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# Superconductivity and magnetism in the $\text{Ho}_{1-x}\text{Er}_x\text{Rh}_4\text{B}_4$ alloy system

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We have used neutron scattering techniques to examine the magnetic transitions in the  $\text{Ho}_{1-x}\text{Er}_x\text{Rh}_4\text{B}_4$  pseudoternary system. A wide variety of behavior is found, ranging from mean-field behavior for  $\text{HoRh}_4\text{B}_4$  to complicated behavior for  $\text{ErRh}_4\text{B}_4$ , where superconductivity and long-range ferromagnetic order coexist between 0.7 and 1.2 K. Long-range ferromagnetic order is found at the lowest temperatures for all alloy compositions. Alloys with more than about 30% Ho order magnetically along the *c* axis and superconductivity is destroyed in these alloys in a sharp transition coincident with magnetic ordering. Alloys near the  $\text{ErRh}_4\text{B}_4$  composition order in the basal plane but undergo a complex ordering process through a sinusoidally modulated state. Because Ho and Er have competing orthogonal magnetic anisotropies, compounds near the composition  $\text{Ho}_{0.25}\text{Er}_{0.75}\text{Rh}_4\text{B}_4$  are near a multicritical point in the magnetic phase diagram.

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Magnetism and superconductivity are very interesting phenomena in their own right; however, the discovery of both magnetism and superconductivity in  $\text{ErRh}_4\text{B}_4$  (1) and  $\text{Ho}_{1-x}\text{Mo}_x\text{S}_8$  (2) has heightened interest in these fields. The interest in these types of materials has been further increased by theoretical predictions of a number of unusual effects in the neighborhood of the superconducting-magnetic transition (3). Neutron scattering is a particularly valuable technique in studying the nature of the magnetic transition since the type of magnetic ordering can be determined and the temperature dependence of the magnetization can be measured. We have undertaken a number of measurements on various compositions of the pseudoternary alloy series  $\text{Ho}_{1-x}\text{Er}_x\text{Rh}_4\text{B}_4$ . A wide variety of phenomena is found through this alloy series varying from magnetism in  $\text{HoRh}_4\text{B}_4$  to reentrant superconductivity in  $\text{ErRh}_4\text{B}_4$ . Figure 1 shows a phase diagram of this alloy series as determined by ac magnetic susceptibility measurements. The compositions that we have investigated by neutron diffraction are shown by the arrows on the diagram.

The neutron scattering measurements are straightforward powder diffraction measurements except for  $\text{ErRh}_4\text{B}_4$  where a single crystal is available. The measurements were made on the triple-axis spectrometers at the High Flux Isotope Reactor at Oak Ridge. For the powder samples care was taken to make the samples as pure and single phase as possible so that the results would be unaffected by impurity phases. Small amounts of impurity phases were found in the samples but they did not affect the neutron diffraction measurements which were based on the  $\text{ErRh}_4\text{B}_4$  unit cell as determined by Vandenberg and Matthias (5). Ferromagnetism was found to be the lowest temperature state for all compositions of the alloy series so that all the magnetic lines coincided with the nuclear lines from the  $\text{ErRh}_4\text{B}_4$  unit cell. It turns out that the first few nuclear structure factors are small for the  $\text{Ho}_{1-x}\text{Er}_x\text{Rh}_4\text{B}_4$  alloy system so that the low temperature neutron diffraction

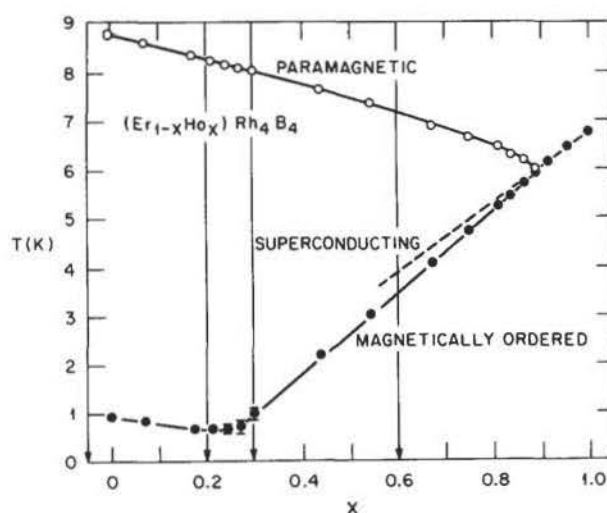


Fig. 1. Phase diagram for the  $\text{Er}_{1-x}\text{Ho}_x\text{Rh}_4\text{B}_4$  alloy system. The arrows show compositions that have been investigated by neutron scattering.

pattern is dominated by the magnetic peaks. For instance, the lowest angle reflection for  $\text{HoRh}_4\text{B}_4$ , the (101), has a magnetic component that is more than 50 times as large as the nuclear component. This makes it easier to determine the temperature dependence of the magnetization from the diffraction peaks and to determine the magnetic structure.

$\text{HoRh}_4\text{B}_4$

Figure 1 shows that  $\text{HoRh}_4\text{B}_4$  is not superconducting but undergoes a magnetic transition at 6.8 K. Earlier

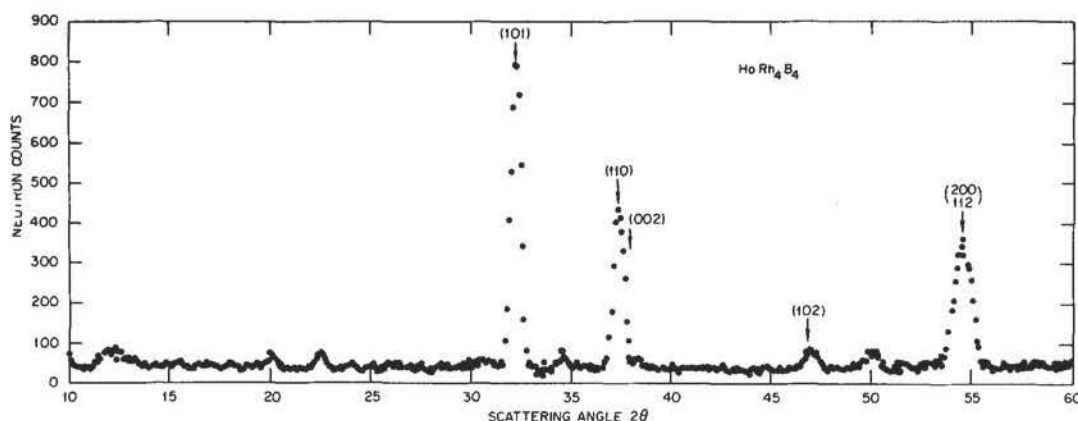


Fig. 2. Neutron diffraction pattern for  $\text{HoRh}_4\text{B}_4$  taken at 1.7 K.

neutron scattering measurements by Lander et al. (6) showed that  $\text{HoRh}_4\text{B}_4$  ordered ferromagnetically with the moment along the c-axis. It was found that the low temperature moment was about  $8.7 \mu_B$  so that Ho ordered with nearly its free ion moment of  $10 \mu_B$ . Our diffraction pattern for  $\text{HoRh}_4\text{B}_4$  taken at 1.7 K is shown in Fig. 2. The absence of the (002) magnetic peak immediately confirms the c-axis ordering. Some small impurity lines are visible but the pattern is dominated by the  $\text{HoRh}_4\text{B}_4$  type reflections. By measuring the temperature dependence of the (101) magnetic peak the temperature dependence of the magnetization or magnetic order parameter can be found. A measurement of this is

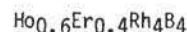
where  $M/M_0$  is the magnetic moment in reduced units,  $g$  is the Lande factor,  $\mu_B$  is the Bohr magneton, and  $\lambda$  is the molecular field constant. Since the neutron intensity is proportional to the square of the magnetic moment, the simple mean-field model would predict that

$$\left(\frac{I}{I_0}\right)^{1/2} = \tanh\left(\frac{I}{I_0}\right)^{1/2} \left(\frac{T_C}{T}\right) \quad (2)$$

where  $T_C$  is the magnetic transition temperature and  $I/I_0$  is the neutron scattering intensity. The solid line in Fig. 3 was calculated using  $I_0 = 3040$  and  $T_C = 6.775$  K. The agreement is excellent. Ott et al. (7) have discussed the mean-field nature of the transition in  $\text{HoRh}_4\text{B}_4$  using the above neutron scattering data as well as other types of measurements such as the electrical resistivity. A discussion of the nature of the magnetic forces necessary to produce mean-field ordering can be found in Ref. 7.

Mean-field theory gives the result that near the magnetic transition the magnetic scattering should go as  $(T_C - T)$ . We find that this is indeed the case and that near  $T_C$

$$I \sim (T_C - T)^{1.08 \pm 0.1} \quad (3)$$



This material is a reentrant superconductor with the magnetic transition taking place at 3.60 K. Our low temperature diffraction pattern also shows c-axis ferromagnetism for this material. The data are consistent with a moment of  $5.0 \pm 0.5 \mu_B$  at 1.6 K. This is below the free ion moment for Er or Ho but is consistent with only the Ho ordering with a moment of  $8.3 \mu_B$  which is about the same moment found in  $\text{HoRh}_4\text{B}_4$ . In more Er-rich compounds two separate orderings are found with the Er ordering at a lower temperature than the Ho. It appears that if the Er orders at all in  $\text{Ho}_{0.6}\text{Er}_{0.4}\text{Rh}_4\text{B}_4$  it must be at temperatures lower than those used in the experiment.

The temperature dependence of the magnetization as determined from the (101) diffraction peak is shown in Fig. 4 for temperatures near the transition temperature. As the temperature is increased, the magnetization decreases in a linear manner similar to  $\text{HoRh}_4\text{B}_4$  but suddenly falls rapidly to zero at about 3.5 K. The temperature at which long-range ferromagnetism disappears (3.60 K) is coincident with the appearance of superconductivity. Thus long-range ferromagnetism destroys superconductivity in a sharp first-order transition and there is no region of co-existence of ferromagnetism and superconductivity. The first-order nature of the transition is apparent in that there is hysteresis in the magnetic order parameter curve with

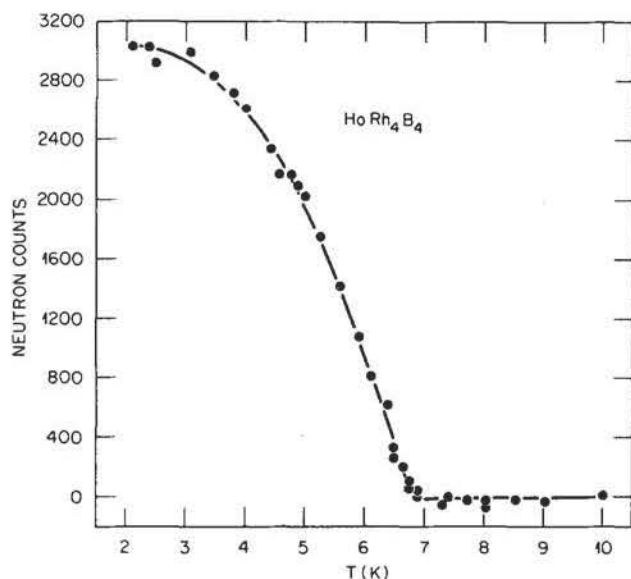


Fig. 3. Magnetic intensity of the (101) reflection vs temperature for  $\text{HoRh}_4\text{B}_4$ . The solid line is a fit to the mean-field expression given by Eq. (2).

shown in Fig. 3. It turns out that the nature of the magnetic ordering as a function of temperature is quite interesting in that a mean-field model gives an excellent account of the magnetic ordering. A simple spin  $1/2$  mean-field model would give

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

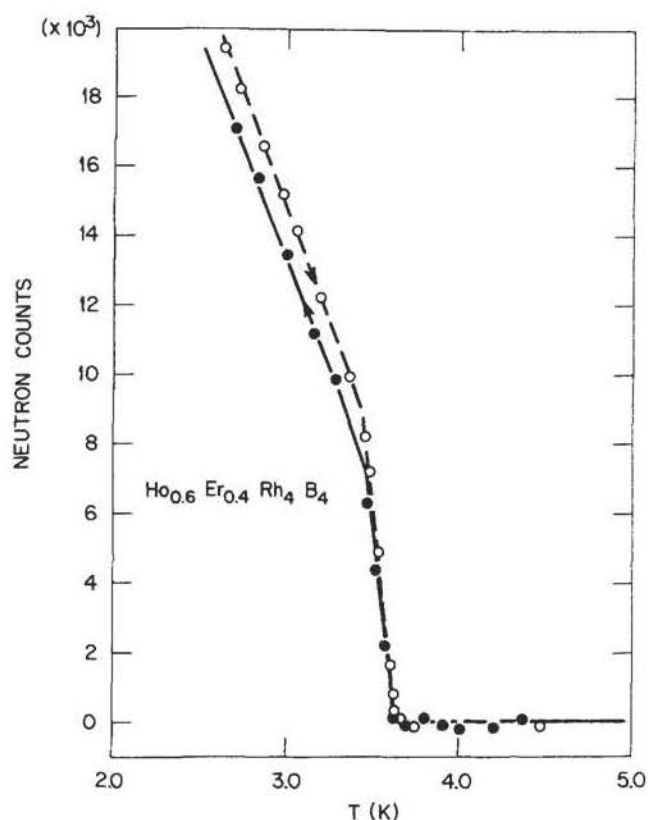


Fig. 4. Magnetic intensity of the (101) reflection vs temperature for  $\text{Ho}_{0.6}\text{Er}_{0.4}\text{Rh}_4\text{B}_4$  for temperatures near the transition.

temperature. The linear range between 2.5 and 3.5 K again has a slope of unity showing that the transition has a mean-field nature in this temperature range but that the mean-field transition is preempted by a first-order transition as the transition temperature is approached. If the linear region is extrapolated to zero counts a transition temperature of around 4 K is found. This suggests that the superconductivity influences the mean-field transition by changing it into a first-order transition and lowering the magnetic ordering temperature from 4 K to 3.6 K. The phase diagram in Fig. 1 has a dotted line extending from high Ho concentrations showing the effect of superconductivity on magnetic ordering. This dotted line crosses the  $\text{Ho}_{0.6}\text{Er}_{0.4}\text{Rh}_4\text{B}_4$  composition at about 4 K which would be the temperature of the mean-field transition if the first-order transition did not take place.

#### $\text{ErRh}_4\text{B}_4$

$\text{ErRh}_4\text{B}_4$  is a reentrant superconductor with the magnetic transition below 1 K. Using powder diffraction the material was found by Moncton et al. (8) to order ferromagnetically in the basal plane in its lowest temperature state with a saturation moment of about  $5.5 \mu_B$ . Later measurements showed small angle satellites near the transition temperature suggesting the presence of an oscillatory magnetic state (9). Theoretical work (3) had suggested that such a state might have a lower energy than the ferromagnetic state near the transition so that the appearance of the satellites seemed to confirm the theoretical predictions.

Our measurements on  $\text{ErRh}_4\text{B}_4$  were made on a high quality single crystal and while the older results were generally confirmed, much more information could be obtained. Figure 5 shows the magnetic order parameter as determined from (101) reflection. In addition, the

satellite intensity is also shown. The satellite peaks appear at positions  $(\pm 0.042 \text{ \AA}^{-1} \pm 0.055 \text{ \AA}^{-1})$  around the nuclear peaks. The satellites are consistent with a transverse-linearly-polarized, sinusoidally modulated structure with a periodicity of  $100 \text{ \AA}$  and the wave-vectors of the modulation making  $45^\circ$  angles with the c-axis and each of the equivalent a-axes. Upon cooling superconductivity is lost at 0.7 K so that long-range ferromagnetism and superconductivity coexist with a modulated phase between 0.7 and around 1.2 K.

The exact physical nature of this state is still under consideration but in any case is very interesting and unusual. Below 0.7 K only long-range ferromagnetism is found and superconductivity is destroyed. Upon warming, superconductivity is regained at about 0.8 K at which time the satellites reappear. The large hysteresis in the (101) magnetic intensity and the sharp jump in the satellite intensity show the first-order nature of the transition. A detailed account of the  $\text{ErRh}_4\text{B}_4$  single-crystal measurements can be found in Ref. 10 so that we will not discuss  $\text{ErRh}_4\text{B}_4$  further at this time.

#### $\text{Ho}_{0.2}\text{Er}_{0.8}\text{Rh}_4\text{B}_4$

Figure 1 shows that there is a minimum in the magnetic ordering temperatures of the  $\text{Ho}_{1-x}\text{Er}_x\text{Rh}_4\text{B}_4$  alloy series in the neighborhood of 75% Er. We know the Er side of the phase diagram has basal plane magnetic ordering while the Ho-rich side has c-axis ordering. c-axis ordering seems to destroy superconductivity in a sharp first-order transition while b-axis ordering may be preceded by a complex superconducting-magnetic state. The temperature dependence of the magnetic contribution of the (101) reflection for  $\text{Ho}_{0.2}\text{Er}_{0.8}\text{Rh}_4\text{B}_4$

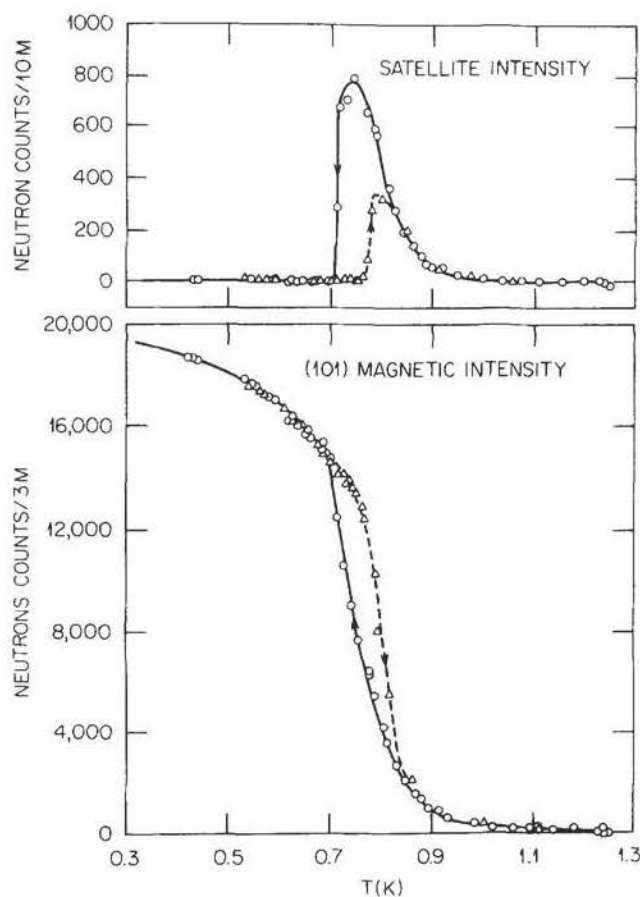


Fig. 5. Magnetic intensity of the (101) reflection and a satellite reflection plotted vs temperature for  $\text{ErRh}_4\text{B}_4$ .

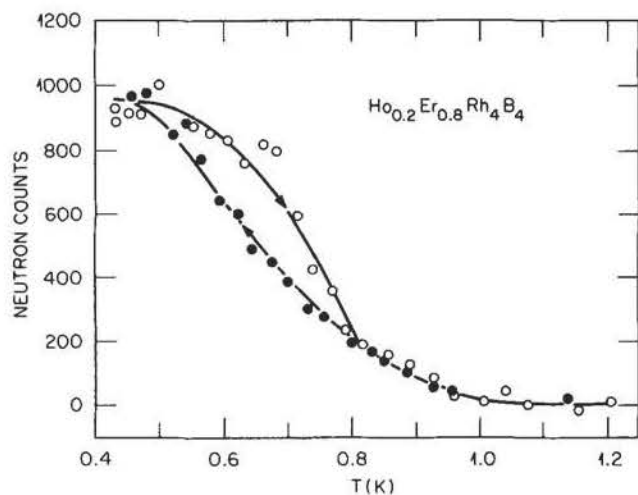
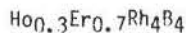


Fig. 6. Magnetic intensity of the (101) reflection vs temperature for  $\text{Ho}_{0.2}\text{Er}_{0.8}\text{Rh}_4\text{B}_4$ .

is shown in Fig. 6. The magnetic order parameter curve looks very similar to that of  $\text{ErRh}_4\text{B}_4$ . The measurements are not as detailed since a single crystal is not available. The Ho seems to depress the ordering temperature somewhat but it appears that there may not be much difference between the two materials. The powder diffraction pattern is consistent with basal plane ordering with a similar Er moment as in  $\text{ErRh}_4\text{B}_4$ .



The addition of 10% more Ho to the previous alloy changes its properties remarkably. The magnetic order parameter curve is shown for  $\text{Ho}_{0.3}\text{Er}_{0.7}\text{Rh}_4\text{B}_4$  in Fig. 7.

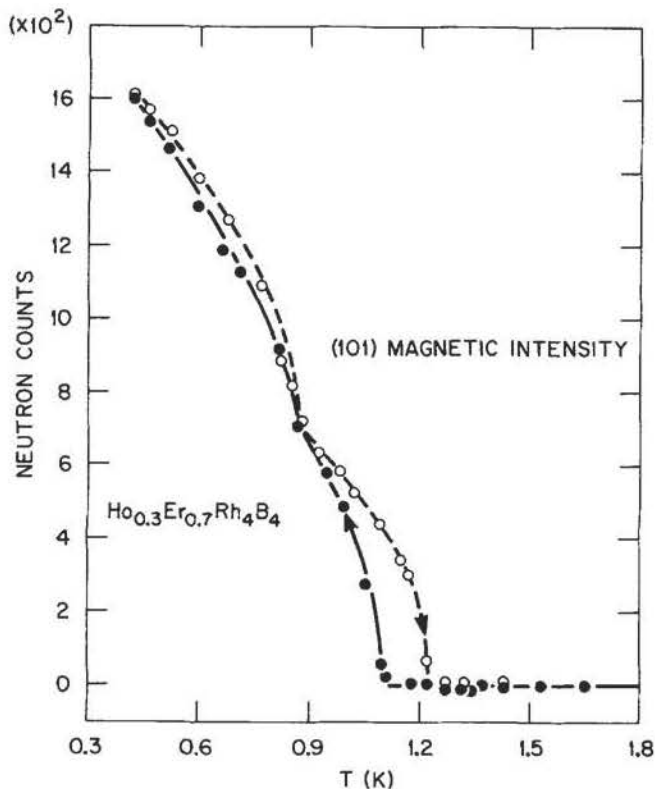


Fig. 7. Magnetic intensity of the (101) reflection vs temperature for  $\text{Ho}_{0.3}\text{Er}_{0.7}\text{Rh}_4\text{B}_4$ .

We now find evidence for two magnetic transitions, one at about 1.2 K and one at 0.85 K. Analysis of the powder diffraction patterns at various temperatures shows that c-axis ordering takes place at the highest temperatures and that ordering perpendicular to the c-axis takes place at about 0.85 K. The large hysteresis is indicative of the first-order nature of the transitions. Superconductivity is destroyed upon cooling at 1.1 K so that no coexistence region is found with c-axis ordering which is similar to  $\text{Ho}_{0.6}\text{Er}_{0.4}\text{Rh}_4\text{B}_4$ . It appears that Ho with its preference for c-axis ordering, orders first in  $\text{Ho}_{0.3}\text{Er}_{0.7}\text{Rh}_4\text{B}_4$  and this destroys superconductivity. Er with its preference for base-plane ordering apparently orders at around 0.85 K. Since the magnetic anisotropies are orthogonal for Er and Ho in the alloy series, there must be a multicritical point in the neighborhood of 75% Ho. The system is then in some respects similar to the competing anisotropy system  $\text{Fe}_{1-x}\text{Co}_x\text{Cl}_2$  studied by Wong et al. (11) except that we have in addition superconductivity.

## CONCLUSION

A wide variety of superconducting and magnetic phenomena occur within the  $\text{Ho}_{1-x}\text{Er}_x\text{Rh}_4\text{B}_4$  system. The magnetic transitions in Ho-rich compounds are mean-field like with c-axis ordering. Long-range ferromagnetism destroys superconductivity in a first-order transition and no coexistence region is found. For Er-rich materials ordering takes place through a complex sinusoidally modulated phase in which superconductivity and long-range basal-plane ferromagnetism coexist. Compositions near 75% Er are near a multicritical point in the phase diagram. We plan more measurements in this region to better determine the phase boundaries near the multicritical point.

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- c. Research sponsored by the U.S. Department of Energy under contract DE-AT03-76ER70227.
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