sample preparation technique, the annealing of the cast sodium samples reduced ρ_d, whereas the annealing of the cast potassium samples did not. This difference between the two is undoubtedly due to the low-temperature martensitic phase transformation of sodium which produces samples having an unstable array of strains.

To test the effect of the martensitic phase transformation on our results, sample N-1*b* was cycled to room temperature and back. The results for the sample, now denoted as N-1*c*, show a 5% increase in both ρ_0 and A. This is, of course, due to the increase in ρ_d caused by the additional strain introduced by cycling through the phase transformation, a phenomenon previously observed by Dugdale and Gugan.[10]

With the assumed starting ratio $\rho_d/\rho_0 = 0.36$, samples N-1*b* and N-1*c* (open squares) are seen to follow the same general behavior as K. This is in accordance with the expectation that electron-electron scattering should be quite similar for both Na and K.

It is a pleasure to thank Nathan Wiser and Moshe Kaveh for many useful discussions. We also thank H. van Kempen and J. H. J. M. Ribot for their valuable help with experimental aspects of the measurement. Finally, we gratefully acknowledge the financial assistance provided by the Israel Commission for Basic Research.

[1] J. A. Rowlands, C. Duvvury, and S. B. Woods, Phys. Rev. Lett. 40, 1201 (1978).

[2] H. van Kempen, J. S. Lass, J. H. J. M. Ribot, and P. Wyder, Phys. Rev. Lett. 37, 1574 (1976).

[3] J. W. Ekin and B. W. Maxfield, Phys. Rev. B 4, 4215 (1971).

[4] D. Gugan, Proc. Roy. Soc. London, Ser. A 325, 233 (1971).

[5] J. M. Ziman, *Electrons and Phonons* (Oxford Univ. Press, Oxford, England, 1960), Chap. IX, Sec. 9.14.

[6] M. Kaveh and N. Wiser, to be published.

[7] B. Levy, M. Sinvani, and A. J. Greenfield, unpublished.

[8] In a separate experiment, with use of a technique which produces virtually strain-free samples, a potassium sample taken from the same stock of starting material was prepared having $\rho_0 = 0.1$ nΩ cm. This value for ρ_0 remained constant to within 3% upon thermal cycling of the sample including warming, further annealing, and recooling. Therefore, the value for ρ_i in both samples taken from this stock cannot be much larger than about 0.1 nΩ cm unless the preparatory process introduces additional impurities. Our technique for sample preparation is not expected to introduce significant amounts of further impurities. Since the present results are not very sensitive to the precise value of ρ_i, it was sufficient to prepare only a single such virtually strain-free sample. A detailed description of the preparation of our samples will be published separately (see Ref. 7).

[9] W. S. C. Gurney and D. Gugan, Philos. Mag. 24, 857 (1971).

[10] J. S. Dugdale and D. Gugan, Proc. Roy. Soc. London, Ser. A 254, 184 (1960).

Anomalous Conduction-Electron Polarization in Superconducting YRh_4B_4

P. K. Tse, A. T. Aldred, and F. Y. Fradin
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 29 June 1979)

NMR and magnetization measurements in $Y_{1-x}Er_xRh_4B_4$ indicate a strong conduction-electron–local-moment interaction with only a weak depression of the superconducting transition temperature T_c. The appearance of large hyperfine interactions below T_c indicates that a grossly uncompensated conduction-electron spin state exists in the superconducting phase of YRh_4B_4. These results are discussed in terms of both itinerant electron antiferromagnetism and non-*s*-wave Cooper pairing.

Since the discovery of re-entrant superconductivity in the ternary compound $ErRh_4B_4$ by Fertig *et al.*,[1] there have been extensive studies of superconductivity and magnetic order in this class of rhodium-boride compounds containing a rare earth with a localized moment. One of the surprising features of this phase is the weak depression of T_c in the presence of localized magnetic moments, even though there is no obvious crystallographic isolation of the rare-earth ion from the transition metal atoms as there is in the Chevrel-phase ternary superconducting compounds.[2] In the present investigation ^{11}B NMR and static magnetization results are reported for the normal and superconducting states of $Y_{1-x}Er_xRh_4B_4$ ($x \leq 0.1$). These results show, for the first time, that the conduction electrons in YRh_4B_4 strongly couple to the local moments, yet there is an extremely weak dependence of T_c on x. Furthermore, the superconducting state is characterized by large hyperfine fields at the boron sites; we show that this novel result is due to an anomalously large uncompensated conduction-electron spin polarization state in the superconducting phase.

The samples used in this investigation were made by repetitive arc melting of the constituent elements. The buttons were given an ordering anneal at 1100°C for ~ 5 days. Metallography and x-ray powder patterns indicate solid solutions are formed between YRh_4B_4 and $ErRh_4B_4$. Static magnetization measurements were made on powder samples by use of a Faraday technique. The NMR measurements were made on powders with a pulsed phase-coherent spectrometer operated at 8 and 12 MHz and a Varian electromagnet with Fieldial control.

In Fig. 1 we show the integrated signal intensity of the ^{11}B nuclear spin echo in $Y_{1-x}Er_xRh_4B_4$ ($x = 0$ and 0.01) at 12 and 8 MHz for temperatures that span $T_c(H)$. Because of the inhomogeneous Knight-shift broadening, we only observe the $\pm\frac{1}{2}$ transition metal atoms as there is in the Chevrel- is a gradual loss of signal with decreasing temperature between 77 K and T_c due to signal components suffering Knight shifts in excess of ~ 1000 Oe. In pure YRh_4B_4 and $LuRh_4B_4$, we are able to see the $\pm\frac{3}{2} \leftarrow \pm\frac{1}{2}$ transition, and the integrated signal intensity follows the nuclear magnetic Curie law above T_c. However, as temperature is reduced, the signal intensity drops rapidly below T_c for all compositions. From the magnetization experiments we find $H_{c1} \approx 1$ kOe and $H_{c2} \approx 20$ kOe at 4.2 K. We estimate the volume flux exclusion at the resonance frequencies $H_{c1} \ll H < H_{c2}$ to be less than 10%, i.e., $B \approx H$. The sharp loss of signal intensity at T_c is quite unusual for a strong type-II superconductor.

Two possible causes of signal loss can be ruled out. First, the loss of signal due to a rapid shortening in the spin-echo lifetime T_2 below T_c

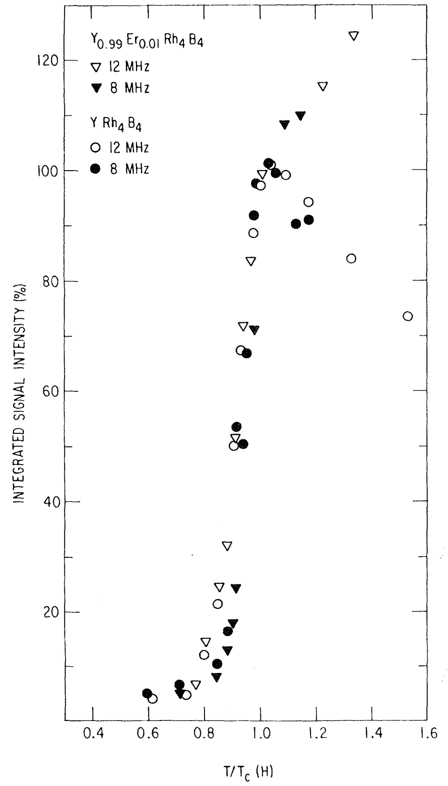

FIG. 1. The reduced temperature $T/T_c(H)$ dependence of the normalized integrated resonance intensity of ^{11}B obtained from the spin echo in YRh_4B_4 and $Y_{0.99}Er_{0.01}Rh_4B_4$ at 8 and 12 MHz. From susceptibility measurements T_c was determined to be 8.2 and 7.2 K at $H \simeq 6$ and $H \simeq 8.8$ kOe, respectively.

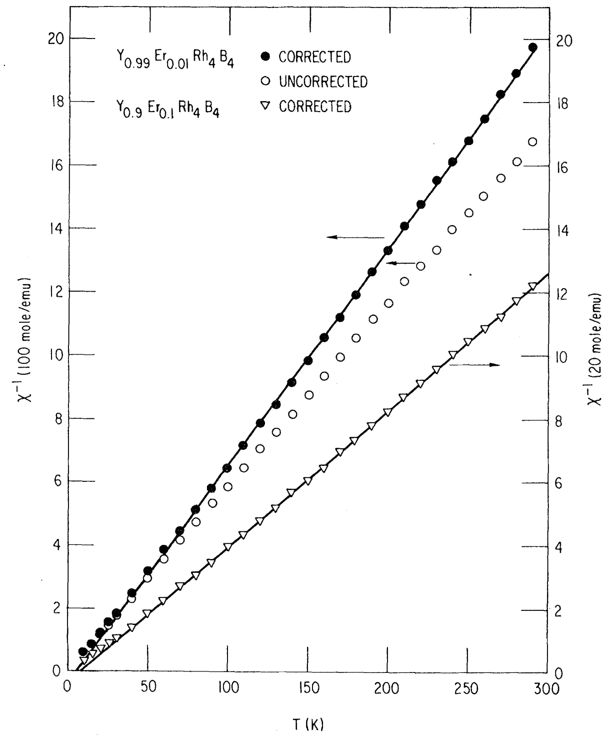

FIG. 2. Reciprocal susceptibility vs temperature data for two $Y_{1-x}Er_xRh_4B_4$ compounds. The uncorrected data for $x = 0.01$ represent the experimentally measured susceptibilities; to obtain the corrected values, which represent the susceptibility per Er ion, a point-by-point subtraction of the measured susceptibility of YRh_4B_4 was made. The corrections for the $x = 0.1$ sample were small.

can be eliminated since we find T_2 constant at 176 μsec (YRh_4B_4) both above and below T_c for 8 and 12 MHz. Second, the effect of field inhomogeneity associated with the vortex state has been estimated following de Gennes[3] for the intermediate field range $H_{c1} \ll H < H_{c2}$. Using a value of the field penetration length $\lambda = 1500$ Å, we find the root-mean-square second moment $\langle \Delta H^2 \rangle^{1/2} = 40$ Oe. This amount of line broadening would not result in signal loss in our experiment. A larger broadening would be predicted for a much smaller λ, but this would be inconsistent with the strongly type-II behavior, i.e., $H_{c2}/H_{c1} \gtrsim 20$.

Another striking feature of our results is the effective moment μ_{eff} per Er atom in the $Y_{1-x}Er_x$-Rh_4B_4 alloys determined from the Curie-Weiss susceptibility obtained in the temperature range 15 to 300 K and fields of 500 to 15 000 Oe, Fig. 2. The giant effective moments (see Table I, line 4) can be compared with the Er^{3+} free-ion moment of $9.58\mu_B$, which is experimentally found for $ErRh_4B_4$. In addition, the ^{11}B relaxation rate T_1^{-1} shows a giant impurity enhancement in the Er-doped compounds and a non–Korringa-like behavior, i.e., $T_1 T \neq$ const (Table I). A clustering of Er ions would not be expected[4] to have such a strong effect on T_1. Further, since $ErRh_4B_4$ ferromagnetically orders at ~ 1 K,[1] we would not expect that Er substituted on the Y sublattice forms superparamagnetic clusters at elevated temperatures. High-field magnetization results (90 kOe, 2.1 K) yield a saturation moment of $9.85\mu_B$/Er in the 1 at.% Er compound, compared to the free-ion value of $9\mu_B$. However, for the tetragonal site symmetry of the Er, crystal field interactions are important. Mössbauer hyperfine splitting of Er in the rhodium-borides indicates a saturation moment of $8.3(2)\mu_B$.[5] Thus, the saturation magnetization indicates a polarization of the conduction electrons of ~ $1.5\mu_B$/Er. These results taken together indicate a strong polarizability of the YRh_4B_4 susceptibility. [The measured YRh_4B_4 susceptibility increases in a non–Curie-Weiss manner from $9(2)\times 10^{-5}$ emu/mole at room temperature to $60(2)\times 10^{-5}$ emu/mole at 15 K.] The large interaction of the host susceptibility with the Er ions appears at odds with the negligible reduction of T_c with Er addition (see Table I), since both are expected to depend on the strength of the conduction-electron–local-moment interaction $H = -J\vec{s}\cdot\vec{S}$.

The sharp drop in signal in Fig. 1 is quite similar to the ^{11}B resonance in CrB_2 at the incommensurate itinerant-electron antiferromagnetic transition.[6] The loss of signal with little shift in position can be ascribed to an extremely broad distribution of magnetic hyperfine fields ($\gg 100$ Oe) at the boron nuclei. A description of YRh_4B_4 as an itinerant-electron antiferromagnet could partially explain a number of the results presented here. The normal-state susceptibility $\chi(q)$ would then have a tendency to go critical in the Stoner sense at finite $q = Q$. For the case when the superconducting coherence length $\xi \gg Q^{-1}$, it has been shown[7] that superconductivity and spiral magnetic order can coexist. However, in the case of YRh_4B_4 and $LuRh_4B_4$, the magnetism would be associated with itinerant electrons instead of localized $4f$ electrons. It is difficult, however, to explain why the apparent Néel temperature T_N (as determined from the sharp loss of the ^{11}B signal) would be depressed with application of a magnetic field in the same manner as T_c. Furthermore, the ^{11}B relaxation rate T_1^{-1} near T_c in YRh_4B_4, which is proportional to $\sum_q \chi(q, \omega_n)$, where ω_n is the nuclear Larmor frequency, has a functional dependence expected of a type-II superconductor and does not show the critical be-

TABLE I. Experimentally determined parameters for $Y_{1-x}Er_xRb_4B_4$.

x	0	0.003	0.01	0.03	0.1
$T_c(H=0)$ (K)[a]	10.28	10.31	10.30	10.36	10.27
μ_{eff} (μ_B/mol)[b]	···	0.60	1.17	1.78	3.07
μ_{eff}(corr) (μ_B/mol)[c]	···	0.52	1.08	1.71	3.03
μ_{eff}(corr) (μ_B/Er)	···	175	108	57	30
T_1T (sec K) at 77 K	53.9	···	8.24	···	0.34
T_1T (sec K) at ~7.7 K and 8.8 kOe	42.8	···	0.022	···	···

[a] Note, for $x = 0.5$ and 1.0, $T_c = 9.52$ and 8.61 K, respectively.

[b] Determined from uncorrected data (Fig. 2).

[c] Determined from corrected data (Fig. 2).

havior anticipated for an itinerant-electron antiferromagnet near T_N.[6]

Because of the appearance of identical behavior for the superconducting and "magnetic" order parameters, we propose an alternative explanation for the ^{11}B signal loss below T_c, which can be cast in terms of a single order parameter associated with non-s-wave pairing, i.e., by considering p-wave or higher-order pairing. Following Balian and Werthamer,[8] we consider p-wave pairing and the full triplet of states. They show that in the p-wave paired phase the thermodynamic properties follow BCS[9] predictions. However, the Knight shift of the NMR line should show little change below T_c inasmuch as the spin susceptibility in the superconducting state is $\frac{2}{3}$ of its value in the normal state. Our results are consistent with this prediction, but represent a weak argument since orbital Knight shifts and spin-orbit scattering can also reduce the fractional change in Knight shift at T_c for the BCS state. However, in the p-wave paired state the triplet contains both parallel and antiparallel spin-paired states. Balian and Werthamer show that the pairs of parallel spins contribute to the spin indefiniteness. We can understand the broad distribution in hyperfine fields at the boron sites, with the p-wave pairing model, as being due to the nuclear coupling to the parallel-spin conduction-electron pairs below T_c. This is consistent with an additional experimental observation that $T_2{}^*$, which is inversely proportional to the root-mean-square moment of the local magnetic field distribution, is constant above T_c but decreases just as sharply as the integrated resonance intensity below T_c.

Although p-wave pairing has been established[10] in ^{3}He, arguments based on the depression of the p-wave pairing transition in superconductors due to normal potential scattering from defects[8] makes p-wave pairing unlikely, unless some special Fermi surface anisotropy[11] favors the p-wave paired state over the isotropic s-wave state. Both phonon-mediated as well as paramagnon-mediated p-wave pairing have been considered.[12] We note that for YRh$_4$B$_4$ we have no evidence for nonmagnetic impurities depressing T_c, but we do have evidence that magnetic solute additions only weakly depress T_c (Table I). Thus, both spin scattering and potential scattering appear to be ineffective.

In summary, we have shown that Er substitutions in YRh$_4$B$_4$ yield large conduction-electron polarizations due to a strong conduction-electron-local-moment interaction. Boron NMR below T_c indicates an extremely large distribution of hyperfine fields that grows in a manner similar to the expected superconducting gap behavior. Both magnetic and nonmagnetic impurities are ineffective at depressing T_c. Two possible explanations of the unusual behavior have been discussed. One involves a simultaneous itinerant-electron antiferromagnetic state coexisting with the superconducting state. The other proposes that an exotic non-s-wave pairing is responsible for superconductivity in the rhodium borides. A full account of the magnetization, NMR relaxation, and high-field ^{11}B and ^{105}Rh NMR in the normal and superconducting state of Y$_{1-x}$Er$_x$Rh$_4$B$_4$, Y$_{1-x}$Gd$_x$Rh$_4$B$_4$, and LuRh$_4$B$_4$ will be published separately.

This work is supported by the U. S. Department of Energy. The authors would like to acknowledge stimulating discussions with Dr. G. S. Knapp, and the experimental assistance of J. W. Downey and L. W. Weber.

---

[1] W. A. Fertig, D. C. Johnston, L. E. DeLong, R. W. McCallum, M. B. Maple, and B. T. Matthias, Phys. Rev. Lett. 38, 987 (1977).

[2] F. Y. Fradin, G. K. Shenoy, B. D. Dunlap, A. T. Aldred, and C. W. Kimball, Phys. Rev. Lett. 38, 719 (1977).

[3] P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).

[4] F. Y. Fradin and T. J. Rowland, Solid State Commun. 8, 1047 (1970).

[5] B. D. Dunlap, G. K. Shenoy, F. Y. Fradin, and C. W. Kimball, J. Phys. (Paris), Colloq. 37, C6-379 (1978).

[6] R. G. Barnes and R. B. Creel, Phys. Lett. 29A, 203 (1969); F. Borsa and R. G. Lecander, Solid State Commun. 20, 389 (1976); S. Funahashi, Y. Hamaguchi, T. Tanaka, and E. Bannai, Solid State Commun. 23, 859 (1977).

[7] L. N. Bulaevski, A. I. Rusinov, and M. Kulic, Solid State Commun. 30, 59 (1979); E. I. Blount and C. M. Varma, Phys. Rev. Lett. 42, 1079 (1979).

[8] R. Balian and N. R. Werthamer, Phys. Rev. 131, 1553 (1963).

[9] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[10] See, for example, A. I. Ahonen, M. T. Haikala, M. Krusius, and O. V. Lounasmaa, Phys. Rev. Lett. 33, 628 (1974).

[11] P. W. Anderson and P. Morel, Phys. Rev. 123, 1911 (1961).

[12] I. F. Foulkes and B. L. Gyorffy, Phys. Rev. B 15, 1395 (1977); D. Fay and J. Appel, Phys. Rev. B 16, 2325 (1977); F. J. Pinski, P. B. Allen, and W. H. Butler, Phys. Rev. Lett. 41, 431 (1978).