Importance of Structural Instability to High-Temperature Superconductivity

A. Bussmann-Holder
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany and University of Bayreuth, D-8550 Bayreuth, Federal Republic of Germany

A. Migliori, Z. Fisk, J. L. Sarrao, and R. G. Leisure[(a)]
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

S.-W. Cheong
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 22 October 1990)

The orthorhombic-tetragonal structural phase transition of $La_{2-x}Sr_xCuO_4$ 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.

PACS numbers: 74.20.−z, 63.20.Kr, 63.20.Ry, 77.80.−e

The origin of the pairing mechanism in high-temperature superconductors [1] is still an open problem. Including the perovskites $Ba_{1-x}K_xBiO_3$ [2] and $BaPb_{1-x}Bi_xO_3$ [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 $La_{2-x}Sr_xCuO_4$. 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 $YBa_2Cu_3O_7$, 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 $H^{(4)}$:

$$H=\sum_i[p_i^2/2M+\tfrac{1}{2}g_2q_i^2+\tfrac{1}{2}g_4q_i^4+\tfrac{1}{2}K(q_{i-1}-q_i)^2] +t\sum_{i,\sigma}(c_{i,\sigma}^{\dagger}c_{i+1,\sigma}+\text{H.c.})+\lambda\sum_{i,\sigma}q_in_{i\sigma} +\tilde{\lambda}\sum_{i,\sigma}(q_{i+1}-q_i)n_{i\sigma}+\sum_i U^in_{i\uparrow}n_{i\downarrow}+H^{(4)} \quad (1)$$

and

$$H^{(4)}=g_4\sum[q_in_{i\sigma}(q_i+n_{i\sigma})+q_i^2n_{i\uparrow}n_{i\downarrow}]\,, \quad (2)$$

where the p_i and q_i are the phonon momentum and displacement coordinates, $c_{i\sigma}^{\dagger}$ and $c_{i\sigma}$ are electron creation and annihilation operators with $n_i=\sum_\sigma c_{i\sigma}^{\dagger}c_{i\sigma}$, and λ 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 those 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 $YBa_2Cu_3O_7$, 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_c. 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

$$H=\sum_i\left\{\frac{p_i^2}{2M_i}+V(w_i)\right\}+\sum_i\sum_j V_{ij}u_iu_j \qquad (3)$$

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 $La_{1.85}Sr_{0.15}CuO_4$ 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.

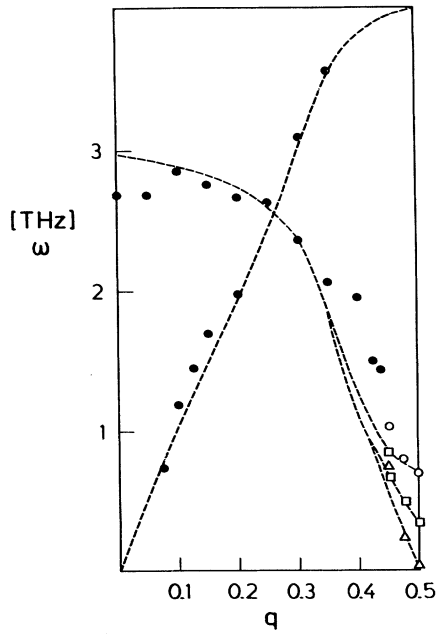

FIG. 1. Comparison of theoretical (dashed lines) and experimental dispersion curves (taken from Ref. [20]) at $T=573$ K (open circles), $T=473$ K (open squares), and $T=432$ K (open triangles). Solid circles are temperature-independent data.

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 $La_{1.86}Sr_{0.14}CuO_4$ 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 $La_{1.90}Sr_{0.10}CuO_4$ [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 $d\omega/dq$ for $q\rightarrow 0$. It displays the same softening for other T_s.

The electron-phonon interaction potential derived self-

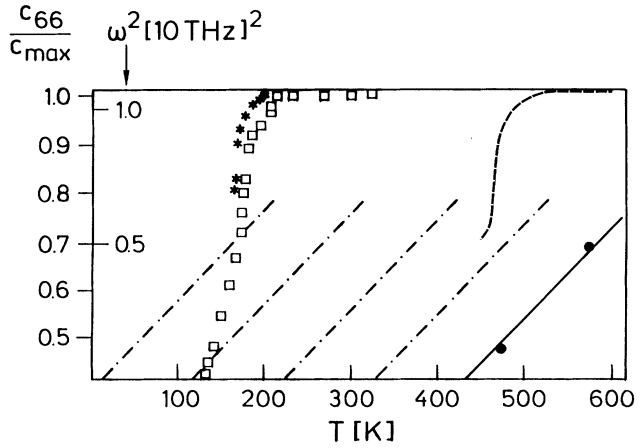

FIG. 2. Calculated temperature dependence of the soft zone-boundary mode for five different T_s. The solid straight line corresponds to the calculated temperature dependence compared to experimental data (solid circles, Ref. [20]) and the related softening of the elastic constant c_{66} (dashed line), 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.

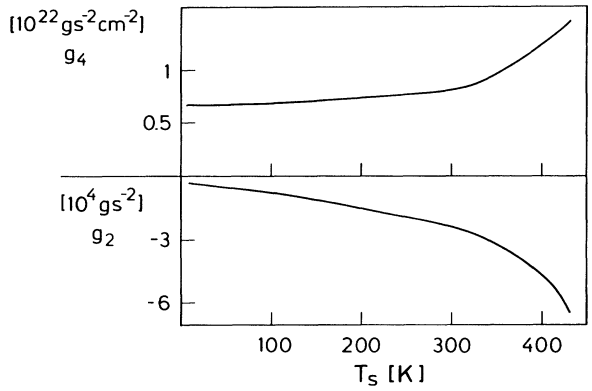

FIG. 3. Harmonic (g_2) and nonlinear (g_4) electron-phonon couplings as a function of structural transition temperature T_s.

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 $T_c \ll T_s$ 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 $T_s \approx T_c$ 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 $La_{2-x}Sr_xCuO_4$ can be described quantitatively on the basis of self-consistent phonon theory using an anharmonic electron-phonon interaction model. In the temperature regimes where $T_c \approx T_s$ 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 λ 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,

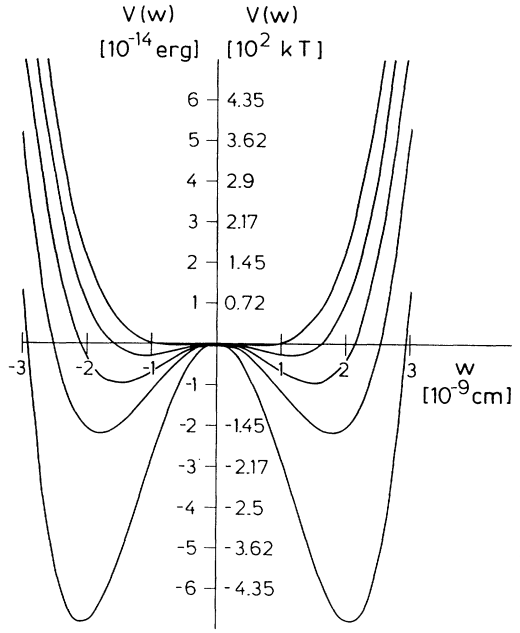

FIG. 4. The double-well potential in the electron-phonon interaction as derived self-consistently from the temperature dependence of the soft mode. Starting from the outermost potential, the corresponding transition temperatures are 432, 330, 220, 116, and 10 K, respectively.

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 α with structural instability as observed by Crawford *et al.* [25] not only for $La_{2-x}Sr_xCuO_4$ but also (and even more pronounced) for $La_{2-x}Ba_xCuO_4$.

Work at Los Alamos was performed under the auspices of the U.S. Department of Energy's Division of Basic Energy Sciences. One of us (A.B.-H.) gratefully acknowledges the hospitality enjoyed at Los Alamos National Laboratory and the financial support of the Deutsche Forschungsgemeinschaft. It is a pleasure to thank P. B. Allen, A. R. Bishop, and H. Büttner for many stimulating discussions and H. Büttner for a critical reading of the manuscript.

[a]Permanent address: Physics Department, Colorado State University, Fort Collins, CO 80523.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986); C. W. Chu, P. H. Hor, R. L. Meng, L. Rao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).

[2] R. J. Cava, B. Batlogg, G. J. Krajewski, R. Farrow, L. W.

Rupp, Jr., A. E. White, K. Short, W. F. Peck, and T. Kometani, Nature (London) **332**, 814 (1988).
[3] A. W. Cox, J. J. Gibson, and P. E. Bierstedt, Solid State Commun. **17**, 27 (1975).
[4] R. Migoni, H. Bilz, and D. Bäuerle, Phys. Rev. Lett. **37**, 1155 (1976); H. Bilz, G. Benedek, and A. Bussmann-Holder, Phys. Rev. B **35**, 4840 (1987).
[5] See, e.g., P. Allen, Z. Fisk, and A. Migliori, in *Physical Properties of High Temperature Superconductors I,* edited by D. M. Ginsberg (World Scientific, Singapore, 1989), p. 213.
[6] V. M. Galitskii and A. B. Migdal Zh. Eksp. Teor. Fiz. **34**, 139 (1958) [Sov. Phys. JETP **7**, 96 (1958)].
[7] W. P. Su, J. R. Schrieffer, and A. G. Heeger, Phys. Rev. B **22**, 2099 (1980).
[8] H. Fröhlich, Phys. Rev. **79**, 845 (1950).
[9] A. Bussmann-Holder, H. Büttner, and A. Simon, Phys. Rev. B **39**, 207 (1989).
[10] A. Bussmann-Holder, A. R. Bishop, and I. Batistíc, Phys. Rev. B **43**, 13728 (1991).
[11] J. R. Hardy and G. W. Flocken, Phys. Rev. Lett. **60**, 2191 (1988); N. M. Plakida, Phys. Scr. **T29**, 77 (1981); S. L. Drechsler and N. M. Plakida, Phys. Status Solidi B **144**, K113 (1987).
[12] A. B. Migdal, Zh. Eksp. Teor. Fiz. **34**, 1438 (1958) [Sov. Phys. JETP **7**, 996 (1958)].
[13] A. Bussmann, H. Bilz, R. Roenspiess, and K. Schwarz, Ferroelectrics **25**, 343 (1980).
[14] I. Batistic, A. R. Bishop, R. L. Martin, and Z. Tesanovic, Phys. Rev. B **40**, 6896 (1989).
[15] For a recent review, see, e.g., R. Micnas, J. Ranninger, and S. Robaskiewiecz, Rev. Mod. Phys. **62**, 113 (1990).
[16] D. Emin and M. S. Hillery, Phys. Rev. B **39**, 6575 (1989).
[17] J. C. K. Hui and P. B. Allen, J. Phys. F **4**, L42 (1974).
[18] J. Enz, Phys. Rev. B **6**, 4695 (1972).
[19] E. Pytte and J. Feder, Phys. Rev. **187**, 1077 (1969).
[20] P. Böni, J. D. Axe, G. Shirane, R. J. Birgenau, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, and T. R. Thurston, Phys. Rev. B **38**, 185 (1988).
[21] A. Migliori, W. M. Vissher, S. Wong, S. E. Brown, S. Tanaka, H. Kojima, and P. B. Allen, Phys. Rev. Lett. **64**, 2458 (1990).
[22] A. Migliori, W. M. Visscher, S. E. Brown, Z. Fisk, S.-W. Cheong, B. Alten, E. T. Ahrens, K. A. Kubat-Martin, J. D. Maynard, Y. Huang, D. R. Kirk, K. A. Gillis, H. K. Kimard, and M. H. W. Chan, Phys. Rev. B **41**, 2098 (1990).
[23] S. W. Cheong, J. D. Thompson, and Z. Fisk, Physica (Amsterdam) **158C**, 109 (1989).
[24] A. Bussmann-Holder and A. Bishop (to be published).
[25] M. K. Crawford, M. N. Kunchur, W. E. Farneth, E. M. McCarron, III, and S. J. Poon, Phys. Rev. B **41**, 282 (1990).