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Hydrogen absorption properties of CeNiAl: influence on its crystal structure and magnetic behaviour

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Abstract

CeNiAl absorbs up to 1.93(5) hydrogen per formula unit at room temperature and at a pressure of 1 MPa. This hydride is stable in air. Hydrogenation induces both: (i) a structural transition hexagonal ZrNiAl-type→hexagonal AlB_2-type; (ii) a valence transition for cerium. At low temperature for $T<7$ K, the hydride $CeNiAlH_{1.93}$ shows a spin fluctuation behaviour.

Keywords: Hydrogen sorption; X-Ray powder diffraction; Magnetization measurements

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1. Introduction

The intermetallic compounds RNiAl (R=rare earth) crystallize, except for R=Eu, in the hexagonal ZrNiAl structure (space group $P\bar{6}2m$) [1]. These compounds are known to absorb hydrogen easily. For instance, the ternary compounds RNiAl with R=Y, Gd, Tb, Dy, Er and Lu absorb hydrogen at normal pressure [2]. Their hydrogenation induces an orthorhombic distortion of the original hexagonal ZrNiAl type and a decrease of their magnetic ordering temperatures as from 59 K in GdNiAl to 20 K in $GdNiAlH_{1.35}$ [2,3].

Hydrogenation of CeNiAl which is considered as an intermediate valence compound [4,5], induces a localization of the 4f(Ce)-electron in the hydride $CeNiAlH_{2.04}$ [6]. The presence of trivalent cerium ions in the hydride was detected by magnetization measurements performed above 77 K but no indication of the crystal structure was reported [6]. In order to obtain more information on this hydride, we have investigated it by X-ray powder diffraction, transmission electron microscopy (TEM) and magnetization measurements between 1.8 and 300 K. We guess that its hydrogenation leads to an expansion of its unit cell favouring the following sequence: intermediate valence state→magnetically ordered state.

2. Experimental

The polycrystalline sample was prepared by melting the constituent elements under a purified argon atmosphere. Its homogeneity was achieved by annealing under vacuum at 1073 K for 1 month. Its characterization by electron microprobe analysis reveals a perfect chemical homogeneity.

The hydriding apparatus used was described previously [7]. After activation in a vacuum of 10^{-3} Pa at 373 K, the CeNiAl sample was cooled down to room temperature and hydrogenated at a pressure of 1 MPa. The amount of H-atom absorbed, i.e. 1.93(5) per CeNiAl mol, was determined volumetrically by monitoring pressure changes in a calibrated volume.

The crystal structures of CeNiAl and $CeNiAlH_{1.93}$ were refined by the Rietveld profile method [8]. The data were collected on a diffractometer using Bragg–Brentano geometry with CuK_α radiation. The patterns were scanned in steps of 0.02° (2θ) from 15 to 120° with a constant counting time of 30 s.

Magnetization measurements were performed using a superconducting quantum interference device (SQUID)

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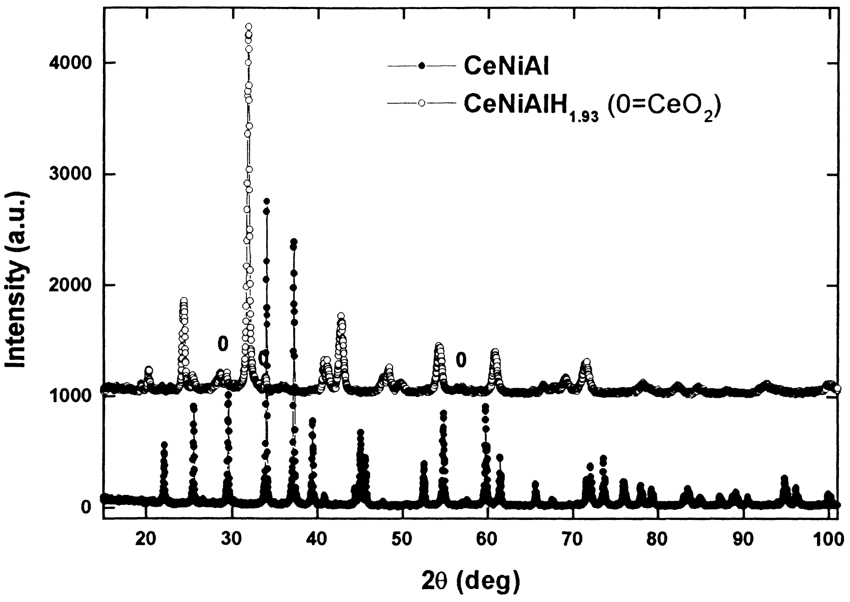

Fig. 1. X-Ray powder pattern of CeNiAl before and after hydrogen sorption.

magnetometer in the temperature range 1.8–300 K and applied fields up to 5 T.

3. Results and discussion

The X-ray powder pattern of CeNiAl, presented in Fig. 1, is easily indexed on the basis of the hexagonal ZrNiAl-type structure. The refined unit cell parameters are $a=0.69760(5)$ nm and $c=0.40187(5)$ nm. Ce-atoms occupy the *3g*-site [0.57886(8) 0 1/2], Ni-atoms are located on both *1b* (0 0 1/2) and *2c* (1/3 2/3 0) sites and finally Al-atoms are on the *3f*-site [0.2106(3) 0 0]. These atomic coordinates are close to those determined previously [1].

Upon exposure to hydrogen gas at room temperature, CeNiAl starts to absorb. The hydride $CeNiAlH_{1.93}$ obtained by introducing hydrogen up to 1 MPa, is stable in air. Its X-ray powder pattern clearly shows that hydrogenation leads to a structural transition (Fig. 1). Several small crystal fragments of $CeNiAlH_{1.93}$ examined by TEM, reveal that its unit cell adopts the hexagonal symmetry with $a=0.427(1)$ nm and $c=0.443(1)$ nm as

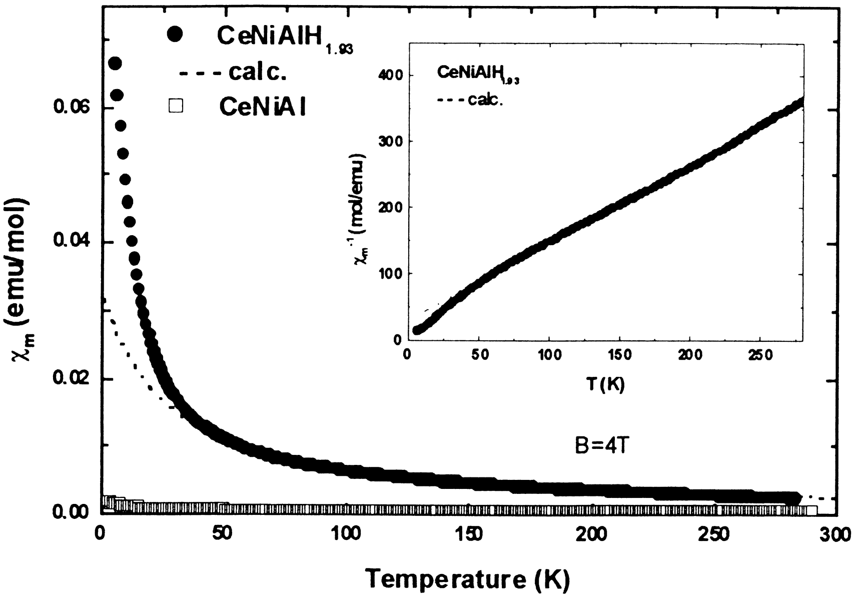

Fig. 2. Temperature dependence of magnetic susceptibility of CeNiAl and $CeNiAlH_{1.93}$ (the insert shows the reciprocal magnetic susceptibility of $CeNiAlH_{1.93}$).

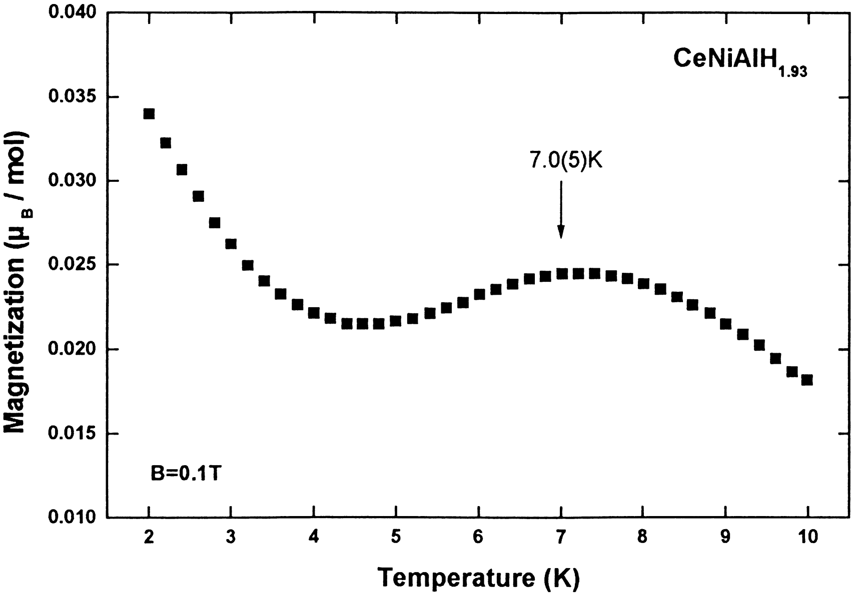

Fig. 3. Temperature dependence of magnetization of $CeNiAlH_{1.93}$ measured in an applied field $B = 0.1$ T.

lattice parameters. Moreover, no systematic extinctions can be distinguished. Using these results, the X-ray powder pattern of $CeNiAlH_{1.93}$ can be indexed on the basis of a hexagonal AlB_2-type structure (space group *P6*/*mmm*); Ce-atoms occupying the *1a*-site (0 0 0) whereas Ni- and Al-atoms being randomly distributed on the *2d*-site (1/3 2/3 1/2). This X-ray diffraction study reveals the presence of some amounts of oxide CeO_2 (the peaks relative to this phase are indicated by 0 in Fig. 1). Also, an investigation of the hydride (deuteride) $CeNiAlH_{1.93}$ by neutron diffraction is in progress in order to locate the hydrogen atoms in the structure and to verify or not the statistically distribution of Ni- and Al-atoms.

The structures ZrNiAl-type and AlB_2-type show some similarities: in these two cases, the cerium three-dimensional network can be described by an intergrowth of trigonal $[Ce_6]$ prisms. In CeNiAl, Ni-atoms are at the centre of the trigonal prism, whereas in $CeNiAlH_{1.93}$ this prism is occupied by a distribution of Ni- and Al-atoms.

The unit cell volume by mol (V_m) varies drastically after hydrogenation: a large increase of V_m is observed (+23.9%) from 0.0565 to 0.0700 nm^3. Moreover, the structural transition ZrNiAl-type→AlB_2-type leads to an increase of both the number of Ce-atoms neighbouring each other (6→8) and the d_{Ce-Ce} interatomic distances (2×0.40187 nm and 4×0.36159 nm→6×0.427 nm and

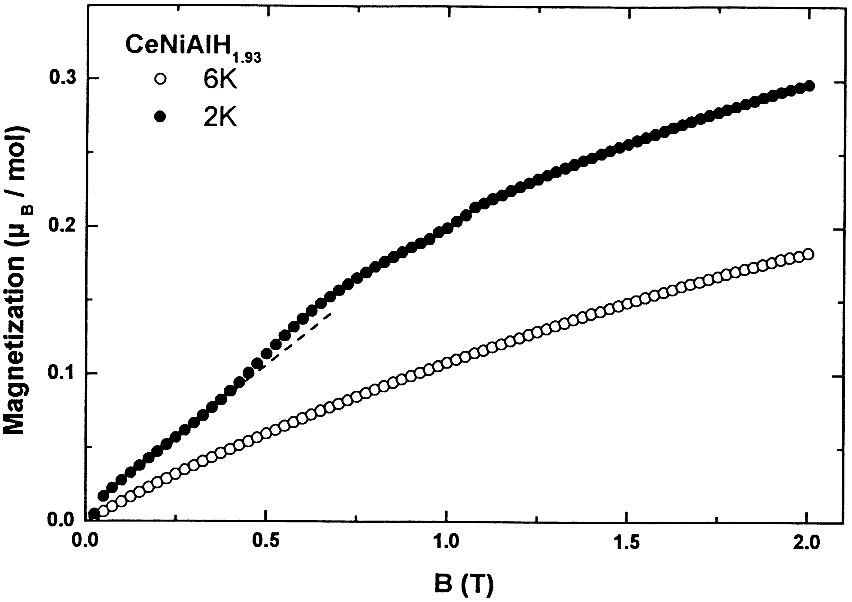

Fig. 4. Field dependence of magnetization of $CeNiAlH_{1.93}$ measured at 2 and 6 K.

2×0.443 nm). This last observation can be ascribed to the presence of trivalent cerium in the hydride.

Fig. 2 compares the thermal dependence of the magnetic susceptibility of CeNiAl and $CeNiAlH_{1.93}$. Above 30 K, the magnetic susceptibility χ_m of CeNiAl is small ($\chi_m = 0.75\cdot10^{-3}$ emu/mol) and practically independent of the temperature in agreement with a nearly tetravalent state of cerium in this compound (increase of χ_m below 25 K can be attributed to the presence of traces of magnetic impurities such as Ce_2O_3). On the contrary, above 40 K the $\chi_m = f(T)$ curve of $CeNiAlH_{1.93}$ follows a Curie–Weiss law having $\theta_p = -25(1)$ K as paramagnetic Curie-temperature and $\mu_{eff.} = 2.59(1)\mu_B$/Ce as the effective moment; a value close to that calculated for free Ce^{3+} ion (2.54 μ_B).

The thermal dependence of the magnetization of $CeNiAlH_{1.93}$, measured in an applied field $B=0.1$ T, exhibits a broad maximum centered around 7.0(5) K (Fig. 3). The saturation of magnetization at low temperature is attributed to spin fluctuations arising from either Kondo or valence fluctuations, or a combination of both. Below 4 K, the increase of magnetization with decreasing temperature is presumably due to small amounts of impurity phase.

With increasing magnetic field at 2 K, the magnetization of the hydride increases linearly at low fields then shows a steep rise around 0.4–0.5 T (Fig. 4). This behaviour is typical of a metamagnetic transition as observed in the heavy fermion compound $CeRu_2Si_2$ [9].

In summary, hydrogenation of CeNiAl leads to a valence transition for cerium: tetravalent→trivalent. No magnetic ordering occurs above 2 K for the hydride $CeNiAlH_{1.93}$. This compound appears to be an interesting system, showing spin fluctuations at low temperatures. Further experiments have to be performed in order to state it more precisely.

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