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Time-dependent magnetic structures of the superconducting mixed ternary system $Ho(Rh_{1-x}Ir_x)_4B_4$

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Magnetic structures have been determined by netron diffraction for several compositions in the superconducting mixed ternary system $Ho(Rh_{1-x}Ir_x)_4B_4$. Two features previously reported to occur in the heat capacity for some compositions are shown to correspond to successive magnetic transitions. For $x=0.30$ and 0.45, neutron diffraction peaks for the lowest temperature structure develop over a timescale of many hours. The results are discussed in terms of magnetic frustration.

INTRODUCTION

The interaction of superconductivity with long-range magnetic order has been the subject of considerable research. Most of this work has concentrated on ternary rare earth (R) compounds such as RRh_4B_4 and RMo_6S_8,[1] in which both superconductivity and long-range magnetic ordering of the R^{3+} ions can occur. Studies of such compounds have revealed many interesting phenomena, including the destruction of superconductivity by long-range ferromagnetic order and the coexistence of superconductivity with long-range antiferromagnetic order.[1] Additional insight has come from work with mixed ternary systems formed by alloying two related compounds. In this way the critical temperatures for superconductivity and magnetic order can be varied considerably. New phenomena revealed in such experiments include transitions from ferromagnetic to antiferromagnetic order, suppression of ferromagnetic order by superconductivity, and competition between different magnetic anisotropies.[1] We present here the most recent results of a continuing investigation of the mixed ternary system $Ho(Rh_{1-x}Ir_x)_4B_4$.

The first investigations of the $Ho(Rh_{1-x}Ir_x)_4B_4$ system[2] established a phase diagram similar to the one shown in Fig. 1, although no magnetic order was reported for $0.2 \lesssim x \lesssim 0.6$. The most striking aspect of this system was the occurrence of antiferromagnetic order at a temperature higher than the superconducting transition temperature for $x > 0.6$, the first materials reported to show this behavior.[2,3] Subsequent work[4] determined the dependence of the magnetic ordering temperature on x through extensive heat capacity experiments. Of special interest was the observation of two distinct magnetic transitions for $0.275 \leq x \leq 0.35$. Neutron diffraction measurements revealed ferromagnetic order for $x=0$ (Refs. 5 and 6) and $x=0.15$ (Ref. 4), while an antiferromagnetic structure was found for $x=0.70$ (Ref. 7). The objective of this investigation was to determine the magnetic structure for two intermediate compositions, $x=0.30$ and 0.45. It was observed in the course of these experiments that the shape of the neutron diffraction peaks corresponding to the low temperature structure was time dependent. Scans at fixed temperature showed that the peaks became larger and more narrow over a timescale of many hours. These changes were most pronounced after rapidly cooling through the magnetic transition temperature. Results of experiments to investigate this phenomenon will be presented after a discussion of the magnetic structures.

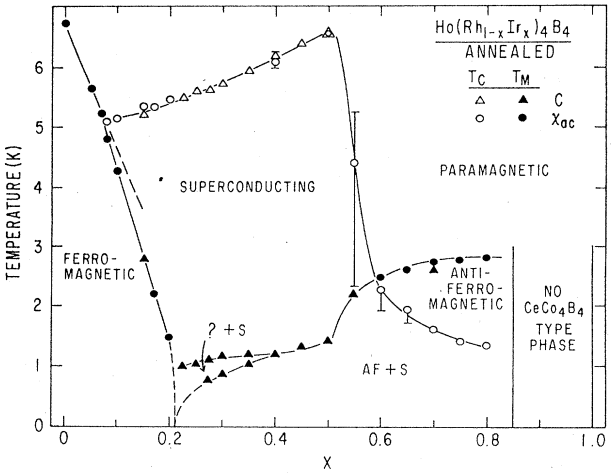

FIG. 1. Phase diagram of transition temperature vs composition x for $Ho(Rh_{1-x}Ir_x)_4B_4$. Data points were determined by measurements of ac magnetic susceptibility χ_{ac} (from Ref. 2) or heat capacity C (from Ref. 4). Regions labeled include superconductivity coexisting with antiferromagnetic order (AFM+S) or an unidentified spin structure (?+S).

EXPERIMENTAL DETAILS

The samples used in these experiments were prepared using stoichiometric quantities of the elements plus a 4% excess of boron by weight to suppress secondary phases.[8] Chunks of boron, isotopically enriched to 98.7% ^{11}B, were

used to reduce neutron absorption by ^{10}B. The elements were arc-melted on a water-cooled copper hearth in a Zr-gettered argon atmosphere, followed by annealing.[7] Heat capacity and ac magnetic susceptibility measurements at the University of California, San Diego (UCSD), yielded values for the critical temperatures in excellent agreement with previous work.[2,4] Measurements at Oak Ridge National Laboratory (ORNL) were performed on crushed samples (< No. 20 sieve) of mass ~ 4.5 g and volume ~ 0.5 cm^3 that had been loaded into a flat aluminum sample holder and cooled in a He^3 refrigerator. The temperature was determined from the dc electrical resistance of a calibrated germanium thermometer. Neutron diffraction measurements were performed using the HB2 triple-axis spectrometer at the High Flux Isotope Reactor at ORNL with an incident neutron wavelength $\lambda = 2.443$ Å. Starting at the monochromator, the neutron beam passed through a 40′ collimator, the sample, a pyrolytic graphite filter to remove higher-order wavelengths, and a second 40′ collimator. Elastically scattered neutrons were selected using a graphite analyzer crystal placed before the detector. Neutrons were counted against a neutron monitor to account for variations in reactor power. The instrumental resolution of the diffractometer was determined after these experiments from measurements at room temperature of a sample of ferrite which exhibited a diffraction peak at $\phi = 29.24°$ with a full width at half maximum (FWHM) of 0.647°. Assuming that we can observe broadening equal to one-half of our instrumental resolution, the minimum range of correlations for a resolution-limited peak can be estimated by $L = 2/\Delta q = 71$ Å, where $\Delta q = 2\pi \Delta\phi \cos(\phi/2)/\lambda$ is obtained by differentiating the Bragg law for diffraction and $\Delta\phi$ = FWHM.

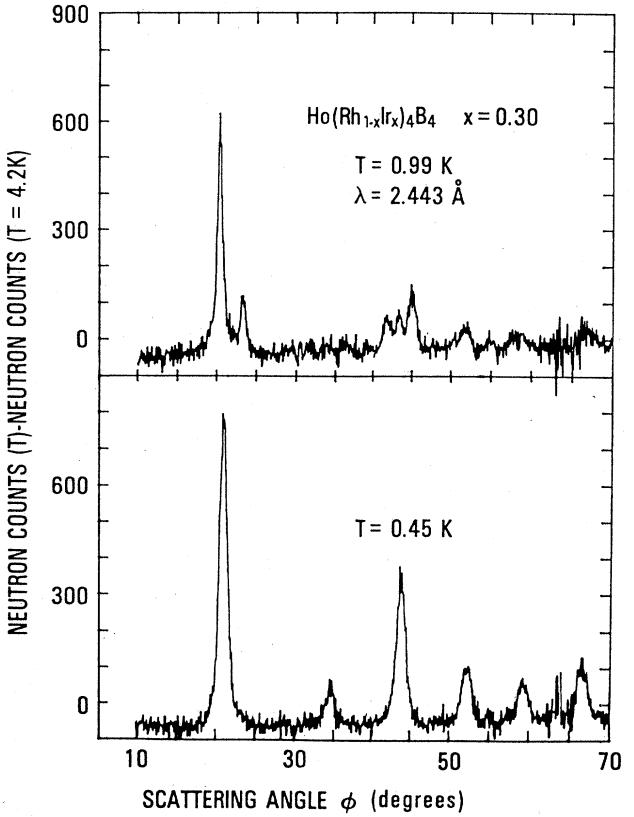

FIG. 2. Powder neutron diffraction patterns for $Ho(Rh_{1-x}Ir_x)_4B_4$ with $x = 0.30$. Neutron counts at 4.2 K have been subtracted, leaving only the magnetic peaks. The lower pattern for $T = 0.45$ K has been determined to correspond to an antiferromagnetic structure (Ref. 7). The spin arrangement yielding the upper pattern for $T = 0.99$ K has not been identified. The counting time for these data points was approximately 80 sec.

RESULTS

The phase diagram in Fig. 1 shows that a single magnetic transition was observed in heat capacity measurements of $Ho(Rh_{1-x}Ir_x)_4B_4$ with $x = 0.45$, while two distinct transitions were found for $x = 0.30$.[4] The neutron diffraction pattern from the magnetically ordered state for $x = 0.45$ and the low temperature state for $x = 0.30$ are very similar to that measured previously for $x = 0.70$.[7] The data for $x = 0.30$ are shown in Fig. 2 after subtracting background counts. The magnetic structure corresponding to this diffraction pattern was determined in Ref. 7 for $x = 0.70$ to consist of antiferromagnetic planes of Ho^{3+} ions stacked along the c axis, with the Ho magnetic moments directed along the c axis. A diagram of this structure is given in Ref. 7. A comparison of the intensities observed here with the expected intensities was made to confirm that the magnetic structure of the samples studied here ($x = 0.30$ and 0.45) is the same as that of the sample with $x = 0.70$ previously investigated. The observed intensity I_{obs} of each diffraction peak was determined from the area of a Gaussian fit to the data. The expected intensity I_{calc} was calculated as before.[7] The results are shown in Table I. Defining the discrepancy factor

$$R = \sum (I_{obs} - I_{calc})^2 \Big/ \sum I_{obs}^2 ,$$

we observe that $R \ll 1$, indicating that the same structure occurs at low temperature for $x = 0.30$, 0.45, and 0.70. This result is depicted in Fig. 1, where the appropriate areas of the phase diagram have been labeled as antiferromagnetic. Also given in Table I is the average magnetic moment per Ho^{3+} ion calculated from the intensities observed at $T = 0.45$ K for the (101) magnetic peak and the (101) nuclear peak. The observed moments are in good agreement with the free-ion value for Ho^{3+} of $10.0\mu_B$.

The diffraction pattern from the high temperature magnetic structure of $Ho(Rh_{1-x}Ir_x)_4B_4$ with $x = 0.30$ is also shown in Fig. 2. The integrated intensity of the largest magnetic peak is ~ 20 times greater than the intensity for nuclear peaks, indicating that these features are magnetic in origin and do not arise from a crystallographic transition. The line positions are different from those for the low-temperature diffraction pattern, and the two sets of peaks do not occur simultaneously at any temperature. Consequently, it can be concluded that two distinct magnetic structures of the same set of Ho^{3+} magnetic moments are found in different temperature ranges for this

TABLE I. Integrated intensities I_{obs} for magnetic diffraction peaks for $x=0.45$ and the low-temperature structure for $x=0.30$ in $Ho(Rh_{1-x}Ir_x)_4B_4$. Uncertainty in I_{obs} comes from uncertainty in the fit of a Gaussian plus a constant to the data used to determine the intensity. Also shown are intensities I_{calc} calculated as in Ref. 7, the discrepancy factor R given in the text, and μ, the average moment per Ho^{3+} ion determined at 0.45 K.

Magnetic cell indices hkl	$x=0.45$ I_{obs}	I_{calc}	Error (%)	$x=0.30$ I_{obs}	I_{calc}	Error (%)
101	1208±32	1087	11.1	1170±29	1071	9.2
103	165±15	152	8.6	150±14	152	1.3
211	706±25	603	17.1	615±23	599	2.7
213,105	341±20	338	0.9	228±22	337	32.3
301	198±22	174	13.8	190±18	174	9.2
R		0.012			0.012	
μ		$(10.25\pm0.53)\mu_B$			$(10.35\pm1.5)\mu_B$	

sample. Another observation is that the largest peak at 20.4° and the small peak at 23.4° cannot be described as the sum of two Gaussians plus a constant background. Instead, three Gaussians must be used with the third also centered at 20.4°. This third peak is extremely broad with FWHM $\sim$3.5° and an integrated intensity comparable to that of the other peak at 20.4°. This may indicate that $\sim$50% of the Ho^{3+} moments are not well ordered at this temperature.

The magnetic structure corresponding to the diffraction pattern from the high temperature structure has not been determined. No reasonably enlarged unit cell of either the ferromagnetic or antiferromagnetic (i.e., low temperature) structure yields the desired pattern. Efforts to describe the structure as a modulated magnetic structure in which a sinusoidal modulation of the magnitude of the spin occurs along a certain direction in the crystal lattice were also unsuccessful. Particularly promising in this respect were modulations along the [111] direction since the low temperature antiferromagnetic structure can be described as a modulation along [111] with a wavelength of 2 times the interplane spacing. Several different wavelengths for a [111] modulation gave positions for diffraction peaks in reasonable agreement with the data. However, calculated intensities were very different from those observed, and substantial intensities were predicted for other peaks which were not found. Among other explanations for this disagreement are that the structure is sinusoidally modulated along a direction that was not considered, that no simple sinusoidal modulation exists, or that there is a superposition of more than one modulation. The small number of lines observed makes the latter possibility seem unlikely. Since the magnetic structure could not be determined for this case, the appropriate region of the phase diagram in Fig. 1 is labeled with a question mark.

A very unusual aspect of the neutron diffraction data for $x=0.45$ and 0.30 is the observation of time dependence in the magnetic diffraction peaks when cooling from the superconducting paramagnetic state into the antiferromagnetic state. This was first noticed when measuring the amplitude of the largest magnetic diffraction peak as a function of temperature for the $x=0.45$ sample. Rapid cooling of the sample resulted in a peak amplitude much smaller than for very slow cooling. The addition of a small amount of ^3He to the ^4He exchange gas already in the low temperature cell containing the sample did not affect this phenomenon, indicating that it was not due to poor thermal contact of the sample to the sample holder. Further work to investigate this behavior included cooling in $\sim$1.5 min from $T=1.6$ K to $T=0.6$

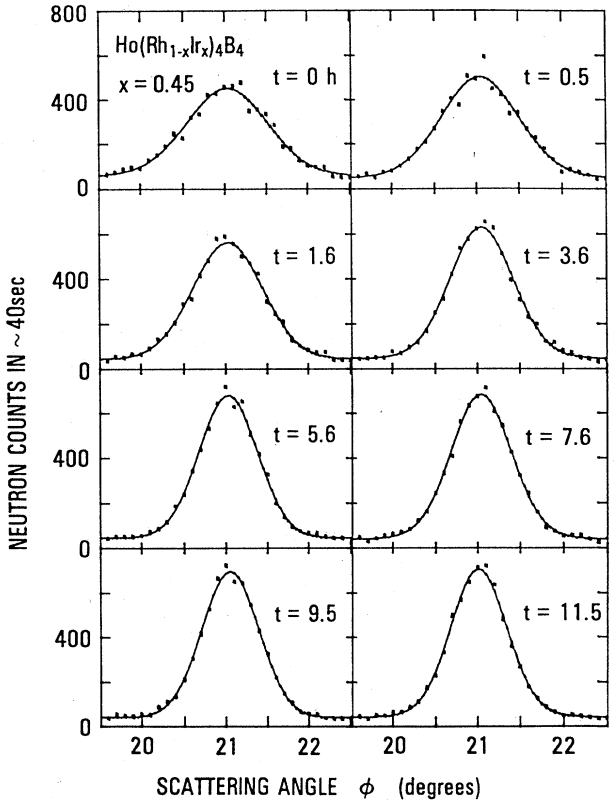

FIG. 3. Scans of the largest magnetic diffraction peak of $Ho(Rh_{1-x}Ir_x)_4B_4$ with $x=0.45$ at various times t in hours after rapidly cooling from 1.6 to 0.6 K. Solid lines are fits of a Gaussian plus a constant to each set of data.

K through the magnetic ordering temperature $T_M = 1.38$ K, followed by scans at $T = 0.6$ K of the largest magnetic diffraction peak for many hours. Examples of some of these scans as a function of time t are shown in Fig. 3, where the solid lines are fits of a constant plus a Gaussian function to each set of data. It can be seen that the form of the diffraction peak changes considerably with time, becoming larger in amplitude and smaller in width. Parameters describing the Gaussian fit to the scans are plotted as a function of time in Fig. 4, where the error bars reflect uncertainty in the Gaussian fit. The amplitude of the peak increases immediately after cooling, reaching saturation only after approximately 10 h. This growth of the peak height is accompanied by a decrease in the FWHM, which also saturates after approximately 10 h. Also plotted in Fig. 4 is the relative area under this peak (i.e., the integrated intensity) which is proportional to (peak amplitude)$\times$(FWHM) which is, in turn, proportional to the square of the average moment per Ho^{3+} ion. The intensity achieves saturation after approximately 4 h, indicating that for $4 < t < 12$ h, the changes seen in the peak height and FWHM correspond to rearrangement of magnetic moments exhibiting an unchanging average value. Finally, the diffraction angle ϕ for this largest magnetic peak is plotted in Fig. 4. This line position remains essentially unchanged despite the considerable variations seen in the other parameters.

The difficulty in measuring the magnetic order parameter as a function of temperature in a system exhibiting time dependence such as that found here is obvious since the peak amplitude changes as a function of time even when the temperature is fixed. Displayed in Fig. 5 is the temperature dependence of the number of neutron counts at the position of the largest magnetic peak for $x = 0.45$. Background counts measured off of the peak which decreased from 250 to 100 when cooling through T_M have been subtracted. These data were obtained by cooling slowly from $T > T_M$ to a minimum temperature of 0.6 K. The temperature was allowed to stabilize for ~ 3 min at each temperature, then neutrons were counted against the neutron monitor for ~ 3 min. The temperature was immediately increased after counting at $T = 0.60$ K to obtain the T-increasing data. Some hysteresis is observed upon warming compared to the cooling curve. This may be an inherent property of the magnetic transition, but it may also be due to the slow increase with time of the peak amplitude. The critical exponent for this transition could not be determined reliably since the onset of magnetic order is somewhat smeared out. Order parameter curves were measured for both faster and slower cooling rates. The shape of the curve is similar whatever the rate of temperature change, with the maximum number of counts

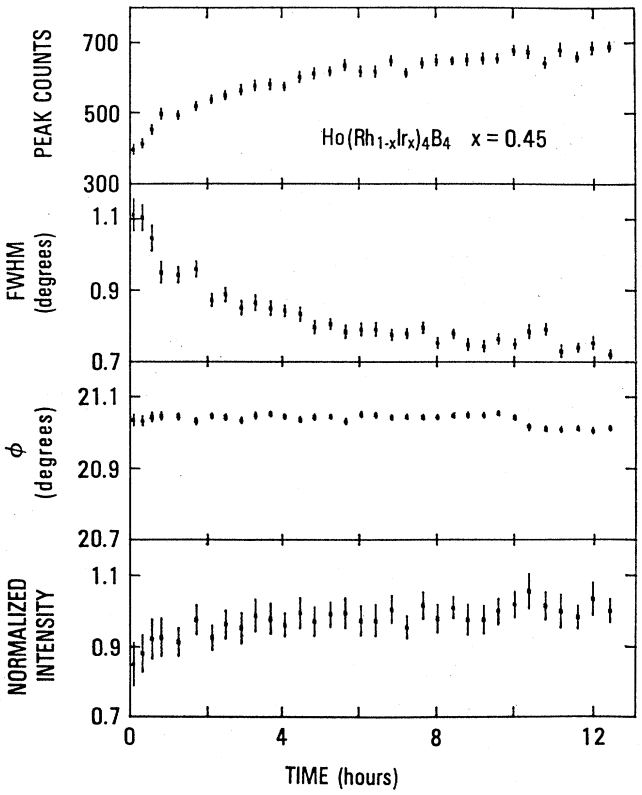

FIG. 4. Parameters describing the diffraction peak in Fig. 3 vs time. The quantities plotted are counts at the peak maximum, full width at half maximum (FWHM), diffraction angle ϕ, and integrated intensity normalized by the intensity for long times. Error bars reflect uncertainty in the Gaussian fit.

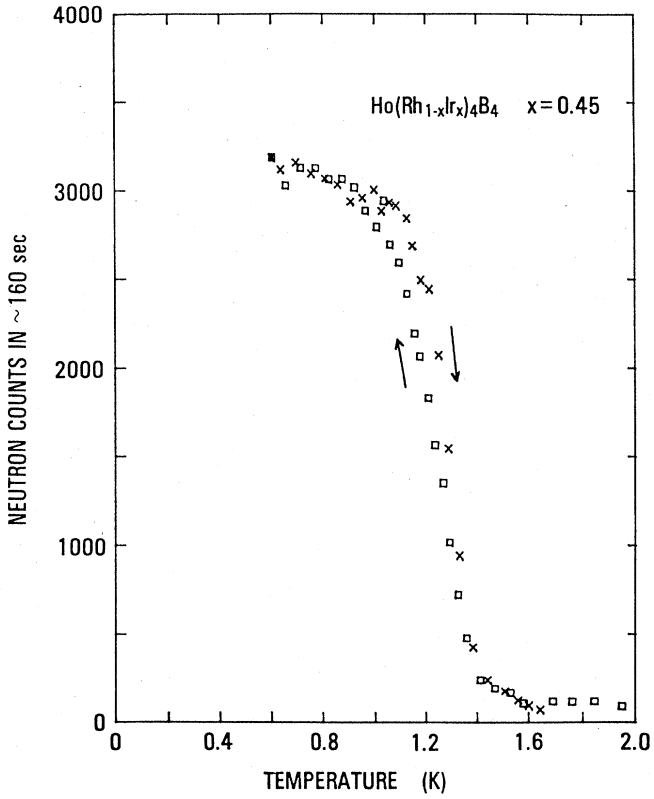

FIG. 5. Neutron counts at the position of the largest magnetic diffraction peak for $Ho(Rh_{1-x}Ir_x)_4B_4$ with $x = 0.45$, vs temperature. Data are given for both cooling and warming as indicated by the arrows. Background counts have been subtracted. For details see text.

at low temperature inversely related to the rate of cooling. Note that no hysteresis was observed in similar order parameter measurements for $x=0.70$.[7] This indicates that no time dependence of the neutron intensities would have been observed for this composition if that possibility had been investigated.

The neutron diffraction data for $x=0.30$ exhibit many similarities to the data for $x=0.45$, although the behavior is more complex due to the occurrence of two distinct magnetic transitions. A similar time dependence of the appearance of the diffraction peaks was observed when the sample was cooled from 1.6 to 0.48 K in ~ 2 min where $T_{M2}=0.89$ K and $T_{M1}=1.12$ K. Parameters describing the largest magnetic peak are shown as a function of time in Fig. 6. The timescale is much longer than for $x=0.45$, however, with the peak amplitude and FWHM approaching saturation only after approximately 20 h. A rather abrupt change in the diffraction angle ϕ from the angle for the high temperature structure to that for the low temperature structure was observed shortly after cooling. At $t=20$ h, the temperature was increased to 0.59 K, after which the peak began to change with time in the same way as before, with saturation again occurring after approximately 20 h. The temperature was increased again to 0.68 K, whereupon a small increase of the peak amplitude and a small decrease of FWHM were observed, both of which saturated after approximately 10 h. The behavior without these temperature increases was investigated when the reactor was shut down for almost 2 days for refueling while this sample was being measured. The sample was rapidly cooled just before the reactor was shut down, and several scans were made showing behavior identical to that seen after the previous rapid cooling. The sample was held at $T=0.48$ K until a scan could be made 44 h later, after the reactor was started up again. The parameters for this scan are also plotted in Fig. 6 and reveal a considerably broader and smaller peak than data for the same time with temperature increases. Holding the temperature at a constant low value clearly results in a considerably less ordered magnetic state. These data also show that the process by which the magnetic structure becomes more ordered is in some sense thermally activated.

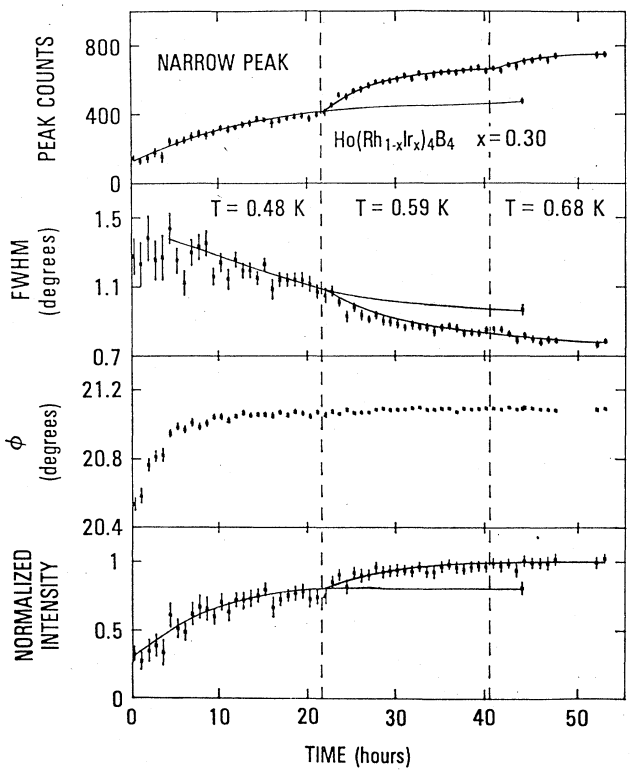

FIG. 6. Parameters describing the largest diffraction peak for the low-temperature magnetic structure of $Ho(Rh_{1-x}Ir_x)_4B_4$ with $x=0.30$, vs time. The quantities plotted are the same as in Fig. 4. Solid lines are guides to the eye, while the dashed lines indicate when the temperature was changed. Isolated data points at $t\sim 45$ h are for a second cooldown to $T=0.48$ K with the temperature subsequently remaining constant. See text for details.

A similar experiment with rapid cooling from 1.44 to 0.95 K in ~ 1 min was performed on the $x=0.30$ sample to investigate the time evolution over 10 h of the high-temperature magnetic structure. Surprisingly, no time dependence was found in the largest magnetic peaks, in strong contrast to the behavior for transitions into the antiferromagnetic structure. The width of the largest peak was constant with an average FWHM=0.788°, comparable to the FWHM observed at the longest times for the antiferromagnetic structure in both samples. This rapid equilibration of the high temperature magnetic structure indicates that the time dependence observed for the antiferromagnetic structure is an inherent property of these materials and is not due to some unknown experimental difficulty.

It should be noted that very long relaxation times (~ 10 min) were observed while measuring the specific heat of some of the $Ho(Rh_{1-x}Ir_x)_4B_4$ samples.[9] This phenomenon occurs for $0.225\leq x\leq 0.40$ for temperatures where ordering into the antiferromagnetic structure is taking place. The relaxation becomes more rapid (~ 1 min) rather abruptly as the temperature approaches T_M for the higher temperature transition.

DISCUSSION

The results which have been presented indicate that a rather abrupt transition from ferromagnetic to antiferromagnetic order takes place in $Ho(Rh_{1-x}Ir_x)_4B_4$ for $x\sim 0.2$. More information about the way in which these phase boundaries meet is not available at present due to the 0.5 K low temperature limit of our calorimeter. However, those portions of the magnetic phase diagram which have been determined so far bear a strong resemblance to some behaviors calculated for systems in which ferromagnetic and antiferromagnetic interactions compete. In some cases, a phase diagram of transition temperature versus relative strength of these interactions exhibits ferromagnetic order and antiferromagnetic order separated

by a region in which a variety of modulated spin structures occur.[10,11] This situation is called the devil's staircase[12] since the number of modulated magnetic structures which are predicted becomes larger as the scale investigated decreases. The phase boundaries expected in such a case[11] are shown in Fig. 1 by the dashed lines. A mechanism which can be proposed for this behavior is that substitution of Ir for Rh in $Ho(Rh_{1-x}Ir_x)_4B_4$ enhances antiferromagnetic interactions of Ho^{3+} ions with one another at the expense of ferromagnetic interactions. Further work at lower temperatures may prove useful in resolving this question, although obtaining samples of sufficient homogeneity may be difficult.

The unusual time dependence of the magnetic neutron diffraction peaks which was found for transitions into the antiferromagnetic structure for $x=0.30$ and 0.45 deserves further consideration. This behavior is especially surprising for two reasons. First, no time-dependent phenomena were observed in measurements for $x=0.70$ (Ref. 7) in which the same antiferromagnetic structure occurs. Second, no time dependence was observed in our measurements of the higher temperature magnetic transition for $x=0.30$. It is difficult to find a consistent explanation that can account for all of these observations.

One obvious possibility is that the observed time dependence is a manifestation of the interaction of superconductivity and magnetism. This does not seem likely for two reasons. First of all, no time-dependent behavior is seen for the transition into the high temperature magnetic state for $x=0.30$. Any mechanism which involved the interaction of superconductivity with magnetic order would be expected to have the same influence on two different magnetic transitions in the same sample. A second reason is that such time dependence has not been reported for any other antiferromagnetic superconductor.[1]

Another explanation is that this time dependence is the result of growth of antiferromagnetic domains after cooling from $T>T_M$ to $T<T_M$. In almost all magnetically ordered systems investigated to date, the magnetic system comes to equilibrium so quickly that it is not possible to observe the growth of domains. A notable exception is recent work on the quasi-two-dimensional ferromagnet $Rb_2(Mg_{1-x}Cl_x)F_4$, where three-dimensional order was observed to develop over a timescale of several hours.[13] This was attributed to weak coupling of magnetic moments occupying different planes in the crystal. The time dependence observed is consistent with a variety of calculations (see, for example, Refs. 14—17) which show that the domain size should increase as $t^{1/2}$ for short times, and $\ln t$ for longer times. Domain growth may be responsible for the time dependence observed in our measurements of the $Ho(Rh_{1-x}Ir_x)_4B_4$ mixed ternary system. However, the size of domains inferred from the FWHM (after correcting for instrumental resolution) never increases as $t^{1/2}$. The domain size may vary as $\ln t$ for long times, but this is not certain because the FWHM approaches the instrumental resolution, resulting in considerable scatter in the data. In addition, various scaling relations that have been proposed[14] are not satisfied. The domain walls for the magnetic structure observed here may be unusually broad or the growth of domains might be inhibited by the disorder introduced by the random substitution of Ir for Rh. It may be difficult to resolve these questions without measurements on single crystals in which the resolution of the neutron diffractometer would be much better. It should be noted that time-dependent neutron diffraction peaks were observed recently in measurements of the metamagnet $Fe_{0.70}Mg_{0.30}Cl_2$ in applied magnetic fields of ~ 5 kG.[18] It was proposed that this effect was caused by the motion of domain walls.

Another physical system in which time-dependent magnetic phenomena have been observed is spin glasses.[19,20] In particular, application of a magnetic field after cooling below the freezing temperature gives rise to a component of the magnetization which increases with time. Subsequently turning off the field results in a remanent magnetization which decays as $\ln t$. One explanation for this time dependence is magnetic frustration in which competing magnetic interactions permit many different spin configurations with nearly the same energy.[21] The system slowly evolves towards the configuration with the lowest energy by changing the orientation of individual spins or groups of spins. A similar mechanism may be important in the $Ho(Rh_{1-x}Ir_x)_4B_4$ mixed ternary system, where competing magnetic interactions are surely present since long-range ferromagnetic order was observed for $x=0$ (Refs. 5 and 6) and 0.15 (Ref. 4) while long-range antiferromagnetic order was found for $x=0.70$.[7] These competing interactions and the accompanying magnetic frustration may be responsible for the evolution with time towards long-range antiferromagnetic order observed for $x=0.30$ and 0.45. For $x=0$, 0.15, and 0.70, one type of interaction is sufficiently dominant that long-range order develops more quickly than can be observed. The two interactions become more nearly equal and the timescale for growth of magnetic order might increase as the composition approaches $x\sim 0.2$ where a change from ferromagnetic to antiferromagnetic order occurs. This can explain why the timescale for $x=0.30$ is considerably longer than for $x=0.45$. This is not a complete answer since other mixed magnetic systems would be expected to exhibit the same behavior. With the exception of the two cases mentioned earlier, we are aware of no reports of time-dependent phenomena involving the development of magnetic order in other studies of a considerable number of mixed magnetic systems (see, for example, Ref. 22 and references therein).

The $Ho(Rh_{1-x}Ir_x)_4B_4$ mixed ternary system may prove to be a very fruitful testing ground for investigations of competing magnetic interactions. The Ho^{3+} moments are strongly constrained to the tetragonal c axis by crystal field effects[23] and so behave as Ising spins. For $x=0.70$, the critical exponent for the growth of the magnetization with temperature decreasing below T_M is precisely the value expected for Ising spins.[7] In addition, the ferromagnetic ordering for $x=0$ shows the behavior expected from mean field theory for all measurements that have been performed.[6] Furthermore, the measurements presented here suggest that the relative strength of ferromagnetic and antiferromagnetic interactions can be adjusted by varying x. One difficulty is that random substitution of Ir for Rh results in considerable disorder in the crystal lattice.

CONCLUSION

Neutron diffraction measurements on the mixed ternary system $Ho(Rh_{1-x}Ir_x)_4B_4$ have been presented for $x=0.30$ and 0.45. A rather abrupt transition from ferromagnetic to antiferromagnetic order occurs for $x\sim0.20$. An antiferromagnetic structure occurs at low temperature for $0.2\leq x\leq0.8$, while for $0.225\leq x<0.4$ there is another transition at higher temperature into a different structure which has not been identified. An unusual time dependence of the magnetic diffraction peaks was observed for both $x=0.30$ and 0.45 upon cooling into the antiferromagnetic state. The explanation for this behavior may be magnetic frustration.

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[1] *Superconductivity in Ternary Compounds I,* Vol. 32 of *Topics in Current Physics,* edited by Ø. Fischer and M. B. Maple (Springer, New York, 1982); *Superconductivity in Ternary Compounds II,* Vol. 34 of *Topics in Current Physics,* edited by M. B. Maple and Ø. Fischer (Springer, New York, 1982).

[2] H. C. Ku, F. Acker, and B. T. Matthias, Phys. Lett. **76A**, 399 (1980); H. C. Ku, H. F. Braun, and F. Acker, Physica **108B**, 1231 (1981).

[3] L. D. Woolf, S. E. Lambert, M. B. Maple, H. C. Ku, W. Odoni, and H. R. Ott, Physica **108B**, 761 (1981); L. D. Woolf, S. E. Lambert, M. B. Maple, F. Acker, H. C. Ku, W. Odoni, and H. R. Ott, J. Low Temp. Phys. **51**, 117 (1983).

[4] K. N. Yang, S. E. Lambert, H. C. Hamaker, M. B. Maple, H. A. Mook, and H. C. Ku, in *Superconductivity in d- and f-Band Metals 1982,* edited by W. Buckel and W. Weber (Kernforschungszentrum, Karlsruhe, 1982).

[5] G. H. Lander, S. K. Sinha, and F. Y. Fradin, J. Appl. Phys. **50**, 1990 (1979).

[6] H. R. Ott, G. Keller, W. Odoni, L. D. Woolf, M. B. Maple, D. C. Johnston, and H. A. Mook, Phys. Rev. B **25**, 477 (1982).

[7] H. C. Hamaker, H. C. Ku, M. B. Maple, and H. A. Mook, Solid State Commun. **43**, 455 (1982).

[8] D. C. Johnston and H. F. Braun, in *Superconductivity in Ternary Compounds II,* Vol. 34 of *Topics in Current Physics,* edited by M. B. Maple and Ø. Fischer (Springer, New York, 1982), p. 11.

[9] K. N. Yang (private communication).

[10] P. Bak and J. von Boehm, Phys. Rev. B **21**, 5297 (1980).

[11] M. H. Jensen and P. Bak, Phys. Rev. B **27**, 6853 (1983).

[12] B. B. Mandelbrot, *Fractals: Form, Chance and Dimension* (Freeman, San Francisco, 1977).

[13] H. Ikeda, J. Phys. C **16**, 3563 (1983).

[14] G. F. Mazenko and O. T. Valls, Phys. Rev. B **27**, 6811 (1983).

[15] K. H. Fischer, Solid State Commun. **46**, 309 (1983).

[16] S. A. Safran, Phys. Rev. Lett. **46**, 1581 (1981).

[17] G. S. Grest, D. J. Srolovitz, and M. P. Anderson, Phys. Rev. Lett. **52**, 1321 (1984).

[18] P. Wong and J. W. Cable, Phys. Rev. B **28**, 5361 (1983).

[19] C. N. Guy, J. Phys. F **8**, 1309 (1978).

[20] P. J. Ford, Contemp. Phys. **23**, 141 (1982).

[21] J. Villain, J. Phys. C **10**, 1717 (1977); G. Toulouse, Commun. Phys. **2**, 115 (1977).

[22] E. F. Sarmento and C. Tsallis, Phys. Rev. B **27**, 5784 (1983).

[23] B. D. Dunlap, L. N. Hall, F. Behroozi, G. W. Crabtree, and D. G. Niarchos, Phys. Rev. B **29**, 6244 (1984).