Enhanced Electron-Phonon Coupling and its Irrelevance to High $T_c$ Superconductivity

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It is argued that the origin of the buckling of the CuO$_2$ planes in certain cuprates as well as the strong electron-phonon coupling of the $B_{1g}$ phonon is due to the electric field across the planes induced by atoms with different valence above and below. The magnitude of the electric field is deduced from new Raman results on YBa$_2$Cu$_3$O$_{6+x}$ and Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_y$ with different O and Y doping, respectively. In the latter case it is shown that the symmetry breaking by replacing Ca partially by Y enhances the coupling by an order of magnitude, while the superconducting $T_c$ drops to about two third of its original value.

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Recently there have been several suggestions [1] that out of plane oxygen vibrations of the CuO$_2$ plane may play an important role in mediating superconducting pairing in certain high temperature superconductors. It is also known that the presence of buckling (when the oxygen atoms are placed outside of the plane of the copper atoms) correlates with a strong interaction of a particular out-of-phase c-axis vibration (the so-called $B_{1g}$ phonon) with planar quasiparticles [2]. As such, considerable attention has been focused on the strong interaction of electrons with this particular phonon and its connection to phonon-mediated $d_{x^2-y^2}$ superconductivity [3,4].

The present paper provides the first direct experimental evidence to support that the buckling and consequent large value of the electron-phonon interaction are indeed correlated as a result of a local crystal electric field surrounding the vibrating atoms. Using the above ideas in conjunction with a three band model for the electron system, the strength of the electron phonon coupling and consequently the value of the electric field perpendicular to the plane can be determined by fitting the Fano interference in the $B_{1g}$ Raman spectra. We find that even though the electron-phonon coupling can be engineered in different materials to increase by an order of magnitude, the effect has essentially no correlation with $T_c$ of the material. Therefore we argue that the $B_{1g}$ phonon is irrelevant to superconductivity in the cuprates.

Raman scattering data are presented in the normal state for different doping levels of YBa$_2$Cu$_3$O$_{6+x}$ (Y-123) and Bi$_2$Sr$_2$CaCu$_2$O$_y$ (Bi-2212). Experimentally the electron-phonon coupling can be determined from the line shape of the $B_{1g}$ Raman phonon for both Y-123 where the surroundings of the CuO$_2$ plane is highly asymmetrical and Bi-2212 where the plane is placed in a more symmetrical environment with respect to the charges of the nearby atoms.

The resulting electron-phonon coupling is then used to interpret the Fano interference in the Raman spectra of Y-123, where the light is scattered by both the $B_{1g}$ phonon and the electronic charge fluctuation in the plane described above.

However, for Bi-2212 the $B_{1g}$ phonon has an almost Lorentzian line shape indicating the lack of any substantial coupling between that phonon and the charge transfer between the two oxygens in accordance with the absence of a significant electric field. This striking difference in the data taken on these two groups of materials can be considered as strong evidence in favor of the linear (involving one phonon) electron-phonon coupling due to the electric field. In order to complete this argument, the data for a Bi-2212 sample with the calcium partially (38%) substituted by yttrium are presented, where the doping most likely breaks locally the reflection symmetry through the CuO$_2$ plane, thereby making this material similar to the asymmetrical ones.

Finally, the value obtained for the electron-phonon coupling is in excellent agreement with the value calculated using the electric field value determined by the experimentally observed buckling [3,4] and the restoring force calculated from the frequency of the $A_{1g}$ phonon. The change in the doping is essential in light of the close-ness of the Fermi level to a van Hove singularity in the density of states.

Much of the development of the crystal field model was given in Ref. [5]. However, the electronic dispersion is now calculated for a three band model including direct $O-O$ hopping $t'$ as well as $Cu-O$ hopping $t$. As
in Ref. [6] we consider only a reduced one band model appropriate for near half filling and take only the upper band into account. The electron - phonon reduced Hamiltonian for the $B_{1g}$ $q = 0$ phonon was given as

$$H_{el-ph} = \frac{1}{\sqrt{N}} \sum_{k,\sigma} g(k)d_{k,\sigma}^\dagger d_{k,\sigma}[c + c^\dagger],$$

(1)

where $d_{k,\sigma}$ annihilates an electron of spin $\sigma$ and momentum $k$, and $c$ creates a $B_{1g}$ phonon mode of wavevector $q = 0$. The coupling constant $g(k)$ of the $B_{1g}$ mode to an electron with momentum $k$ was evaluated in Ref. [6] and is given by

$$g(k) = eE \sqrt{\frac{\hbar}{2M\omega_{B_{1g}}}} \sqrt{\frac{1}{2}} \left| \phi_x(k) \right|^2 - \left| \phi_y(k) \right|^2,$$

(2)

where $M$ is the oxygen mass, $\omega_{B_{1g}}$ is the phonon frequency, and $E$ is the $\hat{z}$ component of the electric field at both the $O(2)$ and $O(3)$ sites. The functions $\phi_{x,y}$ are the amplitudes of the $O$-orbitals in the wave functions from the three band model [3].

In Ref. [6] a generalized form of the Breit-Wigner or Fano lineshape describing the interaction of a discrete excitation (phonon) with an electronic continuum was given in terms of the channel dependent electronic susceptibility $\chi_\lambda$, the electron-phonon coupling constant, the effective phonon-phonon coupling constant $g_{\lambda-\lambda}$, and the intrinsic damping $\Gamma_\lambda$ of the phonon lineshape due to e.g. an anharmonic lattice potential. The expression for the full Raman response measured in channel $\lambda$ was given as

$$\chi_{\lambda, full}(\omega) = \frac{(\omega + \omega_\lambda)^2}{(\omega - \omega_\lambda)^2 + 4\omega_\lambda \Gamma_\lambda(\omega)^2} \times \left\{ 2\lambda\chi''(\omega) \left[ (\omega - \omega_\lambda)^2 + 4\Gamma_\lambda^2(\omega) \left( \frac{\omega_\lambda}{\omega + \omega_\lambda} \right) \right] \right\} + 4g_{\lambda-\lambda}^2 \Gamma_\lambda \left( \frac{\omega_\lambda}{\omega + \omega_\lambda} \right)^2 [1 + \lambda(\omega)/\beta]^2,$$

(3)

The parameters are chosen to model the background spectrum seen of the normal state measured via Raman scattering. Then the remaining parameters are chosen to fit the Fano profile. Specifically, the effect of the parameters is as follows: the photon-phonon coupling constant $g_{\lambda-\lambda}$ determines the position of the antiresonance $\omega_\alpha$ of the Fano profile, the electron-phonon coupling constant $g$ determines the asymmetry of the lineshape around the phonon position $\omega$, which differs from its position $\omega$ in the absence of electron-phonon coupling, and the photon-electron coupling constant $\gamma$ determines the overall strength of the background continuum under the phonon measured via Raman scattering [5]. Here $\gamma_{B_{1g}}$ is the projected part of the electron-phonon vertex $\gamma(k)$ which possesses $B_{1g}$ symmetry. $g_{B_{1g}}^2$ is the average of the coupling $|g(k)|^2$ over the Fermi surface including the electron density for the two spins at a temperature $T$. We can now evaluate the Fano lineshape as a function of doping.

Before a comparison of the theoretical predictions with the data is made a few experimental details are given and the results are summarized. The Raman experiments were performed in back-scattering geometry, with the resolution set at 8 cm$^{-1}$ being completely sufficient for the observation of the changes. The coordinate system is locked to the Cu - O bonds with $x = [100]$, $x' = [110]$, etc. All symmetries refer to a tetragonal point group. The $B_{1g}$ phonon and continuum are projected out with $x'y'$ polarization. The samples we used were of superior quality which manifests itself in a small transition width to the superconducting state and a large intensity ratio $I_{phonon}/I_{continuum}$. Y-123 in particular was prepared in BaZrO$_3$ resulting in an unprecedented purity of 99.995% [4]. More details of the samples will be described in another publication.

Results obtained at $B_{1g}$ symmetry for Y-123 are plotted in Fig. 2 (a)-(c). All spectra are divided by the Bose-Einstein thermal function in order to get the response $\chi''_{\lambda, full}$ as described in Eq. (3). As a result of doping the shape of the $B_{1g}$ phonon at approximately 330 cm$^{-1}$ changes considerably. At low doping it is narrow and close to a Lorentzian. When carriers are added the line broadens and becomes more asymmetric exhibiting a Fano-type dependence on frequency. $I_{phonon}/I_{continuum}$ decreases since the $B_{1g}$ continuum gains intensity [1]. Excellent fits to the data on optimally-doped Y-123 in both the superconducting and normal states were given in [6], which, when interpreted, supported evidence for $d_{x^2-y^2}$-pairing in this material. We now extend these results by examining fits to the normal state data of different samples and dopings. We find that once again excellent fits to the data can be obtained (Fig. 2). The respective fitting parameters for $\chi_\lambda$ (see [6]) are given in Table I.

We now can make a comparison to the crystal field model predictions for the electron-phonon coupling constant. We see from the fits that for Y-123 the coupling
weaker spontaneous symmetry breaking is also possible. Themselves in the larger linewidth of the phonon. A symmetry and also to local inhomogeneities which manifest electron-phonon coupling to a much smaller local asym-
Y-123) in this compound. We attribute then the small and below the planes are not so drastically different as in electric field must be much weaker (the charges above to experimentally observed Fermi surfaces.

Indeed, in our model we would expect that the electron-phonon coupling for Bi-2212 obtained from the mirror plane symmetry is broken and we would expect the charges of oxygen and copper are different. For an estimation of the buckling [5], a simplified model is sufficient [6] where Cu is pinned rigidly to the elementary cell, and the oxygen moves in a harmonic potential be-
estimated by replacing the Ca with (CaO_{0.62}Y_{0.38}) in Bi-2212. It is expected that significant parts of the CuO_2 planes experience a stronger local field loosing the reflection symmetry through that plane. Most likely, the Y replaces big regions of the Ca planes, just like in Y-123 where upon oxygen doping of the chains some of the chains are more doped than the others [3].

To test this idea we look at the measurements of Bi-2212 which has been doped with Y in place of Ca. When Y is doped in for Ca the line gains intensity and shifts by 15-20 cm^{-1} (Fig. 2 (e)). A reminder of the line found in Y-free crystals is still seen as a shoulder on the left-hand side of the new line. Since here the valence of the Y (+3) is different from that of Ca (+2), once again the mirror plane symmetry is broken and we would expect a much larger electron-phonon coupling than in the undoped compound. The fit to the B_{1g} data using Eq. (3) is given in Fig. (2e). The coupling constant (see Table I.) is indeed increased over that of the undoped compound when Y is introduced, and in accordance the intensity of the phonon line is also essentially enhanced. The fact that the Fano effect increases gives strong support for the crystal field coupling model as the driving source of electron-phonon coupling.

The electric field E perpendicular to the CuO_2 plane results in an A_{1g}-type static distortion of the plane since the charges of oxygen and copper are different. For an estimation of the buckling [3], a simplified model is sufficient [6] where Cu is pinned rigidly to the elementary cell, and the oxygen moves in a harmonic potential being characterized by the frequency of the A_{1g} phonon at \( \omega_{A_{1g}} = 435 \text{ cm}^{-1} \). The restoring force at the buckling amplitude \( \Delta z \) must balance the electric force acting on the oxygen with charge \( q = -1.75e \). Thus, \( qE = M\omega_{A_{1g}}^2\Delta z \) must hold. With the experimental value \( \Delta z = 0.24\text{A} \), \( E = 1.53V/A \) is obtained which is close both to the 1.3V/A used for estimating the electron-phonon coupling strength and to the theoretically calculated number [3]. On the other hand, in the case

FIG. 2. Comparison of the theory from the crystal field model to the B_{1g} Raman results on (from left to right) under-doped, optimally-doped, over-doped YBa_{2}Cu_{3}O_{6+x}, respectively, and optimally-doped (second panel from right) and Y-doped Bi_{2}Sr_{2}(Ca_{1-x}Y_{x})Cu_{2}O_{8+\delta} (right panel), respectively, and the scales for each are arbitrary. The parameters used are listed in Table I.
of CuO$_2$ planes in a more symmetrical environment as in Bi-2212 and the infinite-layer compound CaCuO$_2$ the buckling, if it exists at all, is at least an order of magnitude smaller as found in structural studies [14].

In summary, studying Y-123 with different doping levels we have shown that the electric field across the CuO$_2$ planes is sufficiently strong to produce both the observed buckling and the strong electron-phonon coupling for the Fano line shape. In order to check this idea experiments were performed on Bi-2212 with and without Y doping. While the sample without Y shows very weak electron-phonon coupling, the interaction is enhanced by an order of magnitude and becomes comparable to the one in Y-123 if the local reflection symmetry is broken more substantially by replacing part of the Ca by Y. As doping Bi-2212 with Y results in a change of $T_c$ from $T_c = 91.5K$ to $T_c = 57K$ along with a large increase of the coupling $\lambda$, the $B_{1g}$ phonon can not play an important role for the superconductivity, in agreement with the conclusion of Savrasov and Andersen [3].

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![Table I. Summary of fitting parameters used in Fig. (2). All quantities except $\alpha, \beta, \lambda$, and the scale factor (dimensionless) are given in units of cm$^{-1}$. Also $\omega_c = 12,000$ cm$^{-1}$ and $\beta' = 3.3$ have been used. A scale factor was multiplied to Eq. (3) to account for the overall magnitude of the cross section. Since the experimentally determined response is in arbitrary units, this has no effect on the conclusions.](image-url)

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$$\tilde{\chi}_f^{\alpha}(\omega) = N_F \omega \tilde{\tau}_\alpha^{-1}/[\tilde{\omega}^2 + \tilde{\tau}_\alpha^{-2}],$$

where

$$\tilde{\tau}_\alpha^{-1} = \tau_\alpha^{-1} + \sqrt{(\beta/T)^2 + \omega^2},$$

and

$$\tilde{\omega} = \omega m(\omega)/m, with \quad m^*(\omega)/m = 1 + 2\alpha B \pi [\omega(\sqrt{(\beta T)^2 + \omega^2})].$$

Here $1/\tau_\alpha^{-1} = 1/\tau_{m=0} - 1/\tau_\alpha$ is the channel-dependent impurity scattering rate reduced by vertex corrections [A. Zawadowski and M. Cardona, Phys. Rev. B 42, 10732 (1990)], and $\alpha, \beta$, and $\omega_c$ are constants determined by a fit to the electronic continuum in the normal state. This form for the Raman susceptibility provides an adequate description to the continuum in the normal state of both Y-123 and Bi-2212.

[9] These parameters are related as in [14] by

$$\beta = 2g_p\gamma g_{B_{1g}}[\gamma B_{1g} \omega B_{1g}]^{-1}, \quad \omega^2 = \omega_{B_{1g}}^2[1 + \beta],$$

$$\lambda(\omega B_{1g}) = \tilde{g}_{B_{1g}}/\omega B_{1g},$$

$$\Gamma_{B_{1g}}(\omega B_{1g}) = \Gamma_{B_{1g}} + g_{B_{1g}}^2 \tilde{\chi}_f^{\alpha}(\omega B_{1g})/N_F,$$

with $N_F$ the density of states per spin at the Fermi level.

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**Table I.** Summary of fitting parameters used in Fig. (2). All quantities except $\alpha, \beta, \lambda$, and the scale factor (dimensionless) are given in units of cm$^{-1}$. Also $\omega_c = 12,000$ cm$^{-1}$ and $\beta' = 3.3$ have been used. A scale factor was multiplied to Eq. (3) to account for the overall magnitude of the cross section. Since the experimentally determined response is in arbitrary units, this has no effect on the conclusions.

| Fig. | $\alpha$ | $\omega$ | $\omega_c$ | $\omega_{B_{1g}}$ | $\Gamma$ | $\lambda$ | scale |
|------|---------|---------|---------|---------------|-------|--------|-------|
| (2a) | 0.55    | 343     | 347.5   | 3000           | 352.5 | 4      | 0.0257 | 22   |
| (2b) | 0.95    | 340.5   | 348     | 1200           | 349.3 | 6.5    | 0.0426 | 20   |
| (2c) | 0.75    | 342     | 352     | 900            | 352.5 | 6      | 0.056  | 30   |
| (2d) | 0.1     | 305     | 305.2   | 1600           | 306.5 | 28     | 0.00131 | 20 |
| (2e) | 0.2     | 320     | 322     | 1200           | 326   | 20     | 0.0124 | 10   |