

Valence state of Ce and the magnetism in CeRh_3B_2

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The compound CeRh_3B_2 orders magnetically with a high Curie temperature (T_C) of 115 K but with a low moment of only $0.4\mu_B$. L_{III} absorption-edge measurements show a dominant absorption peak at the energy corresponding to trivalent cerium. Magnetic studies on the compounds $\text{Ce}(\text{Rh}_{1-x}\text{T}_x)_3\text{B}_2$ with $T = \text{Ru}$ and Os reveal that the magnetic state is very rapidly broken up with the replacement of Rh by Ru and Os. These results, along with the observation of a high T_C in CeRh_3B_2 , suggest that magnetism in this compound arises from a strong hybridization of nearly localized or slightly delocalized Ce 4*f* electrons with conduction electrons. The small moment may be due to a Kondo-type interaction coupled with crystal-field effects.

Recently, the crystal structure¹ and magnetic behavior of a series of ternary borides represented by the formula RRh_3B_2 ($R = \text{La}$ to Gd) has been reported.² These compounds crystallize in the hexagonal CeCo_3B_2 -type structure with space group $P6/mmm$. In this series, the compound LaRh_3B_2 shows superconducting behavior below a temperature of about 2.5 K, while the remaining compounds, including CeRh_3B_2 , are magnetically ordered. The Nd compound may be antiferromagnetically ordered, while the magnetism in the Eu compound is very sensitive to stoichiometry and may be due to stabilization of divalent Eu ions.³ The unit-cell volume of CeRh_3B_2 is lower¹ than that expected for trivalent Ce ions, which led to the belief that Ce in this compound may be in a mixed-valent state. Therefore, the observation of magnetic ordering in CeRh_3B_2 was rather unexpected.

The compound CeRh_3B_2 has some unusual features in its magnetism. Its saturation moment is only about $0.4\mu_B$ per formula unit, which is much smaller than the Ce^{3+} free-ion moment. This is also much smaller than the value of about $7\mu_B$ per formula unit in isostructural GdRh_3B_2 . Yet it is remarkable that the ordering temperature of CeRh_3B_2 is higher than that of GdRh_3B_2 (91 K). In fact, this is, to date, the highest known ordering temperature for any cerium compound with nonmagnetic elements. In the paramagnetic state, the susceptibility follows a non-Curie-Weiss behavior. However, much above the Curie temperature (T_C), the susceptibility has been fitted to the Curie-Weiss law, which yields an effective moment (μ_{eff}) of about $3.0\mu_B$, and a large and negative paramagnetic Curie temperature. Consideration of the unit-cell volume anomaly (or the possible intermediate valence state of Ce), the low saturation moment, and the high ratio of the effective paramagnetic moment to the saturation moment, led to the suggestion that the magnetism in this compound is of the itinerant type arising primarily from the Rh *d* band, which is hybridized with delocalized Ce 4*f* electrons. Resistivity⁴ and heat capacity⁵ measurements are also consistent with these ideas.

The above picture relies very heavily on the assumption of an intermediate valence state of cerium. Therefore, in

order to gain further understanding of the nature of the valence state of cerium and the magnetism in CeRh_3B_2 , we have carried out L_{III} absorption-edge studies on this compound, and also investigated the effect of partially substituting other elements at various sites (e.g., La for Ce;⁶ Ru, Os,³ Ir, etc., for Rh; and Si for B³) on the magnetism of this compound. From absorption-edge studies, we find that Ce is nearly trivalent in CeRh_3B_2 . Furthermore, the magnetic state can be rapidly broken up, and a collapse of the magnetic moment occurs in $\text{Ce}(\text{Rh}_{1-x}\text{T}_x)_3\text{B}_2$ ($T = \text{Ru}, \text{Os}$), even with small replacement of Rh by Ru and Os (around $x = 0.167$). These results suggest that the magnetism in CeRh_3B_2 and $\text{Ce}(\text{Rh}_{1-x}\text{T}_x)_3\text{B}_2$ arises from strong hybridization of nearly localized (or slightly delocalized) Ce 4*f* electrons, with *sp* conduction electrons and/or transition-metal-derived 4*d*, 5*d* electrons. The magnetic state is strongly influenced by the changes in the 4*f*-4*d*, 5*d* hybridization.

The compounds $\text{Ce}(\text{Rh}_{1-x}\text{T}_x)_3\text{B}_2$, where $T = \text{Ru}, \text{Os}$ ($x = 0.0, 0.033, 0.067, 0.1, 0.133, 0.167$), were prepared by repeated arc melting of stoichiometric amounts of the high-purity constituent elements in a purified argon atmosphere. Powder x-ray diffraction patterns obtained using $\text{Cu K}\alpha$ radiation on a Rigaku x-ray diffractometer showed the presence of single-phase materials with the CeCo_3B_2 -type structure. X-ray absorption-edge studies were carried out using the C2 beam line at CHESS. Magnetization studies on the as-cast samples were carried out using a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 5–300 K. The magnetization versus field isotherms were obtained at 5 K up to 50 kOe applied field.

The lattice parameters as a function of x are plotted in Fig. 1. On Ru or Os substitution, the *a* lattice parameter increases and the *c* parameter decreases. The unit-cell volume slightly decreases, or remains nearly constant with increasing x (within the range of values of x investigated).

The L_{III} near-edge spectra show an intense white-line peak arising from the transition of a 2*p* core electron to the empty 5*d* states at the Fermi level. In intermediate- or mixed-valent rare-earth compounds, a double peak structure is generally observed because of the presence of two final

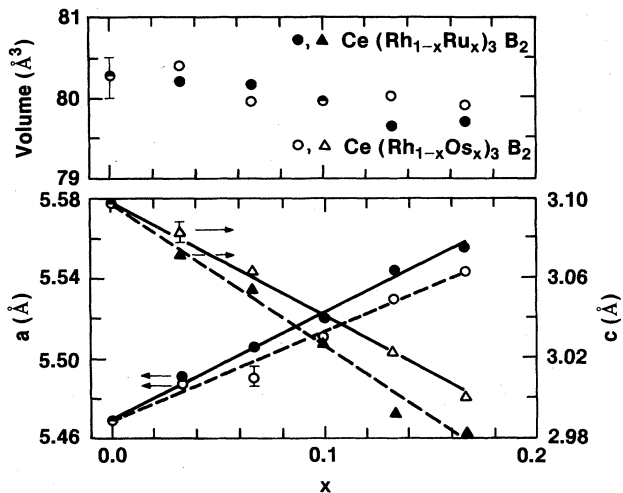


FIG. 1. Lattice parameters and unit-cell volume of $\text{Ce}(\text{Rh}_{1-x}\text{T}_x)_3\text{B}_2$ compounds ($T = \text{Ru}, \text{Os}$) as a function of x .

states. The separation ΔE between the two peaks is given by the difference in the Coulomb energies of those states. In the case of Ce, this separation is typically of the order of 7–10 eV. The room-temperature L_{III} absorption-edge spectrum of CeRh_3B_2 is shown in Fig. 2(a). Contrary to the expectations based on the unit-cell anomaly, a dominant single

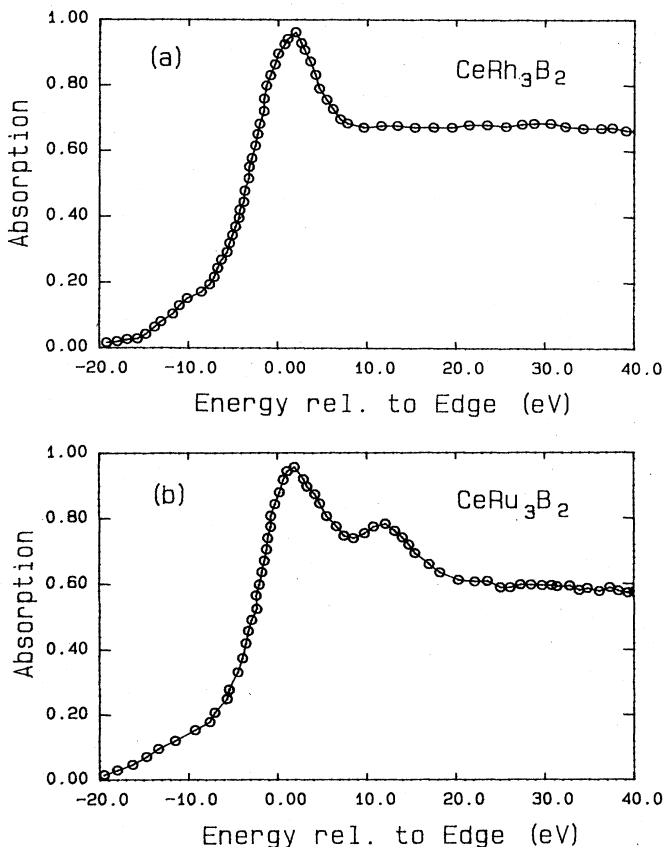


FIG. 2. L_{III} absorption-edge spectra of Ce in (a) CeRh_3B_2 and (b) CeRu_3B_2 .

peak is observed at the trivalent cerium energy position. The intensity of the second line expected at the Ce^{4+} position is very small and buried in the noise. Similar results have been obtained by others.⁷ By contrast, superconducting⁵ CeRu_3B_2 shows a pronounced anomaly in the unit-cell volume, and the presence of two prominent peaks in the L_{III} near-edge absorption spectrum [Fig. 2(b)].

Magnetic studies on $\text{Ce}(\text{Rh}_{1-x}\text{T}_x)_3\text{B}_2$ (where $T = \text{Ru}$ or Os) show that the magnetic state is strongly influenced when Rh is replaced by other $4d$ or $5d$ elements which are nonisoelectronic to Rh. Figure 3(a) shows the plot of the magnetic moment per formula unit versus temperature for $\text{Ce}(\text{Rh}_{1-x}\text{Ru}_x)_3\text{B}_2$ compounds in an applied field of 5 kOe. Similar results are obtained in the $\text{Ce}(\text{Rh}_{1-x}\text{Os}_x)_3\text{B}_2$ system [Fig. 3(b)]. As mentioned above, the compound CeRh_3B_2 is magnetically ordered with a low moment but a high T_C of 115 K. As Ru or Os is substituted for Rh, both the magnetization and the transition temperature show a drop. The decrease in T_C is so large that the compounds in which 16%–17% Rh is replaced by Ru or Os do not show magnetic

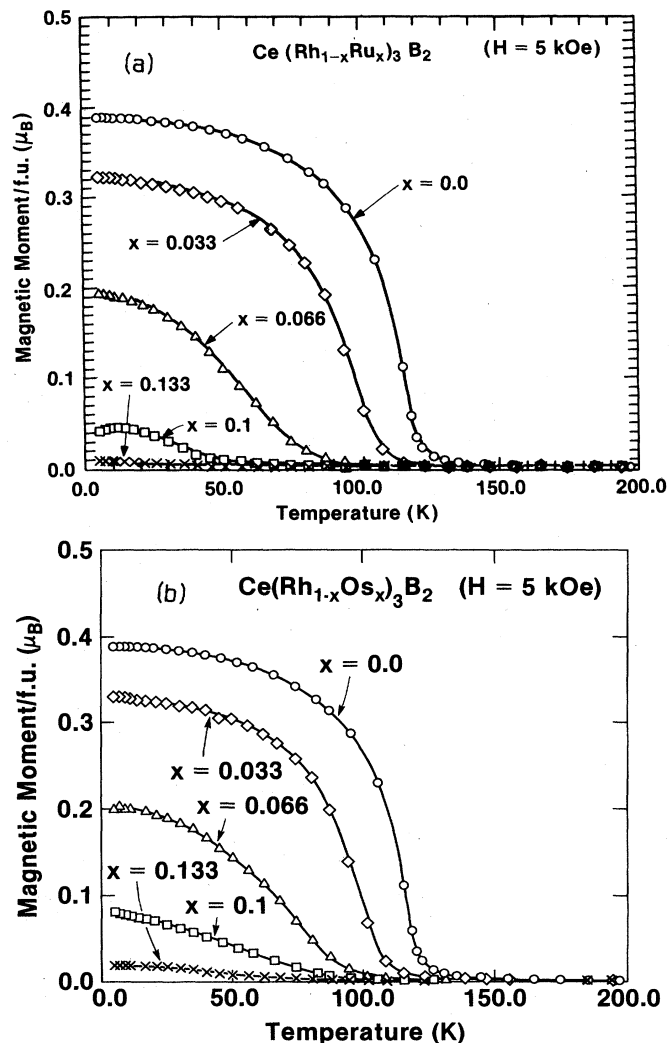


FIG. 3. Magnetic moment per formula unit vs temperature in 5 kOe applied field for (a) $\text{Ce}(\text{Rh}_{1-x}\text{Ru}_x)_3\text{B}_2$ alloys and (b) $\text{Ce}(\text{Rh}_{1-x}\text{Os}_x)_3\text{B}_2$ alloys.

order down to 5 K. In compounds showing magnetic order, the transition broadens with increasing x , possibly due to disorder in the lattice, and it is not possible to obtain the exact value of T_C . Therefore, the point of steepest descent in the M - T curve has been defined as the transition temperature. For some values of x the magnetization shows a broad maxima at low temperatures. The Curie temperature and the saturation moment per formula unit are plotted in Fig. 4 as a function of x . It is observed that a collapse of the moment and a breakdown in the magnetic state occur with substitution of Rh by Ru or Os. Such effects related to the replacement of Rh by Ru have been noted by other researchers also.^{8,9}

The origin of magnetism in these compounds is of great interest. The magnetism can arise from the (i) Rh d band, (ii) Ce $4f$ electrons (either localized or band type) strongly interacting with the conduction electrons or hybridized with the transition metal d electrons, or (iii) localized Ce moments interacting in the usual Ruderman-Kittel-Kasuya-Yosida (RKKY) manner. The magnetism cannot be solely attributed to the Rh d band, because the remaining RRh_3B_2 compounds ($R = La$ to Gd) do not show such a behavior, in particular, the high Curie temperatures. The T_C of $GdRh_3B_2$ is, in fact, lower than that of $CeRh_3B_2$, while $LaRh_3B_2$ exhibits superconductivity. Moreover, recent band-structure calculations¹⁰ and the Rh $4d$ derived valence-band photoemission studies⁷ on $CeRh_3B_2$, reveal that the Fermi energy lies in a region of low density of states, which precludes satisfying the Stoner-Wohlfarth criteria for itinerant magnetism from the Rh d band alone. If the magnetism is attributed to localized trivalent Ce ions interacting in the usual (RKKY) manner, then according to the de Gennes rule its T_C should have been smaller by a factor of 100 from the measured value.

The lattice volume anomaly in $CeRh_3B_2$ has been taken to indicate that Ce in this compound is not in a completely trivalent state, but may exist in a mixed-valent state. Because of this, it was earlier suggested that the magnetism

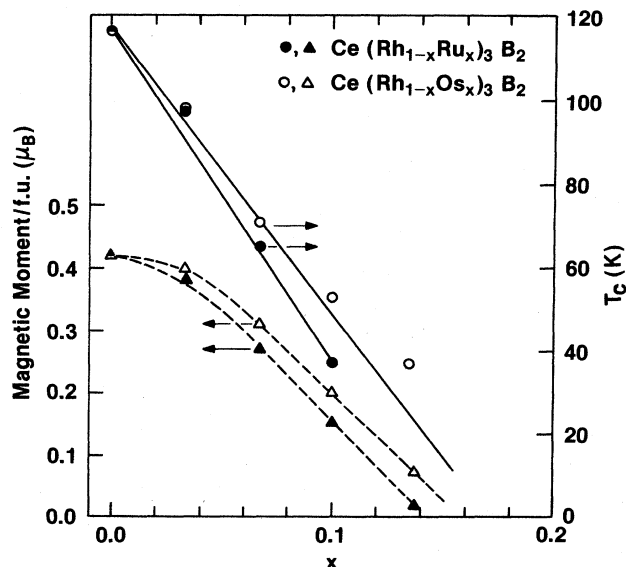


FIG. 4. Curie temperature and saturation moment vs x in $Ce(Rh_{1-x}T_x)_3B_2$ alloys ($T = Ru, Os$).

presumably arises from the Rh d band, with Ce $4f$ electrons playing an important role² (implying hybridization of delocalized or band-type Ce $4f$ electrons with Rh d band). However, the present L_{III} absorption-edge studies and those of others⁷ reveal the presence of a dominant single-valence state. Usually there are ambiguities in the interpretation of L_{III} edge spectra of Ce compounds, and even when two absorption peaks are observed it is not straightforward to estimate the relative amounts of the two valence states.¹¹ Furthermore, these studies do not reveal anything about the delocalization of $4f$ levels. The Ce-Ce distance in the c direction in $CeRh_3B_2$ is already small enough to give rise to some delocalization of the $4f$ electrons. Therefore, what we can infer at present from the L_{III} edge spectra is that the $4f$ count in $CeRh_3B_2$ is close to unity as would be expected for trivalent Ce ions. Therefore, the magnetism in $CeRh_3B_2$ should have its origin in the Ce $4f$ electrons (either localized or slightly delocalized). But, as remarked above, the usual RKKY interaction between Ce local moments cannot give rise to such a high T_C . Therefore, one has to further invoke strong hybridization between local or nearly localized Ce $4f$ electrons (with f occupation close to 1) and the conduction electrons or the transition-metal d electrons. Band-structure calculations on $CeRh_3B_2$ have indeed shown¹⁰ that there is considerable hybridization between the Ce $4f$ band and the Rh d band. (This hybridization is also partly responsible for the lattice volume anomaly, particularly in the lattice parameter in the c direction.) In view of the f count of nearly one in $CeRh_3B_2$, this compound should fall in the class of nearly trivalent or "Kondo lattice" systems such as $CeCu_2Si_2$.¹² The reduced magnetic moment of $CeRh_3B_2$ may be a consequence of Kondo-type interaction coupled with crystal-field effects on cerium ions, or it may be due to unusual spin arrangement. In this regard it may be mentioned here that neutron diffraction measurements on this compound are underway.¹³

It appears that the role of Rh is to provide proper hybridization so that magnetic ordering becomes possible. The hybridization changes when Rh is replaced by Ru or Os, and for some concentration of the transition metal a collapse in the magnetic moment occurs. On replacing Rh by Os and Ru the c lattice parameter decreases further, resulting in larger $4f$ - $4f$ overlap in the c direction, and presumably larger $4f$ bandwidths. This may result in further reduction of the magnetic moment. The system $Ce_{1-x}La_xRh_3B_2$ was also investigated,^{6,8,9} but the reduction in T_C and magnetic moment is not as pronounced as in the $Ce(Rh_{1-x}T_x)_3B_2$ ($T = Os, Ru$) system. In fact $Ce_{0.2}La_{0.8}Rh_3B_2$ is still magnetically ordered.

In conclusion, the L_{III} absorption-edge studies reveal a $4f$ count of nearly one in $CeRh_3B_2$. Furthermore, the magnetic state of $CeRh_3B_2$ is rapidly broken up by the substitution of Rh by a small amount of Os or Ru. The magnetism is thought to arise from strong hybridization of Ce $4f$ electrons with sp conduction electrons and the transition-metal d band. It is suggested that this compound may represent another nearly trivalent or Kondo lattice system. From Ce valence considerations, $CeRu_3B_2$ is similar to superconducting $CeCo_2$ and $CeRu_2$.¹⁴

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