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Change in valence of Ce ions induced by hydrogen absorption : CeRu₂ (*)

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Résumé. — On a préparé les hydrures ternaires des composés supraconducteurs de structure cubique phase de Laves, CeRu₂ et LaRu₂. On constate, avec la conservation de la structure cubique, une forte dilatation du réseau. Pour les deux hydrures, des mesures de susceptibilité révèlent la disparition de la supraconductivité et, dans le cas de CeRu₂, l'apparition d'une transition magnétique à $T \sim 1,4$ K. Le CeRu₂H_x a pu être désorbé. Après désorption de CeRu₂, la supraconductivité est rétablie. Les mesures de l'aimantation du CeRu₂H_x et la valeur de sa constante de réseau, comparée à celle du LaRu₂H_x, semblent indiquer qu'avec l'hydrogénation, le cérium a changé de valence pour devenir trivalent.

Abstract. — Ternary hydrides of superconducting cubic Laves-phases CeRu₂ and LaRu₂ have been prepared. The cubic structure is preserved and a considerable lattice expansion is observed. Magnetic susceptibility measurements show the disappearance of the superconducting transition for both hydrides, and in the case of CeRu₂, the appearance of a susceptibility peak at $T \sim 1.4$ K. For CeRu₂ hydride, the hydrogen could be removed and superconductivity reestablished. Magnetization measurements of CeRu₂ hydride and comparison of its lattice parameter with that of LaRu₂ hydride indicate that, with hydrogenation, the valence of Ce has changed from 4 to 3.

Rare-earth intermetallic compounds are well-known to absorb large quantities of hydrogen. Such hydrides are of great interest for technological reasons (for example energy storage). From a more fundamental point of view, controlled introduction of hydrogen into these compounds is a good tool for modification of the structure of the material and hence, some physical properties like superconductivity and magnetism.

We have studied the cubic Laves-phase compounds CeRu₂ and LaRu₂. From a comparison of its lattice parameters with those of the trivalent RE-Ru₂ it appears that cerium is tetravalent in CeRu₂ [1]. Both Ce and La have no localized 4f electrons in these compounds. Furthermore, these two compounds are superconducting and are reported to absorb large quantities of hydrogen [2].

The samples were prepared by induction melting.

The CeRu₂ was sealed in a tantalum container and annealed at 1 100 °C for 10 days, and at 1 300 °C for few hours. The LaRu₂ was annealed at 1 150 °C for 3 hours in the induction furnace.

Different values of the superconducting transition temperature (T_c) have been published for these compounds. The T_c varies between 4.9 K and 6.2 K for CeRu₂ and between 3.08 K and 4.4 K for LaRu₂ [3-4]. We have obtained a T_c of 5.8 K for CeRu₂ and 3.6 K for LaRu₂. A careful investigation in the case of CeRu₂ has revealed that this lower value is due to contamination by tantalum. We are uncertain as to the reason for LaRu₂.

For hydrogenation small pieces of the sample were placed in a stainless steel reactor connected to a vacuum line. After each hydrogenation the structure of the compounds was checked by X-ray analysis. Attempts to hydrogenate from 200 to 700 °C with pressures above 1 atm., have all led to the dissociation of the starting materials. Lines associated with Ru could be identified in the X-ray patterns of both compounds. However, hydrogenation at room temperature has been conducted successfully. The sample is

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activated by going several times through pressure (10 bars)-vacuum cycles. Then hydrogen pressure (10 bars) is introduced and the sample is left for four days. A second method which consists in using higher pressure (110 bars) and letting the sample absorb for one day has led to the same results concerning the data presented in this paper. The samples are broken into tiny particles by hydrogenation.

X-ray diffraction measurements have been carried out at room temperature, in a vacuum chamber. For both hydrogenated compounds, the X-ray diagrams show that the cubic Laves-phase structure is preserved upon the formation of the ternary hydrides CeRu_2H_x and LaRu_2H_x , where $x \approx 4$, as found by preliminary volumetric measurements. A lattice expansion and a significant line broadening is observed.

As can be seen from table I the relative increase of the lattice parameter $\Delta a/a$ of CeRu_2H_x is larger than that of the hydride LaRu_2H_x . It is important to notice that the lattice parameters for the two hydrides are much nearer the same value than those of the starting materials. The present experiments do not allow us to determine the location of the hydrogens.

Table I.

	a_0	a	$\Delta a/a$
CeRu ₂	7.535 Å ± 0.001 Å	8.40 Å	12 %
LaRu ₂	7.711 Å ± 0.001 Å	8.42 Å	9 %

a_0 : lattice parameter of the starting material.

a : lattice parameter of the hydride.

$\Delta a/a$: relative expansion of the lattice.

Desorption experiments under vacuum have been attempted for both hydrides. The sample is introduced into a quartz tube and heated at a fixed temperature for more than 3 hours. In the case of CeRu_2H_x no change in the X-ray diagrams is observed for temperatures below 150 °C. Desorption starts at 150 °C with the X-ray diagram showing lines both of the initial compound and the hydride. When increasing the desorption temperature we observe that the relative intensity of the two series of lines changes in favour of CeRu_2 . After desorption at 200 °C only the lines of CeRu_2 were seen. During this evolution, the values of the lattice parameters of both phases, respectively a_0 and a , do not change. The width of the lines of CeRu_2 are as sharp as those of the starting material.

For LaRu_2H_x , after a desorption experiment at 150 °C, the X-ray patterns give evidence of Ru as well as the hydride. Thus, desorption of LaRu_2H_x was not successful.

The temperature dependence of the AC (20 Hz) susceptibility is measured by a sensitive mutual inductance bridge. Hydrogenation leads to a sudden disappearance of the superconducting transition as

Fig. 1. — Temperature dependence of the AC susceptibility. *a* : Hydride of CeRu_2 , obtained by hydrogenation, at 10 bars during 4 days. *b* : Desorbed hydride of CeRu_2 at 200 °C. *c* : Desorbed hydride of CeRu_2 at 200 °C, followed by thermal treatment at 700 °C.

shown in figure 1 (in figure 1*a* the small superconducting transition at $T \sim 5.8$ K is probably a contribution of non-hydrogenated grains) and to a clear paramagnetic susceptibility. Furthermore, a peak of susceptibility is observed at $T \sim 1.4$ K indicating the onset of magnetic ordering. Desorption at 200 °C reduces the paramagnetic part of susceptibility, and no peak is observed down to 1.3 K (Fig. 1*b*). To reestablish the superconducting transition, a thermal treatment at 700 °C is needed.

The T_c defined at the mid-point of the transition is the same as that of the starting material, i.e. $T_c \sim 5.8$ K (Fig. 1*c*) but the transition is broader. However at 4.5 K almost 15 % of the compound is still normal and the transition is completed only at 2.5 K. The reason for this is not known. For the hydride of LaRu_2 , the disappearance of the superconducting transition is not associated with any special feature in the susceptibility, within the temperature range explored.

In order to investigate the paramagnetic susceptibility of the CeRu_2H_x , magnetization measurements in a field up to 80 kOe have been conducted in the temperature range 1.4-4.2 K. Figure 2 shows the magnetization *versus* the applied field at 1.47 K.

In contrast to the Pauli like paramagnetism of CeRu_2 [4], the hydrogenated compound shows a Brillouin like magnetization, which must be due to trivalent cerium ions. By assuming that all cerium ions in the sample have the same moment we have derived

Fig. 2. — Magnetization measurements of the hydride of CeRu_2 at 1.47 K. Insert shows the reciprocal susceptibility versus temperature.

the magnetic moment per cerium atom from the saturation magnetization. The calculated value, $0.65 \pm 0.03 \mu_B$, is lower than the moment of $2.14 \mu_B$ for free Ce^{3+} ion. This is possibly due to the fact that the ground state of trivalent cerium in the hydride is the Γ_7 as found in cubic CeAl_2 [5] and $\text{Ce}_x\text{La}_{1-x}\text{Th}$ [6].

In the high field region, we observe a Van Vleck type susceptibility which may be due to the presence of crystalline field effects.

From the curve $1/\chi$ versus T plotted in the insert of figure 2 we have deduced a Curie constant which is slightly lower than that of a Γ_7 ground state. This curve seems also to confirm the appearance of magnetic ordering at about 1 K. The nature of this ordering is yet to be investigated.

In conclusion, the disappearance of superconductivity, the appearance of the paramagnetic susceptibility, with a saturation magnetization of $0.65 \mu_B$ per Ce ion, and the very close values of the lattice parameters of CeRu_2H_x and LaRu_2H_x lead one to conclude that hydrogen absorption has induced an almost perfect change of valence of cerium from tetravalent into trivalent ion. Other experiments are in progress to test the validity of this interpretation.

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