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

G. X. Tessema, J. Peyrard, A. Nemoz
Centre de Recherches sur les Très Basses Températures, C.N.R.S., B.P. 166X, 38042 Grenoble Cedex, France

J. P. Senateur, A. Rouault and R. Fruchart
Equipe de Recherches du C.N.R.S. (**), Section du Génie Physique de l'ENSEGP, INPG, B.P. 46, 38042 Saint-Martin-d'Hères, France

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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 $T \approx 1.4$ K. Le CeRu2Hx a pu être désorbé. Après désorption de CeRu2, la supraconductivité est rétablie. Les mesures de l'aimantation du CeRu2Hx et la valeur de sa constante de réseau, comparée à celle du LaRu2Hx, 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 $T \approx 1.4$ 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 1100 °C for 10 days, and at 1300 °C for few hours. The LaRu2 was annealed at 1150 °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...
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$_2$H$_x$ and LaRu$_2$H$_x$, 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$_2$H$_x$ is larger than that of the hydride LaRu$_2$H$_x$. 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.

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ (Å)</th>
<th>$a$ (Å)</th>
<th>$\Delta a/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeRu$_2$</td>
<td>7.535 ± 0.001</td>
<td>8.40</td>
<td>12%</td>
</tr>
<tr>
<td>LaRu$_2$</td>
<td>7.711 ± 0.001</td>
<td>8.42</td>
<td>9%</td>
</tr>
</tbody>
</table>

$a_0$ : 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$_2$H$_x$ 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$_2$H$_x$, after a desorption experiment at 150 °C, the X-ray patterns give evidence of Ru as well as the hydride. Thus, desorption of LaRu$_2$H$_x$ 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 shown in figure 1 (in figure 1a 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. 1b). 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. 1c) 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$_2$H$_x$, 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
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 $\Gamma_7$ state found in cubic CeAl$_2$ [5] and Ce$_2$La$_{1-x}$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 $1/T$ versus $T$ plotted in the insert of figure 2 we have deduced a Curie constant which is slightly lower than that of a $\Gamma_7$ 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$_2$H$_x$ and LaRu$_2$H$_x$ 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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References