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Metal–Nonmetal Transitions: Theoretical Models*†

ROBERT A. BARI‡

Physics Department, SUNY at Stony Brook, Stony Brook, New York 11794

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Current theoretical models for metal–nonmetal transitions are reviewed. Variational approaches to the half-filled band Hubbard model are discussed. Another electron-correlation model, the spinless Fermion model, is also discussed. Unlike the Hubbard model, the spinless Fermion model exhibits an insulator–metal transition in the one-dimensional ground state for nonzero interaction strength. A discussion of lattice-distortion models is given. In the distorted phase there are two types of spatial configurations for a magnetic singlet but only one (the polar singlet) forms at the expense of the intrasite repulsion energy. The role of soft phonons in a crystalline distortion is briefly discussed.

I. Introduction

There have been many developments in the last several years in the theories of metal–nonmetal (MNM) transitions. Since the 1968 International Conference on the Metal–Nonmetal Transition (*1*) several articles (*2–7*) have appeared which have reviewed the state-of-the-art with respect to descriptions of MNM transitions of various types (e.g., Slater's model of band antiferromagnetism (*8*), lattice distortion models, electron correlation models, etc.). In this paper I will attempt to present, rather than an updated systematic review of these topics, a discussion, as space permits, of certain aspects of recent theoretical developments related to mechanisms for MNM transitions.

As is evidenced in nature and also in the simplest theoretical models, there are many ways in which the transport properties of a crystalline solid can be catastrophically altered. As a consequence, the theoretical study of MNM transitions is the study of many different models which reflect in each instance the underlying phenomenon that the model builder is attempting to describe.

There are several ways of classifying MNM transitions. For example, they can be classified according to whether the gap in the one-electron density of states in the insulating state is due to crystal structure (the Fermi level occurs at the Brillouin zone edge) or whether it is due to an electron-correlation effect (e.g., the Mott–Hubbard (*9*, *10*) gap). Note, however, that it is also possible to have a gap due to crystal structure, but a MNM transition that results from electron correlation e.g., the Falicov–Kimball model (*11*). It is also possible to have a gap in the one-electron density of states at the Fermi energy and not have an insulating state, e.g., the BCS model (*12*). Is it necessary to have a gap in the one-electron density of states in order to have an insulating state?

Another method of classifying MNM transitions is according to whether there is some phase transition (in the thermodynamic sense) at which the transport properties are significantly changed. Is there an order parameter associated with the Mott transition from a nonmagnetic metal to a nonmagnetic insulator?

In addition to these classifications, one may wish to distinguish a MNM transition from a nonmetal–nonmetal transition. In this con-

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† Invited paper.

‡ Present address: Brookhaven National Laboratory, Upton, NY 11973.

nection one must give a definition of the term metal (*13*).

In this paper we shall review theories of MNM transitions in terms of three models: the Hubbard model (*10*), the spinless Fermion model, and the lattice distortion model. For the Hubbard model we shall mainly discuss variational approaches to the MNM transition that have been developed in recent years. The spinless half-filled band Fermion model is the only nontrivial model that rigorously exhibits a MNM transition (*14*) (in the one dimensional ground state). It is interesting to compare this model with the Hubbard model. The model may also provide a reasonable basis for the description of some real materials.

Lattice distortion models have received considerable recent attention in connection with a possible Peierls instability (*15*) in quasi one dimensional solids (*16*, *17*). We shall relate this more recent work to earlier work done in connection with the transition-metal oxides and also discuss the role of a soft-phonon mode in this transition.

II. The Hubbard Model

The single-band Hubbard–Gutzwiller–Kanamori (*9*, *18*, *19*) model has been widely studied in connection with correlation effects in narrow-band solids. The model is

$$H = \sum_{i,j,\sigma} t_{ij} C_{i\sigma}^{+} C_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}, \quad (1)$$

where the notation is that of Ref. (*13*). The model has the distinct conceptual advantage of being quantitatively simple in both the $t_{ij} = 0$ (Heitler–London) limit and $U = 0$ (band) limit. This simplicity invites and challenges theorists to interpolate between these limits and thereby study the competition between localized and itinerant electronic behavior.

Perhaps one of the most significant results since the appearance of Ref. (*1*) is the exact solution for the one-dimensional ground-state energy. Lieb and Wu (*20*) found that under the assumption that the hopping parameter is restricted to nearest-neighbor sites on the linear chain, the one-dimensional Hubbard model is a Mott insulator for all $U > 0$. They based their conclusion on the fact that $\mu_+ > \mu_-$ for the half-filled band and noted that this property is characteristic of an insulator and not a conductor. Here μ_+ and μ_- are the chemical potentials associated with adding and removing an electron from the half-filled band. Thus, the only exact result on the possible MNM transition in the Hubbard model testifies against this possibility. As Lieb and Wu pointed out, the failure of obtaining a MNM transition as a function of U for $U > 0$ in the ground state is *not* connected with the familiar taboos (*21*, *22*) against phase transitions at finite temperature. As we shall see in the next section, it is possible to have a phase transition (as a function of a parameter) in a one-dimensional ground-state with short range interactions. The finite temperature theorems (*21*, *22*) do not extend to the ground state.

There are several approximate treatments of the MNM transition in the higher-dimensional Hubbard model. Hubbard's improved decoupling approximation (*10*) yielded the first description of MNM transition in the sense that beyond a critical value of U a gap opens in the pseudoparticle density of states. Hubbard employed an "alloy analogy" in making his approximation. (He assumed that the opposite-spin electrons were instantaneously frozen into random configuration in considering the interaction between electrons.) It is now known (*23*) that this approximation is equivalent to the coherent potential approximation (CPA) that was independently developed later in the theory of random alloys (*24*). Hubbard's result is exact in both limits ($t_{ij} = 0$ and $U = 0$) but failed (*25*) to give a discontinuity in the single-particle momentum distribution function at the Fermi surface on the metallic side of the transition for finite U.

While Hubbard's approach was based on local concepts and perhaps treated the insulating side of the transition (*26*) better than the metallic side, Brinkman and Rice (*27*) studied the MNM transition in an approximation that emphasized correlations on the metallic side of the transition but gave a naive description of the insulating side of the transition. Their approach is based on the

variational scheme of Gutzwiller (*18*, *28*). Gutzwiller constructed a trial wave function that was based on the exact wave function for $U = 0$ (Bloch waves) but modified to distinguish the doubly occupied (polar) states in the usual Bloch wave construction. This scheme builds in the Fermi surface at the outset and describes the metallic state in terms of a single-particle momentum distribution function for which the discontinuity at the Fermi surface decreases with increasing U. Brinkman and Rice (*27*) applied Gutzwiller's (*28*) approach to the MNM transition in the half-filled band and found a critical value of U for which the discontinuity vanished. They also argued that the effective mass should diverge at the critical value of U. In this sense the MNM transition could be described in terms of a plasmon mode in the metallic state that becomes soft as the transition to the insulator is approached with increasing U.

With regard to the theories of Hubbard (*10*) and Brinkman and Rice (*27*) we note the following. Both predict a MNM transition in the one-dimensional ground state in contradiction to the exact result of Lieb and Wu (*20*). Hubbard (*10*) originally used a parabolic density of noninteracting states model, but Shiba and Pincus (*29*) showed that the MNM transition persists even if one used the appropriate density of states to the one-dimensional cosine band. The result of Brinkman and Rice (*27*) only depends on the average kinetic energy of a half-filled Bloch band and makes no further distinction with regard to dimension.

The MNM transition at finite temperature was studied in the context of a variational scheme (*30*) by Kaplan and Bari (*31*, *32*). This variational scheme (referred to here as the TSDA (*33*)), like the standard thermal Hartree–Fock variational scheme, is based on trial wavefunctions that are single Slater determinants. In the Hartree–Fock scheme the "trial Hamiltonian" is of the form

$$\tilde{H} = \sum_{\lambda} \varepsilon_{\lambda} n_{\lambda}$$

and the free energy

$$F(\rho) = \mathrm{Tr}\,\rho(H - \mu N) + kT\,\mathrm{Tr}\,\rho \ln \rho \geqslant F_{\mathrm{exact}}$$

is varied with respect to the one-electron energies, ε_{λ}, and the one-electron occupation number n_{λ}. Here H is given by Eq. (1) and ρ is the density operator appropriate to $\tilde{H}$. In the TSDA, $\tilde{H}$ is allowed to be an arbitrary function of the n_{λ}. This function and the single determinant wave functions are then varied to achieve stationarity of $F(\rho)$. Unlike the Hartree–Fock approximation, the TSDA gives the physics correctly for both limits of the Hubbard model. The Hartree–Fock approximation fails to give the thermodynamics of the zero-bandwidth limit correctly (*30*, *31*). In fact it predicts a spurious second-order phase transition at $kT = 1/4\ U$.

Kaplan and Bari (*31*, *32*) considered the stability boundaries between various thermodynamic phases, including magnetic and paramagnetic insulating states, a magnetic semiconducting state and a paramagnetic metal. Although they were not able (due to calculational difficulties) to completely determine the phase diagram for all of the trial states that they considered, the phase boundaries that they did obtain are of interest in connection with mechanisms for MNM transitions. Of particular interest is the phase boundary between the paramagnetic metal and the paramagnetic insulator (*32*) since it highlights the role of entropy as the driving mechanism for a metal to nonmetal transition with increasing temperature.

In Fig. 1, the phase boundary between these states is shown for (a) linear chain, (b) body-centered cubic, and (c) simple-cubic lattices. To the left of each boundary the phase is nonmetallic and to the right it is metallic. If, at $T = 0°\mathrm{K}$, the value of Δ/U is such that the energy of the metallic phase is slightly less than the insulating, it is seen from Fig. 1 that a transition to the nonmetallic phase will occur upon increasing temperature. (Here the rms bandwidth, Δ, is defined by $\Delta^2 = \sum_j t_{ij}^2$). This transition will be first order within the approximation scheme and occurs even in one dimension. It occurs even in the one-dimensional ground state, again in contradiction to the exact result of Lieb and Wu (*20*). The transition is easily understood from the facts that (a) the zero-temperature entropy per particle for the nonmetallic state is $k \ln 2$

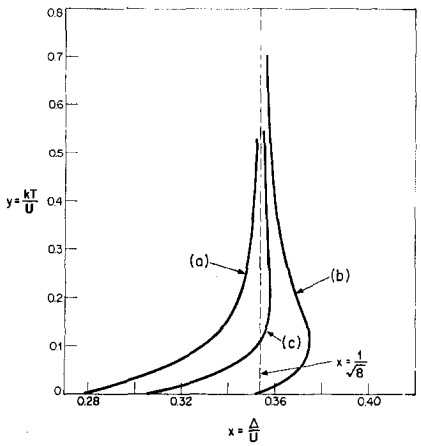

FIG. 1. Phase boundary between localized and extended states for (a) linear chain, (b) body-centered cubic, and (c) simple cubic.

(this state is described by $\tilde{H} = U \sum_i n_{i\uparrow} n_{i\downarrow}$) and for the metallic (Bloch) state it is zero, (b) the ground-state energy (per particle) difference $E_{\mathrm{M(etal)}} - E_{\mathrm{N(onmetal)}}$ decreases with increasing bandwidth (*34*). Thus, at low temperature, the free energies (per particle) of the metal F_{M} and nonmetal F_{N} are given by $F_{\mathrm{M}} = E_{\mathrm{M}} + 0\ (T^2)$ and $F_{\mathrm{N}} = E_{\mathrm{N}} - kT\ln 2$, respectively. Hence, on the phase boundary

$$\partial T/\partial \Delta = -1/(k \ln 2)\,(\partial)/(\partial \Delta)\,(E_{\mathrm{M}} - E_{\mathrm{N}}) > 0.$$

Kaplan and Bari (*32*) noted that this prediction for the phase transition is in qualitative disagreement with one due to Mott (*35*). Mott considered a transition metal from a magnetically ordered insulating state to a paramagnetic metal. In that case the entropy associated with the population of Bloch states ($\propto T$) exceeds the low-temperature entropy associated with the population of spin waves ($\propto T^3$, in three dimensions) in the magnetic insulator. Consequently, Mott obtained a phase boundary with opposite slope at low temperature.

We can compare the predictions of the various theories for the critical value of U/Δ for the paramagnetic MNM transition at zero temperature. In Table I we give the critical values of U/Δ for both the one and three-dimensional cases. The one-dimensional case is given for the simple cosine band for which the density of states is singular at the band

TABLE I

	1 dimension	3-dimensions
Hubbard	3.46	3.39
Brinkman and Rice	7.20	6.79
Kaplan and Bari	3.62	3.46
Exact	0	

edges. The three-dimensional case is given for the parabolic density of states used by Hubbard (*10*). We see that the prediction of Hubbard (*10*) and Kaplan and Bari (*31, 32*) are in close agreement in both one and three dimensions but that the prediction of Brinkham and Rice (*27*) differs by roughly a factor of two in both cases. Is the exact value of the critical U/Δ nonzero in three dimensions? Better approximation schemes would probably include magnetic correlations on both sides of the transition. In fact, in the scheme of Kaplan and Bari (*31*), which reduces to the Hartree–Fock approximation at $T = 0°\mathrm{K}$, a lower variational solution is found for all U/Δ, which is just Slater's (*8*) description of band antiferromagnetism. In one dimension, this solution will yield an insulating state for all $U/\Delta > 0$ and the ground state energy is in good agreement (*36*) with the exact result of Lieb and Wu (*20*).

Although it may not be relevant to oxides (for which $U \simeq 10\,\mathrm{eV}$) there has been discussion in recent years of a gradual metal–nonmetal transition (*13, 29, 37, 38*) in the narrow band regime ($U \gg \Delta$) of the Hubbard model at $kT \simeq 1/4\,U$. This is of particular interest in connection with experimental studies (*38*) of organic charge transfer salts based on the molecule tetracyanoquinodimethan (TCNQ). In such organic solids, $U \simeq .1$ eV and there can be real thermal effects associated with this energy.

Although the specific heat of the narrow-band Hubbard model exhibits a smooth maximum at $kT \simeq 1/5\,U$, perhaps suggestive of a "gradual" phase transition, Bari and Kaplan (*13*) noted that it would be unreasonable to regard the high-temperature regime ($kT \gtrsim 1/3\,U$) as a metal since, among other reasons, $kT \gg \Delta$ (since $U \gg \Delta$). In the high-temperature regime, the direct current is

carried by thermally induced doubly occupied sites and empty sites. They also noted that the fact that the temperature coefficient of the conductivity is negative (observed in most metals) was not sufficient to conclude that the high-temperature phase is metallic. They pointed out that this property is also shared with an ordinary two-band intrinsic semiconductor at temperatures comparable to the crystal structure energy gap.

III. The Spinless Fermion Model

In addition to being a model on which the MNM transition may be studied, the Hubbard model has occasioned much interest in the study of cooperative magnetic effects in itinerant-electron solids. This represents an additional richness and complication at the same time. A simpler model, devoid of spin, has been advocated by Kohn (*39*) for the purpose of studying just the MNM transition.

In the spinless Fermion model, one imagines a lattice of N nuclei, each with charge $+e/2$ and $N/2$ spinless electrons, each with charge $-e$. In the single-band model, only one electron is allowed on a site and in the absence of interactions the system is a half-filled band metal. Since there can be no intrasite interaction, the shortest range interaction is among nearest neighbors. The model can be written as

$$H = -t \sum_{\langle i,j \rangle} c_i^\dagger c_j + V \sum_{\langle i,j \rangle} n_i n_j, \qquad (2)$$

where $c_i^\dagger$ creates a spinless Fermion on the ith site and $n_i = c_i^\dagger c_i$. The brackets denote that the summation is restricted to nearest-neighbor i and j and we have also taken the one-electron hopping to be restricted to nearest neighbors as well.

Although the model may appear to be somewhat unrealistic, Callen and Cullen (*40*) pointed out that it is actually not an unreasonable model for the study of the Verwey transition in Fe_3O_4 (*41*). We see from Eq. (2), that in the limit $t = 0$, the ground state is just $N/2$ localized electrons segregated on one sublattice. Here it is assumed that the lattice can be divided into two sublattices such that all nearest-neighbor sites are on different sublattices. An ordering of this type can be taken to represent the Verwey ordering of Fe^{2+} and Fe^{3+} ions. Sokoloff (*42*), in fact, originally described the Verwey transition (in a mean-field approximation) in terms of Eq. (2) with $t = 0$ by noting that the Hamiltonian is then equivalent to a spin-$\frac{1}{2}$ Ising antiferromagnet. The transformation to spins is given by $S_i^z = n_{i-\frac{1}{2}}$.

Thus, unlike the Hubbard model, the spinless Fermion model can exhibit a phase transition (in two dimensions and higher), as a function of temperature, in the zero-bandwidth limit. Callen and Cullen (*40*) studied Eq. (2) in the (broken symmetry) Hartree–Fock approximation and found an insulating ground state described in terms of a charge–density-wave. In the one-dimensional model, they found that the ground state is insulating for all $V/t > 0$.

In one dimension, Eq. (2) has a very interesting feature. In addition to the fact that the interaction term can be simply represented by an Ising Hamiltonian, the hopping term (in one dimension and with nearest-neighbor coupling) can be represented by the spin-$\frac{1}{2}$ XY model (*43*). As a consequence Eq. (2) is equivalent (in one dimension only) to the anisotropic Heisenberg–Ising model. Apart from an additive constant, Eq. (2) is given by

$$H = J_\perp \sum_i (s_i^x s_{i+1}^x + s_i^y s_{i+1}^y) + J_\parallel \sum_i s_i^z s_{i+1}^z + J_\parallel \sum_i s_i^z. \qquad (3)$$

Here $J_\perp \equiv 2t$ and $J_\parallel \equiv 2V$. The last term in Eq. (3), which represents a uniform magnetic field in the z direction of spin, is apart from an additive constant, the chemical potential times the total number operator (μN) for the half-filled band.

In the context of the Heisenberg–Ising model the ground state energy and low-lying excitations of $H-\mu N$ have been exactly determined (*44*). The interesting results are the following. For $J_\parallel > J_\perp$ there is a gap in the excitation spectrum which vanishes as $J_\parallel \to J_\perp$. Des Cloizeaux noted (*14*) that in terms of the spinless Fermion representation, this is a gap in the one-electron excitation spectrum and represents an insulator to metal transition

at $t = V$. Thus, the ground state of the one-dimensional spinless Fermion Hamiltonian is the only nontrivial model that rigorously exhibits a MNM transition! Des Cloizeaux (*14*) also noted that since the ground state energy is an analytic function of V/t on either side of the transition, perturbation theory is valid. He also explicitly verified the validity of the Landau theory of the Fermi liquid on the metallic side of the transition. It is also interesting to note that the Hartree–Fock charge–density-wave description of Eq. (2) yields a ground state energy that is in good quantitative agreement (*14*) with the exact result for all V/t; however, there is a qualitative disagreement for $V/t < 1$ because the (lowest energy) Hartree–Fock solution predicts insulating behavior in that regime. In comparison, the spin–density-wave Hartree–Fock description of the half-filled band Hubbard model appears to give both qualitative and quantitative agreement (*36*) with the exact result (*20*) for all U/t.

In summary, the spinless Fermion model is a system, not unrelated to real materials (*45*), for which it is known that a MNM transition exists. Consequently, it provides a starting point for further understanding of MNM transitions due to electron correlation.

IV. Lattice Distortion Models

Peierls (*15*) showed that a one-dimensional band would be unstable to a distortion that increases the size of the unit cell when an (arbitrarily weak) electron–phonon interaction is taken into account. He argued that this system would be an insulator because the occupied one-electron states would be split off from the unoccupied states because of the introduction of a gap in the one-electron energy spectrum due to the electron–phonon perturbation. He predicted that the fractional reduction of the Brillouin zone would correspond to the fractional filling of the energy band, e.g., the Brillouin zone would be halved for an originally half-filled band.

Although he had intended it to be an explanation of the as then yet not understood phenomenon of superconductivity, Frohlich (*46*) gave a quite detailed microscopic description of the instability that Peierls (*15*) had in mind. Frohlich started from the Hamiltonian

$$H = H_o + \sum_{q,k} g_q(a_q + a_q^+)\, c_{k+q}^+ c_k, \qquad (4)$$

where H_o is the one-electron band Hamiltonian plus the free-phonon Hamiltonian. g_q is the electron–phonon coupling constant and a_q destroys a phonon with wavevector q and c_k destroys an electron with wavevector k. We have suppressed the spin index for brevity. Frohlich singled out the phonon mode that corresponds to $q = 2k_F$, twice the Fermi wavevector, and treated it as a macroscopic parameter ($\propto (N)^{\frac{1}{2}}$). This led, through the electron–phonon interaction to the mixing of degenerate states across the Fermi surface and a consequent splitting of this degeneracy in the reduced zone scheme. For the half-filled band $2k_F$ corresponds to the zone-boundary phonon and the crystallographic distortion can be described in terms of a macroscopic occupation of the zone-boundary phonon mode. This theory was extended to finite temperature by Kuper (*47*), who showed that the distortion (and electronic energy gap) vanishes at a second-order, mean-field transition temperature.

In order to explain the insulating behavior of certain transition-metal oxides, Goodenough (*48*) proposed a covalent-type bond formation between cation pairs. He noted that cation pair cluster formation introduced the required changes in the translation symmetry of the crystal and the spin pairing of the trapped bonding electrons gave rise to a magnetic singlet state. Subsequently, Goodenough (*49*) gave a more quantitative description of this state starting from the one-dimensional band model.

Adler and Brooks (*50*) started from the one-dimensional Kronig–Penney model and showed that a lattice distortion that doubled the unit cell could give rise to an insulating state provided the gain in electronic energy exceeded the loss of elastic energy upon such a distortion and they found this to be most favorable in very narrow bands. They examined the thermodynamics of the crystallographic phase transition in detail and con-

cluded, under the assumption that the energy subbands (of the lower symmetry phase) were spherical around the valence and conduction band edges, that the phase transition would be of first order. On the other hand, Mattis and Langer (*51*), starting from a description similar to that of Refs. (*46*) and (*47*), found that the transition would be second order for the simple-cubic and body-centered-cubic tight binding band structures. They also discussed how the order of the transition would be changed (to first order) as a result of deviations from the above band structures.

The role of electron–electron interactions in a crystalline distortion that involves a splitting of the electronic energy band was considered by Zinamon and Mott (*7*) and also by Goodenough (*5*). These authors suggested that in the presence of Hubbard's (*9*) intrasite electron–electron repulsion, a distorted phase would not occur if U were sufficiently large compared to the band (bonding–antibonding) splitting that is induced by the crystalline distortion. The distorted state would be quenched and the system would be a Mott insulator with electrons localized one per site. On the other hand Rice, McWhan, and Brinkman (*52*) argued that the distorted phase would compete favorably with the Mott insulator even for very large values of U. Their reasoning is based on the fact that lowering of energy due to correlations in a bonded (singlet) pair has the same origin as the antiferromagnetic exchange splitting in the Mott insulator. Furthermore, the distortion of the bonded pair would lead, since the lowering of electronic energy is linear in the distortion and the raising of elastic energy is quadratic in the distortion, to the possibility of the distorted phase being preferred over the Mott insulator.

We also note that Bari (*53*) constructed a lattice-distortion model, in which the Bloch energy term in Eq. (4) is replaced by the interaction term of the Hubbard model. He also included the nearest-neighbor intersite Coulomb integral as well. Bari found that a distorted phase could occur and that the phase (semiconductor-to-semiconductor) transition to the undistorted (Mott insulator) phase could be first or second order, depending on the parameters. The distorted phase was obtained only for values of U less than a critical value. This quenching of the distorted state is consistent with the arguments presented by Zinamon and Mott (*7*) and Goodenough (*5*). It is interesting to note however that the structure of the distorted state (at zero bandwidth) is that of $N/2$ doubly occupied sites on one sublattice. Thus, although this state forms a spin singlet it is not of the same structure of the bonded state discussed in Refs. (*48*) and (*52*). In order to illustrate the difference, consider a two-site two-electron model with zero bandwidth. The states

$$|a> = (c_{1\uparrow}^{\dagger} c_{2\downarrow}^{\dagger} - c_{1\downarrow}^{\dagger} c_{2\uparrow}^{\dagger})|0>$$

and

$$|b> = (c_{1\uparrow}^{\dagger} c_{1\downarrow}^{\dagger} + c_{2\uparrow}^{\dagger} c_{2\downarrow}^{\dagger})|0>$$

are both singlets in the sense that they are eigenstates of s^2 (total) and of s^z (total) with eigenvalue zero in each case. State $|a>$ is the limiting form, as $t_{ij} \to 0$, of the bonding state discussed by Goodenough (*5*) (it is also, within the single band, the limiting form of the ground state wave function of the H_2 molecule). State $|b>$, although also a singlet state, is a polar state and requires an energy U for formation. In terms of these states, then, it is clear why Bari's (*53*) charge-ordered-state must form at the expense of U; however, it is less clear why, if Zinamon and Mott (*7*) and Goodenough (*5*) are describing a single state based on $|a>$, the criteria suggested by them should apply.

The charge-ordered-state discussed by Bari (*53*) is a consequence of the assumed form of the electron–phonon interaction. Bari started with the interaction given by Eq. (4); in Wannier-site representation this can be rewritten as

$$H_{\text{int}} = \sum_{q,l} g_q (a_q + a_q^{\dagger}) e^{iqR_l} n_l. \qquad (5)$$

If the zone boundary mode is singled out, then Eq. (5) represents an external staggered potential (in the linear chain take $q = \pi/a$) with spatial dependence $\exp\{i\pi R_l/a\}$. This potential will favor segregation of electrons onto one sublattice (at the expense of U). Mitra (*55*) and Barisic (*56*) have discussed the form of the electron–phonon interaction

in the narrow-band regime. They argued that in addition to Eq. (5), a site nondiagonal (in electron operators) term would arise from the modulation of the one-electron hopping integrals in a vibrating lattice. These terms should be taken into account in order to obtain the description of the nonpolar singlet.

Finally, we consider the role of a soft phonon in a crystalline distortion involving the rearrangement of electronic energy states. In the weak-coupling regime, the renormalization of the phonon frequencies due to the coupling to electrons is given by (*57*)

$$\omega_q^2 = \Omega_q^2 + 2\Omega_q |g_q|^2 \chi(q, \omega_q). \qquad (6)$$

Here Ω_q and ω_q are the unrenormalized and renormalized phonon frequencies, respectively, and $\chi(q,\omega_q)$ is the density response function (*57*) of the electron system. For tight-binding band structures such that $\varepsilon(k) = -\varepsilon(k+Q)$ for some Q and all k, the response function for wavevector Q becomes large and negative as T decreases from high temperatures. If at some temperature, T_c, the second term in Eq. (6) exactly cancels the first term the renormalized phonon mode of wavevector Q softens to zero, and the lattice structure becomes unstable.

This description of softening of the phonon in the higher temperature phase is based on the time-dependent Hartree–Fock approximation. The description of the distorted phase in the mean field (Hartree–Fock) approximation (*46*, *47*) is then the *stable* Hartree–Fock solution below T_c. Thus, within the Hartree–Fock approximation the phonon softening in the high-temperature phase and the description of the distorted low-temperature phase are two aspects of the generalized Hartree–Fock description of an instability.

Although the dynamical softening of a lattice mode would certainly favor an instability of the lattice, it is not a necessary condition for achieving a distorted phase. In the zero-bandwith case, the distorted phase can be achieved without any dynamical softening of the phonon modes at all. As can be seen from the description given by Bari (*53*), the displaced oscillator transformation does not effect phonon frequencies, and the phase transition is achieved as a result of the lowering of one-electron energy against the raising of elastic energy required for the distortion. Of course if the elastic constant becomes smaller this will certainly favor the transition, but this need not be a necessary condition for the transition to occur.

V. Remarks

We have reviewed some mechanisms for MNM transitions in the oxides. We offer an apology in advance for any work that was inadvertently missed in connection with the topics discussed.

We have not discussed polaronic effects at all; hopefully a review will be given by Emin (*58*) in these Proceedings. Zinamon and Mott (*7*) have emphasized the concept of strong correlations on the "metallic" side of the MNM transition and have stressed the importance of small polaron effects in some materials. Brinkman and Rice (*27*) were the first to emphasize strong correlations due to the electron–electron interaction in the metallic regime.

There has been much interest recently in the Peierls transition in pseudo-one-dimensional solids (*16*, *17*). We also note the recent neutron scattering work on NbO_2 (*59*) in which a soft excitation has been observed from above the transition (in the rutile phase) to the distorted structure in which niobium ions pair along the *c*-axis.

In regard to model analysis, we have shown that for each model considered here, particular care must be taken in applying Hartree–Fock or mean theory to the models themselves, especially when the interactions are short-ranged (*13*, *14*, *60*).

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