Neutron-diffraction study of the magnetic superconductors $Dy(Ru_xRh_{1-x})_4B_4$

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Powder neutron-diffraction measurements have been performed for several concentrations on the system $Dy(Ru_xRh_{1-x})_4B_4$, which displays varied and interesting types of magnetic and superconducting behavior. For the concentration $x=0.15$, acollinear antiferromagnetic order with a peculiar temperature dependence of order parameters, including pronounced thermal hysteresis, coexists with the superconducting state. The nonsuperconducting $x=1.00$ compound also develops long-range magnetic order, but with a ferromagnetic as well as an antiferromagnetic component. The diffraction pattern corresponding to a concentration $x=0.60$, however, shows no long-range magnetic order for $T>0.3$ K, but rather the development of a broad peak suggesting the onset of some short-range magnetic correlation.

I. INTRODUCTION

The interaction of superconductivity and magnetic order has been a subject of intense study in recent years. Two groups of ternary rare-earth (R) compounds, RMo_6X_8 (X=S,Se) and RRh_4B_4, have been investigated extensively by a variety of experimental techniques.[1–5]

The logical extension of these studies involves the partial substitution of a second rare-earth or transition-metal element. This often results in a wide variety of superconducting and magnetic behavior as a function of substitution concentration. These pseudoternary compounds are, therefore, important for the study of the interaction of magnetism and superconductivity. A number of interesting studies have already been done on systems such as $(Ho_xEr_{1-x})Rh_4B_4$,[6] $Ho(Rh_xIr_{1-x})_4B_4$,[7,8] $R(Ru_{0.15}Rh_{0.85})_4B_4$,[9] and $Dy(Ru_xRh_{1-x})_4B_4$.[10,11]

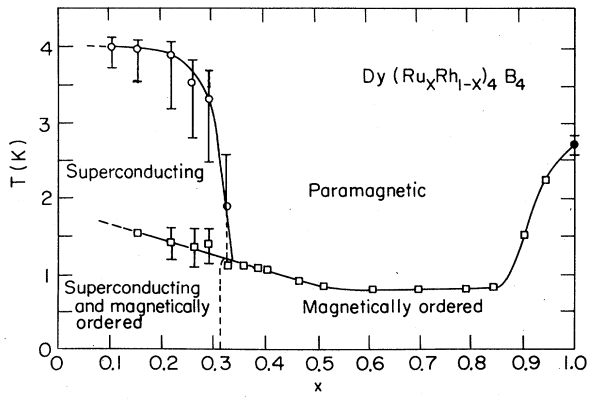


FIG. 1. Low-temperature phase diagram for $Dy(Ru_xRh_{1-x})_4B_4$ determined from ac magnetic susceptibility and heat-capacity measurements (Refs. 10 and 11).

In the case of $Dy(Ru_xRh_{1-x})_4B_4$, the bulk magnetic and superconducting properties have been studied by means of ac magnetic susceptibility, magnetization, heat capacity, and other measurements, resulting in the determination of the low-temperature phase diagram (Fig. 1).[10,11] According to the above work, superconductivity occurs for $x \lesssim 0.35$, whereas long-range magnetic order exists over the entire range of concentration x. Furthermore, a change in the magnetic order from ferromagnetism for $x=1.00$ to antiferromagnetism for $x \lesssim 0.5$ has been indicated. We have performed powder neutron-diffraction measurements for the concentrations $x=0.15$, 0.30, 0.60, and 1.00 in order to obtain microscopic information about the magnetic structure.

II. EXPERIMENTAL DETAILS

The pseudoternary compounds were made by arc melting the appropriate ratio of $DyRh_4B_4$ and $DyRu_4B_4$, where each ternary compound had been previously synthesized by arc melting of the high-purity transition-metal element and single crystals of DyB_4, followed by heat treatments as described in Ref. 10. The isotope ^{11}B was used in order to avoid the high-absorption cross section for slow neutrons of natural boron. The small amounts of impurity phases detected in the neutron-diffraction patterns were of no consequence to the subsequent study of the magnetic structure of the primary phase. For the neutron-scattering experiment, the samples were ground into a fine powder and placed in a flat aluminum container mounted in a pumped liquid-^{3}He cryostat. For all x, the sample thickness was chosen to be 1 mm, which results in a neutron transmission of the order of 0.2. Sample temperature was controlled to within 0.005 K in the range $0.34\ \text{K} \leq T \leq 1.5$ K, and to within 0.05 K in the range $1.5\ \text{K} \leq T \leq 3.5$ K.

The neutron-diffraction measurements were performed at the Brookhaven High Flux Beam Reactor on a triple-axis spectrometer in the elastic scattering mode with a pyrolytic graphite monochromator, analyzer, and filter (to remove higher-order contamination). The incident wave vector was 2.635 Å^{-1} and the horizontal beam collimation 20'-40'-40'-60' unless specifically noted otherwise. The crystal structure of $Dy(Ru_xRh_{1-x})_4B_4$ pseudoternary compounds was determined by Johnston[9] to belong to the space group $P4_{2/nmc}$, with a c/a ratio for a body-centered-tetragonal Bravais lattice very close to 2.

III. EXPERIMENTAL RESULTS

A. $DyRu_4B_4$

Diffraction patterns for scattering angles $2.0° \leq 2\theta \leq 70.0°$ were taken at temperatures of 0.34 and 5.0 K. Major parts of the diffraction pattern are shown in Fig. 2. Positions and relative intensities of the observed peaks at 5.0 K fit the calculated nuclear-diffraction pattern based on the crystal structure cited in the preceding section.[9]

At 0.34 K, additional peaks appear which indicate the presence of long-range magnetic order. All of the new peaks can be indexed in terms of the chemical unit cell (except for several weak peaks identified as impurities). The widths of the peaks are instrument limited, thereby placing a lower limit of 200 Å on the range of coherence. The magnetic peaks are found to belong to one of two groups; one group of peaks having positions coincident with those of nuclear peaks, and another group having positions where no nuclear peaks occur. This observation excludes a simple ferromagnetic model.

We assumed, therefore, a magnetic structure with a ferromagnetic and an antiferromagnetic component. All of the possible simple collinear antiferromagnetic structures with the same unit cell as the chemical one (which are illustrated in the upper part of Fig. 5) were tried. A calculation based on a model having the antiferromagnetic structure of E with the spin direction perpendicular to the c axis in addition to a ferromagnetic component gives the best agreement with observation. In the calculation, the magnetic form factor of the Dy^{3+} ion as obtained by the

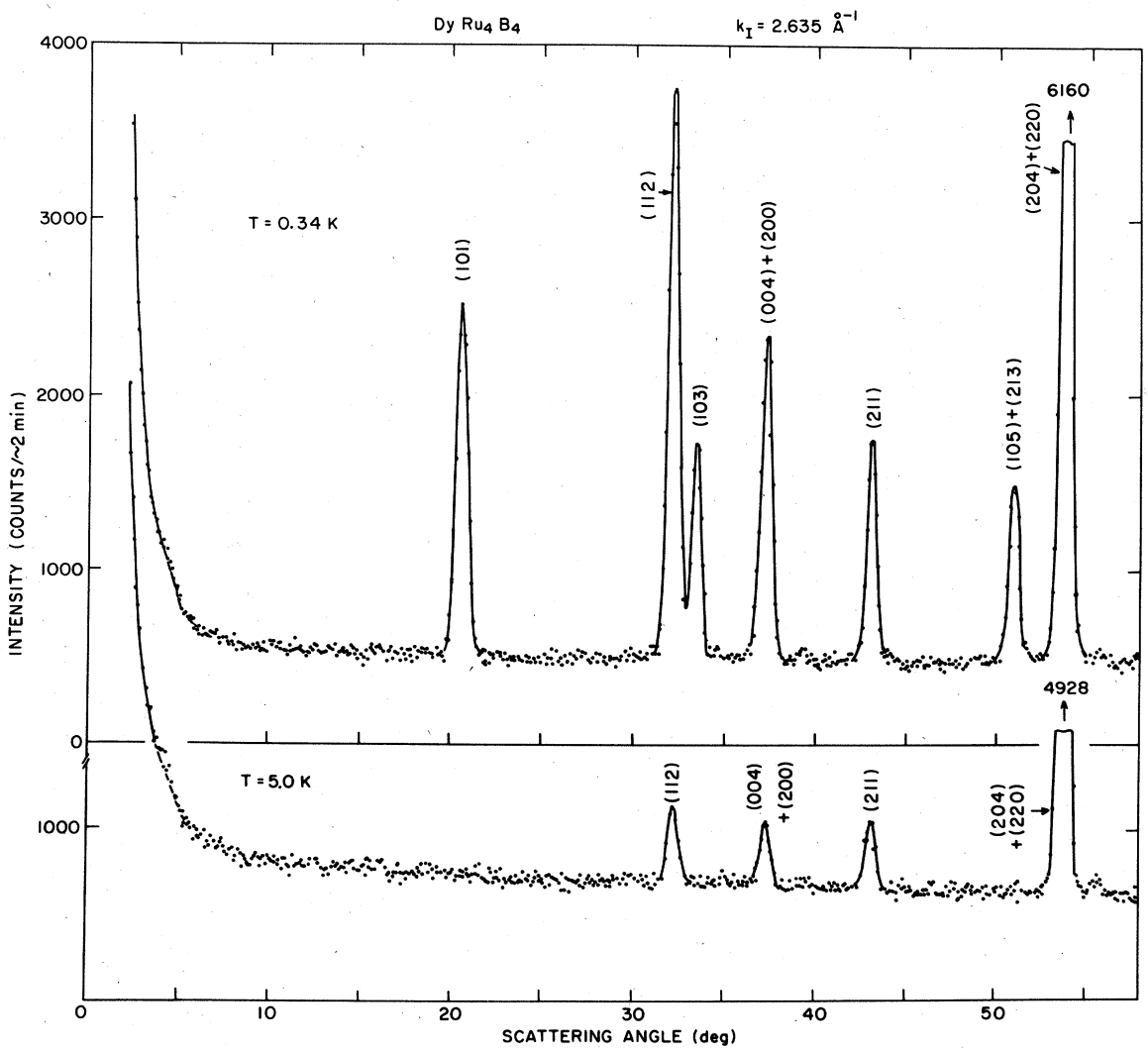


FIG. 2. Neutron-diffraction patterns of $DyRu_4B_4$ at 0.34 and 5.0 K.

TABLE I. Comparison of the observed and calculated peak positions 2θ and integrated intensities I corresponding to the magnetic structure model described in the text for $DyRu_4B_4$. AF and F designate whether the peaks are antiferromagnetic or ferromagnetic, respectively.

		$DyRu_4B_4$			
hkl	$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I_{obs}	I_{calc}	Component
101	20.65	20.61	75±3	78.3	AF
112	32.2	32.14	100±4	113.0	F
103	33.45	33.39	43±3	38.3	AF
004,200	37.3	37.06,37.40	56±4	60.4	F
211	43.05	43.08	28±4	26.0	AF
105,213	50.95	50.73,50.99	35±3	36.4	AF
204,220	53.75	53.67,53.92	49±4	47.9	F
301	58.3	58.34	5±3	5.9	AF
116,312	64.05	63.73,64.18	86±5	77.2	F
215,303		64.70,64.92			AF
224	67.2	67.24	19±4	16.9	F
		$k_i=2.635$ Å^{-1}, $a=7.4390$ Å, $c=15.008$ Å			
		$\mu_F=5.9\mu_B$, $\mu_{AF}=4.5\mu_B$,			

Hartree-Fock calculation[12] was used.

Since the c/a ratio is very close to 2, a tetragonal unit cell becomes nearly cubic. Therefore, the direction of the spins of the ferromagnetic component cannot be determined from the powder diffraction data alone.[13] However, we have already determined the antiferromagnetic component to be perpendicular to the c axis. If the constraint that the set of different magnitudes of the ferromagnetic component, antiferromagnetic component, and net moment of a given atom be identical for all atoms is imposed, then it follows that the ferromagnetic component must be parallel to the c axis.

In Table I, a comparison of the observed and calculated peak positions and integrated intensities is given. Figure 3 shows the temperature variation of intensities for the (101) peak (ferromagnetic component) and for the (112) peak (antiferromagnetic component). The behaviors of both peaks are similar and the critical temperature agrees with the one obtained from bulk measurements.[9–11]

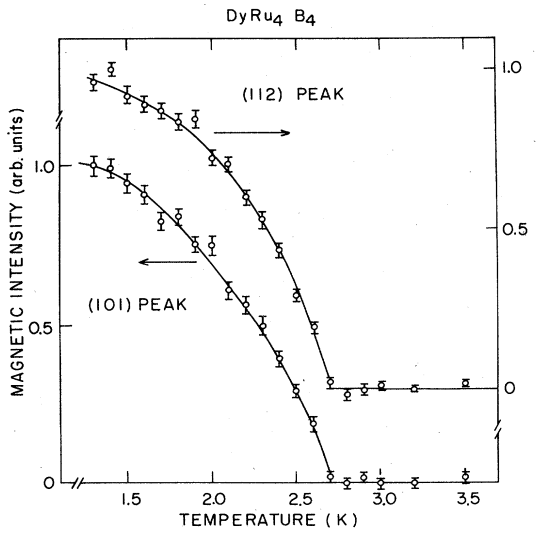


FIG. 3. Temperature dependence of the magnetic scattering intensities for the (101) peak (antiferromagnetic component) and (112) peak (ferromagnetic component) of $DyRu_4B_4$.

B. $Dy(Ru_{0.15}Rh_{0.85})_4B_4$

Diffraction patterns for scattering angles $2.0° \leq 2\theta \leq 70.0°$ were obtained at temperatures of 0.34 and 3.0 K with the standard beam collimation (20′-40′-40′-60′). The lower angles were also scanned with finer collimation (20′-10′-10′-60′) at temperatures of 0.45 and 12 K. The pertinent parts of these diffraction patterns are shown in Fig. 4. The patterns at 3.0 K agree with the calculated nuclear-diffraction pattern as in the case of $DyRu_4B_4$. Additional peaks in the diffraction patterns at low temperatures consist of a group of peaks which can be indexed in terms of the chemical unit cell except for the three peaks appearing at $2\theta=2.9°$, 7.10°, and 11.10°. The intensities of the nuclear peaks show no change between 0.34 and 3.0 K within experimental accuracy, which indicates the absence of a ferromagnetic component.

Assuming that the three unindexed peaks are due to a modulated structure, we first tried to find a basic magnetic structure which accounts for all the observed indexed peaks. Since any collinear antiferromagnetic structures in the framework of the chemical unit cell could not account for the observed diffraction pattern, acollinear models were examined in the following way. An acollinear structure was composed of two or three collinear antiferromagnetic structures in which the spin direction corresponding to each component structure is orthogonal to that of each of the other component structures. After trying all possible combinations of the component structures illustrated in the upper part of Fig. 5, the best agreement with the observed pattern was found to be obtained from a combination of structures *A*, *C*, and *E*, the amplitude and direction of each component as illustrated in Fig. 5. In Fig. 5 the composite structure is also shown, while a comparison of the observed and calculated peak positions and

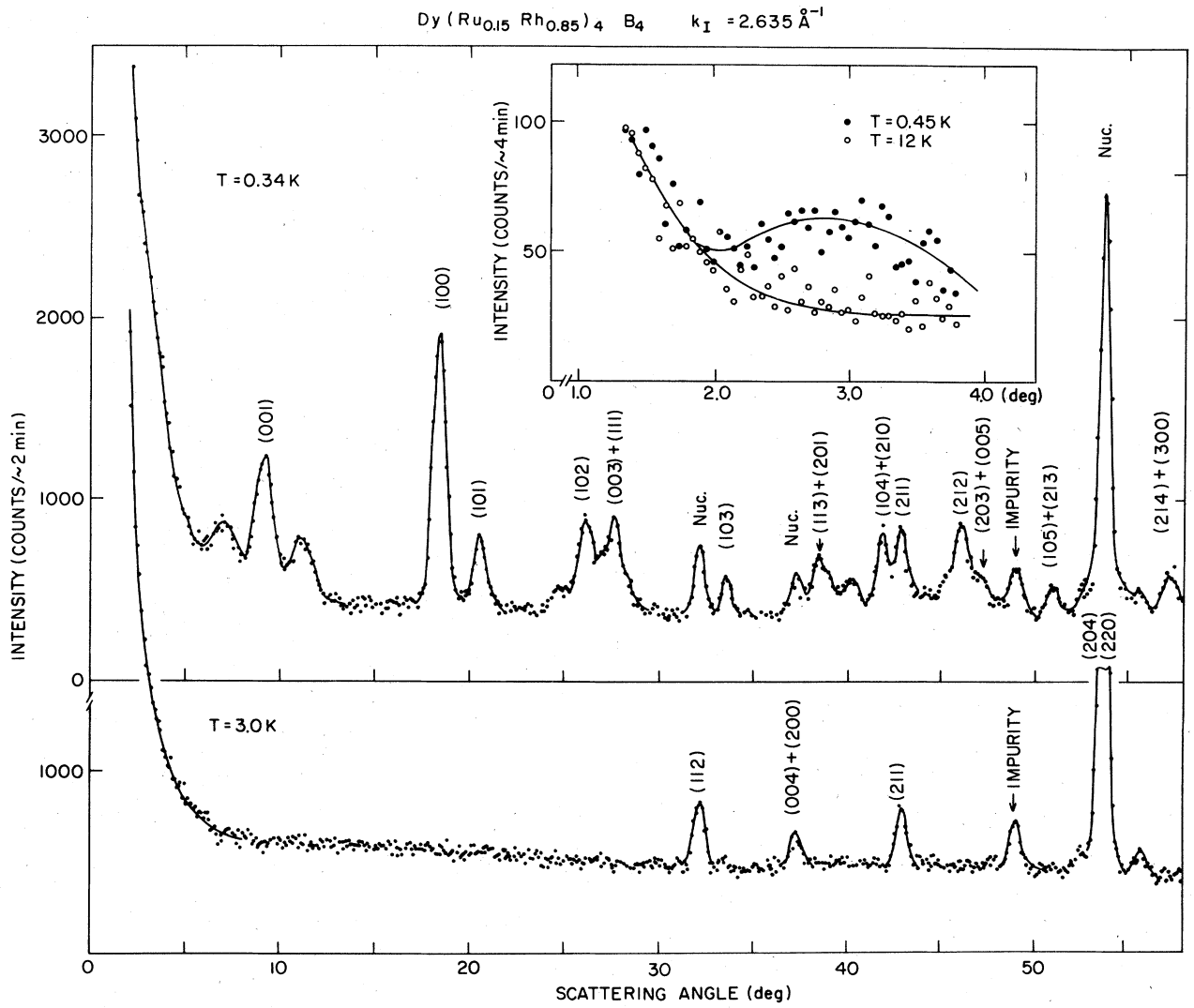


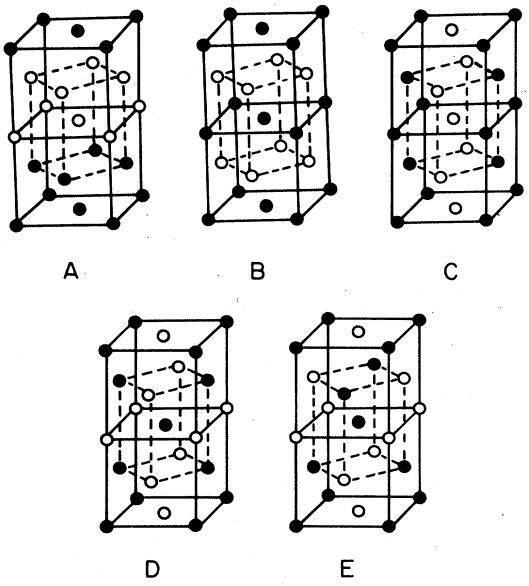
FIG. 4. Neutron-diffraction patterns of $Dy(Ru_{0.15}Rh_{0.85})_4B_4$ at 0.34 and 3.0 K. A higher resolution scan at lower angles is shown in the inset.

intensities is given in Table II (in which an assignment of each peak to a component structure is also given).

The amplitude of the modulation wave vector calculated from the low-angle peaks is $|\vec{q}_M| = 0.133$ Å^{-1}. A structure in which one basic antiferromagnetic component A is modulated along a direction parallel to either the [102] or [012] direction gives satellites about the (001) peak at positions $2\theta = 7.36°$ and 11.36° which are close to the observed peak positions. A modulation of the A component should also give rise to satellites about other indexed peaks. However, the presence of other satellites, because of low intensities and/or poor resolution, was not observed. The temperature dependence of peak intensity was measured for three kinds of peaks, each representing one of the three component structures described above. Figure 6 shows the normalized magnetic peak intensities as a function of temperature where a correction for the temperature-dependent background level was made. Behavior quite different than that of $DyRu_4B_4$ is observed; the intensities of (001) and (100) peaks undergo a discontinuous change near 1.3 K and exhibit pronounced thermal hysteresis below that temperature. However, the intensity of the (101) peak shows no such discontinuity nor appreciable thermal hysteresis.

C. $Dy(Ru_{0.30}Rh_{0.70})_4B_4$

The diffraction pattern for $x = 0.3$ is essentially the same as that for $Dy(Ru_{0.15}Rh_{0.85})_4B_4$, except for the absence of a low-angle satellite about the (001) peak position. A possible reason for the absence of one satellite is a change in the modulation direction to [100] (or one of the directions perpendicular to [001]). Figure 7 shows the temperature variation of the magnetic peak intensities. In this compound, discontinuous changes in intensity for the (001) and (100) peaks were also observed, as in the case of $Dy(Ru_{0.15}Rh_{0.85})_4B_4$. However, no thermal hysteresis was detected within the experimental uncertainty.



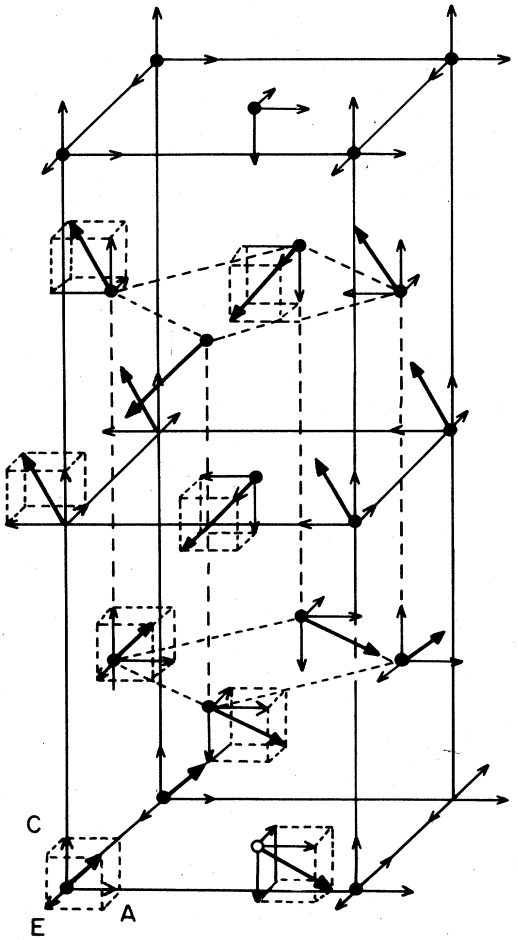


FIG. 5. A proposed antiferromagnetic structure for $Dy(Ru_{0.15}Rh_{0.85})_4B_4$. Fine arrows show individual component spins while bold arrows show composite spins. The component collinear antiferromagnetic structures mentioned in the text are shown in the upper part of the figure where open and solid circles correspond to spin up and spin down, respectively.

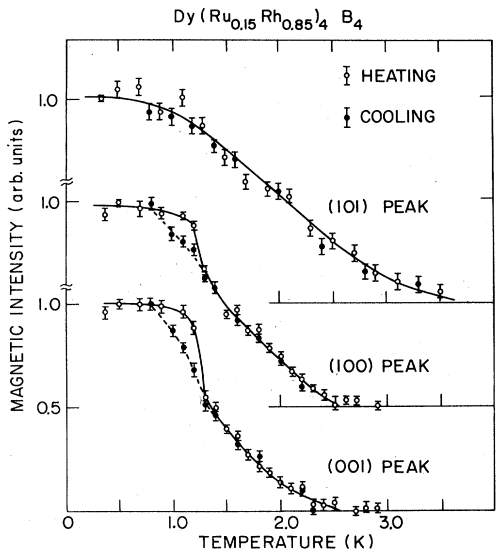


FIG. 6. Temperature dependence of peak intensities for $Dy(Ru_{0.15}Rh_{0.85})_4B_4$. Corrections for the temperature-dependent background have been made.

D. $Dy(Ru_{0.6}Rh_{0.4})_4B_4$

Diffraction patterns above and below the predicted magnetic transition temperature of 0.8 K are shown in Fig. 8. No new Bragg peaks nor additional intensity at nuclear peak positions appeared at 0.34 K, although a very broad peak was observed in the range of $6° \lesssim 2\theta \lesssim 30°$.

IV. DISCUSSION

The present neutron-diffraction experiment has resolved the microscopic magnetic structures of several

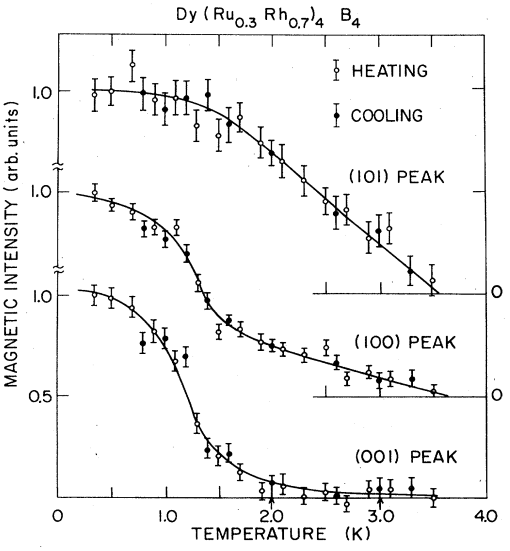


FIG. 7. Temperature dependence of peak intensities for $Dy(Ru_{0.30}Rh_{0.70})_4B_4$. Corrections for the temperature-dependent background have been made.

TABLE II. Comparison of the observed and calculated peak positions 2θ and integrated intensities I for $Dy(Ru_{0.15}Rh_{0.85})_4B_4$. Calculations were based on the structural model described in the text. A, C, and E denote the collinear antiferromagnetic structural component (illustrated in the upper part of Fig. 5) with which a given peak is associated.

		$Dy(Ru_{0.15}Rh_{0.85})_4B_4$			
hkl	$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	I_{obs}	I_{calc}	Component
001	9.1	9.12	164±31[a]	166.6	A
100	18.4	18.41	100± 4	100.0	C
101	20.5	20.59	26± 4	29.4	E
102	26.1	26.08	46± 3	47.2	C
003,111	27.7	27.61,27.75	52± 5	52.0	A
103	33.55	33.39	14± 3	13.9	E
113,201	38.5	38.40,38.50	41± 6	38.7	A
104,210	41.9	41.72,41.93	34± 3	37.4	C
211	42.8	43.00	23± 4	9.5	E
212	46.1	46.10	63±11	40.6	C
005,203	47.0	46.87,47.05	9± 5	16.8	A
105,213	51.0	50.77,50.94	15± 3	12.7	E
115,221		54.46,54.71	b	17.3	A
214,300	57.2	57.21,57.37	26± 4	21.6	C
301	58.3	58.23	8± 8	2.1	E
106,302		60.44,60.75	b	13.0	C
205,223,311		61.39,61.54,61.62	c	21.1	A
215,303	64.0	64.68,64.83	23± 8	6.2	E
007,313		67.67,68.03	b	9.0	A
		$k_i=2.635$ Å^{-1}, $a=7.4530$ Å, $c=14.9920$ Å			
		$\mu_A=4.30\mu_B$, $\mu_C=4.86\mu_B$, $\mu_E=2.70\mu_B$			

[a]Including satellites.
[b]Cannot be obtained because of insufficient instrumental resolution.
[c]Cannot be obtained due to the presence of Al peak from the sample container.

concentrations of the $Dy(Ru_xRh_{1-x})_4B_4$ system. The compound $DyRu_4B_4$, which was classified as a ferromagnet on the basis of bulk measurements, has been shown to possess a magnetic structure with an antiferromagnetic component as well as a ferromagnetic one.

In $Dy(Ru_{0.15}Rh_{0.85})_4B_4$ and $Dy(Ru_{0.30}Rh_{0.70})_4B_4$, acollinear antiferromagnetic structures with a long period modulated component coexist with superconductivity. The peculiar temperature dependence of the magnetic order parameters observed in this acollinear antiferromagnetic phase suggests that the interaction between each basic antiferromagnetic structure might be rather weak. At low temperature, order parameters for the structure E and structures A and C behave almost independently, as if they possessed individual, hypothetical transition temperatures. Between these two hypothetical transition temperatures, the order of one structural component is sustained by interaction with the other. However, the magnitude of the interaction is not sufficient to maintain order all the way up to the transition temperature of the latter component. A sharp peak in the specific-heat curve, from which the magnetic transition temperatures in Fig. 1 were determined, appears to correspond to a sudden change of order parameter. However, the magnetic transition temperature obtained in the present study of this antiferromagnetic phase is actually higher than that determined from the bulk measurements.

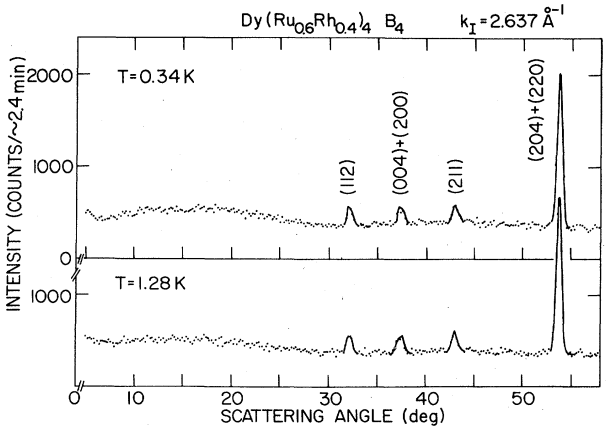


FIG. 8. Neutron-diffraction patterns of $Dy(Ru_{0.60}Rh_{0.40})_4B_4$ at 0.34 and 1.28 K.

As stated in the Introduction, superconductivity coexists with the antiferromagnetic order which occurs in the Rh-rich compounds, but the nature of the interaction between the two phenomena is quite complex. The T_c versus x behavior shown in Fig. 1 is virtually identical to that for the nonmagnetic, isostructural $Y(Ru_xRh_{1-x})_4B_4$ system,[9,14,15] which suggests that the superconductivity and magnetism in the $Dy(Ru_xRh_{1-x})_4B_4$ compounds are only weakly coupled. At the same time, other transport property measurements have indicated that the magnetic order can strongly influence the superconductivity. In particular, an enhancement of the upper critical magnetic

field below ≈ 2 K (Ref. 11) appears to correspond to the change in the antiferromagnetic order parameter. Also, it has been noted elsewhere that for $x \approx 0.33$, reentrant superconductivity occurs,[10,16] presumably due to the antiferromagnetic ordering as indicated by this study. In contrast, there is no clear evidence that the superconductivity has any discernible effect upon the nature of the magnetic order in these compounds.

In the $Dy(Ru_{0.6}Rh_{0.4})_4B_4$, sample, no long-range magnetic ordering of the Dy^{3+} moments occurs. However, the broad peak in the neutron-diffraction data coupled with the ac magnetic susceptibility studies by Hamaker and Maple[10] indicate that some spin-glass-like behavior is observed for intermediate values of x. Since in this region superconducting effects are apparently unimportant, the absence of long-range order is most likely the result of the competing antiferromagnetic and ferromagnetic exchanges. Such behavior has been predicted theoretically by Harris *et al.*,[17] Chen and Lubensky,[18] and Fishman and Aharony.[19] Referring to Fig. 1, the region from $0.5 < x < 0.85$, which exhibits frustrated spin-glass order, separates the antiferromagnetic and ferromagnetic regions at the Rh- and Ru-rich ends, respectively. The $Dy(Ru_xRh_{1-x})_4B_4$ system apparently is the first experimentally observed frustrated system of this kind.

Finally we note that the magnitudes of the ordered magnetic moments observed in $DyRu_4B_4$ and $Dy(Ru_{0.15}Rh_{0.85})_4B_4$ are much smaller than those which would be expected given that the free-ion moment for Dy^{3+} is $10.6\mu_B$. This suggests that crystal-field effects are important in these compounds as has been shown for similar materials.[6,20]

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