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$HoRh_4B_4$: A model mean-field ferromagnet

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Experimental results of specific heat, zero-field magnetization, electrical resistivity, and thermal-expansion measurements reveal the mean-field character of the ferromagnetic phase transition of $HoRh_4B_4$. The data can be described very accurately with the use of mean-field theory and the assumption that the effective spin $S=\frac{1}{2}$.

In recent investigations, metallic compounds of the type RRh_4B_4 (R denotes rare earth) have revealed at low temperatures superconductivity, magnetic ordering, or both. Originally, RRh_4B_4 compounds with $R=$Nd, Sm, Er, Tm, and Lu were found to be superconductors, while those with $R=$Gd, Tb, Dy, and Ho were reported to be ferromagnets.[1] Reentrant superconductive behavior was later discovered in $ErRh_4B_4$ (Ref. 2) and coexistence of long-range magnetic order and superconductivity was observed in $NdRh_4B_4$,[3] $SmRh_4B_4$,[4,5] and $TmRh_4B_4$.[6] Most of the studies on this class of compounds focused on the interplay between superconductivity and magnetism, and comparatively little effort has been made to investigate those substances which exhibit only superconductivity or magnetic order. In magnetic superconductors it is of particular interest to study the nature of the magnetic transition in the presence of a superconducting matrix. Therefore, it seems very important to establish the nature of magnetic ordering in those materials where superconductivity is absent.

One such example is the compound $HoRh_4B_4$ whose low-temperature physical properties have recently been investigated in some detail.[7] $HoRh_4B_4$ orders ferromagnetically at 6.7 K (Ref. 1) due to a spontaneous alignment of the localized $4f$-electron magnetic moments of the Ho^{3+} ions along the tetragonal axis of the crystal lattice.[8] Various measurements have indicated that the $4f$-electron Hund's-rule ground-state multiplet of the Ho^{3+} ions is split by a crystalline-electric field (CEF) leading to a doublet ground state and two singlet states at energies 40 and 60 K above the ground state, respectively. The other excited states, above 80 K, have little influence on the magnetic properties in the region of the ordering temperature.

A rather unexpected feature of the magnetic phase transition was the almost ideal $S=\frac{1}{2}$ mean-field behavior of the magnetic specific heat at and below the magnetic ordering temperature. The entropy associated with this anomaly amounts to 96% of $R\ln 2$ per mole, the expected entropy loss with decreasing temperature due to the splitting of the doublet ground state upon magnetic ordering. The thermal-expansion coefficient below the ordering temperature was found to scale with the specific heat, so that the strain associated with the phase transition also follows mean-field behavior very closely.

In order to further characterize the ferromagnetic phase transition of $HoRh_4B_4$, we have measured the temperature dependence of the spontaneous magnetic moment M of the Ho^{3+} ions and the electrical resistivity in zero magnetic field between 1.5 and 8 K. The temperature dependence of M was determined by monitoring the neutron-diffraction counting rate of the [101] powder Bragg peak as a function of temperature, while the electrical resistivity of a polycrystalline sample of

$HoRh_4B_4$ was measured with a low-frequency four-probe technique. In Fig. 1(a) we show the temperature dependence of the [101] powder Bragg peak intensity with background subtracted and in Fig. 1(b) the corresponding temperature dependence of the Ho^{3+} ion magnetic moment is displayed in reduced units M/M_0 versus T/T_C. Here M_0 is the magnetic moment at $T=0$ K and T_C is the Curie temperature. For an $S=\frac{1}{2}$ system, formally equivalent to the above-mentioned $4f$-electron doublet ground state, mean-field theory gives the following temperature dependence of the spontaneous magnetic moment below T_C (Ref. 9):

$$M/M_0=\tanh(g\mu_B\lambda M/2kT) , \quad (1)$$

where g is the Landé g factor, μ_B is the Bohr magneton, and λ is the molecular field constant. With

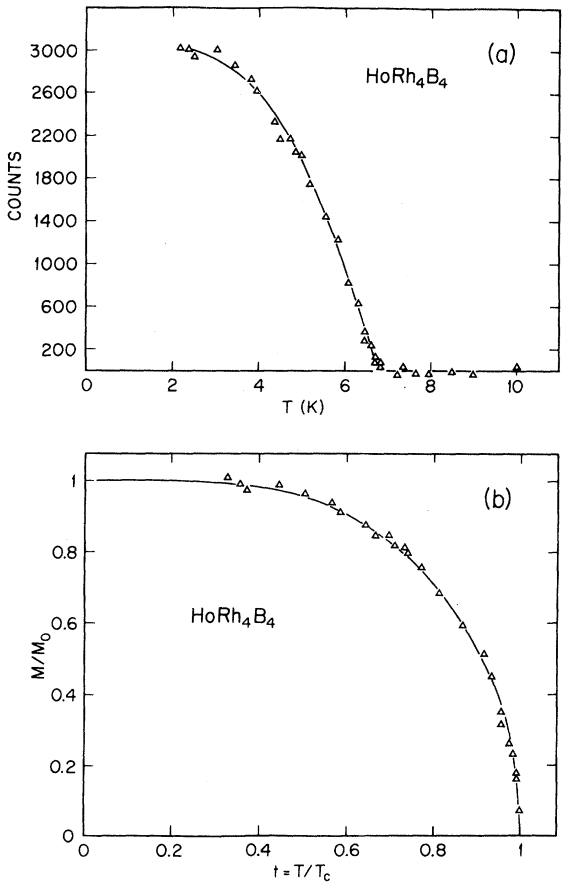

FIG. 1. (a) Temperature dependence of the neutron counts of the [101] powder Bragg peak of $HoRh_4B_4$ below 10 K. The background has been subtracted. The line is to guide the eye. (b) Resulting reduced magnetization M/M_0 in the ferromagnetic phase of $HoRh_4B_4$. The solid line is the mean-field prediction for an $S=\frac{1}{2}$ ferromagnet.

the use of the condition that

$$M_0=2kT_C/\lambda g\mu_B , \quad (2)$$

Eq. (1) can be written as

$$y=\tanh(yT_C/T) , \quad (3)$$

where $y=M/M_0$. The solid line in Fig. 1(b) is calculated from Eq. (3) with $M_0=55.5$ in arbitrary units, $T_C=6.775$ K, and is in excellent agreement with the experimental data over the entire temperature range covered.

The resistivity ρ of our sample was constant below 2.5 K with value ρ_0 and also between T_C and 10 K; hence the temperature dependence of ρ below 10 K is due only to a magnetic-scattering term $\rho_m(T)$ which is constant above T_C and the total resistivity is therefore $\rho(T)=\rho_0+\rho_m(T)$. Shown in Fig. 2 is a plot of ρ_m versus temperature which reveals the gradual change between $\rho_0+\rho_m(T_C)$ and ρ_0 due to developing magnetic order with decreasing temperature. The solid line in Fig. 2 is calculated from

$$\rho-\rho_0=\rho_m(T_C)(1-y^2) , \quad (4)$$

where y is given by Eq. (3). It is thus quite obvious that the decrease of the resistivity of $HoRh_4B_4$ below T_C is proportional to the square of the magnetic moment. This temperature dependence of ρ implies directly that $\partial\rho/\partial T$ is proportional to the magnetic specific heat (see below), not only close to T_C, but at all temperatures below the ordering temperature. The temperature dependence of magnetic contributions to the electrical resistivity has recently been discussed by Hessel-Andersen and co-workers.[10] From their general expression for $\rho_m(T)$ derived using the ionic susceptibility func-

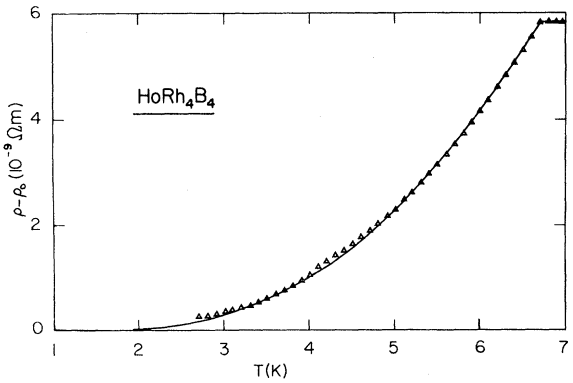

FIG. 2. Temperature dependence of the magnetic contribution to the electrical resistivity of $HoRh_4B_4$. The solid line is a fit using $\rho-\rho_0=\rho_m(T_C)(1-y^2)$.

tion, they argue that in the case of a mean-field Hamiltonian the decrease in the resistivity below T_C should be proportional to M^2. This can also be understood by considering the work of Fisher and Langer[11] who found that the temperature-dependent incoherent scattering of electrons is dominant below T_C and leads to the same behavior of the resistivity. The constant value of ρ just above T_C also indicates that either short-range correlations are not important in $HoRh_4B_4$ or they are confined to a very small temperature range around T_C if they are present.

The temperature dependence of the specific heat C_M due to magnetic ordering after nuclear Schottky anomaly, electronic Schottky anomaly, conduction electron, and lattice contributions have been subtracted from the raw experimental results[7] is shown in Fig. 3. As in Ref. 7, we note that this remaining part C_M is well described by

$$C_M = T_C y \frac{\partial y}{\partial T} , \tag{5}$$

the mean-field result for an $S=\frac{1}{2}$ system.[12] From the thermodynamic relationship between the specific heat and the thermal expansion, it follows directly that the spontaneous strain $\epsilon = \Delta l / l$ (where $\Delta l = l(T+\Delta T) - L(T)$ and l is the length of the sample) accompanying the magnetic transition should be proportional to the square of the reduced magnetic moment $M/M_0 = y$. In Fig. 4 we show that this is indeed observed in $HoRh_4B_4$, namely, $\epsilon \sim -y^2 = -(M/M_0)^2$ below T_C.

Summarizing the experimental results we conclude that the magnetic phase transition of $HoRh_4B_4$ is a model case for an $S=\frac{1}{2}$ mean-field

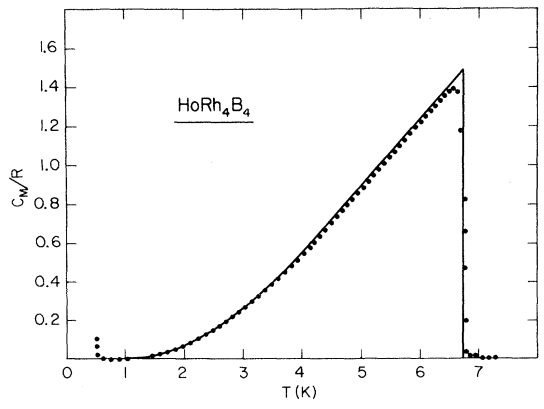

FIG. 3. Temperature dependence of the specific heat anomaly of $HoRh_4B_4$ due to the ferromagnetic ordering. The solid line is the mean-field result for an $S=\frac{1}{2}$ ferromagnet (from Ref. 7).

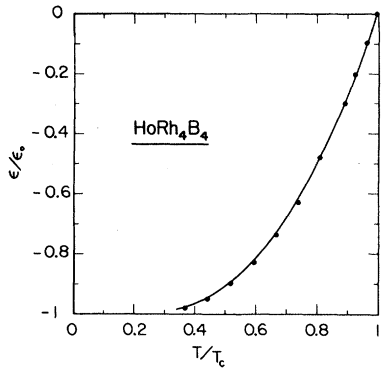

FIG. 4. Temperature dependence of the reduced strain ϵ/ϵ_0 of $HoRh_4B_4$ in the ferromagnetic phase, where $\epsilon_0 = -\epsilon(T=0)$. The solid line is a fit using the mean-field approximation and $S=\frac{1}{2}$.

ferromagnetic transition with virtually no fluctuations above the critical temperature as indicated by both thermal and transport properties. To our knowledge, this is the first such example for a metallic ferromagnet.

Our experimental data, of course, provoke the very obvious questions about the reasons for this particular phase transition to be so mean-field-like. A discussion of this problem is probably best started by recalling some results concerning phase transitions invoking renormalization group theory (RGT).

A simple and straightforward statement of renormalization group theory is that classical behavior of a phase transition is only expected if the dimensionality d of the system investigated is larger than the corresponding marginal dimensionality d^*.[13] Almost classical behavior is expected for the case where $d^* = d$ and RGT provides the necessary logarithmic corrections to Landau behavior in the critical region. A very nice example of this latter case is the magnetic phase transition in $LiTbF_4$, a substance which displays the typical features of a dipolar coupled Ising ferromagnet.[14,15] Theoretically it was shown[16,17] that for a dipolar coupled Ising ferromagnet, $d^* = 3$. The theoretical predictions for the logarithmic corrections were later confirmed experimentally by Ahlers and co-workers[18] and, to a certain extent, by Als-Nielsen and Laursen.[19]

If, as was more or less assumed in earlier work,[7] rather short-range isotropic exchange interactions among nearest and next-nearest neighbors are responsible for the magnetic ordering in $HoRh_4B_4$, RGT predicts that $d^* = 4$.[13] A mean-field-like transition is then certainly not expected. Therefore

it seems that the magnetic phase transition in $HoRh_4B_4$ can be described by RGT arguments only if plausible reasons for a reduction of d^* to 3 or 2 in this system can be found. As mentioned above, the doublet $4f$-electron ground state of the Ho^{3+} ions is an almost pure $|\pm 7\rangle$ state,[7] quite well separated from higher excited CEF states. Therefore it forms an effective spin $S=\frac{1}{2}$ pair with a strongly anisotropic magnetic response, characteristic of an Ising-type magnet. Experimental evidence for the strong anisotropy of the ground state is provided by high-field magnetization measurements, which showed that externally applied magnetic fields of 100 kOe are not strong enough to align all the Ho^{3+} magnetic moments along the field direction.[7] Although we have convincing evidence that $HoRh_4B_4$ is an Ising system, not much can be said about the characteristics of the interactions leading to magnetic ordering. In order to obtain a marginal dimensionality of 2 or 3, the *symmetries* and the *range* of these interactions have to fulfill certain requirements (e.g., long-range character of the interaction is needed). As mentioned above, dipolar interactions would lead to $d^*=3$ in our case, but the value of T_C (6.775 K) as compared to the estimated dipolar interaction energy of a few tenths of a Kelvin and previously published magnetic properties of RRh_4B_4 compounds[7] indicate that Ruderman-Kittel-Kasuya-Yoshida (RKKY) type interactions are likely to be primarily responsible for the phase transition. Since an isotropic and rather short-range RKKY interaction cannot lead to a mean-field transition, we should like to conjecture that a very anisotropic Fermi surface might provide the desired features. A theoretical investigation of the interplay of dipolar and RKKY-type interactions would probably be useful to establish the value of the marginal dimensionality of our system. Further and more elaborate measurements are also needed at temperatures close to T_C.

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