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Review

Various magnetic behaviors of the hydrides deriving from the tetragonal CeFeSi-type compounds

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ABSTRACT

The hydrides *RETX*H (*RE* = rare earth, *T* = transition metal and *X* = Si, Ge) crystallizing in the tetragonal ZrSiCuAs-type are obtained by hydrogen absorption of the intermetallics adopting the tetragonal CeFeSi-type. The H-insertion induces interesting magnetic transitions governed by two effects: the increase of the unit cell volume linked to the H-absorption and the occurrence of the *RE*-H chemical bonding. Some typical examples are reported in this present brief review.

Contents

1. Introduction

The hydrides *RETX*H (*RE* = rare earth, *T* = transition element and *X* = Si, Ge) deriving from the CeFeSi-type, crystallize in the tetragonal ZrSiCuAs-type structure where the H-atoms occupy the RE_4 tetrahedra sites. For instance, the structure of CeCoGeH, presented in Fig. 1, can be described as a stacking along the *c*-axis of two layers formed by [Ce_4Co_4] antiprisms inserting Ge-atoms and separated by one layer of [Ce_4] tetrahedral units inserting H-atoms [1]. The hydrides *RETX*H present similar structural properties to those recently reported for the superconductor phosphide oxide LaNiPO where O-atoms are inserted in the [La_4] tetrahedral units and P-atoms in the [La_4Ni_4] antiprisms [2].

The hydrogenation of the compounds adopting the CeFeSi-type allows to study the influence on their physical properties of two effects: (i) the increase of the unit cell volume induced by the H-insertion and (ii) the occurrence of the *RE*-H chemical bonding. Some examples showing the influence of hydrogenation on the magnetic properties of *RETX* intermetallics are reported here.

2. Results and discussion

2.1. Transition from antiferromagnetic (CeCoSi) to intermediate valence behavior (CeCoSiH)

Hydrogenation of the antiferromagnet CeCoSi ($T_N = 8.8\,K$) involves an expansion of the unit cell volume of 7.8%. The investigation of the hydride CeCoSiH by magnetization, specific heat and electrical resistivity reveals an intermediate valence character (see for instance, Fig. 4 in Ref. [3] showing that its magnetic

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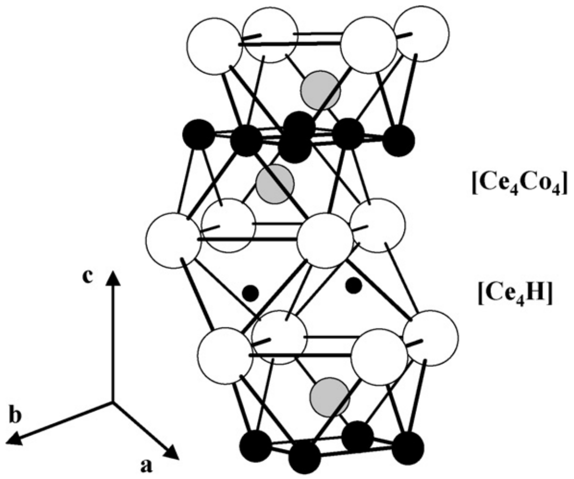

Fig. 1. Crystal structure of CeCoGeH (Ce, Co, Ge and H atoms are, respectively, represented by white large, black medium, grey medium and black small circles).

susceptibility presents a broad maximum around 70 K, characteristic of valence fluctuating systems) [1,3]. In other words, the H-absorption by CeCoSi induces a valence transition for Ce from trivalent to intermediate valent state. The comparison of the temperature dependence of the thermoelectric power $S(T)$ of CeCoSi and its hydride, evidences that the electronic state of cerium is different in these two compounds (Fig. 2). $S(T)$ curve for CeCoSi is mainly characterized by the existence of two extrema: a positive broad maximum of about $1\,\mu V\,K^{-1}$ near 83 K and a pronounced negative $-20\,\mu V\,K^{-1}$ around 26 K. Similar behavior, characteristic of almost trivalent Ce-based intermetallics having a low Kondo temperature, has been observed for $CeCu_2Si_2$ [4]. On the contrary, the $S(T)$ curve for CeCoSiH clearly presents a different behavior. In the temperature range 4.2–290 K, S is always positive but shows a minimum at low temperature ($S = 8\,\mu V\,K^{-1}$ near 31 K) and a broad peak at higher temperature ($S = 23\,\mu V\,K^{-1}$ around 109 K). This last feature characteristic of the canonical intermediate valence compound $CePd_3$, is comparable to that reported for $CeCu_2Si_2$ under isostatic pressure. This transition on S can be qualitatively understood in terms of the Coqblin–Schieffer model which describes the dynamics of conduction electrons due to the exchange and potential scattering on incoherent 4f(Ce)-states [4].

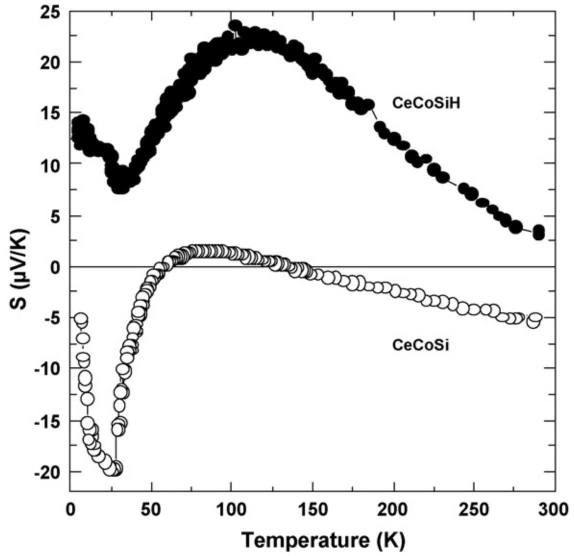

Fig. 2. Temperature dependence of the thermoelectric power of CeCoSi and its hydride.

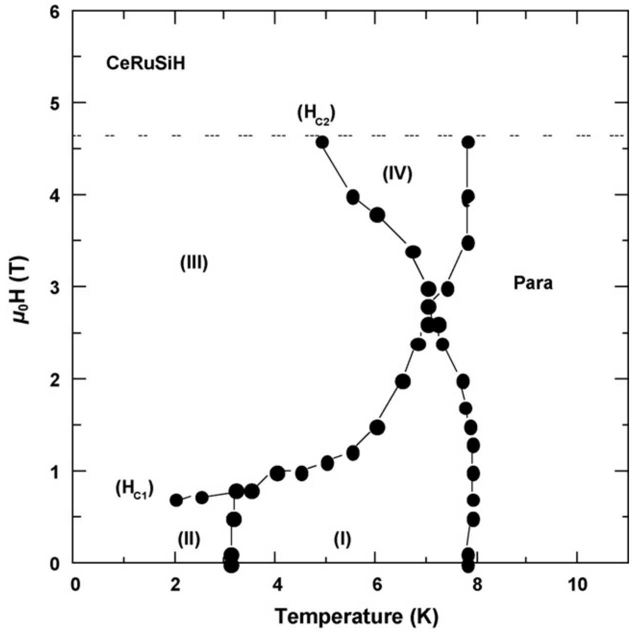

Fig. 3. Field-temperature phase diagram of CeRuSiH deduced from the magnetization measurements [5].

The demagnetization of Ce at low temperatures in CeCoSiH can be associated with the strong Ce–H interaction, which is bonding throughout the conduction band [1,3]. The recent investigation of this hydride by ^1H NMR reveals a significant Knight shift contribution suggesting a transfer of some density of electron spin from Ce to proton via orbital overlap [1].

2.2. Transition from heavy-fermion (CeRuSi) to antiferromagnetic behavior (CeRuSiH)

The hydride CeRuSiH was synthesized by exposure at 523 K of the heavy-fermion ternary silicide CeRuSi under 4 MPa of hydrogen gas. Its investigation by X-ray and neutron powder diffraction reveals that the hydrogenation induces a pronounced anisotropic expansion of the unit cell [5,6]. Moreover, CeRuSiH presents a complex magnetic phase diagram (Fig. 3): two antiferromagnetic transitions are respectively evidenced at $T_{N1} = 7.5(2)$ K and $T_{N2} = 3.1(2)$ K (phases (I) and (II)) and a metamagnetic double transition appears at low temperature (ferrimagnetic and ferromagnetic character respectively for the phases (III) and (IV)). Hydrogenation changes the moderate heavy-fermion compound CeRuSi ($\gamma = 220\,mJ/(mol\,K^2)$) to an antiferromagnet which has a smaller electronic coefficient (e.g. $\gamma = 26\,mJ/(mol\,K^2)$). In other words, the H-insertion diminishes the influence of the Kondo effect. The transition heavy fermion behavior → antiferromagnet can be well understood in terms of the classical Doniach diagram where the hydrogenation plays a role opposite to the applied pressure. The expansion of the lattice induced by H-insertion into CeRuSi is much more important than the role of Ce–H chemical bonding observed in other hydrogenated compounds as CeCoSiH.

Below antiferromagnetic transition at $T_{N1} = 7.5$ K, the neutron diffraction patterns reveal a collinear magnetic structure with $\mathbf{k} = (k_x = 0.318,\ k_x,\ 1/2)$ as propagation vector and with a Ce-magnetic moment along the c-axis. The k_x value increases when the temperature decreases until the second transition at T_{N2} corresponding to the sequence incommensurate → commensurate

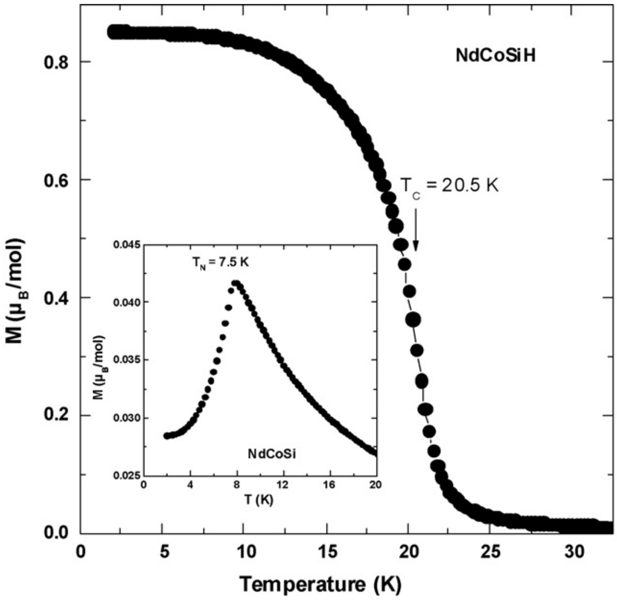

Fig. 4. Temperature dependence of the magnetization M of hydride NdCoSiH measured at applied field of 0.1 T. The inset presents the $M(T)$ curve for NdCoSi.

($\mathbf{k}$ = 1/3, 1/3, 1/2) for the magnetic structure which also becomes square wave modulated [6].

2.3. Huge influence of hydrogenation on the magnetic properties and structure of NdMnSi

Neutron diffraction investigation on NdMnSiH shows, in accordance with the magnetization measurements, that the Mn antiferromagnetic ordering temperature occurs at very high temperature since T_N = 564(5) K. The Nd-sublattice orders antiferromagnetically at T_{t1} = 103(3) K and, at the same time, a spin reorientation of the Mn-sublattice appears.

The hydrogenation of NdMnSi does not change the nature of the magnetic ordering since in both compounds NdMnSi and NdMnSiH, the Mn- and Nd-sublattices order antiferromagnetically. Nevertheless, it is noteworthy that the T_N-temperature increases from 280 K to 564 K after H-insertion. This is linked to the increase of the Mn–Mn exchange interaction induced by the decrease of the intralayer distance $d_{\text{Mn–Mn}}$ from 2.901 Å to 2.847 Å. On the other hand, the Nd ordering T_{t1}-temperature decreases from 185 K to 103 K as well as the Nd-magnetic moment from 2.59μ_B to 1.88μ_B at 1.4 K. Moreover, the propagation vector is $\mathbf{k}$ = (0 0 1/2) in NdMnSi [7] and $\mathbf{k}$ = (0 0 0) in the hydride; as a consequence, the Mn–Mn and the Nd–Nd nearest interplane interactions are respectively antiferromagnetic and ferromagnetic in NdMnSi but inverse for NdMnSiH. On the contrary, the Mn–Mn and the Nd–Nd nearest intraplane interactions are antiferromagnetic and ferromagnetic respectively in both compounds. Thus the magnetic structure and the ordering temperature have much changed after the hydrogenation of NdMnSi. Electronic structures calculations have been done in order to try to understand the role of the Mn–Mn, Nd–Nd and the Nd–Mn exchange interactions in the thermal evolution of the Mn- and Nd-moments.

2.4. Transition from antiferromagnetic (NdCoSi) to ferromagnetic ordering (NdCoSiH)

One maximum is clearly visible on the curve presenting the temperature dependence of the magnetization M for NdCoSi (inset of Fig. 4). This result confirms the occurrence of an antiferromagnetic transition for this ternary silicide; the Néel temperature is estimated at T_N = 7.5 K in agreement with that reported previously [8]. On the contrary, the curve $M(T)$ for the hydride NdCoSiH exhibits a sharp increase of M at the Curie temperature T_C = 20.5 K. Below T_C, the preliminary investigation of NdCoSiH by neutron diffraction reveals a ferromagnetic structure with a Nd-magnetic moment along the c-axis.

3. Conclusion

The H-insertion into the [RE_4] tetrahedral sites of the compounds *RETX* adopting the CeFeSi-type, induces a pronounced anisotropic expansion of the unit cell. These structural changes provoke a higher separation along the c-axis of the [RE_4T_4] antiprism blocks modifying strongly the physical properties of the initial intermetallic.

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