RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 1 1 JANUARY 1989

Temperature dependence of the Raman spectra for $Bi_2CaSr_2Cu_2O_8$

Gerald Burns, G. V. Chandrashekhar, F. H. Dacol, and P. Strobel*
IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598-0218
(Received 2 September 1988; revised manuscript received 18 October 1988)

We report an anomaly at T_c (≈ 85 K) in the temperature dependence of the A_{1g} phonon mode at 464 cm^{-1} in $Bi_2CaSr_2Cu_2O_8$. It behaves similarly to the B_{1g} phonon mode previously found in $YBa_2Cu_3O_7$. However, the anomalously behaving phonon reported here has two different characteristics. First, it has a considerably higher energy than the B_{1g} phonon, and hence should be considerably higher in energy than the superconducting band gap. Second, this phonon involves motion primarily of the oxygen atoms above and below the Cu-O planes rather than those in the Cu-O planes as is the case for the B_{1g} phonons in $YBa_2Cu_3O_7$.

INTRODUCTION

In an early Raman study of $YBa_2Cu_3O_7$ ceramics, Macfarlane, Rosen, and Seki[1] reported an anomalous temperature dependence of the 340 cm^{-1} phonon mode. As the temperature is lowered from room temperature, the mode frequency increases until approximately T_c (≈ 90 K). Below this temperature the frequency decreases by several wave numbers. This type of temperature dependence was also observed in infrared measurements by Bonn *et al.*,[2] and confirmed by Wittlin *et al.*[3] (for both the Raman line, and an ≈ 333 cm^{-1} infrared line) and other authors.[4-6]

Using single-crystal data, Cooper *et al.*[4] have analyzed their Raman spectra of $YBa_2Cu_3O_7$ in considerable detail. They also find an anomalous temperature dependence of the position, as well as the linewidth (and shape) of the 340 cm^{-1} line. They interpret their results as an interference effect due to interband-electronic scattering interfering with the phonons.

The 340 cm^{-1} Raman line in $YBa_2Cu_3O_7$ is interesting because it has B_{1g} symmetry[7,8] (tetragonal notation, which is used throughout this paper). Thus, the normal mode involves *only atomic motion of the oxygen atoms in the Cu-O planes*,[9] and this motion is only along the z direction. The eigenvector can be visualized by considering a single Cu-O plane. If O_x and O_y are the oxygen atoms in the x and y directions, respectively, then the motion consists of O_x moving in the $+z$ direction and O_y moving in the $-z$ direction; the mirror image of this motion occurs for the oxygen atoms in the closely coupled neighboring Cu-O plane. This phonon transforms as x^2-y^2 and so has a first-order coupling to the x^2-y^2 hole states on Cu atoms.

$Bi_2CaSr_2Cu_2O_8$ also has two Cu-O planes per primitive unit cell and thus a Raman active B_{1g} mode, as well as $6A_{1g}+7E_g$ Raman active modes[10] assuming tetragonal symmetry. With crossed polarization measurements at 45° to the crystal axes, the B_{1g} mode has been determined[11] at 282 cm^{-1}. Its position as a function of temperature was measured, but no anomalous behavior could be detected.[11] However, as the authors note, the large linewidth of this B_{1g} mode observed in $Bi_2CaSr_2O_8$ could obscure any anomalous behavior.

We report anomalous temperature dependence of another Raman active line in single crystals of $Bi_2CaSr_2O_8$. The line arises from the motion of atoms that are not in the Cu-O planes, and we discuss some implications of this result.

RESULTS

We have previously measured[10] the room-temperature A_{1g} Raman spectra of single-crystal $Bi_2CaSr_2O_8$. Experimental details are described in Ref. 10. Of the four observed A_{1g} modes, the line at 464 cm^{-1} is the narrowest and most intense.[10] As we show in another paper,[12] this phonon mostly involves the motion of the oxygen atoms

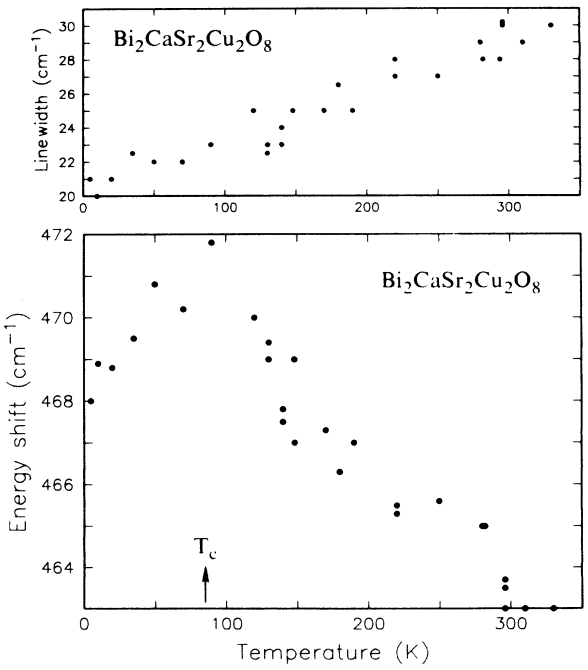

FIG. 1. The temperature dependence of the linewidth and position of the A_{1g} phonon at 464 cm^{-1} in $Bi_2CaSr_2Cu_2O_8$. T_c of the crystal is 85 K, as indicated.

(labeled O_z), which are above and below the Cu-O planes. A similar phonon is found in all the high-temperature copper oxide superconductors.[12]

Figure 1 shows the temperature dependence of the frequency and linewidth of this phonon taken with increasing and decreasing temperature. There is a clear anomaly in the temperature dependence of its frequency in the vicinity of T_c (=85 K, indicated by the arrow). The difference between the highest frequency measured (at T_c) and that at 0 K is about 4 cm^{-1}, but the anomaly is about twice as large if the extrapolated (to 0 K) frequency is used. The linewidth in Fig. 1 is the full width at half power and it exhibits the simple temperature dependence, without any anomaly. Note that the anomaly in the position of the phonon is less than the linewidth which is characteristic of these superconductors.

DISCUSSION

Anomalous behavior of phonon positions in the high-temperature copper oxide superconducting materials is not at present understood. However, it suggests the possibility of electron-phonon interactions in these systems although it may just parametrize other properties of the superconductivity. In all previous studies of anomalous behavior,[1-6] the phonon involved only motion of the oxygen atoms in the Cu-O planes. The phonon anomaly reported here has two different characteristics, which we think may be of some significance. First, at 464 cm^{-1}, this phonon is considerably higher in energy than the B_{1g} phonon (≈ 340 cm^{-1}) reported previously in $YBa_2Cu_3O_7$. Thus, its energy should be considerably higher than the superconducting gap. Second, this phonon mostly involves the motion of the O_z atoms.[12] These atoms are directly above and below the Cu-O plane, but not in the plane. Yet the anomaly is of the same order as observed previously.[1-6]

It would be interesting to see if a similar anomaly is found for phonons that involve the motion of atoms that are even farther from the Cu-O planes. Some of the phonons in other Bi and Tl compounds are certainly candidates for such a study.[12]

---

*On leave from the Laboratoire de Cristallographie, Centre National de la Becherche Scientifique, Grenoble, France.

[1]R. M. Macfarlane, H. Rosen, and H. Seki, Solid State Commun. **63**, 831 (1987).

[2]D. A. Bonn, J. E. Greedan, C. V. Stager, T. Timusk, M. G. Doss, S. L. Herr, K. Kamaras, and D. B. Tanner, Phys. Rev. Lett. **58**, 2249 (1987).

[3]A. Wittlin, R. Liu, M. Cardona, L. Genzel, W. König, and F. Garcia-Alvarado, Solid State Commun. **64**, 477 (1987).

[4]S. L. Cooper, M. V. Klein, B. G. Pazol, J. P. Price, and D. M. Ginsberg, Phys. Rev. B **37**, 5920 (1988).

[5]C. Thomsen, M. Cardona, B. Gegenheimer, R. Liu, and A. Simon, Phys. Rev. B **37**, 9860 (1988).

[6]M. Krantz, H. J. Rosen, R. M. Macfarlane, and V. Y. Lee, Phys. Rev. B **38**, 4992 (1988).

[7]G. Burns, F. H. Dacol, F. Holtzberg, and D. Kaiser, Solid State Commun. **66**, 217 (1988).

[8]R. Liu, C. Thomsen, W. Kress, M. Cardona, B. Gegenheimer, F. de Wette, J. Prade, A. D. Kulkarni, and U. Schöder, Phys. Rev. B **37**, 7971 (1988).

[9]G. Burns, F. Dacol, P. P. Freitas, T. S. Plaskett, and W. König, Solid State Commun. **64**, 471 (1987).

[10]G. Burns, G. V. Chandrashekhar, F. H. Dacol, M. W. Shafer, and P. Strobel, Solid State Commun. **67**, 603 (1988).

[11]M. Cardona, C. Thomsen, R. Liu, H. G. Von Schnering, M. Hartweg, Y. F. Yan, and Z. X. Zhao, Solid State Commun. **66**, 1225 (1988).

[12]G. Burns, P. Strobel, G. V. Chandrashekhar, F. H. Dacol, F. Holtzberg, and M. W. Shafer, Phys. Rev. B (to be published).