RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 1 1 JULY 1987

Antiferromagnetism and oxygen deficiency in single-crystal $La_2CuO_{4-\delta}$

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(Received 15 May 1987)

Two single crystals of undoped La_2CuO_4 are studied by neutron diffraction between $T=5$ and 300 K. In one crystal oxygen vacancies are created by heat treatment and the magnetic properties are found to depend strongly on this treatment. While the untreated sample is found to order antiferromagnetically at $T_N \simeq 50$ K, the heat-treated crystal orders at $T_N \simeq 150$ K with a somewhat larger moment. The magnetic structure is the same for the two crystals and supports previously reported powder results.

The discovery of high-T_c superconductivity[1-4] in materials of the type $La_{2-x}B_xCuO_{4-\delta}$, where B is Ba or Sr, has initiated a major effort in the study of these and related compounds. It is of great interest to explore the origin of the superconductivity, whether it may arise from spin fluctuations or electron-phonon interactions. Recently, Vaknin *et al.*[5] discovered superlattice peaks below $T=220$ K in a powder sample of pure $La_2CuO_{4-\delta}$ and interpreted this as antiferromagnetic ordering. Any doubt about the peaks being of magnetic origin was later removed by polarized-beam measurements.[6]

It has been suggested that the oxygen deficiency δ in these materials may play a role for the superconducting[4] and magnetic[7] properties. To investigate the oxygen dependence of the antiferromagnetism, two single crystals of the parent compound $La_2CuO_{4-\delta}$ have been studied with neutron diffraction. One crystal was grown under conditions to maintain the oxygen content ($\delta=0$), while the other crystal was heat treated in a vacuum in order to remove oxygen ($\delta>0$). It is of interest to study the undoped compound La_2CuO_4 since it provides the basis for an understanding of the physics of the superconducting materials, particularly because the electrons forming the Cu—O bonds are believed to be responsible for the superconductivity. There are also indications that undoped La_2CuO_4 may be superconducting.[8]

The structure[9,10] of La_2CuO_4 is tetragonal at high temperatures, while it undergoes an orthorhombic distortion at lower temperatures. An anomaly in the dc susceptibility has been observed,[7] and it is found that the temperature at which this anomaly occurs is strongly dependent on the oxygen deficiency δ. If the susceptibility anomaly is a signature of the antiferromagnetic transition, this suggests a strong coupling between the amount of oxygen present and the magnetic properties. It is also of interest to study the relation, if any, between the orthorhombic distortion and magnetic ordering.

The two crystals, each with a volume of ~ 1 mm^3, were grown in a flux, and one was thereafter sealed in an evacuated quartz capsule and heated to 400 °C for 16 h. The high-temperature tetragonal phase has the K_2NiF_4 structure (space group $I4/mmm$). In the orthorhombic phase (space group $Cmca$) the unit cell doubles so that if the tetragonal unit cell is (a,a,c), the orthorhombic cell corresponds to $(\sqrt{2}-\epsilon, c, \sqrt{2}a+\epsilon)$. This means that, e.g., the orthorhombic (200) reflection corresponds to the tetragonal (1,1,0). In the following, the orthorhombic notation is exclusively used.

During the neutron-diffraction experiments the crystals were kept in air in sealed aluminum containers and oriented in the $[hk0]$ scattering plane [see Fig. 1(a)]. The orthorhombic distortion in the crystal creates domains with interchanging orientations of [100] and [001]; hence, both directions are always represented in essentially equal proportions.

For the untreated crystal superlattice peaks at the (100), (120), (031), and (140) positions are observed below $T \simeq 50$ K, and for the heat-treated sample equivalent peaks develop below $T \simeq 150$ K. This observation is in agreement with the conclusion reached by Vaknin *et al.*[5] of an antiferromagnetic structure with the spin direction along the [001] orthorhombic axis and ferromagnetic sheets of Cu spins alternating along the [100] orthorhombic axis [see Fig. 1(b)].

The peak intensities for the (100) reflection corrected for background are shown in Figs. 2(a) and 2(b) for the untreated and heat-treated crystals, respectively. To exclude the possibility of double scattering events being responsible for the observed peak, several incident neutron energies E_i were applied around 41, 30.5, and 5 meV, and while sporadic occurrence of a peak at the (001) position was observed, the (100) peak remained unchanged by the choice of incident neutron energy. With $E_i=4.9$ meV we find a clean signal and have sufficient instrumental resolution to clearly demonstrate the difference between originally equivalent tetragonal reflections, i.e., (200) and

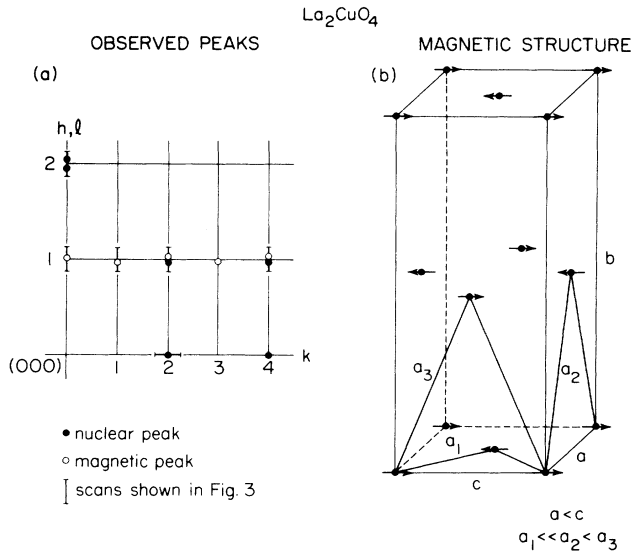

FIG. 1. (a) Sketch of the scattering plane for the alignment of the crystals in the present neutron-diffraction experiment. Also, the observed nuclear and magnetic Bragg peaks are shown. Note the displacements along the vertical (h,l) axis due to the orthorhombic distortion. The common indexing (h,l) of the vertical axis is due to the creation of domains with interchanging orientations of [100] and [001] in the orthorhombic distorted phase. (b) Magnetic spin structure of antiferromagnetic La_2CuO_4 proposed by Vaknin *et al.* (Ref. 5). Only copper atoms in the orthorhombic unit cell are shown for clarity.

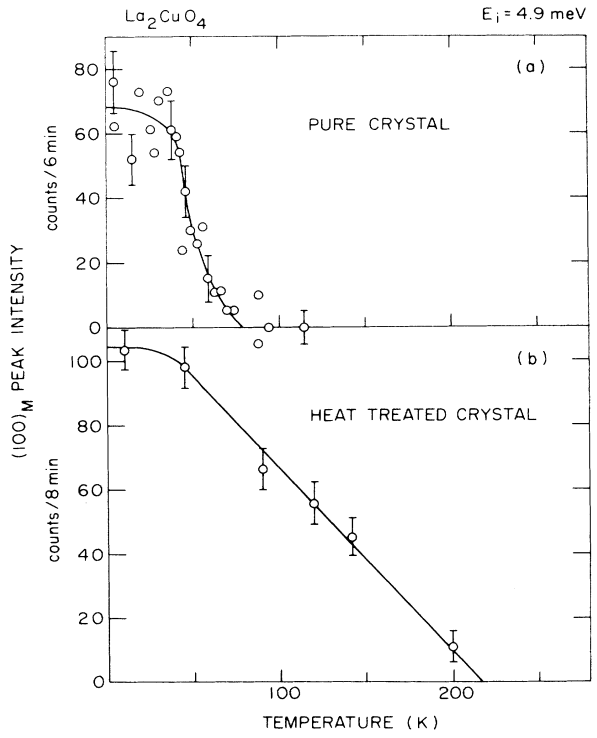

FIG. 2. Peak intensity as a function of temperature of the (100) magnetic Bragg reflection for (a) the untreated crystal, and (b) the crystal heat treated at 400 °C.

(002), (100) and (001), etc. In any case, the appearance of a peak at the (100) position can never originate from multiple nuclear scattering due to the selection rules for the allowed reflections of the present crystal structure.

The data in Fig. 2(a) for the untreated sample are interpreted as an order parameter for an antiferromagnetic phase transition with $T_N \simeq 50$ K. For the heat-treated crystal the data in Fig. 2(b) have a more linear dependence on temperature. We suggest that this is caused by inhomogeneities of the oxygen vacancies in the crystal. The transition temperature is therefore spread over the range between 100 and 200 K.

In Figs. 3(a)–3(f) a selection of scans is shown to demonstrate the indexing and accuracy of the positions of the measured peaks. All data in Fig. 3 are taken at $T=10$ K and incident neutron energy $E_i=4.9$ meV. The horizontal collimation was 20′-40′-20′-80′ providing a Q resolution better than 0.01 $Å^{-1}$ (full width at half maximum). Figure 3(a) shows the splitting of the (002) and (200) nuclear peaks caused by the orthorhombic distortion. The indexing is chosen so that $h=2$ corresponds to $2[(a^*+c^*)/2]$, i.e., the (200) and (002) reflections appear symmetrically around $h=2$. [This is the position of the tetragonal (110) reflection.] Figure 3(b) shows the undistorted nuclear (020) reflection. In Fig. 3(c) the reflection is clearly shifted to higher momentum transfer showing that the observed peak is (100) [rather than (001)]. The magnetic (011) peak in Fig. 3(d) is barely visible with the applied counting time. According to the

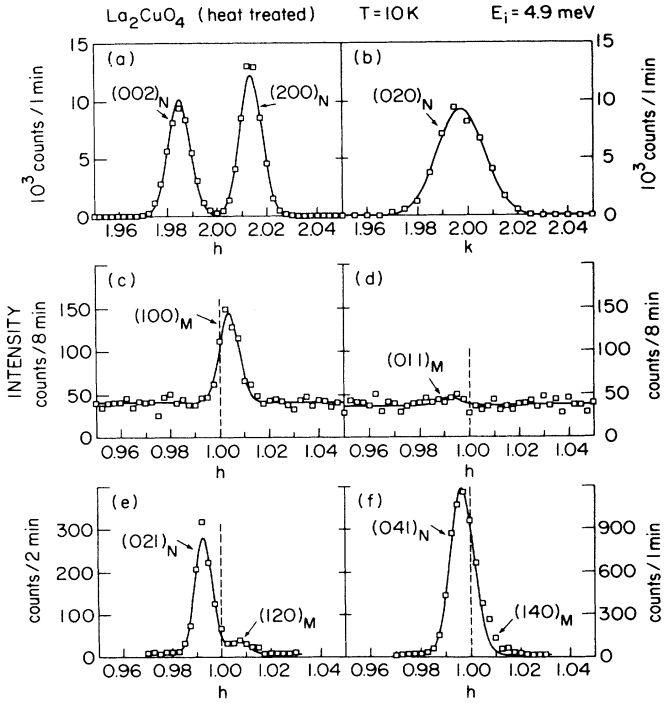

FIG. 3. Neutron-diffraction scans at $T=10$ K of various Bragg reflections in the La_2CuO_4 crystal heat treated at 400 °C. The scans shown are depicted in Fig. 1(a). Solid lines are least-squares fits of Gaussians [(b), (c), (d), and (f)] or sums of Gaussians [(a) and (e)].

TABLE I. Structural and magnetic properties from different La_2CuO_4 samples.

Sample	Lattice const. a(Å) $T=10$ K	Distortion $(c/a)-1$ $T=10$ K	T_N (K)	Moment[a] (μ_B)
Untreated crystal[b]	5.362	1.41%	50	0.17 ± 0.05
400 °C treated crystal[b]	5.324	1.48%	150	0.23 ± 0.05
Vaknin *et al.* powder (Ref. 5)	5.333	1.43%	220	0.40
Yang *et al.* powder (Ref. 12)	5.377	1.51%	250	0.40 ± 0.05

[a]All moments are calculated assuming the magnetic form factor (Ref. 11) $f(100)=0.835$.
[b]This work.

magnetic structure the intensity of this peak is expected to be 7 times weaker than (100). The solid lines in Fig. 3 are all least-squares fits of Gaussians or sums of Gaussians, and the amplitudes of the magnetic peaks are in agreement with the magnetic structure calculations. The two last scans, Figs. 3(a) and 3(f), show the nuclear (021) and (041) reflections split (to lower momentum transfers) from the much weaker magnetic (120) and (140) reflections, which appear at higher momentum transfers.

The integrated intensities of several nuclear peaks are used to calculate the ordered moment from the intensity of the (100) magnetic reflection. It was found that extinction effects were of little or no significance even for the strongest nuclear reflections. The magnetic form factor[11] used to calculate the ordered moment at $T=10$ K was that of pure Cu^{2+}, $f^1(100)=0.835$, and the moment is $\mu=0.17\pm0.05\mu_B$ per Cu atom for the untreated crystal and $\mu=0.23\pm0.05\mu_B$ per Cu atom for the crystal heat treated at 400 °C.

In Table I the results for the structural and magnetic properties of various samples of La_2CuO_4 are summarized. The two powder samples were both heat treated in different ways. It may be seen that the structural parameters, the lattice constant a, and the distortion $(a/c)-1$, are not very different at $T=10$ K for the four samples. The distortion is within $\pm3\%$, which may not be significant. If the distortions are followed as a function of temperature, all four curves run strictly parallel, and no relation seems apparent between the distortion and the antiferromagnetic ordering temperature. However, the magnetic properties are clearly related to the heat treatment of the La_2CuO_4 crystals, i.e., the deficiency of oxygen increases both the Néel temperature and the ordered moment significantly. Very recently we have been informed that similar results concerning Néel-temperature dependency of oxygen content in La_2CuO_4 have been obtained by Endoh.[13]

The authors wish to acknowledge very helpful discussions with B. X. Yang, S. Mitsuda, A. I. Goldman, A. R. Moodenbaugh, Y. Endoh, and especially G. Aeppli and D. C. Johnston. Work at Brookhaven National Laboratory was supported by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

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