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Possibility of optical evidence for charge-transfer excitations in $YBa_2Cu_3O_{7-\delta}$

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We present a three-level model that addresses the possibility that charge-transfer fluctuations are responsible for the anomalously large intensity of the 155 cm^{-1} Ba mode observed by Genzel *et al.* The model also addresses the accompanying Raman signature and the c-axis lattice constant variations with oxygen content.

Optical spectroscopy is a probe of the microscopic properties of a system. In the case of high-T_c superconductors these measurements have already suggested several unusual features, including the existence of a midinfrared band,[1-4] anomalously strong ir activity of certain phonon modes,[4,5] etc. Some of these features disappear or become less prominent in insulating (nonsuperconducting) samples.[1,5]

Here we propose a simple model to account for the anomalously strong infrared activity of a phonon mode observed in $YBa_2Cu_3O_{7-\delta}$ at 155 cm^{-1}. This mode has been labeled as the "barium" mode, and it can be quite accurately described as a rigid motion of the $[CuO_3]$ cluster [chain plus two O(4)] in one direction and Ba^{2+} ions in the opposite direction[5] (Fig. 1). The oscillatory strength of this mode was found to be ~ 15 times larger than the prediction of a pure lattice dynamics calculation.[5,6] This is consistent with our earlier discussion[7] of the importance of the c-axis activity. In this work, we develop a simple local cluster model, building on the suggestion of Genzel *et al.*[5] that such anomalous oscillatory strength is a result of the charge-transfer fluctuations within the "chain" cluster $[CuO_3]$. However, different from them, we assume that the charge of a CuO_3 cluster in the $YBa_2Cu_3O_7$ system is -4. There are several reasons for such a thesis. If the charge of the cluster is equal to -3, then the charge of the conducting planes CuO_2 should be -2, which implies half-filling of the conducting band, and the appearance of the antiferromagnetism. This is in contradiction with the observation of superconductivity in $YBa_2Cu_3O_7$. However, if the charge of the cluster is -4, or more realistically the average is between -3 and -4, then the charge of the planes is less than -2. The finite density of holes in the conducting band may then lead to superconductivity as in doped La_2CuO_4. In oxygen-deficient samples, a part of the electrons from the oxygens lacking in the $CuO_{3-\delta}$ cluster is presumably transferred to the plane. This transfer will suppress the superconductivity, but will also result in a structural transformation along the c axis, as has indeed been observed by Cava *et al.*[8] Additional experimental support for our proposal are the x-ray absorption measurements of Tranquada *et al.*[9] They have found that the "doping" (amounting to a reduction of oxygen content) increases the number of Cu^{1+} ions per unit cell from zero to one on account of the reduction in the number of Cu^{2+} ions; they have attributed Cu^{1+} ions to the chains [Cu(1)].

Assuming therefore that the total charge of the CuO_3 cluster is -4, we have only four formal charge states of the cluster with the charge configurations,

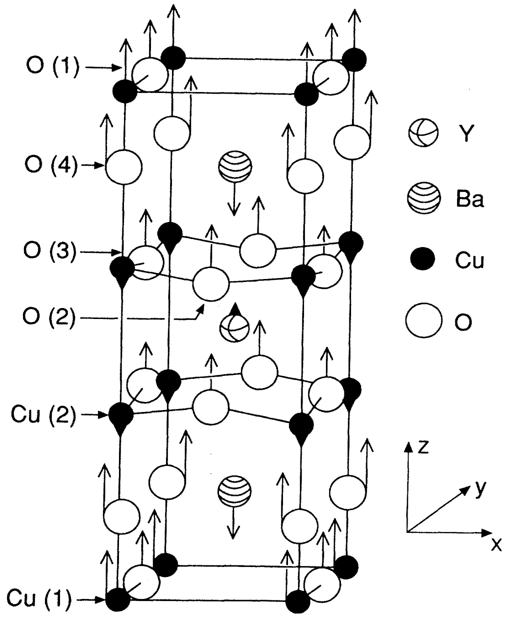
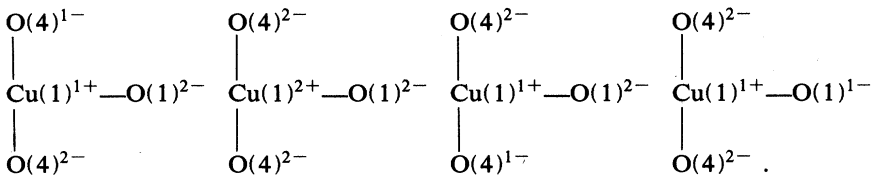


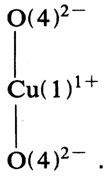
FIG. 1. Unit cell of $YBa_2Cu_3O_7$ with the relative ionic displacements of the "barium mode" at 155 cm^{-1} (after Ref. 5).



$$\begin{array}{llll}
\mathrm{O(4)^{1-}} & \mathrm{O(4)^{2-}} & \mathrm{O(4)^{2-}} & \mathrm{O(4)^{2-}} \\
| & | & | & | \\
\mathrm{Cu(1)^{1+}{-}O(1)^{2-}} & \mathrm{Cu(1)^{2+}{-}O(1)^{2-}} & \mathrm{Cu(1)^{1+}{-}O(1)^{2-}} & \mathrm{Cu(1)^{1+}{-}O(1)^{1-}} \\
| & | & | & | \\
\mathrm{O(4)^{2-}} & \mathrm{O(4)^{2-}} & \mathrm{O(4)^{1-}} & \mathrm{O(4)^{2-}}\ .
\end{array}$$

Note that the first and third state are asymmetric in charge distribution, and hence possess a dipole moment along the c axis. The fourth state also has a dipole moment but along the chain. For simplicity we shall neglect this state in our qualitative model since it does not contribute directly to ir activity of the 155-mode polarized along the c direction.

In the $YBa_2Cu_3O_6$ system we have quite a different situation. The oxygens O(1) are removed from the chains, and one part of their electrons fills the d shells of Cu(1) ions, while the remainder is transferred to the conducting sheets CuO_2. The total charge of our cluster is then reduced to -3. Consequently both the p shells on O(4) oxygens and d shell on Cu(1) copper ion in the cluster are completely filled and no low-energy charge-transfer fluctuation is possible. There exists only one formal charge state of the cluster,



$$\begin{array}{l}
\mathrm{O(4)^{2-}} \\
| \\
\mathrm{Cu(1)^{1+}} \\
| \\
\mathrm{O(4)^{2-}}\ .
\end{array}$$

The fluctuations between formal charge states in the $YBa_2Cu_3O_7$ cluster can be described by the following Hamiltonian:

$$H_{\rm el}=\begin{bmatrix} e_2 & t & 0 \\ t & e_1 & t \\ 0 & t & e_2 \end{bmatrix} . \tag{1}$$

Here, the diagonal matrix elements e_1,e_2 correspond to the energies of the microscopic states, while the off-diagonal term t is the transition amplitude from one state to another. The Hamiltonian (1) can also be associated with a "single-particle" Hamiltonian describing the motion of a hole among the Cu(1) and two O(4) ions. In this sense e_1 and e_2 are on-site energies of the hole on the Cu(1) and O(4) ions, respectively, while t is the hopping amplitude between the Cu(1) and O(4) ions. The direct hopping between two O(4) oxygens is neglected. Note that the microscopic state of the $YBa_2Cu_3O_6$ cluster is the situation when the hole is removed from the system. We shall frequently refer to Hamiltonian (1) as an "electronic" part of the total Hamiltonian, since the charge-transfer fluctuations are nothing but electron motion within the cluster. Including electron correlation effects within the cluster (e.g., Hubbard U and V) will be reported elsewhere. Here we only note that their main effects are to renormalize the parameters in Eq. (1): It is important to appreciate that the levels used are implicitly fully dressed many-body ones.

The matrix elements of $H_{\rm el}$ quite generally depend on the lattice deformation of the unit cell of $YBa_2Cu_3O_{7-\delta}$. We are particularly interested in the coupling of the charge-transfer fluctuations to the 155 mode. The 155 mode is associated with almost rigid motion of the whole CuO_3 cluster between the CuO_2 sheets. This motion will primarily change the energies e_1,e_2, rather than the hopping amplitude t.[10] The counterpart of the 155 mode is the Raman active mode corresponding to the symmetric oscillation of the O(4) ions within the cluster. The frequency assigned to this Raman mode is 515 cm^{-1}.[11] We should also note that there is strong experimental evidence[12] for the coupling between this Raman mode and perpendicular charge-transfer fluctuations. Both modes can be described approximately by the asymmetric and symmetric oscillations, respectively, of the O(4) oxygens in the c direction. Let Δ_1 and Δ_2 denote shifts of the O(4) oxygen ions from their equilibrium positions. Keeping only terms linear in $\Delta_{1,2}$ in a Taylor expansion of e_1,e_2, we obtain the interaction Hamiltonian between the phonon and charge-transfer fluctuations,

$$H_{\text{el-ph}}=-\frac{\lambda_{\rm ir}}{2}(\Delta_1+\Delta_2)\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} -\frac{\lambda_R}{2}(\Delta_1-\Delta_2)\begin{bmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix} , \tag{2}$$

where $\lambda_{\rm ir}$ and λ_R are the coupling constant corresponding to the symmetric and asymmetric modes, respectively. Our estimates of $\lambda_{\rm ir}$ and λ_R (the Evjen-Frank method) indicate that they are slightly different. Other forms of electron-phonon couplings can also be included (e.g., through t) and lead to similar results, as will be shown elsewhere.

We assume that the "phonon part" of the Hamiltonian is given by the familiar expression

$$H_{\rm ph}=\tfrac{1}{2}K(\Delta_1^2+\Delta_2^2)+\tfrac{1}{2}M(\dot{\Delta}_1^2+\dot{\Delta}_2^2) , \tag{3}$$

where M and K are effective mass and elastic constant, respectively.

The Hamiltonians (2) and (3) can be rewritten in terms of coordinates corresponding to the asymmetric (ir) and symmetric (Raman) modes,

$$\begin{bmatrix} u \\ v \end{bmatrix} = \frac{\Delta_1 \pm \Delta_2}{\sqrt{2}} , \tag{4}$$

respectively. Notice that both modes have the same frequency, as a result of the neglect of the motion of other ions in the unit cell. For example, the ir-active mode involves the motion of the Ba ion. This will considerably increase the effective mass, and consequently reduce the frequency of that mode, as observed. We can include this in the model by the appropriate choice of effective masses: charge transfer to the Ba ion is unlikely.

The model defined by Eqs. (1)–(3) is quite general. It can alternatively be associated with the charge-transfer fluctuations between the CuO_2 planes and CuO_3 cluster. In this case we assign the following formal charge states:

$$\begin{array}{lll} [CuO_2]^{1-} & [CuO_2]^{2-} & [CuO_2]^{2-} \\ \vert & \vert & \vert \\ [CuO_3]^{4-} & [CuO_3]^{3-} & [CuO_3]^{4-} \\ \vert & \vert & \vert \\ [CuO_2]^{2-} & [CuO_2]^{2-} & [CuO_2]^{1-} \end{array}$$

described again by Hamiltonian (1). The phonon modes Δ_1 and Δ_2 now correspond to the motion of the sheets CuO_2 with respect to the chain unit CuO_3, which is also part of displacements involved in the 155 mode. Conradson and Raistrick[13] have emphasized the importance of this charge-transfer channel from an analysis of their EXAFS/XANES data. Presumably this charge-transfer fluctuation also contributes to the ir activity of the 155 mode. The most important charge transfer has yet to be unambiguously assigned. *Ab initio* quantum chemistry calculations[14] support this scenario. The infrared intensity estimated from the dipole derivation for the rigid *c*-axis motion of the central unit of a Cu_3O_{12} cluster[7] shows a dramatic enhancement (~64) over the lattice dynamics prediction. The enhancement arises from the vibration-induced mixing of the symmetric and antisymmetric (a_g and b_{1u}) molecular orbitals composed primarily of Cu $d_x2_{-u}2/02p$ hybrids in the two planes. This plane-plane charge fluctuation is reminiscent of other mixed-valence situations where either double-well or highly anharmonic potential surfaces are found. Note that anharmonic electron-phonon coupling is also often used to mimic the inherent oxygen polarizability, in the spirit of shell models.[15]

Our model is a generalization of a two-level system arising in many physics contexts. In fact, a similar two-level system has already been applied for the anomalous ir activity of the 240 mode in La_2CuO_4.[16] The scenario presented here can apply in a plane cluster through coupling to an appropriate phonon.

The interaction Hamiltonian (2) will result in the renormalization of both ir and Raman-phonon frequencies. It can also cause a static deformation of the cluster, which may be important for understanding of the structural transformations observed by Cava *et al.*[8] The renormalized frequency can be found within the usual random-phase approximation (RPA) treatment of the interaction (2), Fig. 2(a). In the case of the ir mode the renormalized frequency is given by

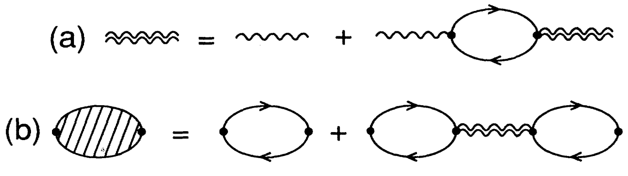


FIG. 2. (a) Dyson's equation for the phonon Green function. (b) The contribution of the electronic polarizability to the polarizability of the ir mode.

$$\omega_{\rm ir}^2 = \omega_0^2 - \frac{\lambda_{\rm ir}^2}{M_{\rm eff}} \Pi_{\rm MM}(\omega) , \tag{5}$$

where ω_0 is the bare phonon frequency, $\sqrt{K/M_{\rm eff}}$, while Π_{AB} is the electron polarization,

$$\Pi_{AB} = i \int \frac{d\varepsilon}{2\pi} {\rm Tr}[G(\omega+\varepsilon) A G(\varepsilon) B] . \tag{6}$$

In the above expression, $G(\omega)$ is the electron Green function equal to

$$G(\omega) = (\omega - H_{\rm el})^{-1} . \tag{7}$$

The pole of $G(\omega)$ with the lowest real part is shifted into the upper part of the complex ω planes, while the other poles are shifted into the lower part of the ω plane. The matrix M in expression (5) is the part of the interaction (2) corresponding to the ir mode, viz.,

$$M = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} . \tag{8}$$

From expression (6) we obtain that the real part of the electron polarization is given by

$$\Pi_{\rm MM}(\omega) = \frac{t^2}{\{2t^2 + [(e_2 - e_1)/2]^2\}^{1/2}} \frac{1}{\omega_{\rm CT}^2 - \omega^2} , \tag{9}$$

where

$$\omega_{\rm CT} = \frac{e_2 - e_1}{2} + \left[2t^2 + \left[\frac{e_2 - e_1}{2} \right]^2 \right]^{1/2} \tag{10}$$

is the frequency of the charge-transfer fluctuation within the cluster. The imaginary part of $\Pi_{\rm MM}$ can be found from Kramers-Kronig relations or directly from the formula (6). The frequency $\omega_{\rm CT}$ is typically much larger than ω_0, so that the change of frequency of the ir mode due to the electron-phonon interaction (2) is

$$\frac{\delta(\omega^2)}{\omega^2} = \frac{\lambda_{\rm ir}^2}{M_{\rm eff}\omega_0^2} \Pi_{\rm MM}(0) . \tag{11}$$

In $YBa_2Cu_3O_6$ there are no relevant charge-transfer fluctuations, and consequently the frequency of the ir mode (and the frequency of any other mode) remains unchanged, i.e., ω_0. The above expression is therefore the relative difference between the frequencies of the 155 mode for $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ systems. It has been found experimentally that this difference is $\simeq 10\%$ (for $YBa_2Cu_3O_7$ $\omega_{ir} \simeq 155\ cm^{-1}$, while for $YBa_2Cu_3O_6$ $\omega_{ir} \simeq 168\ cm^{-1}$).[5] The right-hand side of Eq. (11) is proportional to a conventional definition of the dimensionless electron-phonon coupling constant,

$$\tilde{\lambda}_{ir} = \frac{\lambda_{ir}^2}{M_{eff}\omega_0^2 W} ,$$

where W is the width of the excitation spectrum of the charge-transfer fluctuations

$$2\left[2t^2+\left[\frac{e_2-e_1}{2}\right]^2\right]^{1/2} .$$

In order to find the polarizability we need to determine the operator $\hat{P}$ of the dipole moment of the system. This contains several terms of different origins,

$$\hat{P} = \sqrt{2}(Qu - p_0 M) . \tag{12}$$

The first term is the dipole moment induced by the asymmetric motion of O(4) ions. Here Q is the oxygen charge and u is the displacement of the ir mode defined in Eq. (4). The second electronic term depends on the microscopic state of the cluster. The quantity p_0 is the dipole moment of the first (third) microscopic state; it is of the order of the electron charge multiplied by the distance between Cu(1) and O(4) ions. M is a matrix defined by Eq. (8). In the case of the plane-chain-plane cluster, Q is the averaged charge of the CuO_2 planes per unit cell, while p_0 is of the order of the electron charge multiplied by the distance between Cu(1) and Cu(2) ions.

The polarizability α of the system is given by the correlation function of the dipole momenta. The phonon part of $\hat{P}$ leads to the familiar lattice dynamics term

$$\alpha_{ph}(\omega) = 2\frac{Q^2}{M_{eff}}\frac{1}{\omega_{ir}^2-\omega^2} . \tag{13}$$

The electron part of the polarizability is proportional to the polarization Π_{MM},

$$\alpha_{el}(\omega) = 2p_0^2\Pi_{MM}(\omega) . \tag{14}$$

This is the zeroth-order term in the electron-phonon interaction. The RPA treatment of the interaction (2), Fig. 2(b), results in an additional term with the pole at the phonon frequency ω_{ir},

$$\delta\alpha_{el}(\omega) = 2\frac{(p_0\lambda_{ir}\Pi_{MM})^2}{M_{eff}}\frac{1}{\omega_{ir}^2-\omega^2} . \tag{15}$$

In $YBa_2Cu_3O_6$ this additional term is absent because the charge-transfer fluctuations are suppressed. The combination of Eqs. (13) and (15) gives the polarizability with an effective oscillator strength equal to

$$f = 2\frac{Q^2}{M_{eff}\omega_0^2}\left[1+\left[\frac{p_0\lambda_{ir}\Pi_{MM}(0)}{Q}\right]^2\right] \tag{16}$$

for the 155 mode. The difference δf between the oscillator strengths of this phonon mode in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ systems is therefore given by

$$\frac{\delta f}{f} = \left[\frac{p_0\lambda_{ir}\Pi_{MM}(0)}{Q}\right]^2 . \tag{17}$$

According to the measurements of Genzel *et al.*[5] the quantity (17) is equal to 15.

Equations (11) and (17) can be used for independent estimates of the coupling constant λ_{ir} for $YBa_2Cu_3O_{7-\delta}$. If we assume that the polarization $\Pi_{MM}(\omega=0)$ is given by the inverse of the typical energy of the charge-transfer fluctuations,[17] i.e., of the order of $(0.1\ eV)^{-1}$, then, according to Eq. (11) the coupling constant is

$$\lambda_{ir} \simeq 0.12 M_{eff}/M_O ,$$

in eV/Å, while from Eq. (19) it follows that

$$\lambda_{ir} \simeq 0.19\ \frac{eV}{Å} .$$

Here, M_O stands for the oxygen mass. In order to improve agreement between these two estimates it is necessary to assume that the effective mass M_{eff} of the 155 mode is of the order of four oxygen masses: this effective mass requirement increases if the energy of the charge-transfer fluctuations increases (i.e., $\Pi_{MM}^{-1} > 0.1$ eV). The estimated values of λ_{ir} are relatively small in comparison to coupling constants in some other materials, e.g., polyacetylene. Interestingly, other estimates of electron-phonon coupling based on the superconducting transition temperatures lead to similar values.[18]

The static deformation of the corresponding symmetric (Raman) mode is given by the averaged value of its interaction with CT fluctuations,

$$v_0 = \frac{\lambda_R}{\sqrt{2}K}\left\langle\begin{bmatrix}1 & 0 & 0\\ 0 & -2 & 0\\ 0 & 0 & 1\end{bmatrix}\right\rangle_0 . \tag{18}$$

For $YBa_2Cu_3O_7$, v_0 exists for any finite value of the coupling constant λ_R, and is equal to

$$v_0 = -\frac{\lambda_R}{2\sqrt{2}M_{eff}\omega_0^2}\left[1+\frac{3(e_2-e_1)}{2\{2t^2+[(e_2-e_1)/2]^2\}^{1/2}}\right] . \tag{19}$$

However, this deformation is equal to zero in $YBa_2Cu_3O_6$. Expression (19) corresponds, therefore, to the difference of the Cu(1)-O(4) distances in $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ systems, which is found experimentally to be equal to 0.04 Å,[8] or $\approx 2\%$. The static deformation of the Raman mode will also renormalize the on-site energies, so that the energies e_1 and e_2 are shifted by $2\lambda_R v_0/\sqrt{2}$ and by $-\lambda_R v_0/\sqrt{2}$, respectively. For self-consistency we must take into account these corrections in all previous expressions. Alternatively, for the plane-chain-plane cluster the static deformation (19) is measured to be equal to 0.13 Å,[8] or $\approx 3\%$.

A static deformation of the asymmetric (ir) mode is possible only for sufficiently large coupling constants λ_{ir}. The critical value of λ_{ir} can be estimated from expression (5) by requiring that the renormalized frequency ω_{ir} is equal to zero. Since the change in the frequency of the ir mode is proportional to the dimensionless coupling constant, we find that the necessary condition for this transition is $\tilde{\lambda}_{\mathrm{ir}} \geq \omega_{\mathrm{CT}}^2/t^2 \sim 1$. Note that such a static deformation of the ir mode will induce a permanent dipole moment in the unit cell, and it is therefore to be associated with a ferro-antiferroelectric transition.[19] In this region of parameter space, the dynamics of the ir phonon mode is essentially nonlinear. The corresponding equation of motion of this mode can be found in an adiabatic approximation valid for $t^2 \gg \lambda_{\mathrm{ir}}\dot{u} \approx \lambda_{\mathrm{ir}} u\,\omega_{\mathrm{ir}}$. For small phonon displacements, we obtain an equation with a dominant cubic nonlinearity

$$M\ddot{u} = -Ku + K\tilde{\lambda}_{\mathrm{ir}}\frac{2t^2}{\omega_{\mathrm{CT}}^2}u\left[1-\left[\frac{u}{u_0}\right]^2\right] , \tag{20}$$

where the coefficient of the nonlinear term is

$$u_0^{-2} = \frac{\lambda_{\mathrm{ir}}^2}{W^2\omega_{\mathrm{CT}}^2}[2t^2+W(e_1-e_2)] .$$

The three-level model defined by Eqs. (1)–(3) can be used only for some special composition of the $\mathrm{YBa_2Cu_3O_{7-\delta}}$. Namely, the number of the holes within the cluster can be changed only discontinuously, in our case from the one hole to the case with no holes. As we have already discussed, these two cases correspond to the compositions with $\delta=0$ and 1, respectively. However, in a case with an intermediate composition $0<\delta<1$, the crystal of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ consists of the clusters with one hole and the clusters without holes. The most simple approach to such a situation is the *virtual crystal approximation.*[20] (Extension to a coherent potential approximation[20] is also straightforward.) According to this approximation, the overall electron Green function is given by the linear interpolation of the Green functions of two limiting known cases,

$$G(1\geq\delta\geq 0)=xG(\delta=1)+(1-x)G(\delta=0) .$$

Here parameter x is the fraction of the clusters with no holes. According to the measuremets of Tranquada *et al.*,[9] this parameter is nothing but the number of the Cu^{1+} ions per unit cell, and it is equal approximately to δ for $\delta<0.6$, while for $\delta>0.6$ it is $\approx 2\delta-1$. By using the formula (6) for the electron polarization, we find that Π_{MM} is proportional to $(1-x)$,

$$\Pi_{\mathrm{MM}}(1\geq\delta\geq 0)=(1-x)\Pi_{\mathrm{MM}}(\delta=0) .$$

The composition dependence of the frequency of the ir mode can be obtained from Eq. (5). It is given by a linear interpolation of the frequencies for $\delta=0$ and $\delta=1$,

$$\omega_{\mathrm{ir}}(1\geq\delta\geq 0)=x\,\omega_{\mathrm{ir}}(\delta=1)+(1-x)\omega_{\mathrm{ir}}(\delta=0) .$$

A nonlinear behavior in δ of the frequency ω_{ir} is expected only for δ close to 0.6, when an orthorhombic-tetragonal transition occurs. The electron contribution to the oscillatory strength of the ir mode is quadratic in the electron polarization Π_{MM}, and consequently it will show a more dramatic δ behavior. It decreases linearly for $\delta\geq 0$, and eventually for $\delta\leq 1$ it disappears as $(\delta-1)^2$. The virtual crystal approximation also predicts the linear x behavior of the static deformation of the Raman mode, v_0. Associated with such a static deformation there is also a self-consistent change in the hole density in the planes and/or chains,

$$n_{\mathrm{hole}}(\delta)=n_{\mathrm{hole}}(\delta=1)+\frac{K}{3\sqrt{2}\lambda_R}v_0(\delta) .$$

This is presumably reflected in the rapid change in T_c at $\delta\sim 0.5$.

Finally, the data discussed here certainly do not prove that the superconductivity is driven by the axial charge-transfer fluctuations. However, coupling to the plane has been considered.[7] It is also curious to note the claim of Ref. (21) that $T_c(\delta)\sim\delta\omega_R$, where ω_R is precisely the Raman mode we have considered.

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[19] It is interesting to note that anomalously enhanced dielectric constants have been reported for $YBa_2Cu_3O_{7-\delta}$ materials in the *c* direction [L. R. Testardi *et al.*, Phys. Rev. B **37**, 2324 (1988)] and also for La_2CuO_4 materials in the plane [D. Reagor *et al.* (unpublished)]. It is tempting to suppose that a ferro- or antiferroelectric distortion, typical of perovskites, is nearby.

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