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Study of Coexistence of Ferromagnetism and Superconductivity in Single-Crystal $ErRh_4B_4$

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Neutron-diffraction and bulk resistivity measurements on single crystals of $ErRh_4B_4$ have revealed an intermediate phase below 1.2 K, where both a ferromagnetic structure and a transverse linearly polarized modulated structure, with a wavelength of ~ 100 Å, are observed. The modulated moment disappears suddenly below 0.71 K, with loss of superconductivity and a transition to a normal ferromagnetic state. The intermediate phase is interpreted as being one of coexisting ferromagnetic domains and superconducting domains.

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Early measurements[1-6] on polycrystalline samples of $ErRh_4B_4$ indicated that, in zero external magnetic field, it exhibits a superconducting transition at 8.7 K (T_{c1}) and orders ferromagnetically with apparent loss of superconductivity at approximately 0.9 K (T_{c2}) with some hysteresis at the lower transition. Several theoretical analyses of the superconducting-ferromagnetic (S/FM) transition[7] predicted the occurrence of an intermediate spirally ordered magnetic state, still in the superconducting phase, followed at lower temperature by a first-order transition to a normal ferromagnetic state. More recently, the treatment was generalized[8] to admit the possibility of a linearly polarized sinusoidal phase as the intermediate superconducting state. Other authors[9,10] considered an intermediate *vortex* state, which may undergo a further transition to a purely ferromagnetic state. Recent small-angle neutron-diffraction studies by Moncton *et al.*[6] on a powder sample show the growth of a peak at $Q = 0.06$ Å^{-1} at temperatures below 1.1 K, and a rapid decrease of the peak intensity below 0.65 K. They observed that the peak exhibits temperature hysteresis which is mirrored in a complementary fashion by the ferromagnetic Bragg-peak intensity. Moncton *et al.* concluded that the small-angle peak corresponded to fluctuations into a modulated structure of the type proposed by Blount and Varma,[7] with a wavelength of ~ 100 Å. They also proposed that both ferromagnetic and superconducting regions coexist in this sample over the temperature interval defined by the hysteresis loop.

The samples used in the present studies were grown from an Er-Rh-B melt. The ingot was found to contain a bicrystal, which was spark cut along its grain boundary. The larger of the resulting single crystals (mass 0.3 g) was used for neutron-diffraction studies, and the smaller for resistivity and magnetic measurements. The neutron-diffraction sample was mounted with the [010] axis vertical inside a pumped-^{3}He refrigerator on the HB-2 spectrometer at the high-flux isotope reactor. The measured nuclear structure factors of the (101) and (102) reflections obtained from integrated rocking-curve intensities in the paramagnetic phase at 1.5 K were within 1% of those expected from the crystal structure. For the (200) and (002) reflections, corrections of 9% and 46%, respectively, were required for the high absorption cross section and the irregular sample geometry. The magnetic structure factors were obtained from the ratio of the measured magnetic and nuclear intensities and the known nuclear structure factors. While secondary extinction is not a major problem for the nuclear intensities of the innermost Bragg peaks, it is very likely that the strong ferromagnetic intensities at the lowest temperatures are affected by extinction, precluding an accurate determination of the ordered moment.

Our results are as follows: For $T < 1.2$ K (T_m), ferromagnetic intensity begins to be observed at the (200), (101), and (002) reflections, but not at (102). Four satellite peaks are also observed around (200), (101), and (002) in the horizontal a^*-c^* plane at positions $\pm 0.042\vec{a}^* \pm 0.055\vec{c}^*$. The satellite positions indicate a modulation propagating symmetrically at 45° to the [001] and each of the [100] and [010] axes, with a wavelength of 91.8 ± 2.7 Å. The periodicity of the modulated moment showed very little temperature dependence over most of the observed range. There was a slight increase in its wavelength at the highest temperatures, to 103.6 ± 3.0 Å at 0.97 K. High-resolution scans of the satellite peak taken at 0.78 K indicated no significant peak width beyond the instrumental resolution width of 0.005 Å^{-1}. Assuming that a broadening of half this amount would have been observable, we conclude that at this temperature both the ferromagnetic and satellite peaks correspond to magnetically ordered regions coherent over at least 2400 Å. In spite of careful scans to find them, no higher harmonics or combinations of the basic periodicities associated with the satellites were observed, to within an estimated threshold of 2% of the main satellite intensities. As shown in Fig. 1, the modulated moment disappears suddenly on cooling below 0.71 K and reappears suddenly on warming back to 0.775 K. This first-order transition is mirrored in the opposite sense by the behavior of the ferromagnetic intensity. The intensity curves were quite reproducible, provided the temperature was changed gradually, and one warmed or cooled well beyond T_m or T_{c2}, respectively. Bulk dc resistivity measurements shown in Fig. 1 establish that the modulated moment disappears and reappears with bulk superconductivity in the sample. Note that the satellite and ferromagnetic intensities coexist for temperatures higher than that at which the hysteresis loop closes, and so the coexistence is not restricted only to the hysteretic region.

The concave upward shape of the ferromagnetic intensity below T_m is unusual in conventional ferromagnets. It is suggestive of critical scattering, similar to the "central-mode" critical scattering observed[11] at the structural phase transition in $SrTiO_3$. Another possibility is that the ferromagnetic scattering near T_m comes from only a small fraction of the sample. As the temperature is lowered, these ferromagnetic regions grow in size, forcing the scattered intensity to grow faster than the square of the ordered moment. In both the intermediate phase ($T_{c2} < T < T_m$) and the purely ferromagnetic phase, a broad diffuse component appears around each ferromagnetic reflection. We ascribe this scattering to small ferromagnetic regions which are incoherent with the main ferromagnetic regions. These may arise from domain walls, as already suggested by Moncton *et al.*,[6] or from small *disordered* regions of size 100 Å inside the large coherent ferromagnetic domains.

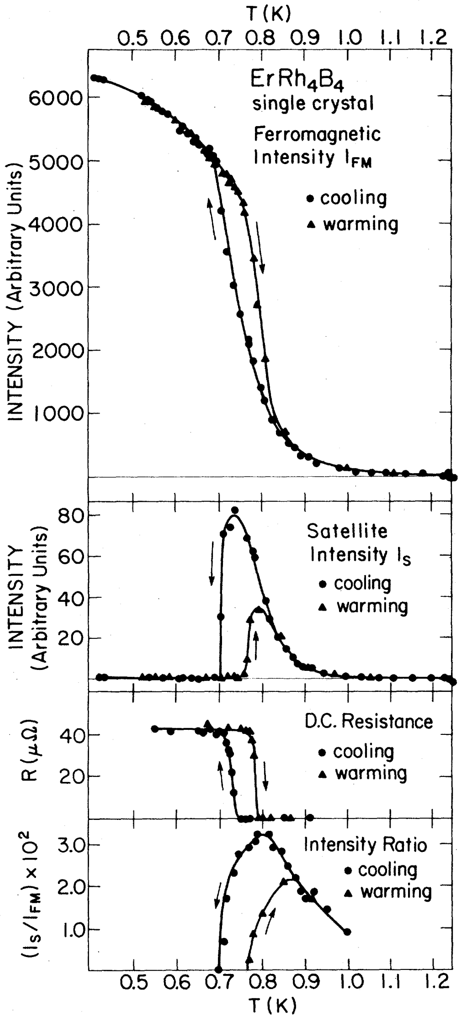

FIG. 1. Temperature dependence of the ferromagnetic and satellite intensities, the bulk dc resistivity, and intensity ratio of satellite and ferromagnetic peaks. The ferromagnetic and satellite peaks are at (101) and $(101) + \vec{q}_s$, respectively.

The effect of a magnetic field on the intermediate state was tested by the application of an external field of 200 Oe along the vertical [010] axis at a temperature of 0.74 K (reached on cooling). The satellite periodicity was unchanged but its intensity decreased by 45% while the ferromagnetic intensity increased by 8.8%. On switching off the external magnetic field the intensity pattern did not restore itself to the previous zero-field values until the sample had been warmed beyond T_m and recooled.

Finally, we turn to the quantitative analysis of the intensity data and the nature of the intemediate state. Table I lists the square of the magnetic structure factor for the observed ferromagnetic reflections at three different temperatures below T_m. They are consistent within experimental error with a uniform ferromagnetic structure with the moment along the (vertical) [010] axis. The absence of moments along the equivalent [100] a axis is surprising, but may be due to slight stresses arising from sample mounting. If so, the magnetic anisotropy in the "easy" plane must be extremely weak. We also show in Table I, $|F_{\mathrm{mag}}|^2$ for one particular satellite as observed from around the (200), (101), and (002) positions. These are consistent with a linear polarization along the [010] axis, i.e., transverse to the propagation vector $\vec{q}$.

Our data are consistent with a model where superconductivity and ferromagnetism coexist in separate domains, with the superconducting domains further divided into subdomains with one of the four observed propagation vectors $\vec{q}$ for the modulated moment. We favor this model over the vortex model for the following reasons: (1) The observed intensities of the four satellites around a given Bragg peak are not equal, one pair being roughly twice as intense as the other. This cannot be explained by the vortex model, but is consistent with the domain model if the superconducting subdomains are not equally divided among the four propagation vectors. (2) No harmonics of the satellites were observed, nor is there a significant temperature or magnetic field dependence to the period, both of which are expected in the vortex model. Also the magnetization grows in continuously below 1.2 K, unlike the predictions of the vortex model.[9,10]

TABLE I. Magnetic structure factors $|F_{\mathrm{mag}}|^2$ and derived ferromagnetic moments per Er atom for the innermost Bragg peaks at three different temperatures, and the magnetic structure factors for a particular satellite reflection $\vec{q}_s$ for three Bragg reflections at 0.75 K.

Temp. (K)	Reflection	$\|F_{\mathrm{mag}}\|^2$	μ_{FM}
0.54	002	5.106	$4.8\mu_B$[b]
	200	6.676	
	101	5.310	
0.75	002	2.914	$3.2\mu_B$
	200	2.977	
	101	2.834	
0.95	002	0.174	$0.77\mu_B$
	200	[a]	
	101	0.161	
0.75	$002+\vec{q}_s$	0.035	
	$200+\vec{q}_s$	0.046	
	$101+\vec{q}_s$	0.044	

[a] Too weak to measure.

[b] Extinction effects likely.

Within the domain model, the relative intensities of the satellite and ferromagnetic scattering shown in Fig. 1 would be proportional to $\mu_S{}^2 V_S / \mu_{FM}{}^2 V_{FM}$ where μ is the moment and V the volume of each domain. The initial rise in I_S/I_{FM} as T is lowered means that the sinusoidal moment increases faster than the ferromagnetic moment, since it is unlikely that V_S/V_{FM} would increase once ferromagnetism sets in.

From the changes in the satellite and ferromagnetic intensities at 0.74 K upon application of the magnetic field, we calculate from the domain model and from the assumption that the field simply changes sinusoidal domains to ferromagnetic domains, that at this temperature $\mu_S \simeq \mu_{FM}$, and that $V_S/V_{FM} \simeq 0.2$.

To summarize, we have shown that in a narrow temperature range $ErRh_4B_4$ exhibits both superconductivity *and* long-range ferromagnetic order, but in a spatially inhomogeneous manner. The *coexistence* of two phases over a finite temperature region appears to be an intrinsic phenomenon rather than a result of sample inhomogeneities and indicates a remarkable new pseudophase, namely a mosaic of microscopic superconducting and ferromagnetic regions (of size $\gtrsim 2000$ Å) presumably stabilized by the lowered free energy of their interfaces. Such mixed phases have already been considered.[12,13] A different possibility is that in the intermediate state, a macroscopic vortex lattice exists, with a periodicity of several thousand angstroms (which cannot be resolved from a ferromagnetic peak in the present experiment) and with large flux-free superconducting regions between the fluxoid tubes in which the modulated moment exists.[14,15] This would explain why the superconducting regions always stay connected down to T_{c2}. A further possibility is that the intermediate phase consists of a self-induced laminar structure (with the moments in each domain modulated along one direction only) as recently proposed by Tachiki.[16]

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[1] 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).

[2] H. R. Ott, W. A. Fertig, D. C. Johnston, M. B. Maple, and B. T. Matthias, J. Low Temp. Phys. 33, 159 (1978); H. G. MacKay, L. D. Woolf, M. B. Maple, and D. C. Johnston, Phys. Rev. Lett. 42, 918 (1979); L. D. Woolf, D. C. Johnston, H. B. MacKay, R. W. McCallum, and M. B. Maple, J. Low Temp. Phys. 35, 651 (1979).

[3] F. Behroozi, G. W. Crabtree, S. A. Campbell, M. Levy, D. R. Snider, D. C. Johnston, and B. T. Matthias, Solid State Commun. 39, 1041 (1981).

[4] G. K. Shenoy, B. D. Dunlap, F. Y. Fradin, S. K. Sinha, C. W. Kimball, W. Potzel, F. Probst, and G. M. Kalvius, Phys. Rev. B 9, 3886 (1980).

[5] D. E. Moncton, D. B. McWhan, J. Eckert, G. Shirane, and W. Thomlinson, Phys. Rev. Lett. 39, 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] E. I. Blount and C. M. Varma, Phys. Rev. Lett. 42, 1079 (1979); M. Tachiki, A. Kotani, H. Matsumoto, and H. Umezawa, Solid State Commun. 31, 157 (1979); R. A. Ferrell, J. K. Bhattacharjee, and A. Bagchi, Phys. Rev. Lett. 43, 154 (1979).

[8] H. S. Greenside, E. I. Blount, and C. M. Varma, Phys. Rev. Lett. 46, 49 (1981).

[9] M. Tachiki, H. Matsumoto, T. Koyama, and H. Umezawa, Solid State Commun. 34, 19 (1980).

[10] C. G. Kuper, M. Revzen, and A. Ron, Phys. Rev. Lett. 44, 1545 (1980).

[11] T. Riste, E. J. Samuelsen, K. Otnes, and J. Feden, Solid State Commun. 9, 1455 (1971).

[12] C. M. Varma, private communication.

[13] A. J. Freeman and T. Jarlborg, Appl. Phys. 50, 1876 (1979).

[14] C. R. Hu and T. E. Ham, Physica (Utrecht) 108 B+C, 1041 (1981), Proceedings of the Sixteenth International Conference on Low Temperature Physics, Los Angeles, 1981.

[15] B. Patton, private communication.

[16] M. Tachiki, Physica (Utrecht) (to be published), Proceedings of the Sixteenth International Conference on Low Temperature Physics, Los Angeles, 1981.

Sensitivity of Orthopositronium Annihilation Rates to Density Fluctuations in Ethane Gas

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Orthopositronium annihilation rates have been measured in ethane gas for densities in the range 1.8 to 286 amagats at 306.4 K. The behavior of the measured annihilation rates at densities up to about 70 amagats can be explained in terms of a simple density fluctuation model. New features are observed at higher densities of ethane at 306.4 K.

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In this Letter we present results from a continuing series of experiments whereby positron annihilation techniques are used to investigate the influence of density fluctuations on the annihilation of orthopositronium (*o*-Ps) atoms formed in ethane gas. We present new results that are the first to show a complex dependence of orthopositronium annihilation rates ($\lambda_{o\text{-Ps}}$) on the density of the gas over a wide range of densities at a temperature that is only about 1 K above the critical temperature of the gas. These results support the sensitivity of $\lambda_{o\text{-Ps}}$ to density fluctuations in ethane gas and allow us to study the application of a simple density fluctuation model to $\lambda_{o\text{-Ps}}$ at sufficiently high densities of the gas that density fluctuations are expected to be large and highly correlated. The behavior of *o*-Ps annihilation rates has been reported recently as a function of density and temperature in methane[1] and ethane[2] gases. However, these measurements were made only for limited ranges of densities and temperatures of the gases. Nevertheless, they have indicated that the annihilation rates of *o*-Ps atoms in methane and ethane gases are sensitive to density fluctuations. Generally at low densities, *o*-Ps annihilation rates increase linearly with the density of the gas up to certain temperature-dependent values of gas density