RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 13 1 NOVEMBER 1987

Antiferromagnetic order in $DyBa_2Cu_3O_7$

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(Received 7 August 1987)

Neutron diffraction measurements on the high-temperature superconductor $DyBa_2Cu_3O_7$ have revealed antiferromagnetic ordering of the Dy moments below 1 K. The magnetic unit cell is obtained from doubling the orthorhombic chemical unit cell along all three basis vectors; $\mathbf{q}_{\text{magnetic}}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Within experimental error, the moments are aligned along the c axis of the structure and the ordered moment is $7.2\pm0.6\mu_B$, which is smaller than the full moment of $10\mu_B$.

In most known superconductors, even dilute concentrations of paramagnetic impurities suppress the superconducting transition temperature T_c or destroy the superconductivity completely.[1] Therefore, the discovery of coexistence between magnetic ordering and superconductivity in magnetic rare-earth (R) compounds such as $R\text{Mo}_6X_8$ (X=S, Se) and $R\text{Rh}_4\text{B}_4$ stimulated intense investigation of the interplay between magnetism and superconductivity.[2] The recent discovery[3] of superconductivity above 90 K in $YBa_2Cu_3O_7$ has generated great excitement, and was soon followed by the substitution of magnetic rare earths (RE) such as Gd, Dy, Ho, and Er for Y. Studies[4,5] of the magnetic and superconducting properties of several of the $R\text{Ba}_2\text{Cu}_3\text{O}_7$ compounds have shown that these substitutions result in little or no effect on the superconductivity. In these materials, the RE sites are well removed from the copper-oxygen planes and so the exchange interaction between the moments and the conduction electrons is weak, in analogy with the situation for the ternary systems mentioned above. Specific-heat measurements performed on the Gd-, Dy-, and Er-based systems display anomalies at low temperature consistent with the onset of magnetic ordering,[5] and structure in the specific heat of the Dy and Er compounds suggests the presence of crystalline electric field effects.[6] For both $ErBa_2Cu_3O_7$ and $DyBa_2Cu_3O_7$ the entropy associated with the magnetic transition is significantly less than that expected for ordering of the full moment, of $9\mu_B$ and $10\mu_B$ respectively, as determined from the high-temperature susceptibility measurements. In particular, measurements by Brown *et al.*[5] on $DyBa_2Cu_3O_7$ found a specific-heat anomaly at approximately 0.8 K, and estimated the entropy of ordering to be $1.24R\ln2$, far reduced from the full magnetic entropy of $R\ln16$ expected for $J=\frac{15}{2}$. This is again most likely attributed to a partial removal of the degeneracy of the angular momentum states due to the crystal field. In the case of $GdBa_2Cu_3O_7$ the full entropy is obtained, consistent with the absence of crystal-field effects for $L=0$.

Neutron diffraction measurements have been employed to probe the nature of the magnetic order in these systems. Lynn *et al.*[7] have recently demonstrated the onset of long-range two-dimensional antiferromagnetic correlations in $ErBa_2Cu_3O_7$ below approximately 0.5 K. Unfortunately, it was not possible to extend the measurements to lower temperature to determine the magnetic structure of the fully ordered state. In this paper we report the results of neutron diffraction measurements on $DyBa_2Cu_3O_7$, which orders antiferromagnetically at $T_N=1.0\pm0.05$ K. The magnetic unit cell is obtained from doubling the orthorhombic chemical unit cell along all three basis vectors, so the ordering wave vector is $\mathbf{q}_m=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The moments lie along the c axis of the structure, and the magnitude of the moment/Dy ion ($7.2\pm0.6\mu_B$) is smaller than the full moment.

Single-phase polycrystalline samples of $DyBa_2Cu_3O_7$ were produced by the solid-state reaction of high-purity DyO_3, $BaCO_3$, and CuO powders. The powders were first mixed, pressed into pellets, and sintered in air at 900 °C for 24 h. Next, the pellets were reground, mixed, pressed into pellets, and sintered under a flow of oxygen at 900 °C for 16 h, followed by a second annealing in oxygen at 600 °C for 16 h. The pellets were then slow cooled to room temperature under oxygen flow. X-ray measurements showed the sample to be essentially single phase, with no evidence of any impurity phase. Resistivity measurements show a sharp drop at 95 K (≈1 K width) signifying the onset of superconductivity. Susceptibility measurements indicate bulk superconductivity with the flux exclusion reaching 60% of the full Meissner effect. High-temperature specific-heat measurements on several of the heavy $R\text{Ba}_2\text{Cu}_3\text{O}_7$ superconductors exhibit a sharp jump at T_c of the same size as that obtained for $YBa_2Cu_3O_7$. These results certainly indicate that the superconductivity in the magnetic $R\text{Ba}_2\text{Cu}_3\text{O}_7$ is a bulk phenomenon.

Several pellets were placed into an aluminum sample holder which was then back filled with ^{4}He gas to ensure good thermal transfer at low temperature, and attached to the cold finder of a pumped ^{3}He cryostat. The temperature was controlled from 0.47 to 1.65 K to within ±0.01 K by regulating the pumping speed on the ^{3}He pot. Neutron scattering measurements were made on the H4M Triple-axis spectrometer at the Brookhaven High-Flux Beam Reactor using 14.7 meV neutrons, a pyrolytic graphite (PG) monochromator and analyzer, and a PG filter after the sample to suppress higher-order contamination of the diffracted beam.

Diffraction scans taken below and above the ordering temperature are shown in Fig. 1. At 1.3 K, all peaks can be indexed to nuclear scattering from either the $DyBa_2Cu_3O_7$ sample or the aluminum can. A few very weak impurity lines are also observed. The measured lattice constants of the orthorhombic chemical unit cell of $DyBa_2Cu_3O_7$ are $a=3.812$ Å, $b=3.887$ Å, and $c=11.678$ Å respectively. Below 1 K, additional peaks appear, and have been isolated by subtracting the data taken at 1.3 K from that taken at 0.49 K as shown in the difference plot in Fig. 1. All peaks can be indexed to a magnetic unit cell obtained by doubling the $DyBa_2Cu_3O_7$ chemical unit-cell dimensions in all directions. This means that nearest-neighbor Dy ions, both in and out of the (a,b) basal planes, are antiferromagnetically coupled. The suppression of the background below zero in the difference plot is attributed to the expected reduction of the diffuse paramagnetic scattering below the Néel temperature.

Fortunately, the low symmetry of the orthorhombic structure allows a unique determination of the moment direction in this compound. Only the component of the magnetic moment perpendicular to the momentum transfer ($\mathbf{Q}$) can be probed in neutron measurements. Qualitatively, one can see from the difference plot in Fig. 1 that the moment direction is along the c axis. For instance, the sequence of relative intensities of the $(hhl)_m$ reflections, $I(111)_m > I(113)_m > I(115)_m > I(117)_m$ is understood by recalling that the angle between $\mathbf{Q}$ and the c axis decreases as l increases. Here, the subscript means that the indices of the reflections are based on the magnetic unit cell of the structure rather than the chemical unit cell. Furthermore, the observation that the intensities of reflections $(hkl)_m$ and $(khl)_m$ are the same within experimental error, implies that the projection of the moments along the a and b basis vectors must be the same, or absent.

We can quantify the above remarks by using the nuclear reflections, and known nuclear structure factors, to put the magnetic scattering cross section in absolute units. The integrated intensity of each magnetic peak is proportional to the magnetic structure factor squared,

$$F_m^2 = \gamma_0^2 M_{\text{eff}}^2 \, |f(Q)|^2 \left[\sum_j e^{i\mathbf{Q}\cdot\mathbf{R}_j} \right]^2 (1 - \langle (\hat{\mathbf{Q}}\cdot\hat{\mathbf{M}})^2 \rangle) \ .$$

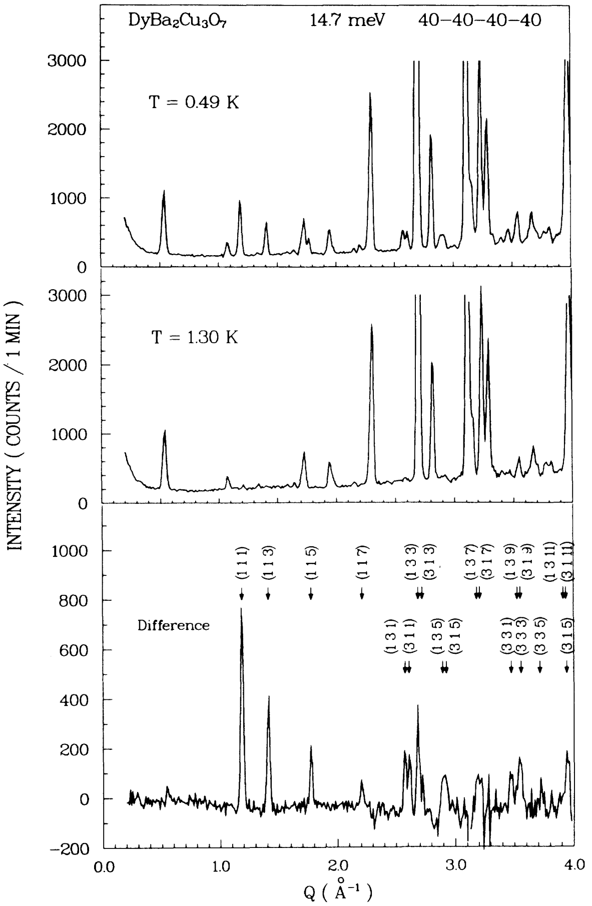

FIG. 1. Neutron diffraction patterns of $DyBa_2Cu_3O_7$ taken at $T=0.49$ K (top panel) and $T=1.3$ K (middle panel). The difference, $I(0.49\text{ K}) - I(1.3\text{ K})$ is shown in the bottom panel along with the indexing based on the doubled orthorhombic unit cell. The intensities of the higher-order reflections [particularly (133)] are less reliable due to the close proximity of strong nuclear reflections, and have not been used in the fit (see Table I).

Here, $\gamma_0^2 = 0.073$ barns/μ_B^2, M_{eff} is the effective moment per ion, $f(Q)$ is the magnetic form factor for Dy,[8] and the sum is performed over all Dy atoms in the magnetic unit cell. Since these measurements were performed on a polycrystalline sample, the angle between the moment direction and $\mathbf{Q}$ must be averaged over all equivalent

TABLE I. Observed and calculated magnetic structure factors for $DyBa_2Cu_3O_7$ at $T=0.5$ K expressed in barns per magnetic unit cell. The calculated structure factors are for an ordered moment of $7.2\mu_B$ directed along the orthorhombic c axis. The magnetic form factor for Dy^{3+} is taken from Ref. 8.

$(hkl)_m$	$\langle Q \rangle$ ($Å^{-1}$)	$1-\langle(\hat{\mathbf{Q}}\cdot\hat{\mathbf{M}})^2\rangle$	$\lvert f(Q) \rvert^2$	F_m^2(calc) barns/magnetic	F_m^2(obs) unit cell
111	1.184	0.95	0.92	206	215 ± 12
113	1.407	0.67	0.86	136	148 ± 12
115	1.771	0.42	0.79	78	76 ± 34
117	2.208	0.27	0.72	46	46 ± 14
131	2.575	0.99	0.67	157	146 ± 15
311	2.608	0.99	0.67	157	127 ± 15

reflections.[9] Table I compares the measured intensities, corrected for self-shielding (absorption) effects, with the magnetic structure factor calculated for $M_{\text{eff}} = 7.2\mu_B$ and $\hat{\mathbf{M}} \| \hat{\mathbf{c}}$. The agreement is quite good.

Figure 2 shows the temperature dependence of the $(111)_m$ reflection between 0.5 K and 1.65 K. From these data we determine the Néel temperature to be 1.0 ± 0.05 K, which is close to the ordering temperature obtained from specific-heat measurements on this compound.

The three-dimensional (3D) magnetic order in $DyBa_2Cu_3O_7$ is in sharp contrast to the 2D long-range correlations observed in $ErBa_2Cu_3O_7$ by Lynn *et al.*[7] In another well-known layered compound, K_2NiF_4,[10] the magnetic scattering above T_N is characteristic of a 2D antiferromagnet with very long-range correlations in the planes of Ni atoms, and no measurable correlations between the planes along the c axis of this tetragonal structure. Below 97 K, long-range 3D order is established in K_2NiF_4, but no accompanying 3D critical scattering is observed on approaching T_N from above or below. With this, and the magnetic scattering data on the Er compound in mind, we have performed preliminary measurements of the diffuse scattering around the $(111)_m$ antiferromagnetic reflection and the $(100)_m$ and $(110)_m$ points at temperatures slightly above 1 K. Diffuse scattering about $(111)_m$ was clearly evident, while no scattering was observed at either $(100)_m$ or $(110)_m$. This indicates that the magnetic interactions in $DyBa_2Cu_3O_7$ are 3D-like.

What is the nature of the interactions which produce antiferromagnetic ordering of the RE sublattice in these materials? This is a complex issue. The fact that no substantial effect on the superconductivity is observed upon the substitution of magnetic RE ions indicates that the exchange interaction between the RE ion moment and the conduction electrons is weak. In turn, this will reduce the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between RE ions substantially. One must consider magnetic dipolar interactions along with anisotropy due to crystal-field effects; both may be significant at these low ordering temperatures. The reduction in the ordered moment of both the Er- and Dy-based compounds, as well as the reduced entropy of ordering, provides strong evidence of the importance of crystal fields in these systems. Several groups have considered the importance of dipolar interactions.[4,7] In particular, Lynn *et al.*[7] point out that since the distance between the RE ions along the c axis is three times larger than the in-plane separations, the dipolar interaction between planes is much smaller, consistent with the observation of long-range magnetic correlations only in the (a,b) planes.

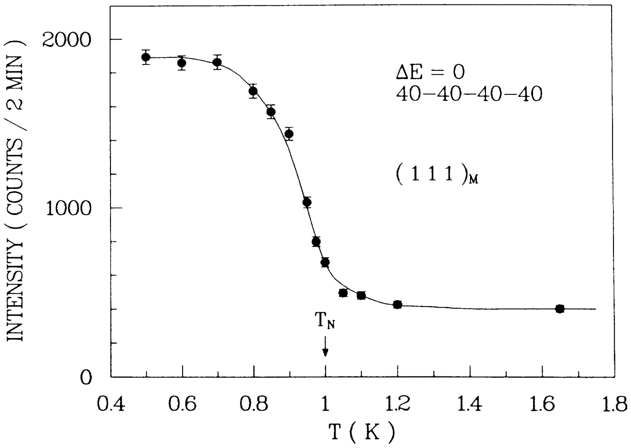

FIG. 2. Temperature dependence of the $(111)_m$ magnetic reflection.

While the immediate interest in the $RBa_2Cu_3O_7$ compounds of course lies in the high superconducting transition temperatures, the magnetic properties and interplay between magnetism and superconductivity deserve further investigation. In particular, the effects of the crystalline electric field at the RE site seem to strongly influence the magnetic properties of these systems. The level scheme appropriate to each $RBa_2Cu_3O_7$ compound needs to be established in order to determine the anisotropies and ground states of the RE ions. It seems likely that the striking difference between the magnetic structures of $DyBa_2Cu_3O_7$ and $ErBa_2Cu_3O_7$ is at least partly due to differences in the respective crystal-field schemes. Inelastic neutron scattering measurements on the $RBa_2Cu_3O_7$ series, as well as diffraction measurements on the Gd-based compound are currently underway.

We gratefully acknowledge useful interactions with D. E. Cox, V. J. Emery, J. Hurst, J. W. Lynn, A. Moodenbaugh, R. N. Shelton, and G. Shirane. Work at Brookhaven was supported by the Division of Material Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76Ch00016. Work at Temple University was supported under the National Science Foundation Grant No. DMR 8219782.

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