Destruction of Superconductivity at the Onset of Long-Range Magnetic Order in the Compound $ErRh_4B_4$

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The compound $ErRh_4B_4$ becomes superconducting at a critical temperature T_{c1} of 8.7 K followed by a return to the normal state at a second critical temperature T_{c2} of 0.9 K. The return to the normal state at T_{c2} is coincident with the occurrence of long-range ordering of the magnetic moments of the Er^{3+} ions which completely occupy a set of equivalent lattice sites.

Recently, a new crystallographic system of ternary compounds with the general formula MRh_4B_4 was reported,[1,2] with M = Th, Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu. Whereas Th, Y, Nd, and Sm formed superconducting compounds, Gd through Ho yielded ferromagnetic phases, and Er, Tm, and Lu again formed superconducting compounds.[1] La, Ce, Pr, Eu, and Yb do not form MRh_4B_4 compounds.[1,2] This behavior is in sharp contrast to that previously observed for the ternary Chevrel-phase compounds $M_xMo_6S_8$[3] and $M_xMo_6Se_8$.[4] Here, each rare earth (M) has been found to form a Chevrel-phase sulfide and selenide and, with the exception of the Ce and Eu members of each series, they are all superconducting.

A comparison between the two MRh_4B_4 compounds formed by the neighboring rare earth (RE) ions Ho and Er is particularly interesting. The ~6-K Curie temperature of the Ho compound is in juxtaposition with the 8.6-K superconducting transition temperature of the Er compound,[1] even though the effective magnetic moments of both RE ions, $10.6\mu_B$ for Ho and $9.6\mu_B$ for Er, differ by only 10%. In this Letter we report the results of new measurements which show that upon cooling $ErRh_4B_4$ far below its superconducting transition temperature, a second transition occurs at 0.9 K where superconductivity disappears and the compound exhibits long-range ordering of the Er^{3+} magnetic moments.

In the past, efforts to explore the interaction between superconductivity and magnetic order were carried out by introducing low concentrations of magnetic impurity ions into superconducting elements and compounds.[5] However, in these dilute matrix-impurity systems, the random spatial distribution of magnetic impurity ions resulted in clustered and/or glassy magnetic structures with ill-defined magnetic ordering temperatures and other physical properties which have proved difficult to interpret. In the ternary RE molybdenum chalcogenides and now the ternary MRh_4B_4 compounds, the RE ions are distributed periodically in the lattice, so that ordering of the RE magnetic moments should be of *long-range* rather than diffuse "spin-glass" type encountered in a dilute substitutional alloy. Thus these systems afford a unique opportunity to investigate the conditions under which superconductivity and long-range magnetic order can coexist.

Samples of $ErRh_4B_4$ were synthesized from the high-purity elements by conventional arc melting and annealing techniques. X-ray and metallographic analysis showed that with the exception of several percent of unidentified impurity phases, a representative sample possessed the tetragonal YRh_4B_4 structure,[2] with lattice constants a = 5.299(3) Å and c = 7.388(4) Å. In separate experiments, a 15-Hz biphase impedance bridge was used to monitor the ac magnetic susceptibility and four-probe electrical resistance between 0.07 and 10 K. Magnetization measurements were made between 0.69 and 294 K in fields up to 10 kG with a Faraday magnetometer. Specific-heat measurements were performed between 0.7 and 17 K in a He^3 semiadiabatic calorimeter using a heat-pulse technique.

Shown in Fig. 1 are plots of the ac magnetic susceptibility χ_{ac} and electrical resistance of $ErRh_4B_4$ as functions of temperature in zero ap-

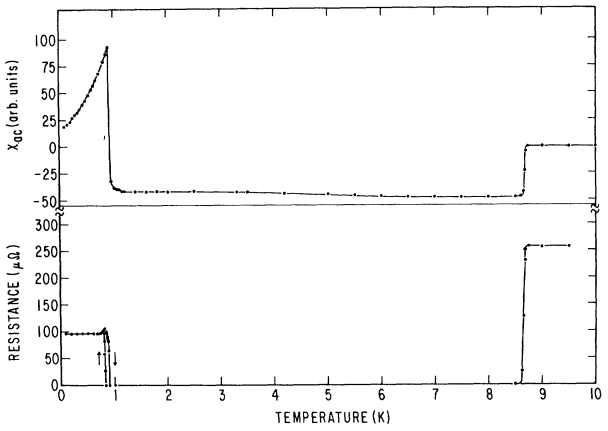

FIG. 1. ac magnetic susceptibility χ_{ac} and ac electrical resistnace vs temperature for $ErRh_4B_4$ in zero applied magnetic field.

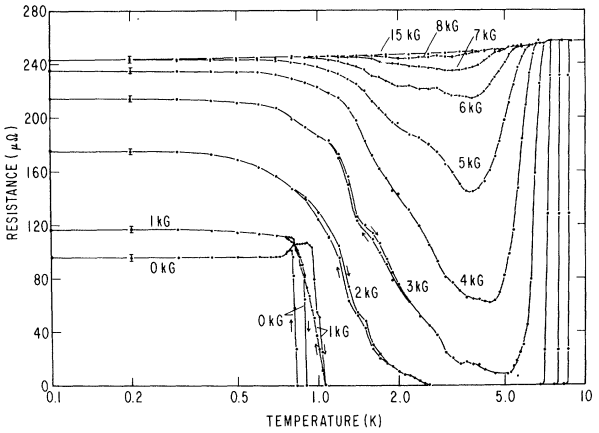

FIG. 2. ac electrical resistance vs temperature for $ErRh_4B_4$ in various applied magnetic fields between 0 and 15 kG.

plied magnetic field. Both measurements reveal a normal- to superconducting-state transition at 8.7 K $\equiv T_{c1}$, followed by a loss of superconductivity at 0.9 K $\equiv T_{c2}$. In addition, χ_{ac} exhibits a large positive value just below T_{c2} and rapidly becomes less paramagnetic with decreasing temperature. The latter behavior indicates that a transition to a magnetically ordered state accompanies the superconducting- to normal-state transition at T_{c2}. A noteworthy feature of the electrical resistance data is that the value of the resistance below $T_{c2} = 0.9$ K is ~40% of the value above the upper critical temperature T_{c1}. This is consistent with the above indication of magnetic ordering at T_{c2}, since the spin-disorder contribution to the resistance should disappear below the magnetic ordering temperature.

Three other salient features of the resistance data near T_{c2} are (1) the marked hysteresis (~0.1 K) which occurs as this transition is traversed with increasing and decreasing temperature; (2) the small peak at the transition; and (3) the constancy of the resistance below 0.7 K. Further measurements of the electrical resistance as a function of temperature were made in various fixed magnetic fields between zero and 15 kG. The measurements were made on a sample of nonuniform geometry with an uncertain demagnetizing factor, and the results are shown in Fig. 2. In magnetic fields of 0, 1, and 2 kG, the transitions at T_{c1} are relatively sharp; in fields of 0 and 1 kG, the transitions at T_{c2} are also relatively sharp and still appreciably hysteretic. In a 1-kG field, the peak which is clearly evident in the zero-field data at T_{c2} has disappeared and is replaced by a steplike feature. In fields between 3 and 8 kG, the data indicate that the sample no longer becomes completely superconducting at any temperature; the latter data exhibit minima at temperatures between 3.5 and 5 K. In the temperature range below 0.4 K, the resistance is independent of temperature at each applied field; its magnitude increases monotonically with increasing field and tends to saturate above 5 kG to a constant value which is slightly lower than the normal-state value near 9 K. The sign of the magnetoresistance below T_{c2} may reflect either antiferromagnetic order, or superconducting fluctuations[6] extending into the temperature region below T_{c2}.

Shown in Fig. 3(a) is a plot of the inverse low-field susceptibility as a function of temperature for $ErRh_4B_4$ between 7 and 294 K. These data can be described by a Curie-Weiss law with an effective magnetic moment μ_{eff} of $(9.62 \pm 0.15)\mu_B$ per Er ion and a small Curie-Weiss temperature of 1 ± 1 K. The value of μ_{eff} is identical within experimental error to that ($9.58\mu_B$ per Er ion) predicted for the Hund's-rule ground state of Er^{3+}.

Plots of the magnetization M versus applied magnetic field obtained below 9 K are shown in Fig. 3(b). The apparent negative M intercepts of the low-field data at temperatures between T_{c1} and T_{c2} reflect the superconductivity of the sample in this temperature range. Below 1 K, the data indicate that the Er moments are not easily saturable in the magnetic field, and the magnetization at each applied field below 1 K is nearly independent of temperature.

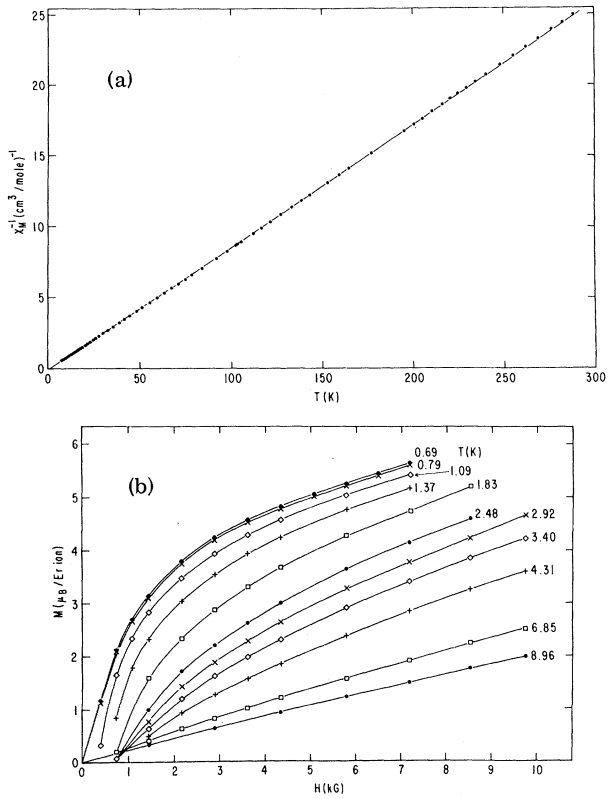

FIG. 3. (a) Inverse static low-field molar magnetic susceptibility χ_M^{-1} vs temperature T for $ErRh_4B_4$. The solid line represents a Curie-Weiss law with $\mu_{eff} = (9.62 \pm 0.15)\mu_B$ per Er ion and $\theta = 1 \pm 1$ K. (b) Magnetization M vs applied magnetic field H isotherms for $ErRh_4B_4$ at temperatures between 0.69 and 8.96 K. Data were obtained with increasing field.

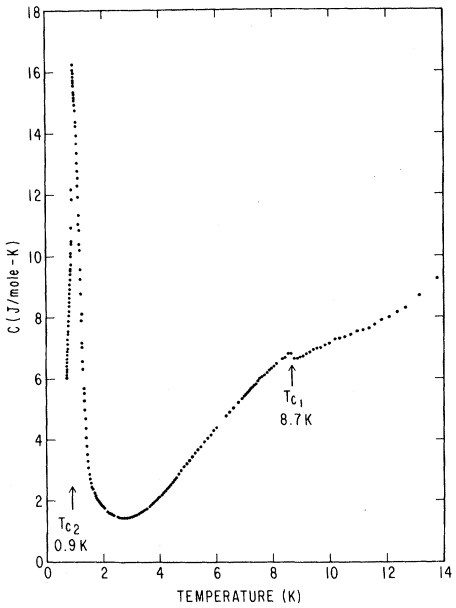

FIG. 4. Specific heat C vs temperature for $ErRh_4B_4$ in zero applied magnetic field.

Shown in Fig. 4 is a plot of the heat capacity of $ErRh_4B_4$ as a function of temperature between 0.7 and 14 K in zero applied magnetic field. The data reveal a specific-heat jump at the upper critical temperature $T_{c1} = 8.7$ K, followed by a pronounced λ-type anomaly at the lower critical temperature $T_{c2} = 0.9$ K. In order to extract the entropy arising from the magnetic degrees of freedom of the Er ions, we roughly estimate an upper limit to the normal-state heat capacity in the absence of these degrees of freedom to be $C_0 = \gamma T + \beta T^3$ arising from electronic and lattice contributions, where $\gamma = 29$ mJ/mole K^2 and $\beta = 3.1$ mJ/mole K^4. A lower limit on the magnetic contribution to the entropy between 0.7 and 15 K was then computed by substracting the calculated normal-state host entropy from the measured entropy, and was found to be $S_{mag}(0.7\text{–}15\ \text{K}) = 13.6$ J/mole K. This value is 59% of $S = R \ln 16 = 23.1$ J/mole K expected for the entropy associated with magentic ordering of Er ions possessing the full sixteen-fold Zeeman degeneracy of the Er^{3+} Hund's-rule ground state.

All of the above data are consistent in revealing (1) a normal- to superconducting-state transition at an upper critical temperature $T_{c1} = 8.7$ K; (2) the destruction of superconductivity at a lower critical temperature $T_{c2} = 0.9$ K; and (3) the onset of long-range magnetic order at T_{c2}. The data thus far obtained do not, however, allow an unambiguous and self-consistent determination to be made of the type of magnetic order which occurs at T_{c2}. The positive Curie-Weiss temperature obtained from the static susceptibility measurements suggests ferromagnetic order; however, the magnetoresistance observed below T_{c2} is opposite in sign to that expected for ferromagnetic order. Below T_{c2}, the magnitude and temperature dependence of χ_{ac}, the temperature independence of the magnetization at constant field, and the difficulty of saturating the magnetization are consistent with either antiferromagnetic order, or with ferromagnetic order if the ferromagnet is of the "hard" type (large coercive force).

Although the disappearance of superconductivity at a second lower critical temperature T_{c2} has been observed previously, this phenomenon has always been restricted to matrix-impurity systems which simultaneously exhibit supercon-

ductivity and the Kondo effect.[7] The disappearance of superconductivity reported here at a second transition temperature T_{c2} in $ErRh_4B_4$ is due to a new and entirely different mechanism. The reasons we exclude the Kondo mechanism for reentrant superconductivity in $ErRh_4B_4$ are as follows: (1) Kondo behavior has been observed only for the RE ions with unstable valence, i.e., for Ce, Sm, Eu, Tm, and Yb ions, but not for Er or any of the other RE ions. (2) There is no evidence in the resistance data presented here or in resistance data up to room temperature for a normal-state resistance minimum which would suggest a Kondo effect. (3) The static magnetic susceptibility does not exhibit a negative Curie-Weiss temperature which might reflect a Kondo effect. (4) The pronounced specific-heat anomaly at T_{c2} does not even remotely resemble the very small specific-heat jump previously observed for superconducting Kondo systems at T_{c2}.[7] (5) T_{c1} is inordinately high compared to the value expected for a superconducting Kondo system with the relatively large concentration for RE ions encountered in $ErRh_4B_4$.[7]

In contrast to the results reported here, the long-range magnetic ordering which occurs in the superconducting state in $M_xMo_6Se_8$ compounds (probably antiferromagnetic) does not lead to the destruction of superconductivity at the magnetic-ordering temperatures.[8] Thus, the type of magnetic ordering which accompanies the return to the normal state at T_{c2} in $ErRh_4B_4$ is apparently different from the type which occurs in the $M_xMo_6Se_8$ compounds. The results reported here are the first evidence for the occurrence of reentrant superconductivity associated with magnetic ordering in any material. It is remarkable that the Er ions which stabilize the superconducting tetragonal phase of $ErRh_4B_4$ are the same ions which lead to the destruction of superconductivity in this compound at low temperatures. Experiments are both planned and in progress to further elucidate the nature and origin of the transition at T_{c2}.

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[6]We are indebted to G. W. Webb for this suggestion.

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