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Raman-forbidden mode and oxygen ordering in $Bi_2Sr_{2-x}La_xCuO_{6+y}$ single crystals annealed in oxygen

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A Raman-forbidden phonon mode at about 840 cm^{-1} is observed popularly on the surface of pure and La-doped $Bi_2Sr_{2-x}La_xCuO_{6+y}$ $(0 \leqslant x \leqslant 0.8)$ single crystals annealed in oxygen. A remarkable excitation dependence of this additional line is found. Based on the properties of the structure of the Bi-O layer with excess oxygen atoms and the similarity in the appearance of the Raman-forbidden modes between $RBa_2Cu_3O_x$ (R = Y, Nd, Gd, Pr) and $Bi_2Sr_{2-x}La_xCuO_{6+y}$ systems, we attribute the manifestation of this additional line to the ordering of the interstitial oxygen in the Bi-O layers. Our results provide Raman evidences for confirming that the ordering of the movable oxygen may exist universally in high-temperature superconductors.

It is well known that Raman experiments can provide rich useful information in the study on the rare-earth copper oxide high-temperature superconductors. And, because of the sensitivity of the Raman mode to the local atomic-site coordination, the change of the atomic-site coordination will result in significant changes of the Raman frequency and the violation of some selection rules, which will allow the forbidden Raman processes. A kind of Raman-forbidden mode related to the oxygen vibration has been studied in $RBa_2Cu_3O_x$ (R = Y, Nd, Gd, Pr) (Refs. 1–11) and $R_{2-x}Ce_xCuO_4$ (R = Gd, Sm, Nd, Pr) (Refs. 12–15) systems. It has been pointed out that the forbidden modes are activated in Raman from the infrared-active phonon branches due to the order and/or disorder of the movable oxygen atoms.[5–15]

Another interesting phenomenon is the striking resonant enhancement of these additional Raman lines, especially in $YBa_2Cu_3O_x$. Wake *et al.*[3] studied the resonant behavior of two additional lines, at 232 and 597 cm^{-1}, for the fully oxygenated $YBa_2Cu_3O_7$, and found their resonance at 2.2 eV, although Panfilov *et al.*[11] argued that the sample of Wake *et al.* seems to be a slightly oxygen-deficient $YBa_2Cu_3O_x$ with $x = 6.9$. Käll *et al.*[8] extended this study to the underdoped $YBa_2Cu_3O_x$ with $6.35 \leqslant x \leqslant 6.87$. Recently, Panfilov and co-workers[9,11] reported the intensity ratio between additional 230-cm^{-1} line and main 340-cm^{-1} one becomes as large as 30 in $YBa_2Cu_3O_x$ with $T_c = 66$ K and found the temporal changes of these forbidden modes under exposure of polarized laser light obeys the exponential-decay law well. They attributed the phenomena to a metastable state and a kind of balance between photoinduced disordering and self-ordering processes of the oxygen in imperfect Cu-O chains.

In this paper we report the finding of the similar Raman additional phonon mode at about 840 $cm^{-}1$ on the surface of the pure and La-doped Bi-2201, $Bi_2Sr_{2-x}La_xCuO_{6+y}$ with $0 \leqslant x \leqslant 0.8$, single crystals annealed in oxygen. This additional line also shows a marked resonance at the excitation energy no more than 2.4 eV. We suggest this mode could come from an infrared-active phonon branch due to a kind of distribution of the interstitial oxygen in the Bi-O layers.

Samples of pure and La-doped Bi-2201 single crystals were prepared as described in Ref. 16. Some cleaved crystals were then annealed in O_2 for 10 and/or 36 h at 953 K. The Raman spectra were recorded by the Dilor Super Labram with a typical resolution of $1 \sim 2$ cm^{-1} in backscattering geometry at room temperature. The system consists of holographic notch filters for Rayleigh rejection and a microscope with 50× objective lens allowing a spatial resolution of less than 3 μm. The sources are an Ar^+ laser at 488.0 and 514.5 nm and a He-Ne laser at 632.8 nm. The laser power arrived at the samples is about 0.8 mW. On the sample surface, the local overheating is no more than $5 \sim 10$ K controlled by recording the anti-Stokes spectra.

Figure 1 presents the typical micro-Raman spectra of La-doped Bi-2201 single crystals with and without being annealed in oxygen. For all spectra in Fig. 1, in addition to the well-known intrinsic phonon modes at about 120, 460, and 615 cm^{-1}, there are also several bands centered at about 155, 202, 330, 400, 655, and 720 cm^{-1} induced by orthorhombic distortion, superstructural modulation and/or extra oxygen in samples. Our spectra are similar to those recorded in pure and Pb and/or La-doped Bi-2201 samples,[17–20] except the 720-cm^{-1} band, which we have found popularly in La-doped samples, and the peak at about 840 cm^{-1} in the oxygen-

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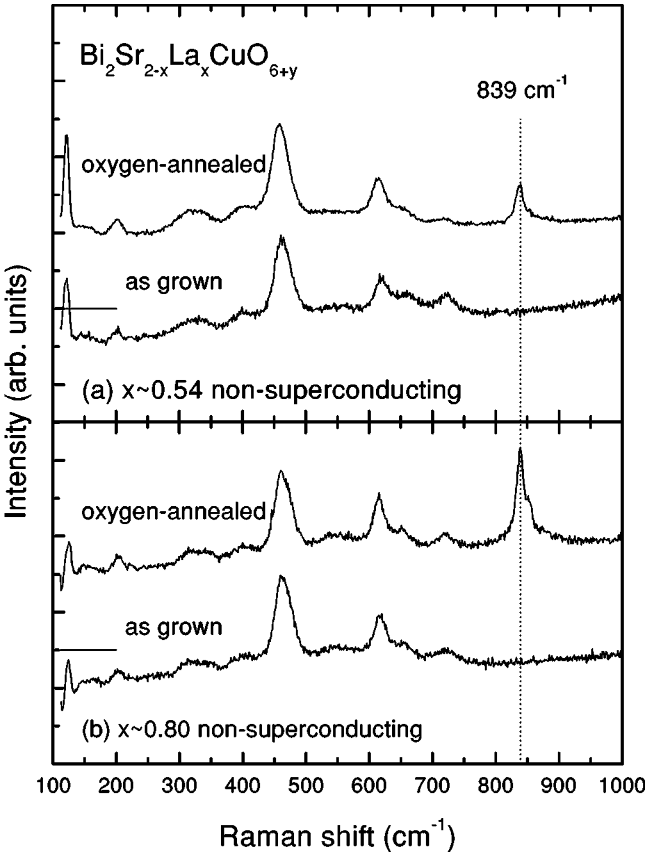

FIG. 1. Raman spectra of $Bi_2Sr_{2-x}La_xCuO_{6+y}$ single crystals with and without being annealed in oxygen. The excitation line $\lambda_{exc}=488.0$ nm. (a) $x\sim0.54$. (b) $x\sim0.80$. The short lines denote the zero-intensity level for the spectrum immediately above.

annealed samples. Because the assignment of the observed phonon features is still ambiguous and sometimes controversial, although phonons in Bi-2201 have been intensively studied by using Raman measurements,[17–23] we will discuss the common phonon modes elsewhere and focus our attention on the 840-cm^{-1} peak appearing in the annealed samples in this paper.

The additional 840-cm^{-1} line is popularly observed on the surface of more than 20 oxygen-annealed $Bi_2Sr_{2-x}La_xCuO_{6+y}$ crystals with various La content x from 0 to 0.8, with or without superconductivity, in our experiments (see also Figs. 3 and 4). There is no such mode in the Raman spectra of the as-grown samples. And, we also find that the Raman spectra recorded from the cleaved surfaces of the annealed crystals are almost same as that of the as-grown samples and no additional lines have been observed. It is implied that our annealing treatment has little influence on the Raman behavior of the inner of the samples. maybe due to the relatively high dense of the single crystal.

Figure 2 gives the corresponding x-ray-diffraction (XRD) patterns recorded on the surfaces of the same annealed crystals shown in Fig. 1. It can be seen that few peaks from any possible secondary phase can be found with the 2θ from 5–80°, even the diffraction intensity is plotted logarithmically versus the 2θ angle indicating the existence of only one single phase. Polarized Raman measurements, as shown in Fig. 3, indicate the additional 840-cm^{-1} mode has almost the same perfect A_{1g} symmetry as other main phonon modes.

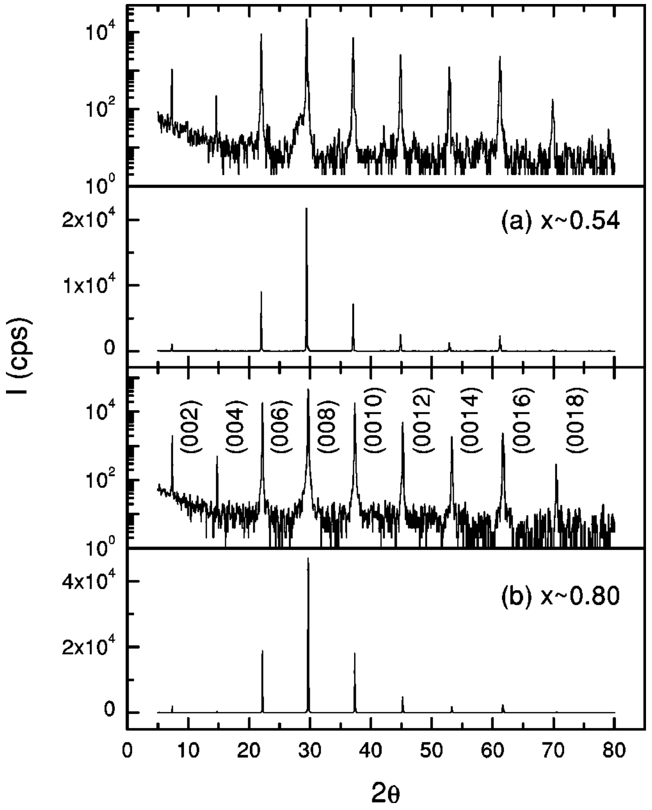

FIG. 2. XRD patterns of the same samples in Fig. 1. The logarithmic diffraction intensity is also plotted.

We also plot the dependence on the excited laser power for the lines at about 460, 620, and 840-cm^{-1} in the inset of Fig. 3. It can be seen that the 840-cm^{-1} line intensities linearly depend on the excitation power. As discussed in Refs. 2 and 11, this linear dependence implies that the possibility of nonlinear effects, which take place at higher excitations, can be ruled out. All these results strongly suggest that the additional 840 cm^{-1} line should be an intrinsic property of the oxygen-annealed Bi-2201 samples rather than a feature due to other phases.

We plot the observed resonant enhancement of the additional line in Fig. 4. The spectra are normalized to the intensity of the 460-cm^{-1} mode, respectively. From the inset of Fig. 4(b), it can be seen that the additional line is noticeably enhanced at (or a little less than) the 2.4 eV line (514.5 nm). The resonance effect is popular and reproducible although its amplitude is sample dependent. The most pronounced resonance, with the intensity ratio for the 840- and 460-cm^{-1} lines as large as about 20, is found in several $Bi_2Sr_{2-x}La_xCuO_{6+y}$ crystals with $x\sim0.5$.

Because of its high frequency and no indication for being a two-phonon mode, the 840-cm^{-1} mode can be assigned unambiguously to oxygen vibrations in Bi-2201. In the IR study of Bi-based glasses an 840-cm^{-1} mode has been extensively discussed and assigned to the totally symmetric stretching vibration of the BiO_3 pyramidal group with the C_{3v} symmetry.[24] And, an accompanied band around 860 cm^{-1} is due to the vibrations of strongly distorted BiO_6 octahedral group. At the same time, Miyaji *et al.* have pointed out that the distorted BiO_6 octahedron involves a BiO_3 species when three Bi-O distances in the BiO_6 octahedron are nearly equal.[25]

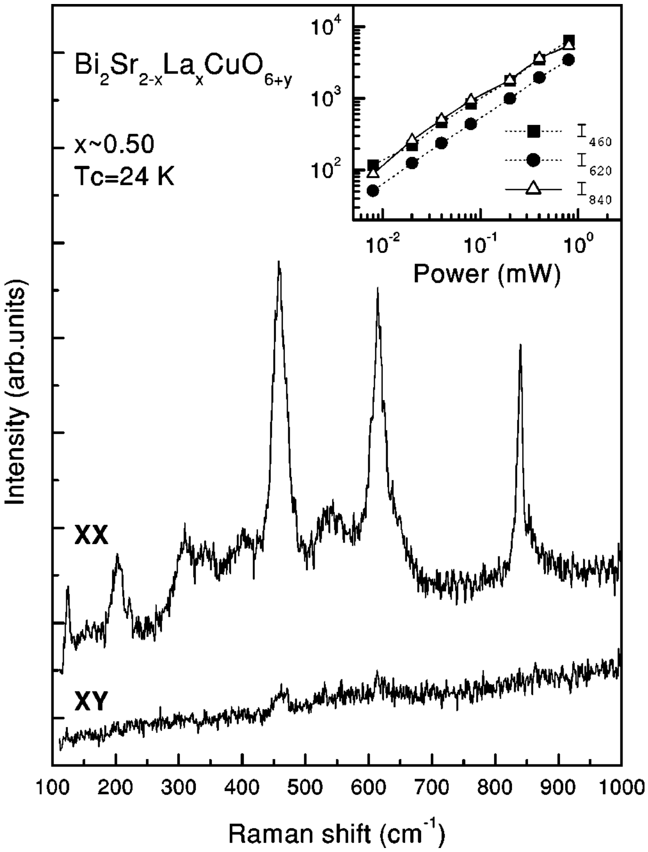

FIG. 3. Raman spectra of oxygen-annealed $Bi_2Sr_{2-x}La_xCuO_{6+y}$ single crystal ($x \sim 0.50$, $T_c = 24$ K) in the xx and xy polarization under the excitation $\lambda_{exc} = 488.0$ nm. The inset shows the dependence on the laser power for the 460-, 620-, and 840-cm^{-1} line intensity, respectively.

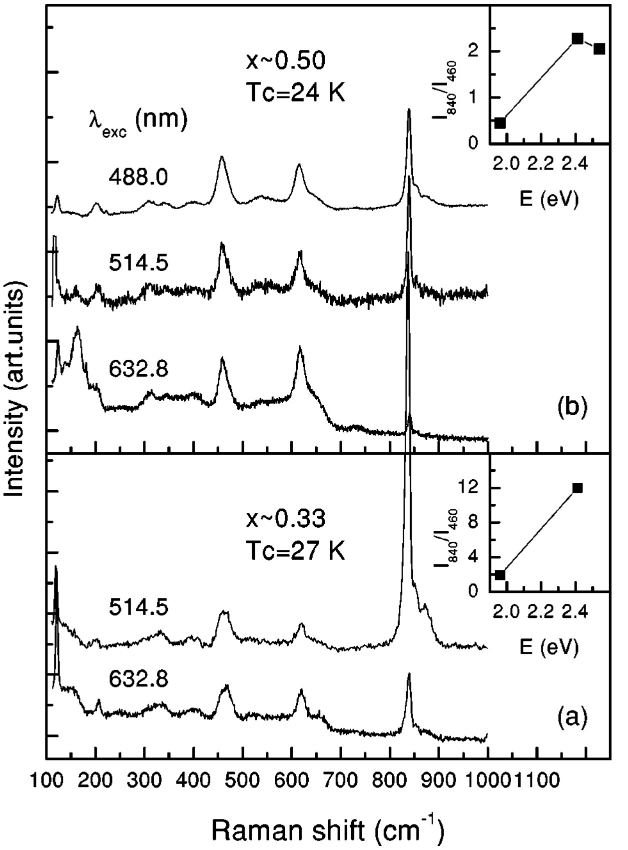

FIG. 4. Raman spectra of oxygen-annealed $Bi_2Sr_{2-x}La_xCuO_{6+y}$ single crystals for different laser-wavelength excitation. Inset shows the ratio of 840-cm^{-1} line intensity to that of 460 cm^{-1} versus the excitation energy. (a) $x \sim 0.33$, $T_c = 27$ K. (b) $x \sim 0.50$, $T_c = 24$ K.

On the other hand, the structure of superconducting Bi-2201 and its larger family $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+y}$ (generally $n = 1$, 2, or 3) were investigated energetically and systematically (see Refs. 26,27, and references therein). XRD, neutron-diffraction, and high-resolution electron microscopy measurements have been used to analyze the structure of the double Bi-O layers and the location of the extra oxygen.[26–35] Studies on $Bi_{2.13}Sr_{1.87}CuO_{6+y}$ and $Bi_{2.05}Sr_{1.54}La_{0.41}CuO_{6+y}$ by Beskrovnyi *et al.*[35] and $Bi_{2+x}Sr_{2-x}CuO_{6+y}$ by Yamamoto *et al.*[34] have revealed that the structure in the Bi-O layer of Bi-2201 is quite similar to that of Bi-2212. And, although lots of open questions still exist, it is generally believed that the Bi-O planes consist of zigzag Bi-O chains, based on the work of Bordet *et al.*,[28] with the repeated appearance of so-called rocksalt-type and oxygen deficient perovskite-type regions when excess oxygen atoms exist.[29–36]

The neutron-diffraction study of $Bi_2(Sr,Ca)_3Cu_2O_{8+x}$ has revealed that the Bi cations are situated in a highly distorted octahedron.[31,36] Of the three nearly perpendicular bonds of 2.0–2.2-Å length, two of them are directed towards the oxygen neighbors in the Bi-O plane and the third to oxygen in atoms in the Sr-O plane. Other two oxygen atoms are in the Bi-O plane and one in the neighboring Bi-O plane and these three anions are situated at the nonbonding distances 2.7–3.4 Å . The study of $Bi_{2.13}Sr_{1.87}CuO_{6+y}$ gave a similar picture in Bi-2201 (see Table 3 and Fig. 3 in Ref. 35). The schemes of the BiO_3 group chains according to these experimental results are illustrated in Fig. 5, where only one possible kind of chain with extra oxygen atoms is given.

In the $YBa_2Cu_3O_x$ system, several explanations have been proposed for the appearance of additional lines in Raman spectra. As discussed and summarized in Ref. 11, the reasonable explanation is that the short-range ordering of the chain oxygen in underdoped $YBa_2Cu_3O_x$ gives rise to the Brillouin-zone folding effect and thus makes a few Γ-point phonon states from an infrared-active phonon branch, which can be seen in Raman spectra.

Based on the above discussion, similarly, we propose a model for the manifestation of the additional 840 cm^{-1} in the Raman spectra of the oxygen-annealed Bi-2201 crystals

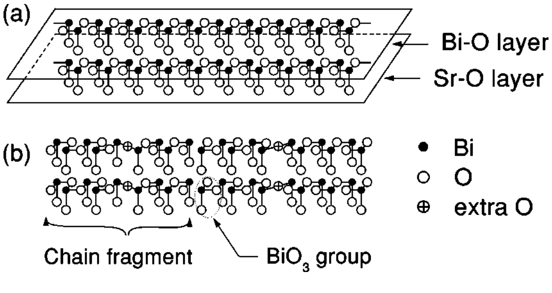

FIG. 5. Scheme of the BiO_3 chains in Bi-2201. (a) Ideal chain arrangement without extra oxygen. (b) A kind of model of the BiO_3 chains with extra oxygen.

due to the ordering of the interstitial oxygen in the Bi-O layers. In the Bi-O layer of Bi-2201, the excess oxygen atoms will break the ideal BiO_3 chains, as shown in Fig. 5(b), and chain fragments appear. These will change the site symmetry of BiO_3 group, for example, the BiO_3 groups at the end of chain fragments, and Γ-point odd-parity phonons could become Raman active when only the inversion is lost. Thus the 840-cm^{-1} mode of BiO_3 group may appear in Raman spectra due to Raman-infrared conversion when the appropriate distribution of excess oxygen forms. The reason that appropriate distribution or ordering of the extra oxygen is taken into consideration instead of a simple explanation by using the Fröhlich electron-phonon interaction is that no additional lines could be found in the as-grown samples where enough excess oxygen also exists. We consider that the annealing process in oxygen used in this study may be helpful for the formation and distribution of the extra oxygen on the surface of the crystals.

In summary, we have found a Raman-forbidden phonon mode at about 840 cm^{-1} on the surface of oxygen-annealed pure and La-doped Bi-2201 single crystals. A remarkable resonance effect of this additional line is observed. We assign this line to the phonon mode of oxygen vibrations in the BiO_3 group and a kind of excess oxygen ordering in Bi-O layer make this mode Raman active from the conversion of an infrared active phonon branch. Our results provide Raman evidences for confirming that the ordering of the movable oxygen may exist universally in high-temperature superconductors.

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