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Neutron-diffraction study of the magnetic ordering in superconducting $TmRh_4B_4$

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The results of neutron-diffraction measurements are reported which confirm that superconducting $TmRh_4B_4$ orders magnetically at $T_M \simeq 0.7$ K. The modulated antiferromagnetic structure deduced from the data is of particular interest, considering the similarity of certain other physical properties of $TmRh_4B_4$ to those of the ferromagnetic, reentrant superconductor $ErRh_4B_4$.

I. INTRODUCTION

The magnetic and superconducting properties of the rare-earth ($\mathscr{R}$) rhodium boride $\mathscr{R}Rh_4B_4$ compounds, discovered by Matthias and co-workers,[1,2] have been described in a recent review article by Maple.[3] Four of these compounds, namely those for which $\mathscr{R}$ =Nd, Sm, Er, or Tm, are especially interesting because they exhibit both superconductivity and magnetic order. Two members of this series have been examined previously by neutron diffraction. In the case of $ErRh_4B_4$, the superconducting

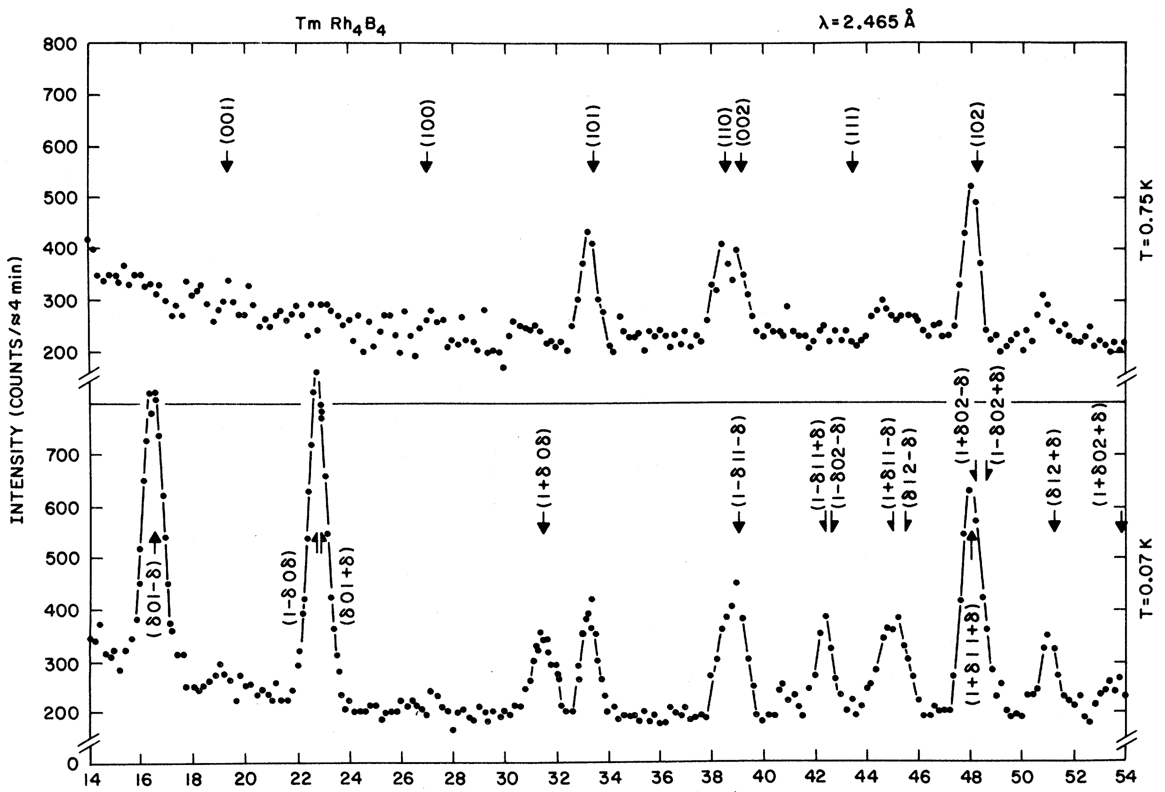

FIG. 1. Neutron-diffraction data above and below the magnetic phase transition temperature for the angular range over which magnetic peaks were observed. δ labels the magnetic satellites and is in units of $2\pi/a$ and $2\pi/c$, respectively, as described in the text.

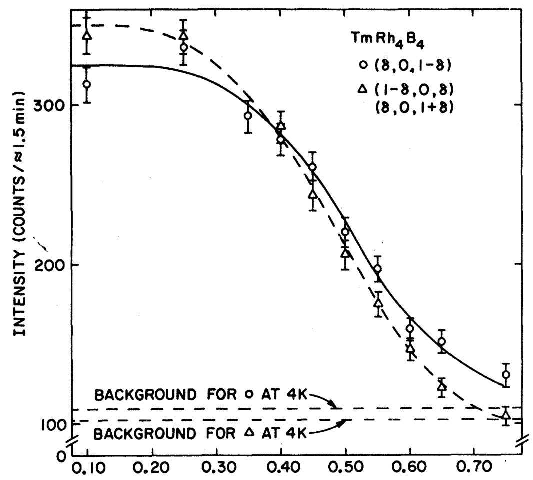

FIG. 2. Temperature dependence of the peak intensities of three magnetic satellites.

state is quenched with the onset of long-range ferromagnetic order.[4,5] More precisely, Moncton *et al.*[6] showed that the competition between ferromagnetism and superconductivity produces a compromise, long-wavelength oscillatory magnetic phase at intermediate temperatures. Recently, Sinha *et al.*[7] concluded, from a neutron-diffraction study of a single-crystal sample of $ErRh_4B_4$, that the intermediate phase consists of coexisting normal ferromagnetic domains and superconducting domains with a transverse, linearly polarized, sinusoidally modulated magnetic structure.

Measurements of the electrical resistance, heat capacity, thermal conductivity, and linear thermal expansion coefficient of $TmRh_4B_4$ by Hamaker *et al.*[8] indicate that superconductivity ($T_C=9.8$ K) and magnetic order coexist in this compound at temperatures below approximately 0.4 K. Furthermore, the striking similarity of several of the abovementioned properties of $TmRh_4B_4$ to those of $ErRh_4B_4$,[4,9,10] as discussed in Refs. 8 and 11, suggests that superconductivity and *ferromagnetic* order coexist in $TmRh_4B_4$. However, the neutron-diffraction data reported in this paper are consistent with the development of a modulated *antiferromagnetic* structure in the superconducting state in zero applied magnetic field. This structure is similar to that reported for superconducting $NdRh_4B_4$.[12,13] Nevertheless, in an applied magnetic field neutron-diffraction data show that a ferromagnetic component can be induced at field strengths for which the electrical resistivity is still zero.

II. EXPERIMENTAL

The preparation of the $TmRh_4B_4$ compound is similar to that of other $\mathscr{R}Rh_4B_4$ neutron-diffraction samples and has been described elsewhere.[14] The particular sample used in this study was ground into

TABLE I. Comparison of the observed to the theoretical integrated intensities I corresponding to the model for the magnetic structure of $TmRh_4B_4$ proposed in the text. The angular dependence of the Tm^{3+} form factor was obtained from Ref. 15. Angles are given in degrees and intensities in arbitrary units. $\lambda=2.465$ Å, $\mu_{max}=6.56\ \mu_B$.

hkl	2θ	I_{obs}	I_{calc}
$(\delta,0,1-\delta)$	16.58	50 ± 5	50
$(1-\delta,0,\delta)$	22.80	52 ± 3	51
$(\delta,0,1+\delta)$	22.93		
$(\delta,1,\delta)$	27.47	0 ± 1	0
$(1+\delta,0,\delta)$	31.50	11 ± 3	13
$(1-\delta,1,1-\delta)$	39.07	2 ± 6	8
$(1-\delta,1,1+\delta)$	42.38	8 ± 3	14
$(1-\delta,0,2-\delta)$	42.66		
$(1+\delta,1,1-\delta)$	45.01	8 ± 5	14
$(\delta,1,2-\delta)$	45.51		
$(1+\delta,1,1+\delta)$	47.97		
$(1+\delta,0,2-\delta)$	48.22	10 ± 7	16
$(1-\delta,0,2+\delta)$	48.65		
$(\delta,1,2+\delta)$	51.25	5 ± 4	6
$(1+\delta,0,2+\delta)$	53.75	3 ± 4	4

a fine powder and several grams were loaded into a flat aluminum container mounted inside a ^{3}He-^{4}He dilution refrigerator, the thermometry of which had been previously calibrated. Diffraction measurements were performed at the Brookhaven high-flux beam reactor using a triple-axis spectrometer in the elastic scattering mode with an incident neutron wavelength of 2.465 Å. Satisfactory suppression of higher-order wavelengths was achieved with a pyrolytic graphite filter. The spectrometer collimation was, from source outward, 20′, 40′, 40′, and 60′, respectively. The transmission of the sample was measured to be approximately 0.20.

III. RESULTS

Complete diffraction patterns for scattering angles from 2° to 68° were obtained at temperatures above and below the magnetic phase transition temperature $T_M \simeq 0.7$ K. Structure factors obtained from the nuclear peak intensities measured by neutron diffraction at a temperature above T_M are consistent with those calculated on the basis of the tetragonal structure of $TmRh_4B_4$ reported by Vandenberg and Matthias,[2] in which the magnetic Tm^{3+} ions occupy the corner and body-centered tetragonal positions with $a=5.287$ Å and $c=7.359$ Å. Figure 1 shows diffraction data at $T=0.75$ and 0.07 K over the angular range where magnetic peaks were observed.

The new peaks which appear below T_M cannot all be indexed in terms of the chemical cell or any simple enlarged cell, thereby ruling out a simple ferromagnetic or antiferromagnetic arrangement. However, all of the new peaks can be accounted for as satellites about the (001), (100), (111), and (102) positions. In Fig. 1 (and also Fig. 2 and Table I), δ is used to label the satellites where $\delta=0.163$ in units of $2\pi/a$ and $2\pi/c$, respectively. The *absence* of a single satellite about (010) at a scattering angle of approximately 27.47° is evidence that the Tm^{3+} moments are aligned along the [010] direction. The measured positions and intensities of the satellites are consistent with a body-centered tetragonal, antiferromagnetic sublattice of Tm^{3+} moments which are sinusoidally modulated along the [101] direction with a modulation wave vector of magnitude $|\vec{q}_M|=0.238$ Å^{-1}.

The maximum amplitude of the magnetic moment at saturation was determined to be 6.6 ± 1.0 Bohr magnetons (μ_B), whereas the free-ion value is $7.57\mu_B$. The temperature dependence of the intensities of three representative satellites is plotted in Fig. 2. Table I compares the observed integrated intensities to those calculated on the basis of the model for the magnetic structure proposed above. The theoretical and measured integrated intensities are in good agreement except for some of the weaker peaks at higher scattering angles where the uncertainty is relatively large. It should be noted that within experimental error $|\vec{q}_M|$ is one-sixth the length of the (1,0,1) reciprocal-lattice vector. Although no higher-order harmonics were observed, the accuracy of the present data is not sufficient to completely eliminate the possibility of their existence. The existence of a small ferromagnetic component ($\lesssim 0.7\mu_B$) also cannot be precluded on the basis of the present data.

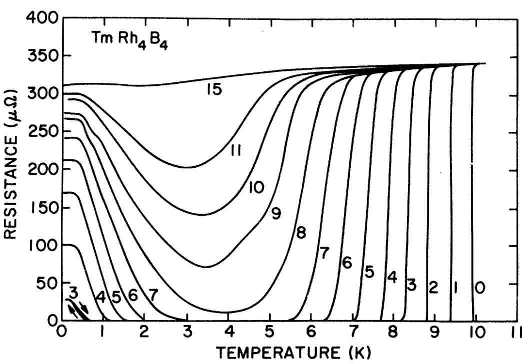

FIG. 3. ac electrical resistance vs temperature for $TmRh_4B_4$ in various applied magnetic fields between 0 and 15 kOe (after Hamaker *et al.*, Ref. 8).

IV. DISCUSSION

As stated in the Introduction, a number of the physical properties of $TmRh_4B_4$ and the reentrant ferromagnet $ErRh_4B_4$ are strikingly similar. Hamaker *et al.*[8] measured the zero-field linear thermal expansion coefficient α as a function of temperature and observed a negative anomaly at 0.4 K. Because applied magnetic fields greatly enhance this anomaly,[11] an association with the long-range ordering of the Tm^{3+} magnetic moments is suggested. Furthermore, ferromagnets tend to have much smaller α anomalies than antiferromagnets.[16] The anomaly in $TmRh_4B_4$ is comparable to that of $ErRh_4B_4$ (Ref. 9) and significantly less than those reported for other metallic rare-earth compounds which order antiferromagnetically in this temperature range.[17,18] Small magnetic fields also influence the temperature dependence of the thermal conductivity as measured by Hamaker *et al.*[8] In a 1-kOe external magnetic field a hysteretic transition having a reentrant characteristic similar to that found at the ferromagnetic transition of $ErRh_4B_4$ (Refs. 10 and 19) was observed. Low-field magnetization experiments have further demonstrated that in applied fields $TmRh_4B_4$ (Ref. 20) and $ErRh_4B_4$ behave similarly.[9] Finally, consider the ac electrical resistance versus temperature for $TmRh_4B_4$ in various applied

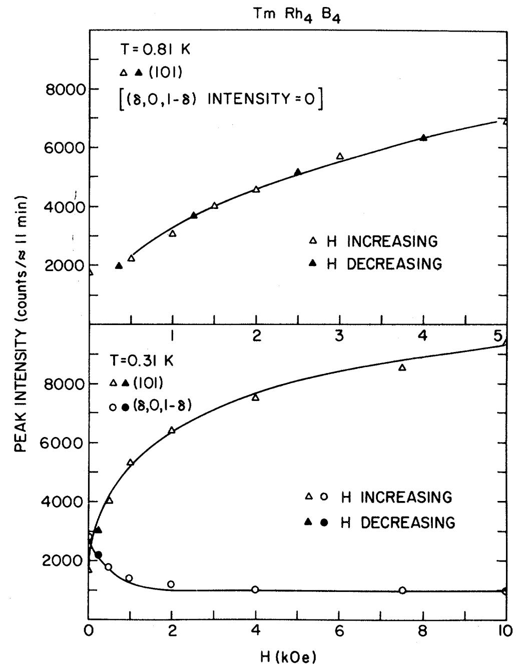

FIG. 4. Peak intensity of the (101) reflection as a function of applied magnetic field, at temperatures above and below the Néel temperature, showing the growth of an induced ferromagnetic component. Also shown is the corresponding decrease in the intensity of the antiferromagnetic reflection $(\delta,0,1-\delta)$ below T_M. Background intensity has not been subtracted.

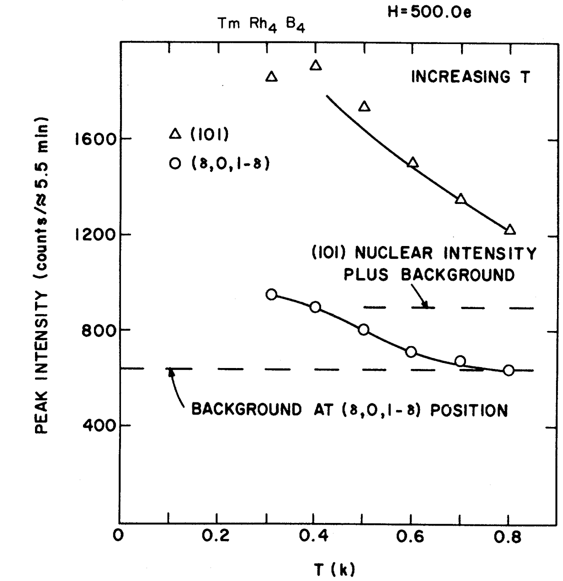

FIG. 5. Temperature dependence of the peak intensities of the (101) and $(\delta,0,1-\delta)$ reflections for $H=500$ Oe.

magnetic fields as shown in Fig. 3 (after Hamaker *et al.*[8]). For $H\leq 2$ kOe, the data reveal a single normal-to-superconducting state transition, but for $H\geq 3$ kOe, reentrant superconductivity occurs. This reentrant behavior in an applied field is similar to that of $ErRh_4B_4$ in zero applied field.[4,9] In view of the ferromagnetic behavior in applied fields and the comparatively small linear thermal expansion anomaly, it might be expected that superconductivity and long-range ferromagnetic order coexist in $TmRh_4B_4$. Hamaker *et al.*[8,11] have conjectured that although superconductivity coexists with antiferromagnetism in zero applied field, as shown by the present neutron-diffraction data, applied magnetic fields might induce a metamagnetic transition from antiferromagnetism to ferromagnetism which is complete by $H\simeq 3$ kOe.

Figures 4 and 5 show preliminary neutron-diffraction data for $TmRh_4B_4$ in applied magnetic fields. It is observed that a ferromagnetic component can be induced at field strengths for which electrical resistivity is still zero. However, thermal-conductivity data[8,11] indicate that normal regions also exist. Induced ferromagnetic components have also been observed in $Dy_{1.2}Mo_6S_8$ and $Tb_{1.2}Mo_6S_8$.[21,22] Higher instrumental resolution is required, however, to determine whether the coherence length of an antiferromagnetic domain is affected by the induced ferromagnetic moment. It has not yet been proven whether normal domains possessing a net ferromagnetic moment coexist with separate, superconducting antiferromagnetic domains or, for temperatures above T_M, with separate, nonmagnetic superconducting regions. Higher resolution and small-angle scattering experiments are being planned in order to resolve these questions.

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[1] B. T. Matthias, E. Corenzwit, J. M. Vandenberg, and H. E. Barz, Proc. Natl. Acad. Sci. USA 74, 1334 (1977).
[2] J. M. Vandenberg and B. T. Matthias, Proc. Natl. Acad. Sci. USA 74, 1336 (1977).
[3] M.P. Maple, in *Ternary Superconductors,* edited by G. K. Shenoy, B. D. Dunlap, and F. Y. Fradin (North-Holland, New York, 1981), pp. 131–139.
[4] 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).
[5] D. E. Moncton, D. B. McWhan, J. Eckert, G. Shirane, and W. Thomlinson, Phys. Rev. Lett. 19, 1164 (1977).
[6] D. E. Moncton, D. B. McWhan, P. H. Schmidt, G. Shirane, W. Thomlinson, M. B. Maple, H. B. MacKay, L. D. Woolf, Z. Fisk, and D. C. Johnston, Phys. Rev. Lett. 45, 2060 (1980).
[7] S. K. Sinha, G. W. Crabtree, D. G. Hinks, and H. A. Mook, Phys. Rev. Lett. 48, 950 (1982).
[8] H. C. Hamaker, H. B. MacKay, L. D. Woolf, M. B. Maple, W. Odoni, and H. R. Ott, Phys. Lett. 81A, 91 (1981).
[9] H. R. Ott, W. A. Fertig, D. C. Johnston, M. B. Maple, and B. T. Matthias, J. Low Temp. Phys. 33, 159 (1978).
[10] W. Odoni and H. R. Ott, Phys. Lett. 70A, 480 (1979).
[11] H. C. Hamaker, H. B. MacKay, M. S. Torikachvili, L. D. Woolf, M. B. Maple, W. Odoni, and H. R. Ott, J. Low Temp. Phys. 44, 553 (1981).
[12] H. C. Hamaker, L. D. Woolf, H. B. MacKay, Z. Fisk, and M. B. Maple, Solid State Commun. 31, 139 (1979).
[13] C. F. Majkrzak, D. E. Cox, G. Shirane, H. A. Mook, H. C. Hamaker, H. B. MacKay, Z. Fisk, and M. B. Maple, Phys. Rev. B 26, 245 (1982).
[14] H. A. Mook, W. C. Koehler, M. B. Maple, Z. Fisk, D. C. Johnston, and L. D. Woolf, Phys. Rev. B 25, 372 (1982).
[15] M. Blume, A. J. Freeman, and R. E. Watson, J. Chem. Phys. 37, 1245 (1962).
[16] K. P. Belov, *Magnetic Transitions* (Consultants Bureau, New York, 1961), p. 135.
[17] H. R. Ott and B. Lüthi, Z. Phys. B 28, 141 (1977).
[18] M. E. Muller, B. Lüthi, P. S. Wang, E. Bucher, L. D. Longinotti, J. P. Maita, and H. R. Ott, Phys. Rev. B 10, 186 (1974).
[19] H. R. Ott and W. Odoni, in *Superconductivity in d- and f-Band Metals,* edited by H. Suhl and M. B. Maple (Academic, New York, 1980), pp. 403–408.
[20] H. R. Ott, H. Rudigier, H. C. Hamaker, and M. B. Maple, in *Ternary Superconductors,* edited by G. K. Shenoy, B. D. Dunlap, and F. Y. Fradin (North-Holland, New York, 1981), pp. 159–162.
[21] W. Thomlinson, G. Shirane, D. E. Moncton, M. Ishikawa, and Ø. Fischer, J. Appl. Phys. 50, 1981 (1979).
[22] M. Ishikawa and J. Muller, Solid State Commun. 27, 761 (1978).