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Phonon modes in corrugated planes

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Under certain reasonable assumptions, the phonon modes due to the small vibrations of the bond angles associated with the corrugation in the Cu-O plane of high-T_c superconductors are investigated. Two distinct modes are obtained. While one of them has a linear dispersion relation, the other has a quadratic one. Both modes may be relevant to a possible enhancement of T_c. Even more relevant, perhaps, is the linear temperature dependence of the heat capacity due to the quadratic mode at low temperatures. This may provide an alternative explanation of the recent experimental findings.

One experimentally observed but seldom emphasized feature of high-T_c oxide superconductors,[1–3] such as La-Sr-Cu-O, Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, Tl-Ca-Ba-Cu-O, etc., is the corrugation in the Cu-O planes[4] where the z coordinates of O and Cu are slightly different, the z direction being perpendicular to the Cu-O planes. In contrast, it is intriguing to note that in a parent nonsuperconducting compound such as La-Cu-O, the Cu-O planes are flat. In other words, the onset of superconductivity seems to be accompanied by the simultaneous appearance of the corrugation. So far, this corrugation has been ignored in the current theories.[5–9]

In this paper we propose to study the effect of the new degrees of freedom associated with the corrugation. In a flat plane, the implicit assumption is that there is no vibration mode consisting of particle motion normal to the plane. In the presence of corrugation, the angular stiffness pertaining to the deformation of the bond angles becomes nonzero. This gives rise to new phonon modes in which the bond angles execute small collective oscillations while the bond lengths remain practically unchanged. It is not difficult to visualize that as long as the bond angles are not far from 180° the angular stiffness is relatively small, rendering the change of bond angles much easier than the change of bond lengths. We may postulate an angular stiffness k defined by $\tau = -k\delta\theta$ where τ is the restoring torque when the bond angle is deformed by $\delta\theta$. There would then be phonon modes associated with these $\delta\theta$ degrees of freedom. We expect these phonon frequencies to be much lower than the usual phonon frequencies which involve changes in bond lengths. We also expect that the electrons would be strongly coupled to one of these modes since it generally involves distorted charge configurations. Hence it may help to enhance[10] the electron-electron attraction and T_c. More significantly, perhaps, it is found that the lower mode has a parabolic dispersion relation at long wavelengths. In two dimensions, this yields a linear temperature dependence in the heat capacity which may be relevant to some recent experimental findings.[11] At least it demonstrates that a linear T term is not necessarily of electronic origin.[5]

Since the qualitative features of the dispersion relation of the phonon are only dependent on the types of interaction but not so much on the dimensionality, we consider, for simplicity, a corrugated one-dimensional (1D) Cu-O chain (Fig. 1). Also, we shall be interested in the collective motion associated with the $\delta\theta$ degrees of freedom, i.e., small vibration of the bond angles, assuming that the bond lengths l remain unchanged.

Since each atom in the corrugated Cu-O chain can move in a plane and there are two atoms (Cu and O) and two bonds in each unit cell, by assuming fixed bond lengths we are left with two degrees of freedom in each cell. In view of the restoring torque, it is natural to choose the two orientational angles α_j and β_j of the two bonds Cu_{j-1}-O_j and O_j-Cu_j (as shown in Fig. 1) as the generalized coordinates. Correspondingly, we call the two atoms Cu_{j-1} and O_j together with their connecting bond the A_j bar for its rigidity and similarly the two atoms O_j and Cu_j together with their connecting bond the B_j bar. The two bond angles at the vertices O_j and Cu_j are then expressed in terms of α_j and β_j as

$$\theta_{o,j} = \alpha_j + (\pi - \beta_j), \quad \theta_{c,j} = \alpha_{j+1} + (\pi - \beta_j) .$$

Accordingly, the restoring torques due to deformations of the two bond angles will have the forms

$$\tau_{o,j} = -k_o \delta\theta_{o,j} = -k_o(\delta\alpha_j - \delta\beta_j) , \quad (1)$$

$$\tau_{c,j} = -k_c \delta\theta_{c,j} = -k_c(\delta\alpha_{j+1} - \delta\beta_j) , \quad (2)$$

where $\delta\theta_{o,j} = \theta_{o,j} - \theta_0$, $\delta\theta_{c,j} = \theta_{c,j} - \theta_0$, $\delta\alpha_j = \alpha_j - \alpha_0$, and $\delta\beta_j = \beta_j - \beta_0$, with θ_0, α_0, and β_0 $[= \alpha_0 = (\frac{1}{2})\theta_0]$ denoting the equilibrium values of $\theta_{o,j}$ or $\theta_{c,j}$, α_j, and β_j, respec-

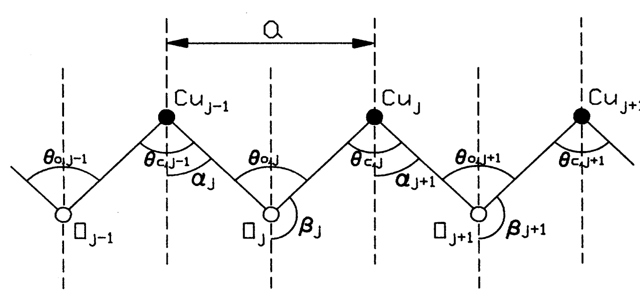

FIG. 1. The corrugated one-dimensional Cu-O chain with a denoting the lattice constant.

tively; k_o and k_c are the angular stiffnesses of the two bond angles at the vertices O and Cu, respectively. As mentioned above, the bond angular stiffnesses k_o and k_c depend on the bond angle θ_0 and should go to zero for $\theta_0 = 180°$.[12]

We now look at the relative motion between the centers of mass of the B_{j-1} bar and the B_j bar, which can be shown to be governed, after linearization, by the equation

$$I_o(\ddot{\alpha}_j - \ddot{\beta}_{j-1}\cos\theta_0) + I_c(\ddot{\alpha}_j - \ddot{\beta}_j\cos\theta_0) = k_o[(\delta\alpha_{j+1} - \delta\beta_{j+1}) - 2(\delta\alpha_j - \delta\beta_j) + (\delta\alpha_{j-1} - \delta\beta_{j-1})] + k_c[(\delta\alpha_{j+1} - \delta\beta_j) - 2(\delta\alpha_j - \delta\beta_{j-1}) + (\delta\alpha_{j-1} - \delta\beta_{j-2})], \quad (3)$$

where $I_o = m_o l^2$, $I_c = m_c l^2$ are the rotational inertias. Since the motion is constrained by intermediate bars, the rotational inertia enter. Angle differences such as $\delta\alpha_j - \delta\beta_j = \delta\theta_{o,j}$ and $\delta\alpha_{j+1} - \delta\beta_j = \delta\theta_{c,j}$ enter because they represent bond angle deviations that invoke the restoring torque. All generalized forces are now expressed in torques. This is why the time rate of change of the generalized momenta is expressed in terms of the product of rotational inertia and angular accelerations. For brevity, the detailed derivation of this equation is omitted here.

The other independent linearized equation describing the relative motion of two successive A bars can be similarly obtained as

$$I_o(\ddot{\beta}_j - \ddot{\alpha}_{j+1}\cos\theta_0) + I_c(\ddot{\beta}_j - \ddot{\alpha}_j\cos\theta_0) = k_0[(\delta\beta_{j+1} - \delta\alpha_{j+1}) - 2(\delta\beta_j - \delta\alpha_j) + (\delta\beta_{j-1} - \delta\alpha_{j-1})] + k_c[(\delta\beta_{j+1} - \delta\alpha_{j+2}) - 2(\delta\beta_j - \delta\alpha_{j+1}) + (\delta\beta_{j-1} - \delta\alpha_j)]. \quad (4)$$

Assuming $\delta\alpha_j = \mathcal{A}e^{i(kja - \omega t)}$, $\delta\beta_j = \mathcal{B}e^{i(kja - \omega t)}$; and substituting into (3) and (4) we obtain as usual the determinantal equation

$$\omega^4 L + \omega^2[-4(1-\cos ka)]M + 4(1-\cos ka)^2 N = 0, \quad (5)$$

where

$$L = (I_o + I_c)\sin^2\theta_0 + 2(1-\cos ka)\frac{I_o I_c}{I_o + I_c}\cos^2\theta_0, \quad (6)$$

$$M = (k_o + k_c)(1-\cos\theta_0) + (1-\cos ka)\frac{I_o k_o + I_c k_c}{I_o + I_c}\cos\theta_0, \quad (7)$$

$$N = 2(1-\cos ka)\frac{k_o k_c}{I_o + I_c}. \quad (8)$$

The roots ω^2 are found to obey the dispersion relations

$$(\omega_\pm)^2 = 2(1-\cos ka)[M \pm (M^2 - LN)^{1/2}]/L. \quad (9)$$

Correspondingly the amplitudes $\mathcal{A}$, $\mathcal{B}$ for the two modes are given by

$$\left(\frac{\mathcal{A}}{\mathcal{B}}\right)_\pm = \frac{[M \pm (M^2 - LN)^{1/2}](I_o e^{-ika} + I_c)\cos\theta_0 - L(k_o + k_c e^{-ika})}{[M \pm (M^2 - LN)^{1/2}](I_o + I_c) - L(k_o + k_c)}. \quad (10)$$

In the limit of $ka \ll 1$ we have $LN \ll M^2 \cong [(k_o + k_c) \times (1-\cos\theta_0)]^2$ and $L \cong (I_o + I_c)\sin^2\theta_0$, the dispersion relations (9) therefore reduce to

$$(\omega_+)^2 \cong 2(1-\cos ka)\frac{2M}{L} \cong (ka)^2\frac{2(k_o + k_c)}{(I_o + I_c)(1+\cos\theta_0)}, \quad (11)$$

$$(\omega_-)^2 \cong 2(1-\cos ka)\frac{N}{2M} \cong 4(1-\cos ka)^2\frac{k_o k_c}{2(I_o + I_c)(k_o + k_c)(1-\cos\theta_0)} \cong (ka)^4\frac{k_o k_c}{2(I_o + I_c)(k_o + k_c)(1-\cos\theta_0)}; \quad (12)$$

while the two corresponding normal modes (10) reduce to

$$\left(\frac{\mathcal{A}}{\mathcal{B}}\right)_+ \cong -1, \quad (13)$$

$$\left(\frac{\mathcal{A}}{\mathcal{B}}\right)_- \cong 1. \quad (14)$$

In the long-wavelength limit, we see from (13) that the ω_+ mode describes the motion of the A bar relative to the B bar within the same unit cell. For example, $\mathcal{A} = -\mathcal{B} > 0$ represents the uniform positive angular deformations at the O-atom vertices (i.e., $\delta\theta_{o,j} = \delta\alpha_j - \delta\beta_j = \delta\theta_o$ for every unit cell j) and the similar uniform deformations ($\delta\theta_{c,j} = \delta\alpha_{j+1} - \delta\beta_j = \delta\theta_c$) at the Cu-atom vertices or equivalently, the out-of-phase deformations of $\pi - \theta_{o,j}$ and $\theta_{c,j} - \pi$, which describe the orientations of the B bars and A bars relative to their neighboring bars, respectively. However, the geometric constraints imposed by the rigid, unbendable bars are such that the $\delta\theta_c$ must then be equal to $\delta\theta_o$ as $ka \rightarrow 0$.[13] This means that although there is strain in the chain, the strain is uniform throughout the entire endless chain, thereby incurring no net local restoring torque, thus leading to zero frequency. This is, in fact, the physical origin of the extra $(1-\cos ka)$ factor in (11) and (12). We might call the ω_+ mode the optical mode in view of the relative motion of the A and B bars within each and the same unit cell, provided we keep in mind, in contrast to the usual optical phonon, the vanishing frequency in the limit $ka \rightarrow 0$. From (14) we see that the ω_- mode describes instead the bodily rotational motion of each unit cell as a whole relative to the next unit cell or the in-phase deformations of $\pi-\theta_{o,j}$ and $\theta_{c,j}-\pi$, which is analogous to the usual acoustic phonons. In the limit $ka \rightarrow 0$, the ratio of the deformation of each cell given by $\mathcal{A}-\mathcal{B}$, to the amplitude $\mathcal{A}$ of the angular deviation of α or $\mathcal{B}$ of β is proportional to ka, whereas the same ratio for the ω_+ mode is of the order of magnitude 1. This one more power of ka is also present when we compare the usual acoustic phonons versus the optical phonons. In addition, the geometric constraints as represented by the extra $(1-\cos ka)$ factor mentioned above, again cause ω_- to vary as k^2 rather than k.

So far we have dealt exclusively with a one-dimensional chain (see Fig. 1). Since our real object is the modes of the corrugated two-dimensional plane, one might question whether the added dimension or the interchain coupling[14] would alter qualitatively the characteristics of the $\omega_\pm$ modes. The answer is no, based on the following physical reasons. We recall first the analogous cases of the phonon modes of a lattice of atoms with either two different atoms per unit cell but all connected by the same springs, or two similar atoms per unit cell connected alternately by two different kinds of spring. In the former case, there are intrinsically two possibilities for the movements of the two different atoms in the same cell. They either move in phase (i.e., relative phase angle $<\pi/2$) or out of phase (i.e., relative phase angle $>\pi/2$). In the latter case, it is more appropriate to treat each unit cell as containing the two different springs. Again there are only two possibilities for the deformations (lengthening or shortenings) of the two springs in each unit cell. They are either in phase or out of phase. For both cases, the in-phase motion gives rise to the acoustic mode, the out-of-phase motion to the optical mode. As usual, the out-of-phase mode entails larger restoring forces and has, therefore, the higher frequency. Such arguments are essentially independent of dimensionality. The change from a 1D chain to a 2D plane merely adds a y degree of freedom to each x degree of freedom that is present in the original chain. The in-phase and out-of-phase possibilities associated with each degree of freedom remain the same.

Our present corrugated system resembles more the case of two different springs rather than two different atoms in one unit cell, since the two bars in each unit cell are of the same moment of inertia but the two angular stiffnesses k_o and k_c are different. One thus expects similarly only the two possibilities, the in phase and out of phase of the two angular deformations of $\pi-\theta_{o,j}$ and $\theta_{c,j}-\pi$ (rather than α_j and β_j). Any added dimension would simply add another angular deformation variable to every previously existing one. Hence the lower-frequency acoustic mode and the high-frequency optical mode again emerge. Of course, for our model of the corrugated system, there is this geometric constraint imposed by the rigid, unbendable bars. Since this constraint is present independently of dimensionality, the extra $(1-\cos ka)$ factor in (11) and (12) should also be independent of dimensionality. We thus conclude that qualitatively the $\omega_\pm$ modes predicted here should persist in 2D corrugated planes.

It is interesting to compare with magnon. The ω_- branch has a $(ka)^2$ long-wavelength behavior, so does the dispersion relation of ferromagnetic spin wave (magnon). However, the latter is due to a quite different sort of interaction. The linearized equations of motion for ferromagnetic spin lattice[15] are

$$\dot{S}_j^{\pm} = \pm(2JS/\hbar)(2S_j^{\pm} - S_{j-1}^{\pm} - S_{j+1}^{\pm}), \tag{15}$$

where $S_j^{\pm} = S_j^x \pm iS_j^y$. The wave solutions $S_j^{\pm} = \omega^{\pm} e^{i(jka-\omega t)}$ lead to

$$\omega^{\pm} = \pm(4JS/\hbar)(1-\cos ka). \tag{16}$$

We observe that the $(1-\cos ka)$ factor appearing here in $\omega^{\pm}$ is the same as the extra $(1-\cos ka)$ factor in $(\omega_\pm)^2$ of (9). The right side of Eq. (15) is analogous to those of Eqs. (3) and (4). The physical origin of this $(1-\cos ka)$ factor comes from the nature of the interaction potential in the form of a scalar product of consecutive vectors. In

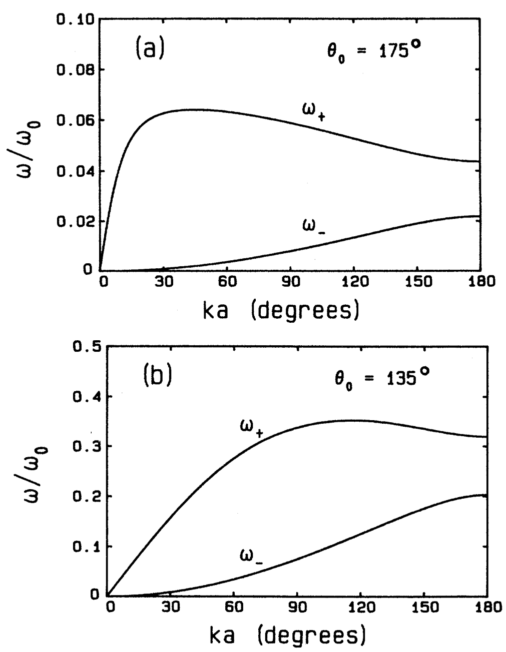

FIG. 2. A plot of $\omega_\pm/\omega_0$ vs ka. Here we take $I_c/I_o = 4$ and $k_c/k_o = 1$; $\theta_0 = 175°$ in (a), $\theta_0 = 135°$ in (b). Notice the difference in the vertical scale.

the magnon case, these vectors are just the spins at neighboring lattice sites; in the corrugated-chain case, the vectors are $l_{co,j}$ and $l_{oc,j}$, i.e., the directed A_j and B_j rigid bars constrained to be joined together at the O and Cu vertices. On the other hand, while the left sides of Eqs. (3) and (4) are the usual second time derivatives of the angles of orientation of the A and B bars yielding a factor ω^2, the left side of (15) is only a first time derivative of the spins yielding a factor ω because it represents the time rate of change of the angular momentum or of the spin itself. Thus this $(1-\cos ka)$ factor yields directly $\omega \sim k^2$ in the magnon case whereas it constitutes the previously mentioned extra factor in Eqs. (11) and (12) [or Eq. (9)] that gives rise to $\omega_+^2 \sim k^2$ and $\omega_-^2 \sim k^4$, respectively.

The $\omega_\pm$ dispersion relations as computed according to Eq. (9) are shown in Figs. 2(a) and 2(b) in which the normalized frequencies $\omega_\pm/\omega_0$ are plotted against ka, where

$$\omega_0 = 2\left[\frac{k_o}{I_o \cos^2(\theta_0/2)}\right]^{1/2} .$$

The factor $\cos^2(\theta_0/2)$ is put in to eliminate the θ_0 dependence of k_o.[12] Here we have adopted $I_c/I_o = 4$, $k_c/k_o = 1$, but $\theta_0 = 175°$ for Fig. 2(a) and $\theta_0 = 135°$ for Fig. 2(b). The linear k and the quadratic k^2 dependences for small k of ω_+ and ω_- are demonstratably clear. We see that as θ_0 increases from 135° to 175° but with I_c/I_o and k_c/k_o kept fixed, the ω_- curves change very little while the ω_+ curves develop a higher and higher hump.

As we saw from Figs. 2(a) and 2(b), the ω_- curves lie considerably below the ω_+ curves, and varies as k^2 for a considerable range of k. We may, therefore, calculate the contribution to the low-temperature heat capacity by using the mode $\omega_- = Dk^2$ alone. In a two-dimensional plane, it contributes a linear T term to the heat capacity per unit area

$$c_- \cong \frac{\pi}{6} k_B^2 \left[\frac{T}{\hbar D}\right] . \qquad (17)$$

Before experimental confirmation of this ω_- mode it is difficult to estimate the coefficient D which involves the angular stiffnesses k_o and k_c. Experimentally, it has been found that there exists a linear term in T in the specific heat for various high-T_c superconductors[11] with the coefficient γ of order of magnitude ranging from 10^{-3} to 10^{-2} J/K^{2}mol. When the doping is not sufficient for the onset of superconduction, the linear term is found to be absent. If corrugation indeed appears together with the superconduction, it is tempting to ascribe the linear T in the specific heat to our unusual phonon mode. If this is the case, the coefficient D should be of order of magnitude about 10^{-5} to 10^{-6} m^{2}sec^{-1}, and the angular stiffnesses k_o and k_c should be of order of magnitude about 10 eV or higher.

In conclusion, the unusual phonon modes we have found here are based on the relative angular motions between neighboring bonds in the corrugated structure, where the bonds are assumed rigid. We saw that it was the special constraints imposed by the assumed rigid, unbendable A and B bonds that gives rise to the extra factor $(1-\cos ka)$ which, in turn, leads to the extra k dependences compared to the usual phonon modes. These unusual modes, aside from their possible relevance to the observed linear heat capacity and enhanced T_c, are interesting in their own rights. Experimental detection may be challenging and rewarding.

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[12] We may assume that $k_c = k_{o-o}[l\cos(\theta_0/2)]^2$ in spirit of the equivalence of the restoring torque $\tau_{c,j}$ and a restoring force $\mathbf{f}_{o;j,j+1}$ (between O_j and O_{j+1}) with a θ_0-independent force constant k_{o-o}, such that $\tau_{c,j} = |\mathbf{f}_{o;j,j+1}|\, l\cos(\theta_0/2)$; and similarly for k_o.
[13] If the bars were not unbendable, an additional degree of freedom describing the relative orientations of the tangential directions of the two ends of each bar would have to be introduced. Then the constraint would be relaxed, no longer requiring the equality of $\delta\theta_o$ and $\delta\theta_c$.
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