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Change in valence of Ce ions induced by hydrogen absorption : $CeRu_2$ (*)

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Résumé. — On a préparé les hydrures ternaires des composés supraconducteurs de structure cubique phase de Laves, $CeRu_2$ et $LaRu_2$. 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 $CeRu_2$, l'apparition d'une transition magnétique à $T \sim 1,4$ K. Le $CeRu_2H_x$ a pu être désorbé. Après désorption de $CeRu_2$, la supraconductivité est rétablie. Les mesures de l'aimantation du $CeRu_2H_x$ et la valeur de sa constante de réseau, comparée à celle du $LaRu_2H_x$, semblent indiquer qu'avec l'hydrogénation, le cérium a changé de valence pour devenir trivalent.

Abstract. — Ternary hydrides of superconducting cubic Laves-phases $CeRu_2$ and $LaRu_2$ 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 $CeRu_2$, the appearance of a susceptibility peak at $T \sim 1.4$ K. For $CeRu_2$ hydride, the hydrogen could be removed and superconductivity reestablished. Magnetization measurements of $CeRu_2$ hydride and comparison of its lattice parameter with that of $LaRu_2$ 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 $CeRu_2$ and $LaRu_2$. From a comparison of its lattice parameters with those of the trivalent RE-Ru_2 it appears that cerium is tetravalent in $CeRu_2$ [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 $CeRu_2$ was sealed in a tantalum container and annealed at 1 100 °C for 10 days, and at 1 300 °C for few hours. The $LaRu_2$ 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 $CeRu_2$ and between 3.08 K and 4.4 K for $LaRu_2$ [3-4]. We have obtained a T_c of 5.8 K for $CeRu_2$ and 3.6 K for $LaRu_2$. A careful investigation in the case of $CeRu_2$ has revealed that this lower value is due to contamination by tantalum. We are uncertain as to the reason for $LaRu_2$.

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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(**) N° 155.

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 $x \simeq 4$, 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 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.

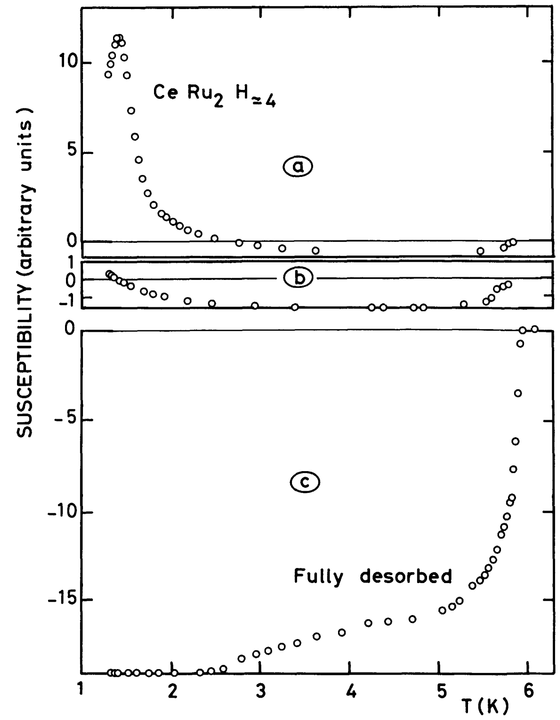

Fig. 1. — Temperature dependence of the AC susceptibility. *a* : Hydride of $CeRu_2$, obtained by hydrogenation, at 10 bars during 4 days. *b* : Desorbed hydride of $CeRu_2$ at 200 °C. *c* : Desorbed hydride of $CeRu_2$ at 200 °C, followed by thermal treatment at 700 °C.

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

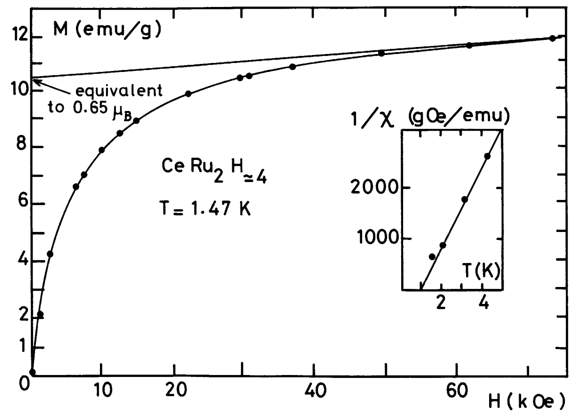

Fig. 2. — Magnetization measurements of the hydride of $CeRu_2$ at 1.47 K. Insert shows the reciprocal susceptibility *versus* temperature.

the magnetic moment per cerium atom from the saturation magnetization. The calculated value, 0.65 ± 0.03 μ_B, is lower than the moment of 2.14 μ_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 $Ce_xLa_{1-x}Th$ [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 $1/\chi$ *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 μ_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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