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Magnetic ordering in $GdBa_2Cu_3O_{6.14}$

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Neutron scattering has been used to determine the magnetic order of the Gd in the oxygen-deficient compound $GdBa_2Cu_3O_{6.14}$. The ordering is found to be identical to that found earlier for the superconducting composition by Paul *et al.* This differs from a result by Chattopadhyay *et al.*, who found a variation in the magnetic structure of the oxygen-deficient compound.

The discovery of high-temperature superconductivity[1] in $YBa_2Cu_3O_7$ resulted in many studies being made of this material and similar materials with chemical substitutions on the various sites. Certainly one of the more interesting results was that the yttrium atom could be replaced entirely by almost all of the rare earths, with the exception of Ce, Pr, and Tb, without altering the superconducting properties.[2,3] The superconducting properties are not affected by the substitution of Gd for Y despite the fact that the Gd ion carries a large magnetic moment.

Specific-heat measurements for $GdBa_2Cu_3O_7$ showed an anomaly at 2.22 K which was interpreted as evidence for antiferromagnetic ordering.[4,5] Neutron scattering measurements by Paul *et al.*[6] showed long-range three-dimensional order in which the chemical cell doubles in all three directions. It was shown that dipole forces could not account for this magnetic structure so that some type of exchange mechanicism is necessary. Liu[7] has suggested that a modified RKKY interaction is responsible for the ordering. The standard RKKY interaction is not appropriate because the rare-earth moments do not interact with the conduction electrons at the Fermi surface.

When oxygen is removed from $GdBa_2Cu_3O_7$ the material becomes tetragonal and insulating. However, the heat-capacity feature signifying the magnetic transition remains unchanged,[8,9] and magnetic measurements show no difference in the rare-earth magnetism.[10] This is not unreasonable since the wave functions of the band electrons at the Fermi level are devoid of rare-earth $5d$ and $6s$ components. Since the heat-capacity feature has the same shape in both the superconducting and insulating material, and since the transition temperature is unchanged, it would seem likely that the magnetic structure would be unchanged as well. However, it has been reported by Chattopadhyay *et al.*[11] that the magnetic structure changes in the oxygen-deficient state. They studied a single-crystal sample that was weakly superconducting and thus probably had an oxygen concentration near 6.5. In their structure, the Gd moments are antiferromagnetically coupled to their nearest neighbors in the a-b plane, but are ferromagnetically coupled along the c axis. This is in contrast to the measurements on the O_7 material where the coupling along the c axis was found to be antiferromagnetic.

In view of the heat-capacity results, it seems surprising that the magnetic structure should depend on the oxygen concentration. Thus, we decided to remove some of the oxygen from our sample of $GdBa_2Cu_3O_7$ that was originally used to determine the magnetic structure and repeat the measurement. Oxygen was removed from the sample by heating it in high-purity helium. The oxygen concentration was determined by observing the weight loss during the heat treatment. The oxygen content was further checked using thermogravometric analysis while replacing the oxygen to the O_7 level after the experiment was completed. The oxygen content was determined to be 6.14 ± 0.04. High-resolution neutron-diffraction measurements showed a tetragonal unit cell as would be expected for this oxygen concentration.

To measure the magnetic structure the sample was placed in the same sample cell used in the earlier measurement. This was then placed in a low-temperature cryostat installed on the IN3 spectrometer at the Institut Laue Langevin. The neutron wavelength was 2.360 Å, and pyrolytic graphite filters were placed before and after the sample to avoid $\frac{1}{2}\lambda$ and $\frac{1}{3}\lambda$ contamination from the monochromator. Since IN3 is installed on a thermal guide, a very clean beam is available for the experiment. Measurements were first made at room temperature and showed the expected nuclear reflections from the $GdBa_2Cu_3O_{6.14}$ lattice.

The sample was then cooled to 1.5 K and additional reflections were observed from the magnetic ordering of the Gd. These were found to be the same reflections as

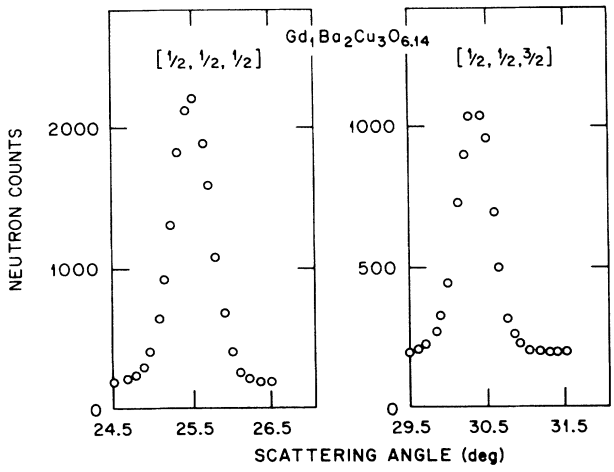

FIG. 1. Measurement of the first two magnetic Bragg reflections for 1.5 K.

observed in the earlier measurement of $GdBa_2Cu_3O_7$ except the splitting of the reflections from the orthorhombic distortion had disappeared. Figure 1 shows the two lowest angle reflections, the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and the $(\frac{1}{2},\frac{1}{2},\frac{3}{2})$. The counting time per point is about 45 seconds giving nearly 3000 counts per minute for the peak of the first reflection. The temperature dependence of the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ reflection is shown in Fig. 2. We were able to measure this temperature dependence more accurately than our earlier measurement with the superconducting sample because, while the IN3 spectrometer has only one detector, it has a higher neutron intensity. A measurement of one peak is

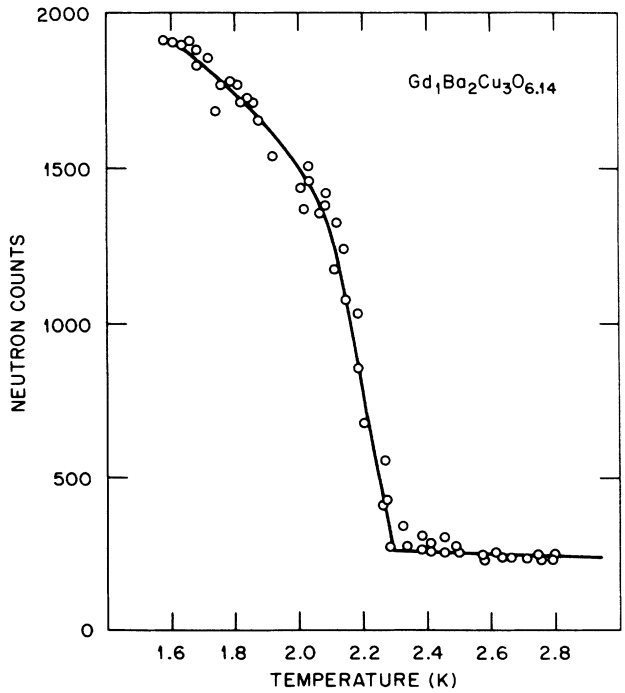

FIG. 2. Temperature dependence of the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ reflection.

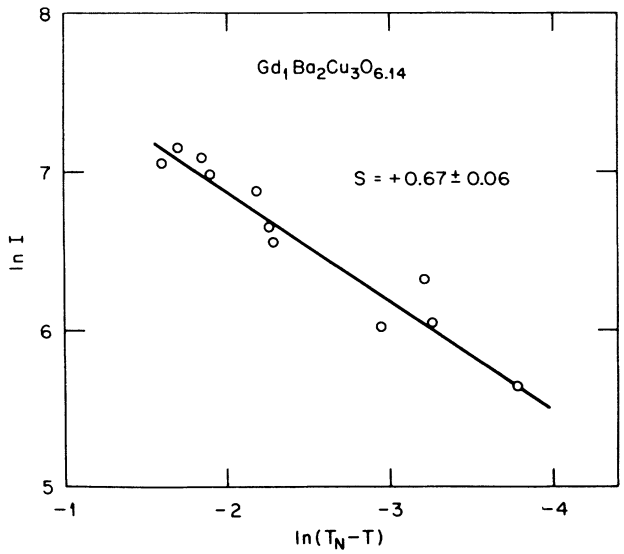

FIG. 3. Logarithmic plot of the temperature dependence of the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ reflection in the temperature region just below the transition. The slope S was determined by a least-squares fit to a straight line.

thus easier on IN3 than with the multidetector spectrometer used before. The lowest temperature was about 1.5 K. We note the intensity appears to be not saturated even at this low temperature. As the temperature increases, the neutron intensity decreases gradually until about 2.1 K, at which point it decreases faster until the transition T_N at 2.27 ± 0.03 K. Figure 3 shows a logarithmic plot of this temperature region. The data appear to be consistent with a straight line and a least squares fit gives a slope of $+0.67 \pm 0.06$. The neutron intensity varies as the square of the sublattic magnetization M, so that M varies as $(T_N - T)^{\beta}$ where β is 0.33 ± 0.03. This exponent is what might be expected for three-dimensional long-range order. As before, the magnetization disappears suddenly at the transition without much critical scattering being observed. No sign of any sizable two- or three-dimensional fluctuations was observed.

The result of the experiment makes sense in view of the previous heat capacity and magnetization measurements, and it is, therefore, difficult to reconcile the contradictory finding of Chattopadhyay *et al.*[11] Since they used a single crystal, normally one would expect that this would be the better measurement. However, since they did not use an isotopically enriched sample, their experiment was much more difficult. Counting times for their peaks were hours compared to a few minutes for our sample. Our experiment thus had a far superior signal to noise ratio. Furthermore, they used a very short neutron wavelength, giving much poorer resolution. Of course, it is possible that materials that have an oxygen concentration somewhere between the 6.14 and 7 values used in our experiments order in a different manner. It is also possible that small impurities may alter the magnetic structure. These are probably more likely in the crystal since our sample, when fully oxygenated, has excellent superconducting properties.

Note added in proof. We have now determined the magnetic structure for the composition $GdBa_2Cu_3O_{6.4}$ and have found it identical to that of the other compositions.

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