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Itinerant magnetism in CeRh_3B_2

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Spin-polarized energy-band calculations, including spin-orbit coupling in the band Hamiltonian, have been performed on CeRh_3B_2 . Good agreement is obtained between theory and experiment concerning the magnetic moment. It is also found that the magnetic moment varies strongly with volume and from this a qualitative explanation for the anomalously high Curie temperature of the compound is proposed. Furthermore, the spin density is found to be highly nonspherical.

In the RRh_3B_2 series ($R = \text{La}$ to Gd) all compounds except LaRh_3B_2 order magnetically.^{1,2} The susceptibility follows a Curie-Weiss law at temperatures higher than the critical temperature for all compounds except LaRh_3B_2 (which is actually a superconductor at low temperatures). The effective moment deduced from the Curie-Weiss law is close to the free-ion value with the exception of CeRh_3B_2 . Here the effective moment is about $1\mu_B$.³ CeRh_3B_2 also seem anomalous in that the effective Curie temperature Θ_C estimated from the high-temperature susceptibility is -373 K.³ Specific-heat and susceptibility measurements at low temperatures indicate a critical temperature of 112 K in CeRh_3B_2 , which is in accordance with the Curie temperature deduced from magnetization measurements as well as from hyperfine-field data.⁴ This critical temperature for magnetic ordering is, however, higher than in any of the other RRh_3B_2 compounds, and considerably higher than would be expected from a de Gennes behavior through the series of compounds.

The magnetization measurements at low temperatures gave a moment of $0.38\mu_B/\text{f.u.}$ (f.u. is a formula unit),^{1-3,5} whereas the magnetic moment deduced from the hyperfine field was $0.4\mu_B/\text{f.u.}$ ⁴ These hyperfine-field measurements also demonstrated that the moment was located on the Ce atom in CeRh_3B_2 . At the critical temperature, CeRh_3B_2 showed a magnetic entropy equal to $0.11Nk_B \ln(2J+1)$ where J is $\frac{5}{2}$. This is only half of the value found in GdRh_3B_2 (Ref. 6). Furthermore, from magnetization measurements on a single crystal it was concluded that the moment lies in the c plane with a magnitude of $0.56\mu_B/\text{f.u.}$ ⁷

The magnetic and transport properties of the compound CeRh_3B_2 have also been found to show a strong dependence on alloying. For instance the resistivity of $\text{Ce}_{0.95}\text{La}_{0.05}\text{Rh}_3\text{B}_2$ shows typical features of a Kondo behavior.⁷ With a 10–25% substitution of Rh with Co the magnetic moment drops to $0.3\text{--}0.12\mu_B/\text{f.u.}$ ⁸ Furthermore, it was

found that the magnetism disappears when 15% Ru or Os replaces Rh.⁹

The crystal structure of CeRh_3B_2 is the CeCo_3B_2 type with the space group $P6/m\bar{m} (D'_{6h})$ (Ref. 10). The Ce atoms form linear chains along the c axis and the interatomic Ce-Ce distance is unusually small in this direction, only 3.09 Å. This is actually shorter than the Ce-Ce distance in, for instance, $\alpha\text{-Ce}$ and is less than the so-called Hill limit for Ce compounds, below which nonmagnetic behavior is expected.¹¹ On these grounds it has been suggested that the Ce $4f$ electrons are delocalized and bonding. This seems to fit with the decreased volume of CeRh_3B_2 , in comparison to the volume one would expect from a typical trivalent Ce ion in the compound. However, since this effect is less pronounced in CeRh_3B_2 than in the isostructural systems containing Ru and Co, it was suggested that CeRh_3B_2 is mixed valent with accompanying localized moments.⁸ However, this mixed-valence picture can be questioned, since L_{III} absorption-edge measurements show a $4f$ occupation of about one for the Ce atom.^{4,12} Finally, the hypothesis that the magnetism in CeRh_3B_2 originates from the Rh $4d$ band was ruled out by x-ray photoelectron spectroscopy (XPS).¹² The basis for this was the fact that no strong Rh $4d$ signal was detected at the Fermi level (E_F). Therefore, the Stoner criterion for the onset of ferromagnetism could not be obeyed for the Rh d electrons.

On the theoretical side, energy-band calculations showed that the $4f$ band in CeRh_3B_2 is about 2–3 eV broad.¹³ Furthermore, it was concluded that the Ce $4f$ -Rh $4d$ hybridization is the most dominating factor giving rise to this relatively broad $4f$ band. In another work the magnetic moment of CeRh_3B_2 was also calculated by a semiempirical method, which used a fitted Coulomb interaction parameter U to describe the interatomic repulsion between the $4f$ electrons.¹⁴ Depending on the choice of U , magnetic moments between

$(0.5-1.7)\mu_B$ could be obtained. Here it was also found that the $4f$ states showed the strongest dispersion along the hexagonal axis in the Brillouin zone (BZ), which reflects the influence of the large overlap between the $4f$ wave functions along the hexagonal axis in the Wigner-Seitz cell.

In the present work we will report on *ab initio* spin-polarized energy-band calculations for this compound. The electronic structure was calculated using the linear muffin-tin-orbital (LMTO) method.¹⁵ The frozen-core approximation was adopted and we used the analytical tetrahedron method¹⁶ to calculate the density of states (DOS) from eigenvalues at 45 k points in the irreducible wedge of the Brillouin zone. The self-consistent calculations were done at two levels of approximations. First a scalar relativistic approach was used and then the spin-orbit coupling¹⁷ was included. This offers the possibility to study the influence of this term in the band Hamiltonian. For the calculation without spin-orbit coupling several types of local approximations to the exchange and correlation potential were used.¹⁸ We first calculated the DOS of CeRh_3B_2 in the paramagnetic state. This DOS looks very much like the one reported from a Korringa-Kohn-Rostoker (KKR) calculation¹³ and therefore we choose not to show it. The $4f$ band width is about 2 eV, the Rh $4d$ band has a width of about 7 eV, and the B sp band is very broad. The $4f$ band is pinned at E_F whereas the main spectral weight of the Rh $4d$ band lies about 3 eV below E_F . The calculated Stoner product¹⁹ is 0.3, and this suggests that the paramagnetic state should be stable. However, since a magnetic ground state can coexist with a locally stable paramagnetic state, one has to split the spin-up and spin-down bands and iterate to see if a magnetic moment develops, even if the Stoner product is less than one. Hence, we tried several different magnitudes of the ferromagnetic splitting (antiferromagnetism was not considered since the system is reported to be a ferromagnet) and iterated to self-consistency. In none of the attempts did a finite magnetic moment develop, but instead the paramagnetic state was found to be an absolute minimum. Next we tried several different exchange and correlation potentials¹⁸ together with the above mentioned technique of splitting the spin bands. In none of the investigated cases did a magnetic moment develop. Hence this would suggest a deficiency in the presently known local approximations to the exchange and correlation potential or possibly a failure in describing the $4f$ electrons in CeRh_3B_2 as band states, since from this approach we could not reproduce the experimental findings of a ferromagnetic ground state.

However, when we include the spin-orbit interaction in the band Hamiltonian¹⁷ together with the Barth-Hedin-Janak¹⁸ exchange and correlation potential, a nonzero moment is calculated self-consistently (the state at zero moment is still, however, locally stable and hence is the relativistic Stoner product²⁰ less than one). The magnitude of the magnetic moment is $0.27\mu_B/\text{f.u.}$ and it can be decomposed into a Ce moment of $0.25\mu_B/\text{atom}$ and a Rh moment of $0.02\mu_B/\text{atom}$. The orbital contributions to the magnetism in this system are very small, for instance on the Ce atom the orbital moment is only $-0.04\mu_B/\text{atom}$.

In Table I we show the $4f$ occupation number for the spin-up and spin-down bands, decomposed on the different azimuthal quantum numbers. Here we note that the occupation is largest for the $l=3, m_l=0$ state, and the partial moment is also dominating for this orbital. Since this orbital has a spatial extension that is pointing in the direction along the c axis, this indicates that the chemical bonding of the $4f$ states is of a rather covalent character.

The orbitals that have the second largest occupation are the $l=3, m_l=\pm 2$ states. In Ref. 13 it was realized that these orbitals are pointing in a direction which approximately coincides with the direction between the Ce atom and the neighboring Rh atoms. This also shows that the covalent character of the $4f$ bonding is pronounced and that charge density builds up between the Ce-Ce atoms and the Ce-Rh atoms. The total number of f electrons is somewhat larger than one, typical for the f occupancy given by the local spin-density approximation on Ce metal and compounds involving Ce.²¹ The spin density in the Ce-Rh direction is low, contrary to the charge density, while the spin density in the Ce-Ce direction is rather high (Table I).

This can clearly be seen from the lm -projected state densities for the Ce atom. In Fig. 1 we show the total DOS from our calculation together with the lm -projected DOS for the Ce $4f$ states. In Fig. 1 we have summed all states having m_l nonzero, to one joint DOS. Here we notice that the $m_l=0$ states lie about 0.5 eV lower in energy than the other m_l states. We also see that the exchange splitting is quite large for the $m_l=0$ states and most of the spin moment is therefore located on this orbital. This suggests that the spin density in CeRh_3B_2 is highly nonspherical, something that should be possible to probe, using for instance, neutron scattering experiments.

The agreement between the computed and the experimental moment is quite acceptable but a bit too low. However, this discrepancy may be explained by the strong volume dependence of the magnetic moment. This is illustrated in Fig. 2 where we show the calculated magnetic moment as a function of volume. This strong dependence is especially apparent for volumes close to the experimental low-temperature volume. For instance, it is clear from Fig. 2 that a volume increase of somewhat less than 1% gives a magnetic moment of $0.38\mu_B/\text{f.u.}$, i.e., the experimental value. In connection with this strong dependence of the magnetic moment with volume, we comment upon the reported anomalously high Curie temperature. Due to

TABLE I. Self-consistently computed occupation numbers for the different $4f$ azimuthal quantum numbers m_l for Ce.

m_l	Spin up	Spin down
-3	0.08	0.04
-2	0.11	0.07
-1	0.08	0.05
0	0.34	0.09
1	0.07	0.08
2	0.09	0.10
3	0.05	0.07

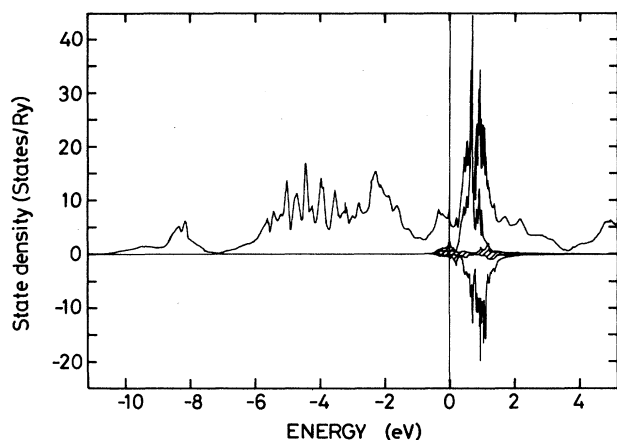


FIG. 1. Calculated state density (DOS) of CeRh_3B_2 . The upper curve is the total DOS. The partial 4f DOS for the up and down spins are also given, with the spin-up DOS positive and the spin-down DOS negative. The 4f partial DOS is divided so that all states with azimuthal quantum number not being zero are collected into one curve, whereas the partial DOS with zero azimuthal quantum number is plotted separately (hatched area). The energies are given in units of electron volts and the Fermi level is located at zero energy.

thermal effects a magnetic moment will almost always decrease with increasing temperature. For CeRh_3B_2 the lattice constant at room temperature is about 0.6% larger than the low-temperature volume. Since the magnetic moments depend strongly upon volume, the temperature induced increase in volume will suppress the normal decrease of the magnetic moment due to thermal excitations. Hence, this might be an explanation to the anomalously high Curie temperature. The found sensitivity to volume suggests that the ferromagnetism should disappear at a relatively low pressure. To our knowledge no such experiments have so far been reported.

This work provides additional support for the delocalized picture of the 4f electrons in CeRh_3B_2 , with a 4f

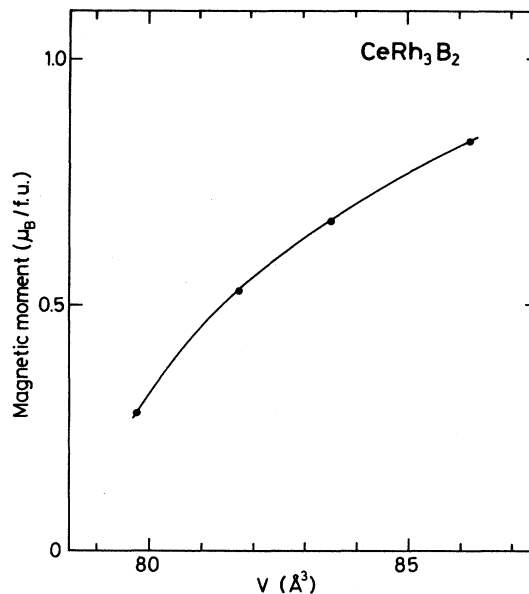


FIG. 2. Calculated magnetic moment per formula unit for CeRh_3B_2 as a function of volume. The point at 79.8 \AA^3 corresponds to the experimental volume at low temperatures.

band pinned at the Fermi level (in contrast to the mixed-valent picture). Our calculations show that treating relativistic effects correctly (i.e., spin-orbit coupling) in the band Hamiltonian has a surprisingly large influence on the results. Furthermore, the found strong volume dependence of the moment might offer an explanation for the anomalously high Curie temperature. The spin density in CeRh_3B_2 is also found to be highly nonspherical.

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