Importance of Structural Instability to High-Temperature Superconductivity

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The orthorhombic-tetragonal structural phase transition of La$_{2-x}$Sr$_x$CuO$_4$ is quantitatively analyzed as a function of composition $x$ within an anharmonic electron-phonon interaction model. The correct temperature dependence of the soft mode and the elastic constant $c_{66}$ is obtained. The double-well potential in the electron-phonon interaction is derived self-consistently and found to vary strongly with $x$. In the vicinity of the superconducting transition temperature $T_c$ electron–two-phonon interactions dominate the harmonic ones which may explain the high $T_c$'s observed.

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The origin of the pairing mechanism in high-temperature superconductors [1] is still an open problem. Including the perovskites Ba$_{1-x}$K$_x$BiO$_3$ [2] and BaPb$_{1-x}$Bi$_x$O$_3$ [3] in the class of “high-temperature” superconductors that show BCS-like properties would suggest that a phonon-mediated mechanism may also be responsible for the layered superconducting compounds with much higher $T_c$’s. In this work we derive an electron-phonon interaction model that quantitatively describes the phonon-mediated structural phase transition observed in La$_{2-x}$Sr$_x$CuO$_4$. This transition is analyzed on the basis of a local $\phi^{(4)}$ potential in the electron-phonon interaction (not nonlinear phonon-phonon interaction) [4] which induces the substantial structural instability observed in all high-$T_c$ compounds [5]. It will be shown that this electron-phonon-induced structural instability requires an extension of the Migdal theorem [6], leading to a BCS-type superconducting state, where the harmonic electron-phonon interaction is enhanced by electron-density–two-phonon couplings. (For example, in YBa$_2$Cu$_3$O$_y$, the high dielectric constant and high pyroelectric coefficients point to an incipient dipolar instability.)

The model Hamiltonian we start with represents a combination of two different electron-phonon models [7,8] extended by higher-order interaction terms $H^{(4)}$:

$$H = \sum_i \left[ p_i^2/2M + \frac{1}{2} g \sum_{\alpha} q_i q_i^\alpha + \frac{1}{2} g \sum_{\alpha} q_i^4 + \frac{1}{2} K (q_{i-1} - q_i)^2 \right] + i \sum_{\alpha} (c_i^\dagger c^{\dagger}_{i+1,\alpha} + H.c.) + \sum_i q_i n_{i\alpha} + \sum_{\alpha} (q_{i+1} - q_i) n_{i\alpha} + \sum_i U n_{i1} n_{i1} + H^{(4)}$$

and

$$H^{(4)} = g_4 \sum_i \left[ q_i n_{i\alpha} (q_i + n_{i\alpha}) + q_i^2 n_{i1} n_{i1} \right],$$

where the $p_i$ and $q_i$ are the phonon momentum and displacement coordinates, $c^\dagger_{i\alpha}$ and $c_{i\alpha}$ are electron creation and annihilation operators with $n_i = \sum_{\alpha} c^\dagger_{i\alpha} c_{i\alpha}$, and $\lambda$ and $\tilde{\lambda}$ represent on-site and intersite couplings of phonon coordinates with the electron density. The fourth-order term in the phonon coordinates $q_i$ is a consequence of the nonlinear electron-phonon interaction potential [9,10]. Higher-order interactions in the electron density have been omitted. The potential in the $q_i$ is equivalent to those used by Hardy and Flocken, Plakida and coworkers, and various other groups [11]. However, in contrast to these models, and an important consequence of this electron-phonon interaction potential, are the terms appearing in Eq. (2) describing electron-density–two-phonon interactions. The Migdal theorem, where higher-order perturbation corrections [12] in the electron-phonon interaction are considered on the basis of the Fröhlich Hamiltonian [8], which resembles (1) with neglect of $H^{(4)}$, is not applicable to our Hamiltonian as the higher-order interactions do not result from perturbation methods but from the $\phi^{(4)}$ potential in the electron-phonon interaction. This means that $\lambda \neq g_4$. Microscopically the Hamiltonian (1) has its origin in the instability of the oxygen $2p^6$ configuration [13], which, due to small phonon displacements, may easily change its character from bound to unbound thus inducing a polarizability catastrophe. The electronic configuration $2p^6$ of O$^{2-}$ is only stable in a crystal where Coulomb interactions with the surrounding ions provide the ionic stability. In an isotropic environment the $p_x$, $p_y$, $p_z$ orbitals are also isotropic. Anisotropy and covalency strongly favor the tendency of an elliptic ground state. For example, in YBa$_2$Cu$_3$O$_y$, the $p_z$ orbitals of the apical oxygen ion O(4) are strongly delocalized towards the CuO$_2$ planes which then provide a mechanism for the pairwise attraction of holes in the planes [10,14].

We note also that our Hamiltonian may change the
picture of bipolaron formation [15] (and especially large bipolaron formation [16]) drastically because the higher-order electron-phonon interaction terms of \(H^{(4)}\) are usually neglected. Furthermore, early calculations of Hui and Allen [17], using a Hamiltonian with \(g_4\) terms in the phonon coordinate \(q_i\) only, did not lead to an enhancement of the electron-phonon coupling. The calculations by Hardy and Flocken, Plakida, and others [11] start from a double-well potential in the phonon coordinates \(q_i\), and an enhancement was found, yet not large enough to explain high \(T_s\). Our analysis is based on the classical equivalent of Hamiltonian (1), and the procedures of Enz [18] and Pytte and Feder [19] are used. The classical Hamiltonian is given by

\[
H = \sum_i \left( \frac{p_i^2}{2M_i} + V(w_i) \right) + \sum_{i,j} V_{ij} u_i u_j
\]

(3)

with

\[
V(w_i) = \frac{g_2}{2} w_i^2 + \frac{g_4}{4} w_i^4
\]

and \(w_i = u_i - v_i\), where \(u_i\) and \(v_i\) are the classical core and shell displacement coordinates and \(V_{ij}\) represents the ionic interaction potential with neighboring cells.

Within the framework of the self-consistent phonon approximation (SPA), which corresponds to an expansion in the first cumulant of the relative electron-ion displacement \(w_i\), the structural phase transition of \(\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4\) is quantitatively described. A comparison of inelastic-neutron-scattering data with model calculations is shown in Fig. 1. The softening of the acoustic branch at the zone boundary with decreasing temperature is self-consistently calculated (Fig. 1). Together with the softening of the zone-boundary frequency the elastic constant \(c_{66}\) softens [21] and shows perfect Curie-Weiss behavior, which also results in quantitative agreement with the model.

To find the temperature dependence of the soft mode related to the structural transition for other compositions and thus other \(T_s\), resonant ultrasound spectroscopy (RUS) [22] was used to confirm a universal behavior of the softening of \(c_{66}\) and thus of the related soft mode. Because previous RUS studies [21] of a well-characterized single crystal of \(\text{La}_{1.86}\text{Sr}_{0.14}\text{CuO}_4\) established that only \(c_{66}\) softened at \(T_s\), we could, for this work, use an unoriented flake from a very small single crystal of Cu-O flux-grown \(\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_4\) [23] in the RUS system. Any observed temperature dependence could then be taken to be that of \(c_{66}\). Again a Curie-Weiss-like temperature dependence of \(c_{66}\) was obtained. Thus the power law (exponent of unity) is correctly determined. The confirmation of a universal temperature dependence of the soft mode as depicted in Fig. 2 (where the new results on \(c_{66}\) are inserted) enabled the self-consistent determination of the relevant electron-phonon couplings \(g_2, g_4\) as a function of \(T_s\) and \(x\). Note that both quantities are nonlinearly dependent on \(x\) and \(T_s\) (Fig. 3). Also shown in Fig. 2 is the predicted temperature dependence of \(c_{66}\), derived from \(\omega^2/\omega(q)\) for \(q \to 0\). It displays the same softening for other \(T_s\).

The electron-phonon interaction potential derived self-

![FIG. 1. Comparison of theoretical (dashed lines) and experimental dispersion curves (taken from Ref. [20]) at \(T=573\) K (open circles), \(T=473\) K (open squares), and \(T=432\) K (open triangles). Solid circles are temperature-independent data.](image)

![FIG. 2. Calculated temperature dependence of the soft zone-boundary mode for five different \(T_s\). The solid straight line corresponds to the calculated temperature dependence compared to experimental data (solid circles, Ref. [20]) and the related softening of the elastic constant \(c_{66}\) (dashed line), while dash-dotted lines represent extrapolations of this temperature dependence for other \(T_s\) as confirmed by RUS methods. Open squares and stars correspond to new experimental data.](image)
consistently from extrapolations of these data to other compositions is shown in Fig. 4 for five different \( T_s \)'s. For high \( T_s \) the potential is a deep double well. Thus at the superconducting transition temperature \( T_c \) where \( T_s \ll T_c \) the potential can be approximated pseudoharmonically as either of the two wells is occupied close to the minimum. With decreasing \( T_s \) the potential flattens and for \( T_s = T_c \) the nonlinear electron-phonon interactions dominate the harmonic ones. The system becomes extremely sensitive to the anharmonicity (i.e., \( g_2 \) and \( g_4 \) are of the same order of magnitude) and a pseudoharmonic treatment of the electron-density–two-phonon interactions should no longer be valid.

Summarizing, it has been shown that the soft-mode-induced structural instability observed in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) can be described quantitatively on the basis of self-consistent phonon theory using an anharmonic electron-phonon interaction model. In the temperature regimes where \( T_s \approx T_c \) the pseudoharmonic treatment is no longer valid as here the higher-order electron-phonon interactions are of the same order of magnitude (or even greater) as the harmonic ones. In this regime strong deviations from BCS-like properties are expected and from first estimates an isotope effect of \( \alpha = 0.1 \) is found. Solving the Eliashberg equations for the electron-phonon coupling \( \lambda \) of this specific mode and deriving the corresponding \( T_c \), definite limitations on \( T_c \) are obtained due to the pseudoharmonic approximations imposed from the soft-mode treatment [24]. This points to the importance of seriously considering the higher-order electron-phonon interactions which require an extension of the Migdal theorem.

As long as these terms are large compared to the harmonic ones, pseudoharmonic treatments are not applicable like the SPA discussed above and consequently pronounced phonon anomalies with temperature (like the soft modes discussed above) are not to be expected in the vicinity of \( T_c \) [24]. Because of the two-phonon interaction terms, line-shape broadenings in Raman scattering, high oscillator strengths in infrared measurement, and bound states (i.e., biphonons) are predicted from the present model. These conclusions also provide an explanation for the interrelation of the isotope effect \( \alpha \) with structural instability as observed by Crawford et al. [25] not only for \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) but also (and even more pronounced) for \( \text{La}_{2-x}\text{Ba}_x\text{CuO}_4 \).

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