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Single-crystal neutron-diffraction investigation of the magnetic ordering of the high-temperature superconductor $ErBa_2Cu_3O_{7-\delta}$

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Neutron-diffraction experiments on single crystals of $ErBa_2Cu_3O_{7-\delta}$ ($T_c \simeq 88$ K) show that Er moments order at about 500 mK with an antiferromagnetic structure with the wave vector $\mathbf{k}=(\frac{1}{2},0,0)$. The magnetic moment of Er atoms is determined to be $4.8(2)\mu_B$ and is oriented perpendicular to the wave vector, i.e., along the b axis. This result differs from that of our previous powder investigations.

Following the discovery of the high-temperature superconductivity in $YBa_2Cu_3O_{7-\delta}$ ($T_c=90$ K) (Ref. 1) it has been found that Y atoms can be substituted entirely by almost all of the rare-earth elements, except for Ce, Pr, and Tb, without changing the superconducting properties.[2,3] The magnetic moments carried by the rare-earth atoms have apparently no influence on the superconducting properties. Many of these rare-earth substituted compounds show magnetic ordering[4] at low temperatures and the ordered antiferromagnetic state coexists with the superconducting state. Three-dimensional magnetic ordering[5,6] has been reported in $GdBa_2Cu_3O_{7-\delta}$ and $DyBa_2Cu_3O_{7-\delta}$. Two-dimensional magnetic ordering in $ErBa_2Cu_3O_{7-\delta}$ has been reported by Lynn *et al.*[7] in the temperature range $0.3\ \text{K} < T < 0.5$ K. We have recently reported[8] three-dimensional ordering of $ErBa_2Cu_3O_7$ in a powder sample. Two independent wave vectors $\mathbf{k}_1=(\frac{1}{2},0,0)$ and $\mathbf{k}_2=(\frac{1}{2},0,\frac{1}{2})$ were required to describe the magnetic reflections. The model (model 1 of Ref. 8) which gave the best fit between observed and calculated structure factors is one in which Er moments are inclined at an angle of 32° to the crystallographic c axis. However, we showed that another model (model 3 of Ref. 8) in which the magnetic moments are oriented along b also gave a close fit. The observation of two independent wave vectors indicates the existence of both ferromagnetic and antiferromagnetic coupling between moments along the c axis. We preferred to interpret the presence of two independent wave vectors as showing that the powder consists of two separate phases each having a single wave vector. An alternative interpretation would be that two different wave vectors coexist in the crystal. This would result in a structure in which alternate layers of Er atoms perpendicular to the c axis have no ordered magnetic moment and the remaining layers couple ferromagnetically giving a sequence $(+0+0)$ along the c axis. Such a model would explain the equivalence of the moments corresponding to the two wave vectors, but seems physically unlikely. In short, no unique magnetic structure for $ErBa_2Cu_3O_7$ could be derived from these powder investigations. Therefore, we decided to reinvestigate the magnetic structure of $ErBa_2Cu_3O_7$ with single crystals as soon as single crystals became available to us. In this Rapid Communication we describe and discuss the results of our single-crystal neutron investigation.

Single crystals of $ErBa_2Cu_3O_{7-\delta}$ were prepared using a flux growth technique. The flux consisted of excess CuO and BaO, and the growth composition that produced the crystals used in the present study was 0.03 mol $ErO_{1.5}$, 0.12 mol $BaCO_3$, and 0.3 mol CuO. Powders of high-purity Er_2O_3, $BaCO_3$, and CuO were intimately ground together by making a methanol-powder slurry which was loaded into an automatic powderizing chamber containing agate cylinders. The well-mixed powder was loaded into a high-density zirconia crucible and heated in air to 985 °C. After soaking for 5 h at 985 °C, the partially molten material was cooled at 800 °C at 2.5 °C/h after which the furnace was turned off. The only crystals that could be successfully separated from the flux were found in small cavities along the sides or within the bulk of the solidified mass. The crystals grew as thin square plates with typical dimensions of $3\times3\times0.2$ mm, although in removing the crystals from the flux some breakage often occurred that resulted in thin crystal plates with a more irregular shape. The as-grown crystals were oxygen deficient and hence, were heated in flowing oxygen at 490 °C for 2 weeks to obtain the optimum superconducting properties. The superconducting transition temperature T_c measured magnetically was 88 K (midpoint) and 89.5 K when 90% in the normal state. Two such crystals were fixed on an aluminum plate which was fixed to the cold tip of the ^{3}He-^{4}He dilution fridge at the diffractometer $D15$ at the Institut Laue-Langevin. The b axis of the crystal was parallel to the ω axis of the diffractometer. Ten centered

nuclear reflections yielded the lattice parameters $a=3.82(2)$ and $c=11.85(6)$ Å. Because of the twinning of the crystal we could not distinguish between the a and b axes and we have arbitrarily chosen the axis in the scattering plane to be the a axis.

The search for magnetic reflections yielded intensities corresponding to the wave vector $\mathbf{k}=(\frac{1}{2},0,0)$. No intensities were observed at $(\frac{1}{2},0,\frac{1}{2})$ or $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ positions. Both the single crystals gave the same single wave vector $\mathbf{k}=(\frac{1}{2},0,0)$ in contradiction to our previous powder investigations[8] which gave two wave vectors $(\frac{1}{2},0,0)$ and $(\frac{1}{2},0,\frac{1}{2})$. We measured 14 and 8 independent magnetic reflections from the two domains $k_1=(\frac{1}{2},0,0)$ and $k_2=(0,\frac{1}{2},0)$, respectively, from one of the crystals along with 9 independent nuclear reflections, at about 90 mK.

The magnetic reflections were put in the absolute scale by determining the scale factor using 9 independent nuclear reflections from the known crystal structure model. Several magnetic structure models were tried. Since there is only one Er atom in the chemical cell the magnetic coupling is uniquely determined by the wave vector $(\frac{1}{2},0,0)$. The Er moments couple antiferromagnetically along a and ferromagnetically along b and c. Model 1 is a model in which the magnetic moments lie in the b-c plane and their direction in this plane is determined. It is to be noted that in our powder investigations[8] on $ErBa_2Cu_3O_7$ this model gave the best fit with moments inclined to c by 32°. In model 2 the magnetic moments are fixed along c, and in model 3 the magnetic moment is confined to the a-b plane and its orientation in the plane determined. Model 2 did not give a good fit between the observed and calculated structure factors whereas model 3 gave an excellent fit with the orientation of the magnetic moment parallel to b. The best fit with model 1 was obtained when the magnetic moments were at an angle of $82\pm5°$ from c and, therefore, is almost equivalent to model 3. Figure 1 illustrates this magnetic structure model which gave the agreement factor $R=0.061$. All these refinements were performed with the reflections from both $(\frac{1}{2},0,0)$ and $(0,\frac{1}{2},0)$ domains. Table I gives the observed and calculated structure factors based on the three models. The magnetic moment per Er atom determined from model 3 is $4.8(3)\mu_B$ at 90 mK, and is in good agreement with that obtained from specific-heat data.[9] This reduction of moment to about half of the free ion value of 9 μ_B is due to crystal-field effects.

Figure 2 shows the temperature variation of the intensity of the $(\frac{1}{2}00)$ magnetic reflection as a function of temperature. The Néel temperature is determined from this intensity variation to be about 500 mK. This result is clearly in variance with those of Lynn *et al.*[7] who observed only two-dimensional magnetic ordering in $ErBa_2Cu_3O_7$ down to 300 mK. Our results clearly establish that the three-dimensional magnetic ordering in $ErBa_2Cu_3O_{7-\delta}$ ($T_c\simeq88$ K) takes place at about 500 mK. The temperature variation of the sublattice magnetization shows a typical two-dimensional behavior.

Our present single-crystal investigation shows that the magnetic structure of $ErBa_2Cu_3O_{7-\delta}$ ($T_c\simeq88$ K) is very simple in variance with our results for polycrystalline samples[8] in which two independent wave vectors $\mathbf{k}_1=(\frac{1}{2},0,0)$ and $\mathbf{k}_2=(\frac{1}{2},0,\frac{1}{2})$ were found. In the analysis of the powder data the best fit was obtained for a model in which the magnetic moments are oriented at 32° to the c axis in the b-c plane although the model with magnetic moments parallel to b gave a reasonable fit. This illustrates that magnetic structure determination with a few poorly resolved intensities should be treated with caution. A recent powder-diffraction experiment[10] on $ErBa_2Cu_3O_{6.53}$ ($T_c=54$ K) showed the presence of a single wave vector $k=(\frac{1}{2},0,\frac{1}{2})$. It is therefore tempting to ascribe the presence of two wave vectors in our first powder investigation[8] due to the presence of two phases, one with the almost full oxygen stoichiometry 7 and the other with the oxygen stoichiometry of about 6.5. In fact, this was our preferred conclusion and we rejected the idea of having two wave vectors in the crystal. However, this interpretation does

TABLE I. Observed and calculated magnetic intensities for different structure models. Model 1 is the model in which the magnetic moments of Er atoms are restricted in the b-c plane and their orientation is refined (angle from the c axis $=82\pm5°$). Model 2 is the one in which the moments are parallel to c. In model 3 the spins are restricted in the a-b plane and their orientation is refined which gave the best fit for orientation parallel to b, i.e., perpendicular to the wave vector. The final line of the table gives the goodness of fit parameter χ^2 for the three models. χ^2 is given by $\chi^2=[1/(n_{obs}-n_{par})]\sum_{obs}(F_{obs}-F_{calc})^2/\Delta F_{obs}^2$, where n_{obs} and n_{par} are the number of observation and the number of parameter, respectively, and ΔF_{obs} is the standard deviation of F_{obs}. χ^2 should approach 1 for the best fit.

				F_{calc}		
h	k	l	F_{obs}	Model 1	Model 2	Model 3
$\frac{5}{2}$	0	0	7.7(2)	7.6	8.3	7.5
$\frac{3}{2}$	0	0	9.6(1)	9.4	10.4	9.4
$\frac{1}{2}$	0	0	10.6(1)	10.7	11.8	10.7
$\frac{1}{2}$	0	1	10.7(1)	10.6	9.8	10.6
$\frac{3}{2}$	0	1	9.4(2)	9.4	10.1	9.4
$\frac{5}{2}$	0	1	7.0(3)	7.5	8.2	7.5
$\frac{1}{2}$	0	2	10.2(2)	10.3	7.0	10.4
$\frac{5}{2}$	0	2	6.9(4)	7.4	7.9	7.4
$\frac{1}{2}$	0	3	9.9(2)	10.0	5.0	10.0
$\frac{3}{2}$	0	3	10(1)	8.9	8.2	8.9
$\frac{1}{2}$	0	4	9.1(4)	9.5	3.8	9.6
$\frac{3}{2}$	0	4	8(1)	8.5	7.1	8.5
$\frac{5}{2}$	0	4	6(1)	6.9	6.8	6.9
$\frac{1}{2}$	1	0	5.0(3)	5.0	6.8	5.0
$\frac{1}{2}$	1	1	5.6(3)	5.6	6.5	5.6
$\frac{1}{2}$	2	1	2(2)	2.9	5.6	2.8
$\frac{1}{2}$	1	2	6.9(2)	6.7	5.7	6.7
$\frac{1}{2}$	2	2	2(1)	3.6	5.3	3.5
$\frac{1}{2}$	1	3	7.1(4)	7.5	4.8	7.5
$\frac{1}{2}$	2	3	3.3(8)	4.2	4.9	4.2
$\frac{1}{2}$	2	4	3.8(8)	4.8	4.4	4.7
	χ^2			0.915	85	0.926

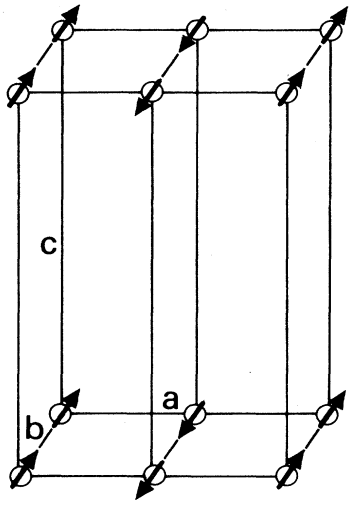

FIG. 1. The magnetic structure of $ErBa_2Cu_3O_{7-\delta}$ ($T_c = 88$ K) determined from single neutron-diffraction investigations.

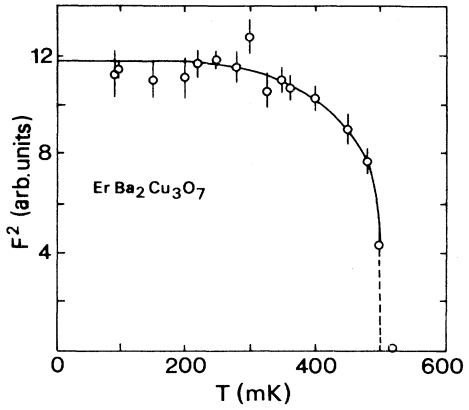

FIG. 2. Temperature variation of the intensity of $(\frac{1}{2}00)$ magnetic reflection.

not explain why the two phases were present in equal amounts in our powder investigation[8] and is not compatible with the sharp superconducting transition[8] at about 90 K. It has to be noted that the difference between these two magnetic structures lies in the stacking of the antiferromagnetic planes. This stacking is ferromagnetic for the wave vector $\mathbf{k}_1 = (\frac{1}{2},0,0)$ and is antiferromagnetic for $\mathbf{k}_2 = (\frac{1}{2},0,\frac{1}{2})$. The energy difference between these two types of structures is very small and it is therefore not surprising to find these two wave vectors coexisting in the same sample. This argument may also be relevant to the observation of different magnetic structures for $GdBa_2Cu_3O_{6.53}$ obtained from single crystal[11] $[k = (\frac{1}{2},\frac{1}{2},0)]$ and powder[5,12] $[k = (\frac{1}{2},\frac{1}{2},\frac{1}{2})]$ investigations. Similarly, both ferromagnetic and antiferromagnetic coupling of the copper moments along c have been observed[13,14] in oxygen deficient $YBa_2Cu_3O_{6+x}$ and $NdBa_2Cu_3O_{6+x}$ corresponding to the wave vectors $(\frac{1}{2},\frac{1}{2},0)$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

The origin of the magnetic interaction between the rare-earth atoms in $RBa_2Cu_3O_{7-\delta}$ along the c axis, for which rare-earth atoms are separated by about 12 Å is still not resolved. The present results provide further evidence that the sign of the exchange interactions depends rather strongly on the oxygen content and hence, that some degree of superexchange is involved.

Note added in proof. Recently, Paul *et al.*[15] have reported the observation of both $(\frac{1}{2},0,0)$ and $(\frac{1}{2},0,\frac{1}{2})$ wave vectors in $ErBa_2Cu_3O_{7-\delta}$. However, they have performed experiments on five crystals fixed together and, therefore, these two different wave vectors may originate from two groups of crystals with different oxygen content.

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