Anomalous ferromagnetism in $CeRh_3B_2$: Possibility of a new Kondo-lattice state

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(Received 2 November 1984)

Information on the nature of the highly anomalous ferromagnetic state of $CeRh_3B_2$ below 115 K is gained by studying the evolution of the magnetic, superconducting, and structural properties across the quasiternary series $La_xCe_{1-x}Rh_3B_2$ and $Ce(Ru_yRh_{1-y})_3B_2$. The present results offer considerable evidence that this ferromagnetism originates from the ordering of Ce local moments and not, as has been claimed, from itinerant magnetism in the Rh $4d$ band.

Cerium and its alloys and compounds exhibit a fascinatingly broad spectrum of unusual physical phenomena which include both reentrant[1] and heavy fermion[2] superconductivity, Kondo and mixed-valence behavior,[3] and more recently, an anomalous ferromagnetic state in $CeRh_3B_2$ below $T_c = 115$ K,[4-7] by far the highest magnetic ordering temperature of any known Ce system with nonmagnetic constituents. This T_c value lies, in fact, above that of $GdRh_3B_2$ with $T_c = 90$ K,[5] and is two orders of magnitude above the value $T_c \simeq 1$ K expected from simple de Gennes factor considerations. The high Curie temperature, the apparently small ratio of the saturation to effective moment (~ 0.12),[4,5] and a volume anomaly interpreted as indicative of a mixed-valence Ce state[5,8] have led to the suggestion[4-6] that the ferromagnetism of $CeRh_3B_2$ is not local moment but itinerant in nature and arises primarily from the Rh $4d$ band. An itinerant $4d$-band ferromagnetism has also been proposed in isostructural $EuRh_3B_2$ where Eu reportedly exists in a trivalent (nonmagnetic) $4f^6$ state.[5] However, recent static magnetization and Mössbauer effect studies show that Eu in stoichiometric $EuRh_3B_2$ is in a nearly divalent (magnetic) $4f^7$ state and that the ferromagnetism originates from the ordering of Eu local moments.[9] Previous reports of Rh $4d$-band ferromagnetism in $LaRh_6B_4$ and $EuRh_6B_4$ (Ref. 10) were later refuted by investigations[11] on samples prepared from ultrapure starting materials; other similar reports[12] have yet to be confirmed. Claims of itinerant $4d$-band magnetism in $CeRh_3B_2$ should thus be examined with due skepticism.

In the present work we attempt to shed light on the origins of the anomalous ferromagnetism in $CeRh_3B_2$ by studying the evolution of the magnetic and structural properties across the two quasiternary series $La_xCe_{1-x}Rh_3B_2$ and $Ce(Ru_yRh_{1-y})_3B_2$. Pair-breaking effects in superconducting $LaCeRh_3B_2$ are also investigated. We conclude that the ferromagnetic state in $CeRh_3B_2$ arises not from an itinerant magnetism but rather from the ordering of Ce local moments coupled together by unusually strong Ce $4f$-conduction electron hybridization. These conclusions are consistent with the results of recent L_{III}-edge x-ray absorption and valence-band photoemission studies[13] as well as band-structure calculations.[14]

The samples used in the present study were prepared by argon-arc melting stoichiometric amounts of high-purity

Ames Lab rare earths (< 15 ppm of any single metallic impurity) together with commercial rhodium and ruthenium (99.9%, Thiokol Corp., Alfa Products) and boron (99.995%, Research Organic-Inorganic Chemical Corp.). Each sample was turned over and remelted six times to promote homogeneity. Powder x-ray diffraction studies confirm the anticipated hexagonal ($P6/mmm$) structure[8] with no trace of a secondary phase in the as-cast samples. Annealing $LaRh_3B_2$ at 1200 °C for three days resulted in the introduction of a small concentration of a secondary phase accompanied by a degradation of the superconducting transition temperature T_{sc} from 2.6 to 1.9 K. The static magnetic properties were thus determined on as-cast samples employing a standard Faraday technique. The present magnetization measurements on as-cast $CeRh_3B_2$ agree closely with previous studies on both as-cast[4,5] and annealed[6] samples.

It would seem reasonable to assume that the anomalous ferromagnetic state in $CeRh_3B_2$ has its principal origins in one of three mechanisms: (1) ordering of Ce local moments, (2) Rh $4d$ itinerant magnetism, and (3) Ce $4f$ itinerant magnetism. The third alternative suggests itself because of the unusually small Ce-Ce separation (3.09 Å) along the c axis which is well below the Hill limit.[15] A $4f$ contribution to the crystalline binding would be, in fact, consistent with anomalies observed in both the unit-cell volume[5,7,8] and the specific heat.[7] The fact that the Ce-Ce separation is small only along the c axis direction would dictate that such a $4f$ band must be quasi-one-dimensional in character. The substitution of La for Ce should thus rapidly break up the $4f$ chains and destroy the $4f$ itinerant magnetism. That this does not occur is seen in Fig. 1 where with increasing La concentration the Curie temperature T_c decreases only very slowly, $La_{0.8}Ce_{0.2}Rh_3B_2$ being, in fact, still ferromagnetic. This is clear evidence against $4f$ itinerant magnetism in $CeRh_3B_2$. On the contrary, the gradual linear increase of T_c with Ce concentration is suggestive that the ferromagnetic state involves the ordering of Ce local moments.

One of the simplest but most convincing arguments against Rh $4d$ itinerant magnetism in $CeRh_3B_2$ is the fact that its neighboring compounds, $LaRh_3B_2$ and $PrRh_3B_2$, show no anomalous magnetism,[8] the former being, in fact, a superconductor at $T_{sc} = 2.5$ K (Refs. 7 and 8) with a conventional slow suppression of T_{sc} under pressure.[7] The ex-
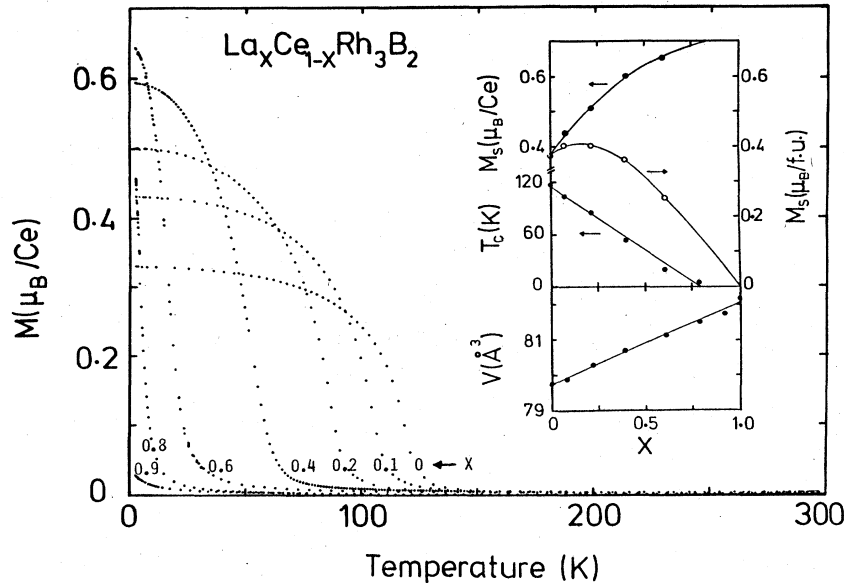
FIG. 1. Temperature dependence of magnetization at 8 kOe in units μ_B per formula unit across series La$_x$Ce$_{1-x}$Rh$_3$B$_2$. Inset shows as function of x saturation moment M_s at 4 K per Ce ion and per formula unit, Curie temperature T_c and unit-cell volume V. Solid lines are guides to eye.

change enhancement factor S of LaRh$_3$B$_2$ is estimated[16] to be less than 2, underscoring the lack of any appreciable tendency towards magnetism in the Rh $4d$ band. Recent valence-band photoemission studies on RRh$_3$B$_2$ with R = La, Ce, Pr by Sampathkumaran et al.[13] reveal essentially identical Rh $4d$ bands for all three compounds and thus speak against a $4d$ itinerant magnetism in CeRh$_3$B$_2$ alone. That the electronic structure in CeRh$_3$B$_2$ is unfavorable for $4d$ itinerant magnetism is also indicated by the relatively low value[13,14] of the Rh contribution to the electronic density of states $N_{Rh}(E_F) \approx 0.68$ states/eV-Rh$_3$ and the fact that the Fermi energy E_F appears to lie in a minimum of $N(E)$.[14]

That, on the other hand, Ce does indeed possess a local moment in the series La$_x$Ce$_{1-x}$Rh$_3$B$_2$ is underscored by the observation that the superconducting state in LaRh$_3$B$_2$ is sharply suppressed by the addition of Ce impurities, as seen in Fig. 2. The $T_{sc}(x)$ dependence observed is characteristic for reentrant superconductors.[1] The initial rate of decrease of T_{sc}, -5.6 K/at.% Ce, is among the largest ever observed for Ce impurities in compounds and alloys at ambient or high pressure. These results establish that Ce impurities in LaRh$_3$B$_2$ possess a well-defined local moment which interacts strongly with the conduction electrons. The observed $T_{sc}(x)$ dependence implies that this interaction contains a prominent covalent mixing (Kondo) component.

That Ce retains its local moment across the La$_x$Ce$_{1-x}$Rh$_3$B$_2$ series is evidenced by magnetic susceptibility measurements where the paramagnetic effect moment is found to equal $1.6\mu_B$ per Ce ion for 8% Ce ($x = 0.92$) and decreases somewhat with increasing Ce concentration.[16] That the Ce ion remains in a nearly trivalent state across the series is also indicated by the linear volume increase with x (Fig. 1) and the relatively small magnitude of the volume anomaly for CeRh$_3$B$_2$ (Fig. 3). Recent L_{III}-edge x-ray absorption results by Sampathkumaran et al.,[13] in fact, reveal less than 5% tetravalent Ce component in CeRh$_3$B$_2$. Taken

together the above results provide considerable evidence that across the entire La$_x$Ce$_{1-x}$Rh$_3$B$_2$ series (1) Ce retains a nearly trivalent local-moment state and (2) the observed ferromagnetism originates from the ordering of the Ce local moments. The reduced values of both the effective and saturation moments could be due to peculiarities in the spin alignment, Kondo moment compensation, loss of some local $4f$ charge along the c axis, crystal-field splittings, and other effects.
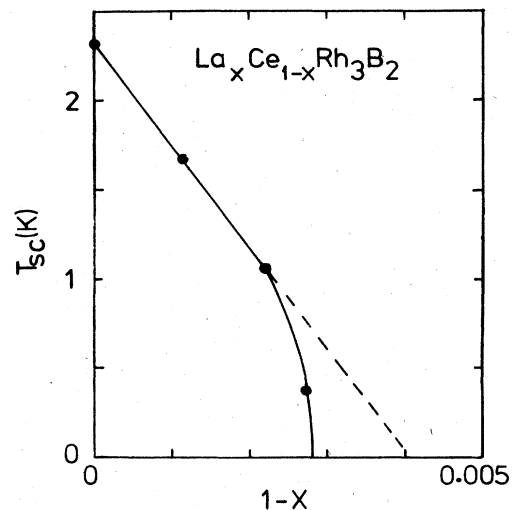
To further test the above picture of local-moment magne-

FIG. 2. Dependence of superconducting transition temperature T_{sc} of LaCeRh$_3$B$_2$ on concentration of Ce impurities. Solid line is guide to eye. Dashed line is linear extrapolation.

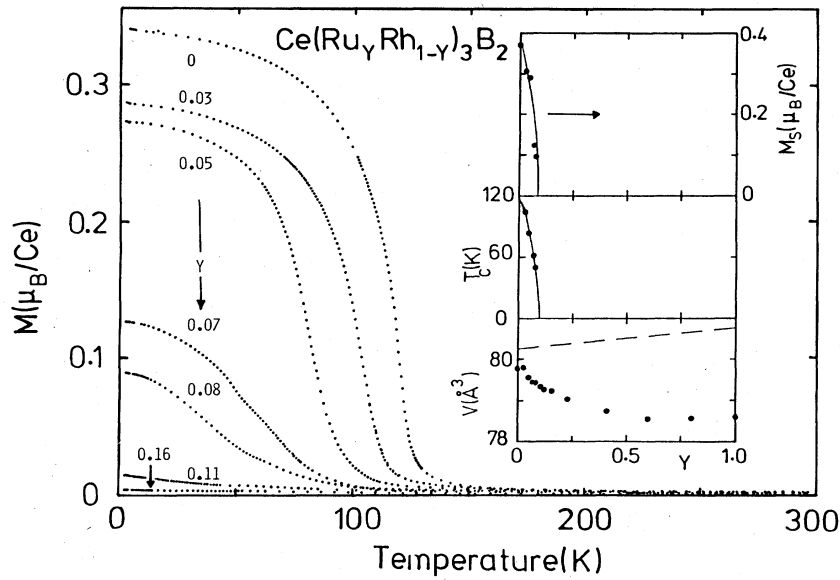S. A. SHAHEEN, J. S. SCHILLING, AND R. N. SHELTON

FIG. 3. Temperature dependence of magnetization of 8 kOe across series $Ce(Ru_yRh_{1-y})_3B_2$. Inset shows as function of y saturation moment M_s at 4 K, Curie temperature T_c and unit-cell volume V. Solid line is guide to eye. Dashed line gives expected y dependence of V for trivalent Ce ions based on x-ray data on $GdRh_3B_2$ and $GdRu_3B_2$ from Ref. 8.

tism in $CeRh_3B_2$ it would be useful to substitute Rh with an element which would be capable of destabilizing the Ce moment, as in the $\gamma \rightarrow \alpha$ transition in pure Ce, and would lead to intermediate valence behavior with its accompanying anomalies in atomic volume, loss of magnetism, and the possible appearance of superconductivity.[3] That the substitution of Rh with Ru can destabilize the Ce moment is known from susceptibility studies on $CeRh_2$ and $CeRu_2$ (Ref. 17) and is also evidenced by the observed superconductivity of $CeRu_2$ (Ref. 17) and $CeRu_3Si_2$.[18]

In Fig. 3 it is seen that the above expectations are confirmed and that the substitution of Ru for Rh across the quasiternary series $Ce(Ru_yRh_{1-y})_3B_2$ leads to a rapid suppression of both the Curie temperature and the saturation moment, the ferromagnetic state being quenched for $y > 0.11$. In the concentration range $0.16 \leq y \leq 0.23$ a susceptibility maximum is observed which may be related to antiferromagnetic ordering or spin-fluctuation effects. Athreya[19] points out that $CeRu_3B_2$ is superconducting below 0.95 K, a value somewhat larger than that (0.68 K) reported by Yang, Torikachvili, Maple, and Ku,[6] reflecting perhaps the difference in heat treatment. That the superconducting state in $CeRu_3B_2$ is conventional and arises because of the demagnetization of the Ce local moment, and not from heavy fermion behavior, is clear from the low value of its specific-heat coefficient $\gamma = 17.6$ mJ/mol K^2 (Ref. 6) and the observed weak Pauli paramagnetic susceptibility.[16] We also note that the relatively weak temperature dependence of the resistivity of $CeRh_3B_2$ for $T > T_c$ relative to that of $CeRu_3B_2$ (Ref. 6) suggests a Kondo anomaly in the former which is removed as Ru is substituted for Rh and Ce demagnetizes.

The variation of unit-cell volume V across a compound series gives important information on possible changes in magnetic state (valence).[3] For stable-valence rare earths like $R = Gd$, substituting Ru for Rh in $R(Ru_yRh_{1-y})_3B_2$

leads to a slow increase in V.[8] The anomalous decrease in V for $R = Ce$ seen in the inset in Fig. 3 indicates that the valence of Ce is increasing from a nearly trivalent value for $y = 0$ to a higher value which saturates for $y > 0.5$. The destruction of ferromagnetism in $Ce(Ru_yRh_{1-y})_3B_2$ as Ru is substituted for Rh thus goes hand in hand with a progressive destabilization of the Ce local-moment state.

We would like to propose the following qualitative picture of the anomalous ferromagnetic state of $CeRh_3B_2$. The very close proximity of Ce ions along the c axis would be expected to lead to some delocalization of $4f$ charge along that direction accompanied by a volume depression and lattice bonding anomalies. However, because of the large Ce separation in the plane perpendicular to the c axis, each Ce ion is able to retain a major portion of its local moment state. Both the $4f$ charge overlap along the c axis and a strong Ce $4f$-Rh $4d$ hybridization result in a particularly intense magnetic interaction between Ce ions. Self-consistent band-structure calculations[14] indicate, in fact, that $\sim 20\%$ of the Ce $4f$ charge is directed along the c axis, where $\sim 40\%$ is towards neighboring Rh ions. In addition, as shown by the experimental evidence discussed above, the $4f$ wavefunction hybridization contains significant covalent mixing (negative J) components which we suggest may be at least partially responsible for the anomalously high value of the Curie temperature. In a simple Kondo-lattice picture, J depends on the mixing matrix element V_{sf} and the Ce $4f^1$ stabilization energy E_{ex} as $J \propto - |V_{sf}|^2 / E_{ex}$.[20] As a Ce ion approaches the mixed-valence state, $E_{ex} \rightarrow 0$ and J grows appreciably in magnitude. As a result, the magnetic ordering temperature $T_c \propto J^2$ would be expected to show an anomalous increase until $|J|$ becomes so large that the Ce moment is quenched.[21] This effect has been observed experimentally on CeAg under pressure by Eiling and Schilling.[22] The extremely small pressure dependence of T_c (Ref. 7) is consistent with the very high T_c value of

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