ROLE OF PHONONS AND BAND STRUCTURE IN METAL-INSULATOR PHASE TRANSITION*†

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We present a soluble model of electrons interacting with lattice vibrations which displays metallic, superconducting, and insulating phases. We solve the thermodynamics of this model and discuss its properties. The metal-insulator phase transition is second order for sc and bcc tight-binding bands. With sufficient deviation [(5-10)% for coupling constant $\tilde{g}=0.1$] from such band structure the transition becomes first order. Above this, the "collective insulator" ceases to exist. Our model might apply to certain transition-series metal oxides, such as VO_2.

We treat several aspects of a soluble model which exhibits an insulator-metal phase transition, polaron effects, low mobility, and a tendency toward superconductivity. This model has several features of certain transition-series oxides such as Ti_2O_3 and VO_2.[1,2] Unlike the Hubbard model,[3,4] the present model has no significant magnetic properties, so that it is only applicable to nonmagnetic oxides.[4,5] Based as it is on the electron-phonon interaction, we believe this model to apply when the effective coupling parameter $\tilde{g}=g^2/\hbar\omega$ exceeds the Coulomb parameter U by a sufficient amount so that qualitatively it is legitimate to ignore U. Otherwise, the Hubbard model is applicable and one obtains antiferromagnetic ordering in the ground state.[4,6] In the present model, the ground-state insulating phase is associated with finite crystallographic distortion, whereby the unit cell is doubled. The bands then split and what might have been mistaken for a metal with a half-filled band becomes an insulator. Moreover, the density of states near the band edges become anomalously large, resulting in surprising thermodynamic and transport properties. We shall later show that the details of the metal-insulator phase transition depend sensitively on band structure. At first, however, we assume a high-

ly symmetric sc or bcc band structure. We start with

$$H=\sum\epsilon_k n_{k,m}+U\sum C_{k+q\uparrow}{}^{*}C_{k\uparrow}C_{k'\downarrow}{}^{*}C_{k'+q\downarrow}+\hbar\omega\sum a_q{}^{*}a_q+gN^{-1/2}\sum(a_q+a_{-q}{}^{*})C_{k+q,m}{}^{*}C_{km}-\mu\sum n_{k,m}. \quad (1)$$

The subscript m refers to the spin of the electron, the momentum subscripts $\vec{k}$ are understood to belong to a set of N vectors in a three-dimensional Brillouin zone. The first term is the energy of Bloch-state electrons [i.e., for tight binding in a simple-cubic structure $\epsilon_k\sim(\cos k_x+\cos k_y+\cos k_z)$ and n_{km} is the number operator]. The second term is the repulsive interaction between pairs of electrons on the same site, treated in a previous paper[4]; in the balance of this work we set $U=0$. The phonons (creation and destruction operators $a_q{}^{*}$ and a_q) are assumed to have an Einstein spectrum. In the fourth term, electrons are scattered from $\vec{k}$ to $\vec{k}+\vec{q}$ by an appropriate phonon. We adjust particle number by means of a chemical potential μ.

With our neglect of the Coulomb repulsion terms this Hamiltonian might be expected to have a superconducting ground state and a metallic high-temperature phase. But we shall show that in some crystal structures (sc or bcc with tight-binding band structures) a dominant phonon mode affects the lattice, causing a gap in the electronic density of states, and unusual insulating properties. Some superconducting features will also be found. In sc and bcc lattices, the vector $\vec{Q}=(\pi/a)(\pm1,\pm1,\pm1)$, where a = lattice spacing, has the property that $2\vec{Q}$ is a vector in the reciprocal lattice, and that $\vec{Q}$ itself splits the Brillouin zone into two subzones. Because $\epsilon(\vec{k}+\vec{Q})=-\epsilon(\vec{k})$, we can take $\epsilon<0$ in the first zone and $\epsilon>0$ in the second. For a half-filled band, the Fermi level lies at $\epsilon=0$. Thus, in crystals with the above mentioned symmetries the phonon mode Q plays a potentially important role and must be singled out. We write

$$H_0=\sum_{km}(\epsilon_k-\mu)n_{km}+gN^{-1/2}\sum_{km}C_{k+Q,m}{}^{+}C_{k,m}(a_Q+a_{-Q}{}^{*})+\hbar\omega a_Q{}^{*}a_Q \quad (2)$$

$$H_1=gN^{-1/2}\sum_{q\neq0,Q}(a_q+a_{-q}{}^{*})C_{k+q,m}{}^{+}C_{k,m}+\hbar\omega\sum a_q{}^{*}a_q. \quad (3)$$

We study the insulating state inherent in H_0 and compare it with the usual superconductor in which H_0 and H_1 are treated by the techniques of the Bardeen-Cooper-Schrieffer (BCS) theory.[7] We start by assuming a macroscopic lattice distortion, setting $a_Q=a_Q{}^{*}=-xN^{1/2}$, and determining the parameter x by minimizing the free energy. [Quantum fluctuations in this single phonon mode contribute only a fraction $O(1/N)$ to the free energy and are ignored.] Writing H_0 in terms of the two half-zones it can be diagonalized exactly by a unitary transformation $c_k=A_kb_k+B_kb_{k+Q}$, where the b's are the new operators. We find

$$A_k{}^{2}=\tfrac{1}{2}+\tfrac{1}{2}|\epsilon_k|(\epsilon_k{}^{2}+\Delta^2)^{-1/2} \text{ and } B_k{}^{2}=\tfrac{1}{2}-\tfrac{1}{2}|\epsilon_k|(\epsilon_k{}^{2}+\Delta^2)^{-1/2}, \quad (4)$$

where $\Delta\equiv2gx$, and $B_k\gtrless0$ for $\epsilon_k\gtrless0$, whereas A_k is always positive. H_0 now has the form

$$H_0=\sum_{\epsilon<0}[-(\epsilon^2+\Delta^2)^{1/2}-\mu^{*}]b_{km}{}^{*}b_{km}+\sum_{\epsilon>0}[(\epsilon^2+\Delta^2)^{1/2}-\mu^{*}]b_{km}{}^{*}b_{km}+N\Delta^2/4\tilde{g}, \quad (5)$$

in which $\tilde{g}=g^2/\hbar\omega$ and $\mu^{*}\equiv(\mu^2+\Delta^2)^{1/2}$ for a more than half-filled band and $=-(\mu^2+\Delta^2)^{1/2}$ for a less than half-filled band, with $\mu^{*}=\mu=0$ for a precisely half-filled band. Setting $f(x)=(1+\exp\beta x)^{-1}$, we construct the free energy F for H_0,

$$F=N\Delta^2/(4\tilde{g})-2/\beta\sum_{\epsilon>0}\ln\{f(-\mu^{*}-(\epsilon^2+\Delta^2)^{1/2})f(-\mu^{*}+(\epsilon^2+\Delta^2)^{1/2})\} \quad (6)$$

and solve for Δ^2 by minimizing F with respect to Δ^2. Replacing summations by integrations over the density of states of the appropriate band structure, the equation for the insulating gap can be written

$$1=2\tilde{g}\int_{-w}^{w}\rho(\epsilon)d\epsilon(\epsilon^2+\Delta^2)^{-1/2}\{f(\mu^{*}-(\epsilon^2+\Delta^2)^{1/2})-f(\mu^{*}+(\epsilon^2+\Delta^2)^{1/2})\}, \quad (7)$$

where $2w$ = bandwidth. From F we also derive the electron density $\bar{n}$:

$$\bar{n}=\int_{-w}^{w}\rho(\epsilon)d\epsilon\{f(\mu^{*}-(\epsilon^2+\Delta^2)^{1/2})+f(\mu^{*}+(\epsilon^2+\Delta^2)^{1/2})\}. \quad (8)$$

In the important example of a half-filled band, $\bar{n}=1$, $\mu=\mu^{*}=0$. We evaluate these expressions for $\bar{n}=1$ using a square density of states ($\rho=1/2w$), an approximation which we have found, by comparison

with exact computer calculations, to be very accurate for the parameters of interest to us in the sc structure.[8] Labeling the insulator parameters by I, we find

$$\Delta_I = w/\sinh(w/2\tilde{g}), \quad kT_I = 0.57\Delta_I, \tag{9}$$

and the change in ground-state energy (δF at $T=0$)

$$\delta E_I = -N\left\{\frac{\Delta^2}{4\tilde{g}} - \tfrac{1}{2}[(\Delta^2+w^2)^{1/2}-w] - \frac{\Delta^2}{2w}\ln\left[\frac{w+(w^2+\Delta^2)^{1/2}}{\Delta}\right]\right\}, \tag{10}$$

and T_I is the nominal metal-insulator critical temperature.

An alternative calculation is to set $x=0$ and use the BCS solution for the superconductor (labelled "s"):

$$\Delta_s = \frac{\hbar\omega}{\sinh(w/\tilde{g})}, \quad kT_s = 0.57\Delta_s, \quad \delta E_s = \frac{-2N(\hbar\omega)^2/2w}{\exp(2w/\tilde{g})-1}. \tag{11}$$

In Fig. 1 we plot $|\delta E_s/\delta E_I|$ and T_s/T_I against $\tilde{g}$ for various values of $\hbar\omega$. When both these ratios are less than unity there is no superconductivity for a half-filled band. We observe that for a coupling constant and phonon energy substantially less than the bandwidth there is no superconductivity, the insulator is preferred, and thus $x \neq 0$.

Next we query, what is the maximum deviation from a half-filled band for which we still have a nonvanishing x in the ground state? Clearly there is a critical density n_c beyond which the ground state is a metal or superconductor, but not an insulator. We plot $|n_c-1|$ as a function of $\tilde{g}$ in Fig. 2(a), as well as Δ_I vs n for $\tilde{g}=0.1$, Fig. 2(b). This figure shows that for this choice of $\tilde{g}$, the insulating phase ceases to exist when the deviation from a half-filled band exceeds 5%. We now assume that $\bar{n}$ is within this range, but not precisely equal to 1, so that the ground state is that of a degenerate semiconductor. We shall now calculate the superconducting properties of such a semiconductor. It is necessary

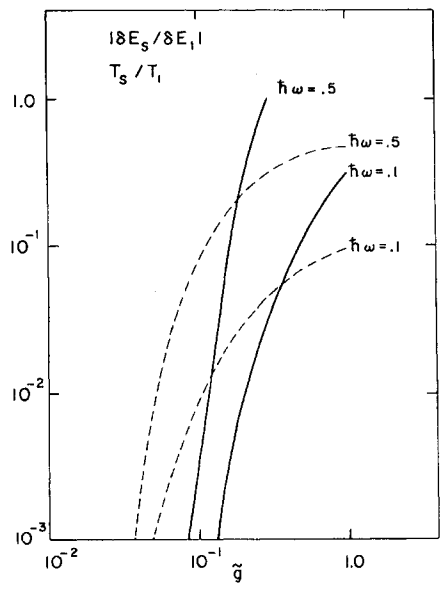

FIG. 1. Ratio of ground-state energy for a half-filled band at $|\delta E_s/\delta E_I|$, solid line; and critical temperatures T_s/T_I, dashed line, for two values of $\hbar\omega$, over a range of $\tilde{g}$. The superconducting phase cannot exist when these ratios are both less than unity, so the insulating phase is clearly preferred in weak coupling (small $\tilde{g}$). All energies are in units of $2w=1$.

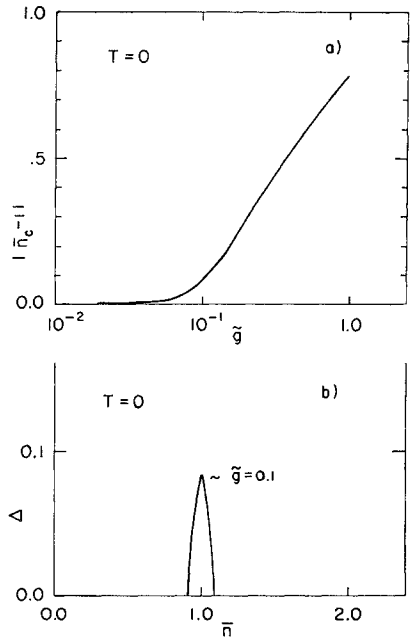

FIG. 2. (a) The insulating phase disappears at a density n_c if we deviate too much from a half-filled band. This plot shows the dependence of n_c on $\tilde{g}$. (b) The insulating gap Δ_I at $T=0$ as a function of electron concentration away from a half-filled band. Δ_I vanishes at $n=n_c$.

to apply to H_1 the canonical transformation which diagonalized H_0 [Eq. (5)], yielding

$$H_1=\tilde{g}N^{-1/2}\sum_{\lambda}(a_\lambda+a_{-\lambda}^*)\sum_{km}\{b_{k+\lambda m}^*b_{km}(A_{k+\lambda}A_k+B_{k+Q+\lambda}B_{k+Q}) + b_{k+\lambda m}^*b_{k+Qm}(A_{k+\lambda}B_k+B_{k+Q+\lambda}A_{k+Q})\}+\hbar\omega\sum a_q^*a_q. \quad (12)$$

We eliminate the phonons to obtain the effective electron-electron interaction, as in the work of Bardeen and Pines[9]:

$$H_s'=-g^2\frac{\hbar\omega}{N^2}\sum_{\lambda}\sum_{km}\left\{\frac{S_\lambda(k)}{(E_{k+\lambda}-E_k)^2-(\hbar\omega)^2}\right\}\sum_{k'm}S_{-\lambda}(k'), \quad (13)$$

where $E_k=\pm(\epsilon_k^2+\Delta_I^2)^{1/2}$ are the energies found in H_0, and

$$S_\lambda(k)=b_{k+\lambda m}^*b_{km}(A_{k+\lambda}A_k+B_{k+Q+\lambda}B_{k+Q})+b_{k+\lambda m}^*b_{k+Qm}(A_{k+\lambda}B_k+B_{k+Q+\lambda}A_{k+Q}). \quad (14)$$

Substituting for A and B and retaining only the BCS reduced interaction, we find an effective Hamiltonian H_s:

$$H_s=H_0+2g^2\frac{\hbar\omega}{N}\sum_{kk'}\frac{b_{k'\uparrow}^*b_{-k'\downarrow}^*b_{k\downarrow}b_{-k\uparrow}}{(E_{k'}-E_k)^2-(\hbar\omega)^2}\left(1+\frac{\Delta_I^2}{E_kE_{k'}}\right). \quad (15)$$

When $w\gg\Delta_I\gg\mu>\hbar\omega$, we find for the parameter of the superconducting semiconductor

$$\Delta_s(T=0)=\frac{\hbar\omega\,\mu/\Delta_I}{\sinh(w\mu/2\tilde{g}\Delta_I)},\quad kT_s=0.57\Delta_s(T=0). \quad (16)$$

The factor μ/Δ_I from the insulator decreases the effective $\hbar\omega$ but greatly enhances the exponential factors, so that T_s could be unusually high.

We have also studied the order of the metal-insulator thermodynamic phase transition in our model. (Experimentally it is first order in most materials which exhibit this phenomenon, with the gap jumping from zero to a finite value at T_I, with a jump in conductivity of as much as six orders of magnitude. However in exceptional cases, such as Ti_2O_3, it appears to be second order.)[1,5] As it stands the transition in our model is second order, with Δ_I going smoothly to zero at T_I. We have however studied many additional mechanisms and have found that the following all preserve the second-order transition, even though they have nontrivial effects on Δ_I, T_I, etc.: (1) pressure and strain (e.g., the strain dependence of $\tilde{g}$, $\hbar\omega$, w, with one exception—II below), (2) nonvanishing Coulomb repulsion U, and (3) deviation from precisely half-filled band. We have also found that the following mechanisms do change the transition to first order: (I) deviation of the band structure from perfect tight-binding sc or bcc, and (II) strain, provided $\tilde{g}\geq w$. This second presupposes an unphysically large coupling constant and we have not pursued it further, even though it is commonly believed, and has been often[5] stated, that the discontinuities are due to strain. Our model does not bear this out, and suggests that mechanism I—i.e., the effect of next-nearest-neighbor overlap on the band structure—is sufficient to explain the experimental facts. We shall assume the following simplified band structure:

$$\epsilon(k)=\epsilon^{sc}(k)+\lambda\delta\epsilon(k), \quad (17)$$

where

$$\delta\epsilon(k+Q)=+\delta\epsilon(k)\ \text{ and }\ \langle\delta\epsilon(k)\rangle_k=0, \quad (18)$$

where $\langle\rangle_k$ stands for an average taken over a surface $\epsilon^{sc}(k)=\text{const}$. For a half-filled band $\mu=\mu^*=0$ once more, and replacing (7) we have

$$1=2\tilde{g}\int_{-w}^{w}\rho(\epsilon)d\epsilon(\epsilon^2+\Delta^2)^{-1/2}\{\langle f(\lambda\delta\epsilon-(\epsilon^2+\Delta^2)^{1/2})\rangle_k-\langle f(\lambda\delta\epsilon+(\epsilon^2+\Delta^2)^{1/2})\rangle_k\}. \quad (19)$$

If the function $\lambda\delta\epsilon(k)$ is replaced by a step function $\pm\lambda$ the angular averages can be performed exactly and numerical evaluation of (19) for $\tilde{g}=0.1$ yields a discontinuous phase transition for λ in the range $0.05<|\lambda/2w|<0.1$.

For smaller λ the transition is second order. When λ increases T_I decreases, until for $|\lambda/2w|\geq 0.1$ the insulating phase ceases to exist even at $T=0$. These effects are expected to depend on the magnitude of $\tilde{g}$. The effects of band structure on $\Delta_I(T)$ are shown in Fig. 3.

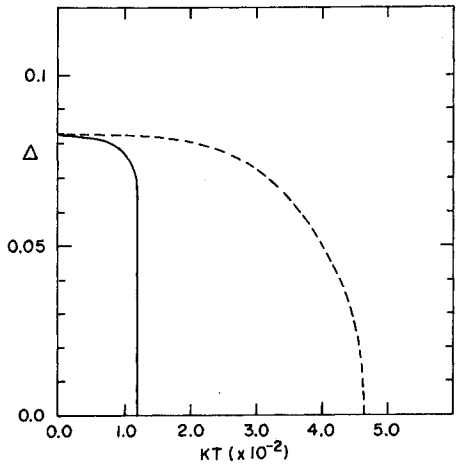

FIG. 3. Temperature dependence of the gap Δ_I for sc band structure (dotted curve) and for 6% deviation from sc ($\lambda/2w = 0.06$, solid curve). At less than 5% deviation the Δ_I curve becomes second order again, whereas at or above 10% $T_I \to 0$ and the insulating phase disappears. This calculation is for $\tilde{g} = 0.1 \times 2w$. The temperature is plotted in units of $kT = 2w \times 10^{-2}$.

We conclude that the observed effects of pressure and strain on T_I are explained by the strain dependence of the band structure (i.e., the "mix" of next-nearest-neighbor to nearest-neighbor overlap depends sensitively on lattice parameter) rather than by the effects of strain on the absolute or relative magnitudes of $\tilde{g}$, $\hbar\omega$, bandwidth, or U.

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[1]F. J. Morin, Bell. Syst. Tech. J. 37, 1047 (1958).

[2]R. Bartholomew and D. Frankel, Phys. Rev. 187, 828 (1969).

[3]J. Hubbard, Proc. Roy. Soc., London, Ser. A 276, 238 (1963), and 277, 237 (1963), and 281, 401 (1964), and 285, 542 (1965).

[4]Several authors have applied the Hubbard model to the problem of the metal-insulator phase transition, first J. des Cloizeaux, J. Phys. Radium 20, 606, 751 (1959); later D. R. Penn, Phys. Rev. 142, 350 (1960); W. Langer *et al.*, Phys. Rev. Lett. 23, 1448 (1969); and others. While there is no exact solution of this model in three dimensions, it is clear that the insulating properties, if any, are related to the spin degree of freedom of the electrons.

[5]A review of the transition-series oxides is given by D. Adler, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1968), Vol. 21, and of the transition and rare-earth series by S. Methfessel and D. Mattis, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1969), Vol. 18A. See also D. Adler, Rev. Mod. Phys. Phys. 40, 714 (1968). Discussion of VO_2 is given in C. Berglund and A. Jayaraman, Phys. Rev. 185, 1034 (1969).

[6]This is also discussed, in perturbation theory, in D. Mattis, *The Quantum Theory of Magnetism* (Harper and Row, New York, 1965), pp. 193-194.

[7]J. Bardeen, L. Cooper, and J. Schrieffer, Phys. Rev. 108, 1175 (1957).

[8]Highly accurate formulas have been developed by R. Jelitto, J. Phys. Chem. Solids 30, 609 (1969). We are grateful to Dr. F. Martino for this reference.

[9]J. Bardeen and D. Pines, Phys. Rev. 99, 1140 (1955).