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2000 J. Phys.: Condens. Matter 12 9637

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Temperature-induced frequency shift of the Raman-active CuO_2 planar oxygen vibrational modes of Bi-2212 related to a change of the Cu–O bonding

C Boulesteix†, K C Hewitt‡ and J C Irwin‡

† MATOP/CNRS B151, Faculté des Sciences de Saint Jérôme, F13397 Marseille Cédex 20, France

‡ Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Received 3 August 2000, in final form 2 September 2000

Abstract. A change, with temperature, of the Cu–O or Bi–O bondings was previously suggested because irregular variations, with temperature, of the lattice parameters and of the electrical resistivity were observed in Bi-2212 crystals. To check the validity of this hypothesis, a study of the variation, with temperature, of the positions of Raman peaks associated with vibrations of the different kinds of O atom has been performed at room and at low temperature. It is shown here that the 285 cm^{-1} Raman peak (B_{1g}), associated with the out-of-plane vibrations of O atoms of the CuO_2 plane, is shifted by +2% upon decreasing from 294 K to 96 K while the 466 and 627 cm^{-1} peaks (both A_{1g}) associated with the other O atoms are not shifted. So Raman spectroscopy confirms a possible change of the Cu–O bonding, in the CuO_2 plane, with temperature, while the Bi–O bonding appears to be unchanged. A hardening of the Cu–O bond is observed at low temperature.

1. Introduction

Compared to normal metals, high- T_c superconductors (HTSC), in their normal state, present many differences and different kinds of anomaly which render this normal state still a matter of controversy. For a better understanding of the normal state of HTSC, the study of these anomalies is of primary importance. Their study is especially interesting when only Cu–O planes and no Cu–O chains exist, because in that case only one kind of Cu–O bond is prominent and interpretation may be easier. This is the case, for example, for the bismuth cuprates. In the case of Bi-2212 crystals two kinds of anomaly occur at low temperature (between 200 and 100 K and below):

- (i) an anomalous variation of the lattice parameters with temperature and an anomalous thermal expansion [1–3];
- (ii) an anomalous variation with temperature, in the normal state, of both the in-plane [4–7] and the out-of-plane resistivities [8–11].

On the basis of these measurements, and no structural change being observed in this temperature range, several authors have suggested a change either in the Cu–O or in the Bi–O bonds [1, 2, 6, 11] to explain the existence of these anomalies, that can give rise to a ‘hole filling’ with decreasing temperature. Some other, very different, kinds of explanation have also been given. For the parameter variation anomaly a mismatch between the rock-salt-type Bi–O layers

and the perovskite part of the structure was suggested [3]. For both of the electrical anomalies observed for underdoped crystals a great variety of explanations have been given. For the anomaly in the a - b plane (i) a possible misorientation of the surface of crystals related to the a - b plane [4] or (ii) an intrinsic granularity of crystals [5] or (iii) both of them [7] were suggested. For the electrical anomaly along c (i) a possible diffusion of free electrons by Cooper pairs just above T_c [8]; and (ii) a consequence of thermal fluctuations in an anisotropic medium [9] were suggested. Under such conditions, as no decisive proof of the existence of a change of the Bi-O bondings or of the Cu-O bondings has been given, a study of the variation, with temperature, of the positions of the Raman peaks of the different kinds of oxygen atom could clarify the situation because, if a change in the bonding occurs, a related Raman frequency shift is expected.

2. Experimental method and sample characterization

Raman spectra of HTSC have been extensively studied [12–16] and, in particular, the phonon Raman spectra of Bi-2212 crystals have been the subject of numerous investigations. Generally, three different kinds of study have been performed on HTSC: (i) studies carried out to identify the different possible lattice vibrations and their symmetries for all doping levels [12]; (ii) studies of the electron–phonon interaction and its dependence on temperature [13, 15]; and (iii) electronic Raman scattering studies carried out to investigate the nature of the superconducting gap and the normal-state electronic properties [16]. In the present paper we suggest another use of Raman spectroscopy for HTSC: a study of the variation of the Cu–O (or Bi–O) bondings with temperature. It has been possible to study these bondings because intense Raman peaks have been clearly associated with vibrations of oxygen atoms in Bi-2212 crystals [17–23]. It will be shown here that the peak associated with vibrations of oxygen atoms of the CuO_2 plane is shifted with temperature while two peaks associated with the oxygen atoms in the Bi and Sr planes are not. The most direct method for determination of the variation, with temperature, of the Cu–O and Bi–O bondings would be a direct determination of Cu–O and Bi–O distances using x-rays or neutron diffraction. This requires the use of crystals of very high quality, which are difficult to obtain in the case of bismuth cuprates. Raman spectroscopy is less sensitive to lattice defects and crystal inhomogeneities and appears then to be the most suitable method in the present case.

Single crystals of Bi-2212 were prepared by a travelling-solvent floating-zone method [22–24] using an infrared imaging furnace. Oxygen was unloaded, for underdoped crystal preparation, by high-temperature anneals in low oxygen pressures, with rapid quenching. The T_c of each crystal was determined via magnetic susceptibility measurements. Two underdoped crystals ($T_c = 51$ K, $T_c = 85$ K) and one optimally doped crystal ($T_c = 90$ K) were used for obtaining experimental results. The transition in the $T_c = 51$ K crystal was quite broad (over about 25 K), while the transition in the 82 K crystal was over about 10 K and it was over a few K in the 90 K crystal. However, for these measurements a 5 Oe field was used, applied parallel to the c -axis so as to provide a larger signal. This field is high in comparison to the values (about 0.1 Oe) generally used in transition width determination, so these values may be higher than what could be obtained under standard experimental conditions. X-ray diffraction revealed in some cases the existence of an impurity phase (Bi-2201), but this impurity phase was found to completely disappear upon cleavage near both surfaces (also upon Scotch tape cleavage), so, in the present case, Bi-2201 is a surface impurity. Samples were cleaved immediately before the Raman scattering investigation, to ensure that in the experiments a fresh uncontaminated surface of a pure Bi-2212 crystal was used.

3. Experimental results

Raman vibrational spectra have been taken for two underdoped ($T_c = 51$ K, $T_c = 85$ K) and one optimally doped ($T_c = 90$ K) Bi-2212 crystal at three different temperatures: 294 K, 96 K (only in the case of $T_c = 85$ K) and 22 K (17 K in the case of $T_c = 90$ K). These spectra, in the frequency range 20–1000 cm^{-1} , were obtained using the 514.5 and 488.0 nm lines of an argon-ion laser as the excitation source. Since the results are similar in the two cases, only results obtained with the 514.5 nm line will be given here. Bi-2212 has an orthorhombic structure with a - and b -axes oriented at 45° to the Cu–O bonds. The difference between a and b is related to the incommensurate modulation of the BiO layers that only marginally affects the Cu–O bond. In Raman experiments, since the orthorhombic distortion is small, it is customary to assume a tetragonal structure for the discussion of symmetry properties. We will do so here and to facilitate comparison with other cuprates we will use a set of x' - and y' -axes rotated by 45° with respect to the Cu–O bonds. The $x'x'$ and $x'y'$ scattering geometries allow the couplings to $A_{1g} + B_{2g}$ and to B_{1g} excitations respectively. As in many previous papers, O atoms of the CuO_2 plane will be labelled O1, O atoms close to Sr will be labelled O2 and O atoms of the BiO layers will be labelled O3. The frequencies of the three important peaks, with nominal frequencies 285 cm^{-1} (O1), 465 cm^{-1} (O3) and 630 cm^{-1} , have been obtained by fitting the experimental peaks with Lorentzian profiles. Since all three peaks are relatively strong and good fits are obtained with the Lorentzian, the resulting uncertainty in the peak frequency is estimated to be 1.0 cm^{-1} . In the case of weaker phonons, the fits are not as good and the uncertainty is between 2.0 and 5.0 cm^{-1} .

4. Underdoped crystal 1 ($T_c = 51$ K) in the xx' and $x'y'$ geometries

For the first underdoped crystal, for which $T_c = 51$ K (figure 1), Raman spectra have been taken in the $x'x'$ ($A_{1g} + B_{2g}$) and $x'y'$ (B_{1g}) geometries at 294 K and 17 K.

In the $x'x'$ geometry a very strong peak is observed at 465 cm^{-1} at 294 K. This peak is unchanged within the experimental error (466 cm^{-1}) at 17 K. Many authors [17–19] assigned this mode to vibrations of the O2 atoms, but more recently it has been shown on the basis of experiments carried out on O-isotope-exchanged crystals [20, 21] that this mode is associated with c -axis vibrations of the O3 atoms in the BiO planes. Several other broad peaks are visible near 60, 120, 300, 395 and 627 cm^{-1} . The most intense peak near 627 cm^{-1} is attributed [20, 21] to vibrations of O2, although it was earlier assigned to O3 atoms [17–19]. It is not shifted at low temperature. The other rather intense peak near 300 cm^{-1} is forbidden in tetragonal symmetry and grows with orthorhombic distortion [22, 23]. It is shifted to 295 cm^{-1} (a 1.6% shift) at 17 K, which is within the experimental uncertainty for this kind of peak. All the other peaks are weak and their measured shifts with temperature are smaller than the experimental uncertainty (the weak peak at 60 cm^{-1} is shifted to 57 cm^{-1} ; the other weak peak at 120 cm^{-1} is shifted to 124 cm^{-1}).

In the $x'y'$ geometry three peaks are visible at 108, 279 and 586 cm^{-1} at 294 K. The first one, attributed to b -axis vibrations of Bi atoms, is unchanged at 17 K [13–19]. The second, which is the strongest, shifts to 285 cm^{-1} (a 2.1% shift) as the temperature is lowered to 17 K. This B_{1g} mode is associated with out-of-phase c -axis vibrations of O1 atoms [17–19]. The third peak is shifted to 590 cm^{-1} (a 0.6% shift), which is again within the experimental uncertainty because of the weakness of this feature at room temperature. It has been previously attributed to O-atom deficiency (in the BiO layer) [19, 22, 23]. To conclude, only in the case of O1 atoms (atoms of the CuO_2 planes) is the frequency of the phonon clearly affected by a temperature shift from 294 to 17 K.

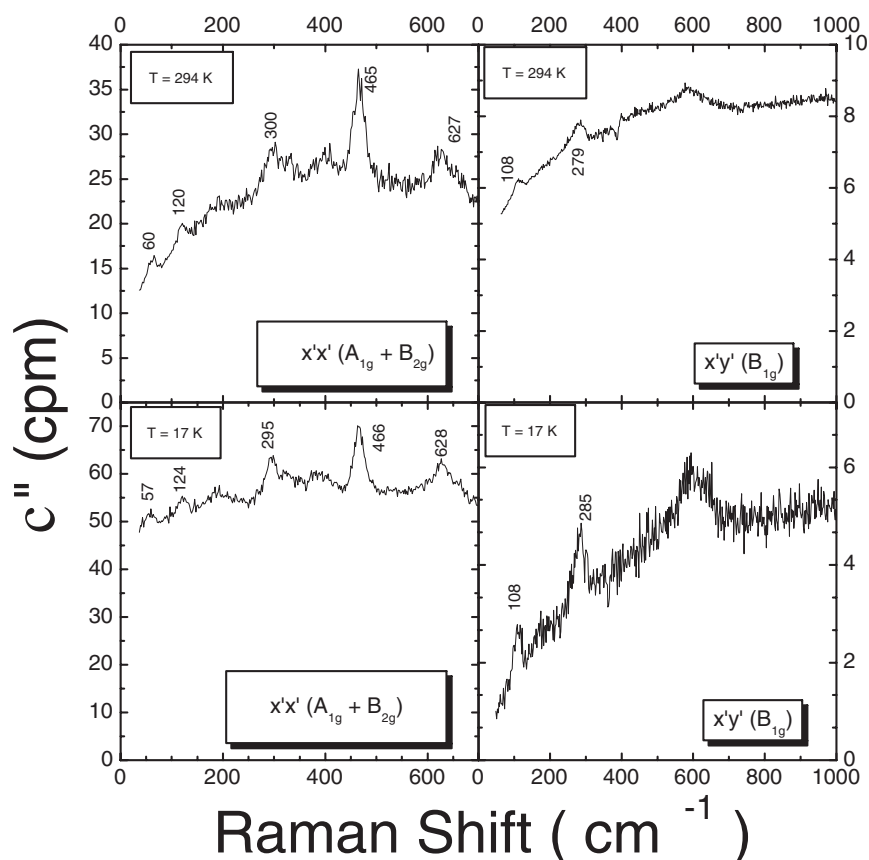


Figure 1. Raman spectra of an underdoped Bi-2212 crystal ($T_c = 51$ K) taken in the $x'x'$ ($A_{1g} + B_{2g}$) and $x'y'$ (B_{1g}) geometries at 294 K and 17 K. The Bose factor is divided out.

5. Underdoped crystal 2 ($T_c = 85$ K) in the $x'y'$ geometry

The shift between high- and low-temperature Raman peaks in the $x'y'$ geometry has also been studied at 96 K in the case of a second underdoped crystal having $T_c = 85$ K (figure 2). As the peak at 590 cm^{-1} has been previously attributed to O-atom deficiency [19, 22], only the peak at 279 cm^{-1} at 296 K will be considered here. The latter, attributed to vibrations of O atoms of the CuO_2 layers is shifted to 284 cm^{-1} at 96 K (1.8% on 188 K: $0.0096\% \text{ K}^{-1}$) and to 287 cm^{-1} at 22 K (2.8% on 265 K: $0.01\% \text{ K}^{-1}$), so we can consider the percentage shift per degree to be constant between room temperature and 22 K and equal to $0.01\% \text{ K}^{-1}$. It must be noted that a peak at 110 cm^{-1} which is not related to the Cu–O bond is unchanged whatever the temperature. The energy of the coupling increases with decreasing temperature which corresponds to Cu–O bond hardening with decreasing temperature. This occurs regularly and begins above the superconductive transition.

6. Optimally doped crystal ($T_c = 90$ K) in the $x'y'$ geometry

So as to be sure that the existence of the shift of the peak at 279 cm^{-1} is not related to O-atom deficiency, the same experiment has been performed between 296 K and 22 K on an

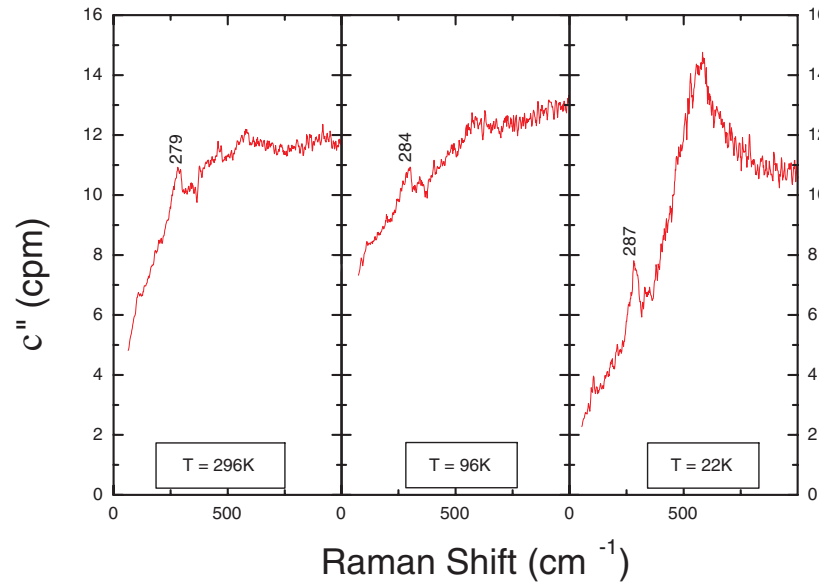


Figure 2. Raman spectra of an underdoped Bi-2212 crystal ($T_c = 85$ K) taken in the $x'y'$ (B_{1g}) geometry at 294 K, 96 K and 22 K. The Bose factor is divided out.

optimally doped crystal ($T_c = 90$ K). The same shift is observed from 282 cm^{-1} to 288 cm^{-1} (2.1%) between 296 K and 22 K (figure 3). Thus, the results are the same for O1 atoms, within experimental error, as in the case of underdoped crystals, so the shift is not related to underdoping.

7. Discussion and conclusions

Experimental results clearly show that (i) a shift of the Raman peak associated with vibrations of O1 atoms of the CuO_2 planes occurs between room and low temperature in the case of Bi-2212 crystals (in agreement with the previous results of Leach *et al* [25] and Opel *et al* [26]); (ii) nothing similar exists for the other Raman peaks associated with vibrations of other atoms in the structure. The observed Raman shift clearly begins above the superconductive transition, so it is independent of the superconductive transition itself. It must be noted nevertheless that it continues in the same way below this superconductive transition. Experimental results show also that it is independent of the oxygen doping of the samples, which is not surprising because only O1 atoms (of the CuO_2 planes) are involved, while under(/over)doping mainly concerns O atoms of the BiO layers and not O atoms of the CuO_2 planes.

As regards the change, with temperature, in the Cu–O bonding inside the CuO_2 planes (or in Bi–O bonding inside the BiO layers) suggested previously, we can consider our experimental results to confirm this hypothesis in the case of the Cu–O bonding and not in the case of the Bi–O bonding. The increase of the coupling energy, with decreasing temperature, should be due to a hardening with decreasing temperature of the Cu–O bonding inside the CuO_2 planes. Such a hardening in the Cu–O bond with temperature can explain simultaneously (i) the anomalous dilatation and lattice parameter variations with temperature and (ii) the anomalous resistivity variation observed in the a – b plane as well as along c . In the latter case the increase of the Fermi level, previously suggested [6, 11] to be at the origin of these resistivity anomalies, can

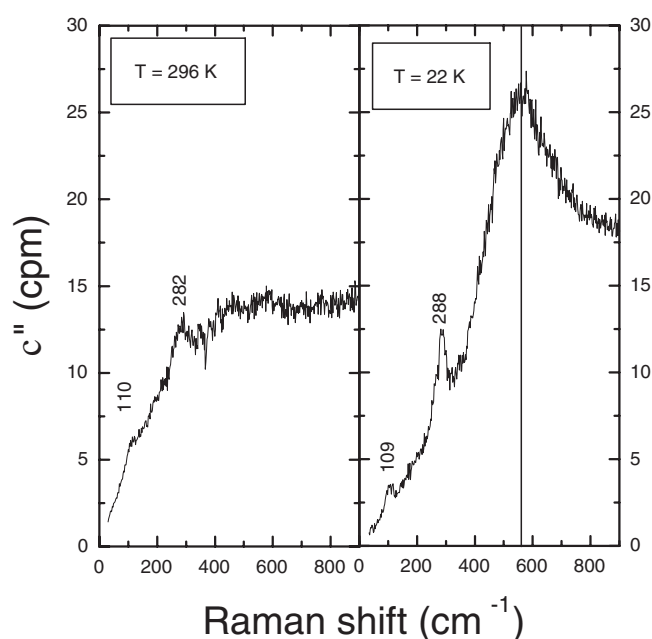


Figure 3. Raman spectra of an optimally doped Bi-2212 crystal ($T_c = 90$ K) taken in the $x'y'$ (B_{1g}) geometry at 294 K and 22 K. The Bose factor is divided out.

be directly related to the change in the Cu–O bonding. For similar reasons a ‘phase transition in the Cu–O ligands’ was recently suggested to occur, by Owens [27], in cuprates with ladder-like structure. A change in the bonding can leave more electrons to behave as free electrons and lead to an increase of the Fermi level in the valence band. Unlike previously given explanations concerning the origin of the anomalies observed in Bi-2212 crystals, the one that we give here explains, uniquely, all of these anomalies. A more classical method for the investigation of chemical bonding variation with temperature would be a determination of the variation of the Cu–O and Bi–O distances with temperature. The rather poor quality of Bi-2212 crystals makes this method more difficult to perform in that case than Raman spectroscopy. Raman spectroscopy has also clarified another point: the change in the bonding occurs in the case of optimally doped crystals as well as in the case of underdoped crystals, which was not obvious from the study of electrical anomalies. The change in the Cu–O bond is extended over a rather large temperature range; it clearly appears far above T_c and continues below T_c . It is not obvious whether the two phenomena are completely independent. To clarify this point, some more studies must be performed—for example, looking for the existence of similar shifts of Raman peaks in the case of some other HTSC (with and without Cu–O chains) above or in the temperature region of T_c .

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