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Magnetic fluctuations and two-dimensional ordering in $ErBa_2Cu_3O_7$

J. W. Lynn, W-H. Li, and Q. Li
Department of Physics, University of Maryland, College Park, Maryland 20742
and National Bureau of Standards, Gaithersburg, Maryland 20899

H. C. Ku,* H. D. Yang, and R. N. Shelton
Department of Physics and Ames Laboratory-U.S. Department of Energy,
Iowa State University, Ames, Iowa 50011
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Neutron-diffraction and small-angle scattering techniques have been used to study the magnetic properties of $ErBa_2Cu_3O_7$. Below the superconducting transition of 95 K there is a decrease in the small-angle scattering, which has the correct amplitude, temperature dependence, and q dependence to be interpreted as the screening of the paramagnetic fluctuations by the superconducting electrons. At low temperatures ($\sim \frac{1}{2}$ K) the Er moments become ordered two dimensionally, with chains of spins coupled ferromagnetically, while adjacent chains align antiparallel.

The discovery[1] of superconductivity in $YBa_2Cu_3O_7$ has generated unprecedented excitement in the physics community both because of the possible new fundamental phenomena this class of systems represents as well as the enormous potential for applications. The substitution of the heavy rare-earth elements for yttrium has little if any detrimental effect on the superconducting transition temperature,[2,3] and hence these are ideal materials to investigate the interplay between magnetism and superconductivity.[4] In the low-T_c systems this coupling is thought to be primarily electromagnetic in origin, but the direct London screening of the long-wavelength magnetic fluctuations by the superconducting electrons has so far eluded detection. Our present small-angle neutron scattering results show that the intensity at small wave vectors q does in fact decrease when the sample becomes superconducting. Furthermore, the overall amplitude, temperature dependence, and q-dependent shape of this change in the scattering is consistent with the expected suppression effect. However, this interpretation would require a London penetration depth λ_L which is much smaller than expected, and suggests that another length scale might be relevant to describe the magnetic screening. At very low temperatures, on the other hand, we find that the Er moments exhibit a two-dimensional ordering which is driven by the dipolar coupling of the moments. The configuration of spins is such that chains form which are aligned ferromagnetically, but with adjacent chains antiparallel.

The neutron experiments were conducted at the research reactor at the National Bureau of Standards. The small-angle neutron scattering (SANS) data were obtained with a neutron wavelength of 6.0 Å using the high-resolution focusing-beam configuration, while the conventional diffraction data were taken with a wavelength of 2.3509 Å and a pyrolytic graphite monochromator and filter. The sample was enclosed in an aluminum canister which contained an atmosphere (standard temperature and pressure) of helium exchange gas to allow adequate thermal conduction at low temperatures. For the SANS experiments the sample was mounted in a Displex helium refrigerator, while for the diffraction data a pumped ^3He cryostat was employed. To prepare the sample, high-purity Ames Laboratory powders of Er_2O_3, BaO, and CuO were used. The predried powders were mixed to give the stoichiometric ratios of metal constituents, and they were then pressed into $\frac{3}{8}$-in. pellets and sintered in air at 900 °C for one day in alumina crucibles. The pellets were subsequently reground, repressed to pellet form, and annealed in air at 900 °C for 1 day. This second heat treatment was followed by a final regrinding and repressing and anneal at 900 °C in oxygen for 36 h. At the end of the 36-h period the furnace was turned off and the samples allowed to slow cool to room temperature in oxygen. Powder x-ray diffraction patterns were indexed on an orthorhombic unit cell (*Pmmm*), with room-temperature lattice parameters of (3.845, 3.884, 11.53) Å. A minor amount ($< 5\%$) of a secondary ternary oxide phase was barely detectable in the x-ray pattern, although it was easily detected with neutrons when the impurity ordered magnetically ($T_M \sim 12$ K). Magnetization measurements showed an onset temperature for superconductivity of 95 K, with a Meissner exclusion of 75% at low temperatures.

We begin by discussing the development of the magnetic correlations at low temperatures. In addition to determining the nature of the magnetic order, these measurements serve to establish the overall energy scale of the fluctuations. It is also important to establish that the rare earth carries a significant moment, which is not a completely trivial consideration (except for Gd) in the present systems since the site symmetry is low and the crystal field ground state might be a singlet. Indeed we have carried out experiments on a sample of $HoBa_2Cu_3O_7$ and found no evidence for the development of magnetic correlations down to 0.3 K, while preliminary measurements of the crystal field transitions suggest a singlet ground state.[5] To isolate the magnetic scattering in $ErBa_2Cu_3O_7$ we have employed the subtraction technique.[6] Well above any magnetic ordering temperature the magnetic moments will be completely uncorrelated, so that the diffraction

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pattern will consist of nuclear Bragg peaks and "background." At low temperatures, on the other hand, magnetic peaks will develop in the scattering due to magnetic order or correlations, which will appear in addition to the nuclear Bragg peaks. A subtraction of the high-temperature data from the data at low T then isolates the magnetic response. Such a subtraction is shown in the top portion of Fig. 1. We see a rapid rise in the scattering, with a maximum at an angle of 17.8°, and then a long tail of scattering which extends towards larger angles. The position of the peak coincides with a $(\frac{1}{2},0,0)$-type reflection, so that we can determine immediately that the scattering is antiferromagnetic in nature. Note also that the net scattering at the lowest angles is negative, which simply reflects the sum rule on the magnetic response; in some regions of q the magnetic scattering must decrease in order to produce peaks elsewhere.

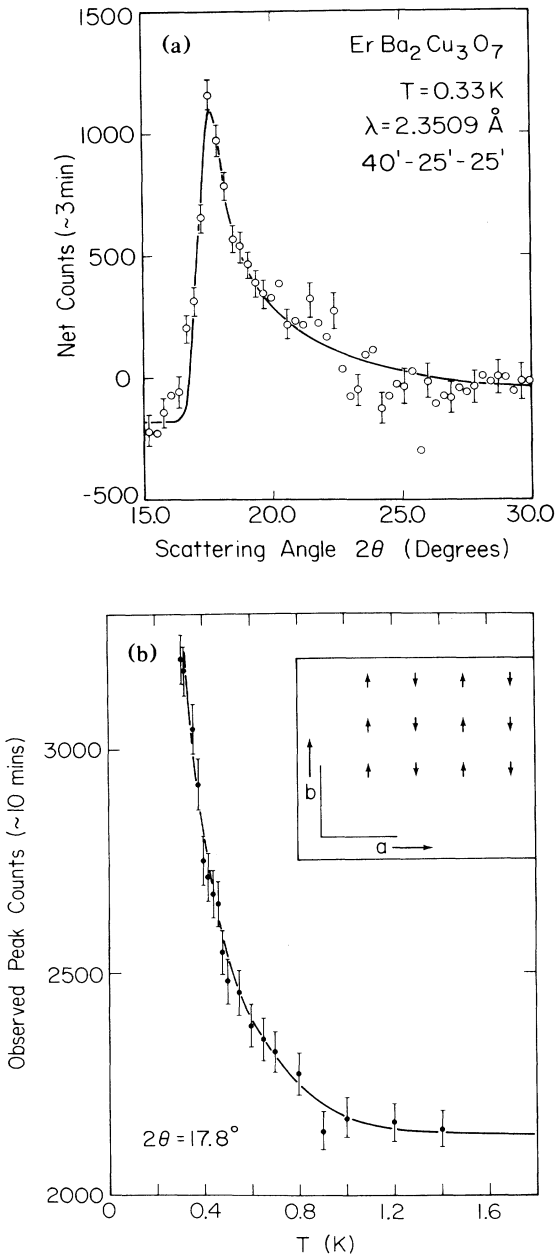

FIG. 1. (a) Magnetic intensity observed at low temperatures. The solid curve is a least-squares fit of the data to the two-dimensional model as described in the text. The data were taken with an in-pile collimation (FWHM) of 40′ and 25′ before and after the sample. (b) Temperature dependence of the peak intensity. The solid curve is a guide to the eye. The inset shows the magnetic configuration of spins.

The pronounced asymmetry of the observed peak is a classic profile of a two-dimensionally ordered system.[7] To understand the origin of this behavior we note that there is only one Er ion per unit cell, so that the Er sublattice is simple orthorhombic. The lattice parameters then show that the separation of the Er ions along the a and b lattice directions is nearly the same, while the distance along the c axis is about three times longer. Hence the dipolar interactions will be very much smaller along this direction, and two-dimensional order seems likely. If the spin structure is collinear, then there are only two possible spin configurations. The first is where the nearest neighbors are antiparallel, while the next nearest neighbors are parallel as shown in the inset to the figure. The unit cell will be doubled along one direction, and this will give rise to peaks like $(\frac{1}{2},0)$, $(\frac{1}{2},1)$, etc., and is consistent with the data in Fig. 1. Note that the spins form chains along the b axis which are parallel, while adjacent chains along the a axis are antiparallel. The other possible spin configuration is obtained by reversing all the next nearest neighbors along the b direction, so that the unit cell doubles along both directions. The lowest-order peak in this model is the $(\frac{1}{2},\frac{1}{2})$ peak, which is inconsistent with the data.

To quantitatively fit these data we have employed a model which assumes that the scattering originates from a Bragg line. We remark that since the orthorhombic distortion of this system is small and the scattering profile from a 2D powder is quite broad, we cannot unambiguously determine if the peak is a $(\frac{1}{2},0)$ or a $(0,\frac{1}{2})$-type reflection. The solid curve in the figure is a least squares fit, assuming there is no intrinsic width to the Bragg line, and no correlations along the line. The fit is excellent, and hence we conclude that there are strong correlations in the a-b plane, while the correlation length along the c axis is small.

The bottom portion of the figure shows the temperature dependence of the intensity at the peak position. We see that the scattering is still increasing rapidly down to 0.3 K, which is the lowest temperature we could achieve. Comparing the magnetic intensity with the (001) nuclear intensity establishes that the ordered magnetic moment $\langle\mu^z\rangle$ is already $2.9\mu_B$. We would expect the intensity to continue to increase until the full ground-state moment is obtained, and then become independent of temperature. At sufficiently low temperatures the peak intensity would presumably start to increase again as 3D order eventually sets in, with the data in Fig. 1 narrowing into a set of resolution limited Bragg peaks. The only related system which has been investigated so far is La_2CuO_4, where the Cu moments exhibit 3D order ($T_N \approx 220$ K) with a similar doubling of the unit cell.[8] In the present system we

would also expect a 3D type of order if the Cu ions aligned, since nearest-neighbor spacings are comparable in all three directions. However, we have no evidence in the present experiments that the Cu ions order.

We now turn to our results at small wave vectors. In a SANS experiment we would expect to observe a paramagnetic signal, which would be superposed on metallurgical scattering which rises steeply at very small q. Since the ordering temperature is so low, the magnetic correlations caused by the Er magnetism will be negligible in the vicinity of the superconducting transition. Above T_c the magnetic scattering is independent of q, which means that fluctuations of all wavelengths are equally likely to occur. Below T_c, however, it will cost additional energy to make fluctuations with wavelengths which are comparable to or larger than the London penetration depth, and hence we would expect the fluctuations for $q \lesssim 1/\lambda_L$ to be suppressed in amplitude. Subtracting the data above T_c from the data below T_c will then emphasize any changes in the observed scattering, while the metallurgical scattering should cancel.[9] Some difference data at two temperatures are shown in Fig. 2. Above T_c we did not detect any change in scattering, while at 75 K we see a small effect which is statistically significant; all the data points are below zero or within one standard deviation of zero. Reducing the temperature to 60 K clearly suppresses the scattering further, while little additional change was found at lower T. We remark that one important check is to compare the magnitude of the decrease in the scattering at small Q with the observed intensity of the raw data at large Q, where the nuclear scattering is small and the paramagnetic scattering dominates. For the paramagnetic suppression interpretation to be valid, we can certainly not reduce the scattering at small q more than the paramagnetic intensity that was originally there, so that the intensity at large Q places an upper bound on the overall size of the possible effect.[9] The data of Fig. 2 are well within this bound.

The results for the temperature dependence of the scattering are shown in the top portion of Fig. 3. The data at each Q exhibit the same T dependence, so we have summed the data over a range of wave vectors from 0.023 to 0.037 Å^{-1} to improve the statistics. The intensity

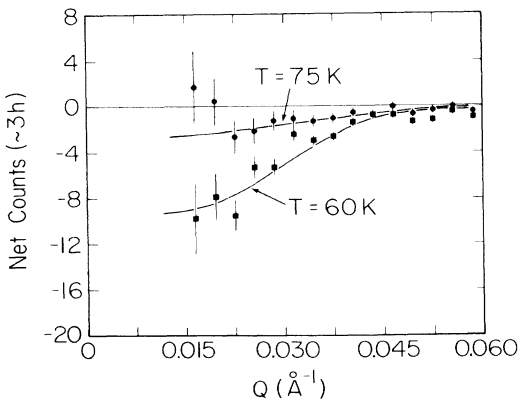

FIG. 2. Wave-vector dependence of the net intensity for two temperatures below T_c.

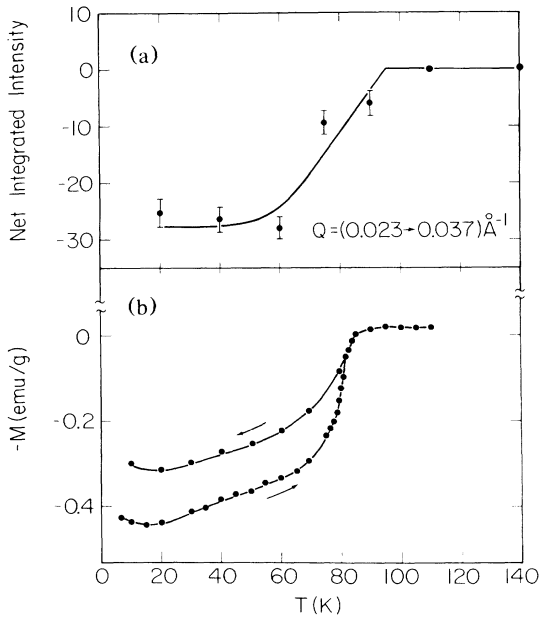

FIG. 3. (a) Temperature dependence of the scattering, integrated over the Q range of 0.023 to 0.037 Å^{-1}. (b) Temperature dependence of the magnetization.

clearly decreases below the superconducting transition temperature, and exhibits behavior which is quite similar to the behavior of the magnetization as shown in the bottom portion of the figure. Here the cooling data were taken in an applied field of 100 Oe, while the warming data were obtained by cooling in zero field, and then applying a field of 100 Oe.

Experimentally we have demonstrated that the SANS scattering decreases below the superconducting transition. If it is correct to interpret this change as due to magnetic screening, then we can use the data of Fig. 2 to estimate the magnetic screening length in this material. The screening in real space should be described by an exponential, which yields a squared Lorentzian scattering function with $\lambda_L = (\sqrt{2}-1)^{1/2}/q_{hw}$. A fit to this functional form yields $\lambda_L \approx 22$ Å, which would be a very small London length. We can compare this value to the related oxide superconductor $La_{1.85}Sr_{0.15}CuO_4$, where λ_L has been measured[10,11] to be 2000–2500 Å. This range is typical for a strong type-II superconductor, and suggests that our screening length is not a direct measure of λ_L. Another relevant length scale is, of course, the superconducting coherence length ξ_0, which is the correct order of magnitude. A second possibility is that the screening in these magnetic superconductors occurs on the length scale of $(\gamma\lambda_L)^{1/2}$, where γ is the magnetic stiffness parameter.[4] This is the quantity which controls the size of the oscillatory wave vector in the "low T_c" magnetic superconductors, and is also the correct order of magnitude. A more interesting possibility, however, is that the change we observe originates from another property of these oxide superconductors unrelated to the Er magnetism. It would be very useful to have a direct measurement of the London penetration depth of this material.

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*Permanent address: Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China.

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