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Dynamic instabilities in high-T_c superconductors

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A simple microscopic model of local structural instabilities in high-T_c materials, which involves the existence of more than one local state, is proposed, and the effects of dynamic fluctuations between these states on the electron and phonon properties are studied. These results give new insight into several important general features of these materials, including their large anharmonicity and also their structural transformations which often limit the attainable values of T_c.

I. INTRODUCTION

The correlation between the superconducting (and other) properties of high-T_c superconductors and the presence of structural phase instabilities and lattice transformations has been widely discussed and is now well established as an *empirical rule*; see especially the work of Matthias[1-4] and of Testardi.[5] Such empirical rules have produced virtually all advances in raising T_c. On the one hand, nearly all high-T_c materials ($T_c \gtrsim 10$ K) seem to have these instabilities,[1,4,5] and crudely speaking, the higher the value of T_c, the greater the "degree of instability." On the other hand, relatively minor changes in material parameters can result in structural transformations which reduce the "instability"; such transformations are often accompanied by dramatic decreases in T_c and are thought to form an ultimate limitation[1-5] on the T_c's achievable in a class of materials.

High-T_c superconductors include a variety of kinds of materials such as sputtered films,[5,6] the A-15's,[7,8] and binary and ternary compounds and alloys.[1-5] These materials are often characterized by the existence of more than one phase (as a function of composition and/or temperature), by defects and structural disorder, by nonstoichiometry, and by lack of reproducibility of their properties. Very recently there has been direct evidence for the coexistence of two phases in several systems (A-15's[9,10] and Nb-Zr alloys[11]). It has been found that certain important features are common to most high-T_c materials; these features include (i) large anharmonicity,[5,12] (ii) anomalous heat capacity,[13-15] and (iii) existence of more than a single phase.[1-5,9-11,16-18]

Virtually no theoretical work to date has included lattice instability in any fundamental way. Phillips and co-workers,[10,19] on the other hand, have recently done pioneering work in undertaking the treatment of these aspects of the properties of high-T_c materials. They have pointed out the importance of the coexistence of two phases and of the existence of defects in these materials. They have investigated a model which has microscopic static regions of a second phase located at defects and have studied their effects on the phonon frequencies, on the residual resistivity, and on the lattice constant (particularly in the A-15 materials).

In the present work we consider the effects which the *dynamics* of instabilities and of transformations to other phases can have in high-T_c materials. We will propose a simple microscopic model which incorporates the existence of more than one state locally, and we will consider the effects of dynamic fluctuation between these local states. This situation should be contrasted with the model of Phillips *et al.*,[10,19] in which the coexisting phases are treated as static. This present model of dynamic fluctuations is used to discuss (i) lattice properties such as anharmonicity, heat capacity, and modifications of phonon frequencies, (ii) the relationship of instabilities to high values of T_c, and (iii) the structural transformations which often inhibit[1-5] high values of T_c.

II. MODEL

The model which we propose for instabilities in high-T_c materials is based on the idea that the *local* ground-state configuration (ionic and electronic) is separated from one or more other configurations by a small amount of energy and by a potential barrier. We shall call excitations between these local states "local structural excitations" (LSEs). Transitions between these states can be caused by electrons or by phonons.[20] LSEs have important effects on the electron and phonon properties if their excitation energy and the barrier between their states are sufficiently small.

We propose that there are an appreciable number of LSEs with small excitation energies and small barriers in high-T_c materials which have structural instabilities. These materials invariably exhibit more than one phase as a function of[1-5,9-11,16-19] temperature, pressure, or composition; examples include the cubic and tetragonal phases in the A-15's and the TI, TII, and cubic phases in the alkali tungsten bronzes.[20-22] Experimentally, these materials are characterized by defects such as vacancies,[18,19] impurities,[6] disorder,[6] and/or nonstoichiometry.[16,20-22] Dynamic fluctuations (transitions) between these local states (LSEs) will be important physically if they can be excited easily. The fact that several phases often exist as a function of (relatively small changes in) temperature and other parameters implies that the states are separated by a small energy difference. In addition defects and nonstoichiometry introduce randomness into the local energy difference between states. Another way of inferring the existence of an appreciable number of physically important LSEs is that these materials often are characterized by the coexistence of more than one phase[1-5,8-11,16-19] which is nucleated by the defects. These defects perturb the unstable structure so as to favor the local nucleation of the second phase at preferred sites. This, however, should be considered as one extreme possibility. At other sites the defect perturbations may not be so drastic as to favor nucleation of the second phase, but yet they may randomly modify the local potential barrier and the energy separation between the phases. Further, the materials with larger degrees of instability correspond to cases with larger numbers of LSEs having fast dynamic fluctuations. Anticipating the result of Sec. III A in which we demonstrate a positive correlation between the enhancement of T_c and an effective interaction between LSEs and the lattice, we can already see the physical origin of Matthias's empirical rule.[1-5]

Some of these local states of the LSEs correspond to phases which are realized macroscopically. Examples include some of the A-15's which have a macroscopic cubic to tetragonal phase transformation for temperatures in the neighborhood of T_c. Small volumes of one phase can be maintained within the other by pinning to defects and by strain fields; such a situation corresponds physically to the static model of the A-15's proposed by Phillips.[10,19] A second example is a film sputtered near its phase transition temperature (e.g., Re-Mo alloy[18] at $T \sim 1250$ °K); in this case the two phases corresponding to the phase transformation are "frozen in" and can be maintained metastably to low T. It should be noted that the local phases may not always correspond to phases realized macroscopically but rather may be occupied only locally. In addition, LSEs occur in high-T_c materials which remain in a single macroscopic phase but which are locally unstable with respect to another ("ghost") phase. This local ghost phase may never be physically realized to reveal itself, but it has important physical effects due to the local instability. The local ghost phase forms the upper state of the LSE. Examples of systems in which local ghost phases can be identified include the superconducting alkali tungsten bronzes,[20,21] e.g., the tetragonal I (TI) structure $\mathrm{Na}_x\mathrm{WO}_3$ with x in the range of $0.2 < x < 0.5$. As x is decreased below 0.2 there is a structural transformation from the TI to the semiconducting tetragonal II phase.[21,22] The sodium ions occupy interstitial sites[21,22] in the pentagonal and square tunnels of the TI structure. The site occupancy is random, and there is some possible clustering of Na ions into microscopic inhomogeneities. Hence the Na occupancy will deviate from the uniform random occupancy described by the x value. This implies that for any average value x_0 in the TI phase, there are microscopic regions where the local density x is smaller than the average value x_0 and close to that corresponding to the TI-TII phase boundary, and thus there is local $T\mathrm{I} \rightarrow T\mathrm{II}$ instability and physically meaningful LSE. The local TII structures then serve as the ghost phases for the LSEs in $\mathrm{Na}_x\mathrm{WO}_3$.

The interaction between LSEs and phonons in structurally unstable materials has important effects on the phonon spectrum. These effects (i) are seen in the superconducting properties and (ii) are seen in other thermal properties which provide an independent test of the present model. To illustrate these effects we shall consider the mean squared atomic displacement $\langle u_i^2 \rangle$ and the heat capacity in the present model. Derivations of certain formal results for two model LSE-phonon Hamiltonians are given briefly in the Appendix.

III. CONSEQUENCES OF THE MODEL

A. Lattice and electronic properties

We consider a distribution of isolated LSEs[23,24] interacting with the harmonic phonons by means of

$$H = \sum_j \Delta_j \sigma_j^z + \sum_{\vec{k}\alpha j} g_{\vec{k}\alpha j} \sigma_j^x (a_{-\vec{k}\alpha}^\dagger + a_{\vec{k}\alpha}) e^{i\theta_{\vec{k}j}} , \qquad (1)$$

where $a_{\vec{k}\alpha}$ is the annihilation operator for a phonon of wave vector $\vec{k}$ and polarization α whose energy is $\omega_{\vec{k}\alpha}$. For simplicity the LSEs are taken to have only two levels each which are separated by the energies Δ_j and which are spanned by the Pauli spin operators $\vec{\sigma}_j$. The second term represents transitions between the LSE states caused by phonons. The degree of instability of the LSE is measured by Δ_j and $g_{\vec{k}\alpha j}$ with greater instability associated with smaller Δ_j and larger $g_{\vec{k}\alpha j}$ (smaller barriers). The coupling in Eq. (1) is the simplest form of coupling between the phonons and the LSEs and represents much of the essential physics. The value of the coupling parameter $g_{\vec{k}\alpha j}$ can be estimated from experiment, e.g., ultrasonic attenuation.[25]

The thermodynamic properties of the interacting LSE-phonon system described in Eq. (1) are obtained by using a diagrammatic approach to obtain the free energy in powers of g.[26] (See Appendix for further details.) To order g^2 the free energy is $\beta^{-1}=k_BT$.

$$F^{(2)}=\frac{\beta}{N}\sum_{\vec{k}\alpha j} g^2_{\vec{k}\alpha j}[(e^{\beta\Delta_j}+1)^{-1}(e^{\beta\omega_{\vec{k}\alpha}}-1)^{-1}] \times[(\omega_{\vec{k}\alpha}-\Delta_j)^{-1}(e^{\beta\omega_{\vec{k}\alpha}}-e^{\beta\Delta_j}) + (\omega_{\vec{k}\alpha}+\Delta_j)^{-1}(e^{\beta(\omega_{\vec{k}\alpha}+\Delta_j)}-1)]\,. \tag{2}$$

The mean-squared atomic displacement can be written

$$\langle u_i^2\rangle=\langle u_i^2\rangle_0+\frac{\hbar}{MN}\sum_{\vec{k}\alpha j}\omega^{-2}_{\vec{k}\alpha}E^{(2)}_{\vec{k}\alpha j}\,. \tag{3}$$

Here $\langle u_i^2\rangle_0$ is its value in the harmonic approximation, and $E^{(2)}_{\vec{k}\alpha j}$ is a contribution to the internal energy of the phonon system (to order g^2) which is given by $E^{(2)}_{ph}=\sum_{j\vec{k}\alpha}E^{(2)}_{\vec{k}\alpha j}$. The total internal energy is given by $E^{(2)}=\partial(\beta F^{(2)}/\partial\beta)$, and it has contributions from the phonon system, from the LSE system, and from the LSE-phonon interaction energy.[26] Physically the second term in Eq. (3) can be thought of as resulting from an increase in the occupation of the $\vec{k}\alpha$ phonon modes and to changes in their zero point energies due to the LSE-phonon interaction. The main contributions to the second term in Eq. (3) come from large k; for relatively small Δ_j, the second term in Eq. (3) can then be expanded, which gives

$$\langle u_i^2\rangle-\langle u_i^2\rangle_0=\frac{9\hbar}{vM}\left\{\frac{1}{N}\sum_j\left(\frac{G}{\omega_D}\right)^2-\tfrac{2}{3}\ln\left[6\pi^2\left(\frac{N}{V}\right)\right] \times\frac{1}{N}\sum_j\left(\frac{G}{\omega_D}\right)^2\frac{\Delta_j}{\omega_D}\tanh\frac{\Delta_j}{2kT}\right\}. \tag{4}$$

Here the phonon spectrum has been treated in the Debye approximation ($\omega_{\vec{k}\alpha}=vk$, $g^2_{k\alpha j}=G^2k$, and ω_D is the Debye energy) and the lowest-order term in Δ_j/ω_D has been retained. The first term in Eq. (4) is the leading contribution, and it arises from modifications of the zero point energy.

Materials with considerable local instability have appreciable values of $g_{\vec{k}\alpha j}$, and for them $\langle u_i^2\rangle$ differs considerably from the harmonic value. These large value of $\langle u_i^2\rangle$ imply that an effective anharmonicity has been induced by the phonon-LSE interaction. This anharmonicity has characteristics [e.g., its temperature (in)dependence] which are quite different from that resulting from phonon-phonon interactions. The large value of $\langle u_i^2\rangle$ induced by the LSE-phonon interaction is consistent with recent experimental observations on $PbMo_6S_8$,[12] and the large induced anharmonicity is consistent with results for the A-15's such as V_3Si,[5] and other high-T_c materials. In each case the temperature dependence of the anharmonicity $\langle u_i^2\rangle$ is quite unusual and cannot be explained by ordinary phonon-phonon interactions.[12,5]

The heat capacity gives fairly direct information about both the LSEs and about their effects on the phonon system. For the interacting LSE-phonon system it is calculated in the usual way from the internal energy which is obtained from Eq. (2). The total heat capacity has the form $C=C_L+C_P^{(0)}+C_{LP}^{(2)}$, where C_L is the contribution of the LSE system, and $C_P^{(0)}$ is the usual noninteracting phonon contribution (e.g., the Debye contribution). For many systems C_L will be a substantial contribution, and it gives quite directly important information about the distribution in energy of the LSE splittings. $C_{LP}^{(2)}$ arises from (i) the change in energy of the phonon system and also from (ii) the interaction energy of the LSE-phonon system. We have evaluated $C_{LP}^{(2)}$ for low temperatures, which gives

$$C_{LP}^{(2)}=+k_B3\pi^{2/3}6^{4/3}207.8\left(\frac{N}{V}\right)^{4/3} \times\left(\frac{G}{\omega_D}\right)^2\left(\frac{k_BT}{\omega_D}\right)^3\frac{1}{N}\sum_j\frac{\omega_D}{\Delta_j} \tag{5a}$$

for $k_BT\ll\omega_D$ and $k_BT\ll\Delta_j$, and

$$C_{LP}^{(2)}=-k_B3\pi^{2/3}6^{4/3}13.2\left(\frac{N}{V}\right)^{4/3} \times\left(\frac{G}{\omega_D}\right)^2\left(\frac{k_BT}{\omega_D}\right)^2\frac{1}{N}\sum_j\left(\frac{\Delta_j}{k_BT}\right)^2. \tag{5b}$$

for $k_BT\ll\omega_D$ and $\Delta_j\ll k_BT$. In both cases a Debye spectrum for the phonons was used ($\omega_{\vec{k}\alpha}=vk$ and $g^2_{\vec{k}\alpha j}=G^2k$). Note here in particular that the $C_{LP}^{(2)}$ is positive or negative depending on whether $\Delta_j\gg k_BT$ or $\Delta_j\ll k_BT$. Thus, the contributions to the heat capacity from $C_{LP}^{(2)}$ and those from C_L in the interacting LSE-phonon system are consistent with the existence of "anomalous" contributions to the heat capacity (both negative and positive) seen in high-T_c materials such as the A-15's.[14]

The LSE-phonon interaction may contain higher-order terms in the phonon operators than that in Eq. (1), and these terms have interesting physical effects, including the softening of phonon frequencies.

The form of the LSE-phonon interaction in Eq. (1) is appropriate for cases in which the rate of the dynamic fluctuations between the states of the LSE is slow compared to the phonon frequencies. It is quite conceivable that there are cases in which the transition rate between the LSE states is larger or comparable to the phonon frequency. Then the phonon is strongly coupled to the LSEs, and higher-order terms such as

$$\frac{1}{2}\sum_{\vec{k}\alpha j} h_{\vec{k}\alpha j}\sigma_j^x a^\dagger_{\vec{k}\alpha} a_{\vec{k}\alpha} e^{i\phi_{\vec{k}j}} \tag{6}$$

may be important. Higher-order terms involving more than two phonon operators are not considered here because their effects (such as anharmonicity and phonon softening) are already given by the linear coupling of Eq. (1) or the bilinear form in Eq. (6). The contribution of the interaction in Eq. (6) to $\langle u_i^2\rangle$ is expressed by Eq. (3) with $E^{(2)}_{\vec{k}\alpha j}$ given by (see Appendix for details)

$$\begin{aligned} E^{(2)}_{\vec{k}\alpha j}/\{\omega_{\vec{k}\alpha}(h^2_{\vec{k}\alpha j}/N)[\tanh(\tfrac{1}{2}\beta\Delta_j)/\Delta_j^2]\}^{-1} = {} & [2(e^{\beta\omega_{\vec{k}\alpha}}-1)^{-1}-(e^{\beta\Delta_j}-1)^{-1}-(e^{-\beta\Delta_j}-1)^{-1}] \\ & \times[\beta\Delta_j e^{\beta\omega_{\vec{k}\alpha}}(e^{\beta\omega_{\vec{k}\alpha}}-1)^{-2}]+[(e^{\beta\omega_{\vec{k}\alpha}}-1)^{-1}-(e^{\beta\Delta_j}-1)^{-1}] \\ & \times[(e^{\beta\omega_{\vec{k}\alpha}}-1)^{-1}-(e^{\beta(\omega_{\vec{k}\alpha}-\Delta_j)}-1)^{-1}]+[(e^{\beta\omega_{\vec{k}\alpha}}-)^{-1}-(e^{-\beta\Delta_j}-1)^{-1}] \\ & \times[(e^{\beta(\omega_{\vec{k}\alpha}+\Delta_j)}-1)^{-1}-(e^{\beta\omega_{\vec{k}\alpha}}-1)^{-1}]. \end{aligned} \tag{7}$$

For moderate temperatures the largest contributions to $\langle u_i^2\rangle$ are given by large k, and for small Δ_j we expand in powers of Δ_j/ω_k, which gives

$$E^{(2)}_{\vec{k}\alpha j} = (\omega_{\vec{k}\alpha}/2N)(h_{\vec{k}\alpha j}/k_BT)^2[\cosh^2(\tfrac{1}{2}\beta\Delta_j)/\cosh(\beta\Delta_j)][\cosh(\tfrac{1}{2}\beta\omega_{\vec{k}\alpha})/\sinh^3(\tfrac{1}{2}\beta\omega_{\vec{k}\alpha})]\,. \tag{8}$$

Note that in this case at low temperatures values of k for which $\omega_{\vec{k}\alpha} \gg k_BT$ give exponentially small contributions to $\langle u_i^2\rangle$, and for $k_BT \ll \omega_D$ the acoustic modes give a contribution to $\langle u_i^2\rangle$ which is proportional to $(k_BT/\omega_D)^4$.

The effect of the interaction in Eq. (6) on phonon frequencies can be especially interesting. This interaction gives a phonon self-energy contribution to order $h^2_{\vec{k}\alpha j}$, which is (see Appendix for details)

$$\begin{aligned} \Sigma_{\vec{k}}(i\omega_m) = -\frac{1}{N}\sum_j h^2_{\vec{k}j}\tanh(\tfrac{1}{2}\beta\Delta_j)\{ & [(e^{\beta\omega_{\vec{k}}}-1)^{-1}-(e^{\beta\Delta_j}-1)^{-1}](\omega_{\vec{k}}-i\omega_m-\Delta_j)^{-1} \\ & -[(e^{\beta\omega_{\vec{k}}}-1)^{-1}-(e^{-\beta\Delta_j}-1)^{-1}](\omega_{\vec{k}}-i\omega_m+\Delta_j)^{-1}\}\,. \end{aligned} \tag{9}$$

With this self-energy the phonon Green's function has poles at $\omega_k \pm \Delta_j$. Higher-order terms in $h^2_{\vec{k}\alpha j}$ give poles at $\omega_k \pm n\Delta_j$. These poles can be interpreted as modulations of the phonon frequency by the LSE, and they can lead to dramatic and novel phonon frequency or force constant changes.

Now consider the relevance of these results to the PdH_x system. Here the relatively small heat of formation[27] and the small mass of the proton may give rise to LSEs of at least partly electronic character which have large LSE interactions with the optic modes and which also possibly have rapidly fluctuating low-energy LSE modes. From the above results these factors all imply a large anharmonicity and phonon frequency anomaly in the optic mode which involves the proton motion. Let M_{D} and M_{Pd} be the atomic masses of deuterium and palladium and $\langle\omega^2\rangle$ be the second moment of the phonon frequencies. Since the ratio $M_{\mathrm{D}}/M_{\mathrm{Pd}}$ is small, Pd vibrates in essentially acoustic modes, and D vibrates in essentially optic modes. It was deduced[28] from experiment that $M_{\mathrm{D}}\langle\omega^2\rangle_{\mathrm{D}} \simeq \frac{1}{7}M_{\mathrm{Pd}}\langle\omega^2\rangle_{\mathrm{Pd}}$ contrary to the expectation that they should be roughly equal as in typical binary compounds. This result however is consistent with the novel type of "softening" of the optic-phonon frequency in the present model given in Eq. (9); the interaction between the optic phonon and the LSEs may be particularly large due to the small D mass and to the sensitivity of the local electronic structure to the D position.

The optic phonon "softening" mechanism discussed above is also consistent with the important and unusual difference observed between the Pd-H and Pd-D force constants. The force constants k_i in terms of the optic-mode frequencies are $\omega_i = (k_i/M_i)^{1/2}$, $i = H, D$. From the above results (with $n = 1$) we have $\omega_i = \omega_i^{(0)} - \Delta$ where $\omega_i^{(0)}$ is the frequency in the absence of the phonon-LSE interaction, and Δ is taken to be the same for H and D on the grounds that the electronic structure should not depend much on the mass difference between H and D. Then, $(k_H/k_D) = \frac{1}{2}[(\omega_H^{(0)} - \Delta)/(\omega_D^{(0)} - \Delta)]^2$. Because $\omega_H^{(0)}/\omega_D^{(0)} = \sqrt{2}$, we have that $k_H/k_D > 1$ for nonzero Δ, which is consistent with experiment.

Now consider the relevance of the above results to the effective electron-electron attraction. The anharmonicity and softening of the force constant induced by the LSEs leads to larger electron-phonon interaction and hence to an enhancement in the superconducting transition temperature in T_c. In addition, electrons can also scatter from the LSEs with an interaction of the form $\sum_{kk'} V_{kk'} C_k^\dagger C_{k'} \sigma^x$. Such an electron-LSE interaction will be also mediate an effective electron-electron attraction in addition to that caused by electron-phonon interaction, and T_c can thus be further enhanced. It is interesting to point out that such an electron-LSE interaction has recently been observed experimentally in amorphous metal alloys.[29]

An illuminating example of the enhancement of T_c by LSEs and their interactions can be found in the alkali tungsten bronzes introduced earlier in Sec. II. Shanks[21] has recently observed the dependence of T_c of TI-Na$_x$WO$_3$ on x for values of x from 0.2 to 0.4 and found that T_c increases rapidly as the TI-TII structural phase boundary at $x = 0.2$ is approached. On the other hand, experimental measurements of both the volume spin susceptibility[21,30,31] and specific heat[30-32] indicate a linear dependence of the density of states $N(0)$ at the Fermi energy E_F on x, for the cubic and TI alkali tungsten bronzes including the Na$_x$WO$_3$. The observed nearly exponential increase in T_c as x approaches 0.2 is extremely puzzling in view of the fact that $N(0)$ decreases linearly as x decreases. This behavior, moreover, is not unique to Na$_x$WO$_3$. The same phenomenon was discovered in the TI phase of K$_x$WO$_3$,[21] where as x is decreased to approach the $x = 0.33$ boundary which separates the TI phase ($x > 0.33$) from the hexagonal[22] phase ($x < 0.33$); T_c again increases rapidly. In our present model, recalling from Sec. II the discussion which indicated that the local TI→TII instabilities are due to alkali ion occupancy deviations from the uniform random occupancy x, we note that as x approaches x_c(= 0.2 for Na$_x$WO$_3$), these deviations become more significant thereby increasing both the number of LSEs and their interactions with phonons and electrons; and in the present model this gives a rapidly increasing T_c, consistent with what was observed experimentally.[33]

B. Structural transformations and superconductivity

We now consider the way in which structural transformations can limit the enhancement of T_c which is due to structural instabilities. In the present model the degree of local instability increases as the energy splitting between the LSE states and the barrier between them decreases. As discussed above, when the degree of local instability increases, T_c is enhanced both due to enhanced phonon pairing of electrons and also due to electron pairing directly by LSEs. For sufficiently large local instability, however, the nearly degenerate LSE levels can undergo at low temperature a pseudo Jahn-Teller-like transformation[34] accompanied by a local lattice (structural) distortion.[34] This distortion splits the LSE states thus increasing the local stability and removing the associated enhancement of T_c.

We now consider in some detail the relationship between the enhanced T_c and local instabilities and transformations by using the LSE model. The form of the dependence of T_c on local instabilities is not known in detail. We shall discuss several somewhat arbitrary but physically plausible forms which are adequate to bring out the essential features. For the coupling between the local (harmonic) phonon displacement $\hat{u}$ and a particular LSE we take the simple form

$$H = \tfrac{1}{2}\Delta\sigma^z + \tfrac{1}{2}g\sigma^x \hat{u}\ , \tag{10}$$

which is essentially that in Eq. (1). In a mean-field-like approximation, $\hat{u}$ is taken to be its thermal average $\langle u \rangle$, and the free energy is $F = C\langle u\rangle^2 - k_B T \ln[2\cosh(\Lambda/2k_B T)]$, where $\Lambda = (\Delta^2 + g^2\langle u\rangle^2)^{1/2}$, and the first term is the elastic energy of the phonon displacement. The free energy is minimized with respect to $\langle u \rangle$, which gives

$$2C\Lambda/g^2 = \tfrac{1}{2}\tanh(\Lambda/2k_B T)\ . \tag{11}$$

$\langle u \rangle$ is nonzero for $T < T_c^L$, where

$$2C\Delta/g^2 = \tfrac{1}{2}\tanh(\Delta/2k_B T_c^L)\ . \tag{12}$$

At T decreases below T_c^L the total splitting $\Lambda(T)$ increases as is shown in Fig. 1.

For the dependence of T_c on the total splitting Λ we consider first the simple form

$$T_c = \Lambda e^{-(1+\lambda)/\lambda}\ , \tag{13a}$$

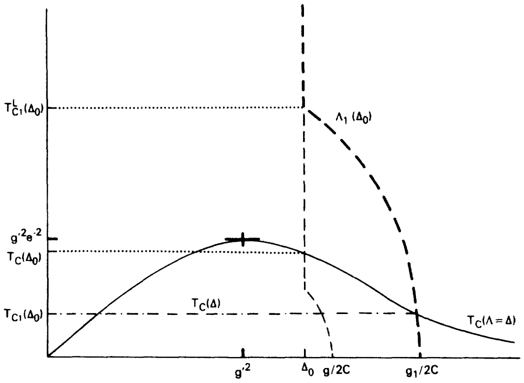

FIG. 1. Enhanced superconducting transition temperature T_c and lattice distortion Λ as given by Eqs. (13) and (11), respectively. $\Lambda_1(T)$ gives the lattice distortion for $\Delta = \Delta_0$ and $g = g_1$; the second dashed curve corresponds a value of $g < g_1$. $T_c(\Lambda = \Delta)$ gives T_c as a function of Δ inthe absence of lattice distortion, and $T_c(\Delta)$ gives T_c as a function of Δ in the presence of lattice distortion.

where

$$\lambda = g'^2/\Lambda\,, \tag{13b}$$

and g' is a constant. Such a form can be motivated by electron pairing via the LSE. The form of T_c in the absence of any lattice distortion is shown by T_c $(\Lambda=\Delta)$ in Fig. 1. To determine T_c in the presence of lattice distortion Eqs. (11) and (13) must be solved self-consistently in such a way that $\Lambda(T)$ in each is evaluated at $T=T_c$. This solution is given by the intersection of $\Lambda(T)$ and $T_c(\Delta)$ in Fig. 1, and the resulting T_c in the presence of lattice distortion is also shown there as a function of Δ.

We now briefly mention results similar to those above for another plausible form of the couplings between LSEs and electrons and phonons. The case of $g=Ke^{-\Lambda/c}$ and $\lambda=g_1^2e^{-\Lambda/C}/\Lambda$ in Eq. (13), which is motivated by the dependence of these couplings on the LSE barrier, has been solved in detail, and the results have all the same general features as those shown in Fig. 1 except that there is now a weak increase of $T_c(\Delta)$ for decreasing Δ after lattice distortion.

We now discuss the physical implications of the results obtained above and shown in Fig. 1. Two different situations can occur: (i) The sample with instability characterized by Δ_0 and g_1 undergoes a pseudo Jahn-Teller distortion at a temperature $T_{c1}^L(\Delta_0)$ higher than the enhanced T_c corresponding to Δ_0. As T decreases below $T_{c1}^L(\Delta_0)$ the lattice distortion increases, and the LSE stability (measured by Λ) increases, and the maximum attainable superconducting transition temperature is $T_{c1}(\Delta_0)$. For T below $T_{c1}(\Delta_0)$ the lattice distortion no longer affects the attainable T_c. (ii) On the other hand a sample with instability characterized by Δ_0 and some $g<g_1$ may not undergo a pseudo Jahn-Teller distortion until T falls below the $T_c(\Delta)$ curve. Then the maximum attainable superconducting transition temperature is $T_c(\Delta_0)$, and the distortion that occurs at lower temperature will have no effect on the attainable enhanced superconducting transition temperature $T_c(\Delta_0)$.

A nice metallurgical example that illustrates cases (i) and (ii) is the sputtering of materials with structural instabilities at elevated temperatures. Examples are[5,6,35] Nb_3Ge, and[18] the Mo-Re alloys. Sputtering enables unstable local structures to be "frozen in" and maintained at low temperatures (i.e., phonon distortion is not allowed to develop). The instabilities (Δ_0) which occur at high temperature are thereby retained at low temperatures, and the LSEs give an enhanced $T_c(\Delta_0)$ corresponding to case (ii). If, on the other hand, the sample is prepared under ordinary metallurgical conditions, these instabilities will not be frozen in, and lattice distortions will have set in at high temperatures. Thus as T decreases from these high values the effective splitting increases, and $g_{k\alpha j}$ decreases. This stabilizes the local structural phases against fluctuation to the higher-energy state and makes the LSEs ineffective in enhancing T_c. This corresponds to case (i) and to a lower value of T_c.

An example given by Matthias[1] of this behavior can be found in the compounds Nb_3Si and Zr_3Sb. These compounds have not yet been synthesized in the β-W form. Instead they crystallize in a tetragonal form with $c/a\approx 2$, and they are no longer superconducting about 1 K. The relatively large distortions of the cubic structure developed in these compounds to give $c/a\approx 2$ is expected in the present model to drastically lower T_c.

Different dependences of T_c in Eq. (13) on Λ can result in rather different features than those discussed above for Fig. 1. For example, the curves for $T_c(\Delta)$ and $T_c^L(\Delta)$ could intersect at more than one Δ. This is the case for

$$T_c = \langle\omega\rangle e^{-(1+\lambda)/\lambda}\,, \tag{14a}$$

$$\lambda = (K/\langle\omega\rangle^2)e^{-\Lambda/a}\,, \tag{14b}$$

where $\langle\omega\rangle$ is a phonon frequency, which is shown in Fig. 2. In this case LSE enhanced superconductivity can be realized only in regions I and III where $T_c(\Delta)\geq T_c^L(\Delta)$. The superconducting transition temperature T_c can be either larger than T_1, or less than T_2. In this simple model there is a forbidden temperature region $T_2<T\leq T_1$ in which superconductivity does not occur. If the material is originally in region I but close to Δ_1 such that external modifications such as compression, cold

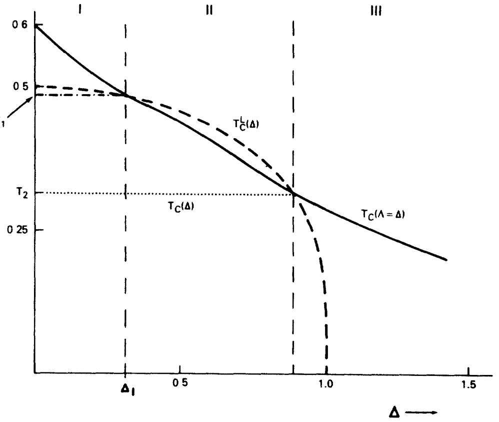

FIG. 2. Lattice distortion temperature T_c^L and the enhanced superconducting transition temperature T_c vs instability parameter Δ for a choice of couplings (see text) which gives two intersections between these curves. The example shown here is given by Eqs. (11) and (14) with parameter values $g^2/4C=1.0$; $K/\langle\omega^2\rangle=1.0$, $\langle\omega\rangle=4.43$, and $a=1.87$.

working, etc., brings Δ from region I to region II, there will be discontinuous drop in the T_c value of at least $T_2 - T_1$. This discontinuous drop in the value of T_c seems to be consistent with some of the observations of McCarthy[4,36] in which residual shear was introduced into the crystals of the $C12$, $C14$, $C15$, and $A12$ structures.

IV. CONCLUDING REMARKS

A simple microscopic model of local instabilities in high-T_c materials which involves the existence of more than one local state has been proposed; the model has been motivated by considering such local phases in several specific materials. The effects of dynamic fluctuations between these local states on the phonon and electron properties have been considered. Effects on the phonon spectrum include large anharmonicity, enhanced heat capacity, phonon frequency softening, and an enhanced electron-phonon interaction. The increased effective electron-electron attraction due to local structural fluctuations can lead to an enhanced superconducting T_c. Finally, the model has been used to discuss the structural transformations which often limit the attainable values of T_c.

ACKNOWLEDGMENT

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APPENDIX

We give here brief derivations of the formal results for the interacting "spin"-phonon systems of Eqs. (1) and (6) which were discussed in the text. In Sec. A 1 we give the diagrammatic formalism used and give some thermodynamic results for the system in Eq. (1); these results have been obtained previously by Sheard and Toombs.[26] In Sec. A 2 we give thermodynamic results and the phonon self-energy for a system with interaction given by Eq. (6); these results have not been derived previously. We give here brief self-contained derivations for both systems; the reader is referred to Ref. 26 for fuller details of the method.

1. Linear phonon-spin interaction

The interacting spin-phonon system of Eq. (1) in the text can be written

$$H = H_s + H_p + H_{sp} \tag{A1}$$

$$H_s = \frac{1}{2}\sum_j \Delta_j \sigma_j^z \tag{A1a}$$

$$H_p = \sum_{\vec{k}\alpha} \omega_{\vec{k}\alpha} a_{\vec{k}\alpha}^\dagger a_{\vec{k}\alpha} \tag{A1b}$$

$$H_{sp} = \sum_{\vec{k}\alpha j} g_{\vec{k}\alpha j}\, \sigma_j^x (a_{-\vec{k}\alpha}^\dagger + a_{\vec{k}\alpha}) e^{i\theta_{\vec{k}j}} \tag{A1c}$$

Here σ_j^α are the Pauli spin operators for "spins" with splittings Δ_j, $a_{\vec{k}\alpha}$ is the annihilation operator for phonons of wave vector $\vec{k}$ and polarization α, and $\theta_{\vec{k}j}$ is a phase factor.

A reliable method for obtaining the thermodynamic quantities is a diagrammatic expansion for the free energy; this can be done by using the drone-fermion representation[37] for σ^α for which the Wick theorem is then available:

$$\tfrac{1}{2}\sigma_j^z = c_j^\dagger c_j - \tfrac{1}{2},$$

$$\tfrac{1}{2}\sigma_j^\dagger = \tfrac{1}{2}(\sigma_j^x + i\sigma_j^y) = c_j^\dagger \phi_j,$$

where the c's are Fermi operators which anticommute with the ϕ's for which $\phi_i\phi_j + \phi_j\phi_i = 2\delta_{ij}$ and $\phi_j^\dagger = \phi_j$. Then $H = H^{(0)} + H_I$, where

$$H^{(0)} = \sum_j \Delta_j c_j^\dagger c_j + \sum_{\vec{k}\alpha} \omega_{\vec{k}\alpha} a_{\vec{k}\alpha}^\dagger a_{\vec{k}\alpha}, \tag{A2a}$$

$$H_I = \sum_{\vec{k}\alpha j} g_{\vec{k}\alpha j}(c_j^\dagger - c_j)\phi_j(a_{-\vec{k}\alpha}^\dagger + a_{\vec{k}\alpha}) e^{i\theta_{\vec{k}j}}. \tag{A2b}$$

Green's functions (propagators) are defined in the usual way

$$C_j(i\omega_n) = \langle \Upsilon[c_j^\dagger(\tau) - c_j(\tau)][c_j^\dagger(0) - c_j(0)]\rangle_{i\omega_n}$$

$$\Phi_j(i\omega_n) = \langle \Upsilon \phi_j(\tau)\phi_j(0)\rangle_{i\omega_n},$$

$$D_{\vec{k}\alpha}(i\omega_m) = \langle \Upsilon[a_{-\vec{k}\alpha}^\dagger(\tau) + a_{\vec{k}\alpha}(\tau)][a_{-\vec{k}\alpha}^\dagger(0) + a_{\vec{k}\alpha}(0)]\rangle_{i\omega_m}.$$

Here Υ is the Wick τ ordering operator, $\langle\ \rangle$ is the ensemble average, and the Fourier components are indicated by $\omega_n = n\pi/\beta$, $\omega_m = m\pi\beta$, where $n(m)$ are odd (even) integers. The unperturbed propagators (corresponding to $H^{(0)}$) are illustrated in Fig. 3(a), and the interaction H_I is shown in Fig. 3(b).

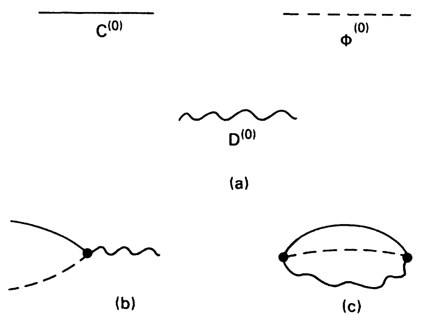

FIG. 3. Diagrammatic representations for the LSE-phonon Hamiltonian in Eq. (1) and in Eq. (A1): (a) unperturbed propagators; (b) vertex; and (c) lowest-order correction to the free energy.

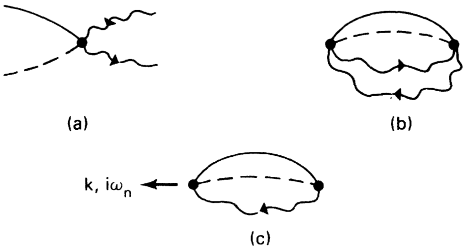

FIG. 4. Diagrammatic representations for the LSE-phonon Hamiltonian in Eq. (6) and in Eq. (A1c′): (a) vertex; (b) lowest-order correction to the free energy; and (c) lowest-order correction to the phonon self-energy.

Thermodynamic quantities are obtained from the free energy which is given by the usual linked cluster expansion.[38] To second order in g, $F^{(2)} = -k_B T \Xi^{(2)}$ where $\Xi^{(2)}$ is shown in Fig. 3(c) and is

$$\Xi^{(2)} = \frac{1}{2\beta N} \sum_{\substack{\vec{k}\alpha j \\ m_1, n_2}} g^2_{\vec{k}\alpha j} D^{(0)}_{\vec{k}\alpha}(i\omega_{m_1}) C^{(0)}_j(i\omega_{n_2}) \times \Phi^{(0)}_j(i\omega_{m_1} - i\omega_{n_2}) . \tag{A3}$$

Evaluating the frequency sums gives the result in Eq. (2) in the text.

The internal energy is given by $E^{(2)} = \partial(\beta F^{(2)}/\partial\beta)$, and it has contributions from the modifications of spin energy, modifications of the phonon energy, and from the spin-phonon interaction energy. For example, by differentiating $F^{(2)}$ appropriately with respect to β in the propagator $D^{(0)}$ one obtains the contribution from the phonon system (which is a contribution to $\langle a^\dagger_{\vec{k}\alpha} a_{\vec{k}\alpha}\rangle$) and is

$$\begin{aligned} E^{(2)}_{\mathrm{ph}} = \frac{1}{N} \sum_{\vec{k}\alpha j} \omega_{\vec{k}\alpha} g^2_{\vec{k}\alpha j} \{ & (\omega_{\vec{k}\alpha} - \Delta_j)^{-2} (e^{\beta\Delta_j} + 1)^{-1} + (\omega_{\vec{k}\alpha} + \Delta_j)^{-2} (e^{-\beta\Delta_j} + 1)^{-1} - 4\Delta_j \omega_{\vec{k}\alpha} (\omega^2_{\vec{k}\alpha} - \Delta^2_j)^{-2} \\ & \times \tanh(\tfrac{1}{2}\beta\Delta_j)(e^{\beta\omega_{\vec{k}\alpha}} - 1)^{-1} - 2\Delta_j (\omega^2_{\vec{k}\alpha} - \Delta^2_j)^{-1} \tanh(\tfrac{1}{2}\beta\Delta_j) [\beta e^{\beta\omega_{\vec{k}\alpha}} (e^{\beta\omega_{\vec{k}\alpha}} - 1)^{-2}] \} \end{aligned} \tag{A4}$$

The results summarized here in Sec. A1 are discussed in more detail in Ref. 25.

2. *Nonlinear phonon-spin interaction*

We now consider both the thermodynamics and the phonon self-energy for the spin-phonon system with interaction given in Eq. (6) in the text; the Hamiltonian is given by Eqs. (A1a), (A1b), and

$$H'_{sp} = \frac{1}{2} \sum_{\vec{k}\alpha j} h_{\vec{k}\alpha j} \sigma^x_j a^\dagger_{\vec{k}\alpha} a_{\vec{k}\alpha} e^{i\theta_{\vec{k}j}} . \tag{A1c′}$$

By using the above formalism, we obtain for the interaction term

$$H'_I = \sum_{j\vec{k}\alpha} h_{k\alpha j} (c^\dagger_j - c_j) \phi_j a^\dagger_{\vec{k}\alpha} a_{\vec{k}\alpha} e^{i\theta_{\vec{k}j}} , \tag{A2b′}$$

which is shown diagrammatically in Fig. 4(a).

The contribution to the free energy to order h^2 is shown in Fig. 4(b) and is given by $F^{(2)\prime} = -k_B T \Xi^{(2)\prime}$, where

$$\Xi^{(2)\prime} = \frac{1}{2n\beta^2} \sum_{\substack{\vec{k}\alpha j \\ m_1, m_2 \\ n_3}} h^2_{\vec{k}\alpha j} G^{(0)}_{\vec{k}\alpha}(i\omega_{m_1}) G^{(0)}_{\vec{k}\alpha}(i\omega_{m_2}) \times C^{(0)}(i\omega_{n_3}) \Phi^{(0)}(i\omega_{m_1} - i\omega_{m_2} - i\omega_{m_3}) . \tag{A5}$$

For convenience the new propagator $G_{\vec{k}\alpha}(i\omega_m) = \langle T a^\dagger_{\vec{k}\alpha}(\tau) a_{\vec{k}\alpha}(0)\rangle_{i\omega_m}$ is introduced here and is shown by the line with an arrow in Fig. 4(b). The internal energy corresponding to the phonon system is given by differentiating $F^{(2)\prime}$ appropriately with respect to β in $G^{(0)}$ which after summing over frequencies gives the result in Eq. (7) in the text.

In calculating the phonon self-energy a multiple scattering approach for the phonon is required. We shall assume that the spins are distributed randomly in space and following Langer[39] calculate an ensemble averaged Green's function over the random spin distributions. Retaining only the lowest-order term in h, we obtain

$$\overline{G}_{\vec{k}}(i\omega_m) = \{ [G^{(0)}_{\vec{k}}(i\omega_m)]^{-1} - \Sigma_k(i\omega_m) \}^{-1} , \tag{A6}$$

where the proper self-energy $\Sigma_k(i\omega_m)$ is shown in Fig. 4(c) and is given by

$$\Sigma_k(i\omega_m) = \frac{1}{N} \sum_j h^2_{kj} \beta^{-2} \sum_{m_1 n_2} G^{(0)}_k(i\omega_{m_1}) C^{(0)}_j(i\omega_{n_2}) \times \Phi^{(0)}_j(i\omega_{m_1} - i\omega_m - i\omega_{n_2}) . \tag{A7}$$

For simplicity the phonon polarization index has been dropped, and an average interaction h_{kj} has been used. When the frequency sums are evaluated this gives the result in Eq. (9) in the text.

The results obtained in (A2) and given in Eqs. (7) and (9) in the text have not been derived previously.

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