2D and 3D Magnetic Behavior of Er in ErBa$_2$Cu$_3$O$_7$

J. W. Lynn, T. W. Clinton, and W-H. Li

*Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742
and National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

R. W. Erwin

National Institute of Standards and Technology, Gaithersburg, Maryland 20899

J. Z. Liu and K. Vandervoort

Argonne National Laboratory, Argonne, Illinois 60439

R. N. Shelton

Department of Physics, University of California, Davis, California 95616

Neutron scattering has been used to study the magnetic order of the Er ions in superconducting ErBa$_2$Cu$_3$O$_7$. Above the 3D Néel temperature ($T_N = 0.618$ K) a rod of scattering characteristic of 2D behavior is unambiguously observed, showing that the magnetic interactions of the rare-earth ions are highly anisotropic; below T_N the order parameter follows the exact Onsager solution for a 2D Ising antiferromagnet. At low T, two separate types of simple 3D antiferromagnetic structures are found, one characterized by a wave vector of $(\frac{1}{2},0,0)$, and the other by $(\frac{1}{2},0,\frac{1}{2})$.

The magnetic properties of the heavy rare-earth ions $\mathcal{R}$ in the $\mathcal{R}$Ba$_2$Cu$_3$O$_7$ superconductors have been of particular interest since the initial experiments which showed that the superconductivity in this system is unaffected by the substitution of $\mathcal{R}$ for yttrium.[1-3] This observation indicates that the rare-earth sublattice is electronically isolated from the superconducting Cu-O planes, while the very weak magnetic interactions yield ordering temperatures of 2 K or less, making these materials ideal candidates to investigate the interplay between the magnetism and superconductivity.[4] The first neutron experiments on ErBa$_2$Cu$_3$O$_7$[5] showed a magnetic phase transition at $T_N \sim 0.6$ K, which agreed with specific-heat data.[6,7] The Er moments exhibited a two-dimensional character in the a-b plane, with an ordering wave vector of $(\frac{1}{2},0)$, while there were no significant magnetic correlations that could be detected along the c axis down to the lowest temperatures that could be achieved at that time (0.33 K). This anisotropic behavior was expected since the interactions are primarily dipolar in origin, and the spacing between Er ions is 3 times larger along the c axis than in the a-b directions. Additional measurements[8] at 140 mK found that the system had 3D order at this lower temperature, with two independent propagation wave vectors of $(\frac{1}{2},0,0)$ and $(\frac{1}{2},0,\frac{1}{2})$. The spin configuration in the a-b plane was the same as we had found[5] at higher temperature, while the spin configuration along the c-axis direction was relatively complicated.

Measurements have also been carried out on the Dy,[9] Gd,[10] and Nd[11] systems,[12] with conflicting interpretations for the results. The specific-heat results for several

systems,[7,11] for example, could be well explained on the basis of a 2D Ising model, while 3D magnetic order with a propagation vector of $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ was clearly observed in the neutron experiments. Moreover, recent results on the Gd system have yielded different spin configurations as observed in powders[10,12] and single crystals.[13] The situation has been further confused very recently by McK. Paul et al.,[14] who reported measurements on small single crystals of ErBa$_2$Cu$_3$O$_7$. They were unable to solve the magnetic structure, or determine the propagation vector in the a-b plane, but claimed that there was in fact no 2D behavior in this system, contrary to our original results.[5] Thus the anisotropy of the magnetic interactions and the nature of the rare-earth ordering were unclear.

In the present Letter we report measurements both on our original powder sample of ErBa$_2$Cu$_3$O$_7$, measured to lower temperatures, and on high-quality single-crystal samples. Above the 3D ordering temperature, we observe a rod of scattering along $(\frac{1}{2},0,l)$, which directly demonstrates the expected strong anisotropy of the magnetic interactions and the concomitant 2D character of the system. In addition, below the Néel temperature the order parameter follows the Onsager solution for the $S = \frac{1}{2}$ 2D Ising model, analogous to the behavior observed for the prototype 2D Ising system K$_2$CoF$_4$.[15] Thus we believe that the physics of the rare-earth ordering in these materials is controlled by the 2D-like character over the entire temperature range of interest. We find that two separate magnetic structures can occur at low T, one characterized by a wave vector $(\frac{1}{2},0,0)$, and the other by $(\frac{1}{2},0,\frac{1}{2})$. Both these structures are ob-

served in our powder, while only the $(\frac{1}{2},0,\frac{1}{2})$ structure is found in our single-crystal samples. The two structures probably occur because the dipolar energies of these configurations are almost identical, as recently calculated explicitly by Felsteiner[16] for the Gd system, and hence the energetics may be influenced by the detailed metallurgical properties of the crystallites such as strains, grain, twin boundaries, etc. We believe the present data elucidate the underlying physics and resolve the conflicts that have been reported for the rare-earth orderings in these systems.

The neutron experiments were conducted at the research reactor at the National Institute of Standards and Technology. The diffraction data were taken with a wavelength of 2.3509 Å and a pyrolytic-graphite monochromator and filter. Triple-axis polarized-neutron measurements were also employed to unambiguously identify the magnetic scattering.[17] A helium dilution refrigerator was used to obtain temperatures as low as 40 mK, while a ^{3}He refrigerator with well-calibrated thermometers was employed for the order-parameter measurements near T_N. The properties of the polycrystalline sample have been described in our earlier report.[5] The nonstoichiometric solid-state reaction technique[18] was employed to grow the single crystals. This technique yields (twinned) crystals which are uniformly and fully oxygenated during the growth process, eliminating the requirement of post-oxygen anneal to make the samples superconducting. The measured superconducting transition temperature for the crystals used in the present measurements was 92.8 K, with a width of less than 1 K. Most of the neutron data were taken on a crystal which weighed 31 mg.

Figure 1 shows two magnetic diffraction peaks, where both h and l are half integral. The solid curves are a least-squares fit with a Gaussian (resolution) peak. The non-Gaussian shape to the experimental data indicate that the mosaic spread of the crystal is not Gaussian, which is of no concern other than that for quantitative comparisons the experimentally summed integrated intensities must be used rather than the integrated intensities obtained from the fitted curves. We remark that in the present case the signal is approximately 20 times higher than that reported by McK. Paul et al.[14]

In the single crystals we have studied, we have not found any peaks with integer l, and hence we assume that the appropriate modulation vector for the ground-state spin configuration is $(\frac{1}{2},0,\frac{1}{2})$. The spin structure for the system is shown in Fig. 2, where $+$ represents a spin in one direction, and $-$ represents a spin pointing in the opposite direction; the specific direction in the crystal in which the spins point may not be one of the primary crystallographic axes, and additional data will be needed before this direction can be uniquely determined. The magnetic structure consists of ferromagnetic "chains" of spins along the b direction, with adjacent chains in the a-b plane coupled antiferromagnetically. In the next lay-
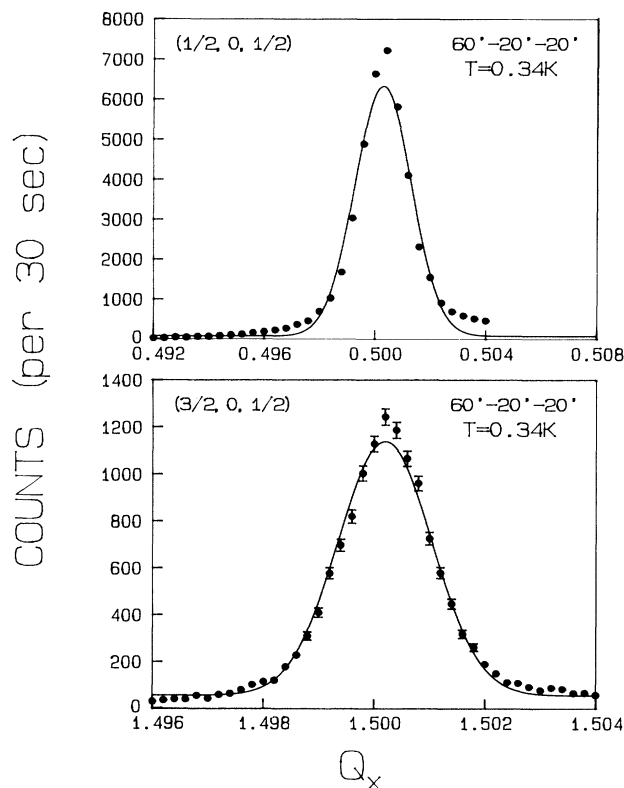

FIG. 1. Magnetic Bragg peaks observed at low temperatures in a single crystal of ErBa$_2$Cu$_3$O$_7$. In these single crystals only peaks with half-integer values of l are observed.

er up, the spins are antiparallel, and we believe that this is the lowest-energy (dipolar) configuration. However, in our powder sample, in the powder data of Chattopadhyay et al.,[8] and in the lower-quality[19] single crystals of McK. Paul et al.,[14] peaks with integer l are observed. This spin configuration corresponds to the spins in adjacent a-b layers being parallel, rather than antiparallel. We remark that the dipolar energies for these two configurations are almost identical, and since the dipolar interaction is long range in nature the energy could be dependent upon defects in the samples such as the density of grain and twin boundaries. We believe that this is the correct explanation for the distinct spin structures which have been observed in the Gd and Er materials, although considerable work will be needed to establish this connection unambiguously. We remark that a similar duality of spin structures, with identical ordering temperatures, has been observed in other planar antiferromagnets such as Rb$_2$MnF$_4$.[20]

We now turn to the two-dimensional character of the system. In the bottom portion of Fig. 2 we present a diagram of reciprocal space, showing positions of the nuclear (crystal structure) and magnetic (spin structure) Bragg peaks. If the system were 2D in character then we would expect to see rods of scattering as shown;
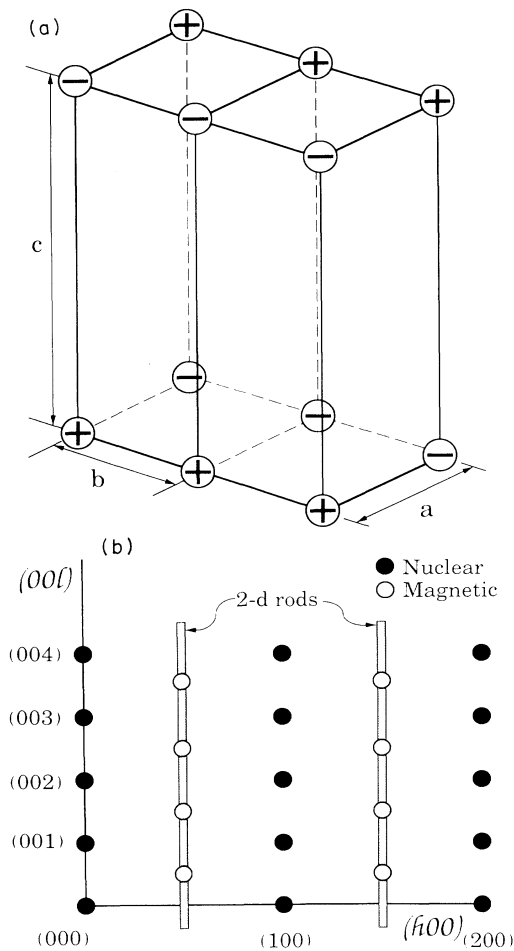
FIG. 2. (a) Spin structure and (b) scattering plane in reciprocal space, where most of our measurements were taken.
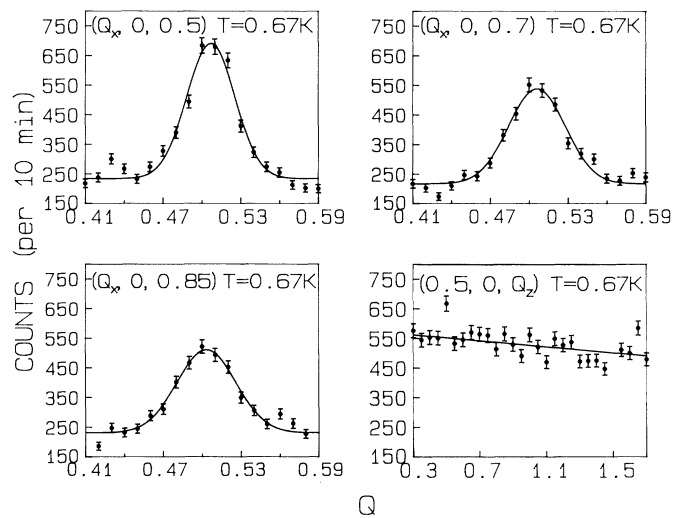

FIG. 3. Three scans across the rod of scattering in reciprocal space, showing the 2D character just above $T_N = 0.618$ K. The fourth scan shows that the scattering intensity does not vary significantly along the rod, indicating that there are no significant spin correlations between planes. The extra intensity at $Q_z = \frac{1}{2}$ is due to a small amount of nuclear contamination via $\lambda/2$ neutrons.

temperature we might expect the anisotropy to be large compared to the magnetic interactions, thus defining a unique spin direction. This would correspond to a 2D Ising model, which of course is the only one that exhibits long-range magnetic order in 2D. The solid curve is a fit of Onsager's exact solution for the $S = \frac{1}{2}$ 2D Ising model,[23] and we see that excellent agreement is obtained. In addition, if we analyze the data in the reduced tempera-

above the ordering temperature this scattering originates from critical fluctuations, while below T_N it originates from low-energy spin waves. Figure 3 shows three scans through the rod, just above the 3D ordering temperature. This strong rod of scattering develops for temperatures $\lesssim 1$ K, and at this temperature the width is solely instrumental in origin. Also shown in the figure is a scan along the rod, which demonstrates that the scattering intensity is essentially uniform. Hence there are no significant correlations between the spins in adjacent a-b layers, even though we are just above T_N. Thus we regard the phase transition at T_N as 2D in character, with the 3D ordering simply being induced as a necessary consequence of the onset of long-range order within the a-b planes.[21] This behavior is prototypical of 2D ordered magnets.[20]

Finally, we turn to the temperature dependence of the order parameter as shown in Fig. 4. Both specific heat[6,7] and inelastic neutron scattering[22] reveal that the ground state is a doublet, so that $S = \frac{1}{2}$ is appropriate. In addition, in an orthorhombic structure with such a low Néel
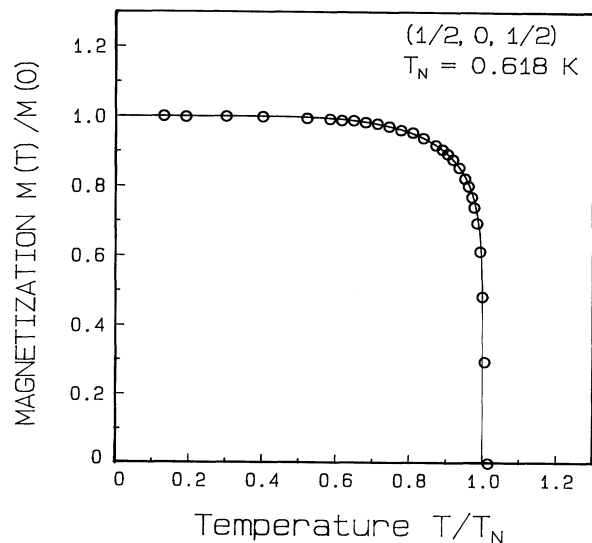

FIG. 4. Sublattice magnetization vs temperature. The solid curve is a fit by Onsager's exact solution for the $S = \frac{1}{2}$ 2D Ising model.

ture range of $1 \times 10^{-3} < (T_N - T)/T_N < 0.11$, we obtain $\beta = 0.122 \pm 0.004$, in excellent agreement with the exact result $\beta = \frac{1}{8}$. We remark that our data are very similar to the "prototypical" $S = \frac{1}{2}$ 2D Ising system K_2CoF_4,[15] and lend additional evidence to the assertion that the ordering in $ErBa_2Cu_3O_7$ is two dimensional in character, with the 3D order simply being induced when the 2D order sets in. However, since the dipolar interaction is long range in nature, the Er system may belong to a different universality class than K_2CoF_4, and we believe a detailed study of the critical properties of $ErBa_2Cu_3O_7$ is warranted.

[1]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[2]P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, Phys. Rev. Lett. **58**, 1891 (1987).

[3]A recent review of the oxide superconductors is given in *High Temperature Superconductivity,* edited by J. W. Lynn (Springer-Verlag, New York, 1989).

[4]For a review, see *Topics in Current Physics,* edited by Ø. Fischer and M. B. Maple (Springer-Verlag, New York, 1983), Vols. 32 and 34.

[5]J. W. Lynn, W-H. Li, Q. Li, H. C. Ku, H. D. Yang, and R. N. Shelton, Phys. Rev. B **36**, 2374 (1987).

[6]See S. E. Brown, J. D. Thompson, J. O. Willis, R. M. Aikin, E. Zirgiebl, J. L. Smith, Z. Fisk, and R. B. Schwarz, Phys. Rev. B **36**, 2298 (1987); B. D. Dunlap, M. Slaski, D. G. Hinks, L. Soderholm, M. Beno, K. Zhang, C. Segre, G. W. Crabtree, W. K. Kwok, S. K. Malik, I. K. Schuller, J. D. Jorgensen, and Z. Sungaila, J. Magn. Magn. Mater. **68**, L139 (1987); B. W. Lee, J. M. Ferreira, Y. Dalichaouch, M. S. Torikachvili, K. N. Yang, and M. B. Maple, Phys. Rev. B **37**, 2368 (1988); H. P. Van der Meulen, J. J. M. Franse, Z. Tarnawski, K. Kadowaki, J. C. P. Klaasse, and A. A. Menovsky, Physica (Amsterdam) **152C**, 65 (1988).

[7]J. van den Berg, C. J. van der Beek, P. H. Kes, J. A. Mydosh, G. J. Nieuwenhuys, and L. J. de Jongh, Solid State Commun. **64**, 699 (1987); S. Simizu, S. A. Friedberg, E. A. Hayri, and M. Greenblatt, Phys. Rev. B **36**, 7129 (1987); M. W. Dirken and L. J. de Jongh, Solid State Commun. **64**, 1201 (1987).

[8]T. Chattopadhyay, P. J. Brown, D. Bonnenberg, S. Ewert, and H. Maletta, Europhys. Lett. **6**, 363 (1988). Our powder data are in good agreement with the data of these authors.

[9]A. I. Goldman, B. X. Yang, J. Tranquada, J. E. Crow, and C.-S. Jee, Phys. Rev. B **36**, 7234 (1987).

[10]D. McK. Paul, H. A. Mook, A. W. Hewit, B. C. Sales, L. A. Boatner, J. R. Thompson, and M. Mostoller, Phys. Rev. B **37**, 2341 (1988); H. A. Mook, D. McK. Paul, B. C. Sales, L. A. Boatner, and L. Cussen, Phys. Rev. B **38**, 12008 (1988).

[11]K. N. Yang, J. M. Ferreira, B. W. Lee, M. B. Maple, W-H. Li, J. W. Lynn, and R. W. Erwin, Phys. Rev. B (to be published).

[12]Pr also orders with the same spin configuration, but it interacts electronically with the Cu-O planes; W-H. Li, J. W. Lynn, S. Skanthakumar, T. W. Clinton, A. Kebede, C.-S. Jee, J. E. Crow, and T. Mihalisin, Phys. Rev. B **40**, 5300 (1989).

[13]T. Chattopadhyay, H. Maletta, W. Wirges, K. Fisher, and P. J. Brown, Phys. Rev. B **38**, 838 (1988).

[14]D. McK. Paul, H. A. Mook, L. A. Boatner, B. C. Sales, J. O. Ramey, and L. Cussen, Phys. Rev. B **39**, 4291 (1989).

[15]H. Ikeda and K. Hirakawa, Solid State Commun. **14**, 529 (1974).

[16]J. Felsteiner, Phys. Rev. B **39**, 7248 (1989).

[17]R. M. Moon, T. Riste, and W. C. Koehler, Phys. Rev. **181**, 920 (1969).

[18]J. Z. Liu (private communication).

[19]They report a rather low value of T_c of 88 K, and the Néel temperature is only 0.5 K instead of 0.6 K.

[20]R. J. Birgeneau, H. J. Guggenheim, and G. Shirane, Phys. Rev. B **1**, 2211 (1970).

[21]For a 2D Ising system with weak coupling J' between layers, there is an energy $\pm J'\langle S\rangle^2(L_D)^2$, where L_D is the average size of a domain in the layers. Hence as soon as the system orders two dimensionally, 3D order is induced. For further discussion, see Ref. 20.

[22]U. Walter, S. Fahy, A. Zettl, S. G. Louie, M. L. Cohen, P. Tejedor, and A. M. Stacy, Phys. Rev. B **36**, 8899 (1987); A. Furrer, P. Bruesch, and T. Unternahreh, Phys. Rev. B **38**, 4616 (1988); A. I. Goldman, Y. Gao, S. T. Ting, J. E. Crow, W-H. Li, and J. W. Lynn, J. Magn. Magn. Mater. **76–77**, 607 (1988).

[23]L. Onsager, Phys. Rev. **65**, 117 (1944).