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CeRhIn: A new mixed-valent cerium compound

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A new ternary equiatomic compound, CeRhIn, has been synthesized which is found to crystallize in the hexagonal Fe_2P-type structure. The unit-cell volume of this compound deviates from that expected on the basis of lanthanide contraction, indicating the nontrivalent state of the Ce ions in this compound. The magnetic susceptibility of CeRhIn shows a broad maximum at about 150 K. Such a maximum is a characteristic feature of the mixed-valent cerium compounds. The resistivity of CeRhIn due to magnetic scattering also shows a broad maximum at about 140 K. Thus from lattice volume, susceptibility, and resistivity measurements, it is concluded that cerium ions are in a mixed-valent state in CeRhIn.

The rare earths and actinides are the most interesting elements in the Periodic Table in terms of their behavior in elemental form as well as in alloys and intermetallic compounds. In the past few years, much attention has been attracted by some of the intermetallic compounds of rare earths (Ce, Eu, and Yb), exhibiting anomalous physical properties such as heavy-fermion behavior, superconductivity, the Kondo effect, magnetic ordering with anomalous ordering temperatures, and valence-fluctuation phenomena, etc.[1-6] These anomalous properties are associated with the instability of the $4f$ shell, which causes a spread of the localized $4f$ level over a certain energy range. The valence fluctuation in rare-earth compounds is one of the most interesting puzzles in the study on the physical and chemical properties of these compounds. Therefore, it is of interest to synthesized new mixed-valent compounds to understand the phenomenon. The mixed-valent behavior of Ce-based compounds is of particular interest, as its $4f$ shell contains only one electron, which may make theoretical models simple. In earlier work, it has been shown that the compound CePdSn is antiferromagnetically ordered with anomalously high Néel temperature ($T_N = 7.5$ K) (Ref. 7) compared with $T_N = 14.6$ K of isostructural GdPdSn. We report here the crystal structure, magnetic susceptibility, and electrical resistivity of a new compound, CeRhIn, prepared for the first time in our laboratory. We find that this compound exhibits the characteristic properties of a mixed-valent cerium compound.

The compound CeRhIn was prepared by arc melting of the stoichiometric amounts of the constituent elements of purity better than 99.99%, on a water-cooled copper hearth under argon atmosphere. For comparison, the compound LaRhIn with nonmagnetic La was also prepared in the same manner. Powder x-ray diffraction patterns were obtained at room temperature using Cu $K\alpha$ radiation. The magnetic susceptibility was measured at various temperatures between 4.2 and 300 K in an applied field of 6 kOe using the Faraday method. Measurements of electrical resistivity were made in the temperature range of 4.2–300 K, using a standard four-probe dc method. The contacts to the samples were made with a conducting silver paint. The temperatures were measured using a carbon-glass thermometer below 30 K and with a platinum-resistance thermometer above 30 K.

Room-temperature powder x-ray diffraction patterns revealed that the compounds CeRhIn and LaRhIn are single-phase materials, crystallizing in the Fe_2P-type structure (space group $P\bar{6}2m$) with three formula units per unit cell. This result is consistent with the crystal structure observed in other RRhIn (R = rare earth) compounds.[8] In the Fe_2P-type structure of RRhIn compounds, the R atoms occupy the ($3g$) sites, In atoms occupy the ($3f$) sites, and Rh atoms occupy the ($2c$) and the ($1b$) sites. The room-temperature lattice parameter values are obtained from the measured d values by applying a least-squares fitting procedure. The lattice parameters obtained are $a = 7.547$ Å and $c = 4.05$ Å for CeRhIn and $a = 7.610$ Å and $c = 4.129$ Å for LaRhIn. Figure 1 shows the plot of the variation of unit-cell volume of RRhIn compounds with a rare-earth ion. The unit-cell volume of CeRhIn deviates from that expected on the basis of normal lanthanide contraction for trivalent rare-earth ions, indicating the nontrivalent nature of the Ce ion in this compound. Since the hypothetical tetravalent lattice constant is not known, it is difficult to make an estimate of the Ce valence in CeRhIn from the present unit-cell volume data. However, evidence for the valence fluc-

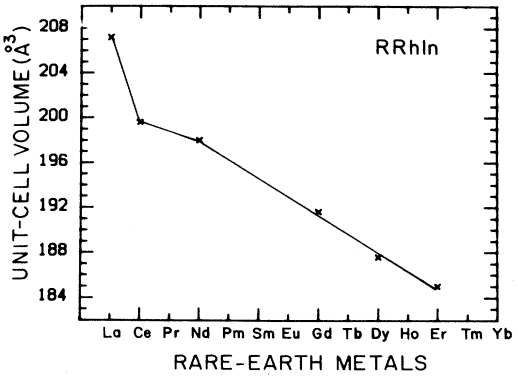

FIG. 1. Variation of unit-cell volume with rare-earth ion (R) in RRhIn compounds.

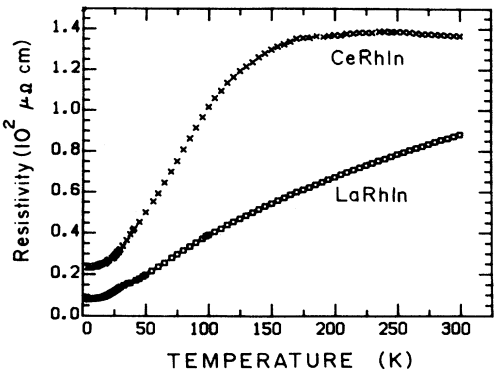

FIG. 3. Resistivity vs temperature for CeRhIn and LaRhIn.

tuation behavior of Ce ions in CeRhIn follows from the magnetic susceptibility and electrical resistivity measurements presented below.

Figure 2 shows the magnetic susceptibility of CeRhIn as a function of temperature in the range of 4.2–300 K. Between 200 and 300 K, the susceptibility follows Curie-Weiss behavior. However, this temperature range is too limited to obtain a meaningful value of the paramagnetic Curie temperature and the effective paramagnetic moment. The susceptibility passes through a broad maximum at about 150 K followed by a rapid rise at low temperatures. The rapid rise may be attributed either to the presence of a small amount of static Ce^{3+} ions stabilized by lattice defects or to traces of other magnetic rare-earth ions. However, this type of behavior may also be intrinsic, as pointed out by Gschneidner[9] in the case of $CeSn_3$. A maximum in the susceptibility is a common feature of Ce- and Yb-based valence-fluctuating compounds.[10,11] For instance, $CeIr_2Si_2$, in which Ce ions are in a mixed-valent state, also shows a broad maximum in the susceptibility at 120 K.[12]

The observed behavior of the magnetic susceptibility of CeRhIn can be understood by the ionic two-level interconfiguration fluctuation model (ICF) proposed by Sales and Wohlleben.[13] According to this model the temperature dependence of the susceptibility is given by the following equation:

$$\chi(T)=(1-n)\left[\frac{\mu_1 P(T)+\mu_2[1-P(T)]}{(T+T_{SF})}\right]+n\frac{C}{T}+\chi_0 , \tag{1}$$

with

$$P(T)=\frac{2J_1+1}{2J_1+1+(2J_2+1)\exp(-E_{ex}/kT)} , \tag{2}$$

where T_{SF} is the spin-fluctuation temperature, n gives the fraction of magnetic impurities which we take to be the stable Ce^{3+} ions, χ_0 is the temperature-independent susceptibility, J_1, J_2, μ_1, and μ_2 are total angular momenta and effective paramagnetic moments of the Ce^{4+} and Ce^{3+} states, respectively, E_{ex} is the excitation energy between the ground-state configuration (Ce^{4+}) and the next excited configuration (Ce^{3+}), and $P(T)$ is the fractional occupation of the Ce^{4+} state. At high temperatures, Eq. (1) predicts a Curie-Weiss behavior of susceptibility. At low temperatures, the susceptibility does not diverge as $1/T$ but rather approaches a temperature-independent value due to the presence of the $T+T_{SF}$ term in the

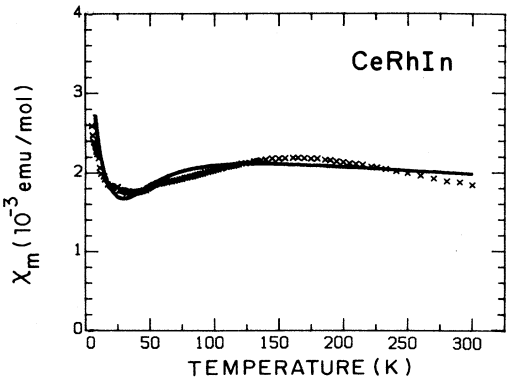

FIG. 2. Magnetic susceptibility of CeRhIn as a function of temperature. The solid line shows fit to the experimental data using Eq. (1) (see text).

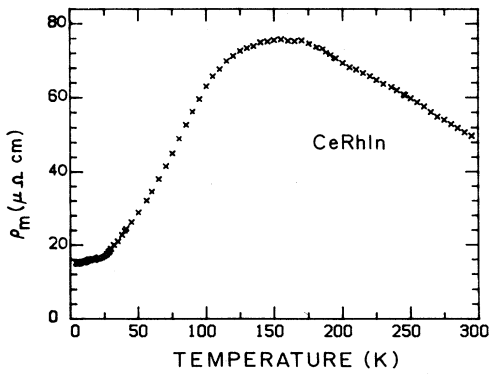

FIG. 4. Magnetic contribution to the resistivity of CeRhIn as a function of the temperature obtained after subtracting the resistivity of LaRhIn.

denominator. The spin-fluctuation temperature is related to the width of the $4f$ level. The $4f$ level is broadened due to the exchange interaction between the conduction electron and the $4f$ electrons. A typical fit to the susceptibility data using Eq. (1) is shown in Fig. 1 as a solid line. The values of the parameters obtained by least-squares fitting of the susceptibility are $E_{ex}=133$ K, $T_{SF}=500$ K, $n=0.016$, and $\chi_0=1.13\times10^{-3}$ (emu/mol).

Four-probe dc electrical resistivity measurements on CeRhIn and LaRhIn were made on a rectangular samples of uniform thickness in the temperature range of 4.2–300 K. Data were collected by applying the current in each direction to eliminate possible thermal effects. The resistivity of the La-based compound was measured in order to estimate the phonon contribution to the resistivity of CeRhIn. The results of resistivity measurements on CeRhIn and LaRhIn are shown in Fig. 3. The room-temperature resistivity of CeRhIn is 140 $\mu\Omega$ cm, which is of the same order of magnitude as the resistivity of other Ce-based mixed-valent systems.[14,15] Further, the resistivity of CeRhIn exhibits a quadratic temperature dependence at low temperatures followed by a linear variation in the temperature range of 30–120 K. Between 200 and 300 K, the resistivity shows weakly temperature-dependent behavior. The overall feature of the resistivity curve for CeRhIn is nearly similar to that reported for mixed-valent $CeIr_2Si_2$.[12] The magnetic or the $4f$ contribution to the resistivity ρ_m in CeRhIn was obtained by subtracting the resistivity of LaRhIn, and the results are shown in Fig. 4. The most prominent feature of this curve is the presence of a broad maximum in the magnetic contribution to the resistivity at a temperature (T_{max}) of about 140 K. The temperature where the susceptibility shows a broad maximum is almost the same where resistivity also shows a broad maximum. The same type of maximum has been observed in some of the mixed-valent cerium compounds.[16] The maximum in the resistivity curve can be interpreted in terms of spin-scattering mechanism in the mixed-valent regime.[16]

In conclusion, a new compound, CeRhIn, crystallizing in the hexagonal Fe_2P-type structure, has been synthesized. The unit-cell volume, magnetic susceptibility, and resistivity measurements reveal that Ce ions are in a mixed-valent state in this compound.

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