# Anharmonicity in the $c$ direction of high-$T_c$ oxides

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The observation of various structural anomalies correlated with the superconducting transition temperature $T_c$ provide a motivation to investigate anharmonic phonon-phonon *and* electron-phonon interactions, and their effect on normal state and superconducting properties. We specifically investigate $c$-axis-related anharmonic lattice fluctuations coupled to the electron density, which provide a charge transfer and interplanar coupling mechanism. Due to the strongly nonlinear phonon fluctuations, the effective interplanar electron (hole) hopping integral becomes temperature dependent and leads to (bi-)polaron formation at high temperatures, followed by a spin density wave instability with decreasing $T$, and finally interplane pair tunneling in the superconducting state. The $c$-axis-related infrared absorption is calculated and it is shown that due to anharmonic effects strong increases in the oscillator strengths, line shape asymmetries and broadening effects are obtained consistent with experimental data.

High-temperature superconducting oxides[1] show a variety of structural anomalies correlated with $T_c$ which clearly demonstrate the importance of electron-lattice interactions. Experimentally it seems clear that the observed structural anomalies are nearly exclusively attributed to oxygen ion displacements, both in and between $CuO_2$ planes. Specifically, pulsed neutron-diffraction results[2] and extended x-ray-absorption fine-structure (EXAFS) experiments[3] have revealed oxygen-related displacements and have suggested two-site distribution functions. The instability of the oxygen $2p^6$ state[4] has not only been shown to be responsible for structural anomalies in ferroelectric perovskites,[5] but also in the context of high-$T_c$ superconductors. Holstein-type electron-phonon interaction models have been derived isolating the special role played by the local instability of $O^{2-}$.[6] Within this context, polaron and bipolaron formation has been attributed to the onset of superconductivity.

The importance of considering lattice and electron-lattice anharmonicity has been demonstrated in a variety of recent work[7] where nonlinear and nonadiabatic effects consistently explain EXAFS, neutron scattering, and optical data.[8] In the following we specifically consider $c$-axis-related effects emphasizing the three-dimensional structure of high-$T_c$ compounds. $c$-axis-related transport properties have been studied in Ref. 9 in order to elucidate normal- and superconducting state properties. In Ref. 10, it has been shown that the plane-chain-plane structure of $YBa_2Cu_3O_7$ provides a suitable scenario for charge-transfer excitations, and thus may reduce the Coulomb repulsion due to interplane Cooper pairing. Here we specifically consider electron-density two-phonon interaction effects, which destabilize the harmonic normal mode frequencies, and thus require higher-order anharmonic interaction terms to prevent lattice instabilities. Simultaneously, these same interactions modify the interplanar hopping integral $t_\perp$ which, within a mean-field approximation, becomes temperature dependent. As a consequence, bipolaron formation takes place at high temperatures.[11] With decreasing temperature a discontinuous change to an ordered antiferromagnetic spin-density-wave state is predicted to take place, again at a mean-field level. With the onset of superconductivity, interlayer pair tunneling occurs, which substantially contributes to an increased pairing.[12,13]

The Hamiltonian we consider for our coupled electron-lattice problem reads

$$H = H_{\rm ph} + H_{\rm el} + H_{\text{el-ph}} , \tag{1}$$

$$H_{\rm ph} = \sum_{i,j} \left\{ \frac{p_i^2}{2m_i} + \frac{k_i}{2} Q_i^2 + \frac{k_4}{4} Q_i^2 Q_j^2 \right\} , \tag{1a}$$

$$H_{\rm el} = \sum_{i,j} t_i (c_i^+ c_j + \text{H.c.}) + \sum_i V_{ii} (\rho_{i\uparrow}\rho_{i\downarrow}) + \sum_{i,j} V_{ij} (\rho_{i\downarrow}\rho_{j\uparrow}) , \tag{1b}$$

$$H_{\text{el-ph}} = -gQ_i\rho_i - g_4 Q_i Q_j (c_i^+ c_j + \text{H.c.}) . \tag{1c}$$

Here $p_i$ and $Q_i$ are the momentum and conjugate displacement coordinate of lattice mode $i$ with mass $m_i$; $k_i$ is the harmonic force constant and $k_4$ is the two-phonon nonlinear interaction term which accounts for the anharmonic effects and structural instabilities. In $H_{\rm el}$, $t_i$ comprises inplane hopping $t_\parallel$ and interplane hopping $t_\perp$; $c^+, c$ refer to electron creation and annihilation operators and $c^+ c = \rho$; $V_{ii}$, $V_{ij}$ are in-plane and interplane Coulomb repulsion terms. Attractive in-plane electron-phonon interaction is attributed to the linear coupling $g$, while an attractive two-phonon mediated interplanar charge transfer is mediated by $g_4$.

For simplicity, we assume that the in-plane Hamiltonian can be decoupled from the interplane Hamiltonian, exhibiting an effective attractive BCS-type phonon-mediated electron-electron (hole-hole) pairing, which is strongly anisotropic due to interband interactions.[14] We

 

note that certain transformation techniques lead to a two-phonon coherent state, derived from the linear electron-phonon interaction only.[15,16] Equation (1) can, at present, be treated approximately only by introducing cumulant expansions in the density terms and carrying out an approximate (mean-field) decoupling of electronic and lattice degrees of freedom. Concentrating on $c$-axis-related phenomena only, this approach yields

$$H_{\rm ph} \hat{=} \sum_{i,j} \left\{ \frac{p_i^2}{2m_i} + \frac{k_i}{2} Q_i^2 - g_4 Q_i Q_j (\langle \rho_i \rangle + \langle \rho_j \rangle) + \frac{k_4}{4} \langle Q_i Q_j \rangle Q_i Q_j \right\}, \tag{2}$$

$$H_{\rm el} \hat{=} \sum_{i,j} (t_\perp - g_4 \langle Q_i Q_j \rangle)(c_i^+ c_j + \text{H.c.}) + \sum_i V_{ij} \rho_{i\uparrow} \rho_{j\downarrow} , \tag{3}$$

where $\langle\ \rangle$ represents thermal averages over phonon or electron density coordinates. The linear coupling $g$ has been neglected in both Eqs. (2) and (3), but as stated above, it is assumed to lead to an attractive electron-electron (hole-hole) interaction in the planes. Note that the mean-field approximation used in Eqs. (2) and (3) induces various limitations, e.g, spurious first-order transitions.[17]

First we consider the consequences arising from electron-density two-phonon interactions on the dynamical lattice properties at the level of Eq. (2). It is assumed that only nearest-neighbor interactions are dominant and that just two phonon modes are crucial for the interplanar or chain-plane related charge transfer. We specifically have in mind for YBCO the planar 340-cm$^{-1}$ buckling mode and the $\approx$500-cm$^{-1}$ apex oxygen-related mode.

From Eq. (2) the equations of motion are derived as

$$\left[ \frac{d^2}{dt^2} + \omega_i^2 \right] A_i = -2\omega_i \sum_{jkl} \frac{k_4}{2} A_j A_k A_e \tag{4}$$

with $A_i = \sqrt{2\omega_i/\hbar}\, Q_i = (a_i + a_i^+)$ the phonon field operators, and $\omega_{i0}^2 = k_i/2m_i$, $\omega_i^2 = \omega_{i0}^2 - g_4(\langle \rho_i \rangle + \langle \rho_j \rangle)$. From Eq. (4) the infrared absorption is calculated using the Green's-function technique (developed in Ref. 18). The dielectric susceptibility with dipole moments up to second order is then given by

$$\begin{aligned} \chi_{\alpha\beta}(\omega) = \sum \frac{2\omega_i M_{i\alpha} M_{i\beta}}{\omega_i^2 - \omega^2 + 2\omega_i [\Delta_i(\omega) - i\Gamma_i(\omega)]} + 2\sum M_\alpha(12) M_\beta(-1-2) \Bigg[ (n_1+n_2+1) \Bigg\{ \frac{1}{(\omega+\omega_1+\omega_2)_p} + \frac{1}{(\omega_1+\omega_2-\omega)_p} \\ - \pi i \delta(\omega+\omega_1+\omega_2) + \pi i \delta(\omega-\omega_1-\omega_2) \Bigg\} \\ + (n_1-n_2) \Bigg\{ \frac{1}{(\omega_2-\omega_1+\omega)_p} + \frac{1}{(\omega_2-\omega_1-\omega)_p} \\ - \pi i \delta(\omega_2-\omega_1+\omega) - \pi i \delta(\omega_2-\omega_1-\omega) \Bigg\} \Bigg] , \end{aligned} \tag{5}$$

where the dipole operator $M_\alpha$ is expanded in powers of the phonon coordinates:[18]

$$M_\alpha = \sum_i M_{i\alpha} A_i + \sum M_\alpha(12) A_1 A_2 + \cdots . \tag{6}$$

$n_i$ are the $i$ phonon occupation numbers and

$$D_T(ij, i\omega_n) = -\frac{\hbar}{kT} \Delta(ij,\omega) + i \frac{\hbar}{kT} \Gamma(ij,\omega) \tag{7}$$

is the self-energy which renormalizes the harmonic normal modes due to anharmonic interactions. Both $\Delta(ij,\omega)$ and $\Gamma(ij,\Omega)$ have been evaluated in the quasiharmonic approximation.[18] Note that the $\omega_i$ are already renormalized by the electron-phonon interaction.

It is clear that the uncoupled harmonic mode frequencies $\omega_{i0}^2 = k_i/m_i$ can be renormalized to zero with strong enough electron-phonon interaction, but also doping may substantially contribute to phonon softening. However, a real lattice instability is prevented by the anharmonic fourth-order phonon-phonon interaction which in a certain temperature regime strongly competes with the electron-phonon interaction. Equation (5) has been investigated numerically for various temperatures and various values of $k_4$ and $g_4$. For both $g_4$ and $k_4 = 0$ the dielectric susceptibility is already strongly affected due to the self-energy effects arising from higher-order terms. With $g_4 = 0$ and $k_4$ finite the oscillator strengths in both modes increases, and phonon sum and difference processes become more pronounced. Experimentally, we expect these processes to be reflected in line-shape broadenings and asymmetries. With $g_4$ and $k_4$ finite the absorption increases strongly and a slight softening of both phonon mode frequencies is observed (Fig. 1). This phonon softening gets stronger with increasing electron-phonon coupling (Fig. 2), but can be compensated by increasing $k_4$ (Fig. 3) which inhibits a lattice instability. With decreasing temperature both phonon modes become more symmetric and sharper, and simultaneously an increase in the oscillator strengths is observed (Fig. 4).

Experimentally, phonon softening, increase in oscillator strengths as well as line-shape sharpening with decreasing $T$ has been observed.[19] From the present

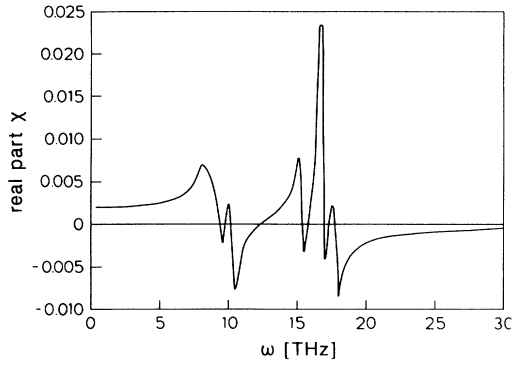


FIG. 1. Real part of Eq. (5) with $k_4=0.1\times10^{22}$ g s$^{-2}$ cm$^{-2}$ and $g_4=1\times10^4$ g s$^{-2}$ at $T=100$ K.

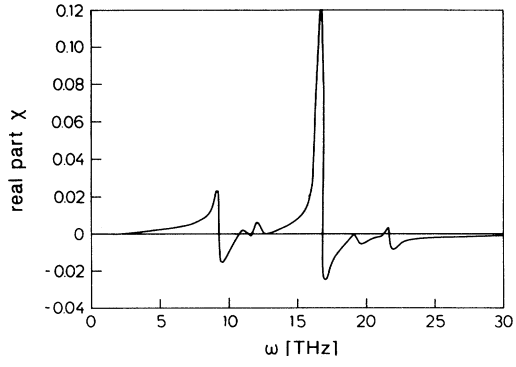


FIG. 3. Real part of Eq. (5) with $k_4=0.5\times10^{22}$ g s$^{-2}$ cm$^{-2}$ and $g_4$ the same as in Fig. 4 at $T=100$ K.

analysis we conclude that the line-shape effects are dominantly due to anharmonic phonon-phonon interactions, phonon softening, and huge increases in the oscillator strengths are attributed to electron-phonon coupling. In the present analysis we assumed that at 90 K a superconducting gap opens which has a value of 325 cm$^{-1}$ at $T=0$ K and a BCS-like temperature dependence. This gap has been observed in $YBa_2Cu_3O_7$ (YBCO) by various techniques.[20,21] This assumption remains, however, a crude simplification as the complex structure and Fermi surface of YBCO will yield a highly anisotropic gap.[22] The temperature dependence of the mode frequency shifts and the oscillator strengths due to the onset of superconductivity are in qualitative agreement with experimental data (Fig. 5). At $T_c$ the oscillator strength of the high-energy apex oxygen mode increases nonlinearly due to the gap opening, which clearly evidences an interrelation of phonon effects and superconductivity in the $c$ direction. A similar temperature dependence of the apex oxygen mode oscillator strength, as shown in Fig. 5, has been observed experimentally in $YBa_2Cu_3O_7$,[19] and more recently in various superconducting compounds of the $Pb_2Sr_2(Y,Ca)Cu_3O_8$ family.[23]

Three different $\tilde{t}_\perp/\hbar\omega_i$ regimes, where $t_\perp=\tilde{t}_\perp-g_4\langle Q_iQ_j\rangle$, are predicted in terms of effects on the lattice modes and have been suggested recently experimentally from $c$-axis polarized Raman scattering and optical reflectivity measurements.[24] (i) In the zero-bandwidth limit $\tilde{t}_\perp\equiv0$, polaronic and bipolaronic states compete with each other.[11] Note that the zero-bandwidth limit does not refer to $t_\perp=0$ but is directly controlled by the fluctuating phonon field. (ii) For $\tilde{t}_\perp\neq0$ and half-filling, a spin-density-wave gap (or charge-density wave) develops, which, within the present approach, will lead to phonon anomalies. Recently, ion channeling and pulsed neutron powder diffraction as well as EXAFS studies have suggested correlated displacements, perhaps related to the onset of the spin gap.[25] (iii) At the superconducting transition the opening of the gap results in softening of both phonon modes considered. Depending on the electron-phonon interaction, a static displacement pattern for the buckling mode may result as well as a correlated displacement of the O(4) ions. It is important to note that the buckling mode and the O(4) mode both show "double-well-type" features, which have been suggested experimentally, and clearly a correlation of the respective displacement patterns with $T_c$ is to be expected. The double well is, here, not a consequence of nonlinear electron-phonon interaction only, but, importantly, also due to nonlinear phonon-phonon interactions,

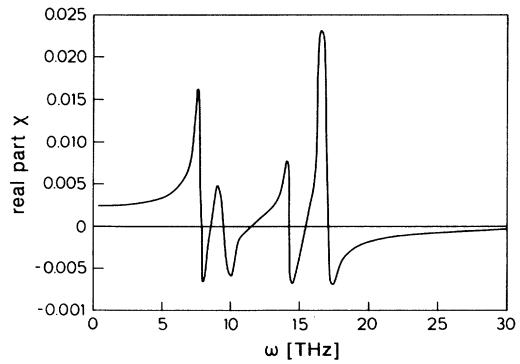


FIG. 2. Real part of Eq. (5) with $k_4$ as in Fig. 4 but $g_4=1.5\times10^4$ g s$^{-2}$ at $T=100$ K.

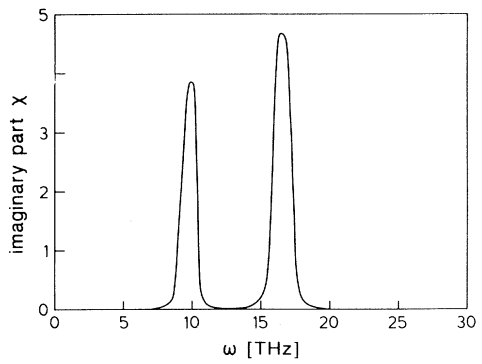


FIG. 4. Imaginary part of Eq. (5) with $k_4$ and $g_4$ as in Fig. 4, but $T=10$ K.

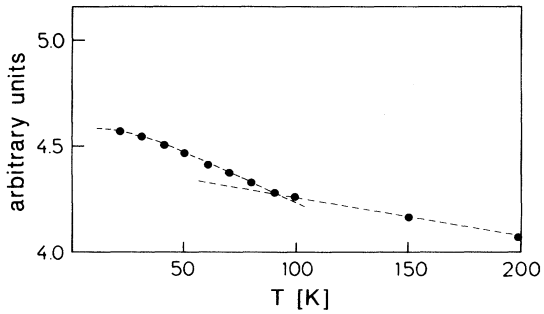


FIG. 5. Oscillator strength of the high-energy mode as a function of temperature with the parameters used in Fig. 1.

which might even induce biphonon bound states.[7]

The consequences for the *electronic* part in Eq. (3) are as manyfold as those arising for the lattice. Here the electron-two-phonon interaction modifies the interplane hopping leading to a temperature dependence of $t_\perp$. Experimentally, this should be observed in the $c$-axis-related transport properties and conductivity measurements. Of course, it has to be kept in mind that the $T$ dependence of $t_\perp$ is dependent on the magnitude of $g_4$ and may thus, in certain limits, be negligible. From the two-phonon-electron coupling term a $c$-axis-related dynamical charge transfer arises which is strongest when lattice mode instabilities occur. On the other hand, the dynamical instabilities are correlated with opening of the superconducting gap. This mechanism introduces a self-consistent interrelation between incipient structural instabilities and enhanced charge transfer between the planes. It is important to note that these incipient structural instabilities strongly affect the electronic densities of states as verified by recent band-structure calculations.[22]

The ideas developed above have certain features in common with models based on deformation-induced charge transfer and strong electron-electron correlation.[26] However, in contrast to these models, the present approach provides a self-consistent description of the coexistence of anomalous lattice effects, a spin gap, and high-temperature superconductivity. Also we have emphasized here phonon-mediated interplanar charge transfer; whereas the in-plane pairing is assumed to be phonon mediated but certainly may also have a different microscopic origin. In linear electron-phonon type models, such as the Holstein[27] or Fröhlich models,[28] strong nonlinear effects can also be generated for sufficiently large coupling strengths. Here we emphasize anharmonicity and nonlinearity as a consequence of density two-phonon interactions, which are not present in the above models.

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