PHYSICAL REVIEW B VOLUME 3, NUMBER 8 15 APRIL 1971

Effects of Short-Range Interactions on Electron-Charge Ordering and Lattice Distortions in the Localized State*

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(Received 26 October 1970)

We investigate the role of electron-lattice interactions in a very narrow half-filled band that would otherwise be described as a Mott insulator. A simple Hamiltonian is presented that incorporates the electron-electron and electron-lattice interactions in the zero-overlap limit. A canonical transformation decouples the electron and lattice systems and we assume that the effective electron-electron interaction is short ranged. It is found that, within an approximation that treats intra-atomic correlations exactly, the Mott insulator can undergo a phase transition to a quite different insulating state as the temperature is lowered. This insulating state is characterized by a charge-density wave in which alternate atomic sites are doubly occupied as opposed to the usual one-electron-per-atom configuration in the Mott state. The phase transition will be either first or second order, depending on the electron-lattice coupling strength. Accompanying the charge-ordered state is a distortion of the crystal lattice that lowers its translational symmetry.

I. INTRODUCTION

The transition-metal and rare-earth compounds contain among them a large group of materials that have been classified as narrow-band insulators. These are materials in which the cation sublattice has partially filled *d* or *f* shells and would exhibit metallic behavior in a description based on ordinary band theory. The low-temperature insulating behavior of these materials has generally been attributed to electron-correlation effects, with or without magnetism, and the interaction of the electrons with the crystal lattice. Rather than systematically reviewing each model or theory that attempts to describe this insulating behavior, we refer the reader to the many reviews[1-5] of this subject that have appeared by now. Instead, we briefly mention those models that have some bearing on the contents of this paper.

Mott[6] argued that electron correlations can give rise to an insulating state in a partially filled band containing an integral number of electrons per cation site. Hubbard[7] presented a single-band or cell model of a crystal that, for a half-filled band, behaved as a metal in the limit of zero correlation energy and behaved as an insulator at zero bandwidth, with each site or cell singly occupied by an electron. In this paper this type of insulator shall be referred to as a Mott insulator.

In order to explain the insulating behavior of certain transition-metal oxides, Goodenough[8] proposed that occupied states of a narrow cation-sublattice band may be split from unoccupied states by the formation of cation clusters, cluster formation introducing the required changes in the translational symmetry of the crystal.

Adler and Brooks[9] started from an itinerant band model of electrons 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 found this to be most favorable in very narrow bands. In this model electron correlations, which are expected to be most important in narrower bands, are ignored.

In this paper we investigate the role of electron-lattice interactions in a very narrow half-filled band that would otherwise be described as a Mott insulator. We present a simple Hamiltonian that describes the electron Coulomb interaction in the zero-overlap limit plus the coupling of these electrons to a lattice system described in the harmonic approximation. The system is treated strictly as a cell model. The electron and lattice systems are formally decoupled via a canonical transformation and after making the assumption that the effective electron-electron interaction is short ranged we analyze the thermodynamics of the decoupled electronic system. It is found that this system can undergo a phase transition from a Mott insulating state to a charge-ordered insulating state as the temperature is lowered, depending on certain parameters relating to the coupling strength. The charge-ordered state is characterized by a ground state in which alternate Wannier sites are doubly occupied. We find that, within an approximation that treats intrasite correlations exactly, the phase transition can be either first or second order, depending on the coupling strength. We also show that the charge-ordered state has an associated lattice distortion that doubles the translational periodicity of the crystal. The effect of finite overlap is briefly 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

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

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

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

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

It has been rigorously shown[10] 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

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

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

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

where

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

This works out simply to be

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

The transformed Hamiltonian is given by

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

where

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

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 $W = U_1 - 2V_1$. Hubbard[7] 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

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

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 transition[11] 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 $-i\langle (c_{i\sigma}(t)c^\dagger_{i\sigma}(t'))_+ \rangle$ when i is on sublattice A and $c^\dagger_{i\sigma}$ is a fermion creation operator. We use the Heisenberg equation of motion for $c_{i\sigma}$ and then approximate $\langle (n_{j\sigma'}(t)c_{i\sigma}(t)c^\dagger_{i\sigma} \times (t'))_+ \rangle$ by $\langle n_{j\sigma'} \rangle \langle (c_{i\sigma}(t)c^\dagger_{i\sigma}(t'))_+ \rangle$ for j, σ' in the equation of motion for $-i\langle (c_{i\sigma}(t)c^\dagger_{i\sigma}(t'))_+ \rangle$. This leads to

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

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

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

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

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

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

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

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 temperature 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 out[12] 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 $-i\langle (n_{i-\sigma}(t)c_{i\sigma}(t)c^\dagger_{i\sigma}(t'))_+ \rangle$ closes because $n^2_{i\sigma} = n_{i\sigma}$. 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 $W \to 0$. 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

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

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

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

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

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

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

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

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

This condition is self-consistently satisfied by

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

(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

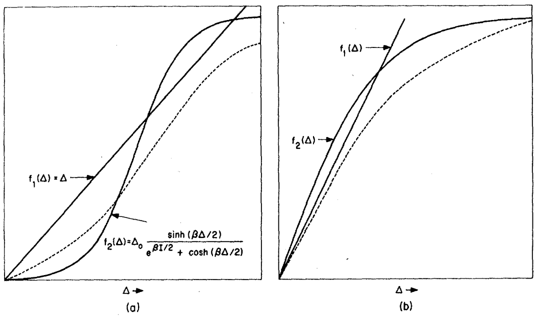

FIG. 1. Solutions of Eq. (4.7) are shown graphically as the intersection of two curves that correspond to the two sides of the equation for the cases (a) $\beta I > 2\ln 2$ and (b) $\beta I < 2\ln 2$. At elevated temperatures the only solution is $\Delta = 0$, as is indicated by the dotted curves which represent the right-hand side of Eq. (4.7).

$$\Delta = 2zW[n_A \tanh\tfrac{1}{4}\beta(I+\Delta) + (1-n_A)\tanh\tfrac{1}{4}\beta(\Delta - I)] \; . \tag{4.5}$$

In terms of Δ, n_A is found [from $G_A(\omega)$ and relation (3.3)] to be

$$n_A = \frac{1}{2}\,\frac{e^{-\beta\Delta/2} + e^{\beta I/2}}{e^{\beta I/2} + \cosh\frac{1}{2}\beta\Delta} \; . \tag{4.6}$$

With Eq. (4.6), the equation determining Δ can be written as

$$\Delta = 2zW \frac{\sinh\frac{1}{2}\beta\Delta}{e^{\beta I/2} + \cosh\frac{1}{2}\beta\Delta} \; . \tag{4.7}$$

We note that the Hartree-Fock order parameter Δ_{HF} is defined slightly differently than the above parameter – the connection is $\Delta_{HF} = (2zW - I)\Delta/2zW$. In terms of Δ_{HF}, Eq. (4.7) reduces to the Hartree-Fock gap equation, Eq. (3.4), to first order in I.

Equation (4.7) can be solved for Δ by numerical means, but first we make certain comments about the nature of the solution. As a function of Δ, the right-hand side of Eq. (4.7) behaves qualitatively similar to $\tanh\frac{1}{4}\beta\Delta$ for $\beta I < 2\ln 2$; i.e., (i) the first derivative is positive and (ii) the second derivative is negative for $\Delta > 0$. However, for $\beta I > 2\ln 2$, the second condition fails for Δ less than some positive number. The function exhibits an inflection point and from simple graphical analysis (see Fig. 1) of Eq. (4.7) one sees that a first-order phase transition is possible for $\beta I > 2\ln 2$. (For $\beta I < 2\ln 2$ only a second-order phase transition is possible.) Equation (4.7) is invariant under the transformation $\Delta \to -\Delta$ and from Eqs. (4.4) and (4.6) the transformation merely interchanges the roles of n_A and n_B. Thus we only consider $\Delta \geq 0$. In the zero-temperature limit Eq. (4.7) can have the solution Δ_0 ($\equiv 2zW$) or zero for $\Delta_0 > I$ and only the solution $\Delta = 0$ for $\Delta_0 < I$. At finite temperatures it can have as many as three solutions (see Fig. 1) depending on the parameters $x \equiv I/\Delta_0$ and $y \equiv kT/\Delta_0$. These solutions are easily determined, but to select the one solution which describes the thermodynamic state for a given set of x and y a free-energy principle must be used.

In Appendix D we start from the variational principle and determine the free energy within our approximation scheme. Further, we demonstrate that this method yields the same physical results as the Green's-function decoupling scheme. (We could have determined the free energy directly from the one-particle Green's function but the variational approach incorporates the important condition that the approximate free energy is a rigorous upper bound on the exact free energy.) The free energy (per particle) is given by Eq. (D8);

$$f = -\frac{\Delta_0}{4}\left(1 - \frac{\sinh^2\frac{1}{2}\beta\Delta}{(e^{\beta I/2} + \cosh\frac{1}{2}\beta\Delta)^2}\right) - \frac{1}{\beta}\ln 2(e^{\beta I/2} + \cosh\tfrac{1}{2}\beta\Delta). \tag{4.8}$$

Figure 2 is a phase diagram in which the stability boundary between the Mott insulating state ($\Delta = 0$) and the condensed (charge-ordered insulator) state is shown. On the left of the dotted line a second-order phase transition occurs, and on the right a first-order phase transition occurs. In Fig. 3 the gap parameter is plotted against temperature for a value of I/Δ_0 (= 0.40) for which the first-order phase transition occurs.

The fact that the transition is first order can be understood in terms of the single-particle excitation levels. In the Hartree-Fock theory, levels ϵ_A and ϵ_B are associated with the two inequivalent sublattices. These levels are self-consistently determined by the differential occupancies of the two sublattices which are proportional to the gap parameter. The gap decreases continuously to zero as the sublattices become equally populated. In the present theory, however, the single-particle levels are

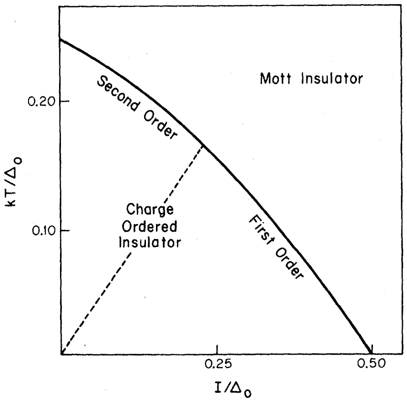

FIG. 2. In this phase diagram a first-order transition occurs across the boundary for that portion of the boundary below its intersect with the dotted line ($\beta I = 2\ln 2$). Above this intersection the phase transition is second order across the boundary.

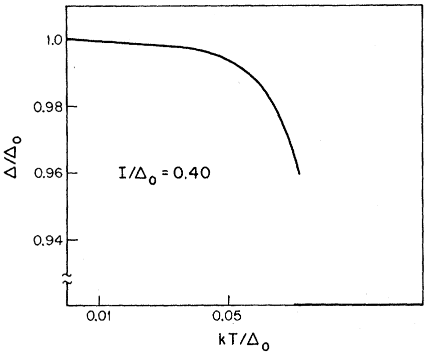

FIG. 3. Gap parameter shows a jump discontinuity (for $I/\Delta_0 = 0.40$) at $kT/\Delta_0 = 0.07$; for $kT/\Delta_0 > 0.07$, $\Delta = 0$.

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

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

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

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

It is easy to see that

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

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 ith 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 Brooks[9] 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 Goodenough[8] and Adler and Brooks[9] 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-

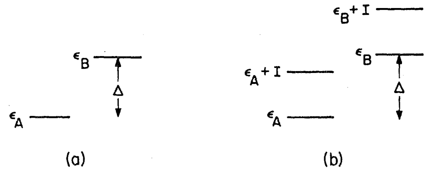

FIG. 4. Single-particle energy levels on sublattices A and B in relation to the gap parameter is shown in (a) the Hartree-Fock theory and (b) the modified Hartree-Fock approach. In case (b) the levels on a given sublattice are split into two quasilevels separated by energy I.

tic energy and that the charge-ordered state may only occur over a limited range of finite bandwidth. We have verified, with a quantitative model, that the charge-ordered state will be quenched at zero bandwidth and have established criteria for the existence of the system in either the Mott or charge-ordered state.

We have worked in the zero-overlap limit in describing the insulating state; however, in materials which are believed to be Mott insulators, finite-overlap effects (e.g., magnetism) play a role in determining the physical properties. It is therefore reasonable to discuss the effects of finite overlap on the charge-ordered state. Finite overlap will introduce the appropriate mixing of states that will modify the alternate doubly occupied site configuration (and its associated cation-cluster formation) and thereby give rise to the homopolar bond formation[8] within each cation cluster. The energy of the charge-ordered ground state will be lowered by approximately $b^2/[(2z-1)W-I]$ because of small overlap (b is proportional to the overlap). Since the spins are paired off in the charge-ordered insulator there is no tendency for further ordering due to finite overlap. Our theory does not describe the situation in which the Mott insulator is magnetically ordered for $I/\Delta_0 < \frac{1}{2}$ (see Fig. 2); but the theory may give a good qualitative description when the magnetic-ordering temperature of the Mott insulator is much less than the critical temperature in Fig. 2, for a particular value of I/Δ_0. The theory does provide criteria for choosing the appropriate zeroth-order (in the bandwidth) state of the system to which finite bandwidth effects can then be incorporated.

ACKNOWLEDGMENTS

The author wishes to thank T. A. Kaplan for stimulating conversations and encouragement and D. Adler and J. B. Goodenough for illuminating discussions of their work. The author also thanks R. V. Lange, A. L. McWhorter, and H. J. Zeiger for reading the manuscript and helpful comments and N. Brine for much assistance providing with the numerical analysis.

APPENDIX A: ELECTRON-LATTICE INTERACTION

We present, in the Wannier-function basis, the usual[14] derivation of the electron-lattice interaction. We do this to make clear our assumptions in deriving the model Hamiltonian H.

The electron-lattice interaction is derived from the one-electron Hamiltonian in the field of the ions

$$H_I = \sum_\sigma \int d\vec{r}\, \psi_\sigma^\dagger(\vec{r})[-\nabla^2/2m + \sum_i V(\vec{r}-\vec{R}_i)]\psi_\sigma(\vec{r}) \,. \tag{A1}$$

Here $\psi_\sigma^\dagger(\vec{r})$ is the creation operator for an electron at point $\vec{r}$ and spin σ and it satisfies the usual fermion anticommutation relations; $V(\vec{r}-\vec{R}_i)$ is the interaction of the electron with a given ion at position $\vec{R}_i$. In the absence of ion motion the set $\{\vec{R}_i^0\}$ denotes the equilibrium ion positions. In the standard fashion we assume first-order displacements and write

$$V(\vec{r}-\vec{R}_i) \approx V(\vec{r}-\vec{R}_i^0) + \delta\vec{R}_i \cdot \nabla V(\vec{r}-\vec{R}_i^0) \,.$$

We now make the assumption that $\psi_\sigma^\dagger(\vec{r})$ is expandable in terms of a single (s band for convenience) band of Wannier functions;

$$\psi_\sigma^\dagger(\vec{r}) = \sum_i \omega(\vec{r}-\vec{R}_i^0)\, c_{i\sigma}^\dagger \,. \tag{A2}$$

$c_{i\sigma}^\dagger$ is the creation operator for an electron at Wannier site $\vec{R}_i^0$ and spin σ. In the Wannier representation H_I is written as

$$H_I = \sum_{ij\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{ij\sigma} \sum_l \delta\vec{R}_l \cdot \vec{e}_{ij}^{\,l} c_{i\sigma}^\dagger c_{j\sigma} \,, \tag{A3}$$

where

$$t_{ij} = \int d\vec{r}\, \omega(\vec{r}-\vec{R}_i^0)[-\nabla^2/2m + \sum_i V(\vec{r}-\vec{R}_i^0)]\,\omega(\vec{r}-\vec{R}_j^0) \,, \tag{A4}$$

$$\vec{e}_{ij}^{\,l} = \int d\vec{r}\, \omega(\vec{r}-\vec{R}_i^0)\nabla V(\vec{r}-\vec{R}_l^0)\,\omega(\vec{r}-\vec{R}_j^0) \,. \tag{A5}$$

We assume the zero-overlap limit and only retain matrix elements in Eqs. (A4) and (A5) for which $i=j$. Without loss of generality we take $t_{ii} = 0$. Thus H_I becomes

$$H_I = \sum_{i,l,\sigma} \delta\vec{R}_l \cdot \vec{e}_{ii}^{\,l} n_{i\sigma} \,. \tag{A6}$$

Since the Wannier functions are assumed to be well localized, we retain only the $l=i$ term in the l summation of (A5). We now write

$$\delta\vec{R}_i = \sum_{\vec{q}} \vec{f}_{\vec{q}}\, (a_{\vec{q}}\, e^{i\vec{q}\cdot\vec{R}_i^0} - a_{\vec{q}}^\dagger e^{-i\vec{q}\cdot\vec{R}_i^0})$$

and with the identification $\vec{f}_{\vec{q}} \cdot \vec{e}_{ii}^{\,i} = V_{\vec{q}}$ obtain Eq. (2.3). The Coulomb integral, Eq. (2.2), also refers to the $\vec{R}_i^0$ positions.

From Eq. (A6) we see that because of the lattice vibrations there is an effective time-dependent external field at each site – and the fields on different sites are related to each other in a manner determined by the collective vibrations of the lattice. A different approach to the electron-lattice interaction is to assume that the Wannier functions are associated with the instantaneous positions (the adiabatic approximation) of the ions, $\vec{R}_i$. The Coulomb integral $U_{ij} = U(\vec{R}_i - \vec{R}_j)$ [see Eq. (2.2)] is then expanded in the small parameter $\delta\vec{R}_i = \vec{R}_i - \vec{R}_i^0$ and the analog of Eq. (A6) is a two-body time-dependent interaction. The derivation is somewhat similar to that given for an Ising spin Hamiltonian in a compressible lattice.[15] A canonical transformation decouples the electronic and lattice systems and leads to effective two-, three-, and four-body electron interactions. The intra-atomic and nearest-neighbor interactions behave similarly to that developed in this paper but we have not investigated this approach further.

APPENDIX B: GROUND-STATE ANALYSIS

In this Appendix we find the lowest-energy eigenstate of

$$H_e = I\sum_i n_{i\uparrow}n_{i\downarrow} + W\sum_{ij} f_{ij}(n_{i\uparrow}+n_{i\downarrow})(n_{j\uparrow}+n_{j\downarrow}). \qquad \text{(B1)}$$

We introduce the new variable $S_i = n_{i\uparrow}+n_{i\downarrow}-1$ into Eq. (B1) and, with the aid of the identity

$$2n_{i\uparrow}n_{i\downarrow} = (n_{i\uparrow}+n_{i\downarrow})^2 - n_{i\uparrow} - n_{i\downarrow}\,,$$

obtain

$$H_e = \tfrac{1}{2}I\sum_i S_i^2 + W\sum_{ij} f_{ij}S_iS_j + \tfrac{1}{2}NzW\,; \qquad \text{(B2)}$$

we have used the condition that the number of electrons is equal to the number of sites, N, and have $\sum_i S_i = 0$. We rewrite Eq. (B2) as

$$H_e = (\tfrac{1}{2}I - \tfrac{1}{2}zW)\sum_i S_i^2 + \tfrac{1}{2}W\sum_{ij} f_{ij}(S_i+S_j)^2 + \tfrac{1}{2}NzW. \qquad \text{(B3)}$$

The variable S_i can take on the values -1, 0, 1 and each summation in Eq. (B3) is a positive quantity. We first consider the case $I > zW$. In this case the minimum energy is obtained by simultaneously minimizing each summation. This is obtained by requiring $S_i^2 = 0$ and $f_{ij}(S_i+S_j)^2 = 0$ for all i and j. These conditions imply that $S_i = 0$ for all i. Thus, for $I > zW$, the minimum-energy eigenstate has each site singly occupied.

For the case $I < zW$ one must maximize $\sum_i S_i^2$ while minimizing $\sum_{ij} f_{ij}(S_i+S_j)^2$. This leads to the conditions $S_i^2 = 1$ and $f_{ij}(S_i+S_j)^2 = 0$ for all i and j. These conditions imply $S_i = 1$ for all i on sublattice A and $S_i = -1$ for all i on sublattice B. Thus $n_{i\uparrow}+n_{i\downarrow} = 2$ for i on sublattice A and $n_{i\uparrow}+n_{i\downarrow} = 0$ for i on sublattice B (the charge-ordered state). For $I > zW$ the ground-state energy is $\tfrac{1}{2}NzW$ and for $I < zW$ it is $\tfrac{1}{2}NI$.

APPENDIX C: ONE-DIMENSIONAL MODEL

The Hamiltonian H_e is quite analogous to a spin Ising Hamiltonian and from Eq. (B2) we see that it resembles a spin-1 Ising Hamiltonian. However, one must be careful since the "spin value" $S_i = 0$ can occur in two ways. This arises from the fact that a singly occupied electron site is twofold spin degenerate. This implies that, if one is to treat the thermodynamics of H_e from Eq. (B2), one must take special care in the counting of states. Rather than work in the representation of Eq. (B2) we work with Eq. (2.9).

In one dimension the partition function is formulated in terms of the transfer matrix.[16] We work in the grand canonical ensemble and write the partition function as

$$Z = \sum_{\substack{n_{1\uparrow}=0,1\\ n_{1\downarrow}=0,1}} \sum_{\substack{n_{2\uparrow}=0,1\\ n_{2\downarrow}=0,1}} \cdots \sum_{\substack{n_{N\uparrow}=0,1\\ n_{N\downarrow}=0,1}} \exp\Big[-\beta I\sum_i n_{i\uparrow}n_{i\downarrow} - \beta W\sum_i (n_{i\uparrow}+n_{i\downarrow})(n_{i+1\uparrow}+n_{i+1\downarrow}) + \beta\mu\sum_i (n_{i\uparrow}+n_{i\downarrow})\Big]\,. \qquad \text{(C1)}$$

Here μ is the chemical potential and we assume periodic boundary conditions such that $n_{N+1,\sigma} = n_{1\sigma}$ (σ equals either spin direction). Since we are only interested in the case $\sum_i(n_{i\uparrow}+n_{i\downarrow}) = N$, μ can be fixed from the outset. The appropriate value for μ is easily found by reexpressing the argument of Eq. (C1) in terms of the S_i variable introduced in Appendix B. We find that

$$\begin{aligned} I\sum_i n_{i\uparrow}n_{i\downarrow} &+ W\sum_i (n_{i\uparrow}+n_{i\downarrow})(n_{i+1\uparrow}+n_{i+1\downarrow}) \\ &- \mu\sum_i (n_{i\uparrow}+n_{i\downarrow}) \\ &= \tfrac{1}{2}I\sum_i S_i^2 + W\sum_i S_iS_{i+1} \\ &- (\mu - \tfrac{1}{2}I - 2W)\sum_i S_i + N(W-\mu)\,. \qquad \text{(C2)} \end{aligned}$$

The number condition $\sum_i S_i = 0$ implies that $\mu = \tfrac{1}{2}I + 2W$. This is the same value obtained in the approximate theories of Secs. III and IV, when specialized to one dimension.

We define a matrix P by the elements

$$\langle n_\uparrow n_\downarrow|P|n'_\uparrow n'_\downarrow\rangle = \exp[-\beta I n_\uparrow n_\downarrow - \beta W(n_\uparrow+n_\downarrow)(n'_\uparrow+n'_\downarrow) + \beta(\tfrac{1}{2}I+2W)(n_\uparrow+n_\downarrow)]\,. \qquad \text{(C3)}$$

Each n takes on the values 0, 1 so that there are 16 elements in all. These elements can be arranged in a 4×4 matrix by the following assignment:

$P_{11} = \langle 00|P|00\rangle = 1\,,$

$P_{12} = \langle 00|P|01\rangle = 1\,,$

$P_{13} = \langle 00|P|10\rangle = 1\,,$

$P_{14} = \langle 00|P|11\rangle = 1\,,$

$P_{21} = \langle 10|P|00\rangle = e^{\beta(I/2+2W)}\,,$

$P_{22} = \langle 10|P|01\rangle = e^{\beta(I/2+W)}\,,$

$P_{23} = \langle 10|P|10\rangle = e^{\beta(I/2+W)}\,,$

$P_{24} = \langle 10|P|11\rangle = e^{\beta I/2}\,,$

$P_{31} = \langle 01|P|00\rangle = P_{21}\,,$

$P_{32} = \langle 01|P|01\rangle = P_{22}\,,$

$P_{33} = \langle 01|P|10\rangle = P_{23}\,,$

$P_{34} = \langle 01|P|11\rangle = P_{24}\,,$

$P_{41} = \langle 11|P|00\rangle = e^{4\beta W}\,,$

$P_{42} = \langle 11|P|01\rangle = e^{2\beta W}\,,$

$$P_{43} = \langle 11 | P | 10 \rangle = e^{2\beta W} ,$$

$$P_{44} = \langle 11 | P | 11 \rangle = 1 .$$

Since $Z = \mathrm{Tr} P^N$ we wish to find the eigenvalues of P. Then we write

$$Z = \lambda_1^N + \lambda_2^N + \lambda_3^N + \lambda_4^N , \tag{C4}$$

where λ_1, λ_2, λ_3, λ_4 are the eigenvalues of P. We look for a phase transition in the $\lim N \to \infty$. If λ_1 is the largest eigenvalue, then in the thermodynamic limit the free energy per particle is $f = -kT \ln \lambda_1$. We show that (a) λ_1 is an analytic function of the parameters βI and βW, and that (b) for all values of the βI and βW, $\lambda_1 >$ any other eigenvalue.

The secular equation that determines the eigenvalues of P is

$$\lambda^3 - 2\lambda^2(1+a) + \lambda[1 - b^4 + 4a(1-b)]$$
$$+ 2a(b^4 - 2b^3 + 2b - 1) = 0 , \tag{C5}$$

where $a = be^{\beta I/2}$ and $b = e^{\beta W}$. The fourth root is $\lambda = 0$ and since we are concerned with the magnitude of the largest root, this root need not concern us further. Since the coefficients in Eq. (C5) are analytic functions of βI and βW, the roots are also analytic functions. From the theory of equations[17] we define the quantity

$$Q = \tfrac{1}{27}(B - \tfrac{1}{3}A^2)^3 + (\tfrac{2}{27}A^3 - \tfrac{1}{3}AB + C)^2, \tag{C6}$$

where A, B, and C correspond to coefficients in Eq. (C5) according to $\lambda^3 + A\lambda^2 + B\lambda + C = 0$. It can easily be shown that $Q < 0$ for all $\beta I > 0$ and $\beta W > 0$. This implies that Eq. (C5) has three different real roots. The possibility of two roots crossing somewhere in the parameter space of βI and βW is ruled out because at such a crossing Q would be zero. This completes the proof.

APPENDIX D: FREE ENERGY

We start from the variational principle of statistical mechanics and write the free energy as

$$F = \mathrm{Tr}\, \rho\, [H - \mu N + (1/\beta) \ln \rho] ; \tag{D1}$$

here ρ is any density operator and F is equal to the exact free energy corresponding to H only if ρ is the exact density operator corresponding to H. For any other ρ, F is an upper bound on the exact free energy.

We approximate

$$\rho = e^{-\beta(\tilde{H} - \mu N)} / \mathrm{Tr}\, e^{-\beta(\tilde{H} - \mu N)} \tag{D2}$$

with

$$\tilde{H} = I \textstyle\sum_i n_{i\uparrow} n_{i\downarrow} + \sum_i e_i (n_{i\uparrow} + n_{i\downarrow}). \tag{D3}$$

This form for $\tilde{H}$ guarantees that the $W = 0$ limit of Eq. (2.9) is treated exactly in Eqs. (D1) and (D2). The second term in Eq. (D3) is written in accordance with the thermal Hartree-Fock approximation – in which we wish to treat the interactions described by W. The $\{e_i\}$ are the variational parameters which are determined by the requirement that $\delta F / \delta e_i = 0$ (stationary condition).

We combine Eq. (2.9) with the above equations and find that the stationary condition implies that

$$e_i = 2W \textstyle\sum_j f_{ij} \langle n_{j\uparrow} + n_{j\downarrow} \rangle , \tag{D4}$$

where the averaging is given by

$$\langle A \rangle \equiv \mathrm{Tr}\, \rho A . \tag{D5}$$

As in the theory of Sec. IV we assume a two-sublattice model and calculate self-consistently the parameters e_A and e_B. If we define an order parameter by $\delta = e_A - e_B$, we obtain conditions, from Eqs. (D4) and (D5), that are mathematically identical to Eqs. (4.6) and (4.7). The condition on the chemical potential is also identical to that obtained in the Green's-function theory.

The free energy from Eq. (D1) then becomes

$$F = -2NWz \langle n_A \rangle \langle n_B \rangle - (1/\beta) \ln Z , \tag{D6}$$

where $Z \equiv \mathrm{Tr}\, e^{-\beta(\tilde{H} - \mu N)}$.

Since we work in the grand canonical ensemble, Z is easily calculated to be

$$Z = (1 + 2e^{\beta(I-\Delta)/2} + e^{-\beta\Delta})^{N/2} (1 + 2e^{\beta(I+\Delta)/2} + e^{\beta\Delta})^{N/2} . \tag{D7}$$

(We have made the identification $\delta = \Delta$.) Thus the free energy per particle ($f \equiv F/N$) is given by

$$f = -\frac{2zW}{4} \left(1 - \frac{\sinh^2 \frac{1}{2}\beta\Delta}{(e^{\beta I/2} + \cosh \frac{1}{2}\beta\Delta)^2}\right)$$
$$-\frac{1}{\beta} \ln 2 (e^{\beta I/2} + \cosh \tfrac{1}{2}\beta\Delta) . \tag{D8}$$

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*Work sponsored by the Department of the Air Force.

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PHYSICAL REVIEW B VOLUME 3, NUMBER 8 15 APRIL 1971

Observed Fine Structure in X Rays Incoherently Scattered by Alkali Halides: Contribution from Color Centers. II

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(Received 1 July 1970)

The spectra of Cu $K\alpha_1$, $K\alpha_2$ and Cr $K\alpha_1$, $K\alpha_2$ radiations scattered by LiF and NaCl single crystals and powders at several angles have been investigated. The spectra of Cr $K\alpha_1$, $K\alpha_2$ scattered radiation were studied for two different color-center concentrations. The spectra of scattered radiation by samples of high color-center concentrations include a new line on the long-wavelength side of the primary spectrum. The line is located at a distance of 5 eV from the primary for LiF, and 2 eV for NaCl. These distances of the new line from the coherent line are independent of the incident radiation energy and scattering angles, and are equal to the F-center excitation energies in the respective crystals. Judging from the position of the new line, and its absence from spectra in which the scatterer had lower F-center concentration, it is concluded that the new line is caused by "x-ray discrete Raman" scattering from the F center. However, because the F-center concentration is at least three orders of magnitude lower than the concentration of the valence electrons, the observed intensity of the line cannot be explained by a simple model in which the isolated F center behaves as a scatterer.

INTRODUCTION; SCOPE OF INVESTIGATION

Previously,[1,2] the author reported on the existence of a new incoherent component in the Cu $K\alpha_1$, $K\alpha_2$ x-ray radiation scattered by LiF which he attributed to x-ray Raman components of F centers. The present investigation has several purposes: (a) to verify the initial observation by extending the research to different radiation and different samples; (b) to demonstrate that the new line can be attributed to the F center by comparing two sets of spectra for two different F-center concentrations; and (c) to study quantitatively the differential cross section of the new incoherent component.

In the present research, the initial observation of a new line in Cu radiation scattered by LiF is verified for the same radiation on NaCl, and for Cr radiation, scattered by LiF and NaCl single crystals and powders at several scattering angles ($\phi = 16°$, $25°$, $40°$, $70°$, $84°$). Cr radiation was chosen because the slow rate of production of F centers permits measurements from samples with low F-center concentrations. The measurement using Cr radiation was then repeated with samples previously irradiated to a saturation concentration of F centers. It is then possible to demonstrate that the fine structure of the spectra depends on color centers by the comparison of Cr $K\alpha_1$, $K\alpha_2$ radiation scattered by samples with two different F-center concentrations. Such a comparison shows that for a concentration one order of magnitude less than the saturation concentration the new line is not observable. The determination of the exact concentration during the measurement is not feasible for several reasons: The spectrum of the incident radiation is not monochromatic; the production rate depends on the energy of the x-ray beam, the F-center lifetime, and the temperature dependence of the lifetime; the perfection of the crystal, etc.

The F-center concentration, as estimated from optical-absorption measurements, was found to be of the order of 10^{17} F centers per cm^3. Since the line characteristic energy loss is equal to the F-center excitation energies in the respective crys-