Al an atomic radius systematically increases which leads to the localization of the f-shell. Therefore the CeTAl and CeTGa can be expected to be magnetic, which was in most cases confirmed [11].

* Corresponding author.
E-mail address: jerzy.goraus@us.edu.pl (J. Goraus).

0966-9795/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.intermet.2012.08.011

Table 1
Rietveld refinement results for CeCoGa (space group $C2/m$); lattice parameters: $a = 10.9983(15)$ Å, $b = 4.35202(57)$ Å, $c = 4.83020(59)$ Å; γ angle: 103.260(7)°; the atomic positions are listed in the table.

Atom	x	y	z
Ce	0.1275(4)	0	0.3250(13)
Co	0.1941(7)	0	0.8658(24)
Ga	0.4151(6)	0	0.1923(21)

In this work we study CeCoGa which crystallizes in the monoclinic structure with the symmetry $C2/m$ [12,13], while the remaining CeTX compounds are mostly orthorhombic. The different symmetry of CeCoGa is the second reason of our investigations, as here we have the possibility to study the influence of the symmetry on the ground state properties of CeTX compounds. For the low structural symmetry of CeCoGa the hybridization effect between Ce 5*d* (and possibly also other Ce conduction states) and 4*f* states is expected to be stronger due to large magnitude of the crystal potential elements V_{lm} with $l = 1$ necessary to couple the 5*d* and 4*f* states (for details see [14]). Therefore, the exchange integral $J_{cf} \sim V_{cf}^2$ should has larger magnitude for CeCoGa than for the CeTX compounds with higher symmetry resulting in the relatively large Kondo temperature. The Kondo temperature obtained for CeCoGa is indeed higher than the Kondo temperature of other CeTX compounds.

Our magnetic measurements suggest that CeCoGa is a moderate heavy fermion system undergoing a complex antiferromagnetic transition below 4.3 K which coexists with the spin-glass-like state. In the magnetic fields of ~0.1 T and ~5 T the magnetization shows a metamagnetic spin–flop transition, which is also visible in the specific heat data (for $B = 5$ T). The metamagnetic behavior is typical for the HF compounds, e.g., it was observed for $CeCoGe_3$ [15], $CeRu_2Si_2$ [16] and UPd_2Al_3 [17].

2. Experimental and calculation details

Polycrystalline CeCoGa sample was prepared by arc melting the constituent elements on a water cooled copper hearth in a high-purity argon atmosphere with an Al getter. The samples were remelted several times to promote homogeneity and annealed at 600 °C for 2 weeks.

The powder diffraction pattern was measured on Rigaku-Denki D/MAX RAPID II-R diffractometer (Rigaku Corporation, Tokyo, Japan) with a rotating anode Ag K_α tube ($\lambda = 0.5608$ Å), an incident beam (002) graphite monochromator and an image plate in the Debye-Scherrer geometry. XRD data were refined using FULLPROF program [18] with pseudo-Voigt line shape and six coefficient polynomial background. The refined lattice parameters and atomic positions given in Table 1 were later used in the band structure calculations.

Magnetization was measured with Quantum Design magnetic properties measurement system (QD-MPMS) above 1.9 K in fields up to 7 T. Heat capacity and resistivity were measured with QD-PPMS, with the He^3 option. AC susceptibility was measured width PPMS ACMS option with the magnitude of magnetic field below 0.1 mT.

The band structure calculations were carried out using both: FP-LAPW/APW + lo method (within the Elk 1.2.15 computer code [19]) and FPLO method (FPLO9-00-34 computer code [20]) within the local spin density approximation (LSDA). The exchange correlation potential V_{xc} was used in the form proposed by Perdew and Wang [21]. For the FP-LAPW calculations the muffin-tin radii of 2.2 atomic units (a.u.) were chosen for Ce and 2.0 a.u. for the Co and Ga elements; the plane wave cut-off factor of $R_{MT} \times K_{max} = 9$ was used, and the convergence with respect to *k*-grid and $R_{MT} \times K_{max}$ was carefully checked. The number of *k*-points in the irreducible wedge of Brillouin Zone were 112 for the FP-LAPW method and 1728 for the FPLO method. The charge convergence in calculations was better than 10^{-4} e, whereas the energy convergence with respect to *k*-grid was better than 1 meV for the FPLO calculations. The results of FPLO and Elk calculations were compared and they were consistent for both methods. For a comparison of experimental valence band X-ray photoemission spectroscopy spectrum with our theoretical results we used the following procedure: calculated partial densities of states (DOS) were summed across corresponding Wyckoff sites and multiplied by a proper cross-section taken from Ref. [22], these weighted total DOS was then convoluted with Lorentztian line shape (FWHM = 0.4 eV) for consideration of finite life time and experimental resolution.

3. Results and analysis

3.1. Magnetic properties

Shown in Fig. 1a is the temperature dependence of the *dc* magnetic susceptibility data measured in a magnetic field of 0.1 T and the real component χ' of the *ac* susceptibility obtained for various frequencies. At the low temperature the susceptibility data exhibit an abrupt increase below 9.3 K and peak at 8 K in χ' with the frequency dependence suggesting some phase transition of spin-glass origin. The real (χ') and the imaginary (χ'') part of the *ac* susceptibility presented in the inset to Fig. 1a show that χ' exhibits

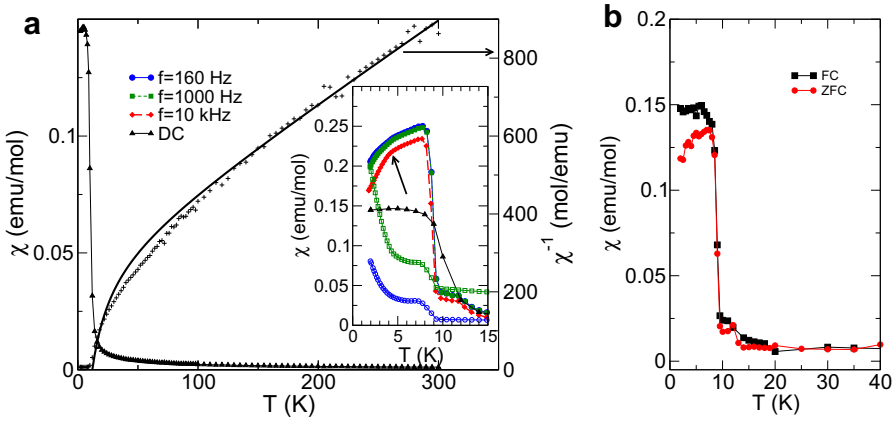

Fig. 1. a) Magnetic susceptibility χ_{dc} (triangles) and inverse susceptibility χ_{dc}^{-1} (crosses) measured in wide temperature range. Solid line denotes ferrimagnetic fit: $1/\chi = (T - \Theta_A)/C - \sigma/(T - \Theta')$ with parameters $\Theta_A = -80.5$ K, $C = 0.41$ emuK mol^{-1}, $\sigma = 3300$ mol K emu^{-1} and $\Theta' = 10$ K. The inset presents real χ'_{ac} (full symbols) and imaginary χ''_{ac} (open symbols) components measured at various frequencies. b) Field cooled (FC) and zero field cooled (ZFC) *dc* susceptibility curves vs. temperature.