

Superconducting $\text{La}_2\text{CuO}_{4+x}$ prepared by oxygenation at high pressure: A Raman-scattering study

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Superconducting crystals of $\text{La}_2\text{CuO}_{4+x}$ prepared by high-pressure oxygenation have been analyzed by Raman spectroscopy. A direct comparison of the role of excess oxygen was made by examining the same crystals with and without excess oxygen. $\text{La}_2\text{CuO}_{4+x}$, like nonsuperconducting $\text{La}_2\text{CuO}_{4.0}$, is found to have a soft phonon associated with a tetragonal-to-orthorhombic phase transition. The A_g phonons of $\text{La}_2\text{CuO}_{4.0}$ and $\text{La}_2\text{CuO}_{4+x}$ occur at essentially the same frequency. At room temperature, $\text{La}_2\text{CuO}_{4+x}$ has no well-defined peak from two-magnon scattering, unlike $\text{La}_2\text{CuO}_{4.0}$. However, in its phase-separated form, $\text{La}_2\text{CuO}_{4+x}$ exhibits well-defined, two-magnon scattering. This establishes that the $\text{La}_2\text{CuO}_{4.0}$ phase present in $\text{La}_2\text{CuO}_{4+x}$ at low temperatures is antiferromagnetic. $\text{La}_2\text{CuO}_{4+x}$ samples prepared by slightly different methods are found to have differing amounts of excess oxygen, as indicated by variations in the intensity of the phonon and magnetic scattering. Certain samples of $\text{La}_2\text{CuO}_{4+x}$ had a phonon peak at 630 cm^{-1} that is absent in $\text{La}_2\text{CuO}_{4.0}$. While a definitive assignment is not possible, the frequency of this peak is consistent with a peroxidelike species in $\text{La}_2\text{CuO}_{4+x}$.

I. INTRODUCTION

High-temperature superconductivity was first achieved by doping nonsuperconducting (NSC) $\text{La}_2\text{CuO}_{4.0}$ with Ba or Sr to give $\text{La}_{2-x}\text{R}_x\text{CuO}_{4.0}$ ($R = \text{Ba}$ or Sr).¹ Illustrated in Fig. 1(a) is the structure of the parent compound $\text{La}_2\text{CuO}_{4.0}$. It is possible, however, to convert $\text{La}_2\text{CuO}_{4.0}$ into a superconductor in another manner, namely, by putting excess oxygen into the structure.^{2,3} When sufficient excess oxygen is introduced by heat treatment in high-pressure oxygen, a stable, bulk superconductor is obtained.⁴ The resulting materials, $\text{La}_2\text{CuO}_{4+x}$, have average oxygen stoichiometries of about 4.03–4.04, superconducting transition temperatures, T_c , of up to 39 K, and superconducting volume fractions of over 50%.⁵ From the viewpoint of charge balance, introducing excess anionic oxygen achieves the same effect as does substituting Ba or Sr (formal valence +2) for La (formal valence +3).

While it is accepted that Ba and Sr substitute for La on the La site,^{6,7} the structural defect and the configuration formed by the excess oxygen of superconducting (SC) $\text{La}_2\text{CuO}_{4+x}$ is not well established. Similar uncertainty is associated with the valence and local bonding of the excess oxygen. Early measurements of oxygen content by gravimetric analysis and chemical titration suggested that the excess oxygen was in the form of superoxide, O_2^{-1} .⁴ This view was supported by analysis using photoelectron spectroscopy.⁸ Zhou, Sinha, and Goodenough⁹ argued that disparities between gravimetric and titration measurements could be explained by surface oxygen, a result that is consistent with more recent single-crystal studies.¹⁰ Other research has suggested that the excess oxy-

gen is in the form of peroxide, O_2^{-2} . For example, neutron-diffraction measurements^{5,10} of a single crystal of average composition $\text{La}_2\text{CuO}_{4.032}$ showed as one interpretation that the excess oxygen resulted in a short O—O bond of 1.59 Å, consistent with bond lengths of peroxides. Fig. 1(b) illustrates the structural position of the excess oxygen as suggested by the neutron-diffraction study. Like NSC $\text{LaCuO}_{4.0}$, SC LaCuO_{4+x} has a tetragonal-to-orthorhombic (T-O) phase transition upon cooling. With further cooling, SC LaCuO_{4+x} undergoes phase separation into two distinct orthorhombic phases.¹¹ One of the two coexisting phases is known to contain the excess oxygen and to be superconducting. While the other phase is known to be essentially stoichiometric $\text{La}_2\text{CuO}_{4.0}$,^{5,11} little is known about its electrical or magnetic properties.

Here, Raman scattering has been used to examine single crystals of $\text{La}_2\text{CuO}_{4+x}$. A direct comparison was made between the same samples with excess oxygen (i.e., superconducting $\text{La}_2\text{CuO}_{4+x}$) and after removing the excess oxygen (i.e., nonsuperconducting $\text{La}_2\text{CuO}_{4.0}$). If the excess oxygen of SC LaCuO_{4+x} is indeed in the form of some dioxygen complex such as O_2^{-2} or O_2^{-1} , then these species should have local vibrational modes associated with them. Since the vibrational frequency of dioxygen complexes is highly sensitive to the valence of the complex, then vibrational analysis of $\text{La}_2\text{CuO}_{4+x}$ should help clarify the nature of the excess oxygen. In addition, this study has investigated the phase transition and phase separation of SC LaCuO_{4+x} using Raman spectroscopy. A soft phonon mode is found to be associated with the T-O phase transition in SC LaCuO_{4+x} . Finally, a comparison is made between light scattering from magnetic spin fluctuations (i.e., magnon scattering) from SC LaCuO_{4+x} and

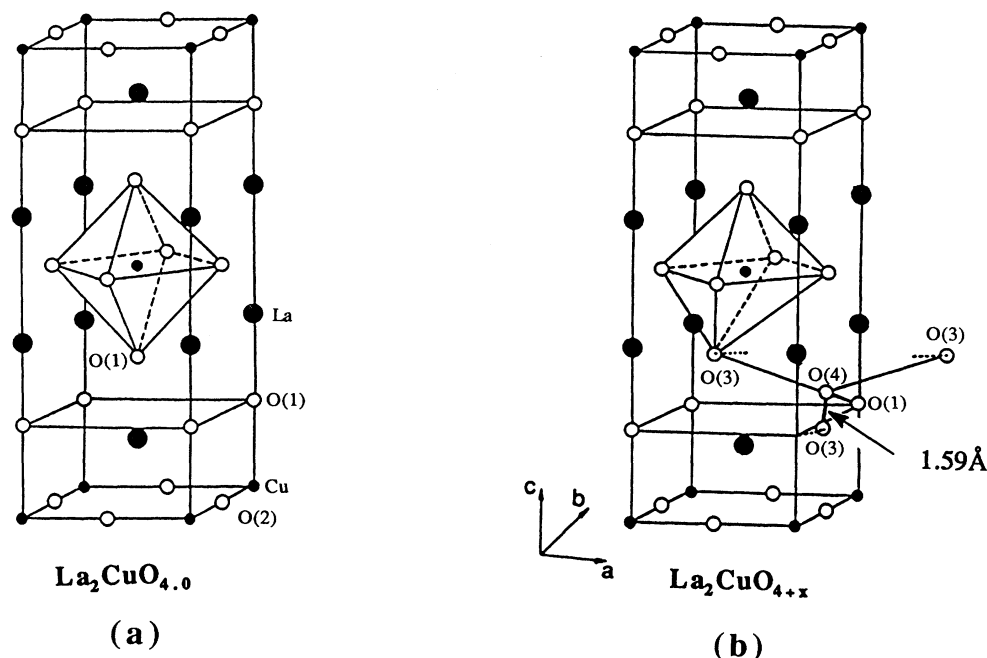


FIG. 1. Structures of tetragonal (a) $\text{La}_2\text{CuO}_{4.0}$, and (b) $\text{La}_2\text{CuO}_{4.048}$ as determined by neutron diffraction. The excess oxygen occupies site O(4), giving a short O(3)—O(4) bond distance of 1.59 Å. Drawings adapted from Chaillout and co-workers (Refs. 5 and 10).

NSC $\text{LaCuO}_{4.0}$. At room temperature, SC LaCuO_{4+x} has no well-defined peak from two-magnon scattering. However, two-magnon scattering is observed from the $\text{La}_2\text{CuO}_{4.0}$ phase of phase-separated SC LaCuO_{4+x} .

II. EXPERIMENTAL

Superconducting crystals of $\text{La}_2\text{CuO}_{4+x}$ were prepared by heating nonsuperconducting single crystals of $\text{La}_2\text{CuO}_{4.0}$ (NSC $\text{LaCuO}_{4.0}$) in either 3 kbar of O_2 at 575°C for 12 h or in 3 kbar of O_2 at 550°C for 60 h.¹² Crystals prepared by the former conditions, referred to as SC LaCuO_{4+x} No. 1, exhibited the onset of superconductivity at 39 K. Crystals prepared in the latter manner, referred to as SC LaCuO_{4+x} No. 2, exhibited the onset of superconductivity at 38 K. A direct comparison of the effect of the excess oxygen was made by examining the SC LaCuO_{4+x} No. 2 crystals by Raman spectroscopy before and after removing the excess oxygen by heating at 700°C in one atmosphere of O_2 . Raman measurements were made in a 180° backscattering geometry using either 488- or 514.5-nm excitation. All the results shown here are for 488-nm excitation. The majority of Raman measurements were made on the interior surfaces of the crystals exposed by mechanical fracture. All spectra of SC LaCuO_{4+x} shown here are from fracture surfaces, while the NSC $\text{LaCuO}_{4.0}$ spectra are from surfaces prepared by mechanical polishing. Polarization geometries are referenced to the axes of the tetragonal structure illustrated in Fig. 1. In (*yy*) polarization, the incident light propagates perpendicular to the *c* axis and the incident and scattered

light are polarized perpendicular to the *c* axis. In (*zz*) polarization, the incident and scattered light are polarized parallel to the *c* axis.

III. RAMAN SCATTERING RESULTS OF SUPERCONDUCTING $\text{La}_2\text{CuO}_{4+x}$

Like $\text{La}_2\text{CuO}_{4.0}$, SC LaCuO_{4+x} undergoes a tetragonal-to-orthorhombic (T-O) transition upon cooling (space group $I4/mmm$ to $Cmca$). The T-O transition temperature is strongly dependent on the exact oxygen content of the sample. For example, the T-O transition occurs at about 530 K for SC $\text{La}_2\text{CuO}_{4+x}$.¹³ In contrast, the SC LaCuO_{4+x} samples of this study are tetragonal at room temperature (295 K) and the T-O transition occurs at about 280 K.¹⁴ The Raman-active phonons allowed in the $I4/mmm$ structure are two of A_{1g} symmetry and two of E_g symmetry (see Table I). In the upper Raman spectrum of Fig. 2, two A_{1g} phonons are observed at 224 and 430 cm^{-1} in tetragonal SC LaCuO_{4+x} at 295 K. The orthorhombic $Cmca$ structure has additional Raman-active phonons (see Table I). The lower spectrum (77 K) of Fig. 2 shows the five A_g phonons of orthorhombic SC LaCuO_{4+x} . The frequencies of the five A_g phonons of orthorhombic SC LaCuO_{4+x} are listed in Table II.

SC LaCuO_{4+x} has an additional feature not present in NSC $\text{LaCuO}_{4.0}$; namely SC LaCuO_{4+x} separates into two distinct orthorhombic phases upon cooling.¹¹ The phase-separation temperature is strongly dependent upon the exact amount of excess oxygen. For example, the material used in the study of Jorgensen *et al.*¹¹ undergoes

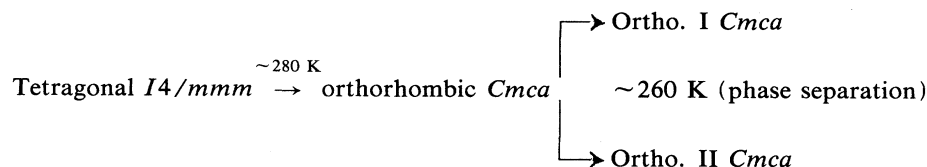
TABLE I. Symmetries of Raman-allowed phonons in different structures of $\text{La}_2\text{CuO}_{4+x}$.

Lattice	Space group	Symmetry			
Tetragonal	$I4/mmm$	$2A_{1g}$	$2E_g$		
Orthorhombic	$Cmca$	$5A_g$	$4B_{1g}$	$3B_{2g}$	$6B_{3g}$
Orthorhombic	$Fmmm^a$	$2A_g$		$2B_{2g}$	$2B_{3g}$

^aIncluded for completeness since $Fmmm$ has been suggested as one of the two phases in phase-separated SC LaCuO_{4+x} (Ref. 11).

the $I4/mmm$ to $Cmca$ transition at about 430 K and phase separation into two orthorhombic phases occurs at about 320 K. In contrast, the samples of the present study contain a greater amount of excess oxygen and the

phase separation occurs at a lower temperature, about 260 K.¹⁴ While originally one phase of the phase-separated material was thought to be $Fmmm$,¹¹ both structures are now thought to be $Cmca$:⁵



Neutron-diffraction analysis^{5,10} of a crystal prepared in a similar manner as those of the present study has established that one of the two coexisting phases is essentially stoichiometric $\text{LaCuO}_{4.0}$. The other coexisting phase contains the excess oxygen and has approximate composition $\text{La}_2\text{CuO}_{4.05}$. Interestingly, the existence of these two coexisting phases is not apparent in the Raman data, even at liquid helium temperatures. Specifically, no splitting of the five A_g phonons is observed in Fig. 2, as might be expected from two different phases with slightly different lattice parameters and vibrational force constants.

The orthorhombic $Cmca$ phases differ from the tetragonal $I4/mmm$ phase by essentially a nearly rigid rotation of the CuO_6 octahedra about the original [110] tetragonal axis.⁶ This rotation is a Raman-active vibration¹⁵ and exhibits soft-mode behavior in SC LaCuO_{4+x} as in NSC $\text{LaCuO}_{4.0}$ (see Sec. IV). As shown in Fig. 2, the A_g phonon at 131 cm^{-1} at 77 K has softened to 112 cm^{-1} at 250 K. This phonon could only be traced to about 250 K; above this temperature the phonon was not observable. Figure 3 shows the temperature dependence of the soft phonons of SC LaCuO_{4+x} and NSC $\text{LaCuO}_{4.0}$. Since the soft A_g mode is allowed only in orthorhombic SC LaCuO_{4+x} but not in the tetragonal phase, the disappearance of the soft A_g mode above about 250 K is consistent with the T-O transition observed by other techniques near 280 K.^{5,14}

IV. COMPARISON WITH NONSUPERCONDUCTING $\text{LaCuO}_{4.0}$

While NSC $\text{LaCuO}_{4.0}$ has been extensively studied by Ramans spectroscopy, the literature is inconsistent. (See review articles by Ferraro and Maroni¹⁶ and Feile¹⁷ for a summary of the literature results.) The five allowed A_g

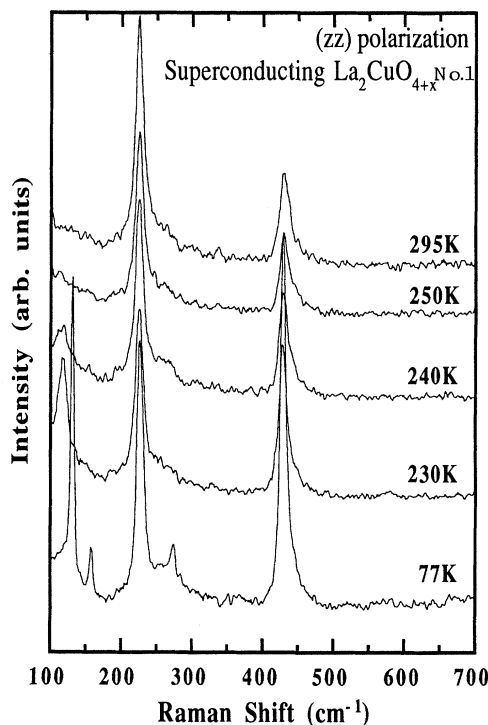


FIG. 2. Raman spectra of SC LaCuO_{4+x} No. 1 in (zz) polarization geometry permitting A_{1g} (tetragonal $I4/mmm$) and A_g symmetries (orthorhombic $Cmca$). The 131-cm^{-1} phonon (77 K) exhibits soft-mode behavior associated with the tetragonal-to-orthorhombic phase transition. Spectra are offset for clarity.

TABLE II. Comparison of frequencies of A_g phonons of SC LaCuO_{4+x} and NSC $\text{LaCuO}_{4.0}$.

Sample	Temp. (K)	Frequency (cm^{-1})					
SC LaCuO_{4+x} No. 2	4	131	155	226	276	429	
NSC $\text{LaCuO}_{4.0}$	13	129	157	228	275	428	

modes of orthorhombic $\text{LaCuO}_{4.0}$ are given in Table II. The frequencies reported here agree extremely well (to within 3 cm^{-1}) with the results of Sugai.¹⁵ This agreement is convincing evidence that these are truly the five A_g phonons of orthorhombic $\text{LaCuO}_{4.0}$. Figure 3 shows the temperature dependence of the soft A_g phonon associated with the T-O transition. This soft phonon has been extensively studied by both Raman spectroscopy^{15,18} and inelastic neutron scattering.¹⁹

Several comments comparing SC LaCuO_{4+x} and NSC $\text{LaCuO}_{4.0}$ are in order. First, the temperature dependence of the soft A_g mode is nearly identical for the two materials below about 250 K. However, the soft mode of SC LaCuO_{4+x} essentially disappears above about 250 K, roughly the temperature at which phase separation and the T-O transition occurs. Second, the A_g phonons of orthorhombic SC LaCuO_{4+x} and orthorhombic NSC $\text{LaCuO}_{4.0}$ occur at essentially the same frequency (see Table II). This insensitivity to the excess oxygen is surprising in view of the rather large structural distortion [see Fig. 1(b)] that the majority [$\sim 70\%$ (Ref. 5)] of the sample has undergone at low temperature. However, differences do exist in the relative intensities of the A_g phonons. Figure 4 shows a comparison between the orthorhombic forms of NSC $\text{LaCuO}_{4.0}$ (upper spectrum), SC LaCuO_{4+x} No. 1 (middle spectrum), and SC LaCuO_{4+x} No. 2 (bottom spectrum). Relative to the axial-oxygen vibration [O(1) in Fig. 1(a)] at 427 cm^{-1} , the peak height of the soft phonon ($\sim 131 \text{ cm}^{-1}$ at 77 K) decreases from NSC $\text{LaCuO}_{4.0}$ to

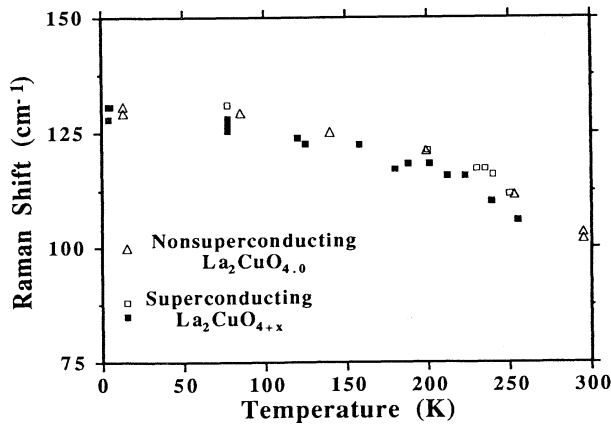


FIG. 3. Temperature dependence of the soft A_g phonon of SC LaCuO_{4+x} and NSC $\text{LaCuO}_{4.0}$. Open squares are from crystal SC LaCuO_{4+x} No. 1 and solid squares are from crystal SC LaCuO_{4+x} No. 2.

SC LaCuO_{4+x} No. 1 to SC LaCuO_{4+x} No. 2. The La vibration (228 cm^{-1}) displays the opposite trend, i.e., it increases in relative intensity. Since SC LaCuO_{4+x} has a higher oxygen content than NSC $\text{LaCuO}_{4.0}$, it is clear that the relative intensity of the soft phonon decreases with increasing oxygen content. Further, as supported in the next section, it is believed that the soft phonon of SC LaCuO_{4+x} No. 2 is weaker than that of SC LaCuO_{4+x} No. 1 due to the higher overall oxygen content of the former material. It is interesting that the same trends observed here in relative phonon intensities as $\text{La}_2\text{CuO}_{4.0}$ is doped with excess oxygen are also observed as $\text{La}_2\text{CuO}_{4.0}$ is doped with strontium.¹⁵

V. MAGNETIC SCATTERING

Raman spectroscopy has been extensively used to study spin fluctuations in the Cu-O based materials. In the parent compound La_2CuO_4 , two-magnon scattering is found as a broad but well-defined peak at about 3000 cm^{-1} with B_{1g} (tetragonal) symmetry. [See Fig. 5(a) and

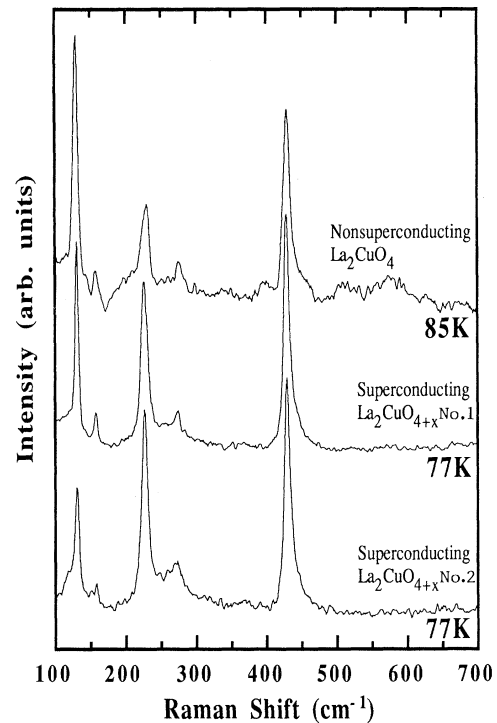


FIG. 4. Comparison of NSC $\text{LaCuO}_{4.0}$ (upper spectrum), SC LaCuO_{4+x} No. 1 (middle spectrum), and SC $\text{LaCuO}_{4.0}$ No. 2 (bottom spectrum) in polarization geometries permitting A_g symmetries (orthorhombic $Cmca$). Spectra are offset for clarity.

Refs. 15 and 20]. Since the two-magnon peak is dominated by short-range magnetic order, it is little affected by temperature and persists above T_N .²¹ As shown in Figs. 5(b) and 5(c) at 295 K neither SC LaCuO_{4+x} No. 1 or SC LaCuO_{4+x} No. 2 exhibit a well-defined two-magnon peak. This is not surprising since Lyons and Fleury²¹ have shown that the two-magnon scattering of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ shifts to lower frequency and greatly broadens upon doping the parent nonsuperconducting compound $\text{YBa}_2\text{Cu}_3\text{O}_6$ with oxygen. For the supercon-

ductor $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ ($T_c \approx 90$ K), there is no well-defined peak from magnon scattering. Similar results are observed in the Tl-based system. That is, the antiferromagnetic insulator $\text{TlYBa}_2\text{Cu}_2\text{O}_7$ has a well-defined two-magnon peak but the doped superconductor $\text{TlCaBa}_2\text{Cu}_2\text{O}_7$ does not.²²

SC LaCuO_{4+x} is more complicated since it separates into two coexisting phases below about 260 K. Neutron-diffraction analysis has shown that from a structural standpoint, one of these two phases is essentially $\text{La}_2\text{CuO}_{4.0}$.^{5,11} The other phase contains the excess oxygen and is known to be superconducting.¹¹ Less is known about the $\text{La}_2\text{CuO}_{4.0}$ phase in phase-separated SC LaCuO_{4+x} , although it has been suggested to be nonsuperconducting.¹² Figures 5(b) and 5(c) illustrate the magnetic scattering observed from SC LaCuO_{4+x} No. 1 and SC LaCuO_{4+x} No. 2 at 77 K, well below the temperature of phase separation. SC LaCuO_{4+x} No. 1 [Fig. 5(b)] has a well-defined two-magnon peak at about 3000 cm^{-1} . At 77 K, SC LaCuO_{4+x} No. 2 [Fig. 5(c)] has an extremely weak two-magnon peak at about 3000 cm^{-1} . Since the phase with the excess oxygen is known to be superconducting, it will not exhibit a well-defined two-magnon peak, as discussed above. Therefore, the two-magnon peak observed in SC LaCuO_{4+x} at 77 K must result from the $\text{La}_2\text{CuO}_{4.0}$ phase and this phase must be antiferromagnetic and nonsuperconducting.

At 77 K, the two-magnon peak of SC LaCuO_{4+x} No. 1 is intense, while the two-magnon peak of SC LaCuO_{4+x} No. 2 is barely discernable. This implies that SC LaCuO_{4+x} No. 2 has less of the antiferromagnetic phase $\text{La}_2\text{CuO}_{4.0}$ than does SC LaCuO_{4+x} No. 1. Since the amount of the $\text{La}_2\text{CuO}_{4.0}$ phase that forms is reduced as the average oxygen content of the material increases,¹¹ it is concluded that the SC LaCuO_{4+x} No. 2 material has a higher oxygen content than does SC LaCuO_{4+x} No. 1. This conclusion is consistent with the observation of Sec. IV, where the intensity of the soft A_g phonon was found to be related to the amount of excess oxygen. Specifically, in Fig. 4, the soft phonon of SC LaCuO_{4+x} No. 2 (bottom spectrum) was weaker than that of SC LaCuO_{4+x} No. 1 (middle spectrum).

As seen in Fig. 5, both SC LaCuO_{4+x} and NSC $\text{LaCuO}_{4.0}$ have numerous Raman features between about 700 and 1500 cm^{-1} . For NSC $\text{LaCuO}_{4.0}$, these high-frequency peaks have been interpreted as either second-order phonons enhanced by some resonance process^{15,23} or magnetic scattering from a spin-density wave in the antiferromagnetic structure.²⁴ These peaks are largely absent in tetragonal $\text{La}_2\text{CuO}_{4.0}$,²⁴ and can be largely eliminated by heat treatment in low pressures of oxygen.²⁵ For SC LaCuO_{4+x} , this high-frequency structure is largely absent at 295 K [Figs. 5(b), 5(c), and 6] but is present at lower temperatures. The intensity of the structure between 700 and 1500 cm^{-1} varies greatly from sample to sample. Compare, for example, Figs. 5(b) (SC LaCuO_{4+x} No. 1) and 5(c) (SC LaCuO_{4+x} No. 2). Even within a sample, the intensity of this structure was variable, for example, the spectra of Figs. 6 and 5(c), taken from different spots on the same crystal.

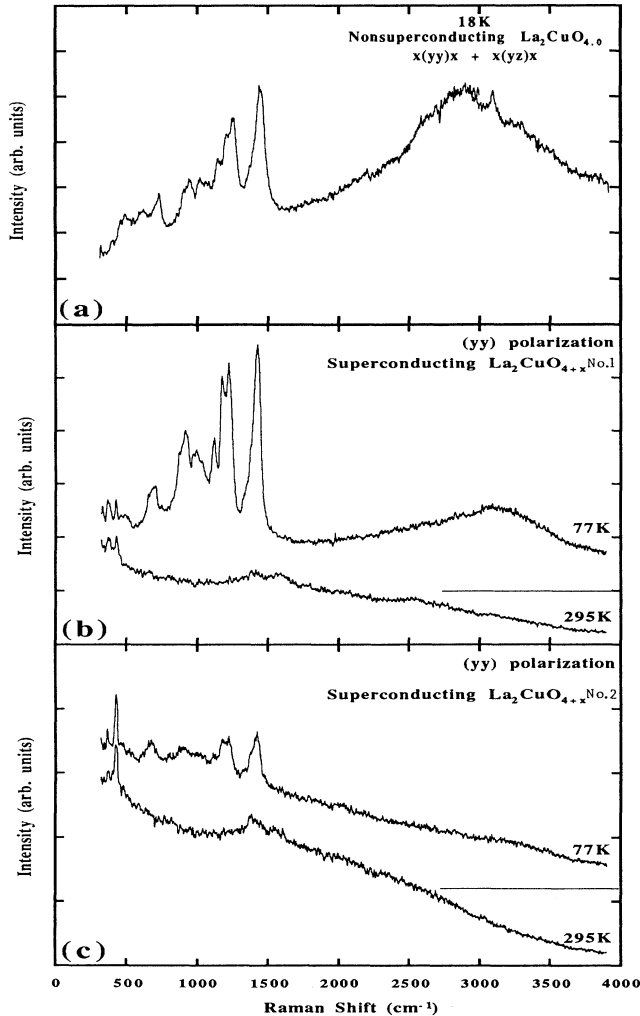


FIG. 5. Comparison of two-magnon scattering in (a) NSC $\text{LaCuO}_{4.0}$, (b) SC LaCuO_{4+x} No. 1, and (c) SC LaCuO_{4+x} No. 2. Spectra were obtained from the same region of each crystal as the corresponding spectra of Fig. 4. The 77-K spectra are offset from the 295-K spectra for clarity. The short horizontal lines in (b) and (c) represent zero intensity for the 77-K spectra. The notation $x(yy)\bar{x}$ refers to polarization of both the incident and scattered light along the $b=y$ axis with the incident laser beam and the scattered light propagating along the $a=x$ axis. $x(yy)\bar{x}$ polarization geometry permits $A_{1g}+B_{1g}$ symmetry in tetragonal $I4/mmm$ and A_g+B_{2g} symmetry in orthorhombic $Cmca$. $x(yz)\bar{x}$ polarization geometry permits E_g symmetry in tetragonal $I4/mmm$ and $B_{1g}+B_{3g}$ symmetry in orthorhombic $Cmca$.

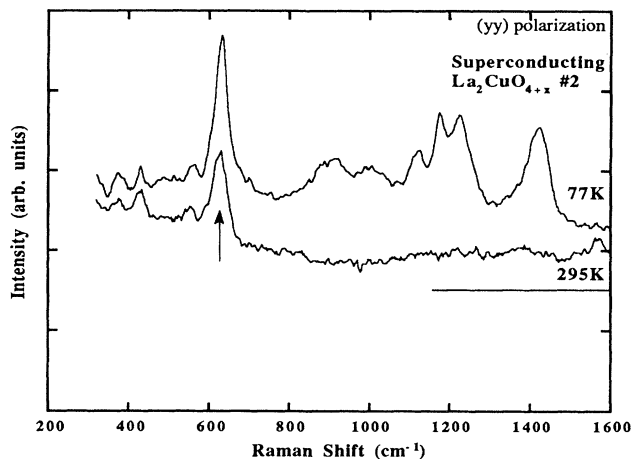


FIG. 6. Raman spectra of SC LaCuO_{4+x} No. 2 at 295 and 77 K. Peak at 630 cm^{-1} , labeled with an arrow, is present in some but not all regions of SC LaCuO_{4+x} No. 2 crystals. This feature was not observed in samples SC LaCuO_{4+x} No. 1 and NSC $\text{LaCuO}_{4.0}$. The spectra are offset for clarity and the short horizontal line represents zero intensity for the 77-K spectrum.

VI. THE 630-cm^{-1} PEAK OF SC LaCuO_{4+x} NO. 2: OBSERVATION AND DISCUSSION

A substantial difference exists between SC LaCuO_{4+x} No. 2 and NSC $\text{LaCuO}_{4.0}$ when examined in a (yy) polarization geometry. As shown in Fig. 6, SC LaCuO_{4+x} No. 2 has a scattering peak at 630 cm^{-1} at both 295 and 77 K, that is, in both the tetragonal and orthorhombic (phase-separated) forms. This peak is totally absent in (zz) polarization spectra. The 630-cm^{-1} feature has been observed in spectra from "as-received" surfaces of two different crystals prepared by heating in 3 kbar of O_2 at 550°C for 60 h (i.e., the conditions denoted by the notation SC LaCuO_{4+x} No. 2). Interestingly, this feature was observed from some but not all fracture surfaces of SC LaCuO_{4+x} No. 2. In contrast, this peak was absent from NSC $\text{LaCuO}_{4.0}$ and SC LaCuO_{4+x} No. 1 at all locations and temperatures examined. Further, this peak has not been observed in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.¹⁵ The presence of the 630-cm^{-1} peak on fracture surfaces and its strong polarization dependence greatly diminish the possibility that the peak is impurity related. Instead, it can be argued that the 630-cm^{-1} peak is observed in regions of high average oxygen content. When the 630-cm^{-1} peak was

observed using (yy) polarization, examination of the same spot using (zz) polarization revealed that the soft A_g phonon was weaker than in any of the spectra of Fig. 4. This includes the bottom spectra of Fig. 4, obtained from a region of SC LaCuO_{4+x} No. 2 where the 630-cm^{-1} peak was not observed. Given the relationship between the intensity of the soft phonon and oxygen content, we conclude that the 630-cm^{-1} peak is associated with regions having the highest amounts of excess oxygen. The absence of the 630-cm^{-1} peak within some regions of the SC LaCuO_{4+x} No. 2 crystals indicates that the crystals are not uniformly loaded with oxygen. This is not surprising, given the size of the crystals (about 1–2 mm in thickness).

There are two sources of Raman-scattering peaks in SC LaCuO_{4+x} : phonon scattering and magnetic scattering. (An additional source of intensity is electronic scattering from charge carriers. However, this scattering, if present, should be in the form of very broad features, i.e., a continuum). It is unlikely that the peak at 630 cm^{-1} results from magnetic scattering. Below its Néel temperature (T_N) of $\sim 300\text{ K}$,¹³ NSC $\text{LaCuO}_{4.0}$ has 3D antiferromagnetic ordering of the Cu^{2+} spins. Above T_N , the spins are still ordered in two dimensions. As discussed in the last section, two-magnon (spin-pair) scattering occurs as a well-defined peak at about 3000 cm^{-1} in nonsuperconducting $\text{La}_2\text{CuO}_{4.0}$.²⁰ The frequency of one-magnon scattering in $\text{La}_2\text{CuO}_{4.0}$ is essentially zero²⁶ near the zone center (i.e., $k \approx 0$), as probed by light scattering. Clearly, the 630-cm^{-1} peak is not associated with two-magnon scattering or one-magnon scattering near the zone center. It is possible that defects such as vacancies could result in observable scattering from a localized, single spin flip. Indeed, a single spin flip next to a vacancy has been suggested as a possible origin of the $\sim 1430\text{-cm}^{-1}$ peak of $\text{La}_2\text{CuO}_{4.0}$.^{27,28} However, a similar explanation is not possible for the 630-cm^{-1} peak. If one takes the exchange parameter $J = 1000\text{--}1300\text{ cm}^{-1}$ (Refs. 26 and 29) and $\text{spin} = \frac{1}{2}$, then 630 cm^{-1} requires more than two vacancies around a copper atom,²¹ an unphysical prospect. Since magnetic scattering can be ruled out, it is concluded that the 630-cm^{-1} peak of SC LaCuO_{4+x} is phonon scattering.

One interpretation is that the peak at 630 cm^{-1} is a local phonon mode associated with the excess oxygen in the structure. Following this possibility and literature suggestions that the excess oxygen forms a dioxygen complex in the structure, it is interesting to compare the frequency of O_2^{-x} vibration as a function of O—O bond dis-

TABLE III. Vibrational frequency of dioxygen complexes of coordination compounds as a function of valence. Data from Nakamoto (Ref. 31).

	$[\text{O}_2^+]\text{AsF}_6$	Molecular O_2	Superoxide $\text{K}[\text{O}_2^-]$	Peroxide $\text{Na}_2[\text{O}_2^{2-}]$	SC LaCuO_{4+x}
Bond distance (\AA)	1.123	1.207	1.28	1.49	1.59^a
ν (cm^{-1})	1858	1555	1108	~ 760	630^b

^aShort O—O bond length as suggested by neutron diffraction (Ref. 5).

^bRaman peak observed in SC LaCuO_{4+x} No. 2 but not in NSC LaCuO_{4+x} .

tance. As seen in Table III, the O—O vibration becomes weaker with increasing O—O bond distance. Table III also lists the 630-cm^{-1} frequency and the short O—O bond length observed by neutron diffraction for $\text{La}_2\text{CuO}_{4.048}$.⁵ While this interpretation cannot be rigorously defended (see below), the relationship would suggest that if the 630-cm^{-1} peak is indeed from dioxygen vibration, then the dioxygen complex is more like peroxide (O_2^{-2}) than like superoxide (O_2^{-1}). The observed polarization dependence of the 630-cm^{-1} peak is qualitatively consistent with the structural model proposed by Chailout and co-workers.^{5,10} As illustrated in Fig. 1, the short O(3)—O(4) bond of 1.59 \AA lies largely within the x - y plane. Therefore, vibration of O(3)—O(4) along this bond should have a large effect on the polarizability measured by (yy) polarization and a smaller influence on the polarizability measured by (zz) polarization. The experimental observations are consistent with this intuition—the 630-cm^{-1} peak is strong for (yy) polarization (Fig. 6) but is absent for (zz) polarization. However, arguments based upon strong scattering for (yy) polarization are weakened by the fact that anomalous scattering peaks are observed with (yy) polarization for $\text{La}_2\text{CuO}_{4.0}$ (see Sec. V).

Despite the reasoning given above, the 630-cm^{-1} peak cannot be definitely assigned to vibration of a dioxygen complex. To begin with, 630 cm^{-1} is within the frequency range expected for vibrational modes of oxygen in the stoichiometric $\text{La}_2\text{CuO}_{4.0}$ structure. For example, an X -point mode of tetragonal $\text{La}_2\text{CuO}_{4.0}$ has been calculated from first principles to occur at 731 cm^{-1} .³⁰ This mode is mainly the planar-breathing vibration of O(2) with some contribution from the axial vibration of O(1). In orthorhombic $\text{La}_2\text{CuO}_{4.0}$, this mode is folded back into the zone center and is Raman allowed. Indeed, Weber *et al.*²³ have assigned a peak observed at 710 cm^{-1} in orthorhombic $\text{La}_2\text{CuO}_{4.0}$ to the planar-breathing mode of O(2). There exist several mechanisms that might allow phonons that are formally Raman inactive to gain Raman intensity even in tetragonal SC LaCuO_{4+x} . The excess oxygen can be viewed as a defect that destroys the long-range order and local symmetry of the lattice and thus relaxes selection rules associated with momentum conservation and phonon symmetry. This could allow vibrational modes that are not at the zone center or are normally only ir-active to gain Raman intensity. In addition, the SC LaCuO_{4+x} structure may have a larger unit cell than even the underlying orthorhombic structure of $\text{La}_2\text{CuO}_{4.0}$. This large unit cell could have additional Raman-allowed phonons not directly related to the speculated dioxygen species and the 630-cm^{-1} peak could be such a phonon. Finally, the 630-cm^{-1} peak could be a

second-order phonon.

Despite the complications discussed above, several conclusions can be drawn. The 630-cm^{-1} peak of SC LaCuO_{4+x} No. 2 is of phonon origin. Since it is not present in NSC $\text{LaCuO}_{4.0}$ or $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$,¹⁵ the 630-cm^{-1} peak results from the introduction of excess oxygen into the structure. Further, the 630-cm^{-1} peak is not related to either the orthorhombic distortion or phase separation since it occurs in tetragonal SC LaCuO_{4+x} .

VII. SUMMARY

In certain aspects, the excess oxygen of SC LaCuO_{4+x} has little influence on the Raman-allowed phonons. For example, at low temperature, five A_g phonons are found at essentially the same frequency in both SC LaCuO_{4+x} and NSC $\text{LaCuO}_{4.0}$. Further, like NSC $\text{LaCuO}_{4.0}$, SC LaCuO_{4+x} has a soft-mode phonon associated with the orthorhombic-to-tetragonal transition and the temperature dependence of this mode below about 250 K is nearly identical in the two materials. However, key differences do exist between SC LaCuO_{4+x} and NSC $\text{LaCuO}_{4.0}$. The soft A_g phonon of SC LaCuO_{4+x} is only observed below about 250 K, approximately the temperature of phase transition and phase separation.^{5,12,14} In contrast, the T-O transition in NSC $\text{LaCuO}_{4.0}$ occurs at about 530 K. At room temperature, SC LaCuO_{4+x} does not have a well-defined peak from two-magnon scattering, in contrast to NSC $\text{LaCuO}_{4.0}$. At 77 K (i.e., in its phase-separated form), SC LaCuO_{4+x} exhibits a well-defined peak from two-magnon scattering. This establishes that the $\text{La}_2\text{CuO}_{4.0}$ present in phase separated SC LaCuO_{4+x} is antiferromagnetic and not superconducting. In both the tetragonal and orthorhombic forms, certain regimes of SC LaCuO_{4+x} have a phonon peak at 630 cm^{-1} , unlike NSC $\text{LaCuO}_{4.0}$. This peak is believed to occur in samples containing the most excess oxygen. If this peak results from a local vibrational mode of a dioxygen species in the structure, then the observed frequency is consistent with peroxide but not superoxide. However, a definitive assignment of the 630-cm^{-1} phonon is not possible at this time.

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