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THE ANOMALOUS MAGNETISM OF $CeRh_3B_2$ UNDER PRESSURE

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Whereas $CeRh_3B_2$ possesses the highest magnetic ordering temperature ($T_c \approx 115$ K) of any Ce-compound with nonmagnetic constituents, $LaRh_3B_2$ becomes superconducting below 2.5 K. Recent magnetization measurements under pressure as well as lattice parameter and specific heat studies shed light on the nature of the anomalous magnetic state in $CeRh_3B_2$.

1. Introduction

Because they possesses the necessary electronic architecture to house distinct and only weakly coupled magnetic and electronic sublattices, ternary compounds have been frequently employed in investigations of the competition between magnetism and superconductivity [1,2]. On the other hand, the potential of ternary systems for supporting exotic new forms of either magnetism or superconductivity has only begun to be tapped. Such multi-component systems, however, can place particularly high demands on the care required for their preparation and characterization, including the purity of the starting materials. As a case in point, the ternary boride $LaRh_6B_4$, which was initially believed [3] to exhibit itinerant ferromagnetism below 6 K, was subsequently shown [4] ro remain paramagnetic to temperatures as low as 40 mK if ultrapure starting materials were used.

Contrary to the results of earlier studies on the hexagonal ternary boride $CeRh_3B_2$ by Ku et al. [5], Dhar et al. [6] have reported ferromagnetism below 115 K. This temperature lies well above the ordering temperature of any known Ce-compound with nonmagnetic constituents. Subsequent resistivity studies [7,8] are consistent with $T_c \approx 115$ K; further magnetization studies [9] on the RRh_3B_2 series with R = La to Gd revealed, in fact, that $GdRh_3B_2$ orders at a *lower* temperature than $CeRh_3B_2$, underscoring the highly anomalous nature of the magnetism in the latter. Lattice parameter studies [5,9] for R = La to Gd indicated that Ce in $CeRh_3B_2$ might be mixed valent and Eu in $EuRh_3B_2$ trivalent. It is thus indeed remarkable that these very two compounds have, relative to the other members of the series, anomalously *high* ordering temperatures.

It is the purpose of the present work both to check the correctness of the previous work [5,6,9] as well as to provide new insight by careful measurements of the magnetization (under pressure), specific heat and lattice parameters on samples prepared from highly purified starting materials.

2. Experiment

The rare earth ternary boride samples used in the present study were prepared by argon arc melting

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stoichiometric amounts of the constituent elements. High purity rare earths from the Ames Laboratory (< 15 ppm of any single metallic impurity) together with commercial rhodium (99.9%, Thiokol Corp., Alfa Products) and boron (99.9995%, Research Organic–Inorganic Chemical Corp.) were used as starting materials. The samples (≈ 1 g mass for the magnetic and ≈ 3 g mass for the specific heat studies) were turned over and remelted six times to promote homogeneity and were then measured in the as cast condition.

Powder X-ray diffraction studies confirmed the anticipated hexagonal (P6/mmm) structure with no trace of a secondary phase. The static magnetic susceptibility was measured using a standard Faraday technique, employing a 90 g Cu–Be pressure clamp for the high pressure investigations [10]. The low temperature heat capacity measurements were performed using a semi-adiabatic heat-pulse calorimeter equipped with a mechanical heat switch and circulating ^{4}He and ^{3}He pots [11]. The high pressure measurements on superconducting $LaRh_3B_2$ were carried out using both an ac technique [12] to 18 kbar and a newly developed [13] diamond anvil clamp with SQUID-sensor to 35 kbar.

3. Results and discussion

In fig. 1 we show the results of the present magnetization measurements on $CeRh_3B_2$. The observed values of both the Curie temperature $T_c \approx 117$ K [14] and the low-temperature saturation moment $M_s(4.2\ \text{K}) \approx 0.37\mu_B$/f.u. are in excellent agreement with the previous studies [6,9], as are also our data well above the Curie temperature where Dhar et al. [6] report $\mu_{eff} \approx 3.0\mu_B$ and $\theta_p = -373$ K. Whereas the saturation moment decreases reasonably rapidly with pressure $\partial \ln M_s/\partial P \approx -0.66\%$/kbar, the Curie temperature increases only slowly $\partial \ln T_c/\partial P \approx +0.09\%$/kbar.

$LaRh_3B_2$ shows a weak paramagnetic susceptibility which rises slowly from $+81 \times 10^{-6}$ emu/mol at 300 K, thru $+110 \times 10^{-6}$ emu/mol at 77 K to $+257 \times 10^{-6}$ emu/mol at 2.5 K, indicating a magnetic impurity concentration in our samples approximately four times less than that reported by Malik et al. [9]. Below 2.55 K $LaRh_3B_2$ becomes superconducting, in agreement with previous studies [5]. To hydrostatic pressures of 35 kbar T_{SC} decreases at the rate $\partial \ln T_{SC}/\partial P \approx -0.32\%$/kbar.

In fig. 2 we display the present results for the ambient temperature lattice parameters and unit cell volume for RRh_3B_2 with R = La, Ce, Pr and compare them with previous results [5,9] across the series R = La to Gd. Our results confirm the existence of a lattice

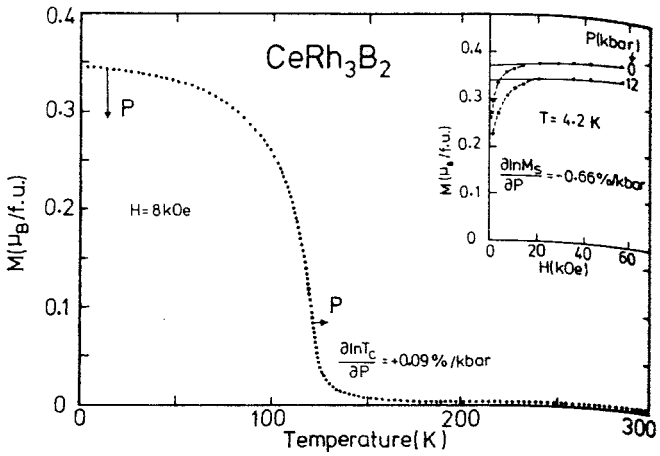

Fig. 1. Magnetization of $CeRh_3B_2$ in units of μ_B per formula unit (per Ce-atom) versus temperature at 8 kOe and ambient pressure. Arrows give direction of pressure dependence. Insert shows magnetization at 4.2 K versus magnetic field for two pressures.

parameter anomaly for the Ce-compound. The value of c for $CeRh_3B_2$ is somewhat depressed from the trivalent value, leading to the relatively small unit cell. The anomalies in lattice parameter for $EuRh_3B_2$ are particularly large. Low-temperature X-ray studies at 80 K on $CeRh_3B_2$ showed no change in crystal structure from

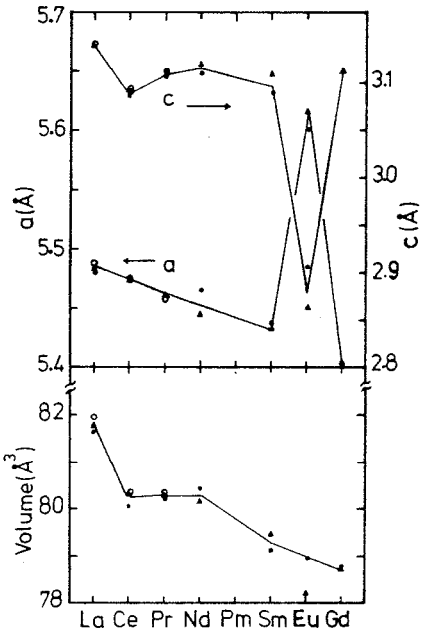

Fig. 2. Lattice parameters and volume of hexagonal unit cell at 300 K across the RRh_3B_2 series with R = La to Gd. (○) present studies, (●) from ref. [5], (▲) from ref. [9]. Solid lines are guide to eye.

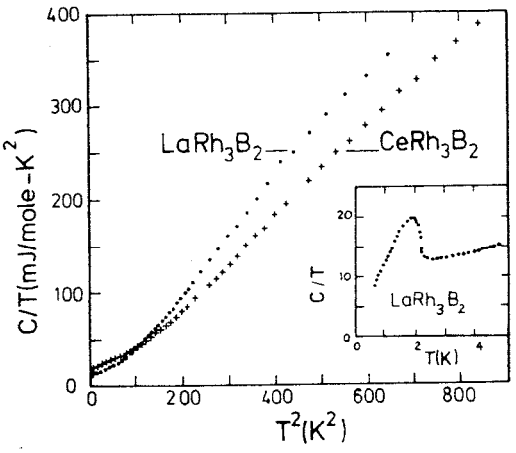

Fig. 3. Specific heat results for $LaRh_3B_2$ and $CeRh_3B_2$ at temperatures below 30 K. Insert shows anomaly below the superconducting transition temperature of $LaRh_3B_2$ in same units as main drawing.

300 K, but did reveal a 1.8% decrease in c coupled with an 0.2% increase in a.

The results of the specific heat measurements in the temperature range 0.7 to 28 K are shown in fig. 3. It is interesting to note that for $T > 10$ K the specific heat of $CeRh_3B_2$ actually lies *below* that of $LaRh_3B_2$, even though it would be expected that the additional (magnetic) degrees of freedom in the former ferromagnetic compound should lead to a specific heat enhancement. The usual low temperature analysis ($T < 5$ K) of the respective data for $LaRh_3B_2$ and $CeRh_3B_2$ gives the γ-coefficients 11.7 and 15.9 mK/molK^2 (2.5 and 3.4 states/eV f.v. spin) and the Debye temperatures 430 and 370 K. The rms-deviation of the data from the best fit was less than 1.5%. The relative softness of $CeRh_3B_2$ at low temperatures contrasts to the apparent stiffness for $T > 10$ K as indicated by the lower specific heat curve for this compound as discussed above. Spin-wave contributions may complicate the analysis below 5 K, however, no clear evidence of a spin-wave contribution was observed. The nonintegral Ce-valence indicated by the lattice parameter anomalies may free electrons to give an additional contribution to the binding energy and lattice stiffness, accounting for the C_P(T)-suppression for $T > 10$ K. The phonon spectrum of the La- and Ce-ternaries may be quite different. The above γ-coefficients are, respectively, factors of 1.3 and 2.7 times those calculated in recent self-consistent non-spin-polarized band structure calculations [15], and for $CeRh_3B_2$ a factor 1.22 times that reported by Yang et al. [7].

The present data shed some light on the origins of the highly anomalous magnetism in $CeRh_3B_2$. It has been suggested [6,8,9] that this magnetism is itinerant in character and arises from the Rh 4d-band, thus accounting for the large value of the ratio $\mu_{eff}/M_s \approx 8$. On this basis, however, it is difficult to understand why the corresponding ternary borides with elements to the left and right of Ce show no anomalous behavior [16]. $LaRh_3B_2$ is, in fact, superconducting at $T_{SC} = 2.55$ K and the observed slow decrease in T_{SC} with pressure can be readily accounted for by the usual lattice stiffening under pressure which leads to a similar T_{SC}-suppression in Pb, In, Sn and also in many transition metal superconductors.

On the other hand, because of the very close separation of the rare earth ions along the c-axis (about 3 Å), one might be tempted to ascribe the anomalous magnetism to the formation of a 4f-band. Such a band should, moreover, be quasi-one-dimensional because of the large separation between the "magnetic chains" in the a and b directions (about 5 Å). Recent experiments [17] on quasi-ternary $Ce_{1-x}La_x(Rh_{1-y}Ru_y)_3B_2$ compounds reveal, however, that the ferromagnetic state is much more effectively weakened by the substitution of Ru for Rh than by La for Ce. This speaks against the formation of a quasi-one-dimensional 4f-band because such a band should be quickly broken up upon La substitution.

From unit cell volume considerations Ce in $CeRh_3B_2$ would appear to have a valence greater than three whereas Eu appears trivalent, the latter conclusion being supported by Mössbauer studies [9]. As discussed above, the anomalous specific heat of $CeRh_3B_2$ could arise from the additional binding from the extra valence charge. The mixed-valence state, however, is normally considered to be detrimental to magnetic order [18], making it particularly difficult to understand anomalously *high* ordering temperatures. One would also expect the ordering temperature to depend sensitively on pressure in a system with unstable valence [19], contrary to the results of the present experiment.

We would like to suggest that the anomalous magnetism of $CeRh_3B_2$ may have its origins in the coexistence of both localized and delocalized band-like 4f-states which arise from the hexagonal symmetry. In this picture the primary magnetic interaction is between the localized Ce-states via a strong covalent mixing with the Rh 4d-states. A similar interaction mechanism was proposed and analyzed in detail by Siemann and Cooper [20] to account for the anomalous magnetic properties of cerium and light actinide monopnictides. A full exposition of the above results will be given elsewhere [21].

Acknowledgments

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Note added in proof

Very recent magnetization and Mössbauer effect studies show that the ferromagnetism of stoichiometric $EuRh_3B_2$ arises from the ordering of the spins of *divalent* Eu (see ref. [17]).

References

[1] See articles in: Superconductivity in Ternary Compounds, eds. Ø. Fisher and M.B. Maple (Springer, Berlin, 1982).
[2] R.N. Shelton, in: Superconductivity in d- and f-Band Metals, eds. W. Buckel and W. Weber (Kernforschungszentrum, Karlsruhe, 1982) p. 123.
[3] I. Felner and I. Nowik, Phys. Rev. Lett. 45 (1980) 2128.
[4] J.S. Schilling, R.N. Shelton, P. Klavins and S.A. Shaheen, Phys. Rev. B28 (1983) 6548.
[5] H.C. Ku, G.P. Meisner, F. Acker and D.C. Johnston, Solid State Commun. 35 (1980) 91.
[6] S.K. Dhar, S.K. Malik and R. Vijayaraghavan, J. Phys. C 14 (1981) L321.
[7] K.N. Yang, M.S. Torikachvili, M.B. Maple and H.C. Ku, Bull. Am. Phys. Soc. 28 (1983) 341.
[8] M. Hakimi, J.G. Huber, L.E. DeLong, S.K. Dhar and S.K. Malik, J. Less-Common Metals 94 (1983) 157.
[9] S.K. Malik, R. Vijayaraghavan, W.E. Wallace and S.K. Dhar, J. Magn. Magn. Mat. 37 (1983) 303.
[10] S.A. Shaheen, J.S. Schilling, S.H. Liu and O.D. McMasters, Phys. Rev. B27 (1983) 4325.
[11] C.B. Vining, PhD. Thesis, Iowa State University (1983).
[12] T.F. Smith, J. Low Temp. Phys. 6 (1972) 171.
[13] J.S. Schilling, in: IX AIRAPT Intern. High Pressure Conf. Albany, NY (July 1983): Materials Research Society Symposium Proc. 22 (1984) part I, p. 79.
[14] As in refs. [6,9] the Curie temperature was estimated from a M^2 versus T plot, giving $T_c = 117$ K for the data shown and 119 K for a second sample. Dhar et al. [6,8] find $T_c = 115$ K.
[15] S. Auluck, D.K. Misemer, S.-I. Kobayashi, B.N. Harmon and C. Vining, Bull. Am. Phys. Soc. 29 (1984) 394.
D.K. Misemer, S. Auluck, S.-I. Kobayashi and B.N. Harmon, Solid State Commun. 52 (1984) 955.
[16] The magnetism of $SmRh_3B_2$ is not yet well established; see ref. [9].
[17] S.A. Shaheen, J.S. Schilling and R.N. Shelton, Phys. Rev. B31 (1985).
[18] J.M. Lawrence, P.S. Riseborough and R.D. Parks, Rep. Prog. Phys. 44 (1981) 1.
[19] J.S. Schilling, in: Physics of Solids under High Pressure, eds. J.S. Schilling and R.N. Shelton (North-Holland, Amsterdam, 1981) p. 345.
A. Eiling and J.S. Schilling, Phys. Rev. Lett. 46 (1981) 364.
[20] R. Siemann and B.R. Cooper, Phys. Rev. Lett. 44 (1980) 1015.
[21] S.A. Shaheen, J.S. Schilling and R.N. Shelton, (in preparation).