Structure and magnetic properties of the ternary gallides CeMGa (M=Mn, Co and Cu) and their hydrides

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Abstract

The ternary gallides CeMGa present various structural properties since CeMnGa, CeCoGa and CeCuGa crystallize, respectively, in the cubic $MgCu_2$-, monoclinic CeCoAl-, and orthorhombic $CeCu_2$-type structure. These compounds absorb hydrogen at room temperature but hydrogenation induces a change of the crystalline structure: (i) $CeCoGaH_{3.0}$ and $CeCuGaH_{0.8}$ adopt the hexagonal AlB_2-type; (ii) on the contrary, the cubic $MgCu_2$ structure is preserved for $CeMnGaH_{1.6}$. Moreover, in some cases hydrogenation leads to a valence change for Ce. For instance, CeCoGa is considered as intermediate valence compound, whereas $CeCoGaH_{3.0}$ contains Ce^{3+}. This paper demonstrates that hydrogenation strongly influences the Kondo effect in these intermetallics.
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1. Introduction

The equiatomic compounds based on cerium and nickel CeNiX with X=Al, Ga and In easily absorb hydrogen at moderate pressure. For CeNiAl and CeNiGa, the absorption of hydrogen induces a structural transition from hexagonal ZrNiAl-type (CeNiAl and CeNiGa low temperature form) or orthorhombic TiNiSi-type (CeNiGa high temperature form) to hexagonal AlB_2-type (CeNiAlH$_{1.93}$ and CeNiGaH$_{1.1}$) [1,2]. On the contrary, the initial ZrNiAl-type is preserved after hydrogen insertion into CeNiIn and a pronounced anisotropic expansion of the unit cell is evidenced (the *a*-parameter decreases, whereas the *c*-parameter increases) [3,4]. As the molar unit cell volume of CeNiAl ($V_m = 56.5$ Å^3) and CeNiGa ($V_m = 55.5$ Å^3 for low temperature form) is smaller than that observed for CeNiIn ($V_m = 65.1$ Å^3), the possible sites for insertion of the H-atom in CeNiAl or CeNiGa are too small and implies the structural transition.

Hydrogenation of the compounds CeNiX induces a change of the electronic configuration of cerium from intermediate valence to a trivalent or nearly trivalent state.

For instance, CeNiAlH$_{1.93}$ shows a spin fluctuation behaviour below 7 K [1], whereas CeNiInH$_{1.8}$ exhibits a ferromagnetic transition at 6.8 K [4]. These results can be explained by a decrease of the Kondo interaction after hydrogen absorption; the valence transition is correlated to a strong increase of the molar unit cell volume inducing a decrease of the hybridisation between the Ce(4f)-electrons and those of the conduction band.

Extending our search on new hydrides deriving from equiatomic compounds CeMX (M=3d transition elements), we have studied the hydrogen absorption properties of ternary gallides CeMGa with M=Mn, Co and Cu. This contribution concerns a preliminary study devoted to the synthesis and crystallographic, electrical and magnetic properties of the hydrides CeMGaH$_Y$. The results are discussed in relation with those obtained recently on CeNiGaH$_{1.1}$ [2].

2. Experimental procedures

All the samples were synthesized by arc-melting a stoichiometric mixture of pure elements (purity above 99.9%) in a high purity argon atmosphere. Then, the samples were turned and remelted several times to ensure homogeneity. Annealing was done for 1 month by enclos-

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Table 1
Crystallographic data relative to the ternary gallides CeMGa (M=Mn, Co and Cu) and their hydrides

Compound	Annealing temp. (K)	Structure type	Unit cell parameters				
			a (Å)	b (Å)	c (Å)	β (Å)	V_m (Å^3)
CeMnGa	1073	MgCu$_2$	7.95(1)				62.81
CeMnGaH$_{1.6}$		MgCu$_2$	8.10(1)				66.43
CeCoGa	1073	CeCoAl	10.987(6)	4.367(5)	4.840(3)	102.99	56.57
CeCoGaH$_{3.0}$		AlB$_2$	4.301(4)		4.273(4)		68.45
CeCuGa	813	CeCu$_2$	4.518(1)	7.409(2)	7.530(2)		63.01
CeCuGaH$_{0.8}$		AlB$_2$	4.368(3)		4.041(3)		66.77

ing the sample in evacuated quartz tubes; the annealing temperatures are given in Table 1.

Hydrogen absorption experiments were performed using the apparatus described previously [5]. An ingot of an annealed sample was heated under vacuum at 473 K for 12 h and then exposed to hydrogen gas at room temperature and 5 MPa as pressure. The amount of H-absorbed was determined volumetrically by monitoring pressure changes in a calibrated volume.

X-ray powder diffraction with the use of a Philips 1050-diffractometer (Cu Kα radiation) was applied for the characterization of the structural type and for the phase identification of the samples. The unit cell parameters were determined by a least-squares refinement method using silicon (5N) as an internal standard. The crystal structures of the samples before and after hydrogenation were refined by the Rietveld profile method [6].

Magnetization measurements were performed using a Superconducting QUantum Interference Device (SQUID) magnetometer in the temperature range 1.8–300 K and applied fields up to 5 T. Electrical resistivity was determined above 4.2 K on a polycrystalline sample using standard dc four probe measurements.

3. Results and discussion

The characterization by X-ray powder diffraction of the samples before hydrogenation confirms that: (i) CeMnGa adopts the cubic MgCu$_2$-type [7]; (ii) CeCoGa crystallizes in the monoclinic CeCoAl-type [8]; (iii) CeCuGa crystallizes in the orthorhombic CeCu$_2$-type [9]. The refined unit cell parameters of these ternary gallides, given in Table 1, are in agreement with those reported previously.

The insertion of hydrogen in CeCoGa and CeCuGa modifies their structural properties. For instance, the X-ray powder pattern of the hydride of CeCuGa (i.e., CeCuGaH$_{0.8}$) (Fig. 1) is easily indexed on the basis of the hexagonal AlB$_2$-type structure (space group $P6/mmm$): Ce-atoms occupying the 1a-site (0 0 0), whereas Co- or Cu- and Ga-atoms are randomly distributed on the 2d-site (1/3 2/3 1/2). The formation of these hydrides is accompanied by a large increase of the molar unit cell volume V_m (Table 1); the expansion is much higher in the case of

CeCoGaH$_{3.0}$ ($\cong 21\%$) than that observed for CeCuGaH$_{0.8}$ ($\cong 6\%$). These results can be compared to those obtained recently on the hydride CeIrGaH$_{1.7}$ [10] or deuteride LaNiSnD$_2$ [11]. These compounds adopt the hexagonal ZrBeSi-type which is a variant of the AlB$_2$-type with an ordering of the iridium (or nickel) and gallium (or tin) atoms. In the present study, the atomic number of Co, Cu and Ga is so close that X-ray powder diffraction does not show if similar ordering exists between Co- (or Cu)- and Ga-atoms in the hydrides CeCoGaH$_{3.0}$ and CeCuGaH$_{0.8}$. In order to solve this question an investigation of these hydrides by neutron powder diffraction is needed.

The hydride CeMnGaH$_{1.6}$ is found to retain the initial cubic MgCu$_2$-type structure (expansion of the V_m volume around 5.8%) (Table 1). Similar result was reported recently upon the hydrogenation of CeMnAl [12].

The expansion of the molar unit cell volume due to the hydrogenation of the ternary gallides CeMGa modifies strongly their magnetic and electrical properties.

Above 200 K, the magnetic susceptibility χ_m of CeCoGa follows a Curie–Weiss law with $\mu_{eff}=1.92(5)$ μ_B and $\theta_p=-92(2)$ K, respectively, as effective moment and Curie paramagnetic temperature (Fig. 2). The μ_{eff} value is lower than that calculated for a free Ce^{3+} ion (i.e., 2.54 μ_B) and indicates that cerium exhibits an intermediate valence state in CeCoGa. This result is confirmed by those obtained by X-ray absorption near-edge spectroscopy
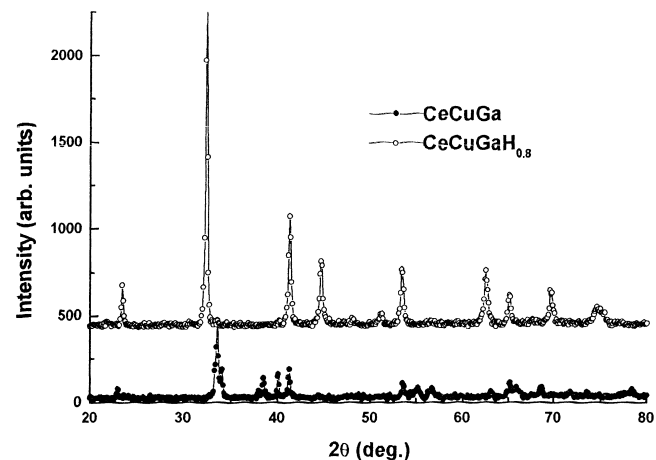

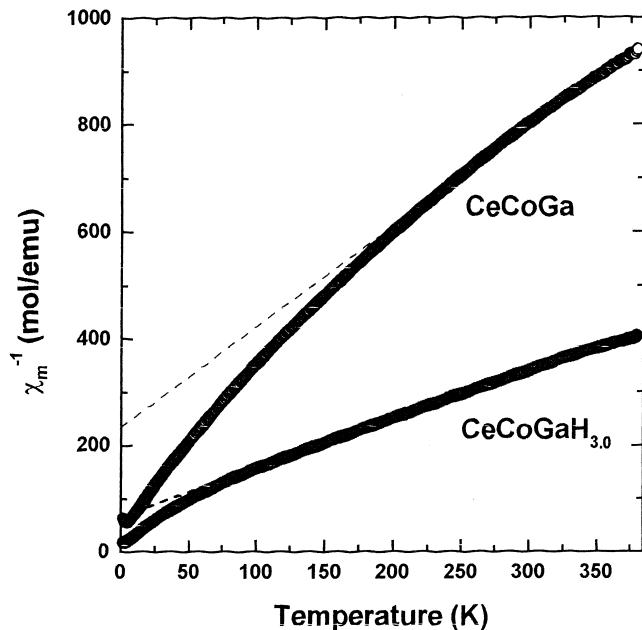Fig. 1. X-ray powder diffraction patterns of CeCuGa and CeCuGaH$_{0.8}$.

Fig. 2. Temperature dependence of the reciprocal magnetic susceptibility, measured with an applied field $\mu_0 H = 4$ T, of gallide CeCoGa and its hydride $CeCoGaH_{3.0}$.

(XANES) measurements showing a valence of 3.17(2) for cerium in this compound [13]. On the contrary, above 60–70 K, the curve $\chi_m^{-1} = f(T)$ relative to $CeCoGaH_{3.0}$ can be fitted with a Curie–Weiss law giving $\mu_{\text{eff}} = 2.60(5)$ μ_B and $\theta_p = -74(2)$ K. The cerium atom is trivalent in this hydride. The change of cerium valence state by hydrogen absorption is confirmed by electrical resistivity measurement (Fig. 3): (i) above 10 K, the reduced resistivity of
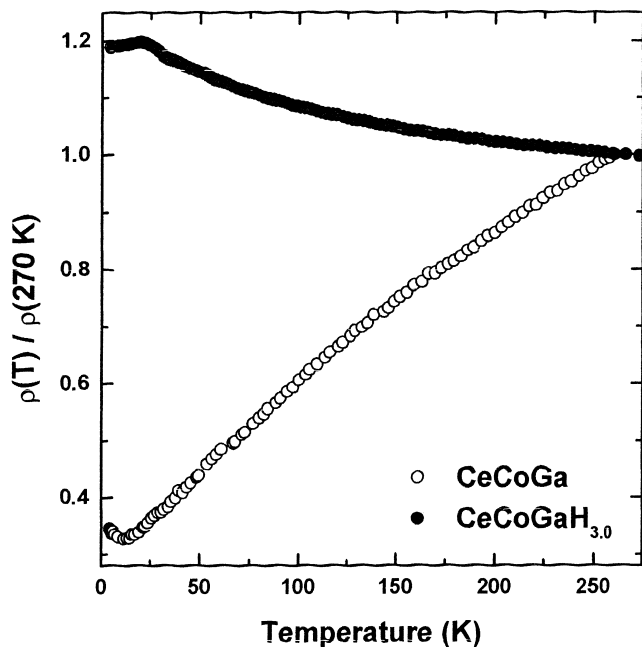

Fig. 3. Temperature dependence of the reduced electrical resistivity of CeCoGa and its hydride $CeCoGaH_{3.0}$.
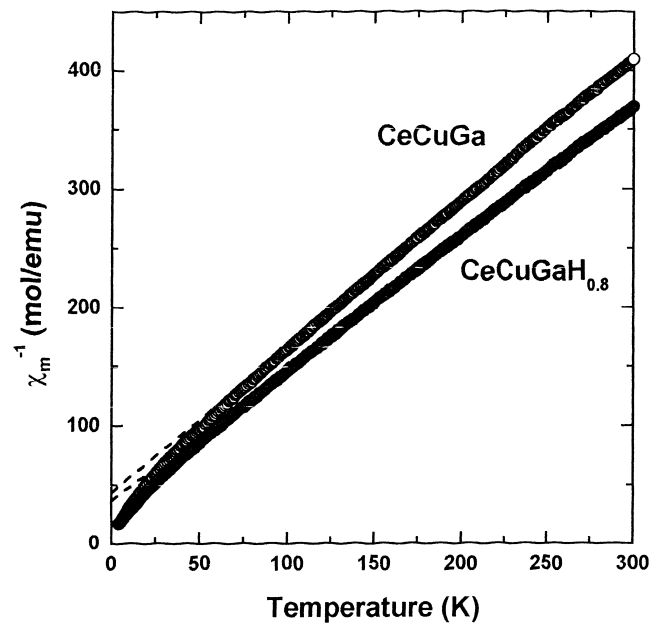

Fig. 4. Temperature dependence of the reciprocal magnetic susceptibility of gallide CeCuGa and its hydride $CeCuGaH_{0.8}$.

CeCoGa increases almost linearly with the temperature characterizing a non-magnetic metal where the 4f(Ce)-electrons are delocalised; (ii) the resistivity of $CeCoGaH_{3.0}$ increases in a Kondo-like manner when the temperature decreases from 270 to about 20 K; this behavior is due to the crystal field and Kondo effect competition.

Above 70 K, the magnetic susceptibility of CeCuGa and its hydride $CeCuGaH_{0.8}$ can be fitted with a Curie–Weiss law $\chi_m^{-1} = (T - \theta_p)/C_m$ giving $\theta_p = -35(2)$ K and $\mu_{\text{eff}} = (8C_m)^{1/2} = 2.55(5)$ μ_B for CeCuGa and $\theta_p = -31(2)$ K and $\mu_{\text{eff}} = 2.62(5)$ μ_B for $CeCuGaH_{0.8}$ (Fig. 4). In both compounds, the cerium shows a trivalent state. In the temperature range 270–30 K, the electrical resistivity of CeCuGa decreases slowly with the temperature (Fig. 5). Below 30 K, a strong increase of the resistivity is observed indicating a Kondo behaviour. These results are in agreement with those reported previously by Nakotte et al. [9]. For the hydride $CeCuGaH_{0.8}$, the increase observed below 20–25 K on the curve $\rho(T)/\rho(270$ K$) = f(T)$ (Fig. 5) is less pronounced suggesting a smaller reduction of the influence of the Kondo effect.

4. Conclusion

We have found that the electronic state of the cerium in the ternary gallides CeCoGa, CeNiGa [2] and CeCuGa, is strongly modified after hydrogenation of these compounds: (i) absorption of hydrogen by CeCoGa and CeNiGa induces a valence transition for cerium from intermediate to trivalent state; (ii) on the contrary, Ce shows a trivalent
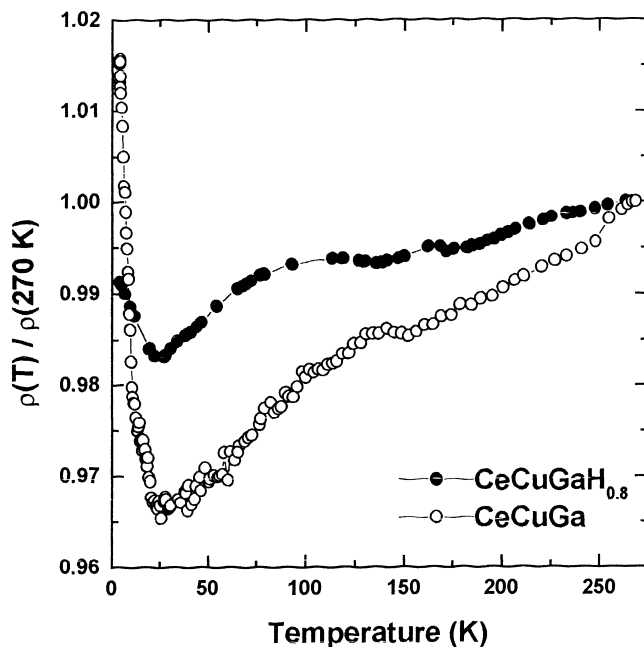
Fig. 5. Temperature dependence of the reduced electrical resistivity of CeCuGa and its hydride CeCuGaH$_{0.8}$.

state in both CeCuGa and CeCuGaH$_{0.8}$ but the Kondo behaviour existing at low temperature is less marked in the hydride. This study confirms that the hybridisation between the Ce(4f)-electrons and those of the conduction band is always reduced after hydrogenation of the intermetallics. In order to check this assumption, an electronic band structure calculation based on spin polarised density functional theory is now in progress for these gallides and their hydrides.

Finally, it is interesting to note that recent studies devoted to the hydrogenation of CeMX compounds (M = transition element and X = Al, Ga or In) confirm a decrease of the interaction J_{cf} between 4f(Ce)-electrons and conduction electrons by insertion of hydrogen in the lattice. This change can lead to: (i) a reduction of the Kondo temperature as in the hydrides CeNiAlH$_{1.93}$ [1] and CeRhInH$_{0.55}$ [14]; (ii) a cerium valence transition from intermediate valence to the trivalent state where Ce shows no magnetic ordering (CeIrAlH$_2$ [15] and CeIrGaH$_{1.7}$ [10]) or ferromagnetic behaviour (CeNiInH$_{1.8}$ [4]); (iii) a strong increase of the Néel or Curie temperature (CePtAlH$_{1.1}$ [16] and CeAuAlH$_{1.4}$ [17]).

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