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Possibility of a common origin to ferroelectricity and superconductivity in oxides

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We describe an extension of a lattice dynamical model for displacive-type ferroelectrics which might be applied to high-temperature superconductors. The model is based on the instability of the oxygen ion O^{2-}, dynamically described by an on-site nonlinear electron-ion coupling, and on the valence instability of the cation [e.g., Cu(I), Cu(III)], represented by a nonlinear electron-electron interaction which provides a pairwise coupling of the electrons. The equivalent quantum-mechanical Hamiltonian describes an extended Peierls-Hubbard system. The most important outcome of the model is that a ferroelectric instability is a necessary condition for paired electron states which indicate the possibility of superconductivity. Depending on the strength of the coupling constants, either a ferroelectric or a superconducting state results.

I. INTRODUCTION

A variety of theories[1-4] have been proposed to explain the superconductivity of high-T_c oxide systems. The microscopic mechanism is still a matter of dispute. We propose a model based on the specific microscopic properties of the oxygen ion O^{2-} (Ref. 5) and the involved cations, copper in particular.[6,7] The model combines the valence instability of the cations and the ferroelectric instability observed in many pervoskite oxides.

II. CHEMICAL ASPECTS

Semiconducting $BaBiO_3$ forms a distorted perovskite structure according to $Ba_2Bi(III)Bi(V)O_6$ with localized electron pairs on half of the Bi sites.[8] The localization and distortion is avoided through a substitution of Bi by Pb or by forcing the Bi into a nonintegral oxidation state, $BaPb_{0.75}Bi_{0.25}O_3$ as well as $Ba_{0.6}K_{0.4}BiO_3$ are metallic and become superconducting at 13 K (Ref. 9) and 29 K (Ref. 10), respectively. The electron pairing mechanism is discussed in terms of the bipolaron model.[4,11,12] Chemically, the attractive interaction between electrons to form singlet electron pairs is due to a (frustrated) tendency for on-site localization of a "lone pair" in a Bi(III) configuration.

The special situation of Bi is the occurrence of intermediate valence states involving oxidation states differing by *two*. The specific property of oxygen is its configurational instability as a free ion O^{2-}. In a crystal the ion is stabilized by the Madelung potential. The inherent instability is reflected in a strong dependence of the oxygen ion polarizability α on its neighboring atoms.[13] In simple cubic oxides like MgO, CaO, SrO, α is proportional to the cell volume V.[14] This dependence is enhanced by covalency and anisotropy to α proportional V^3 or even V^4 as has been observed in spinels and ferroelectrics.[15] This local instability leads to a delocalization of the O $2p$ electrons with increasing cation-anion distance and if combined with transition-metal ions leads to a ferroelectric phase transition or if combined with the cations of intermediate valency results in an electronic resonant state driven by strong electron-phonon interaction. A pseudo-Jahn-Teller active mode[16] enables the Bi ion to attract pairwise electrons while simultaneously the O^{2-} ion delocalizes its p electrons.

The structures of $La_{1.8}A_{0.2}CuO_4$ ($A=$Ba,Sr; $T_c \approx 30$ and 40 K, respectively[17,18]) contain nearly planar CuO_2 layers between $La_{1.8}A_{0.2}O_2$ slabs with a strongly distorted octahedral (4+2) coordination of Cu. The rather square planar coordination is ideally suited to accommodate Cu(III) with a low-spin d^8 configuration present from the doping with A. It is interesting to note that in undoped La_2CuO_4 a considerable amount of d^{10} configuration [Cu(I)] contributes to the ground state.[19]

The ability of Cu to exhibit intermediate valence states involving the oxidation states Cu(I)/Cu(III) [together with Cu(II)] reminds one of the Bi(III)/Bi(V) systems.

The typical coordinations of Cu in oxocuprates[20,21] are shown in Fig. 1(a). The pseudo-Jahn-Teller mode involved in a Cu(I)/Cu(III) valence fluctuation should therefore lead to a quadrupolar distortion (coordination 2+2) for Cu.

In the new system $Tl_2Ba_2CuO_6$ which becomes superconducting at 80 K (Ref. 22), Tl(III) not only oxidizes the Cu but presumably also participates in the valence fluctuations as Tl(I)/Tl(III) (Ref. 23) similar to Bi in the Cu-Bi mixed oxides.[24,25] In the two- and three-layer cuprates, with still higher T_c's, these valence fluctuations are obviously even more enhanced by interlayer interactions.[26,27]

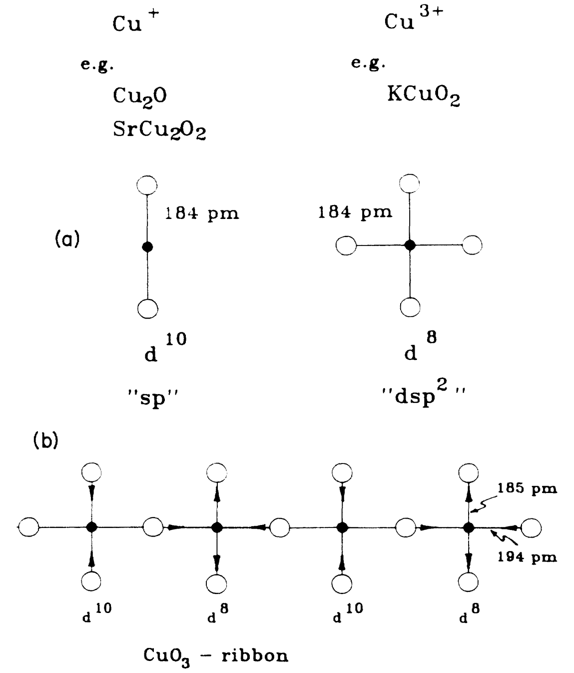

FIG. 1. Linear and square planar coordination of Cu(I) and Cu(III), respectively, in oxocuprates, e.g., SrCu$_2$O$_2$ (Ref. 20) and KCuO$_2$ (Ref. 21). (a) The Cu-O distances are 1.84 Å in both cases. (b) CuO$_{3-x}$ ($x=0$) ribbon in YBa$_2$Cu$_3$O$_{7-x}$. The distances Cu-O(1) and Cu-O(4) are 1.85 and 1.94 Å, respectively. The indicated vibration of O(1) approximates linear and square planar coordination for Cu.

YBa$_2$Cu$_3$O$_7$ [$T_c \approx 90$ K (Ref. 28)] represents a very interesting system, as its structure contains planar CuO$_3$ ribbons together with (strongly buckled) CuO$_2$ twin layers. These ribbons contain Cu in an oxidation state near +3, yet the linear CuO$_2$ units characteristic for Cu(I) are preformed here. Chemical removal of the loosely bound O atoms from the ribbons leads to the stable Cu(I) species. Dynamically this can be simulated by a pairwise removal of O from one Cu site, indicated in Fig. 1(b), thus enhancing the tendency to a d^{10} configuration. Simultaneously the adjacent Cu atoms (with square planar coordination) have the tendency for a d^8 configuration.[7]

We propose that the superconductivity of oxocuprates is due to the configurational instability of the O^{2-} ion together with the intermediate valency of the involved cations, thus leading to a dynamical change in the *p-d* hybridization ("dynamical covalency"[5]). While the d^{10} configuration is metal centered and creates holes in the O 2*p* band, the d^8 configuration of Cu leads to strong mixing with the oxygen *p* states. The crucial interplay of valence fluctuation and local instability has been taken into account in a simple double-shell model described in Sec. III.

III. THE CLASSICAL MODEL

Structurally ferroelectric perovskites and high-temperature superconducting oxides are closely related. Furthermore, it is evident for both that the oxygen ion plays a central role for the specific properties of the system under consideration. For ferroelectrics it has been shown that their soft-mode behavior at the zone center is triggered by the anisotropic nonlinear polarizability of the oxygen ion.[29] Lattice dynamically this is described by a local onsite double-well potential which is characterized by an attractive harmonic electron-phonon coupling g_2 and a stabilizing repulsive electron–two-phonon term g_4. Both quantities do not only account for the oxygen ion polarizability but also include the *p-d* hybridization of oxygen *p* and transition-metal *d* states.[30] The *p-d* hybridization exhibits a different character in superconducting Cu oxides due to the valence instability of the cation. Dynamically this has been simulated by introducing a second shell with *d* character surrounding the polarizable cluster with mass m_1 which is coupled nonlinearly to the original *p* shell. The relevant electron-electron couplings are k_2 harmonic and attractive, and k_4 nonlinear repulsive (Fig. 2). This model seems to be related to the double-shell model proposed by Weber[31] for hard superconductors. However, it differs by the important electron-electron coupling of the shells, which can give rise to two plasmon branches. The nonlinearity of this coupling (k_4) will be shown to lead to a crucial *p-d* density-density interaction. The Hamiltonian for our model reads

$$H=\tfrac{1}{2}\sum_{i,n} m_i \dot{u}_{in}^2+\tfrac{1}{2}\sum_{i,n} m_{ei}\dot{v}_{1n}^{2(i)}+\sum_n [\tfrac{1}{2}f'(u_{1n+1}-u_{1n})^2+\tfrac{1}{2}f(v_{1n}^{(1)}-u_{2n})^2+\tfrac{1}{2}g_2(v_{1n}^{(1)}-u_{1n})^2$$
$$+\tfrac{1}{4}g_4(v_{1n}^{(1)}-u_{1n})^4+\tfrac{1}{2}l(v_{1n+1}^{(2)}-v_{1n}^{(2)})^2+\tfrac{1}{2}k_2(v_{1n}^{(2)}-v_{1n}^{(1)})^2+\tfrac{1}{4}k_4(v_{1n}^{(2)}-v_{1n}^{(1)})^4]\,, \tag{1}$$

where m_i, m_{ei}, u_{in}, $v_{1n}^{(i)}$ ($i=1,2$) are the core and shell masses and their respective displacement in the *n*th cell. f', l, and f are harmonic second-nearest-neighbor core-core, shell-shell, and nearest-neighbor core-shell couplings. From the definitions

$$v_{1n}^{(1)}-u_{1n}=w_{1n}, \quad v_{1n}^{(1)}-v_{1n}^{(2)}=x_{1n} \tag{2}$$

the potential energy can be rewritten as

$$V=\tfrac{1}{2}\left(\sum_n [f'(u_{1n+1}-u_{1n})^2+f(w_{1n}+u_{1n}-u_{2n})^2+l(v_{1n+1}^{(2)}-v_{1n}^{(2)})^2+g_2w_{1n}^2+\tfrac{1}{2}g_4w_{1n}^4+k_2x_{1n}^2+k_4x_{1n}^4]\right). \tag{3}$$

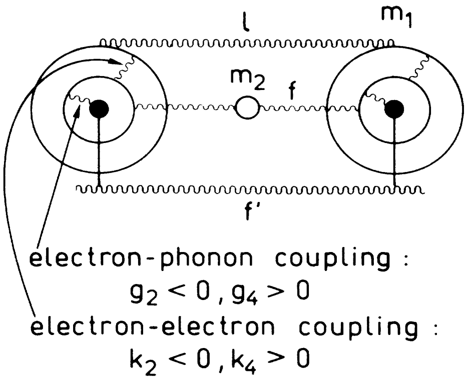

FIG. 2. The model (force constants and masses are explained in the text).

The use of the self-consistent phonon approximation allows the linearization of the nonlinear terms in the potential energy. This corresponds in the equations of motions to the replacement:

$$g_2 w_{1n} + g_4 w_{1n}^3 = (g_2 + 3g_4 \langle w_{1n}^2 \rangle_T) w_{1n} = g w_{1n} , \tag{4}$$

$$k_2 x_{1n} + k_4 x_{1n}^3 = (k_2 + 3k_4 \langle x_{1n}^2 \rangle_T) x_{1n} = k x_{1n} . \tag{5}$$

Here g and k are harmonic but temperature-dependent quantities which define two different types of phase transitions. (i) The limit $g \rightarrow 0$ (Ref. 30) leads to a static electron-ion displacement which induces a dipole moment and thus results in the ferroelectric state. Simultaneously, a soft optic mode is observed. (ii) For $k \rightarrow 0$ a frozen-in shell-shell displacement results which is characterized by the double-well potential defining quantities k_2, k_4. $\langle x_{1n}^2 \rangle_{T_c}$ is given by $-k_2/3k_4$ for $k=0$. As (i) has been discussed extensively in Ref. 30 we restrict ourselves here to (ii). The transition temperature T_c for a frozen-in shell-shell displacement or pairwise correlated electron state can be evaluated by calculating $\langle x_{1n}^2 \rangle_T$ via the eigenvectors U_1^2 and U_2^2 which obey the normalization condition $m_1 U_1^2 + m_2 U_2^2 = 1$. $\langle x_{1n}^2 \rangle_T$ is explicitly given by

$$\langle x_{1n}^2 \rangle_T = \sum_{q,j} \frac{\hbar}{2N\omega_{q,j}} x_1^2(q,j) \coth \left[\frac{\hbar \omega_{q,j}}{2kT} \right] , \tag{6}$$

where the dynamical information is provided by the self-consistent phonon approximation (SPA) eigenvalues $\omega_{q,j}$ and its related eigenvectors $x_1(q,j)$ for all phonon branches j in the first Brillouin zone. An analytical expression for T_c is obtained by using the high-temperature approximation in Eq. (6) which corresponds to $\hbar \omega_{q,j} \ll 2kT$. Within this approximation any mass dependence of T_c vanishes[32] with T_c meaning a classical instability which points to strong pairing of quantum-mechanical Cooper pairs. Furthermore, the electronic degrees of freedom are treated in the adiabatic approximation which reduces the summation over j to two branches. Thus T_c for the correlated electron-electron displacement is defined by

$$kT_c = -\frac{k_2}{3k_4} \frac{4f^2}{(2f-g)^2} (4f'J + 2f) . \tag{7}$$

$$J = \frac{V}{3} \int_0^{2\pi/a} q^2 dq \sin^2(qa) ,$$

V being the unit-cell volume. Obviously the magnitude of T_c is mainly determined by the intermolecular electron-phonon coupling f and the intramolecular coupling g which is intimately related to the oxygen ion polarizability. We distinguish the following cases.

(i) $g \gg 2f$:

$$kT_c = -\frac{k_2}{3k_4} \frac{4f^2}{g^2} (4f'J + 2f) , \tag{8}$$

which corresponds to small values of T_c.

(ii) $g \approx 2f$: kT_c may become very large.

(iii) $g \ll 2f$:

$$kT_c = -\frac{k_2}{3k_4} (4f'J + 2f) . \tag{9}$$

kT_c can exhibit high values. Its magnitude is only determined by the intermolecular electron-phonon coupling.

The above transition temperature can be identified as a transition to a state with pairwise correlated electrons (see below). Summarizing the above discussed results of the SPA treatment it can be concluded that the crucial interplay of inter- and intramolecular electron-phonon coupling determines the magnitude of T_c.

IV. QUANTUM-MECHANICAL MODEL

A connection to conductivity or superconductivity cannot be provided by the lattice-dynamical Hamiltonian discussed above if the electrons are treated as classical degrees of freedom. In this section we discuss how the classical Hamiltonian can provide a description of a state with pairwise-correlated electrons. This can be achieved by first transforming the shell displacement coordinates $v_{1n}^{(1)}$ and $v_{1n}^{(2)}$, respectively, into electron-creation and annihilation operators[33] which corresponds to

$$\begin{aligned} v_{1n}^{(1)} &= \Sigma_\sigma a_{j\sigma}^\dagger a_{j\sigma} = n_j^p , \\ v_{1n}^{(2)} &= \Sigma_\sigma b_{j\sigma}^\dagger b_{j\sigma} = n_j^d . \end{aligned} \tag{10}$$

The indices p,d refer to p and d electrons. It has been shown that this transformation is valid for rather low electron densities and long-range interactions.[34] The basic assumption is that the electronic excitations are approximated bosons although the elementary particles are fermions. Necessarily, at least two electrons are involved in the interactions. Furthermore, we add a quantum-mechanical hopping term which has no classical analog. Then the Hamiltonian reads

$$H = H_h + H_e + H_L + H_{e-e} + H_{e-L} , \tag{11}$$

$$H_h = \sum_{jj'\sigma} \epsilon^p (a^\dagger_{j\sigma} a_{j'\sigma} + \text{H.c.}) + \sum \epsilon^d (b^\dagger_{j\sigma} b_{j'\sigma} + \text{H.c.}) , \tag{12a}$$

$$H_e = \sum_j U^p n^p_{j\uparrow} n^p_{j\downarrow} + \sum_f U^d n^d_{j\uparrow} n^d_{j\downarrow} + \sum_j l (n^d_{j+1} - n^d_j)^2 , \tag{12b}$$

$$H_L = \frac{1}{2} \left[\sum_{i,n} m_i \dot{u}^2_{in} + g(u_{1n+1} - u_{1n})^2 + f u^2_{1n} + g u^2_{1n} \right] , \tag{13}$$

$$H_{e-L} = - \sum_{j,n} \sum_{\sigma} (f u_{2n} a^\dagger_{j\sigma} a_{j\sigma} + g u_{1n} a^\dagger_{j\sigma} a_{j\sigma} + 4 g_4 u_{1n} n^p_{j\uparrow} n^p_{j\downarrow}) , \tag{14}$$

$$H_{e-e} = - \sum_j U^{pd} n^p_j n^d_j - k_4 \sum_{j\uparrow} [n^p_j n^d_j (n^d_j - n^p_j)^2 + 2 n^p_{j\uparrow} n^p_{j\downarrow} n^d_{j\uparrow} n^d_{j\downarrow} + n^p_j n^d_{j\downarrow} n^d_{j\downarrow} + n^d_j n^p_{j\uparrow} n^p_{j\downarrow}] , \tag{15}$$

where the following definitions have been introduced:

$$\epsilon^p = \frac{1}{2} (g_2 + f + k_2 + \frac{1}{2} g_4 + \frac{1}{2} k_4) , \tag{16a}$$

$$\epsilon^d = \frac{1}{2} (k_2 + \frac{1}{2} k_4) , \tag{16b}$$

$$U^p = \frac{1}{2} (2g_2 + 7g_4 + 2f + 2k_2 + 7k_4) , \tag{16c}$$

$$U^d = \frac{1}{2} (2k_2 + 7k_4) ,$$

$$U^{pd} = (k_2 + \frac{1}{2} k_4) .$$

The electronic kinetic hopping H_h term is introduced in analogy to the original Peierl's model. The Hamiltonian now represents an extended Peierls-Hubbard Hamiltonian which is similar to a combination of different models proposed for the description of superconductivity (PIP and IMV, see below). The most important extension here is the fourth order on-site interaction (k_4) of two d electrons with the corresponding p electrons.

The polarization-induced pairing (PIP) mechanism model considers the electronic and electron-electron-interaction parts of the Hamiltonian.[6] In a finite cluster calculation the variation of the model parameters has been investigated to find the existence regions for paired electron and paired hole states.[35] Fully paired states result for large values of the p-d interaction which, in our model, corresponds to k_4. To find paired states a certain minimal critical value for this quantity can be assigned which depends on the energy difference of oxygen and copper orbitals. In contrast to the PIP model this difference is not purely electronic in our model but includes electron-lattice interactions. Furthermore, the repulsion between copper and oxygen electrons and/or holes has to be small which consequently leads to large values of k_2. Thus, it can be concluded from the PIP model that k_2 and k_4 are critical quantities for the electron pairing mechanism which are strongly influenced by the energy difference $\epsilon^p - \epsilon^d$, corresponding to $g_2 + \frac{1}{2} g_4 + f$ in our model.

In the intramolecular vibration (IMV) model the Hamiltonian includes the lattice part and the interaction of the lattice with the electrons.[36] Yet it does not differentiate between oxygen p and copper d electrons and consequently neglects their mutual interactions. A formula for the superconducting transition temperature T_c is evaluated which is a maximum for an intermediate value of the band-filling factor and reduces to zero for the half-filled and full band. The bandwidth of the electron pairs (and simultaneously T_c) can be enhanced by increasing the ratio of f^2 (the intermolecular electron-phonon-coupling constant squared) to f' (intermolecular phonon-phonon interaction constant).[37] Thus T_c can be increased by the intersite electron-phonon interaction. The intrasite electron-phonon coupling (corresponding to g) reduces T_c as now the electrons are dressed by phonon clouds. For strong enough coupling, localized bipolaroniclike states are expected,[37] while a reduction of the coupling leads to a delocalization of electron pairs into extended states.

The results of the classical model can thus be compared to quantum-mechanical models. Furthermore, the important identification of the classical T_c as a possible transition point to a ground state with pairwise correlated electrons has been shown.

V. PHONONS AND PLASMONS

In the following the solutions of the classical Hamiltonian will be investigated. The equations of motion are easily obtained as the derivatives of the potential energy with respect to the corresponding displacements. They are given by

$$\begin{aligned}
m_1 \ddot{u}_{1n} &= f'(u_{1n+1} + u_{1n-1} - 2u_{1n}) + g_2 w_{1n} + g_4 w^3_{1n} , \\
m_2 \ddot{u}_{2n} &= f(w_{1n+1} + w_{1n} + u_{1n+1} + u_{1n} - 2u_{2n}) , \\
m_{e1} \ddot{v}^{(1)}_{1n} &= - g_2 w_{1n} - g_4 w^3_{1n} - k_2 x_{1n} - k_4 x^3_{1n} \\
&\quad + f(u_{2n} + u_{2n-1} - 2w_{1n} - 2u_{1n}) , \\
m_{e2} \ddot{v}^{(2)}_{1n} &= k_2 x_{1n} + k_4 x^3_{1n} + l(v^{(2)}_{1n+1} + v^{(2)}_{1n-1} - 2v^{(2)}_{1n}) ,
\end{aligned} \tag{17}$$

where the definitions of x_{1n} and w_{1n} have been given in Eq. (2). By applying the self-consistent phonon approximation the cubic terms in the displacement coordinates are linearized. After standard Fourier transformation the dynamical matrix is given by

$$\begin{bmatrix}
m_1 \omega^2 - 4f' \sin^2(qa) - g & 0 & g & 0 \\
0 & m_2 \omega^2 - 2f & 2f \cos(qa) & 0 \\
g & 2f \cos(qa) & m_{e1} \omega^2 - g - k - 2f & k \\
0 & 0 & k & m_{e2} \omega^2 - k - 4l \sin^2(qa)
\end{bmatrix} \tag{18}$$

from which the dispersion relations can be deduced. Analytical results for the zone-center and zone-boundary modes can only be obtained by using the adiabatic approximation. Interestingly, the zone-center mode is not affected by the second shell and corresponds exactly to the ferroelectric soft mode. At the zone boundary the situation is changed. While one mode exhibits again the same value as within the original ferroelectric model the other solution contains the electron-electron couplings k and l and is explicitly given by

$$\omega^2\left(q=\frac{2\pi}{a}\right)=\frac{1}{m_1}\,\frac{(4f'+2\tilde{f})(2f+g)(4l+k)+4lk(4f'+g)}{(2f+g)(4l+k)+4lk}\,, \tag{19}$$

with $\tilde{f}=fg/(2f+g)$. Obviously real frequencies are only obtained if $4lk/[(2f+g)(4l+k)]\neq -1$. Simultaneously this implies that $(4f'+2\tilde{f})/(4f'+g)\neq 1$, which only holds for finite and large enough electron-phonon coupling g. Thus, a softening of g is excluded which also excludes a transition to a ferroelectric state with soft-zone-center optic mode. Consequently, the following can be stated.

(i) Ferroelectricity and on-site electron pairing exclude each other.

(ii) The zone-center optic mode has rather high-frequency values which corresponds, for a ferroelectric system, to the saturation limit.[30] Accordingly, it is, if at all, only very weakly temperature dependent.

(iii) The zone-boundary mode [Eq. (19)] cannot become zero but for $k=0$ is pinned at a finite value

$$\omega^2(2\pi/a)_{k=0}=\frac{1}{m_1}(4f'+2\tilde{f})\,.$$

Thus, for $k\rightarrow 0$ a structural phase transition with soft-zone-boundary mode is excluded.[38]

The eigenvalues of the dynamical matrix [Eq. (19)] have been investigated numerically for $\mathrm{YBa_2Cu_3O_{7-\delta}}$. The parameters f,f' were taken from the existing parameter set of $\mathrm{SrTiO_3}$ which has comparable lattice constants to the perovskite substructure of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ (see Table I). The on-site electron-phonon coupling g was fitted to the experimentally determined zone-center mode at approximately 150 $\mathrm{cm^{-1}}$ (Refs. 39 and 40) thus assuming that this corresponds to a pseudoferroelectric mode. g exhibits a rather high value in accordance with Eq. (19). The intersite electron-electron coupling l was chosen arbitrarily as changes in l affect the dispersion only very slightly. The values for k were varied between 100 and 0 and 0 and -10 in order to investigate the temperature dependence of the dispersion curves above and below the transition. Above the transition the phonon branches are only slightly affected by reducing the electron-electron coupling k. The zone-boundary mode [Eq. (19)] softens by very few wave numbers and is pinned for $k\rightarrow 0$ (Fig. 3). Two plasmon modes are related to the shell displacements which both for large enough values of k exhibit high-frequency values. Reducing k shows up in a softening of one branch at $q=0$ which degenerates into a pseudoacoustic branch for $k=0$ (Fig. 4). This branch is mainly determined by the mass of the d shell. The other plasmon branch has p-shell character and behaves like an Einstein oscillator. It softens slightly throughout the whole Brillouin zone for decreasing k. This behavior is well known from ferroelectrics. The acoustic plasmon mechanism as the origin of strong electron-electron attraction has been and is discussed as a possible microscopic mechanism for superconductivity.[41,42] In contrast to the existing models here the acoustic plasmon is a consequence of a classical lattice dynamical model with intersite electron-electron repulsion (1). Thus, the electron pairing is an on-site mechanism while the plasmon branch results from the on-site attraction together with the intersite coupling.

TABLE I. Model parameters for $\mathrm{YBa_2Cu_3O_4}$.

$m_1=1.852\times10^{-22}$ g (CuO_n, $n=3$)
$m_2=4.566\times10^{-22}$ g ($\mathrm{Ba_2}$)
$g=160.48\times10^4$ $\mathrm{g\,s^{-2}}$
$f'=1.7\times10^4$ $\mathrm{g\,s^{-2}}$
$f=16.0\times10^4$ $\mathrm{g\,s^{-2}}$
$k\cong$variable

Below the critical temperature for the frozen-in shell-shell configuration identified above as superconducting phase[6,36] both the phonon and the plasmon dispersions show strong anomalies (Fig. 5). For the optic and the acoustic phonons the anomalies are observed close to the Brillouin zone center for small negative values of k. Decreasing the value of k shifts the anomalies to higher q values and for large enough negative k they smear out.

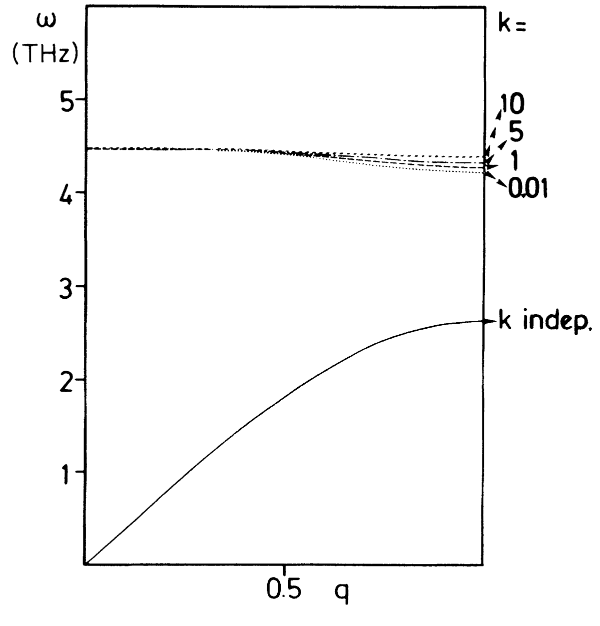

FIG. 3. The dispersion of the acoustic and optic modes for $k>0$. The parameters used are listed in Table I.

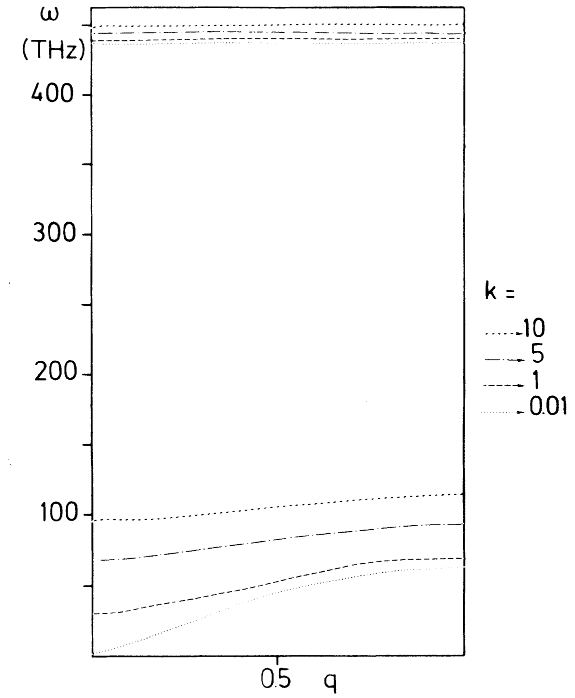

FIG. 4. The dispersion of the two plasmon branches for $k > 0$.

The observed anomalies always appear at the same point in the Brillouin zone for optic and acoustic branch and indicate a tendency of the system to structural instabilities, which has also been observed in superconducting carbides.[5,43,44]

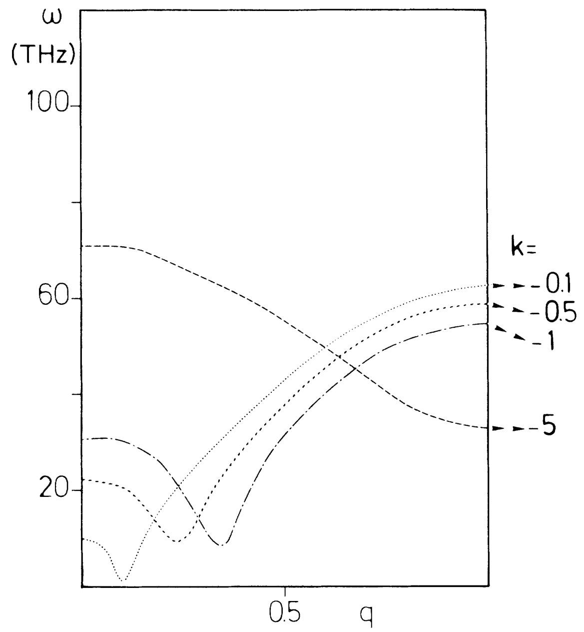

FIG. 6. The dispersion of the "pseudoacoustic" plasmon branch for $k < 0$.

The "optic" plasmon branch is only slightly affected by varying k. It keeps its Einstein-oscillator behavior and changes throughout the Brillouin zone. The pseudoacoustic plasmon branch becomes optic for negative k but also shows anomalies which shift from small to high q values for decreasing k (Fig. 6). For large enough negative k this branch softens at the Brillouin zone boundary indicating the tendency to an electronic superstructure without affecting the ionic lattice.

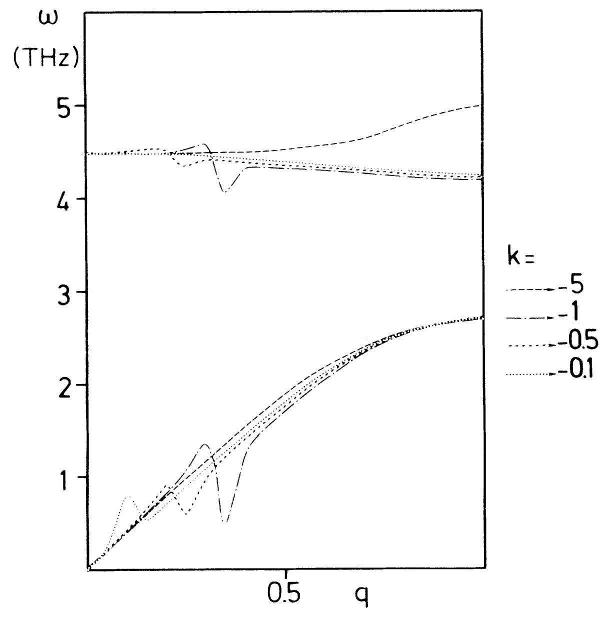

FIG. 5. The dispersion of the acoustic and optic modes for $k < 0$.

Thus, it can be concluded that above the critical temperature the phonons show no anomalies. A structural phase transition cannot occur either at the zone center or at the zone boundary. While one plasmon branch exhibits optic character and has very high-frequency values the other branch softens and finally becomes acoustic for $k=0$. Below the transition phonons and the acoustic plasmon have k dependent anomalies which indicate structural and electronic instabilities.

VI. SUMMARY

It has been shown that a long-known lattice dynamical model for ferroelectric soft modes is equivalent to an extended one-dimensional Peierls-Hubbard model if a quantum-mechanical hopping term is added. The classical model combines the ferroelectric instability with an electron-electron pairing instability thus leading to two competing types of phase transitions. The occurrence of a state with pairwise correlated electrons suppresses ferroelectricity and vice versa. This competition has been confirmed experimentally for $\mathrm{BaBi}_{1-x}\mathrm{Pb}_x\mathrm{O}_3$ (Ref. 45) and seems to be present too in $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-x(x\approx 1)}$.[46] Thus, systems with inherent ferroelectric instabilities are good candidates to observe electron pairing which has first been shown for doped SrTiO$_3$.[47] A result of this simple diatomic model is that soft modes do not occur either at the zone center or at the zone boundary. A softening of a plasmon branch is expected from the model calculations which becomes acoustic at the transition to the paired electron state. Below this transition phonon and plasmon anomalies indicate the tendency of the system to undergo phase transitions to different superstructures.

The equivalent extended quantum-mechanical Hamiltonian combines two different models for superconductivity.[6,36] The results of these models can directly be interpreted in terms of the lattice dynamical model parameters. The electron pairing is caused by the on-site electron-electron *p*-*d* interaction together with the intersite *d*-*d* coupling. The magnitude of the transition temperature is determined by the electron-phonon coupling where strong intersite coupling favors a high T_c while strong on-site coupling decreases T_c. Conclusively, it has been shown that the combination of cationic valence instability including oxidation states differing by 2 together with the configurational instability of O^{2-} may lead to a high-T_c superconducting state.

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