one to treat thermodynamic systems, i.e., systems with finite density of particles, corresponding to mixtures of particles with different charges moving on a loop threaded by a magnetic flux. In this way one can investigate the occurrence of superconductivity.

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Specific-Heat Anomalies at the Lower Critical Temperature in Reentrant Ferromagnetic Superconductors

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A spike-shaped heat-capacity anomaly has been identified at the lower superconducting-to-normal transition temperature T_{c2} of the magnetic superconducting system $(Er_{1-x}Ho_x)Rh_4B_4$. This anomaly can be distinguished from the feature due to long-range magnetic ordering and indicates that the transition at T_{c2} is thermodynamically of first order.

The discovery of the destruction of superconductivity at a second lower critical temperature T_{c2} in the ternary rare-earth (RE) compounds $ErRh_4B_4$[1] and $Ho_{1.2}Mo_6S_8$[2] and in various pseudoternary RE compounds[3-7] due to the onset of long-range ferromagnetic order has prompted recent theoretical[8-13] and experimental[14,15] interest in this new phase transition. In this Letter we present evidence that a spike-shaped anomaly in the heat capacity of these compounds, which can be distinguished from the broader background due to magnetic ordering alone, is associated with the superconducting-to-normal state (SC-N) transition at T_{c2}.

The feature in the heat capacity near T_{c2} for $ErRh_4B_4$ is presented in Fig. 1 which shows much more detail than originally reported in Ref. 1. There is a distinct sharp spike-shaped anomaly that peaks at 0.93 K, within the narrow range of T_{c2} values as inferred from ac electrical resistance and magnetic susceptibility measurements (0.91–0.94 K),[1,16] which appears to be superimposed on a broader feature due to the long-range ordering of the Er^{3+} magnetic moments. The latter feature begins at ~ 1.5 K, close to the onset of precursor scattering at 1.2 K observed in neutron diffraction experiments.[17]

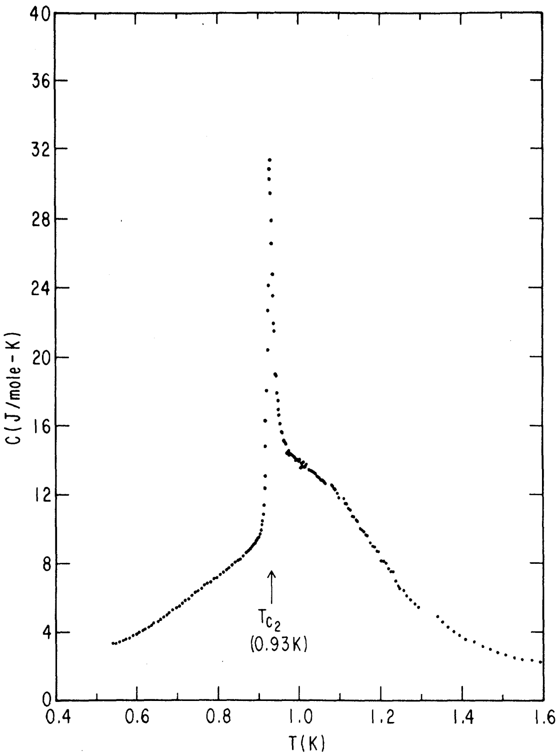

FIG. 1. Heat capacity C vs temperature T near T_{c2} for $ErRh_4B_4$. The arrow indicates the SC-N transition temperature as measured by ac magnetic susceptibility.

To establish that the heat-capacity spike is as-

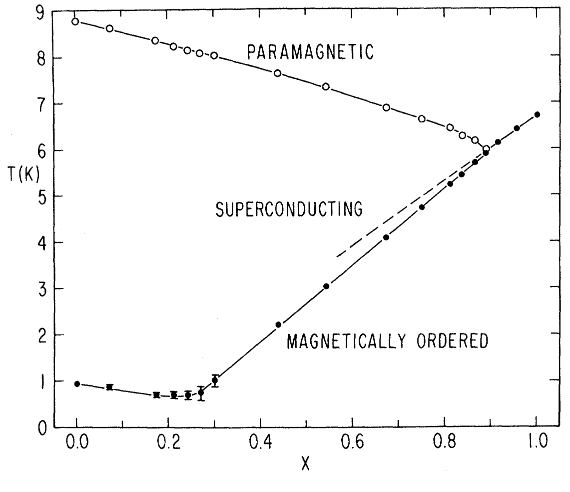

FIG. 2. Low-temperature phase diagram for the system $(Er_{1-x}Ho_x)Rh_4B_4$ determined from ac magnetic susceptibility measurements (from Ref. 3). The vertical bars on the T_{c2} data points indicate the observed thermal hysteresis.

sociated with the SC-N transition at T_{c2}, we have made heat-capacity measurements on a series of $(Er_{1-x}Ho_x)Rh_4B_4$ compounds which are reported herein. The preparation of the compounds has been discussed elsewhere.[3] A ^3He semiadiabatic calorimeter using a heat-pulse technique was employed to make the low-temperature heat-capacity measurements.

The low-temperature phase diagram for the $(Er_{1-x}Ho_x)Rh_4B_4$ system (Fig. 2) was previously reported in Ref. 3. It shows a region of composition $(0 \leq x < x_{cr} = 0.89)$ in which pseudoternary $(Er_{1-x}Ho_x)Rh_4B_4$ compounds behave much as the ternary $ErRh_4B_4$ end member; that is, a sample becomes superconducting with decreasing temperature at T_{c1} and then returns to the normal state at a lower temperature T_{c2} as it orders magnetically. Above the critical concentration $(x > x_{cr})$, the pseudoternary compounds do not become superconducting, but directly order ferromagnetically from the paramagnetic normal state like the ternary $HoRh_4B_4$ end member.

Interpretation of the heat-capacity results of Fig. 3 is simplified by the ternary compound $HoRh_4B_4$ having a characteristic sawtooth-shaped heat-capacity feature which is due to magnetic ordering [Fig. 3(a)].[6] This shape is surprisingly similar to that expected from molecular-field theory. There is also a low-temperature upturn which is apparently the high-temperature tail of a Ho nuclear Schottky anomaly.[6] At $x = 0.912$, just above the critical concentration, $x_{cr} = 0.89$, the same sawtooth shape is evident although reduced in magnitude [Fig. 3(b)]. However, at $x = 0.813$, just below the critical concentration, the sawtooth shape now has superimposed upon it a spike-shaped feature which, within experimental error, is coincident with the destruction of superconductivity at T_{c2} as measured by ac magnetic susceptibility [Fig. 3(c)]. Since there is no indication of a spike-shaped structure for $x > x_{cr}$,

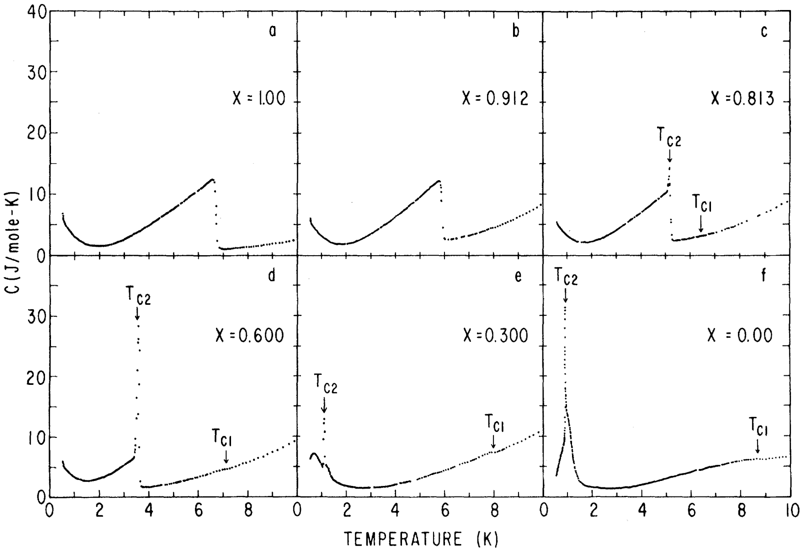

FIG. 3. Heat capacity C vs temperature for certain members of the $(Er_{1-x}Ho_x)Rh_4B_4$ system. The arrows indicate the upper (T_{c1}) and lower (T_{c2}) SC-N transition temperatures as measured by ac magnetic susceptibility.

where ferromagnetic order is established from the normal state, it is reasonable to attribute this spike for $x<x_{\rm cr}$ to the heat capacity associated with the SC-N transition at T_{c2}. At the composition $x=0.60$, the characteristic sawtooth shape can still be observed with an even larger spike superimposed, probably due to a more fully developed superconducting state [Fig. 3(d)].

The situation for $x=0.30$ is more complex because it occurs in a region of concentration in which there is a minimum in the superconducting-to-normal magnetically ordered (SC-NM) phase boundary of Fig. 2. Recent neutron scattering experiments have shown that in the MRh$_4$B$_4$ tetragonal unit cell (where M is a RE element), the ferromagnetic alignment is in the basal plane for ErRh$_4$B$_4$,[17] but along the unique c axis for HoRh$_4$B$_4$.[18] The minimum in the phase boundary evidently indicates where the ferromagnetic alignment that destroys the superconducting state changes direction: Ordering in the basal plane determines the Er-rich boundary, while ordering along the c axis determines the Ho-rich boundary. The heat-capacity curve for $x=0.30$ [Fig. 3(e)] provides evidence that due to this difference in the direction of magnetic alignment of the RE magnetic moments with respect to the crystallographic axes, the Er and Ho magnetic moments order independently at different temperatures for this composition. Although the destruction of superconductivity for the $x=0.30$ compound falls on the boundary determined by the ordering of the Ho magnetic moments showing that these moments order above 1 K, there is a broad, round peak at 0.7 K which resembles the feature due to magnetic ordering in ErRh$_4$B$_4$ without the superimposed spike. In fact, a linear extrapolation of the SC-NM boundary from the Er-rich side of the phase diagram suggests that the latter peak occurs at a temperature where the Er magnetic moments would be expected to order for this composition. The complex nature of the magnetic ordering for the $x=0.30$ composition may be responsible for the reduction of the heat capacity spike at T_{c2}.

Evidence for a spike-shaped anomaly at T_{c2} has also been observed in the heat capacity of the pseudoternary system[6] (Lu$_{1-x}$Ho$_x$)Rh$_4$B$_4$ and the ternary compound Ho$_{1.2}$Mo$_6$S$_8$.[19] However, heat-capacity measurements reported for the (Gd$_x$Er$_{1-x}$)Rh$_4$B$_4$ system[7] do not clearly show a distinguishable spike at the SC-N transition. This may be because the data points were, on the average, taken 50 mK apart, and a narrow spike anomaly some 70 mK wide could therefore have been missed.

Another common feature of these magnetic superconductors is that the SC-N transition at T_{c2} shows thermal hysteresis in the ac electrical resistance and magnetic susceptibility.[1,19] This suggests that the transition at T_{c2} is first order and that the heat-capacity spike is a manifestation of a latent heat of transformation. The latent heat may appear as a *finite* spike because the SC-N transition is not infinitely sharp.

Knowing whether or not the transition is first order is important in assessing the possible mechanisms responsible for this phenomenon. It has been speculated that magnetization fluctuations near the magnetic ordering temperature destroy the superconducting state before a mean exchange field or magnetization can be established.[8] A recent theory by Suhl[10] considers the effect of such fluctuations of the magnetic and superconducting order parameters in a Landau-Ginzburg theory of magnetic superconductors. For strong coupling between the order parameters he finds that fluctuations would destroy the superconductivity in a second-order transition, instead of the first-order transition apparently observed experimentally.

Two well-known mechanisms by which long-range ferromagnetic ordering could cause a first-order SC-N transition are (1) the paramagnetic effect on superconductivity of a mean exchange field, and (2) the orbital effect on superconductivity of the vector potential produced by the magnetization. The paramagnetic effect leads to a first-order transition if the mean exchange field $H_{\rm exch}$ produced by the spontaneous polarization of the RE local magnetic moments exceeds the Pauli paramagnetic limiting field $H_p({\rm kG})=18.4T_c({\rm K})$.[20] For the case of ErRh$_4$B$_4$, these fields can be estimated to be $H_{\rm exch}\gtrsim 300$ kG and $H_p\sim 200$ kG fulfilling the above requirement. On the other hand, if the superconductor is type I, the orbital effects can cause a first-order transition when the magnetization produces an induction field $B=4\pi M$ that exceeds the critical field H_c. The nonmagnetic member of the RE rhodium borides, LuRh$_4$B$_4$, is a type-II superconductor with an upper critical field, $H_{c2}=60$ kG,[21] which might imply that the other superconducting MRh$_4$B$_4$ members are also type II. However, a recent theory by Maekawa, Tachiki, and Takahashi[8] indicates that the large RE spin polarizability of the magnetic superconductors near T_M has the effect of changing even extreme type-II superconductors into type I. Although this theory was intended only for the region $T > T_M$, it is reasonable to extend the results into the region of spontaneous magnetization where there is still a large RE spin polarizability. If one therefore assumes that $ErRh_4B_4$ is a type-I superconductor at T_M, it is only necessary to compare the magnetic induction $B \cong 10$ kG assuming saturated magnetization with the thermodynamic critical field $H_c = 1.8$ kG calculated from the heat capacity of $LuRh_4B_4$[21] to conclude that orbital effects may also be important in the destruction of superconductivity in these magnetic superconductors.

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Effect of Bound Hole Pairs on the *d*-Band Photoemission Spectrum of Ni

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It is shown that the spectral density of the Ni *d* electrons contains a peak due to excitations of bound hole pairs. The spectral density is observed directly in photoemission experiments which show a satellite peak below the bottom of the *d* bands. The observed peak exhibits a strong resonance as a function of photon energy and this behavior is also explained by the present theory.

My purpose is to present a theory for the physical origin of the satellite that is observed at approximately 7 eV below the Fermi energy in photoemission experiments on Ni, and also to explain the observed resonance in the satellite intensity as a function of photon energy. The satellite has been observed[1-6] in both x-ray and ultraviolet photoemission spectroscopy (XPS and UPS), at a binding energy of roughly 7 eV.[7] The amplitude of the satellite has its maximum at a photon energy of 67 eV (Ref. 4) and is unobservably small below roughly 25 eV.[5,6] The *d*-band peak observed in both XPS and UPS is narrowed relative to the calculated *d*-band peak[8] and a narrowing is predicted by the present theory. However, Eastman, Himpsel, and Knapp[9] have also observed a band narrowing at photon energies below 20 eV where the satellite is not seen.

The simplest explanation for the satellite would be the excitation of a 5-eV Ni plasmon (the satel-