5-23-1988

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(Received 13 July 1987; revised manuscript received 4 February 1988)

A new mechanism is proposed to explain high-T_c superconductivity in copper-oxide–based, open perovskitelike systems. It is shown that, should the oxygen ions be moving in a double-well potential, an order-of-magnitude enhancement of the electron-lattice coupling follows automatically from a consistent treatment of this motion. Both theoretical and experimental evidence for the presence of such double wells is cited.

PACS numbers: 74.20.−z, 74.70.Vy, 75.10.Jm

The recent discoveries of superconductivity in lanthanum barium copper oxide (LBCO), at 35–40 K,[1] and then at 90–100 K in yttrium barium copper oxide[2] (YBCO) obviously pose the question as to the origins of this remarkable behavior. Specifically, one is led to ask if the "conventional" BCS phonon-assisted electron pairing[3] could ever produce such high T_c values, and, if not, what novel mechanism has come into play.

In the case of LBCO, use of the Eliashberg formalism[4] for BCS pairing suggests that $T_c \simeq 40$ K is still a possibility,[5,6] given the evidence of strong electron-phonon coupling for modes involving a "breathing" type of motion of the CuO_6 octahedra.[5–7] However, this appears to be close to the limit of what is possible, and 90–100-K values of T_c are probably well above this limit, while still higher values certainly are.

These findings have prompted a broad search for completely novel mechanisms, usually of an electronic nature. However, recently Cohen *et al.*[8] have presented *a priori* lattice-dynamical calculations for both the pure lanthanum compound (LCO) and YBCO which show that each is highly unstable mechanically if confined either to tetragonal symmetry for LCO, or to the *observed* orthorhombic symmetry for YBCO. (Very recently their predictions for LCO have been shown to agree remarkably well with experiment.[9]) This opens a possibility for increasing the magnitude of the electron-lattice coupling, λ, that appears hitherto unexplored. The presence of these strong instabilities indicates that both systems are at the *maxima* of double-well potentials. However, when the Eliashberg formalism is employed to derive λ, it is normally assumed that the lattice response is purely harmonic. Obviously this is completely erroneous for a double well, and it is imperative to determine if this false assumption is leading to *qualitatively* wrong findings.

This can most easily be done by extending a very early study of anharmonic effects on T_c by Hui and Allen[10] whose formulas and notation we adopt. Thus,

$$\lambda = N(0) \sum_{kk'}^{FS} \sum_{n} \frac{|\langle n | M_{kk'} | 0 \rangle|^2}{E_n - E_0}, \quad (1)$$

where $N(0)$ is the density of electron states, $M_{kk'}$ is the electron-phonon matrix element between electronic states $|k\rangle$ and $|k'\rangle$ on the Fermi surface, and $|0\rangle$ and $|n\rangle$ are the ground state and nth excited state of the oscillator corresponding to energies E_0 and E_n, respectively.

For the present qualitative purposes it is sufficient for us, as it was for them, to consider only a one-dimensional potential. They considered three increasingly anharmonic single-well potentials and found small to negligible effects on λ. We shall employ potentials of the double-well form $(-Ax^2+Bx^4)$ and assume an oscillator mass, m, of 20 amu (i.e., we assume that the instabilities are primarily oxygen motions as Cohen *et al.*[8] find them to be).

To proceed further, a finite-temperature generalization of Eq. (1) is necessary. This takes the form

$$\lambda(T) = N(0) \sum_{kk'n'>n}^{FS} \sum \frac{|\langle n | M_{kk'} | n' \rangle|^2}{E_{n'} - E_n} (f_n - f_{n'}), \quad (2)$$

where f_n and $f_{n'}$ are the thermal weighting factors; $f_n = \exp(-\beta E_n)/\sum_{n'} \exp(-\beta E_{n'})$ and $\beta = 1/kT$, T being the temperature. If harmonic eigenstates are used in Eq. (2) it reduces to the harmonic form, $\lambda = (\hbar/2m\omega^2) \times N(0)(M_{kk'})^2$, which is temperature independent (ω being the frequency of transition between nearest levels for the oscillator). However, for more general potentials this is not the case and λ becomes temperature dependent.

In Fig. 1 we show λ as a function of T for four different double wells. The first three have ground states marginally above the central maximum in V. The fourth

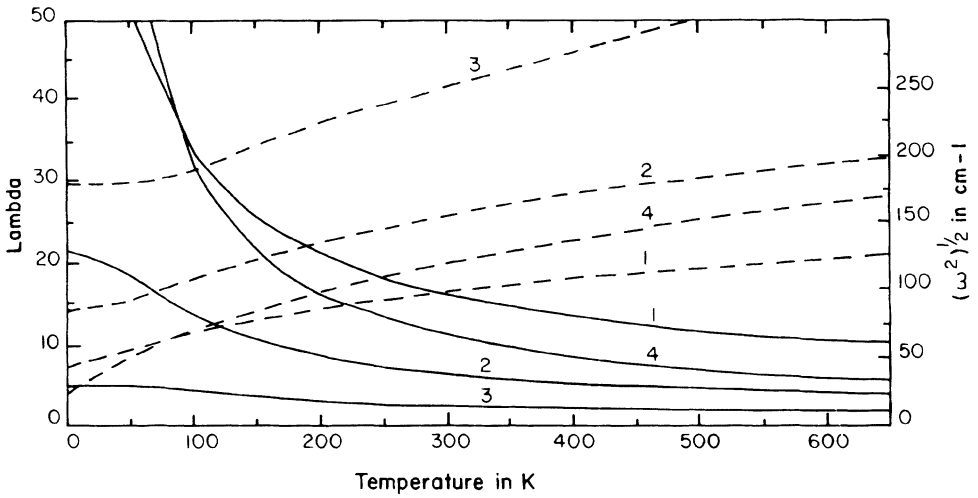

FIG. 1. λ (solid line, left scale) and $\langle\omega^2\rangle^{1/2}$ (broken line, right scale) as functions of T for four double wells: (1) depth =50 K, width =0.5 Å; (2) depth =100 K, width =0.36 Å; (3) depth =200 K, width =0.25 Å; and (4) depth =400 K, width = 0.5 Å. (Widths quoted are total widths of the double well at $V=0.0$.)

has a closely spaced doublet somewhat below this maximum as can be seen from Fig. 2.

In order to perform these calculations we needed to form reasonable estimates of the electron-lattice coupling and the double-well width. We fixed the former by assuming that $\lambda=1$ (a modest strong-coupled value) for the 20-amu mass oscillating at $\omega=400$ cm^{-1}. This would appear reasonable, but it should be noted that everything that follows remains true of the *relative* enhancement of λ irrespective of its absolute value. The widths we estimated from the $O(1)$ thermal ellipsoid parameters (the B values) quoted by Capponi *et al.*[11] for YBCO. Our largest and smallest well widths correspond approximately to the maximum and minimum values, erring on the smaller side for the latter.

It can now be seen that the values of λ we obtain are dramatically enhanced: Specifically, for all four cases $\lambda(100\text{ K})$ is well into, or near the extreme strong-coupling regime ($\lambda>5$) cited in Allen and Mitrovic's definitive review.[4] In this regime the expression for T_c (again from Ref. 4) is, in the present notation,

$$T_c=0.18(\lambda\langle\omega^2\rangle)^{1/2}, \tag{3}$$

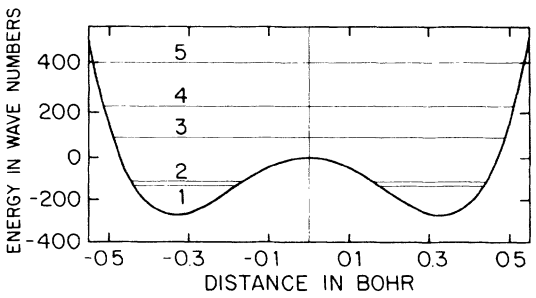

FIG. 2. Linear double well showing the first five energy levels (in wave numbers) for the 400-K well.

where $\langle\omega^2\rangle^{1/2}$ (also shown as a function of T in Fig. 1) is obtained from

$$\langle\omega^2\rangle=\frac{N(0)}{\hbar^2\lambda}\sum_{kk'}^{\mathrm{FS}}\sum_{n'>n}|\langle n|M_{kk'}|n'\rangle|^2 \times(E_{n'}-E_n)(f_n-f_{n'}). \tag{4}$$

If we now employ these expressions a surprising result emerges: T_c vs T is *constant*. This is because the expression for $\langle\omega^2\rangle$ can be shown to reduce to the f-sum rule for *any* set of states. Unless $\lambda>5$, T_c calculated in this manner has no physical meaning; however, if this criterion is met, then superconductivity will occur when $T<T_c$, as calculated from Eq. (3).

In these calculations, the well depths have been fixed by the required energies of the ground states. If we deepen the wells we can obtain values of λ that increase without bound. However, these are not physically relevant since, as the wells are deepened, at some point, the system will undergo a structural transformation to a lower-symmetry phase in which the double wells are replaced by normal "hard" phonons, and λ will revert to a "normal" value. However, this will not occur as soon as the ground state lies slightly inside the wells. A large λ, in the untransformed state, implies strong lattice relaxation about the carriers, and if λ is suddenly "switched off" by the transformation there will be a net increase in this component of the free energy which has to be offset by a larger *decrease* in the potential component. This will only be possible if the wells are relatively deep (i.e., the ground state must be significantly *below* the double-well maximum). Below T_c the transformation will not occur unless it can compensate energetically for the resultant pair-breaking free-energy loss; this again requires a ground state fairly deep in the wells. Our 400-K well is designed to represent this interim situation, hav-

ing levels clearly within the well, but not so far within as to produce a structural change.

It thus appears that high-T_c behavior *could* have as its origin the present, very simple, cause. Obviously one cannot say this unambiguously at this stage; our underlying assumptions, particularly with regard to the absolute values we have assigned to λ, need further investigation. Also, the actual atomic motions are three dimensional and complex; however, it appears likely that, as long as there is a central hump in the potential, order-of-magnitude changes in the values of λ are unlikely.

The most immediate practical consequence is to call into question all conventionally calculated values of λ for these systems as having a basically erroneous form for the lattice response. However, this is done in a very positive sense, since it may mean that λ values capable of producing $T_c \approx 100$ K *can* emerge from the Eliashberg formalism *provided the lattice response is treated realistically.*

Thus far our basic qualitative argument is purely theoretical: Double-well oscillators respond to an external coupling much more strongly than harmonic systems, particularly at low temperatures. This is germane because the results of Cohen *et al.*[8] (again theoretical) show that double wells are present, certainly in YBCO and probably in LBCO since, initially, Ba^{2+} doping will only reduce the LCO instability. Experimentally there are a number of findings that indicate that we may be on the right track. For example, there is evidence that superconductivity in LBCO partially reverses the structural instability in this system,[12] something one might expect, since it could imply more freedom for the oxygen motions and thus enhance T_c. Similarly there is some evidence[13] that in YBCO there is a "frustrated" structural transformation even at 4.2 K. This could be associated with the type of superconducting behavior we described earlier for the case of our 400-K double well.

It is also interesting to note that T_c in YBCO would probably be insensitive to rare-earth substitutions since these are remote from the copper-oxygen chains. Some things, such as the weakness of the isotope effect or the pressure dependence of T_c, do not emerge from the present (again purely theoretical) discussion, since neither can be addressed without more knowledge about the proper form of $M_{kk'}$ in Eq. (1) appropriate to the much larger excursions in double-well systems. It is conceivable, indeed likely, that this greater freedom is employed to maximize λ. If this were the case then one could expect anomalously small effects (second order rather than first order). The fact that both mass and pressure changes have more effect in LBCO than in YBCO *could* be due to the fact that the former has a smaller λ value and less freedom to absorb external perturbations without change in T_c, but no definitive answers are possible at this stage.

One final point which we believe to be of considerable importance, and which is normally not stressed, concerns the occurrence of high-T_c behavior in materials that have been so crudely prepared that they are probably *extremely* impure. Given this, it is likely that the only definite statements possible as to their properties are that they have (locally) the correct structure (particularly the Cu-O chains in YBCO) and a sufficiency of free carriers present. However, these two conditions are the *only requirements* for the present double-well mechanism to produce high T_c: The requirement of the integrity of the Cu-O chain being automatic [since oxygen vacancies in these chains will drastically distort, and quite probably destroy, the double wells] however, it should be noted that chains *per se* are not required, only double wells.

Work at the University of Nebraska was supported by the Office of Naval Research, Contract No. N00014-80-C-0518, and by the Army Research Office, Contract No. DAAL03-87-K0-0070. We wish to acknowledge helpful discussions with L. L. Boyer, W. E. Pickett, Ron Cohen, and Joe Serene, and supporting computations by R. A. Guenther, P. J. Edwardson, and D. Billesbach. We should also like to acknowledge our debt to the late I. Lefkowitz and his intuitive conviction that high-T_c and lattice instability were closely related.

Note added.—Very recently we became aware of work by Plakida, Aksenov, and Drechsler[14] which proposes ideas similar to ours but formulated more qualitatively.

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