

discussed.

II. HAMILTONIAN AND CANONICAL TRANSFORMATION

We shall work in the zero-overlap limit for a single band. In this case the Hamiltonian does not contain any hopping integrals and the only part of the Coulomb interaction that is retained is

$$H_c = \frac{1}{2} \sum_{i,j} U_{ij} (n_{i\uparrow} + n_{i\downarrow}) (n_{j\uparrow} + n_{j\downarrow}), \quad (2.1)$$

where $n_{i\uparrow}$ is the occupation number for an electron on Wannier site i and spin \uparrow . U_{ij} is the long-range Coulomb integral given by

$$U_{ij} = \iint d\vec{r} d\vec{r}' \frac{e^2}{|\vec{r} - \vec{r}'|} \omega^2(\vec{r} - \vec{R}_i) \omega^2(\vec{r}' - \vec{R}_j), \quad (2.2)$$

with $\omega(\vec{r} - \vec{R}_i)$ a Wannier function.

It has been rigorously shown¹⁰ that the minimum-energy eigenstate of H_c has the one-electron-per-site charge configuration when the number of electrons is equal to the number of sites. We shall refer to this state as the Mott insulating state.⁶

We shall now allow the atoms to undergo small vibrations about their equilibrium positions such that the zero-overlap limit still obtains. The vibrational energy is described by the Hamiltonian $H_L = \sum_q \omega_q a_q^\dagger a_q$, where a_q is a phonon destruction operator of wave vector q and ω_q is the energy of the mode of wave vector q . The electron-lattice interaction is derived (see Appendix A) by assuming the usual first-order displacement of the atoms from their equilibrium positions and this leads to the interaction term

$$H_I = \sum_{\vec{q}, i} V_{\vec{q}} (a_{\vec{q}} e^{i\vec{q} \cdot \vec{R}_i} - a_{\vec{q}}^\dagger e^{-i\vec{q} \cdot \vec{R}_i}) (n_{i\uparrow} + n_{i\downarrow}), \quad (2.3)$$

where $V_{\vec{q}}$ is the electron-lattice matrix element. The total Hamiltonian is then $H = H_c + H_L + H_I$.

The electrons and lattice can be decoupled by the familiar (displaced-oscillator) canonical transformation

$$\begin{aligned} b_{\vec{q}}^\dagger &= e^S a_{\vec{q}}^\dagger e^{-S}, \\ \bar{n}_{i\uparrow} &= e^S n_{i\uparrow} e^{-S}, \end{aligned} \quad (2.4)$$

where

$$S = \sum_{\vec{q}, i} \frac{V_{\vec{q}}}{\omega_{\vec{q}}} (a_{\vec{q}} e^{i\vec{q} \cdot \vec{R}_i} + a_{\vec{q}}^\dagger e^{-i\vec{q} \cdot \vec{R}_i}) (n_{i\uparrow} + n_{i\downarrow}). \quad (2.5)$$

This works out simply to be

$$\begin{aligned} b_{\vec{q}}^\dagger &= a_{\vec{q}}^\dagger + (V_{\vec{q}}/\omega_{\vec{q}}) \sum_i e^{i\vec{q} \cdot \vec{R}_i} (n_{i\uparrow} + n_{i\downarrow}), \\ \bar{n}_{i\uparrow} &= n_{i\uparrow}. \end{aligned} \quad (2.6)$$

The transformed Hamiltonian is given by

$$H = \frac{1}{2} \sum_{i,j} (U_{ij} - 2V_{ij}) (n_{i\uparrow} + n_{i\downarrow}) (n_{j\uparrow} + n_{j\downarrow}) + \sum_{\vec{q}} \omega_{\vec{q}} b_{\vec{q}}^\dagger b_{\vec{q}}, \quad (2.7)$$

where

$$V_{ij} \equiv \sum_{\vec{q}} (|V_{\vec{q}}|^2 \omega_{\vec{q}}) e^{i\vec{q} \cdot (\vec{R}_i - \vec{R}_j)}. \quad (2.8)$$

The electron-lattice interaction has been replaced by a long-range electron-electron interaction with matrix elements V_{ij} . In this representation the eigenstates of H are seen to be products of free-phonon wave functions with single Slater determinants of Wannier functions. The partition function is also a product of a phonon contribution and an electron contribution but, although the eigenstates are known, the evaluation of the partition function for the electronic part is nontrivial for general $W_{ij} \equiv \frac{1}{2} U_{ij} - V_{ij}$. Furthermore, the charge configuration of the ground state with interactions described by W_{ij} will not necessarily be that of the Mott state and will depend on the behavior of V_{ij} .

The general W_{ij} will exhibit a long-range behavior but we can expect that the terms with $i=j$ and i,j nearest neighbors will be the largest. Furthermore, in a real system, the long-range tail of the Coulomb interaction is screened by the presence of core and band electrons in the other occupied bands. In order to keep the mathematical analysis simple and to the extent that the further neighbor interactions do not qualitatively change our results and can be ignored, we make the simplifying ansatz that $W_{ij} = \frac{1}{2} I \delta_{ij} + W f_{ij}$, where $f_{ij} = \frac{1}{2}$ for i,j nearest neighbors and $f_{ij} = 0$ otherwise. Here $I = U_0 - 2V_0$ and $W = U_1 - 2V_1$. Hubbard⁷ has estimated that the (unscreened) values of U_0 and U_1 are 20 and 6 eV, respectively, for 3d electrons in transition metals. In the localized regime it is reasonable to expect that I and W are positive (contrary to the usual assumptions made in superconductivity theory).

The electron part of the Hamiltonian can now be written as

$$\begin{aligned} H_e &= I \sum_i n_{i\uparrow} n_{i\downarrow} + W \sum_{i,j} f_{ij} (n_{i\uparrow} + n_{i\downarrow}) (n_{j\uparrow} + n_{j\downarrow}) \\ &\quad + \frac{1}{2} I \sum_i (n_{i\uparrow} + n_{i\downarrow}). \end{aligned} \quad (2.9)$$

The third term represents a constant shift of the energy levels and shall be disregarded in what follows. All further analysis in this paper will be with the specific form H_e and not the more general Eq. (2.7).

When the number of electrons is equal to the number of sites, the first and second terms of H_e separately describe quite different ground states. The ground state Φ_1 of the first term alone has the Mott-state charge configuration. However, for the second term alone, the ground state Φ_2 would have half the sites unoccupied (we assume a lattice in which the z nearest neighbors of any given site lie on a different sublattice). In Appendix B it is rigorously shown that for all $zW < I$, Φ_1 is the ground state of H_e and for all $zW > I$, Φ_2 is the ground state. Furthermore, the ground-state entropy is $Nk \ln 2$

for Φ_1 , whereas it is zero for Φ_2 . It seems possible then that the system described by H_e will exhibit a phase transition¹¹ as a function of temperature for some $zW > I$. In Secs. III and IV we explore this possibility via approximation schemes to H_e .

III. HARTREE-FOCK THEORY

As a first attempt at describing this phase transition we employ the well-known technique of the broken-symmetry Hartree-Fock approximation. In this case we shall look for a solution in which the thermal average of the electron occupancy is not translationally invariant. We specifically assume that $\langle n_i \rangle \neq \langle n_j \rangle$ for i on sublattice A and j on sublattice B and, otherwise, translational invariance within each sublattice.

It is convenient to introduce two-time Green's functions of the form $-i\langle (A(t)B(t'))_+ \rangle$, in which $()_+$ is the fermion time-ordering symbol and $\langle \rangle$ denotes the thermal average. Let $G_A(\omega)$ represent the Fourier transform of $-i\langle (c_{i\sigma}(t)c_{i\sigma}^\dagger(t'))_+ \rangle$ when i is on sublattice A and $c_{i\sigma}^\dagger$ is a fermion creation operator. We use the Heisenberg equation of motion for $c_{i\sigma}$ and then approximate $\langle (n_{j\sigma'}(t)c_{i\sigma}(t)c_{i\sigma}^\dagger(t'))_+ \rangle$ by $\langle n_{j\sigma'} \rangle \langle (c_{i\sigma}(t)c_{i\sigma}^\dagger(t'))_+ \rangle$ for j, σ' in the equation of motion for $-i\langle (c_{i\sigma}(t)c_{i\sigma}^\dagger(t'))_+ \rangle$. This leads to

$$(\omega - I\langle n_A \rangle - 2zW\langle n_B \rangle)G_A(\omega) = 1 \quad (3.1)$$

and, similarly for $G_B(\omega)$,

$$(\omega - I\langle n_B \rangle - 2zW\langle n_A \rangle)G_B(\omega) = 1. \quad (3.2)$$

Since the system is spin invariant we have suppressed spin indices wherever ambiguities do not arise. The number occupancies $\langle n_A \rangle$ and $\langle n_B \rangle$ on each sublattice can be obtained self-consistently from $G_A(\omega)$ and $G_B(\omega)$ in the standard fashion

$$\langle n_A \rangle = i \int (d\omega/2\pi) f(\omega) [G_A(\omega + i0) - G_A(\omega - i0)]; \quad (3.3)$$

here $f(\omega) = (e^{\beta(\omega - \mu)} + 1)^{-1}$. The chemical potential μ is determined by the number condition $\langle n_A \rangle + \langle n_B \rangle = 1$. It is easy to see that the number condition is satisfied by $\mu = \frac{1}{2}(I + 2zW)$. In order to determine the number occupancies on sublattices A and B it is convenient to define an order parameter which is the difference between the poles (single-particle energies) of $G_A(\omega)$ and $G_B(\omega)$. If we define $\Delta \equiv (2zW - I)(\langle n_B \rangle - \langle n_A \rangle)$, then from Eq. (3.3) and μ we get the familiar (from mean-field theories) form

$$\Delta = (2zW - I) \tanh \frac{1}{4} \beta \Delta \quad (3.4)$$

which is the self-consistency condition for Δ . If $2zW < I$, then the only self-consistent solution is $\Delta = 0$, and therefore $\langle n_A \rangle = \langle n_B \rangle$, i.e., the Mott state. For $2zW > I$, a solution $\Delta \neq 0$ is found for $kT (=1/\beta) \leq kT_c$, where $kT_c = \frac{1}{4}(2zW - I)$ is the critical tem-

perature above which $\langle n_A \rangle = \langle n_B \rangle$. The phase transition is, of course, second order.

This approximation, although simple, serves to (a) establish the notation and (b) illustrate that the effective nearest-neighbor energy which is to be compared with I is zW and not just W . Thus, for a bcc lattice, I can be almost an order of magnitude larger than W and yet it is possible that the nearest-neighbor interaction can determine the charge configuration at low enough temperatures.

One obvious way to improve this Hartree-Fock treatment is to break the spin symmetry and therefore give a better description of the intra-atom correlations. However, it has been pointed out¹² that even this improvement fails to give the thermodynamics correctly for the intra-atomic interaction. It is desirable to have a better treatment of (at least) the intra-atomic interactions since they play a fundamental role in determining the physical characteristics of the localized state.

IV. MODIFIED HARTREE-FOCK THEORY

The intra-atomic correlations can be treated exactly by employing a technique first used by Hubbard.⁷ For $W=0$ the Green's-function equation of motion for $-i\langle (n_{i\sigma}(t)c_{i\sigma}(t)c_{i\sigma}^\dagger(t'))_+ \rangle$ closes because $n_{i\sigma}^2 = n_{i\sigma}$. It is this fact that allows a closed exact solution for $G_A(\omega)$ for $W=0$. Our strategy is to make our approximation in terms that vanish as $W \rightarrow 0$. In these terms, which involve correlation between electrons on different sites, we employ a Hartree-Fock type of truncation similar to that in Sec. III.

In a straightforward fashion the decoupled equations of motion are

$$(\omega - 2zW\langle n_B \rangle)G_A(\omega) = 1 + I\Gamma_A(\omega), \quad (4.1)$$

$$(\omega - I - 2zW\langle n_B \rangle)\Gamma_A(\omega) = \langle n_A \rangle; \quad (4.2)$$

$\Gamma_A(\omega)$ is the Fourier transform of $-i\langle (n_{i\sigma}(t)c_{i\sigma}(t) \times c_{i\sigma}^\dagger(t'))_+ \rangle$. After eliminating $\Gamma_A(\omega)$ between Eqs. (4.1) and (4.2) we obtain

$$G_A(\omega) = \frac{1 - n_A}{\omega - \epsilon_A} + \frac{n_A}{\omega - I - \epsilon_A}, \quad (4.3)$$

where $\epsilon_A = 2zW\langle n_B \rangle$.

The number condition is, using Eqs. (3.3) and (4.3),

$$n_A + n_B = 1 = (1 - n_A)[(e^{\beta(\epsilon_A - \mu)} + 1)^{-1} + (e^{\beta(\epsilon_B + I - \mu)} + 1)^{-1}] + n_A[(e^{\beta(\epsilon_A + I - \mu)} + 1)^{-1} + (e^{\beta(\epsilon_B - \mu)} + 1)^{-1}]. \quad (4.4)$$

This condition is self-consistently satisfied by

$$\mu = \frac{1}{2}(I + \epsilon_A + \epsilon_B) = \frac{1}{2}(I + 2zW)$$

(the same value obtained in Hartree-Fock theory). We define an order parameter as $\Delta \equiv \epsilon_A - \epsilon_B$ and straightforwardly obtained the condition

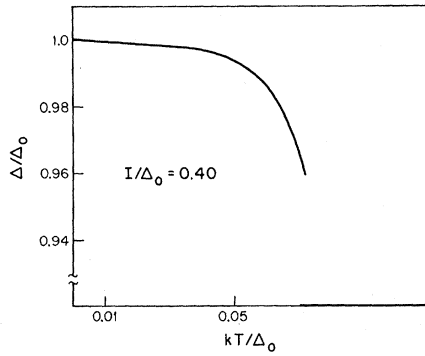


FIG. 3. Gap parameter shows a jump discontinuity (for $I/\Delta_0 = 0.40$) at $kT/\Delta_0 = 0.07$; for $kT/\Delta_0 > 0.07$, $\Delta = 0$.

determined by Eq. (4.3). Each sublattice energy level is split into two quasilevels separated by an energy I . As is illustrated in Fig. 4, in order to have the two sublattices unequally populated, both of the quasilevels on the A sublattice must be occupied. When the gap parameter Δ decreases to I , the lower quasilevel on sublattice B is energetically equal to the upper quasilevel on sublattice A – thereby giving rise to an abrupt population of the B sublattice. Since the gap parameter and differential occupancy are self-consistently determined, a finite value of the gap parameter cannot be maintained and it falls discontinuously to zero.

The charge ordering of the electrons has implications for the lattice degrees of freedom as well. One important consequence is that there is a lattice distortion at the transition from the Mott state to the charge-ordered state. To see this we calculate the deviation of the cation equilibrium position that results from the electron-lattice interaction. In Appendix A we defined this deviation to be

$$\delta \vec{R}_i = \sum_{\vec{q}} \vec{f}_{\vec{q}} (a_{\vec{q}} e^{i\vec{q} \cdot \vec{R}_i} - a_{\vec{q}}^\dagger e^{-i\vec{q} \cdot \vec{R}_i}).$$

We now substitute Eq. (2.6) into this expression and take its thermal average in the presence of the electron-lattice interaction. This gives

$$\langle \delta \vec{R}_i \rangle = 2 \sum_{j, \sigma} \langle n_{j\sigma} \rangle \sum_{\vec{q}} \vec{f}_{\vec{q}} \frac{V_{\vec{q}}}{\omega_{\vec{q}}} \cos[\vec{q} \cdot (\vec{R}_i - \vec{R}_j)]. \quad (4.9)$$

It is easy to see that

$$\langle \delta \vec{R}_{i+l} \rangle = 2 \sum_{j, \sigma} \langle n_{j+l, \sigma} \rangle \sum_{\vec{q}} \vec{f}_{\vec{q}} \frac{V_{\vec{q}}}{\omega_{\vec{q}}} \cos[\vec{q} \cdot (\vec{R}_i - \vec{R}_j)], \quad (4.10)$$

where l corresponds to any lattice translation, i.e., $\vec{R}_{i+l} = \vec{R}_i + \vec{R}_l$.

In the Mott state, which is translationally invariant, it is easily verified from Eqs. (4.9) and (4.10) that $\langle \delta \vec{R}_i \rangle$ is independent of i ; we call this quantity $\langle \delta \vec{R} \rangle_M$. In the charge-ordered state we still have translation invariance within each sublattice and it is easily verified from Eqs. (4.9) and (4.10) that $\langle \delta \vec{R}_i \rangle_c = \langle \delta \vec{R}_j \rangle_c$ for i and j on the same sublattice (the

subscript c denotes the charged-ordered state). If i and j are on different sublattices it is easy to show that $\langle \delta \vec{R}_i \rangle_c - \langle \delta \vec{R}_j \rangle_c$ is proportional to the gap parameter in Eq. (4.7). Furthermore, it follows from Eq. (4.4) that $\langle \delta \vec{R}_i \rangle_c + \langle \delta \vec{R}_j \rangle_c = 2\langle \delta \vec{R} \rangle_M$. The deviation of the equilibrium position of the i th cation relative to that in the Mott state is $\vec{D}_i \equiv \langle \delta \vec{R}_i \rangle_c - \langle \delta \vec{R} \rangle_M$. This gives $\vec{D}_i = -\vec{D}_j$. These results imply that there is a distortion of the original lattice to a situation in which all the cations on sublattice A are equally displaced from all of those on sublattice B . Consequently, the lattice symmetry is lowered since the periodicity of the lattice is doubled. We expected this distortion in the charge-ordered state since the cations must adjust their positions to minimize the potential energy.

V. DISCUSSION

We have shown that within our assumptions concerning the nature of the electron-lattice coupling a Mott insulator is thermodynamically unstable to a charge-ordered insulating state below a certain temperature and for some values of the interaction parameters. By treating the thermodynamic state in an approximation which handles the intra-atomic interaction exactly, we have shown that the phase transition will be either first or second order – depending on the parameters.

We have also shown that the charge-ordered state is accompanied by a distortion of the crystal lattice to lower translational symmetry. It is expected from general physical considerations that a spatially distorted electronic state is accompanied by a distortion of the cationic positions as well. Adler and Brooks⁹ found this to be true in a band model of electrons in which electron correlations were not taken into account. It has been argued^{5,13} that it is important to take electron correlations into account in bands that are sufficiently narrow to sustain a spontaneous lattice distortion of the type that Goodenough⁸ and Adler and Brooks⁹ had discussed. It is expected that the charge-ordered state will be quenched if the electron correlations are sufficiently large compared to the loss of elas-

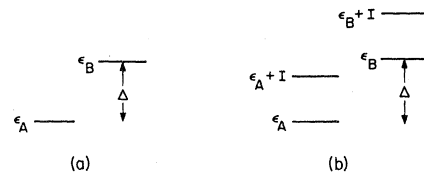


FIG. 4. Single-particle energy levels on sublattices A and B in relation to the gap parameter is shown in (a) the Hartree-Fock theory and (b) the modified Hartree-Fock approach. In case (b) the levels on a given sublattice are split into two quasilevels separated by energy I .

