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Magnetic properties of $RRh_3B_2 (R = La, Ce, Nd, Gd)$ compounds

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Abstract. The ^{11}B NMR results on $RRh_3B_2 (R = La, Ce, Nd$ and $Gd)$ are reported. For $CeRh_3B_2$, specific heat and electrical resistivity are reported. From a comparative study of the ^{11}B NMR Knight shifts and the spin lattice relaxation times of these compounds it is shown that in $CeRh_3B_2$, there is strong hybridization of 4*f* states with the conduction electrons. A local moment on Ce with admixture of 4*f* and 5*d*-6*s* orbitals is suggested.

Keywords. Magnetic properties; rare earth compounds; 4*f*, 5*d*, 6*s* orbitals; hybridization.

1. Introduction

The ternary borides form an interesting class of materials in view of their magnetic and superconducting properties (Maple *et al* 1982). After the synthesis of RRh_4B_4 (R = rare earth) compounds by Matthias *et al* (1977) numerous ternary borides were studied by various workers (Rogl 1979; Maple *et al* 1982). In particular the RRh_3B_2 compounds are known to exhibit interesting magnetic properties (Ku and Shelton 1980; Ku *et al* 1980; Dhar *et al* 1981) $LaRh_3B_2$ is a superconductor with a T_c of about 2·6K, whereas $CeRh_3B_2$ orders ferromagnetically at $T_m \sim 115$ K. This transition temperature is the highest known for any Ce compound with nonmagnetic elements. The other compounds also order magnetically with smaller T_m values. In view of the unusual properties of these compounds, a detailed study using ^{11}B NMR, a.c. susceptibility, specific heat and electrical resistivity with particular emphasis on $CeRh_3B_2$ is undertaken and the results are presented below.

2. Experimental

The alloys $RRh_3B_2 (R = La, Ce, Nd, Gd)$ were made from constituent elements by melting them in stoichiometric proportion in an arc furnace under an inert atmosphere of argon. They were annealed at 700°C for one week. The homogeneity of the samples was checked by x-ray diffraction. The real part of the a.c. susceptibility χ', the specific heat C and the electrical resistivity ρ of these samples were measured. ^{11}B NMR data were recorded for $LaRh_3B_2$, $CeRh_3B_2$, $NdRh_3B_2$ and $GdRh_3B_2$.

3. Results and discussion

The a.c. susceptibility curves $\chi'(T)$ of $CeRh_3B_2$ and $NdRh_3B_2$ are shown in figures 1 and 2 respectively. A peak at 115 K is observed for the Ce compound showing the

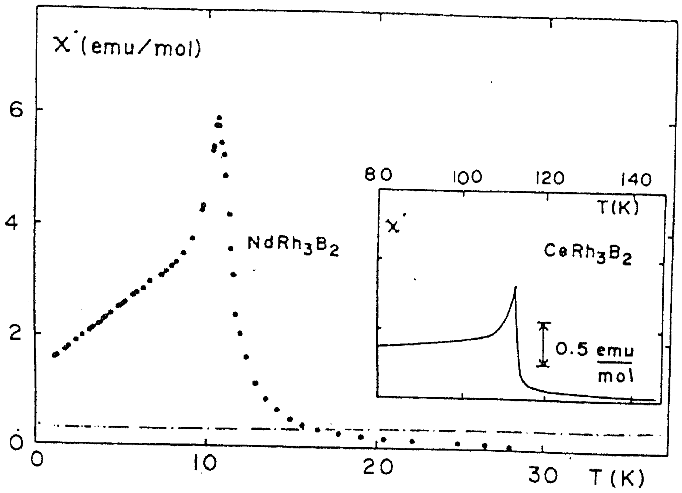

Figure 1. Real part of ac susceptibility χ' of NdRh$_3$B$_2$ and CeRh$_3$B$_2$.

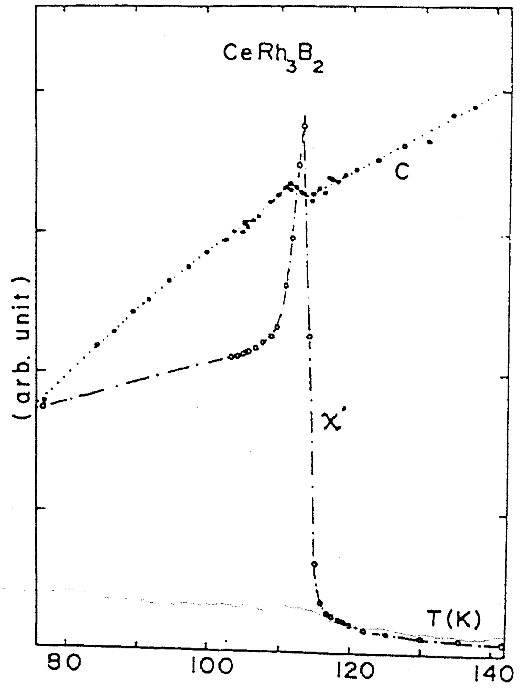

Figure 2. Specific heat C and real part of a.c. susceptibility of CeRh$_3$B$_2$.

onset of ferromagnetic order. Figure 2 also depicts the specific heat of CeRh$_3$B$_2$. The magnetic contribution to the specific heat shows up as a bump near the ordering temperature. The electrical resistivity of CeRh$_3$B$_2$ as a function of temperature is shown in figure 3. We notice the change of slope near $T_m \sim 115$ K. Below T_m the resistivity clearly shows a magnetic contribution. The magnetic contribution to the resistivity has been worked out theoretically by Mott (1935, 1936) and Kasuya (1956). Kasuya (1956) considers an exchange interaction between the conduction electrons and the inner shell electrons. At temperatures above absolute zero, but below T_m the spin wave excitations produce irregularities in the spin orientations and the conduction

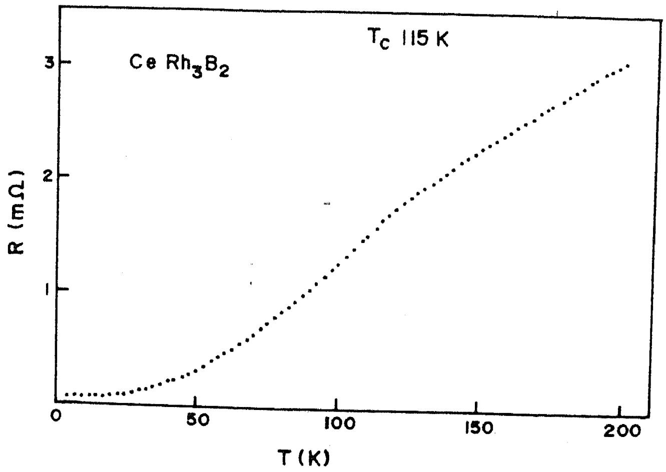

Figure 3. Electrical resistivity (in arbitrary units) of $CeRh_3B_2$.

electrons get scattered at these irregularities, thereby contributing to resistivity. Above T_m the spins are totally random, and that would produce a situation where the electrons are scattered at each lattice point. This would give a contribution similar to that of phonons i.e. proportional to T at higher temperatures. Kasuya's calculation gives the magnetic contribution to resistivity as

$$\rho = \left(\frac{3\pi m^{*2}}{Ne^2\hbar^2}\right)\frac{(S-M)(S+M+1)J_{\text{eff}}^2}{E_F}$$

where S is the spin of the ordering moments per atom, M the thermal expectation value of magnetization; J_{eff} is the effective exchange energy of conduction electrons with the inner shell electrons; and E_F is the fermi energy. The value of M can be deduced from the reported magnetization data (Dhar *et al* 1981). This magnetic contribution when added to the phonon contribution, would result in the experimentally observed resistivity.

The ^{11}B NMR Knight shift for $CeRh_3B_2$ is plotted against temperature in figure 4. The ^{11}B resonance in the magnetically ordered state at 77 K exhibits an anisotropic Knight shift (KS). The shift H_{KS} can be written as

$$H_{\text{KS}} = H_{\text{iso}} + H_{\text{dip}}(3\cos^2\theta - 1)$$

where H_{iso} is the isotropic part and H_{dip} is the dipolar part and θ the angle between the symmetry axis (i.e. c-axis) and the direction of the applied field. It is known that $H_{\text{iso}} = (H_{\parallel} + 2H_{\perp})/3$ and $H_{\text{dip}} = 2(H_{\parallel} - H_{\perp})/3$, where $H_{\parallel}$ and $H_{\perp}$ are the peak and edge fields of the spectrum. H_{dip} is found to be about -300 Oe. This can be simulated by a lattice sum of dipolar fields assuming a moment of $0{\cdot}42\ \mu_B$ at each cerium site. This value is close to the reported bulk value of $0{\cdot}38\ \mu_B$.

The Knight shift in the paramagnetic state is plotted against susceptibility in figure 5 for $CeRh_3B_2$. A linear dependence with $K = 0$ for $\chi = 0$ is observed. If Knight shift is written as

$$K = (A_{hf}/N\mu_B)\chi(T)$$

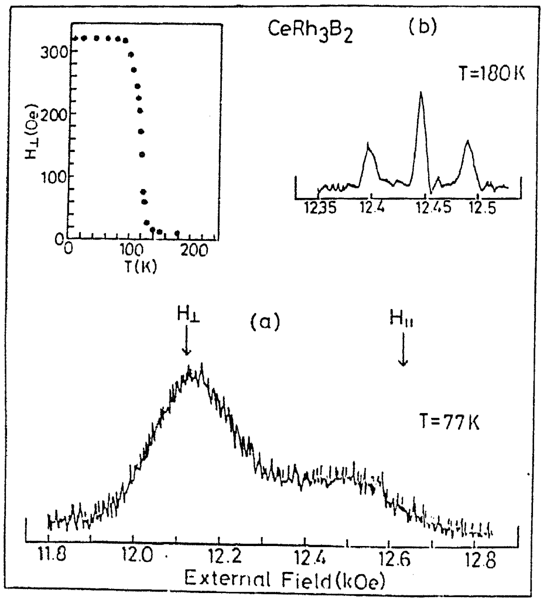

Figure 4. ^{11}B NMR signals at 180 K and 77 K in $CeRh_3B_2$. The inset shows the $H_\perp$ as a function of temperature.

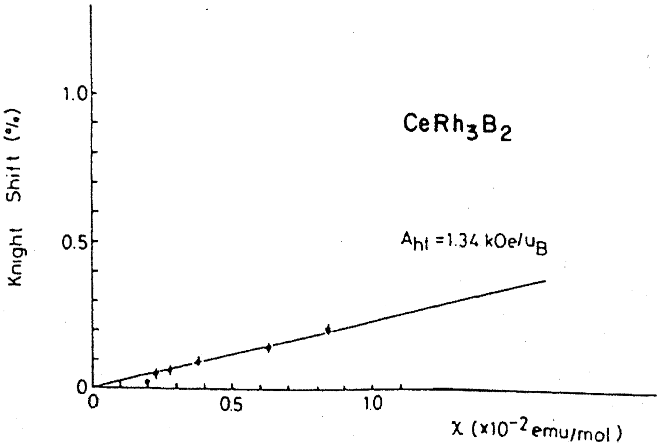

Figure 5. ^{11}B Knight shift versus susceptibility plot for $CeRh_3B_2$.

a value of the hyperfine coupling constant $A_{hf} = 1340\ \mathrm{Oe}/\mu_B$ is obtained for $CeRh_3B_2$. The plots of K vs T for $NdRh_3B_2$ are shown in figure 6. K vs χ for $NdRh_3B_2$ is plotted in figure 7. A_{hf} for $NdRh_3B_2$ and $GdRh_3B_2$ are found to be $609\ \mathrm{Oe}/\mu_B$ and $-610\ \mathrm{Oe}/\mu_B$ respectively. In a simple uniform conduction electron polarization model, A_{hf} can be written (Kohori *et al* 1983)

$$A_{hf} = (1 - 1/g_J) N(E_F) J_{sf} H_{hf}$$

where H_{hf} is the hyperfine field due to s-electrons at the B site and J_{sf}, the $s-f$ exchange constant. From the observed A_{hf} values and the above relation, it is found that $N(E_F) J_{sf}$ in $CeRh_3B_2$ is about six times larger than in other compounds. This shows that the mixing interaction between $4f$ and conduction electrons is rather strong.

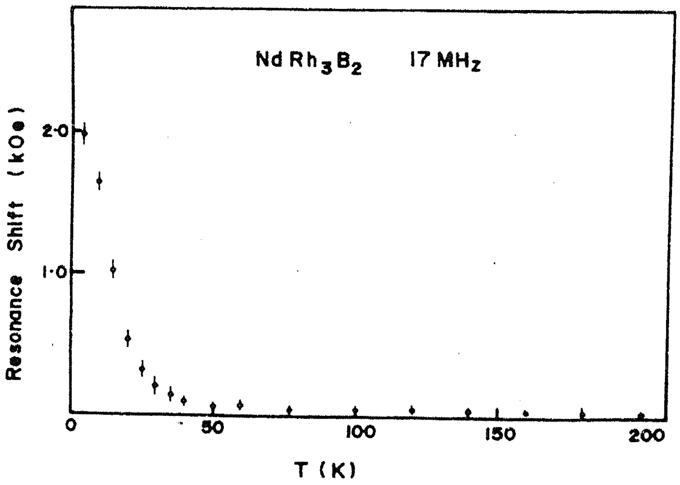

Figure 6. Temperature dependence of ^{11}B Knight shift of $NdRh_3B_2$.

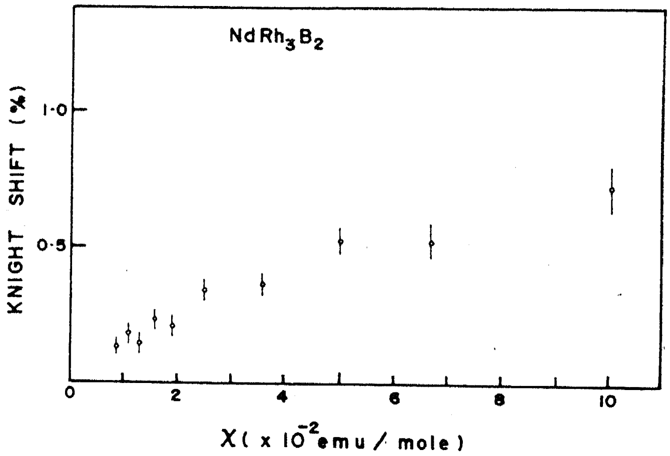

Figure 7. Knight shift versus susceptibility plot for $NdRh_3B_2$.

This would qualitatively account for the reduction of the moment from the free ion value.

The spin lattice relaxation time (T_1) of ^{11}B resonance as a function of temperature is plotted in figure 8 for $CeRh_3B_2$ and $LaRh_3B_2$. The relaxation rate ($1/T_1$) for $CeRh_3B_2$ can be taken to be a sum of Korringa type relaxation due to conduction electrons and a contribution due to $4f$ spin fluctuations:

$$1/T_1 = (1/T_1)_K + (1/T_1)_{4f}$$

As a rough approximation if we take $(1/T_1)_K$ to be equal to that of $LaRh_3B_2$ (i.e. $T_1T = 100$ sec K) we can estimate $(1/T_1)_{4f}$. From figure 8 we can see that the difference between the ($1/T_1$) values of $CeRh_3B_2$ and $LaRh_3B_2$ remains essentially temperature independent at high temperatures. This is consistent with spin fluctuation mechanism. On the other hand for local moments coupled by Rudirman Kittel Kasuya and Yoshida

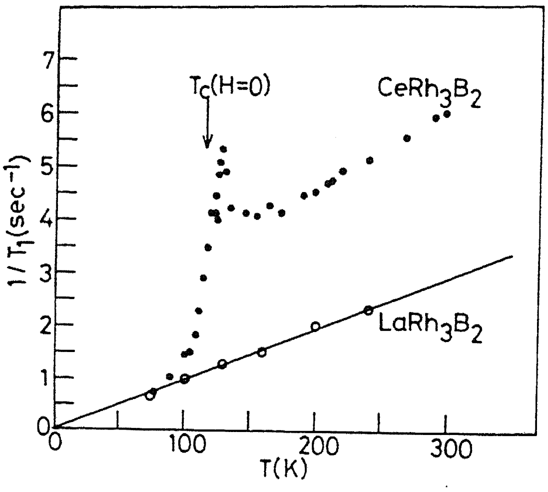

Figure 8. Temperature dependence of the ^{11}B spin lattice relaxation time T_1.

(RKKY) interaction (Moriya 1956) $(1/T_1)$ is a sum of two parts, $(1/T_1)_{\mathrm{RKKY}}$ and $(1/T_1)_{\mathrm{dipole}}$ (Kohori *et al* 1983)

$$(1/T_1)_{\mathrm{RKKY}} = (2\pi)^{1/2} \sum_i (A_i/h)^2 (g_J - 1)^2 J(J+1)/3\omega_e$$

$$(1/T_1)_{\mathrm{dipole}} = \frac{2(2\pi)^{1/2}\gamma^2 (g_J \mu_B)^2 J(J+1)}{3\omega_e} \sum_l r_l^{-6}$$

where $A_i = (\gamma g_J A_{hf})/3(g_J - 1)$ and ω_e the exchange frequency. A rough estimate of ω_e can be made by assuming mean field approximation, using the relation

$$(\hbar\omega_e)^2 = (3kT_m)^2/6z(g_J - 1)J(J+1)$$

where z is the number of nearest neighbours coupled, which is taken to be two along the c-axis. The values of $(1/T_1)_{\mathrm{RKKY}}$ and $(1/T_1)_{\mathrm{dipole}}$ are listed in table 1.

The agreement between calculated values and experimental values is reasonable except for the case of CeRh$_3$B$_2$. The very poor agreement for CeRh$_3$B$_2$ shows that a simple RKKY model assuming well localized moments is not applicable to this compound. This and other factors discussed above suggest a strong hybridization of 4f electrons with conduction electrons for CeRh$_3$B$_2$. This hybridization appears to play an important role in the high ordering temperature and the observed small value of the magnetic moment.

Table 1. Values of $(1/T_1)_{\mathrm{RKKY}}$ and $(1/T_1)_{\mathrm{dipole}}$

Compound	$(1/T_1)_{\mathrm{exp}}$ sec^{-1}	$(1/T_1)_{\mathrm{dipole}}$ sec^{-1}	$(1/T_1)_{\mathrm{RKKY}}$ sec^{-1}
CeRh$_3$B$_2$	2·20	0.57	0.20
NdRh$_3$B$_2$	630	640	110
GdRh$_3$B$_2$	1800	930	160

Dedication and acknowledgements

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