RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 1 1 JULY 1987

Confirmation of antiferromagnetism in La_2CuO_{4-y} with polarized neutrons

S. Mitsuda*
Institute for Solid State Physics, University of Tokyo, Tokyo 106, Japan

G. Shirane
Brookhaven National Laboratory, Upton, New York 11973

S. K. Sinha, D. C. Johnston, M. S. Alvarez, D. Vaknin,† and D. E. Moncton
Corporate Research Laboratories, Exxon Research & Engineering Company, Annandale, New Jersey 08801
(Received 15 May 1987)

We have used neutron polarization analysis to study the superlattice peaks observed recently in undoped La_2CuO_{4-y} using unpolarized powder neutron diffraction. The results confirm that the superlattice peaks are indeed due to antiferromagnetic ordering, which occurs for our sample below $T_N = 290 \pm 30$ K, in agreement with our magnetic susceptibility data which yield $T_N = 290 \pm 10$ K. The low-temperature moment on the Cu ion is estimated as $0.43 \pm 0.13 \mu_B$ in agreement with the previous estimates.

It is by now well known that doping the compound La_2CuO_4 with Ca, Sr, or Ba produces an interesting series of high-T_c superconductors.[1-4] The nature of the ground state of *undoped* La_2CuO_4 is of interest from the point of view of possible new mechanisms for superconductivity in the corresponding superconducting compounds.[5-7] Pure La_2CuO_4 is known[8,9] to have a variable concentration (y), of oxygen vacancies which depends on the method of preparation, and we henceforth refer to it as La_2CuO_{4-y}.

La_2CuO_{4-y} undergoes a second-order structural phase transformation from a tetragonal to an orthorhombic structure well above room temperature.[8-12] Johnston *et al.*[8] have found that this transition temperature (T_0) is extremely sensitive to prior oxygen treatment of the sample. They[8] and others[13,14] also found anomalies in the magnetic susceptibility at temperatures up to ~ 295 K, indicative of antiferromagnetic ordering. The magnitude of the anomaly and the transition temperature (T_N) associated with it increase rapidly with oxygen vacancy concentration (y) in the sample.[8] The anomaly is absent in La_2CuO_{4-y} samples close to full oxygen stoichiometry. Both the magnetic anomaly and the structural transformation appear to be rapidly suppressed as one dopes with Sr and goes over into the superconducting phase.[8,13-15] The undoped La_2CuO_{4-y} with $y \simeq 0$ appears to behave as a semimetal[16] above 100 K, but the carriers appear to localize at lower temperatures.[8,11,13] For $y \simeq 0.03$ the compound is a semiconductor with a large band gap of about 0.72 eV above room temperature.[8]

Powder neutron diffraction using unpolarized neutrons on a pure $La_2CuO_{3.98}$ sample revealed new superlattice peaks which appeared below 220 K and were ascribed to antiferromagnetic ordering of the Cu spins.[12] The peak of the susceptibility anomaly of the same sample occurred at 230 K,[8] and the maximum positive slope occurred near T_N. Similar results were obtained on an independently prepared La_2CuO_{4-y} powder sample by Yang *et al.*[17] Both these studies indicated quite similar values for T_N (220–240 K) and for the low-temperature ordered Cu moment, i.e., about 0.5 $(\pm 0.15)\mu_B$. More recently, superlattice peaks were also observed in single crystals of La_2CuO_{4-y},[18] with T_N appearing to depend on oxygen treatment of the samples. The proposed antiferromagnetic structure inferred from these experiments was a structure with the Cu moments pointing "up" and "down" in successive planes normal to the orthorhombic [100] axis, the moment direction being along the orthorhombic [001] axis. However, in view of other possibilities for the occurrence of superlattice peaks, e.g., further structural phase transitions[19] or possible oxygen vacancy ordering,[9] we felt it was important to carry out a polarized neutron experiment on La_2CuO_{4-y}.

The powder sample used consisted of La_2CuO_{4-y} which was prepared by decomposition of the La and Cu nitrates after dissolving the dried oxides in dilute HNO_3 followed by drying on a hot plate. It was first fired for one hour at 650 °C and reground homogeneously after cooling in air, then fired twice more in air at 950 °C overnight and reground and homogenized between firings. It was finally treated in flowing helium for 15 h at 500 °C in order to increase the oxygen vacancy concentration. The oxygen vacancy concentration in the present sample was found by thermogravimetric analysis to correspond to $y = 0.03 \pm 0.02$. A total of 31 g of the sample was used in the present experiment in order to compensate for the intensity loss inevitable in a neutron polarization analysis experiment. The sample was mounted in a variable-temperature cryostat on the H8 polarized neutron triple-axis spectrometer at the Brookhaven High-Flux Beam Reactor. An incident neutron energy of 14.7 meV was used, together with a pyrolytic graphite filter to remove second-order contamination from the beam.

The polarization analysis setup is schematically indicated in Fig. 1. The method has been discussed in detail in the literature.[20,21] The polarizing crystals used as monochromator and analyzer were Heusler alloy (111) crystals. As the neutron is brought onto the sample, its spin polarization **P** can be arranged to be either parallel to the

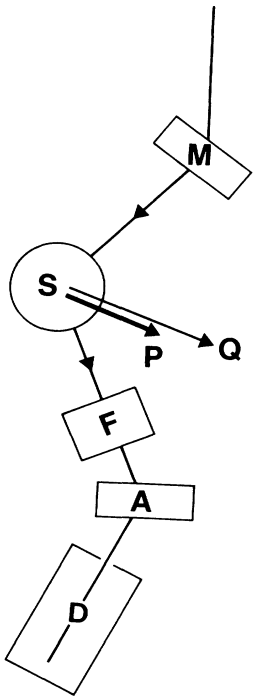

FIG. 1. Schematic of neutron polarization analysis configuration showing sample (S), polarizing monochromator crystal (M), analyzer crystal (A), neutron spin flipper (F), neutron detector (D), and directions of momentum transfer (**Q**) and neutron polarization vector (**P**), for the horizontal field (HF) configuration.

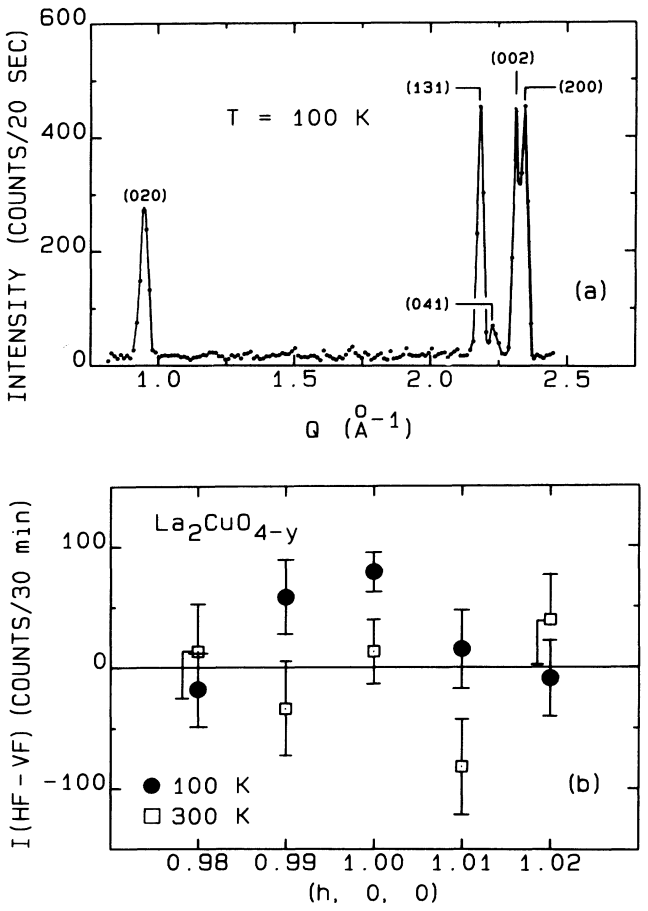

FIG. 2. (a) Nuclear scattering from La_2CuO_{4-y} measured in the horizontal field (HF) non-spin-flip mode. Indicated are the nuclear Bragg peaks. (b) Magnetic scattering from the (100) superlattice peak measured in spin-flip (HF-VF) mode at 100 and at 300 K. The intensities shown are normalized to a given monitor counting time.

momentum transfer **Q**, with a horizontal field (HF) on the sample, or normal to **Q**, with a vertical field (VF) on the sample. The experiment consists in looking at spin-flip (SF) or non-spin-flip (NSF) scattering processes in either field configuration. For HF, the magnetic scattering is all SF and thus the NSF component arises purely from nuclear scattering.[20,21] The NSF scattering intensity in the HF configuration is shown in Fig. 2(a), which thus corresponds to nuclear Bragg peaks superimposed on background consisting of nuclear diffuse scattering from the sample as well as room background, at a sample temperature of 100 K. The orthorhombic splitting of the (002) and (200) nuclear Bragg peaks is evident and there is no obvious nuclear (100) peak. The order parameter $\eta = 2(c-a)/(c+a)$ which is a measure of the orthorhombic distortion was checked at several temperatures and seemed to agree within 2% with previous results.[12] For the (100) magnetic peak, the assumed magnetic spin direction is *normal* to **Q** and the powder averaging for all possible moment (i.e., [001]) directions for a given [100] direction yields the following simple result: The difference in the SF cross sections for the (100) antiferromagnetic peak between the HF and the VF configurations is one-half of the cross section of the (100) antiferromagnetic Bragg peak only. Thus, multiplied by 2, the integrated peak intensity can be compared with that of the HF NSF (nuclear) Bragg peak integrated intensities to obtain (μf) as in conventional magnetic powder diffraction, where μ is the ordered magnetic moment and f is the magnetic form factor of the Cu^{2+} ion. Figure 2(b) shows the above difference in the SF cross sections for a scan through the (100) peak position at 100 and at 300 K. The width of the peak was resolution limited. A corresponding scan through the nuclear (200) peak position shows no difference in the cross sections. Thus Fig. 2(b) establishes that the observed (100) peak *indeed arises from long-range magnetic ordering in the sample.*

Figure 3 shows the temperature dependence of the square of the magnetic (100) structure factor obtained from the difference in the HF and VF spin-flip scattered intensity at the (100) peak position as a function of temperature. From these measurements, we establish a Néel temperature T_N for our La_2CuO_{4-y} sample of 290 ± 30 K. This is higher than that measured in our previous samples and correlates with y being greater in the current sample.[8]

The magnetic susceptibility for the present sample was measured using the Faraday method from 4 to 800 K, and

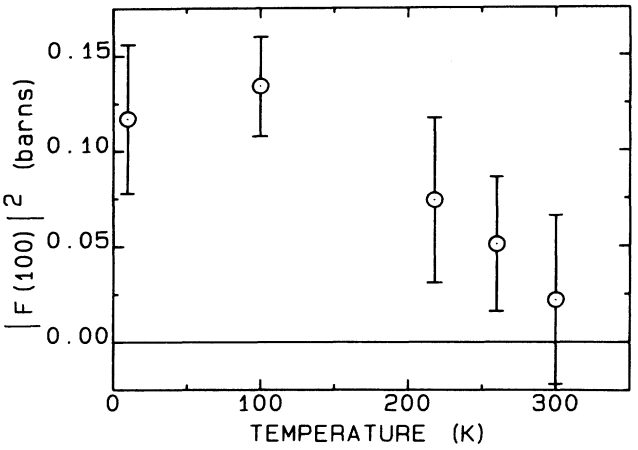

FIG. 3. Temperature dependence of the square of the magnetic (100) structure factor assuming four copper ions in a unit cell.

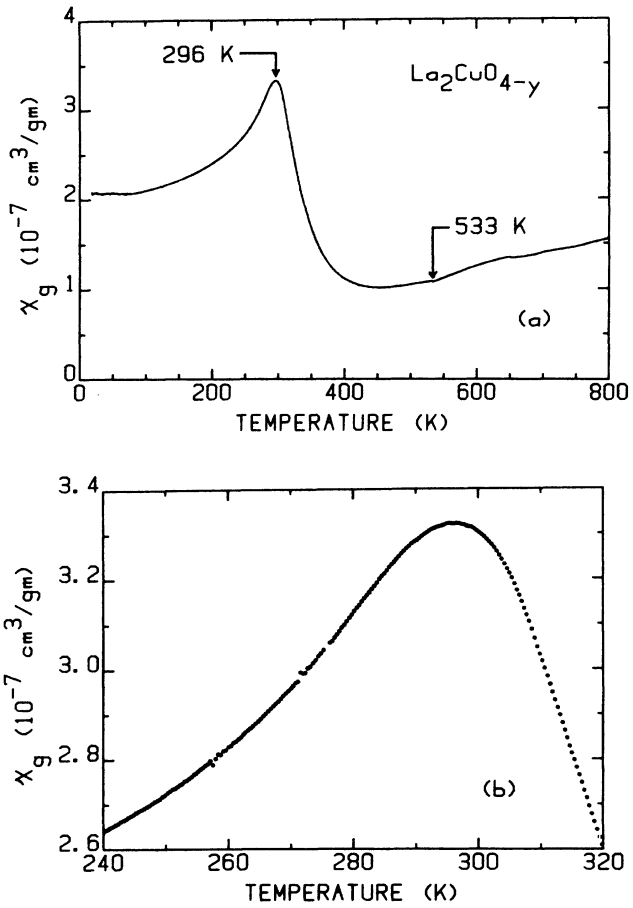

FIG. 4 (a) Gram magnetic susceptibility vs temperature for La_2CuO_{4-y}. This sample is the same as that for which the neutron scattering data in Figs. 2 and 3 were obtained. The Néel temperature near $\simeq$296 K and the tetragonal-orthorhombic transition temperature near 530 K are indicated. The anomaly near 650 K is spurious, resulting from imperfect correction for the ferromagnetic impurity contribution. (b) Expanded view of the data in Fig. 4(a) near the Néel temperature.

the results are plotted in Fig. 4. Here, a small Curie-Weiss impurity contribution $C/(T-\Theta)$ has been subtracted from the data, where $C=1.35\times10^{-6}$ cm^3K/gm and $\Theta=-1.99$ K. The small contribution to the magnetization from ferromagnetic impurities has also been corrected for from magnetization-field isotherms. The peak in the susceptibility occurs at 296 ± 1 K and the temperature of maximum positive slope is about 280 K. The latter temperature is normally associated with the onset of long-range antiferromagnetic order, but the absence of any sharp slope discontinuity and the rounded maximum [see Fig. 4(b)] suggest that magnetic fluctuation effects are important near T_N as suggested previously[12] and/or that the transition is broadened by oxygen inhomogeneity. From the data in Fig. 4, we estimate $T_N=290\pm10$ K, in agreement with the polarized neutron estimate. The data in Fig. 4 are nearly identical with data obtained for a different sample with a final heat treatment at 750 K under 30 Torr of He gas.[8] After correcting for a slight deviation from 100% polarization of the incident neutron beam, the analysis of the (100) integrated intensity yields a low-temperature moment of $0.43\pm0.13\mu_B$/Cu atom using the magnetic form factor of Cu^{2+} obtained in K_2CuF_4 [$f(100)=0.75$],[22] which is the same moment, within the error limits, as the one obtained from earlier unpolarized neutron diffraction data.[12,17] In this calculation, the moment was assumed to be along the [001] crystallographic axis as deduced from the earlier data.

In conclusion, we have confirmed the occurrence of long-range antiferromagnetic order in undoped orthorhombic La_2CuO_{4-y}, in which the Néel temperature is remarkably sensitive to oxygen vacancy concentration. This result points to the importance of electron spin correlations in these materials as initially recognized by Anderson.[5] Thus, there appears to be a possibility of such correlations inducing either magnetic ordering (the Néel state) of Cooper pairing, probably in a mutually exclusive manner as a function of doping or vacancy concentration (see, for example, Ref. 6). The detailed microscopic mechanism remains to be clarified.

The authors wish to acknowledge helpful interactions with G. Aeppli, J. E. Fischer, and B. Yang. This work was supported in part by the U. S.-Japan Collaboration on Neutron Scattering. Work at Brookhaven is supported by the Division of Materials Sciences, U. S. Department of Energy, under Contract No. DE-AC02-76CH00016.

*Visitor at Brookhaven National Laboratory, Upton, NY 11973.
†Also at Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986); J. G. Bednorz, K. A. Müller, and M. Takashige, Science **236**, 73 (1987).

[2]S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. **26**, L1 (1987); H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, *ibid.* **26**, L123 (1987).

[3]C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).

[4]R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[5]P. W. Anderson, Science **235**, 1196 (1987); G. Baskaran, Z. Zou, and P. W. Anderson (unpublished); Y. Hasegawa and H. Fukuyama, Jpn. J. Appl. Phys. (to be published); H. Fukuyama and K. Yosida, *ibid.* **26**, L371 (1987); A. E. Ruckenstein, P. J. Hirschfeld, and J. Appel (unpublished); K. Machida and M. Kato, this issue, Phys. Rev. B **36**, 854 (1987); S. A. Kivelson, D. S. Rokhsar, and J. P. Sethna, *ibid.* **35**, 8865 (1987); D. J. Scalapino, E. Loh, Jr., and J. E. Hirsch (unpublished); D. J. Scalapino, E. Loh, and J. E. Hirsch, Phys. Rev. B **34**, 8190 (1986).

[6]M. H. Cohen and D. H. Douglass, Phys. Rev. B **35**, 8720 (1987).

[7]K. Miyake, S. Schmitt-Rink, and C. M. Varma, Phys. Rev. B **34**, 6554 (1986); P. Prelovsek, T. M. Rice, and F. C. Zhang (unpublished); K. Machida and M. Kato (unpublished); D. J. Scalapino (unpublished); D. H. Lee and J. Ihm (unpublished); J. Ruvalds, Phys. Rev. B **35**, 8869 (1987).

[8]D. C. Johnston *et al.*, in Special Symposium on High-T_c Superconductivity, Meeting of the American Physical Society, March 1987, New York, NY (unpublished); in Special Symposium on High-T_c Superconductivity, Meeting of the Materials Research Society, April 1987, Anaheim, CA (unpublished); D. C. Johnston, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski (unpublished).

[9]C. Michel and B. Raveau, Rev. Chim. Miner. **21**, 407 (1984).

[10]B. Grande, Hk. Müller-Buschbaum, and M. Schweizer, Z. Anorg. Allg. Chem. **428**, 120 (1977).

[11]J. D. Jorgensen, H.-B. Schüttler, D. G. Hinks, D. W. Capone II, K. Zhang, M. B. Brodsky, and D. J. Scalapino, Phys. Rev. Lett. **58**, 1024 (1987).

[12]D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinya, and H. E. King, Jr. (unpublished).

[13]S. Uchida, H. Takagi, H. Yanagisawa, K. Kishio, K. Kitazawa, K. Fueki, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L445 (1987).

[14]R. L. Greene, H. Maletta, T. S. Plaskett, J. G. Bednorz, and K. A. Müller, Solid State Commun. (to be published).

[15]R. M. Fleming, B. Batlogg, R. J. Cava, and E. A. Rietman, Phys. Rev. B **35**, 7191 (1987).

[16]T. Kenjo and S. Yajima, Bull. Chem. Soc. Jpn. **46**, 1329 (1973).

[17]B. Yang, S. Mitsuda, G. Shirane, Y. Yamaguchi, H. Yamaguchi, and Y. Syono (unpublished).

[18]T. Freltoft, J. Remeika, D. E. Moncton, G. Aeppli, A. S. Cooper, J. E. Fischer, D. Harshman, G. Shirane, S. K. Sinha, and D. Vaknin (unpublished).

[19]W. Weber, Phys. Rev. Lett. **58**, 1371 (1987).

[20]R. M. Moon, T. Riste, and W. C. Koehler, Phys. Rev. **181**, 920 (1969).

[21]J. Wicksted, P. Böni, and G. Shirane, Phys. Rev. B **30**, 3655 (1984).

[22]K. Hirakawa and H. Ikeda, Phys. Rev. Lett. **33**, 374 (1974). Note that Yang (Ref. 17) used the magnetic form factor of K_2CuF_4 measured by J. Akimitsu and Y. Ito, J. Phys. Soc. Jpn. **40**, 1621 (1976).