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LETTER TO THE EDITOR

Occurrence of ferromagnetic transition on hydrogen insertion in the ternary indide CeNiIn

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Abstract

The hydride CeNiInH_{1.8(1)} has been studied by magnetization measurements. It exhibits a ferromagnetic behaviour below $T_C = 6.8(2)$ K. In other words, the insertion of hydrogen in CeNiIn induces a cerium valence transition from intermediate valence to the trivalent state.

Recently, several studies have been devoted to the hydrogenation of CeMX intermetallics ($M = nd$ transition element and $X = Al, Ga, In$) where cerium exhibits an intermediate valence state. In all cases, the insertion of hydrogen in the compounds CeNiAl [1], CeIrAl [2], CeNiGa [3] or CeIrGa [4] induces a change of the electronic configuration of cerium from intermediate valence to a trivalent or nearly trivalent state. This behaviour can be explained through the schematic Doniach phase diagram based on the competition between the Kondo interaction, which tends to demagnetize $4f(Ce)$ states, and the magnetic Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction, which drives the compound towards a long-range magnetic ordering [5]. Both interactions depend on the coupling constant J_{cf} between the $4f(Ce)$ electrons and conduction electrons:

- (i) the compound is considered as a valence-fluctuating system for high J_{cf} values;
- (ii) cerium atoms carry a magnetic moment for low J_{cf} values;
- (iii) for intermediate values of J_{cf} , the compound exhibits interesting physical properties such as magnetic or non-magnetic Kondo behaviour, heavy-fermion state, superconductivity etc.

The strength of J_{cf} decreases with rising hydrogen insertion due to an increase of the unit-cell volume, which leads to a trivalent cerium state, but to the best of our knowledge no example exists concerning the transition from intermediate valence state to long-range magnetic ordering induced by hydrogenation of intermetallics.

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The ternary intermetallic CeNiIn is a valence-fluctuating system having a Kondo temperature of 94 K [6, 7]. Moreover, this compound easily absorbs hydrogen at room temperature to give the hydride CeNiInH_{1.8}, which crystallizes in the same hexagonal ZrNiAl-type structure as the pristine CeNiIn compound [8, 9]. However, the hydrogenation causes a pronounced anisotropic expansion of the unit cell; the *a*-parameter decreases whereas the *c*-parameter increases. Previous magnetic susceptibility measurements performed above 90 K on this hydride have indicated that the cerium is in a trivalent state [10].

In this letter, we show for the first time that the insertion of hydrogen in CeNiIn can lead to a transition from an intermediate valence to a ferromagnetic ordering behaviour.

The CeNiIn sample has been synthesized by arc-melting from a stoichiometric mixture of pure elements (purity above 99.9%) in a high-purity argon atmosphere. Then, the sample was turned and remelted several times to ensure homogeneity. The weight loss during the arc-melting process was less than 0.5 wt%. Annealing was performed at 973 K for 1 month by enclosing the sample in evacuated quartz tube. An x-ray powder diffraction (Philips PW 1050-diffractometer, Cu K α radiation) examination confirms that CeNiIn crystallizes in the hexagonal ZrNiAl-type structure with unit-cell parameters $a = 7.531(2)$ Å and $c = 3.976(1)$ Å, in agreement with those reported previously [8].

Hydrogen absorption experiments were performed using apparatus described previously [11]. The annealed sample was crushed (particle size ≤ 100 μ m), heated under vacuum at 473 K for 12 h and then exposed to hydrogen gas at 373 K and 4 MPa. The number of H atoms absorbed, i.e. 1.8(1) moles per mole CeNiIn, was determined volumetrically by monitoring pressure changes in a calibrated volume. After synthesis, the hydride was handled in a dry Ar-filled glove box.

Magnetization measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer working between 1.8 K and 300 K under 0–5 T applied magnetic fields.

The x-ray powder diffraction pattern of CeNiInH_{1.8(1)} can be indexed in the expected hexagonal ZrNiAl structure type. The refined unit-cell parameters $a = 7.308(2)$ Å and $c = 4.630(1)$ Å are slightly higher than those determined previously ($a = 7.291$ Å and $c = 4.624$ Å) [8].

Figure 1 compares the thermal dependences of the magnetic susceptibility χ_m of CeNiIn and CeNiInH_{1.8(1)}. Above 50 K, χ_m relative to CeNiIn is small ($\approx 3 \times 10^{-3}$ emu mol⁻¹) and varies weakly with the temperature in agreement with the intermediate valence character of cerium [6]; its increase below 50 K is mainly attributed to the presence of small amounts of stable moments of Ce³⁺ ions constituting the magnetic impurities (i.e. Ce₂O₃). In contrast, above 100 K, the data relative to CeNiInH_{1.8} can be fitted with a Curie–Weiss law $\chi_m^{-1} = (T - \theta_p)/C_m$, giving $\theta_p = 20$ K and $\mu_{eff} = (8C_m/3)^{1/2} = 2.61\mu_B/\text{Ce}$. The effective moment value μ_{eff} is very close to that calculated for a free Ce³⁺ ion (2.54 μ_B). Moreover, the positive value of the Curie paramagnetic temperature θ_p suggests that the ferromagnetic interactions are dominant in the hydride. This study confirms that the hydrogenation of this ternary intermetallic leads to a change of the valence of cerium from an intermediate to purely trivalent state.

The thermal dependence of the magnetization of CeNiInH_{1.8} measured in low field is characteristic of ferromagnetic behaviour (figure 2). The Curie temperature T_C , determined from the inflection point of the curve, is equal to 6.8(2) K. Below T_C the field dependence of the magnetization (figure 3) shows

- (i) a sharp rise at low fields and
- (ii) then a tendency to attain the full moment value at high fields.

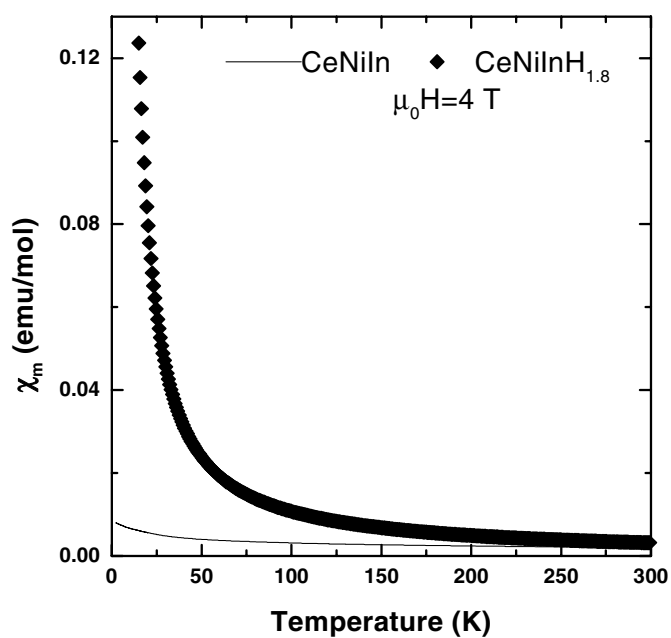


Figure 1. Temperature dependences of the magnetic susceptibility of CeNiIn and CeNiInH_{1.8} measured in an applied field $\mu_0 H = 4$ T.

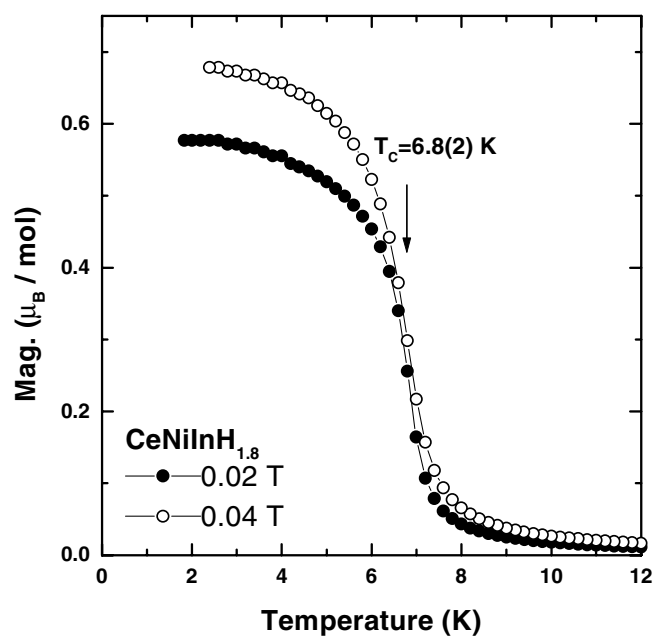


Figure 2. Temperature dependence of the magnetization of CeNiInH_{1.8} measured with a magnetic field $\mu_0 H = 0.02$ and 0.04 T.

At 2 K and $\mu_0 H = 2$ T, the magnetization reaches a value of $1.31 \mu_B \text{ mol}^{-1}$, smaller than that of the free Ce³⁺ ion ($g_J J = 2.14 \mu_B$), suggesting the existence of magnetic anisotropy, as usually observed in some ferromagnets. Also at 2 K, a weak remanent magnetization of

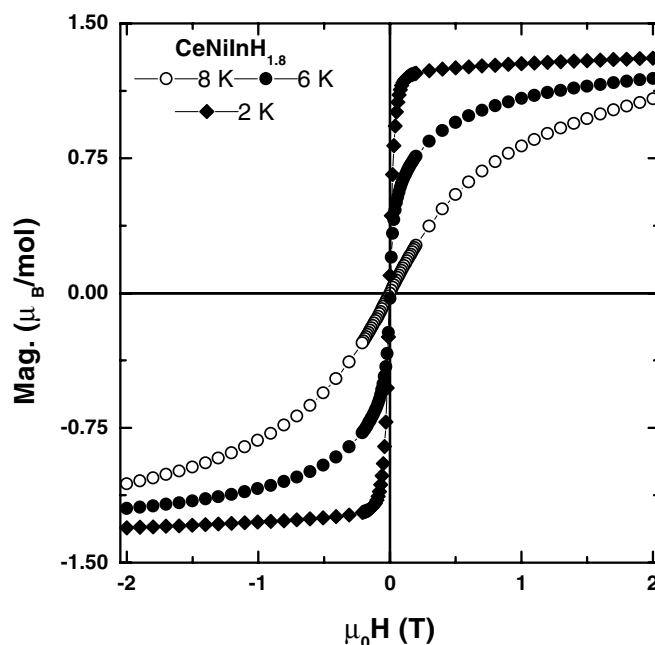


Figure 3. Field dependence of the magnetization of CeNiInH_{1.8} at various temperatures.

about $0.1 \mu_B$ is detected. All these results indicate that CeNiInH_{1.8(1)} is a ferromagnet below $T_C = 6.8(2)$ K, as is NdNiIn, which exhibits a higher Curie temperature of 20 K [6].

This study confirms that the hydrogenation of Ce-based intermetallics leads to a strong reduction of the Kondo effect interaction. The insertion of hydrogen in CeNiIn involves an expansion of the unit-cell volume from 195.3 to 214.1 Å³, allowing a decrease of the hybridization between the 4f(Ce) electrons and conduction electrons. This favours the transition from an intermediate valence state to a ferromagnetic behaviour observed for the first time in this work. The hydrogenation can be considered as an application of ‘negative’ pressure on intermetallics.

References

- [1] Bobet J-L, Chevalier B, Darriet B, Nakhl M, Weill F and Etourneau J 2001 *J. Alloys Compounds* **317/318** 67
- [2] Malik S K, Raj P, Sathyamoorthy A, Shashikala K, Harish Kumar N and Latika Menon 2001 *Phys. Rev. B* **63** 172418
- [3] Chevalier B, Bobet J-L, Gaudin E, Pasturel M and Etourneau J *J. Solid State Chem.* at press
- [4] Raj P, Sathyamoorthy A, Shashikala K, Venkateswara Rao C R and Malik S K 2001 *Solid State Commun.* **120** 375
- [5] Doniach S 1977 *Physica B* **91** 231
- [6] Fujii H, Inoue T, Andoh Y, Takabatake T, Satoh K, Maeno Y, Fujita T, Sakurai J and Yamaguchi Y 1989 *Phys. Rev. B* **39** 6840
- [7] Kurisu M, Takabatake T and Fujii H 1990 *J. Magn. Magn. Mater.* **90/91** 469
- [8] Bulyk I I, Yartys V A, Denys R V, Kalychak Ya M and Harris I R 1999 *J. Alloys Compounds* **284** 256
- [9] Yartys V A, Denys R V, Hauback B C, Fjellvag H, Bulyk I I, Riabov A B and Kalychak Ya M 2002 *J. Alloys Compounds* **330–332** 132
- [10] Sen M, Giri S, Ghoshray K, Bandyopadhyay B, Ghoshray A and Chatterjee N 1994 *Solid State Commun.* **89** 327
- [11] Bobet J-L, Pechev S, Chevalier B and Darriet B 1998 *J. Alloys Compounds* **267** 136