RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 13 1 NOVEMBER 1987

Raman study of La_2CuO_4: Possibility of local symmetry breaking

G. A. Kourouklis,* A. Jayaraman, W. Weber,† J. P. Remeika, G. P. Espinosa,
A. S. Cooper, and R. G. Maines, Sr.
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 27 July 1987)

Raman spectra on flux-grown single crystals of La_2CuO_4 show two modes in the range of O stretch vibrations, near 426 and 526 cm^{-1}. The latter line exhibits a very large intensity and has polarization features consistent with an in-plane O stretch vibration. The 426 cm^{-1} line is assigned to the axial O stretch mode, also found in superconducting $La_{2-x}(Ba,Sr)_xCuO_4$. The prominent 526 cm^{-1} line is observed over the temperature range from 77 to 600 K; i.e., even in the high-temperature tetragonal phase, where, by symmetry arguments, *no* in-plane O stretch mode is Raman allowed. We believe that the presence of this mode indicates local symmetry breaking, possibly due to antiferromagnetic fluctuations.

INTRODUCTION

Since the discovery of high-temperature superconductivity in the system $La_{2-x}B_xCuO_4$ [B = Ba or Sr (Refs. 1-4)] several structural[5] and Raman studies[6-9] on these systems have appeared in the literature. These compounds crystallize in the tetragonal K_2NiF_4 structure (D_{4h}^{17},$I4/mmm$) when $x > 0.15$.[5,10] However, for $x \lesssim 0.15$, they undergo an orthorhombic distortion to the space group D_{2h}^{18}-Pbma (Refs. 10 and 11) due to rotation of the O octahedra. The as-grown La_2CuO_4 undergoes an antiferromagnetic ordering[12-15] near $T_N \simeq 240$ K. Quite surprisingly, superconductivity has recently been reported in La_2CuO_4 near 40 K.[16,17] On the high-temperature side, the compound transforms to the tetragonal lattice between 450 and 520 K depending on the oxygen concentration.[18]

In this study we have investigated single-crystal samples of La_2CuO_4 by Raman spectroscopy in the temperature interval 80-600 K, which covers the region of the antiferromagnetic transition as well as the orthorhombic-to-the tetragonal transition. The interesting finding is the presence of an additional bond-stretching mode with in-plane polarization, which is present over the above-mentioned temperature range. This mode is not expected to be Raman active in the tetragonal phase from group theoretical analysis of the vibrational modes.[6-9,19] We believe that this may be due to the presence of a symmetry-breaking mechanism, possibly connected with antiferromagnetic fluctuations.

EXPERIMENT

Millimeter-size single crystals of La_2CuO_4 prepared by the flux method were available to us. These were jet black in color and were verified by x-ray powder diffraction to have the orthorhombic structure with the a, b, and c parameters characteristic of the stoichiometric compound. Some of these crystals were heated in an evacuated sealed tube for periods greater than 16 h to achieve equilibrium, with a zirconium foil[20] placed inside, to getter the O_2 given off at prescribed temperatures. For Raman studies a fresh surface was obtained by cracking the single-crystal samples with a razor blade. Such freshly exposed surfaces were shiny and jet black in color. For Raman excitation the 488 and the 514.5 nm lines of an Ar^+ laser were used. The laser beam was focused with a lens of 10-cm focal length to a spot size of about 30 μm. The laser line was kept at a power level of 100-150 mW. For high-temperature experiments the crystals were mounted with silver paste onto a copper rod which was enclosed in a silica tube. The latter was surrounded by a resistive heater. For experiments at low temperature, a liquid-nitrogen optical cryostat was used in which the sample was glued on to the cooled copper block. In both cases the temperature was measured with a chromel-alumel thermocouple placed close to the sample. Raman spectra were recorded using a Spex double monochromator equipped with a conventional photon counting system. For recording the spectra, the back scattering geometry was used and the scattered radiation was collected by an F1 focusing lens.

The Raman spectra of La_2CuO_4 obtained at 77, 296, and 600 K are shown in Fig. 1. There are two peaks in these spectra which are reproducible from sample to sample. Of these two the strong peak near 529-516 cm^{-1} appeared only when the incident polarization was in the scattering plane. Although we did not use oriented crystals, we were able to fix the orientation of the c axis in our experiments by using the results of infrared reflectivity measurements[18,21] on oriented single crystals of La_2CuO_4. The latter study has shown that when the incident polarization is perpendicular to the c axis ($\mathbf{E}_i \perp \hat{c}$) the reflectivity is much higher than when it is parallel ($\mathbf{E}_i \parallel \hat{c}$). In Fig. 2 the Raman spectra of La_2CuO_4 obtained for the two different incident polarization directions ($\mathbf{E}_i$) with respect to the c axis are shown (a) and (b), and the Raman spectrum of $La_{1.85}Sr_{0.15}CuO_4$ at room temperature is also shown for comparison (c). In the case of $La_{1.85}Sr_{0.15}CuO_4$, (a ceramic pellet) which has the tetragonal structure, we obtain very reproducibly one Raman peak near 427 cm^{-1}. The strongest peak near 526 cm^{-1} observed in the orthorhombic La_2CuO_4 is totally absent in the tetragonal Sr-doped sample. We could not get any peaks in the lower frequency range because of the high background.

The Raman spectra of two samples annealed in vacuum

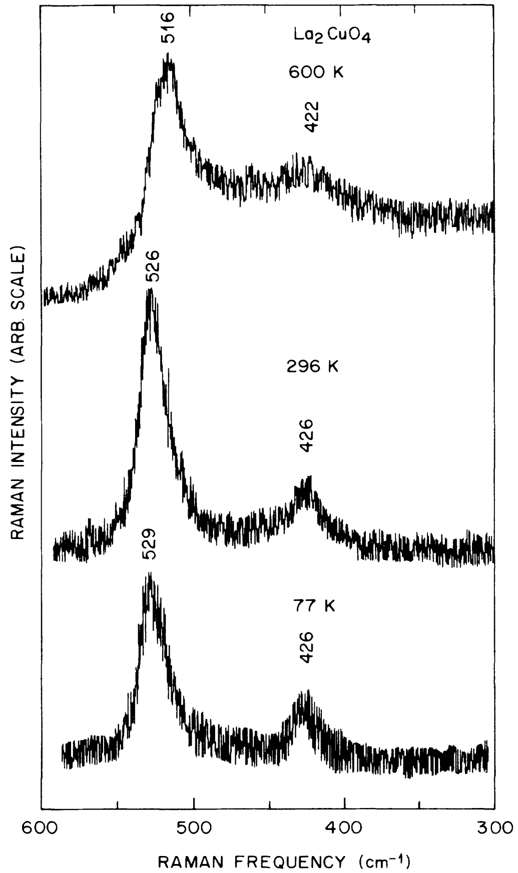

FIG. 1. Raman spectra of La_2CuO_4 at 77, 296, and 600 K. Spectra were recorded from a freshly exposed surface, approximate orientation was determined as described in text. The 488-nm Ar^+ laser line at a power of ~100 mW was used for excitation.

in the presence of zirconium foil to induce oxygen vacancies are shown in Figs. 3(b) and 3(c), along with the spectrum of the stoichiometric (as-grown) La_2CuO_4 (a). The sample that gave spectrum (b) was annealed for 17 h at 300 °C while the one that gave (c) was annealed for 22 h at 350 °C. These treatments were done with Zr foil present in the reaction tube. We believe that in the latter sample the oxygen-vacancy concentration was higher. The annealed samples (oxygen deficient) show the same Raman features as the stoichiometric one but both the 426 cm^{-1} and the 526 cm^{-1} peaks are broadened considerably, in particular the 426 cm^{-1} feature becomes quite broad. In addition, there is a small red shift of the 526-cm^{-1} peak with increasing oxygen-vacancy concentration.

DISCUSSION

For the tetragonal D_{4h}^{17} ($I4/mmm$) phase of the system, group theory predicts two A_{1g} and two E_g Raman active modes at the zone center.[6–9,19] In all these modes, only the La atoms and the O(1) atoms in the axial positions above and below the Cu atoms vibrate, and the atomic displacements are symmetric (gerade) with respect to the Cu atom at the unit-cell center. As a consequence, there is only one high-frequency O(1) stretch mode possible [polarized along c direction and stretching the Cu—O(1) and La—O(1) bonds]. Brun *et al.*[8] have reported a peak near 430 cm^{-1} for the tetragonal $La_{1.85}Sr_{0.15}CuO_4$, which is the highest frequency peak in their data. This feature is present in our spectra of $La_{1.85}Sr_{0.15}CuO_4$ and La_2CuO_4. We, therefore, assign this peak to the O(1) "axial" symmetric-stretch mode. From infrared data on La_2CuO_4 the corresponding O(1) asymmetric-stretch mode is placed near 550 cm^{-1}, while the in-plane asymmetric O(2) stretch mode is found near 690 cm^{-1}.[21–23] [The in-plane stretch modes have higher frequencies due to the shorter Cu—O(2) bond lengths.] We note that inelastic neutron data (representing the phonon density of states) yield a three-peak structure in the range between 400—700 cm^{-1}, confirming the presence of high-frequency modes in this energy range.[24] The symmetric in-plane O(2) stretch modes do not represent $q=0$ phonons, but phonons of the X point at the boundary of the tetragonal Brillouin zone. Consequently, they cannot be Raman active in this symmetry.

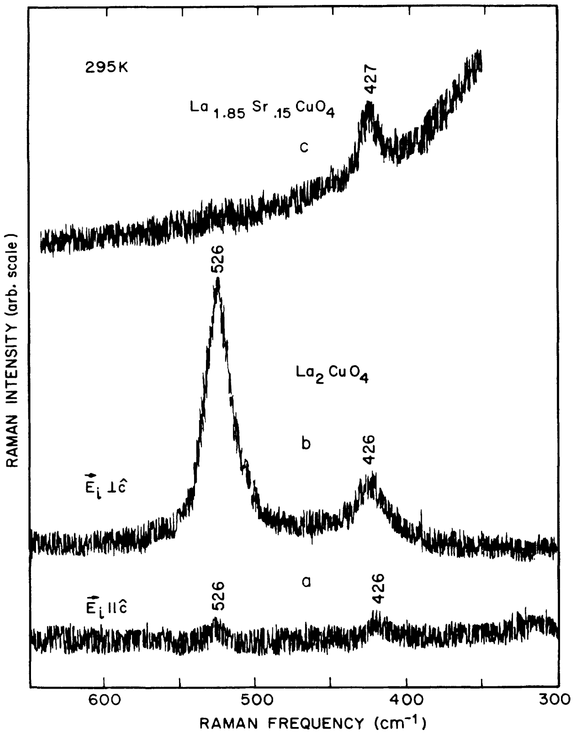

FIG. 2. (a) and (b) Raman spectra of La_2CuO_4 for two different polarizations of the incident beam with respect to the c axis (see text). (c) Raman spectrum of tetragonal $La_{1.85}Sr_{0.15}CuO_4$; sample was a ceramic pellet and the 488 nm Ar^+ laser line and line focus were used for excitation.

However, these modes become Raman active in the low-temperature orthorhombic phase, where the unit-cell volume is doubled, and the X point is folded back to the Γ point. The new Raman active O-stretch modes are (i) a "breathing" mode of the four in-plane O(2) atoms around

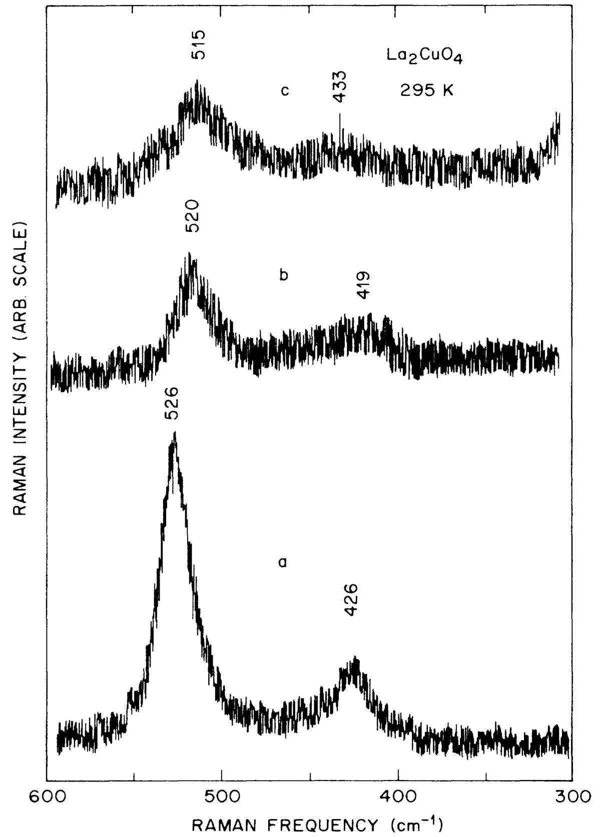

FIG. 3. (a) Raman spectra of stoichiometric La$_2$CuO$_4$, (b) of a sample of La$_2$CuO$_4$ annealed for 17 h at 300 °C, and (c) for 22 h at 350 °C in vacuum in the presence of zirconium foil. Experimental conditions same as in Fig. 1.

the Cu atoms, and (ii) a "quadrupole" vibration of the four O(2) atoms with two opposite O(2) atoms moving towards and the other two O(2) atoms moving away from the central Cu. In addition, there is another axial O(1) stretch mode possible.

In electron-phonon calculations,[25] the "breathing" mode was found to couple very strongly to the conduction electrons, and as a consequence, is very strongly renormalized (the quadrupole mode was much less affected). In fact, a static Peierls distortion of a breathing type was predicted for La$_2$CuO$_4$,[25,26] similar to the case of BaBiO$_3$.[27] However, there is, so far, no crystallographic confirmation of this distortion. Instead, an antiferromagnetic ordering was observed.[13-15] with transition temperatures $T_N \approx 50-290$ K, strongly dependent on the amount of O vacancies. In addition, very small amounts of Sr or Ba doping ($x \approx 0.02$) make the antiferromagnetic ordering disappear.[28] We note that the magnetic ordering also leads to a doubling of the unit cell as compared to the tetragonal symmetry (this would also be true for the "breathing" distortion).

As our polarization analysis clearly identifies the new 526 cm^{-1} line in undoped La$_2$CuO$_4$ as an in-plane vibration (see Fig. 2), the new mode could either be the breathing or the quadrupole vibration. At present we are unable to further identify the symmetry of this mode. However, its large intensity implies that it couples very strongly to the modulated electronic density, which, in turn, suggests that this mode is the breathing vibration.

Our samples were obtained from a batch of La$_2$CuO$_{4-\delta}$ single crystals with $T_N \approx 100$ K and $T_{\rm tr} \approx 450$ K. It is evident from Fig. 1 that the 530 cm^{-1} line does not vanish when going through either of these transitions. The line is still present in the tetragonal phase at 600 K. The only changes are small red shifts with increasing T and a more asymmetric line shape above $T_{\rm tr}$. We can exclude the case that the mode is induced by O vacancies, as the mode intensity decreases drastically with increasing O vacancies (see Fig. 3). In our view, the only remaining possibility is that locally the symmetry is lower than seen in the crystallographic data. For instance, individual Cu-O(2) planes may have a lower symmetry than the crystal, but there is no phase coherence between these planes. It might also be possible that there exist small domains in each of the planes, with dimensions less than the x-ray coherence length. The origin of this symmetry breaking could be static Peierls-type breathing distortions or two-dimensional antiferromagnetic fluctuations. In the absence of any further experimental support for the Peierls distortions, we may argue that, most probably, antiferromagnetic fluctuations persist to temperatures as high as 600 K, and possibly even much higher. It should be mentioned that in K$_2$NiF$_4$, which exhibits a three-dimensional antiferromagnetic ordering temperature $T_N \approx 100$ K, two-dimensional magnetic fluctuations persist at least up to 200 K.[29] However, it is not clear why magnetic fluctuations should cause such a strong coupling to the lattice, as evident from the large intensity of the mode.

The spectra of annealed samples are compared with the spectrum of stochiometric La$_2$CuO$_4$ in Fig. 3. The strong Raman peak near 526 cm^{-1} broadens and shifts to lower frequencies. Since the effect of annealing is quite marked on the intensity of the 426 cm^{-1} peak which corresponds to the Cu-O(1) axial mode, we suggest that the vortex oxygens in the CuO$_6$ octahedra are preferentially removed. Hence, the vacancies occur in these sites and one may therefore expect a strong influence on the axial mode. Any vacancy will affect the force constants of the planar mode, and the substantial change in the frequency of this mode speaks for this effect.

In conclusion, we have presented Raman spectra for La$_2$CuO$_4$ over the temperature range between 77 and 600 K, and as a function of oxygen vacancies. The prominent Raman feature over this temperature range is a peak near 526 cm^{-1}, identified as an in-plane O stretch vibration. This mode persists through all phase transitions known for La$_2$CuO$_4$; both the magnetic and the orthorhombic-to-tetragonal transition. As no in-plane O-stretch mode is symmetry allowed in the high-temperature tetragonal phase, the presence of this mode indicates local symmetry breaking, possibly due to high-temperature antiferromagnetic fluctuation.

[*] Permanent address: Department of Physics, National Technical University, Zografou Campus, Athens GR 15773, Greece.

[†] Permanent address: Kernforschungszentrum Karlsruhe INFP, D-7500 Karlsruhe 1, Federal Republic of Germany.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] S. Uchida, H. Tagaki, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L1 (1987).

[3] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and J. 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] R. J. Cava, A. Santoro, D. W. Johnson, Jr., and W. W. Rhodes, Phys. Rev. B **35**, 6716 (1987).

[6] I. S. Shaplygin and N. V. Porotrikov, Russ. J. Inorg. Chem. **29**, 491 (1984).

[7] S. Sugai, M. Sato, and S. Hosoya, Jpn. J. Appl. Phys. Lett. **26**, L495 (1987).

[8] T. Brun, M. Grimsditch K. E. Gray, R. Bhadra, V. Maroni, and C. K. Loong, Phys. Rev. B **35**, 8837 (1987).

[9] S. Blumenroeder, E. Zirngiebl, J. D. Thompson, P. Killough, J. L. Smith, and Z. Fisk, Phys. Rev. B **35**, 8840 (1987).

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

[11] J. M. Longo and P. M. Raccah, J. Solid State Chem. **6**, 526 (1973).

[12] Y. Yamaguchi, H. Yamauchi, M. Ohashi, Y. Yamamoto, N. Shimoda, M. Kikuchi, and Y. Syono, Jpn. J. Appl. Phys. Lett. **26**, L447 (1987).

[13] D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. Newsam, C. R. Safinya, and H. E. King, Jr., Phys. Rev. Lett. **58**, 2802 (1987).

[14] S. Mitsuda, G. Shirane, S. K. Sinha, D. C. Johnston, M. S. Alvarez, D. Vaknin, and D. E. Moncton, Phys. Rev. B **36**, 822 (1987).

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

[16] J. Beille, R. Cabanel, C. Chaillout, B. Chevalier, G. Demazeau, F. Deslandes, J. Etourneau, P. Lejay, C. Michel, J. Provost, B. Raveau, A. Sulpice, J. L. Tholence, and R. Tournier, C. R. Acad. Sci. (Paris) **304**, 1097 (1987).

[17] P. M. Grant, S. S. P. Parkins, V. Y. Lee, E. M. Engler, M. L. Ramirez, J. E. Vasquez, G. Lim, R. D. Jacontz, and R. L. Greene, Phys. Rev. Lett. **58**, 2482 (1987).

[18] D. C. Johnston, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski (unpublished).

[19] G. Burns, F. H. Dacol, and M. W. Shafer, Solid State Commun. **62**, 687 (1987).

[20] C. Chailloet and J. P. Remeika, Solid State Commun. **56**, 833 (1985).

[21] J. Orenstein, G. A. Thomas, D. H. Rapkine, C. G. Bethea, B. F. Levine, R. J. Cava, A. S. Cooper, D. W. Johnson, Jr., J. P. Remeika, and E. A. Rietman, in *Proceedings of the International Workshop on Novel Superconductivity, Berkeley, 1987,* edited by V. Kresin and S. Wolf (Plenum, New York, 1987), p. 693–698.

[22] P. Ganguly and C. N. R. Rao, J. Solid State Chem. **53**, 193 (1984).

[23] M. Stavola, R. J. Cava, and E. A. Rietman, Phys. Rev. Lett. **58**, 1571 (1987).

[24] B. Renker, F. Gompf, E. Gehring, N. Nücker, D. Ewert, W. Reichardt, and H. Rietschel, Z. Phys. B **67**, 15 (1987).

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

[26] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[27] D. E. Cox and A. W. Sleight, Acta Crystallogr. B **35**, 1 (1977).

[28] T. Fujita, Y. Aoki, Y. Maeno, J. Sakurai, H. Fukuba, and H. Fujii, Jpn. J. Appl. Phys. **26**, L368 (1987).

[29] R. J. Birgeneau, H. J. Guggenheim, and G. Shirane, Phys. Rev. Lett. **22**, 720 (1969).