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Magnetic ordering in the high-temperature superconductor $GdBa_2Cu_3O_7$

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Neutron diffraction has been employed to study the magnetic ordering in the high-temperature superconducting compound $GdBa_2Cu_3O_7$. The compound is found to undergo an antiferromagnetic transition with the Gd magnetic moments ordering at 2.22 ± 0.07 K. The ordering is shown to be three dimensional with a doubling of the orthorhombic unit in all three directions. An analysis of the intensities of the observed magnetic Bragg reflections shows that the ordered magnetic moment per Gd atom is $(7.4 \pm 0.6)\mu_B$ and lies along the c axis of the orthorhombic cell. It is unlikely that dipolar ordering can explain the occurrence of this magnetic phase transition where the system locks into a three-dimensional ordered arrangement at the Néel temperature, since the separation of the Gd atoms along the c axis is approximately three times that along the a,b axes.

The discovery of superconductivity at elevated temperatures in various barium- or strontium-doped samples of lanthanum cuprate ($T_c \sim 35$ K, Ref. 1) and, in the ordered compound $YBa_2Cu_3O_7$ ($T_c \sim 95$ K, Ref. 2) has led to considerable interest and speculation amongst members of the scientific community. Because of the magnitude of the transition temperatures, it is thought that it may not be possible to explain the occurrence of superconductivity in such materials using the conventional electron-phonon coupling model (BCS), and that some other mechanism must be invoked to satisfactorily explain the properties of these compounds.[3] Various alternative models have been proposed based on bipolaronic, excitonic, or antiferromagnetic interactions that might permit electron pairing to exist at high temperatures. Although each of the available models has attractive features for explaining particular aspects of various experimental findings, the fundamental mechanism responsible for the origin of the superconducting state in these novel substances is still not established.

The substitution of other rare-earth ions in these compounds allows the study of the importance of the yttrium atom in maintaining the superconducting state and permits the observation of the coexistence of magnetism and superconductivity in these materials where the superconductivity may be of an unusual type, and arises from a much stronger interaction than is the case for conventional superconductors. Studies of rare-earth substitution in $YBa_2Cu_3O_7$ have shown that the yttrium atom may be entirely replaced by most of all the rare earths, the exceptions being Ce, Pr, and Tb, without substantially altering the superconducting properties of the compound.[4] Measurements of the susceptibility and magnetization of these materials confirm that the superconducting and magnetic properties are effectively independent of each other, and that the critical currents estimated from the magnetic hysteresis loops are similar for several rare-earth compounds.[5,6] Specific-heat measurements for $GdBa_2Cu_3O_7$ exhibit an anomaly at 2.22 K that is interpreted as evidence for antiferromagnetic ordering.[7] Similar anomalies, at lower temperatures, have been noted for other rare-earth compounds (i.e., Er, Ho, Dy).

Neutron scattering is an ideal tool to examine antiferromagnetism since it permits a direct observation of the form of the magnetic ordering and may also be used to estimate the magnitude, direction, and site of the magnetic moment. The experimental results presented in this paper confirm the proposed antiferromagnetic nature of the specific-heat anomaly and are of sufficient accuracy to allow the extraction of information concerning the gadolinium moment.

The superconducting material used in the present measurements was prepared by first mixing and grinding appropriate quantities of the constituents Gd_2O_3, CuO, and $BaCo_3$. The resulting mixture was then repeatedly fired at a temperature of 900 °C in an oxygen atmosphere and was reground between firings. The resulting powder was then cold pressed into cylindrical pellets that were sintered in pure oxygen by heating to 945 °C at a rate of 3 °C/min. The firing cycle consisted of a soak for 16 h at 945 °C followed by cooling to 475 °C at a rate of 0.5 °C/min. After soaking at 475 °C for 12 h, the furnace was turned off and allowed to cool directly to room temperature. Powder x-ray diffraction analysis of the resulting ceramics indicated that the material was single phase (i.e., less than 5% of any impurity phase was present) and that the material had the same structure as $YBa_2Cu_3O_7$. Since naturally

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occurring gadolinium is composed of several isotopes, some of which are highly absorbing for neutrons, the gadolinium oxide was prepared from gadolinium metal that was enriched in the low absorbing isotope ^{160}Gd to a concentration of 98.1% ^{160}Gd. The sample had a superconducting transition temperature of 85.9 K, as determined from the midpoint of a resistive measurement. After cooling the material to 4.2 K in zero magnetic field, a flux exclusion of 0.94 of the ideal Meissner diamagnetism was observed. About 0.5 of the ideal diamagnetism was observed at 82.7 K and 0.1 was found at 85.4 K. The somewhat lower transition temperature determined for this material as compared to other $GdBa_2Cu_3O_7$ samples is thought to result from chemical impurities present in the isotopically enriched ^{160}Gd used in the sample preparation.

The neutron-diffraction studies were performed using the D1a powder diffraction instrument at the Institut Laue-Langevin, Grenoble.[8] The incident wavelength of 3.006 Å was selected by reflection from the [113] plane of a germanium monochromator crystal, thus removing the half-wavelength contamination from the observed spectra. Diffraction spectra were collected at several temperatures (1.3–5 K) and over a scattered angular range of 100 degrees. The sample of $GdBa_2Cu_3O_7$ was crushed to a fine powder and held in a plate sample holder of thickness 3 mm that was aligned at 120° to the direction defined by the incident beam, thus reducing and simplifying corrections to the neutron scattered intensities due to residual absorption.

The nuclear scattering observed at 5 K is well described by the structure of the $YBa_2Cu_3O_7$ compound,[9] and relative intensities are satisfactorily reproduced by a calculation using the known scattering lengths of ^{160}Gd, Ba, Cu, and O. The lattice parameters from the orthorhombic unit cell are found to be $a = 3.844 \pm 0.002$, $b = 3.905 \pm 0.002$, and $c = 11.714 \pm 0.005$ in agreement with previous x-ray studies. The extraction of the magnetic scattering from the observed spectra at lower temperatures was performed by a subtraction technique. The data taken at 5 K were assumed to adequately describe the nuclear scattering at any lower temperature and were subtracted from the accumulated spectra at lower temperatures to leave the magnetic signal. Typical experimental observations at 1.5 K produced by this method are presented in Fig. 1. The quality and statistical significance of the experimental data are evident from this diagram. Eleven magnetic Bragg reflections are present in the angular range up to 90°; these reflections may be indexed, using multiples of half integers, on the orthorhombic unit cell of the nuclear structure. This indexation is included in Fig. 1 and immediately demonstrates that the material is antiferromagnetically ordered at 1.5 K. It is pleasing to note that, under the present experimental conditions, the D1a instrument has sufficient intrinsic resolution to resolve magnetic reflections that are split due to the small difference in the magnitude of the a,b lattice parameters [e.g., $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$, and $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$].

The widths of the Bragg reflections are resolution limited, within the experimental accuracy, and this suggests that the magnetic state corresponds to the development of long-range order in the compound. The remaining background, after the subtraction technique has been applied, is negative with a gradual decline in magnitude over the range of observation. This is to be expected since at a temperature of 5 K paramagnetic correlations still exist and the measurement will integrate over these dynamical processes to a certain extent. At a temperature of 1.5 K, the majority of the magnetic signal is located in the elastic Bragg scattering, and hence a subtraction of data from these two temperatures will produce magnetic Bragg scattering superimposed on a small negative signal from the paramagnetic response.

The magnetic ordering of the gadolinium sublattice in

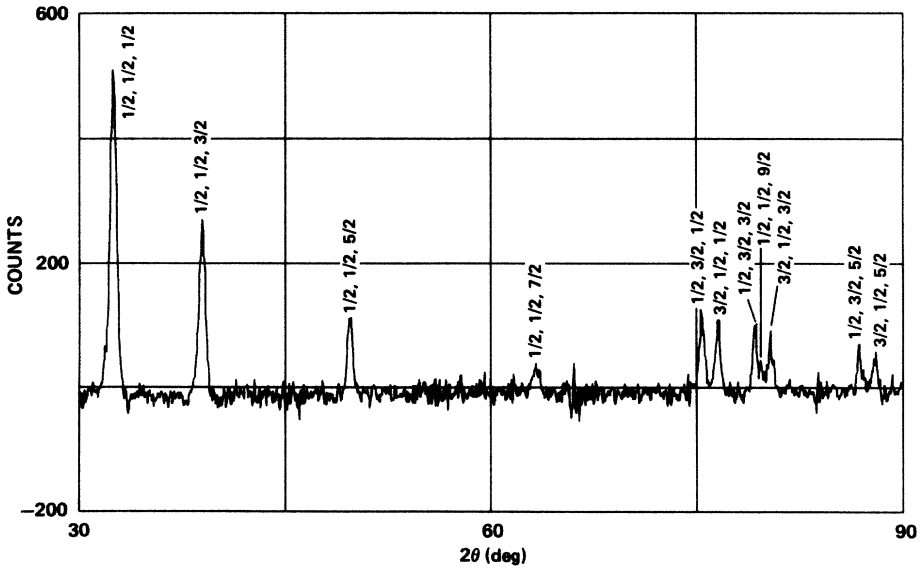

FIG. 1. Difference pattern taken for $GdBa_2Cu_3O_7$ in which data obtained at 5 K are subtracted from 1.5-K data. The result shows the diffraction pattern resulting from the magnetically ordered state.

this material is simply derived from the observed magnetic Bragg reflections. The indexed reflections would all be observed for an ordering that is face-centered orthorhombic on the up-spin sublattice, with all nearest neighbors antiferromagnetically aligned, and a representation of the ordered magnetic structure is presented in Fig. 2. This result shows that the magnetic ordering doubles the unit cell in all three directions, and hence, the magnetic structure is three dimensional. The intensity information contained in the magnetic Bragg scattering permits estimates to be made of the magnitude of the magnetic moment on the gadolinium site and its orientation with respect to the crystallographic axes. Taking into account the effects of absorption, instrumental resolution, and magnetic form factor, assumed to be the same as gadolinium metal,[10] and by scaling to the intensities of low-order nuclear Bragg reflections to place the calculation on an absolute scale, we find that the intensities of all the observed magnetic reflections are well described by a model which has a gadolinium magnetic moment of $(7.4 \pm 0.6)\mu_B$ aligned along the c axis.

The temperature dependence of the order for this magnetic transition, in this case the sublattice magnetization, may be examined by observing the temperature dependence of the intensity of the magnetic Bragg reflections. An example of such a temperature dependence for the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ magnetic Bragg reflection of $GdBa_2Cu_3O_7$ is presented in Fig. 3. From this data, we estimate the Neel temperature of $GdBa_2Cu_3O_7$ to be 2.22 ± 0.02 K. After removing the background intensity component, except for very near the transition, we can represent the intensity, and hence the sublattice magnetization, by a power law of

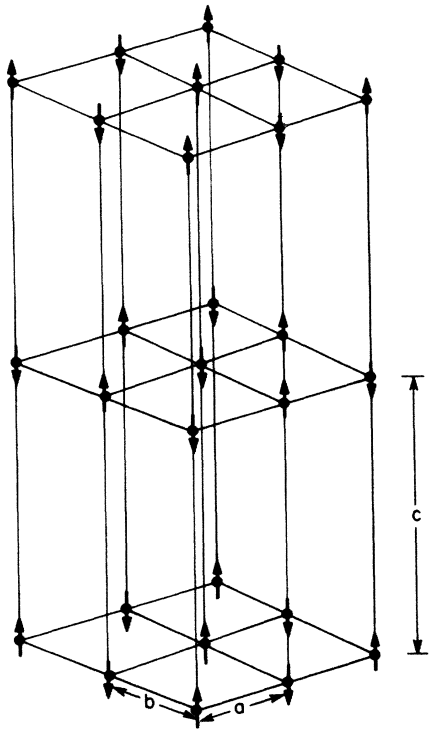

FIG. 2. Magnetic structure of $GdBa_2Cu_3O_7$ showing the moment direction of the Gd atoms at 1.5 K.

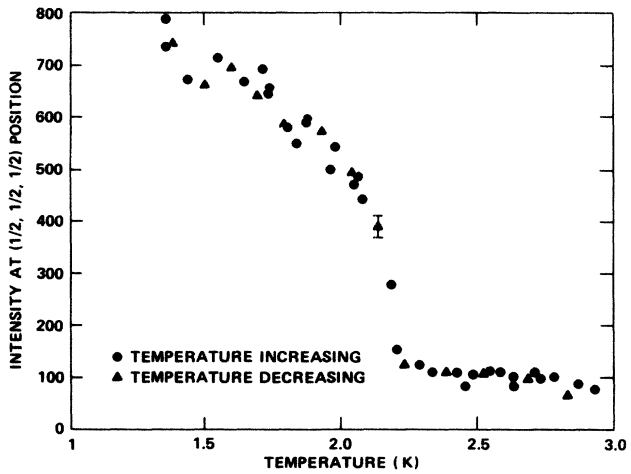

FIG. 3. Measurement of the temperature dependence of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ reflection showing the variation of the sublattice magnetization with temperature.

the form $M = t^{\beta}$, where $t = (T_n - T)/T_n$. An analysis of this form leads to an estimate of the exponent, giving $\beta = 0.15$. This value of the exponent for the power-law dependence of the sublattice magnetization may be strongly affected by small sample imperfections or impurities and indeed the transition could be first order.

A careful check for any hysteresis in this phase transition was made by taking data as the sample was cooled or heated through the Néel transition after allowing sufficient time for the material to come to equilibrium. Within the accuracy of the experimental measurements, there is no hysteresis present at this magnetic transition. Also, no evidence could be found for any precursor two-dimensional magnetic phase transition at temperatures of the Néel temperature (2.22 K) or greater.

The results of this experimental study are in complete agreement with the conclusions drawn from the anomaly observed in the specific heat at 2.22 K and hence validate their assumption that this anomaly is produced by antiferromagnetic ordering of the gadolinium sublattice. A particularly interesting observation drawn from the present measurements is that the magnetic ions lock into a three-dimensionally ordered state at the Néel temperature; no evidence for a higher-temperature two-dimensionally ordered state could be found. In a previous study of $ErBa_3Cu_3O_7$ where the Néel temperature is ~ 0.5 K, the magnetic ordering was found to be two dimensional down to 0.3 K.[11] The magnetic ordering in the a-b plane consisted of ferromagnetic lines of spins along one of the base plane directions which were antiferromagnetically coupled. The differences between the erbium and gadolinium compounds in terms of their magnetic ordering suggests that crystal field effects may play an important role in determining the magnetic ground state.

Calculations of the dipole energy for the observed magnetic structure give a value of 1.4 K. A simple mean-field model would then suggest a magnetic transition temperature of 0.6 K. However, if one shifts one layer of moments so that there are ferromagnetic chains along the c-axis, the dipole energy remains the same to four significant

figures. It thus appears that dipole fields cannot be responsible for the observed three-dimensional ordering. It is, therefore, necessary to appeal to an alternative mechanism such as the RKKY interaction or superexchange, although in the superexchange scenario, a convoluted exchange path would be required to explain the observed magnetic ordering. This interpretation raises the interesting question of how the magnetic interactions succeed in traversing the copper-oxygen layers, which are thought to be responsible for the superconductivity, without influencing the superconducting state.

Note added. After submitting this paper for publication, it was learned that a similar neutron study has been done on $DyBa_2Cu_3O_7$ which showed identical magnetic ordering but at a temperature near 1 K.[12]

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