

**Anomalous shifts of oxygen mode frequencies in
 $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$,
 and $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_8$ studied by photoinduced
 infrared absorption and Raman spectroscopy**

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Comparison of photoinduced local modes (PILM's) of insulating $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_8$ with Raman spectra of their metallic counterparts suggests that carrier injection anomalously increases the frequencies of phonons involving z -axis apex-oxygen motion in both the dilute (insulator) and concentrated (metallic) limit. In La_2CuO_4 , we observe PILM's whose frequencies suggest a correspondence with the "ghost modes" observed in neutron scattering [Rietschel *et al.*, *Physica C* **162-164**, 1705 (1989)]. These data, together with Raman data on apex-oxygen anharmonicity, enable us to discuss the vibronic mode couplings involved in polaron formation in the three materials.

Raman-spectroscopy studies of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as a function of doping have established that the frequency of the symmetric 500-cm^{-1} A_g mode involving the z -axis vibration of the apex-oxygen atom increases with increasing carrier concentration.¹ The observed increase in phonon frequencies is unusual in the sense that it would imply that doping reduces the electronic screening of these out-of-plane modes. In contrast, the red shift of infrared (ir) active modes involving displacements of the apex O(4) (at 155 and 569 cm^{-1}) is consistent with the change in lattice constants upon doping.² The behavior in the ir can be easily understood, since ir modes involve displacements of a relatively large number of ions in the unit cell. Raman modes are simpler in comparison, involving the displacements of a smaller number of ions.¹ In this sense Raman spectroscopy can probe more locally into the electron-phonon interaction of certain ions.

There appears to be a fundamental connection between the unusual behavior of the out-of-plane vibrational Raman modes and superconductivity in the high- T_c oxides. An anomalous increase in the O(4) A_g mode frequency in the immediate vicinity of T_c has recently been found in extended x-ray-absorption fine-structure (EXAFS) spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.³ In addition, a sharp decrease of the a and c lattice constants over a narrow temperature region of a few degrees above T_c has been reported

in x-ray diffraction measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$,⁴ suggesting a structural phase transition just above T_c . Whether these two effects have the same origin is not yet understood, but these structural anomalies in the vicinity of T_c suggest coupling of the lattice, and apex oxygens in particular, to critical fluctuations accompanying the normal-to-superconducting transition. Indeed, the martensitic Jahn-Teller (JT) phase transitions just above T_c in the A15 compounds (V_3Si , V_3Pt , Nb_3Sb , etc.) provide a precedent for such behavior.^{5,6}

The appearance of localized phonon modes and self-localized electronic transitions upon photoexcitation in all high- T_c insulator precursor materials studied to date indicates that the photoinduced carriers form polarons in the insulator materials. The midinfrared optical conductivity $\sigma(\omega)$ of doped superconducting high- T_c materials suggests that this polaronic behavior persists in the doped and superconducting state.^{7,8}

As an explanation for the anomalous behavior of the apical O modes, we have recently suggested⁹ that an interaction between the apex O(4) oxygen vibration and a localized electronic state changes the local crystal field of the O(4) atom upon doping, possibly giving rise to the anharmonicity and anomalous positive frequency shift of the 500 cm^{-1} apex-oxygen modes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

In this paper we attempt to clarify the cause for the

anomalous behavior of the out-of-plane modes by investigating the local deformations caused by carrier photoinjection into insulating La_2CuO_4 , $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$, and $\text{Tl}_2\text{Ba}_2\text{Ca}_{0.98}\text{Gd}_{0.02}\text{Cu}_2\text{O}_8$. A comparison of the photoinduced (vibrational) local modes (PILM's) with Raman spectra on both metallic and insulating material enables us to assign the PILM's and attempt to identify some of the electronic states involved in causing the observed phonon anomalies.

The photoexcitation measurements were done in the usual way.⁸ Similarly, the Raman measurements were done in a way described previously.¹⁰ In Fig. 1, we show Raman spectra and the PILM's obtained from photoinduced absorption on the insulators. The Raman spectra of La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are in agreement with published data. We find the Raman spectrum of insulating $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_8$ (Fig. 1) to be different from the published spectra of metallic $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$.¹¹ In particular, the apical O mode frequencies appear to shift upward in the metal, similar to the already-mentioned behavior in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. (The background scattering in the region below 500 cm^{-1} is mainly due to the substantial scattering from the rough surface of the cold-pressed powder pellets.) The difference in the Raman spectra between the metal and the insulator in the Tl compounds could arguably be caused by the tendency of the Tl material to form different compounds. However,

the very small amount of Gd substitution (2 at. %), as well as the very similar ionic radii of Gd and Ca ions, suggest that the substitution should not significantly affect the structure. Powder x-ray measurements¹² of the insulating samples and the metallic (and superconducting) 2:2:1:2-phase samples show virtually identical patterns with no sign of one- or three-layer Tl impurity phases. In addition, Raman measurements on pressed ceramic pellets of the $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_8$ show very consistent spectra over the whole pellet surface, implying that there are no impurity phases present.

We cannot find any correspondence between the PILM's and the observed Raman modes in the insulator species of any of the three compounds (Fig. 1). In contrast, we do observe a fairly clear correspondence between the PILM's on the insulator phase and ($k = 0$) Raman spectra on the metallic phase of both $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ (Fig. 2). We use this resemblance to assign the PILM's in Table I. In both materials the strongest observed PILM is the apex O(4) oxygen z -axis vibrational mode: at 500 cm^{-1} in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and 490 cm^{-1} in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$. The shift between the PILM's and the Raman frequencies in the insulator from which they are derived, $\Delta\omega$, is $\approx 55\text{ cm}^{-1}$ for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\approx 47\text{ cm}^{-1}$ for $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_8$. The frequency shifts of the Raman modes upon doping are also shown in Table I. For local modes, k is no longer a

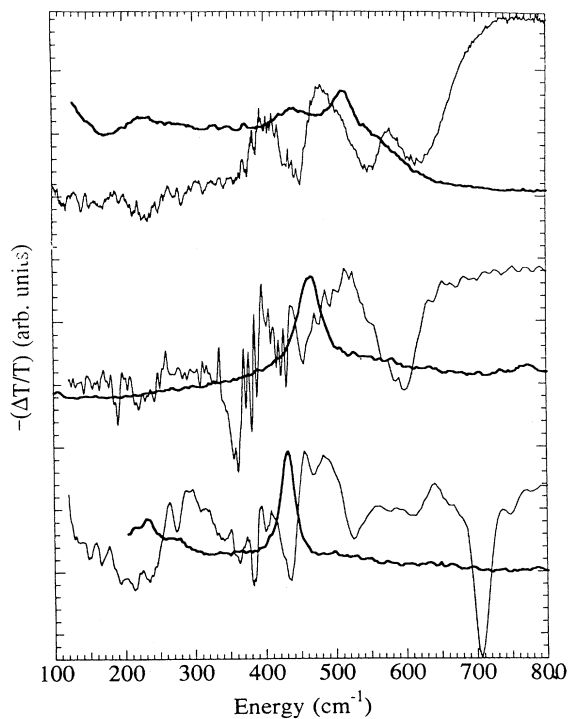


FIG. 1. Photoinduced local vibrational modes (PILM's) (thin lines) in $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_8$ (top), $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$ (middle), and La_2CuO_4 (bottom) are compared with Raman spectra (thick lines) of insulating $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_8$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$, and La_2CuO_4 .

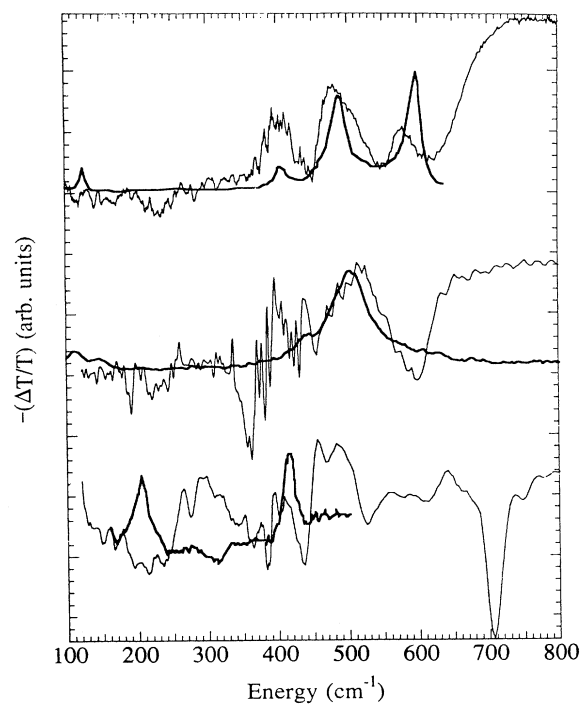


FIG. 2. Photoinduced local vibrational modes (PILM's) (thin lines) in $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_8$ (top), $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$ (middle), and La_2CuO_4 (bottom) are compared with Raman spectra (thick lines) of metallic $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, $\text{YBa}_2\text{Cu}_3\text{O}_7$, and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. The Raman spectra for $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ are taken from Ref. 11.

TABLE I. Frequencies (in cm^{-1}) of the PILM's compared with the symmetric Raman mode frequencies in the insulator and metal.

Compound	Raman ω		PILM ω	Shift		Assignment
	Metal	Insulator	Insulator	$\Delta\omega^a$	$\Delta\omega^b$	
$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$			650			new mode ^c (weak)
			480			new mode ^c
	433 (A_{1g})	430 (A_g)			< 10	apex O(2)-La out of phase \mathbf{c}
			400			new mode ^c (weak)
$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$			300			new mode ^(c)
	229 (A_{1g})	229 (A_g)			< 10	apex O(2)-La in phase \mathbf{c}^1
	505 (A_g)	475 (A_{1g})	510	+55	+40	apex O(4) \mathbf{c}
$\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$	420 (A_g)	460 (A_{1g})	400	-60	-40	planar O(2)-O(3) \mathbf{c}^1
	595 (A_{1g})	520 (A_{1g})	578	+50	+75	Tl-O(3) \mathbf{c}
	490 (A_{1g})	440 (A_{1g})	485	+45	+45	apex O(2) \mathbf{c}
	410 (A_{1g})		410			O(1) \mathbf{c}^{11}

^aPILM: Raman (insulator).

^bRaman (insulator): Raman (metal).

^cSee text.

good quantum number and the range of the Brillouin zone $\Delta\mathbf{k}$ probed by the photoinduced local mode spectroscopy is related to the spatial extent of the distortion (Δx) created by the photoinduced carrier, $\Delta\mathbf{k} \simeq 2\pi/\Delta x$. A correspondence of PILM's with $k = 0$ Raman modes and their relative sharpness thus suggests that the modes from which the PILM's are derived have relatively little dispersion.

The remarkable correspondence between the frequencies of the PILM's in the *insulators* and the Raman spectra of the *metallic* phase of both $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ strongly suggests that the local distortion caused by a photoinjected carrier (dilute limit) is very similar to the change in crystal field caused by doping. Previously, we have shown⁹ that photoexcitation mimics doping behavior in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: both the O(4) apical z -axis PILM and the O(2)-O(3) z -axis PILM appear at the frequencies corresponding to Raman spectra of metallic $\text{YBa}_2\text{Cu}_3\text{O}_7$ (505 and 420 cm^{-1}). Whereas the 500 cm^{-1} O(4) apical mode *hardens*, the 420 cm^{-1} O(2)-O(3) planar mode *softens* upon doping¹ or photoexcitation.

Present work on $\text{Tl}_2\text{Ba}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ -based semiconducting material shows similar behavior. In this material, the three PILM's involving z -axis motion of oxygen atoms are observed at frequencies that are again very close to those of the metal (Fig. 2 and Table I) and are up-shifted with respect to those of the insulator. We note an upward frequency shift also in the Tl-O vibrations (at 595 cm^{-1}), suggesting that the valence fluctuations that are causing the local instability in the Cu-apex O behavior are also present in the Tl-O layers. The increase in the apical oxygen frequencies upon the introduction of carriers observed in both spectroscopies suggests that this behavior is a more general phenomenon in the high- T_c cuprates with pyramidal structure, i.e., the 1:2:3 and 2:2:1:2 compounds. They show an absence of a mirror plane of the apical modes with respect to the CuO_2 planes and give rise to locally polar electron-phonon coupling.¹³ The observation of (otherwise nonpolar) apical O modes in in-

frared spectroscopy is consistent with this interpretation: upon photoinjection they acquire a dipole moment and become observable in infrared absorption.

In La_2CuO_4 , no significant shift of the apical O vibration frequency is seen in Raman spectra with doping (any possible shifts are smaller than 10 cm^{-1}). Also, we observe no clear correspondence between the PILM's and the Raman spectra in either the metal or the insulator. Instead, new additional modes appear at frequencies that cannot be as easily assigned as in the 1:2:3 and 2:2:1:2 structure materials (Fig. 1 and Table I). Perhaps importantly, one of the new modes at 480 cm^{-1} (Fig. 1 and Table I) corresponds in frequency to the "ghost mode," which is observed in the neutron-scattering data of Rietschel *et al.*¹⁴ on La_2CuO_4 . In addition to this mode, we observe a rather broad feature centered around 300 cm^{-1} and a set of weaker modes at 400 and 650 cm^{-1} . More detailed comparisons between these data and neutron-scattering experiments (also including the 1:2:3 and 2:2:1:2 compounds) have to be postponed until more neutron data become available. Nevertheless, the observation of the PILM at 480 cm^{-1} does clearly imply that this mode is coupled to the injected carriers.

Note that in contrast to the 1:2:3 and 2:2:1:2 materials, La_2CuO_4 has an octahedral structure surrounding the planar Cu ion, with no polar terms in the e - p coupling. We conclude that the situation is more complex in La_2CuO_4 than in the other two materials, the complexity arising from the different symmetry of the electron-phonon coupling of the octahedrally coordinated Cu in these materials.¹³

In order to explain the anomalous positive frequency shift of the apex z -axis oxygen vibrations in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, we can invoke two possible mechanisms.

(a) The shift arises from level repulsion (or crossing) between the symmetric vibrational modes and a coupled collective low-frequency electronic excitation of A_g symmetry (e.g., an acoustic plasmon). This could explain the positive frequency shift upon doping of the apical modes

in Raman spectra, but it cannot easily account for the shift observed in our photoexcitation experiments, where the carrier density is probably too low for plasmons to be present.

(b) The shift arises from a more localized Jahn-Teller (JT) or pseudo-JT effect (PJT), where the change in occupancy at (or around) the JT site induces a local distortion of the surrounding structure. As a result of this distortion caused by the introduction of carriers, the oxygen vibration frequencies in the deformed structure are higher than in the nondeformed structure. Equivalently, we can view the effect as a vibronic repulsion between a symmetric low-lying, localized electronic state and coupled apex-oxygen vibrations. With increasing carrier concentration, this local electronic excitation could extend to a band.

There is increasing evidence to support the latter explanation. A JT mechanism causing the phonon anomalies of La_2CuO_4 , observed in neutron-scattering data of Pintschovius *et al.*¹⁴ has been suggested by Weber.¹⁵ That possibility was analyzed in some theoretical detail by Zannen, Oless, and Feiner.¹⁶ A JT or PJT effect in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ involving the apex-oxygen sites is suggested by a variety of other data.¹⁷ A significant change in the mean position of the apex oxygen has been observed in x-ray studies of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ upon doping,¹⁸ with the O ion moving substantially closer to the CuO_2 planes with increasing carrier concentration. This shortening of the apex-O—Cu(2) bond cannot be directly related to the tetragonal-orthorhombic structural phase transition, and is opposite in sign from the change in c lattice constant upon doping. Rather, the observed behavior appears to be a direct carrier-related effect related to the charge transfer (CT) from the charge reservoirs, i.e., chains to the planes through the apex oxygens. The wealth of experimental data showing the presence of carriers (holes) in p_z orbitals on O ions, together with the well-known instability of the O^{2-} ion, clearly suggest the involvement of apical O p_z together with out-of-plane Cu orbitals in the JT coupling.

Anharmonicity of the apex-O vibrations has been found in temperature-dependent Raman scattering experiments of both La_2CuO_4 (Ref. 19) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Ref. 9). Anharmonic behavior is also observed in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ (Ref. 20) where the apex O(2) oxygen mode shows high-temperature softening above 500 K similar to, but somewhat less dramatic than, that observed in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Refs. 9 and 21). The implication is that the common behavior in all three systems is caused by the underlying instability to a JT distortion. The symmetry-breaking effect of such nonadiabatic behavior has also recently been suggested by the observation of a spontaneous polarization (a pyroelectric effect) in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and La_2CuO_4 .²² A suggested adiabatic potential surface for the apex-O ions in the pyramidal structure 1:2:3 and 2:2:1:2 materials is shown in Fig. 3. The position of the apex-O ion (as determined by x-ray diffraction) is as a superposition of the occupation probabilities for the two equivalent or near-equivalent posi-

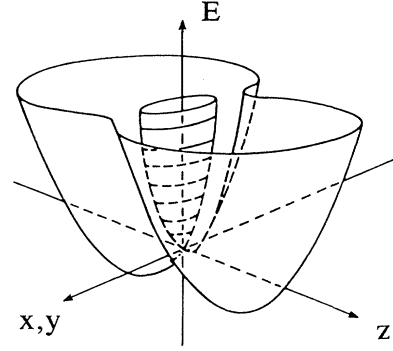


FIG. 3. A suggested possible adiabatic potential surface describing the anharmonicity of the apex-O atom in $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_8$. Assuming a static potential, the barrier height can be estimated from the high-temperature phonon softening (Refs. 9, 20, and 21) to be ~ 500 K (~ 40 meV).

tions. Consequently, the apical O vibrational frequency, as well as the average ion position, will change with local carrier occupancy as the charge balance along z is distorted by a localized carrier. A similar effect seems to occur in the concentrated limit upon doping. A dynamic version of this apical oxygen JT effect may have important implications for superconductivity, with the anharmonic potential along the CT axis providing the necessary retarded nonlinear interaction for real-space Cooper pairing of in-plane carriers.

In conclusion, we find that the presence of a localized carrier in an octahedral unit in La_2CuO_4 manifests itself in the appearance of new local modes. Of interest is the mode in the region of 480 cm^{-1} , which appears to correspond to the “ghost mode” observed in elastic neutron scattering.¹⁴ In contrast, a polaron in the pyramidal unit of insulating $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_8$ appears to result in the observation of coupled apex-oxygen modes, which correspond to the $k = 0$ modes in metallic $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, respectively. A Jahn-Teller interaction involving the level repulsion between a localized low-lying electronic state and the apex-O vibration is suggested as a possible explanation for the anomalous large positive frequency shifts of the photoinduced local modes upon carrier injection as well as the positive frequency shifts in the Raman spectra upon doping. Some kind of an anharmonic potential could then be used to describe the vibronic interaction for the apex oxygens in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$.

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