

PHASE TRANSITION IN STRONG ELECTRON-PHONON INTERACTION

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A macroscopic theory is constructed for a first-order phase transition in a lattice of the displacement type; the phase transition is due to strong electron-phonon interactions within narrow bands. It is shown that the problem reduces to a model of the Ising type. The analysis is carried out in the self consistent field approximation. The phase transition is accompanied by a jump of the carrier density, and account is taken of both current and exciton states. The theory is applied to a discussion of the experimental data on V_2O_3 .

ADLER and Brooks^[1] proposed a phenomenological model of an electronic phase transition in order to explain the jump of the electric conductivity observed in such substances as V_2O_3 , VO, Cr_2O_3 , and others. In^[1], owing to the phenomenological character of the model, there were no indications of the concrete interaction mechanism leading to the phase transition. Only the connection between the transition mechanism and the interaction of the electrons with the lattice was noted. In addition, only the current states of the system were taken into account in^[1]. At the same time it is clear that in the model of extremely narrow bands considered in^[1], which in its physical meaning is a Heitler-London model, currentless states are possible, namely Frankel excitons, and these, as will be shown below, can also lead to thermodynamic instability of the system.

In the present paper we investigate the possibility of a first-order phase transition in the electron system in the presence of a strong electron-phonon interaction, accompanied by a jump of the electric conductivity and by realignment of the lattice, for the case of extremely narrow allowed bands.

1. FORMULATION OF PROBLEM AND HAMILTONIAN

We consider a system of electrons interacting with the lattice vibrations. It is assumed that an electron localized at the site m of the lattice can be in one of two states $\varphi_{1m}(\mathbf{r}) \equiv \varphi_1(\mathbf{r} - \mathbf{m})$ and $\varphi_{2m}(\mathbf{r}) \equiv \varphi_2(\mathbf{r} - \mathbf{m})$ (here $\varphi_{\alpha m}$ -function of the atomic or Wannier type). These states are separated by an energy gap $\epsilon = E_1 - E_2 > 0$, due to the splitting in the crystal field. We shall assume that the widths of the bands produced in the crystal out of states 1 and 2 are small compared with all other energies encountered in the problem, since the width of the band is determined in the tight-binding model by the overlap integral J between the nearest neighbors. When the condition $r_B < a_0$ (where r_B is the radius of the corresponding atomic orbits and a_0 is the characteristic distance between neighboring sites, which is on the order of the lattice constant) is satisfied, the overlap integral, owing to the exponential character of the damping of the atomic functions, will be of the order of

$$\exp(-a_0/r_B) \ll 1. \tag{1}$$

The quantized wave function of the electrons is of the

form

$$\Psi(\mathbf{r}) = \sum_{\alpha m} \varphi_{\alpha m}(\mathbf{r}) a_{\alpha m}, \quad \alpha = 1, 2. \tag{2}$$

The Hamiltonian of the interaction of the electrons with the phonons, according to^[2], is given by

$$V(\mathbf{r}) = \sum_{jm} u_{jm}^\sigma w_j^\sigma(\mathbf{r} - \mathbf{m}) \tag{3}$$

and represents its most general form in the approximation linear in the phonons. Here u_{jm}^σ is the σ component of the displacement of the j -th atom in the m -th unit cell. Going over with the aid of (2) to the second-quantization representation, we rewrite (3) in the form

$$V = \sum_{jmm'} u_{jm'}^\sigma \left[\int \varphi_{\alpha 0}(\mathbf{r}) w_j^\sigma(\mathbf{r} - \mathbf{m}' + \mathbf{m}) \varphi_{\alpha 0}(\mathbf{r}) d\mathbf{r} \right] a_{\alpha m'}^\dagger a_{\alpha m}, \tag{4}$$

where the terms of the type

$$\int \varphi_{\alpha m} w \varphi_{\alpha m'} d\mathbf{r}, \quad m \neq m'$$

have been omitted, since they contain a small quantity such as (1); for simplicity we assume that the functions φ are real, and then

$$\begin{aligned} \sum_{m'} u_{jm'}^\sigma \int \varphi_{\alpha m}(\mathbf{r}) w_j^\sigma(\mathbf{r} - \mathbf{m}') \varphi_{\alpha m'}(\mathbf{r}) d\mathbf{r} &= u_{jm}^\sigma \int \varphi_{\alpha}(\mathbf{r}) w_j^\sigma(\mathbf{r}) \varphi_{\alpha'}(\mathbf{r}) d\mathbf{r} \\ &+ \sum_{m \neq m'} u_{jm'}^\sigma \int \varphi_{\alpha}(\mathbf{r}) w_j^\sigma(\mathbf{r} - \mathbf{m}' + \mathbf{m}) \varphi_{\alpha'}(\mathbf{r}) d\mathbf{r}. \end{aligned} \tag{5}$$

The first term in (5) describes the interaction of the electron with the nuclear vibrations in that cell in which the electron is located, i.e., the fluctuations of the orbits that split in the crystal fields as a result of the vibrations of the ions of the given unit cell. The second term describes the influence exerted on the electron by the oscillations of nuclei of other cells. Therefore the quantity $w_j(\mathbf{r} - \mathbf{m}' + \mathbf{m})$, $m \neq m'$, changes little over distances on the order of r_B , whereas the first term of (5) can vary noticeably over such distances, and consequently $w_j(\mathbf{r} - \mathbf{m}' + \mathbf{m})$, $m \neq m'$, can be expanded in powers of $r_B/a_0 \ll 1$. Then, recognizing that for the d or f orbits that split in the crystal field the matrix elements of the dipole moment are equal to zero, we obtain, accurate to $(r_B/a_0)^2$

$$\begin{aligned} \mathcal{H} &= \sum_{m\alpha} E_\alpha a_{\alpha m}^\dagger a_{\alpha m} + \sum_{q_s} \hbar \omega_{q_s} b_{q_s}^\dagger b_{q_s} \\ &+ \sum_{m \neq m'} u_{jm}^\sigma w_{j\alpha\alpha'}^\sigma a_{\alpha m}^\dagger a_{\alpha' m} + \sum_{m \neq m'} u_{jm'}^\sigma w_j^\sigma(\mathbf{m} - \mathbf{m}') a_{\alpha m}^\dagger a_{\alpha m}; \end{aligned} \tag{6}$$

s—number of branch, \mathbf{q} —quasimomentum of the phonon,

$$w_{j\alpha\alpha'}^\sigma = \int \varphi_\alpha(\mathbf{r}) w_j^\sigma(\mathbf{r}) \varphi_{\alpha'}(\mathbf{r}) d\mathbf{r}, \quad (7)$$

and \mathbf{u}_{jm} is expressed in the usual manner in terms of the normal coordinates

$$\mathbf{u}_{jm} = \sum_{\mathbf{q}_s} \sqrt{\frac{\hbar}{2NM\omega_{\mathbf{q}_s}}} (\mathbf{e}_{\mathbf{q}_s}^j e^{i\mathbf{q}_m \cdot \mathbf{b}_{\mathbf{q}_s}} + \text{h.c.}); \quad (8)$$

M —mass of unit cell, N —number of lattice sites, $\mathbf{e}_{\mathbf{q}_s}^j$ —unit vector of the corresponding mode. The term $w_j(\mathbf{m} - \mathbf{m}')$ describes the long-range part of the interaction potential, whereas the first term in (5) or (6), while determining the short-range part of the interaction, nevertheless leads to an effective long-range interaction between the electrons as a result of the phonon dispersion.

2. HOMOPOLAR CASE. FRENKEL EXCITONS

We consider first the case when all the transitions occur without a change in the number of electrons per site. We assume that in the lattice there is one electron per site, and then this condition takes the form

$$a_{1m}^\dagger a_{1m} + a_{2m}^\dagger a_{2m} = 1. \quad (9)$$

(The electron spin is henceforth disregarded.) Physically this corresponds to the system of Frenkel excitons (homopolar approximation). In this case, assuming that $E_1 - E_2 = \epsilon > 0$, we have¹⁾

$$\begin{aligned} \mathcal{H} = & \sum_{\mathbf{m}} \epsilon n_{\mathbf{m}} + \sum_{\mathbf{m}, \mathbf{j}} u_{jm}^\sigma w_{jm}^\sigma n_{\mathbf{m}} + \sum_{\mathbf{m}, \mathbf{j}} u_{jm}^\sigma [\tilde{w}_j^\sigma a_{1m}^\dagger + a_{2m} \\ & + (\tilde{w}_j^\sigma)^* a_{2m}^\dagger + a_{1m}] + \hbar\omega_{\mathbf{q}_s} b_{\mathbf{q}_s}^\dagger b_{\mathbf{q}_s}; \\ n_{\mathbf{m}} \equiv & a_{1m}^\dagger a_{1m}; \quad w_j^\sigma \equiv w_{11j} - w_{22j}; \quad \tilde{w}_j^\sigma \equiv w_{12j}. \end{aligned} \quad (10)$$

The quantities w_j and \tilde{w}_j are independent, so that in principle two limiting cases are possible: a) $|w_j^\sigma| \gg |\tilde{w}_j^\sigma|$, b) $|w_j^\sigma| \ll |\tilde{w}_j^\sigma|$. In the present paper we confine ourselves to the case a). Then

$$\begin{aligned} \mathcal{H} = & \sum_{\mathbf{m}} \epsilon n_{\mathbf{m}} + \frac{1}{\sqrt{N}} \sum_{\mathbf{q}, \mathbf{m}} \hbar\omega_{\mathbf{q}_s} (\gamma_{\mathbf{q}_s} e^{i\mathbf{q}_m \cdot \mathbf{b}_{\mathbf{q}_s}} + \text{h.c.}) n_{\mathbf{m}} \\ & + \sum_{\mathbf{q}_s} \hbar\omega_{\mathbf{q}_s} b_{\mathbf{q}_s}^\dagger b_{\mathbf{q}_s}; \end{aligned} \quad (11)$$

$$\gamma_{\mathbf{q}_s} \equiv \sum_j (2\hbar M \omega_{\mathbf{q}_s}^3)^{-1/2} w_j^\sigma e_{\mathbf{q}_s}^j \sigma. \quad (12)$$

The Hamiltonian (11) is diagonalized by the linear transformation

$$b_{\mathbf{q}_s} = \tilde{b}_{\mathbf{q}_s} + \alpha_{\mathbf{q}_s}; \quad \alpha_{\mathbf{q}_s} = -\frac{1}{\sqrt{N}} \sum_{\mathbf{m}} \gamma_{\mathbf{q}_s}^* e^{-i\mathbf{q}_m \cdot \mathbf{b}_{\mathbf{q}_s}} n_{\mathbf{m}}, \quad (13)$$

¹⁾Transforming (6) with allowance for (9), we obtain also a term that is linear in the operators $b_{\mathbf{q}}$ and $b_{\mathbf{q}+}$, and which does not contain electronic operators. After eliminating the linear terms in the phonon part of the Hamiltonian, the value of the energy gap ϵ is renormalized; we shall assume that this is done. In addition, in a consistent analysis it is necessary to take into account the Coulomb interaction of the electrons. However, in the considered homopolar case this interaction reduces to quadrupole-quadrupole interaction, which decreases like r^{-6} and is insignificant at low concentrations.

yielding

$$\tilde{\mathcal{H}} = \sum_{\mathbf{m}} (\epsilon - \Delta E_p) n_{\mathbf{m}} + \sum_{\mathbf{m} \neq \mathbf{m}'} \hbar\omega_{\mathbf{q}_s} \tilde{b}_{\mathbf{q}_s}^\dagger \tilde{b}_{\mathbf{q}_s} - \sum_{\mathbf{m} \neq \mathbf{m}'} K(\mathbf{m} - \mathbf{m}') n_{\mathbf{m}} n_{\mathbf{m}'}; \quad (14)$$

$$\Delta E_p = \frac{1}{N} \sum_{\mathbf{q}_s} |\gamma_{\mathbf{q}_s}|^2 \hbar\omega_{\mathbf{q}_s}; \quad (15)$$

$$K(\mathbf{m} - \mathbf{m}') = \frac{1}{N} \sum_{\mathbf{q}_s} \hbar\omega_{\mathbf{q}_s} |\gamma_{\mathbf{q}_s}|^2 e^{-i\mathbf{q} \cdot (\mathbf{m} - \mathbf{m}')}. \quad (16)$$

As a result of the transformation (13), the phonon and electron systems split, and an effective electron-electron interaction of the type (16) appears. The Hamiltonian (14) is analogous to the Ising Hamiltonian or to its equivalent, the Hamiltonian of the lattice-gas problem.

We shall continue the analysis in the self-consistent field approximation²⁾. Setting up the equations of motion for the operator $a_{\mathbf{m}}$, we get

$$\frac{da_{\mathbf{m}}}{dt} = -\frac{i}{\hbar} \left[(\epsilon - \Delta E_p) a_{\mathbf{m}} - 2 \sum_{\mathbf{m} \neq \mathbf{m}'} K(\mathbf{m} - \mathbf{m}') n_{\mathbf{m}'} a_{\mathbf{m}} \right]. \quad (17)$$

This leads to a self-consistent field in the form⁽³⁾

$$\begin{aligned} 2 \sum_{\mathbf{m}' \neq 0} K(\mathbf{m}') \frac{N_e}{N} = & 2 \frac{N_e}{N} \left[\left(\sum_s \hbar\omega_{\mathbf{q}_s} |\gamma_{\mathbf{q}_s}|^2 \right)_{\mathbf{q}=0} - \Delta E_p \right]; \\ N_e = & \sum_{\mathbf{m}} n_{\mathbf{m}}. \end{aligned} \quad (18)$$

Thus, the effective single-particle Hamiltonian is given by

$$\mathcal{H}_0 = \sum (\epsilon_s - 2\tilde{K}x) n_{\mathbf{m}}, \quad x = \frac{N}{N}; \quad (19)$$

$$\tilde{K} = \frac{1}{N} \sum_{\mathbf{q}_s} (|\gamma_{0s}|^2 \hbar\omega_{0s} - |\gamma_{\mathbf{q}_s}|^2 \hbar\omega_{\mathbf{q}_s}), \quad \epsilon_s = \epsilon - \Delta E_p. \quad (20)$$

The quantity \tilde{K} , according to (20) consists of two terms which enter with opposite signs. The first term, corresponding to attraction, describes the indirect electron interaction resulting from the interaction between the electrons and the zeroth Fourier component of the phonons, i.e., with fluctuations of the dipole moment of the crystal as a whole. The second term, corresponding to repulsion, is due to the interaction of the polaron wells and receives contributions from the vibrations with all values of \mathbf{q} .

We note that the model proposed in^[1] is obtained from (7) by retaining in it only the zeroth Fourier component of the phonon coordinates. Such a procedure leads to the loss of the second term of (20), so that the electron interaction is always of the attraction type, and leads also to the incorrect conclusion that the indicated effect differs from zero in the absence of dispersion. Actually, however, it follows from (20) that in this case $\tilde{K} = 0$. It is obvious that the phase transition is possible only when $\tilde{K} > 0$, which we shall assume satisfied. The quantity ϵ_e , as well as all quantities having the meaning of an energy gap, will henceforth be regarded as positive. In this case, the effective energy gap $\epsilon - 2\tilde{K}x$ between the states 1 and 2 becomes a linear decreasing function of the concentration x . It follows from (19) that the mean value of x at a temperature T is determined by

²⁾We emphasize that in our case the Ising Hamiltonian describes interacting elementary excitations, the number of which is determined by the thermodynamic-equilibrium conditions.

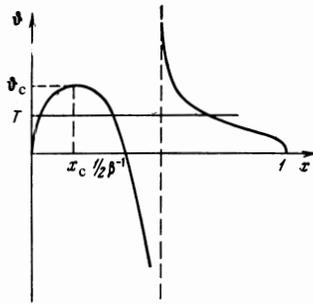


FIG. 1

the Fermi distribution

$$x = \left[\exp\left(\frac{\epsilon_e - 2Kx}{T}\right) + 1 \right]^{-1}. \quad (21)$$

Since the number of excitations is not specified, the chemical potential is equal to zero. From this we obtain an equation for the determination of the equilibrium value of x at the given temperature:

$$\vartheta = \frac{1 - 2\beta x}{\ln(1-x) - \ln x} \equiv f(x); \quad \vartheta = \frac{T}{\epsilon_e}; \quad \beta = \frac{K}{\epsilon_e}. \quad (22)$$

Figure 1 shows a graphic solution of (22). When $\beta < 1$, $f(x)$ is a monotonically increasing function assuming values from zero to infinity, and to each value of ϑ there corresponds a definite x , while x is a monotonically increasing function of ϑ . When $\beta > 1$, the function $f(x)$ vanishes at $x = \frac{1}{2}\beta^{-1}$, and then reverses sign, i.e., $f(x)$ has a maximum at a certain point x_c . It can be shown that the states corresponding to values of x to the right of x_c are absolutely unstable thermodynamically, and the temperature ϑ_c connected with x_c by the relation $\vartheta_c = 2\beta x_c(1-x_c)$ corresponds to the point of absolute instability, in which the state of the system changes jumpwise with further increase of temperature. The approximation under consideration does not make it possible to obtain another branch of states, to which the system should go over when $\vartheta > \vartheta_c$. This final state may be a certain state with $x < 1/2$ (at which the exciton concentration changes jumpwise but the gap remains finite), or a state with $x = 1/2$ ("collapse" of the gap). In the general case the transition is of first order.

Let us see what happens to the unit cell of the lattice. The transformation (13) reflects the fact that when the electron is excited at a site, its interaction with the phonons causes a realignment of the phonons (their centers of gravity shift), leading to the appearance of a static displacement of the nuclei from their positions at $x = 0$ in the unit cell. To obtain this displacement, we substitute (13) in (8), and then

$$u_{jm} = \sum_{q_s} \sqrt{\frac{\hbar}{2NM\omega_{q_s}}} (e_{qs}^j \alpha_{qs} e^{iq \cdot m} + \text{h.c.}).$$

Since $e_{-q}^* = e_q$ and $\alpha_{-q}^* = \alpha_{-q}$, the average displacement of the j -th atom in the unit cell is

$$\begin{aligned} \epsilon_j &= \langle u_{jm} \rangle = \text{Re} \frac{1}{N} \sum_{q, m'} \sqrt{\frac{\hbar}{M\omega_{q_s}}} \gamma_{qs}^* e_{qs}^j e^{iq \cdot (m-m')} \langle n_m \rangle \\ &= \text{Re} \sum_s \sqrt{2} \sqrt{\frac{\hbar}{M\omega_{0s}}} \frac{N_e}{N} \gamma_{0s}^* e_{0s}^j = \text{Re} \sum_s \frac{1}{M\omega_{0s}^2} e_{0s}^j \sum_{j'} w_j \cdot e_{0s}^{*j} x = \Delta u_0^j \cdot x, \end{aligned} \quad (23)$$

i.e., it is proportional to the concentration of the excited excitons. We note that relation (23) is exact. In the transition, x changes jumpwise, and therefore ϵ_j also changes jumpwise. The quantity ϵ_j determines the distortion of the unit cell, and consequently is responsible for the crystal-field change that leads to the decrease of the gap, and is directly connected with the transition temperature. In fact, ϵ_j is the "distortion parameter" introduced in the phenomenological theory^[1]. We note that the quantity ϵ_j , by definition, is much smaller than the lattice constant up to the transition point (the displacement of the j -th atom in the unit cell due to the polaron effect should be small compared with the characteristic dimension of the unit cell, since we have used in the initial Hamiltonian a linear approximation for the electron-phonon interaction). However, the distortion of the unit cell may change by a noticeable amount during the transition, since x changes by an amount on the order of unity. It follows from (23), (16), and (13) that the lattice tends to become realigned with increasing concentration of the excitations, in a manner such as to cause the gap to vanish.

In concluding this section, we note the following circumstance. If we assume that the Hamiltonian (11) with harmonic phonons describes the behavior of the system in the entire region of concentrations ($1 \geq x \geq 0$), then there can be no phase transition, since the problem is equivalent to the ferromagnetic Ising model in an external magnetic field. In this case, the state with the lowest energy is the state with $x = 1$, and the excitation spectrum will have no anomalies leading to a phase transition (it is known that in the Weiss model of a ferromagnet, an external magnetic field eliminates the transition). However, in such a wide range of concentrations (from zero to one) it is essential to take into account the anharmonic terms in the Hamiltonian, for in this case the equilibrium positions of the atoms change significantly. It may turn out that the ground state corresponds to the state with $x = 0$, as was assumed by us. (Such a switch of the ground state as a result of the anharmonicity can be readily demonstrated by means of the model considered in^[1].) It is interesting to note that the Hamiltonian (14) contains a long-range interaction described by the zeroth Fourier component of the potential, thus demonstrating the correctness of introducing the self-consistent field^[3].

3. POLAR (CURRENT) STATES

We consider the case when more than one electron per site can be present. As before, we shall disregard the electron-phonon interaction terms that are non-diagonal in the electrons. In addition, it is now necessary to take into account the Coulomb interaction between the electrons, which can be represented in the form

$$\begin{aligned} V_{\text{Coul}} &= \sum_{m \neq m'} J_{11}(m-m') n_{1m} n_{1m'} + \sum_{m \neq m'} J_{22}(m-m') n_{2m} n_{2m'} \\ &+ 2 \sum J_{12}(m-m') n_{1m} n_{2m'}; \quad n_{\alpha m} \equiv a_{\alpha m}^\dagger a_{\alpha m}. \end{aligned} \quad (24)$$

Here

$$\frac{J_{\alpha\beta}(\mathbf{m})}{e^2} = \int \frac{\varphi_{\alpha\mathbf{m}}^2(\mathbf{r})\varphi_{\beta\mathbf{0}}^2(\mathbf{r}')d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} - (1-\delta_{\alpha\beta}) \int \frac{\varphi_{\alpha\mathbf{m}}(\mathbf{r})\varphi_{\beta\mathbf{m}}(\mathbf{r})\varphi_{\beta\mathbf{0}}(\mathbf{r}')\varphi_{\alpha\mathbf{0}}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}. \quad (25)$$

The omitted terms with $\mathbf{m} \neq \mathbf{m}'$, have, compared with those which are retained, an additional small quantity of the type (1), as a result of the weak overlap of the site functions at the different sites. Taking (10) and (24) into account, the Hamiltonian of the system takes the form

$$\begin{aligned} \mathcal{H} = & \sum \varepsilon n_{\mathbf{m}} + 2 \sum J_{12}(0)n_{\mathbf{m}}(1-\nu_{\mathbf{m}}) + \sum' J_{11}(\mathbf{m}-\mathbf{m}')n_{\mathbf{m}}n_{\mathbf{m}'} \\ & + \sum' J_{22}(\mathbf{m}-\mathbf{m}')(1-\nu_{\mathbf{m}})(1-\nu_{\mathbf{m}'}) + 2 \sum' J_{12}(\mathbf{m}-\mathbf{m}')n_{\mathbf{m}}(1-\nu_{\mathbf{m}'}) \\ & + \sum \mathbf{u}_{j\mathbf{m}}\mathbf{w}_{1j}n_{\mathbf{m}} + \sum \mathbf{u}_{j\mathbf{m}}\mathbf{w}_{2j}(1-\nu_{\mathbf{m}}) \\ & + \sum' \mathbf{u}_{j\mathbf{m}}\tilde{\mathbf{w}}_j(\mathbf{m}-\mathbf{m}')(n_{\mathbf{m}}-\nu_{\mathbf{m}}+1) + \sum \hbar\omega_{\mathbf{q}s}b_{\mathbf{q}s}^+b_{\mathbf{q}s}. \quad (26) \end{aligned}$$

Here

$$n_{1\mathbf{m}} \equiv n_{\mathbf{m}}; \quad n_{2\mathbf{m}} \equiv 1-\nu_{\mathbf{m}}; \quad \sum' \rightarrow \sum_{\mathbf{m} \neq \mathbf{m}'}$$

Now we have three types of independent elementary excitations: 1) excitons, when at a given site the state 2 is empty and 1 is occupied; 2) hole, when there are no electrons at the site; 3) pair, when two electrons, in states 1 and 2 respectively, are located at the site simultaneously. We note that the holes and the pairs correspond in our model to current states. The operators of the numbers of these excitations are of the form:

$$\begin{aligned} \text{Exciton number operator } \nu_{e\mathbf{m}} &= \nu_{\mathbf{m}}n_{\mathbf{m}}; \\ \text{hole number operator } \nu_{h\mathbf{m}} &= \nu_{\mathbf{m}}(1-n_{\mathbf{m}}); \\ \text{pair number operator } \nu_{p\mathbf{m}} &= (1-\nu_{\mathbf{m}})n_{\mathbf{m}}. \end{aligned}$$

The hole and pair operators are connected by the electroneutrality condition

$$N_h = N_p, \quad N_h = \sum_{\mathbf{m}} \nu_{h\mathbf{m}}, \quad N_p = \sum_{\mathbf{m}} \nu_{p\mathbf{m}}. \quad (28)$$

Expressing (26) in terms of the operators (27), we get

$$\begin{aligned} \mathcal{H} = & \hbar\omega_{\mathbf{q}s}b_{\mathbf{q}s}^+b_{\mathbf{q}s} + [\varepsilon - 2(I_{22} - I_{12})]N_e + [\varepsilon \\ & + J_{12}]N_p + \sum' [J_{11}(\mathbf{m}-\mathbf{m}')(\nu_p + \nu_e)_{\mathbf{m}}(\nu_p \\ & + J_{22}(\mathbf{m}-\mathbf{m}')(\nu_e + \nu_h)_{\mathbf{m}}(\nu_e + \nu_h)_{\mathbf{m}'} \\ & - 2J_{12}(\mathbf{m}-\mathbf{m}')(\nu_e + \nu_p)_{\mathbf{m}}(\nu_e + \nu_h)_{\mathbf{m}'}] + \sum \mathbf{u}_{j\mathbf{m}}\mathbf{w}_{1j}(\nu_e + \nu_p)_{\mathbf{m}} \\ & - \sum \mathbf{u}_{j\mathbf{m}}\mathbf{w}_{2j}(\nu_e + \nu_h)_{\mathbf{m}} + \sum' \mathbf{u}_{j\mathbf{m}}\tilde{\mathbf{w}}_j(\mathbf{m}-\mathbf{m}')(\nu_p - \nu_h)_{\mathbf{m}}; \\ I_{12} = & \sum_{\mathbf{m} \neq \mathbf{0}} J_{12}(\mathbf{m}); \quad I_{22} = \sum_{\mathbf{m} \neq \mathbf{0}} J_{22}(\mathbf{m}); \quad J_{12} \equiv J_{12}(0). \quad (29) \end{aligned}$$

As before, we carry out the analysis in the self-consistent field approximation. The last term in (29) can be omitted, since in this approximation it is proportional to $N_p - N_h = 0$, by virtue of the electroneutrality condition. For the same reason, the Coulomb terms with $\mathbf{m} \neq \mathbf{m}'$ in the self-consistent field approximation reduce to a quadrupole-quadrupole interaction, which decreases like $(\mathbf{m}-\mathbf{m}')^{-6}$. It can be shown that such terms contain the small parameter $(r_B/a_0)^5$ (in analogy with Sec. 1) and can therefore be disregarded. The term $I_{22} - I_{12}$ contains a small quantity of the same order³⁾.

³⁾The quantity $I_{22} - I_{12}$ diverges. However, if we add to the Hamiltonian the contribution from the ions, then the diverging term cancels out, and we obtain thereby a small addition to ε , on the order of $(r_B/a_0)^4$.

Expressing $\mathbf{u}_{j\mathbf{m}}$ in terms of the normal coordinates, we obtain

$$\begin{aligned} \mathcal{H} = & \sum \hbar\omega_{\mathbf{q}s}b_{\mathbf{q}s}^+b_{\mathbf{q}s} + \varepsilon N_e + (\varepsilon + 2J_{12})N_p \\ & + \frac{1}{\sqrt{N}} \sum \hbar\omega_{\mathbf{q}s}(\gamma_{\mathbf{q}s1}e^{i\mathbf{q}\mathbf{m}}b_{\mathbf{q}s} + \text{h.c.})(\nu_e + \nu_p)_{\mathbf{m}} \\ & - \frac{1}{\sqrt{N}} \sum \hbar\omega_{\mathbf{q}s}(\gamma_{\mathbf{q}s2}e^{i\mathbf{q}\mathbf{m}}b_{\mathbf{q}s} + \text{h.c.})(\nu_e + \nu_h)_{\mathbf{m}}; \\ \gamma_{\mathbf{q}s\alpha} = & \sum_j \sqrt{\frac{1}{2M\omega_{\mathbf{q}s}\hbar}} e_{\mathbf{q}s}^j \mathbf{w}_{\alpha j}. \quad (30) \end{aligned}$$

Performing a linear transformation of the phonon operators, similar to the transformation (13), with $\alpha_{\mathbf{q}s}$ equal to

$$\alpha_{\mathbf{q}s} = -\frac{1}{\sqrt{N}} \sum_{\mathbf{m}} \gamma_{\mathbf{q}s1}e^{-i\mathbf{q}\mathbf{m}}(\nu_e + \nu_p)_{\mathbf{m}} + \frac{1}{\sqrt{N}} \sum_{\mathbf{m}} \gamma_{\mathbf{q}s2}e^{-i\mathbf{q}\mathbf{m}}(\nu_e + \nu_h)_{\mathbf{m}}, \quad (32)$$

we reduce the Hamiltonian to the form

$$\begin{aligned} \mathcal{H} = & \sum \hbar\omega_{\mathbf{q}s}b_{\mathbf{q}s}^+b_{\mathbf{q}s} + \varepsilon N_e + (\varepsilon + 2J_{12})N_p \\ & - \sum K_1(\mathbf{m}-\mathbf{m}')(\nu_e + \nu_p)_{\mathbf{m}}(\nu_e + \nu_p)_{\mathbf{m}'} \\ & - \sum K_2(\mathbf{m}-\mathbf{m}')(\nu_e + \nu_h)_{\mathbf{m}}(\nu_e + \nu_h)_{\mathbf{m}'} \\ & + \sum L(\mathbf{m}-\mathbf{m}')(\nu_e + \nu_p)_{\mathbf{m}}(\nu_e + \nu_h)_{\mathbf{m}'}; \\ K_1(\mathbf{m}) = & \frac{1}{N} \sum \hbar\omega_{\mathbf{q}s}|\gamma_{\mathbf{q}s1}|^2 e^{i\mathbf{q}\mathbf{m}}; \quad K_2(\mathbf{m}) = \frac{1}{N} \sum \hbar\omega_{\mathbf{q}s}|\gamma_{\mathbf{q}s2}|^2 e^{i\mathbf{q}\mathbf{m}}; \quad (33) \\ L(\mathbf{m}) = & \frac{1}{N} \sum \hbar\omega_{\mathbf{q}s}(\gamma_{\mathbf{q}s1}\gamma_{\mathbf{q}s2}e^{i\mathbf{q}\mathbf{m}} + \text{c.c.}). \quad (34) \end{aligned}$$

In the self-consistent field approximation we have

$$\mathcal{H} = \sum \hbar\omega_{\mathbf{q}s}b_{\mathbf{q}s}^+b_{\mathbf{q}s} + \sum_{\mathbf{m}} \left[\varepsilon_e \nu_{e\mathbf{m}} + \varepsilon_T \nu_{p\mathbf{m}} - 2\mathcal{K} \frac{N_e + N_p}{N} (\nu_e + \nu_p)_{\mathbf{m}} \right]. \quad (35)$$

In the derivation of (35) we used the electroneutrality condition. Here

$$\begin{aligned} \varepsilon_e = & \varepsilon - \Delta E_p; \quad \varepsilon_T = \varepsilon + 2J_{12} - E_{p1} - E_{p2}, \\ \Delta E_p = & \frac{1}{N} \sum_{\mathbf{q}s} \hbar\omega_{\mathbf{q}s}|\gamma_{\mathbf{q}s1} - \gamma_{\mathbf{q}s2}|^2, \\ E_{p1} = & \frac{1}{N} \sum \hbar\omega_{\mathbf{q}s}|\gamma_{\mathbf{q}s1}|^2, \quad E_{p2} = \frac{1}{N} \sum \hbar\omega_{\mathbf{q}s}|\gamma_{\mathbf{q}s2}|^2, \\ \mathcal{K} = & \sum_s \hbar\omega_{0s}|\gamma_{0s1} - \gamma_{0s2}|^2. \quad (36) \end{aligned}$$

Thus, in the self-consistent field approximation, the energy of the system is a function of N_e and N_p only. Recognizing that not more than one excitation can be present at a single site simultaneously, we obtain the following expression for the entropy:

$$\begin{aligned} S = & -N[x_e \ln x_e + 2x_p \ln x_p + (1-x_e-2x_p) \ln(1-x_e-2x_p)]; \\ x_e = & \frac{N_e}{N}, \quad x_p = \frac{N_p}{N}, \quad 0 < x_e < \frac{1}{2}, \quad 0 < x_p < \frac{1}{2}, \\ & 0 < x_e + x_p < 1. \quad (37) \end{aligned}$$

The equilibrium values of x_e and x_p are determined from the condition for the minimum of the free energy $F = E - TS$ with respect to x_e and x_p . Then the equations for the determination of the equilibrium x_e and x_p take the form

$$\begin{aligned} \frac{1}{N} \frac{\partial F}{\partial x_e} = & \varepsilon_e - 2\mathcal{K}(x_e + x_p) + T \ln \frac{x_e}{1-x_e-2x_p} = 0, \\ \frac{1}{N} \frac{\partial F}{\partial x_p} = & \varepsilon_T - 2\mathcal{K}(x_e + x_p) + 2T \ln \frac{x_p}{1-x_e-2x_p} = 0. \quad (38) \end{aligned}$$

The distortion of the unit cell is determined in this case both by the exciton concentration and by the concentration of the holes and pairs; it is given by expression (23), in which x should be replaced by $x_e + x_p$.

Let us consider two limiting cases.

1) $\epsilon_e \ll \epsilon_T/2$. In this case $x_p/x_e \ll 1$ and we can neglect x_p compared with x_e . The system (38) breaks up into Eq. (21) for x_e , and x_p is equal to

$$x_p = (1 - x_e) \exp \left[-\frac{1}{2T} (\epsilon_T - 2Kx_e) \right]. \quad (39)$$

In this case the phase transition is due to the exciton system, and the concentration of the current excitations depends parametrically on x_e . In particular, if the excitons experience a phase transition with a "collapse" of the gap, i.e., the concentration changes jumpwise from $x_e^0 \ll 1$ to $x_e^1 \approx 1/2$, then the electron concentration also changes jumpwise from

$$x_p^0 \approx \exp(-\epsilon_T/2T)$$

to

$$x_p^1 \approx (1 - x_e^1) \exp \{ -(\epsilon_T - 2Kx_e^1) / 2T \},$$

and the gap width decreases by an amount $\tilde{K}x_e^1$. It is important that in this case the carrier spectrum both before and after the transition can be characterized by a nonzero gap, and the jump of the carrier density before and after the transition generally speaking, is not limited in magnitude, i.e., a Mott semiconductor-semiconductor transition takes place. Just as in the homopolar case, the transition is effected by realignment of the unit cell.

2. $\epsilon_e > \epsilon_T/2$. In this case $x_e/x_p < 1$ and we can neglect x_e compared with x_p . The carrier density is determined from the equation

$$x_p = [2 + \exp \{ (\epsilon_T - 2Kx_p) / 2T \}]^{-1}. \quad (40)$$

The exciton concentration depends parametrically on the electron concentration (concentration of the current excitations)

$$x_e = (1 - 2x_p) \exp \{ -(\epsilon_e - 2Kx_p) / T \}. \quad (41)$$

In essence, it is precisely this case which is equivalent to that considered in^[1]. In this case, as noted in^[1] the ratio of the current densities before and after the transition, at reasonable values of the parameters, cannot exceed one or two orders of magnitude.

From the expression for the distortion of the unit cell we see that a noticeable realignment of the cell takes place during the transition regardless of whether the transition is of the "exciton" or electronic type. It is only important that in the final state the number of excitations of any kind be of the order of the number of lattice sites.

If the electron spin is taken into account while the exchange interaction is neglected, then one more branch of current excitations arises, when the pair consists of two electrons in the same lower state but with opposite spins. The corresponding Coulomb energy will now be not $2J_{12}(0)$ but

$$2J_{22}(0) \approx e^2 \int \varphi_2^2(\mathbf{r}) \varphi_2^2(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} d\mathbf{r} d\mathbf{r}',$$

and it can greatly differ from the former. The foregoing

analysis corresponds to the case when $J_{22} > J_{12}$, i.e., the aforementioned branch is not excited. Without account of the spin-orbit interaction, using reasoning similar to that given above, we obtain in lieu of (38), when $J_{22} < J_{12}$ (this corresponds to disregarding the states in which the exciton and the pair are at one site),

$$\begin{aligned} \epsilon_e - 2Kx_e + T \ln \frac{x_e}{1 - x_e - 2x_p} &= 0; \\ J_{22} - E_{p1} + T \ln \frac{x_p}{1 - x_e - 2x_p} &= 0; \\ x_p &= (1 - x_e) \left[2 + \exp \left(\frac{J_{22} - E_{p1}}{T} \right) \right]^{-1}. \end{aligned} \quad (42)$$

If now the exciton system experiences a transition, then x_p also experiences a jump (as a result of the factor preceding the exponential). On the other hand, if the exciton system is stable, then the system of current excitations is also stable, unlike the case considered above.

4. DISCUSSION OF RESULTS

We have considered above, in an approximation equivalent to the self-consistent field approximation, the possibility of phase transitions in an electronic system, of the Heitler-London type. The mechanism causing the loss of thermodynamic stability of the electron system is the indirect electron-electron interaction via the optical lattice vibrations. This interaction leads to an energy gain when the electrons are excited or, in other words, the width of the energy gap decreases with increasing concentration of the excitations. The self-consistent field approximation in our problem is equivalent to the use of an "abbreviated" pair Hamiltonian, retaining only the zeroth Fourier component of the interaction potential, describing the interaction of the electrons with the fluctuations of the dipole moment of the entire crystal.

We have shown that, depending on the relation between the exciton gap ϵ_e , determined by the splitting of the states in the crystal field, and the effective electron (current) gap ϵ_T , which takes into account the Coulomb interaction of two electrons at one site, the transition can be in the limiting cases either of the "exciton" (case 1) or of the "electronic" type (case 2).

When $\epsilon_e = \tilde{K}$, the transition is a second-order one. Inasmuch as the electron system experiences a radical realignment during the phase transition, owing to the interaction with the lattice, the lattice itself becomes realigned, i.e., the electron system causes a transition of the displacement type in the lattice. Apparently, valuable information concerning the electronic nature of the transition can be obtained by investigating the influence of the illumination on the phase transition⁴⁾.

We note that the theory developed by Adler and Brooks^[1] could not explain for example the jump of the electric conductivity at the transition point, amounting to seven orders of magnitude for V_2O_3 and resulting

⁴⁾The possibility of using light to observe the electronic nature of the transition, and also reference 4, were pointed out to us by G. E. Pikus. Thus, if the excitons are photo-excited, then, under the condition that the transition occurs in the carrier system, the problem is described by the second equation of (42), where x_e is given. The shift of the transition temperature is then determined by the expression $\Delta T_C/T_C = 2\chi_e/\epsilon_T$.

from the change of the concentration; as noted by the authors themselves, the theory made it necessary to assume that the mobility of the carriers changes by a factor 10^5 at the transition point, and amounts to 10^{-5} cm²/V-sec in the semiconducting state. In our theory, when the transition is of the "exciton" type, as noted above, the jump of the concentrations is not limited in magnitude. In this case the metallic state should be interpreted as a state in which the current gap vanishes as a result of the finite width of the allowed bands. (In our model, in which the finite width of the bands is not taken into account, a metal corresponds to a Mott semiconductor with a small forbidden band).

Using the values of the transition temperature and of the jump of the electric conductivity^[1], we can estimate the parameters of V₂O₃ in the semiconducting phase, assuming the transition to be of the "exciton" type (case 1) and the jump of the electric conductivity to be connected only with the jump of the concentration of current excitations. From the theory developed above we get three simple relations between the concentration jump σ_M/σ_S and the transition temperature T_c with the constant of the molecular field \tilde{K} , the exciton gap ϵ_e at $T = 0$, and the exciton concentration at the transition point x_{ce} :

$$\frac{\sigma_M}{\sigma_S} = \exp\left(\frac{\tilde{K}}{T_c}\right); \quad T_c = 2\tilde{K}x_{ce}; \quad \epsilon_e = T_c(1 - \ln x_{ce}).$$

The calculated values are given below.

Self-consistent field constant $\tilde{K} = 0.44$ eV.

Concentration of excitons at the transition point $x_{ce} = 0.0015$.

Exciton excitation energy $\epsilon_e = 0.07$ eV

$$\begin{aligned} \epsilon_T/\epsilon_e &= 3.4 - 5.2 > 2. \\ \beta &= \tilde{K}/\epsilon_e = 6.3 > 1. \end{aligned}$$

From the experimental data of^[1] we have:

Transition temperature $T_c = 150^\circ$ K.

Jump of electric conductivity $\sigma_M/\sigma_S = 10^7$.

Activation energy from the temperature dependence of the electric conductivity σ :

$$q = \frac{1}{2}\epsilon_T = 0.12 + 0.18 \text{ eV}, \quad \sigma = \sigma_0 \exp(-q/kT).$$

Position of the absorption peak $\epsilon_0 \approx 0.1$ eV.

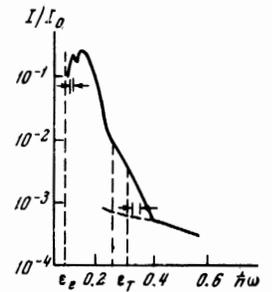


FIG. 2. Absorption spectrum of V₂O₃ [1]. The dashed lines limit the energy region containing the values of the current gap from the electric-conductivity data.

We see that the calculated relations between the parameters of the semiconductor actually agree with the "exciton" nature of the transition.

Similar calculations can be made for such substances as VO, VO₂. The calculated value of ϵ_e can be compared with the independently determined (from optical measurements) position of the exciton peak. Such a comparison is shown in Fig. 2, which indicates both $\epsilon_e = 0.07$ eV and the values (arrows) of the current gap, which should correspond to the absorption edge.

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¹D. Adler and H. Brooks, Phys. Rev. 155, 826 (1967); J. Feinleib and W. Paul, Phys. Rev. 155, 841 (1967); D. Adler, J. Feinleib, H. Brooks, and W. Paul, Phys. Rev. 155, 851 (1967).

²R. E. Peierls, The Quantum Theory of Solids, Oxford, 1955.

³R. Brout, Phase Transitions, Benjamin, 1965.

⁴V. M. Fridkin, ZhETF Pis. Red. 3, 252 (1966) [JETP Lett. 3, 161 (1966)]; L. M. Belyaev, I. I. Groshik, V. V. Lyakhovitskaya, V. N. Nosov, and V. M. Fridkin, ZhETF Pis. Red. 6, 481 (1967) [JETP Lett. 6, 16 (1967)]; B. P. Grigas, I. P. Grigas, and R. P. Belyankas, Fiz. Tverd. Tela 9, 1532 (1967) [Sov. Phys. -Solid State 9, 1203 (1967)].

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