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CHARGED EXCITONS, ANOMALOUS TEMPERATURE SHIFT OF THE ENERGY BANDS, AND THE INSULATOR-METAL TRANSITION

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Some compounds of the transition and rare earth metals are diamagnetic at low temperatures but become paramagnetic with increase of temperature. In a number of cases rearrangement of the partially filled magnetic-ion electron shells, which can be interpreted as excitation of low frequency Frenkel excitons, leads to a fundamental change in the electrical properties of the crystals. The influence of the interaction between excitons and conduction electrons on the state of the latter is investigated. At sufficiently low concentrations the conduction electrons can be regarded as localized magnetic moments with a concentration which depends on the temperature. Bound states are possible between an electron and either a single exciton ("charged excitons") or a whole complex of excitons ("ferromagnetic micro-regions in a diamagnetic crystal"). If the "charged excitons" play the dominant role in the transfer processes then a specific mechanism of charge motion in the crystal by exciton charge transfer becomes possible, leading to a sharp rise in the mobility with temperature. Electron-excitation interaction also leads to an anomalously large shift of the bottom of the conduction band, and this can be used to explain the insulator-metal transition in such materials.

1. FORMULATION OF THE PROBLEM

IONS of the transition and rare-earth elements in some of their compounds do not possess a magnetic moment at low temperatures. However, on increase of temperature, they go over into a state with non-zero moment. Change in the magnetic structure of the ions is accompanied in a number of cases by a fundamental change in the electrical properties of these materials. For example, $LaCoO_3$ crystals at low temperatures are semiconductors with small carrier mobility, which increases sharply with rise of temperature. However, at high temperatures they go over from the semi-conducting state to the metallic state.[1] An analogous transition has also been observed in SmB_6 at a temperature below 3°K.[2]

The rearrangement of the d- or f-shells in these ions can be interpreted as the excitation of low-frequency Frenkel excitons (thus, in $LaCoO_3$, triplet excitons of energy ~ 0.01 eV are excited[1]). These excitons have very small mobility, i.e., they are practically localized magnetic moments, the concentration of which depends on the temperature. Below it will be shown that the anomalous electric properties of crystals of the type $LaCoO_3$ and SmB_6 can be explained by the interaction of the current carriers with these localized moments.

The interaction of conduction electrons with excitons in the case under consideration is of an exchange nature. Earlier, in [3], an investigation was made of the effect on the electronic states of a polarizing electron-exciton interaction inducing the creation or annihilation of Frenkel excitons without change in the ion spin. The difference between these two types of interaction implies that the electron states in the case under consideration are of a type totally different from the exciton-polaron states studied in [3].

A specific feature of the materials considered is the narrowness of the forbidden band (in $LaCoO_3$ it is tenths of an eV[1] and in SmB_6 it is thousandths of an eV[2]). This makes it necessary to use a two-band model, in which states of both the conduction and valence bands are taken into account.

The basic results of the paper can be formulated as follows. Bound states of a conduction electron with a Frenkel exciton ("charged exciton") are possible. For real crystal parameters the binding energy of an electron with an exciton can exceed the excitation energy of the exciton, i.e., the "charged exciton" is energetically more favorable than an electron in the conduction band. A bound state of an electron with a whole complex of Frenkel excitons can turn out to be even more energetically favorable. If the number of excitons in the complex is sufficiently great, it can be regarded as a ferromagnetic micro-region in a diamagnetic semiconductor.

If the level of the conduction electron trapped by an exciton or by a complex of them falls within the valence band, its width becomes finite. Such an electron state is a superposition of a localized state, constructed from states of the conduction band, and a delocalized state, constructed from states of the valence band.

An electron trapped by an exciton can move through the crystal by hopping from exciton to exciton. This mechanism for the motion leads to a sharp increase of mobility with temperature. In this respect current carriers of the above type resemble small-radius polarons,[4] although here the reason for the increase of mobility with temperature is completely different.

The electron-exciton interaction causes an anomalously large temperature shift of the bottom of the conduction band. It is especially great in cases when this interaction results in the appearance of local or resonance levels close to the bottom of the conduction band.

If bound electron-exciton states are not formed, this anomalous temperature shift can explain the insulator-metal transition in the materials with narrow forbidden band under consideration. An insulator-metal transition is also possible in cases when bound electron-exciton states are realized. The reason for this is the destruction of these states at sufficiently high exciton concentrations.

2. BOUND ELECTRON-EXCITON STATES

Unlike the Kondo effect, the problem treated here is a one-electron problem. The Hamiltonian of the system is written in the form

$$\begin{aligned}\mathscr{H} = \omega \sum b_{\mathbf{g}\tau}^{*} b_{\mathbf{g}\tau} + \sum \varepsilon_{\mathbf{k}l} \overset{*}{a}_{\mathbf{k}l\sigma} a_{\mathbf{k}l\sigma} \\ - \frac{1}{2N} \sum A_{ll'}(\mathbf{s})_{\sigma\sigma'}(\mathbf{S})_{\tau\tau'} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{g}} \overset{*}{a}_{\mathbf{k}l\sigma} a_{\mathbf{k}'l'\sigma'} b_{\mathbf{g}\tau}^{*} b_{\mathbf{g}\tau'} \delta(\sigma+\tau, \sigma'+\tau') \\ - \frac{1}{2N} \sum I(\mathbf{g}-\mathbf{f})(\mathbf{S})_{\tau\tau'}(\mathbf{S})_{\lambda\lambda'} t_{\mathbf{g}\tau}^{*} b_{\mathbf{g}\tau'} b_{\mathbf{f}\lambda}^{*} b_{\mathbf{f}\lambda'} \delta(\lambda+\tau, \lambda'+\tau'). \end{aligned} \quad (1)$$

Here $\overset{*}{a}_{\mathbf{k}l\sigma}$ and $a_{\mathbf{k}l\sigma}$ are the operators of creation and annihilation of an electron with quasi-momentum $\mathbf{k}$ and spin projection σ in band l. The conduction band will be denoted by the index $l = 1$, and the valence band by $l = -1$. The operators $\overset{*}{b}_{\mathbf{g}\tau}$ and $b_{\mathbf{g}\tau}$ describe the creation and annihilation of an exciton with spin projection τ at an atom of label $\mathbf{g}$. The symbols $\mathbf{s}$ and $\mathbf{S}$ respectively denote the spin operators of a conduction electron and an exciton and $\delta(n, m)$ is a delta-function of discrete argument. It is assumed that the spin S of the exciton can differ from unity.

It is best to start from the case of a bound state of an electron with one exciton. The calculation is performed by generalizing the Green's-function method developed by Lifshitz[5] to the case of a defect with an internal degree of freedom (spin) and an unperturbed electron-energy spectrum consisting of two bands.

Clearly the states of the system being considered can be classified by the values of the combined spin of the exciton and electron. For a combined spin $S - 1/2$, using the Clebsch–Gordan coefficients,[6] we can represent the wave-function of the system in the form

$$\psi = \sum_{\mathbf{k}l} x_{\mathbf{k}l} \{\sqrt{S-\tau+1}\; \overset{*}{a}_{\mathbf{k}l\uparrow} \overset{*}{b}_{\mathbf{g}\tau-1} - \sqrt{S+\tau}\; \overset{*}{a}_{\mathbf{k}l\downarrow} \overset{*}{b}_{\mathbf{g}\tau}\} |0\rangle, \quad (2)$$

where $|0\rangle$ is the vacuum wave function, $\mathbf{g}$ is the label of the site at which the exciton is excited, and $\tau - 1/2$ is the value of the projection of the combined spin of the system. In writing expression (2), we have used the fact that the Hamiltonian (1) conserves the number of excitons at each atom (as was noted above, the mobility of Frenkel magnetic excitons is very small).

Using expression (1) and (2) and taking account of the equality[6]

$$S_{\tau\tau-1}^{+} = S_{\tau-1\tau}^{-} = \sqrt{(S+\tau)(S-\tau+1)} \quad (S^{\pm} = S^{x} \pm iS^{y}) \quad (2')$$

we obtain the following system of equations for the expansion coefficients $x_{\mathbf{k}l}$:

$$(\varepsilon_{\mathbf{k}l} - E_L) x_{\mathbf{k}l} + \frac{A_l(S+1)}{2} X_l + \frac{A(S+1)}{2} X_{-l} = 0, \quad (3)$$

$$X_l = \frac{1}{N} \sum_{\mathbf{p}} x_{\mathbf{p}l} \quad (A_l \equiv A_{ll},\ A \equiv A_{l,-l}).$$

From the existence condition for the solution of the system (3), we find an equation for the electron energy E_L:

$$\left[1 - \frac{A_1(S+1)}{2} F_1(E_L)\right]\left[1 - \frac{A_{-1}(S+1)}{2} F_{-1}(E_L)\right] = \frac{A^2(S+1)^2}{4} F_1(E_L) F_{-1}(E_L), \quad (4)$$

where for the Green's function of the l-th band we have used the notation

$$F_l(E) = \frac{1}{N} \sum_{\mathbf{p}} \frac{1}{E - \varepsilon_{\mathbf{p}l}}.$$

For a combined spin $S + 1/2$ for the electron and exciton, the wavefunction of the system can be represented in the form

$$\psi = \sum_{\mathbf{k}l} x_{\mathbf{k}l} \{\sqrt{S+\tau}\; \overset{*}{a}_{\mathbf{k}l\uparrow} \overset{*}{b}_{\mathbf{g}\tau-1} + \sqrt{S-\tau+1}\; \overset{*}{a}_{\mathbf{k}l\downarrow} \overset{*}{b}_{\mathbf{g}\tau}\} |0\rangle. \quad (5)$$

It corresponds to the same combined spin projection of the system $\tau - 1/2$. In this case, the expansion coefficients $x_{\mathbf{k}l}$ are determined from the system of equations

$$(\varepsilon_{\mathbf{k}l} - E_L) x_{\mathbf{k}l} - \frac{A_l S}{2} X_l - \frac{AS}{2} X_{-l} = 0, \quad (6)$$

for which the condition for the existence of a non-trivial solution is the equality

$$\left[1 + \frac{A_1 S}{2} F_1(E_L)\right]\left[1 + \frac{A_{-1} S}{2} F_{-1}(E_L)\right] = \frac{A^2 S^2}{4} F_1(E_L) F_{-1}(E_L). \quad (7)$$

Each of the equations (4) and (7) has two solutions, one of which is "genetically" associated with the conduction band, and the other with the valence band. The analysis of them is considerably simplified if we assume that the exchange integral A_1 is much greater than the exchange integrals A_{-1} and A. This is justified by the fact that in the case under consideration the conduction-band electrons move mainly by way of the cations and the valence-band electrons by way of the anions. Since the excitons are localized on cations and the exchange forces are short-range, the conduction-band electrons interact more strongly with excitons than do the valence-band electrons.

In the materials under consideration, the exchange energy of an electron with an exciton V_0, equal to $-A_1S/2$ for $A_1 > 0$ and $A_1(S+1)/2$ for $A_1 < 0$, is several tenths of an eV, and the effective mass m_1 of a conduction electron is several times greater than the mass m_0 of a free electron. For such values of the parameters, a local electron level lying below the bottom of the conduction band is possible, irrespective of the sign of the exchange integral A_1. It splits off from the bottom of the conduction band, starting at the critical value $|V_0|$, which, for a simple cosinusoidal dispersion law for the conduction electrons, is equal to $1.2\, m_0/m_1$ eV. On further increase of $|V_0|$, the level passes through the whole forbidden band and falls into the valence band, after which, like a resonance level, it acquires a finite width. To take this fact into account, it is sufficient to replace E by $E + i\epsilon$ ($\epsilon \to 0$) in expressions (4) and (7). In the leading approximation in A, we obtain the following expression for the imaginary part of the energy of the state:

$$E_L'' = \left| \left(\frac{A}{A_1}\right)^2 \frac{g_{-1}(E)}{dF_1(E)/dE} \right|_{E=E_L'} \quad (8)$$

where $g_{-1}(E)$ is the density of levels in the valence band, and E_L' is the electron level found by solving equations (4) and (7) in the zeroth approximation in A and A_{-1}.1) As has already been pointed out, the electron state under consideration is a superposition of a localized state, constructed from states of the conduction band, and a delocalized state, constructed from states of the valence band. This state, inasmuch as delocalized states take part in its formation, resembles a resonance state, although of course, it is of a completely different type. In particular, in the one-dimensional case, it is well-known that resonance states are not realized, whereas states of the type under consideration are possible.

Clearly, a necessary condition for the system to be stable with respect to formation of bound electron–exciton states is the inequality $E_L + \omega > \epsilon_{0,-1}$, where $\epsilon_{0,-1}$ is the energy of the top of the valence band. Consistent with this inequality is the inequality $E_L + \omega < \epsilon_{01}$, where ϵ_{01} is the energy of the bottom of the conduction band. The latter expresses the fact that if there is an odd electron in the crystal at $T = 0$, its transition to a bound state with an exciton is energetically favorable. The energy expended in exciting the exciton, which in the materials considered is not great, is compensated by the gain in energy due to the exchange interaction of an electron with the exciton.

If the exciton frequencies are sufficiently small, it may turn out that the minimum energy of a crystal with an odd electron is attained when this electron is in a bound state not with one exciton, but with a whole complex of them. This complex must clearly occupy some simply connected microregion in the crystal. To ensure the maximum gain in electron-exciton exchange energy, it is necessary that the spins of all the excitons be parallel to each other. Such an exciton complex can be regarded as a ferromagnetic micro-region in a diamagnetic semiconductor.

To find the energy of the ground state in the case under consideration, we can make use of a technique analogous to that used earlier in an investigation of ferromagnetic microregions in anti-ferromagnetic crystals.[8,9] For definiteness, we consider the case when the quantities A_l are positive. A variational principle is used. In constructing the trial wavefunction we assume that the excitons occupy a microregion of radius R, which is treated as the variational parameter:

$$\psi = \sum_{\mathbf{f}l} \varphi_l(\mathrm{f}) \sum_{\mathbf{k}} a^{*}_{\mathbf{k}l\uparrow} e^{-i\mathbf{k}\mathbf{f}} \prod_{|\mathbf{g}|<R} b_{\mathbf{g}s}{}^{*} |0\rangle. \tag{9}$$

The symbol $|\mathbf{g}| < R$ denotes the ions within the microregion.

If the radius R is much greater than the lattice constant, the quantities $\varphi_1(\mathbf{f})$ can be assumed to be slowly varying functions of the coordinates of the atoms **f**. We can therefore go over to the continuous-medium approximation, replacing the discrete variable **f** by the continuous one **r** in the quantities $\varphi_1(\mathbf{f})$ and $\varphi_{-1}(\mathbf{f})$, which can be regarded as two components of a spinor wavefunction. The wave equation obtained using expressions (1) and (9) then takes the form

$$\begin{aligned} -\frac{1}{2m_1}\Delta\varphi_1(\mathbf{r}) - \left[\frac{A_1S}{2}\varphi_1(\mathbf{r}) + \frac{AS}{2}\varphi_{-1}(\mathbf{r})\right]\theta(R-r) &= (E_L - \varepsilon_{01})\varphi_1(\mathbf{r}), \\ -\frac{1}{2m_{-1}}\Delta\varphi_{-1}(\mathbf{r}) - \left[\frac{A_{-1}S}{2}\varphi_{-1}(\mathbf{r}) + \frac{AS}{2}\varphi_1(\mathbf{r})\right]\theta(R-r) &= (E_L - \varepsilon_{0,-1})\varphi_{-1}(\mathbf{r}). \end{aligned} \tag{10}$$

Here $\theta(x)$ is the unit-step function. The effective mass m_1 of an electron in the conduction band is positive, while that in the valence band m_{-1} is negative.

Stationary states of the system being considered exist if the electron level E_L lies within the forbidden band. The spinor wave function inside a potential well of radius R is sought as an s-wave with, generally speaking, complex wave-number k. Two different values of k correspond to the same value of E, so that the wave function of the system inside the potential well is represented as a superposition of two spherical waves, and outside it as an attenuating spherical wave ($l = \pm 1$):

$$r\varphi_l = \left\{B_l \sin k_l r + B_{-l}\frac{m_l AS}{k_{-l}{}^2 - \chi_l{}^2}\sin k_{-l} r\right\}\theta(R-r) + C_l e^{-\varkappa_l r}\theta(r-R), \tag{11}$$

where we have used the notation

$$\begin{gathered} k_l{}^2 = {}^1\!/_2(\chi_1{}^2 + \chi_{-1}{}^2) + {}^1\!/_2 l\sqrt{(\chi_l{}^2 - \chi_{-l}{}^2)^2 + m_1 m_{-1} A^2 S^2}, \\ \chi_l^2 = 2m_l(E - \varepsilon_{0l} + {}^1\!/_2 A_l S), \qquad \varkappa_l^2 = 2m_l(\varepsilon_{0l} - E). \end{gathered}$$

From the continuity conditions for the two components of the wave function and their normal derivatives at the boundary of the potential well, we obtain the following transcendental equation for the energy:

$$\begin{aligned} &\prod_{l=\pm 1}(k_l\cos k_l R + \varkappa_l \sin k_l R) \\ &= A^2S^2\prod_{l=\pm 1}\frac{m_l}{(k_{-l}^2 - \chi_l^2)}(k_l \cos k_l R + \varkappa_{-l}\sin k_l R). \end{aligned} \tag{12}$$

If E_L lies within the valence band, the solution (12) can be analytically continued from the real-axis cut $\epsilon_{0,-1} < E < \epsilon_{01}$ into the complex E-plane, in a way similar to that used in the theory of resonance states. Then, as in the case of one exciton, the level-width becomes finite.

The radius R of the micro-region is determined from the equation

$$\frac{d}{dR}\left[E_L(R) + (\omega - 3IS^2)\frac{4\pi}{3}\left(\frac{R}{a}\right)^3 - 4\pi\left(\frac{R}{a}\right)^2(3IS^2)\right] = 0, \tag{13}$$

where a is the lattice constant and I is the exchange integral between excited magnetic atoms in the nearest-neighbor approximation. Generally speaking, it can be of either sign. If it is positive, exchange between excited atoms favors increase of the radius of the ferromagnetic micro-region. For $6I \ll \omega \sim 10^{-2}$ eV, $A_1S \sim 0.5$ eV, and $m_1/m_0 \sim 1$, we obtain the value 2a for the radius R, and so the estimates obtained in the continuous-medium approximation are entirely reasonable.

We should note that ferromagnetic micro-regions in a diamagnetic semiconductor can be formed not only near free carriers but also near carriers trapped by charge-centers (i.e., near electron donors). Since there are few ionized donors at low temperatures, only localized electrons can have a noticeable influence on the

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1) One might have formed the impression that there is no broadening of the local level, since electron transitions from it into the valence band, which is completely filled by electrons, are forbidden by the Pauli principle. But, in fact, a localized moment deforms the one-electron states of the conduction band and valence band, causing them to be partially mixed. First it is necessary to find these new one-electron states, including also the localized state with allowance for its damping, and then fill them with electrons. In this respect the situation is completely analogous to the case of a localized moment in a metal. There the d-level lies below the Fermi level, i.e., also falls in a band of filled states. Nevertheless, it has a finite width [7].

magnetic properties of crystals. The reason why the ferromagnetic micro-regions can substantially affect the magnetic susceptibility of the crystal even at relatively small concentrations of them is exactly the same here as in the case of antiferromagnetic semiconductors,[9] namely that their contribution to the magnetic susceptibility is proportional to the square of their moment, which is $^8/_3\pi S(R/a)^3$ times greater than the moment of the electron which caused their appearance. The generalization of the calculation of the radius of a ferromagnetic micro-region to the case of localized electrons is performed in exactly the same way as in paper.[9] Magnetic measurements are clearly the most convenient for detecting ferromagnetic micro-regions and have already made it possible to establish their presence in crystals of EuSe in the paramagnetic state.[10]

Since the Frenkel excitons considered here are practically localized, the conduction electrons trapped by them must have very small mobility. However, a specific charge-motion mechanism is possible here, leading to a sharp rise in the mobility with temperature and can play an important role if charge-transfer by "charged excitons" (electron + exciton) is dominant.

With rise in temperature, there is a decrease in the average distance between a "charged exciton" and neighboring excitons which have appeared as a result of thermal excitation. As a result it becomes possible for an electron to move through the crystal by way of transitions from one exciton to another. The similarity between this mechanism of motion and the motion of a carrier by way of impurities in ordinary semiconductors is obvious.

The probability of transfer of an electron from an exciton to an exciton is determined by the overlap of the electron orbits corresponding to localization of the) electron at these excitons. It increases exponentially with decrease in the distance between excitons. This is the reason for the sharp temperature dependence of the mobility. To establish the nature of the temperature dependence of the mobility u for $kT \ll \omega$, we can make use of the theory of impurity-conduction,[11] according to which, $u \sim \exp\{-cn^{-1/2}r_L^{-3/2}\}$, where n is the defect concentration, assumed to be substantially greater than the carrier concentration, r_L is the radius of a localized electron state, and c is a constant of order unity. The exciton concentration n is given here by the expression

$$\nu \equiv na^3 = \frac{(2S+1)e^{-\omega/kT}}{1+(2S+1)e^{-\omega/kT}} \approx (2S+1)e^{-\omega/kT}, \tag{14}$$

and so their mobility is proportional to

$$u \sim \exp\{-c(2S+1)^{-1/2}(r_L/a)^{-3/2}e^{\omega/2kT}\}. \tag{15}$$

In its rapid increase in mobility with temperature, described by formula (15), a "charged exciton" resembles a small-radius polaron.[4] In $LaCoO_3$ crystals, where the mobility is observed to have this type of behavior,[11] it is more probable that this is due to exactly these "charged excitons," since the exchange energy V_0 is considerably greater than the energy of polarization of the crystal by an electron.

3. SHIFT OF THE BAND EDGE. THE INSULATOR-METAL TRANSITION

The interaction of electrons with excitons, along with the formation of bound electron-exciton states, can bring about an anomalously strong temperature shift in the bottom of the conduction band. A calculation of this effect is performed below by means of a generalization of the calculation of band-shifts caused by defects.[12] Since, however, simultaneous allowance for the two bands and for the Heisenberg character of the electron-exciton interaction leads to very cumbersome expressions, it is appropriate to assume from the outset that the exchange integrals A_{-1} and A can be neglected in comparison with A_1. The wavefunction of the system is constructed in a form which is a generalization of the one-exciton expressions (2) and (5) to the case of a system with N_0 excitons:

$$\psi = \Big\{\sum_{\mathbf{k}} x_{\mathbf{k}} a^*_{\mathbf{k}\downarrow 1} + \sum_{\mathbf{k}m} y_{m\mathbf{k}} (S^-)_{\tau_m-1\,\tau_m} a^*_{\mathbf{k}\uparrow 1} b^*_{\mathbf{g}_m\tau_m-1} b_{\mathbf{g}_m\tau_m}\Big\} \prod_{n=1}^{N_0} b^*_{\mathbf{g}_n\tau_n}|0\rangle, \tag{16}$$

where $\mathbf{g}_n$ and τ_n are the coordinate and spin projection of the n-th exciton. We should note that the exact wave function of the Hamiltonian (1) for $N_0 > 1$ has a more complicated structure than expression (16), so that the latter must be regarded as a trial function in a variational method. For this reason the use of expression (16) must lead to an overestimate for the energy of the bottom of the conduction band.

It is assumed that the exciton concentration is small, so that the interaction between them can be neglected. Using expressions (1), (2′) and (16) leads to the following system of equations for the expansion coefficients $x_{\mathbf{k}}$ and $y_{m\mathbf{k}}$:

$$\begin{gathered}(\varepsilon_{\mathbf{q}1}-E)x_{\mathbf{q}} + \frac{A_1}{2N}\sum_{\mathbf{k}n} e^{i(\mathbf{q}-\mathbf{k})\mathbf{g}_n}\tau_n x_{\mathbf{k}} - \frac{A_1}{2N}\sum_{\mathbf{k}n} e^{i(\mathbf{q}-\mathbf{k})\mathbf{g}_n} f(\tau_n) y_{n\mathbf{k}} = 0,\\ (\varepsilon_{\mathbf{q}1}-E)y_{n\mathbf{q}} - \frac{A_1}{2N}(\tau_n-1)\sum_{\mathbf{k}} e^{i(\mathbf{q}-\mathbf{k})\mathbf{g}_n} y_{n\mathbf{k}} - \frac{A_1}{2N}\sum_{\mathbf{k}} e^{i(\mathbf{q}-\mathbf{k})\mathbf{g}_n} x_{\mathbf{k}} = 0,\end{gathered} \tag{17}$$

where

$$f(\tau) = S(S+1) + \tau - \tau^2.$$

Equations (17) are transformed to the integral form

$$\begin{gathered}X_m - {}^1/_2 A_1 \sum_n \tau_n F_1(\mathbf{g}_n-\mathbf{g}_m)X_n + \sum_n f(\tau_n)F_1(\mathbf{g}_n-\mathbf{g}_m)Y_n = 0,\\ [1+F_1(\tau_n-1)]Y_n + F_1 X_n = 0,\end{gathered} \tag{18}$$

where

$$X_n = \sum_{\mathbf{q}} x_{\mathbf{q}} e^{-i\mathbf{q}\mathbf{g}_n}, \quad Y_n = \sum_{\mathbf{q}} y_{n\mathbf{q}} e^{-i\mathbf{q}\mathbf{g}_n},$$

$$F_1(\mathbf{f}) = \frac{1}{N}\sum_{\mathbf{q}} \frac{e^{i\mathbf{q}\mathbf{f}}}{E-\varepsilon_{\mathbf{q}1}}, \quad F_1 \equiv F_1(0).$$

After elimination of the quantities Y_n from the system (18) and extraction of the terms with n = m from the sum over n, this system takes the form

$$\begin{gathered}Z(E)X_m = \frac{A_1}{2}\Big[1+\frac{A_1}{2}F_1(\tau_m-1)\Big]\\ \times\sum_{m\neq n}\Big\{\frac{\tau_n + {}^1/_2 A_1F_1S(S+1)}{1+{}^1/_2 A_1F_1(\tau_n-1)}\Big\}F_1(\mathbf{g}_n-\mathbf{g}_m)X_n,\end{gathered} \tag{19}$$

where

$$Z(E) = \Big[1-\frac{A_1S}{2}F_1\Big]\Big[1+\frac{A_1(S+1)}{2}F_1\Big].$$

Temperature-averaging of the electron spectrum is carried out in the following way. Since the interaction between the excitons is not taken into account, all exciton coordinates and all exciton spin projections are equally probable. As was pointed out by Lifshitz,[12] at energies close to the bottom of the conduction band the quantity $F_1(\mathbf{f})$ decreases slowly with increase of $|\mathbf{f}|$ and therefore a large number of sites make a contribution to the right-hand side of Eq. (19). Fluctuations in the defect coordinates are thereby smoothed out in Eq. (19). This enables us to assume that the quantities $|X_n|^2$ are approximately equal for all sites with the same exciton spin projection. A direct generalization of the technique proposed in [12] to the case of defects with spin permits us to write

$$X_n \approx X(\tau_n) e^{ip\mathbf{g}_n}. \qquad (20)$$

correct to within a small fluctuating term. After substituting expression (20) into Eq. (19), we replace the kernel of the equation by its value averaged over the exciton coordinates:

$$\sum_{n \neq m} F_1(\mathbf{g}_n - \mathbf{g}_m) \exp\{i\mathbf{p}(\mathbf{g}_n - \mathbf{g}_m)\} \approx \nu/(E - \varepsilon_{\mathbf{p}1}), \quad \nu = N_0/N = na^3. \qquad (21)$$

If the relation (21) is taken into account, Eq. (19) is transformed, in the first approximation in $A_1\nu$, to the form

$$Z(E_p)X(\tau) = \frac{A_1\nu[1 + {}^1\!/_2 A_1 F_1(\tau - 1)]}{2(2S+1)(E_p - \varepsilon_{p1})} \sum_{\tau'} \frac{\tau' + {}^1\!/_2 A_1 F_1 S(S+1)}{1 + {}^1\!/_2 A_1 F_1 (\tau' - 1)}. \qquad (22)$$

Solution of the system of equations (22) leads to the following expression for the shift of the bottom of the conduction band:

$$\Delta E \equiv E_0 - \varepsilon_{01} \approx \frac{A_1^2 S(S+1)\nu(T)}{4NZ(\varepsilon_{01})} \sum_{\mathbf{q}} \frac{1}{\varepsilon_{01} - \varepsilon_{\mathbf{q}1}}, \qquad (23)$$

where the exciton concentration $\nu(T)$ is given by expression (14).

We shall now discuss the results obtained. Clearly, if the exchange energy A_1S is small compared with the width of the conduction band, then $Z(\epsilon_{01}) \approx 1$ and expression (23) coincides with the Born-approximation result (the renormalization of the electron spectrum due to the exchange interaction with localized moments in the Born approximation was found earlier in [13] with an arbitrary type of coupling between these moments). If the energy A_1S is so great that resonance levels exist close to the bottom of the conduction band, the quantity $Z(\epsilon_{01})$ tends to zero and the temperature shift of the edge of the conduction band increases sharply. This resonance effect is an analog of the well-known resonance scattering at a resonance level.[6]

If the energy A_1S exceeds the critical energy necessary for the formation of a bound state of an electron with an exciton, the quantity $Z(E)$ vanishes for $E < \epsilon_{01}$. Therefore, $Z(\epsilon_{01})$ becomes negative and with increase of temperature the bottom of the conduction band is raised, in contrast to the case when there are no bound states, when it is lowered. The assumption, made in deriving expression (23), that there are no correlations in the positions of the excitons does not enable us to take account of the effect on ΔE of bound states of an electron with a complex of excitons, if the latter are possible.

Even in the absence of local or resonance levels close to the bottom of the conduction band, the shift of the bottom of the band due to electron-exciton interaction is anomalously large. Indeed, for $S = 1$, $\omega = 0.01$ eV, $A_1 = 1$ eV, a conduction-band width $E_Z = 2$ eV, and $T = 30$ °K, the quantity ΔE found from formula (23) is greater than 0.1 eV, i.e., two orders of magnitude higher than for Ge or Si at the same temperature (cf., e.g., [14]). As has already been pointed out above, formula (23) was obtained using the variational principle and therefore, if bound electron-exciton states are not formed, underestimates the magnitude of the temperature shift of the bottom of the conduction band.

We should note that an anomalously strong temperature shift of the conduction band due to interaction with localized magnetic moments has already been observed in ferromagnetic semiconductors. Naturally, its magnitude and temperature dependence are completely different from those given by formula (23). The temperature shift in crystals of the type considered here have not yet, to the author's knowledge, been investigated experimentally.

As already stated, in the considered crystals the width E_g of the forbidden band is small. Therefore, the anomalously sharp decrease in the width of the forbidden band with rise of temperature, brought about by a shift of the bottom of the conduction band is, in itself, without drawing on the ideas of Mott, sufficient to explain the insulator-metal transition. In accord with what is stated above, a necessary condition for the realization of such a transition mechanism is the absence of bound electron-exciton states. If, as before, we assume the quantities A_{-1} and A to be negligibly small, the transition temperature T_M, when it is small compared with ω/k, is determined from the condition

$$E_g \approx \Delta E(T_M), \qquad (24)$$

where the temperature shift of the conduction band is given by expression (23). If the condition $|A_1|S \ll E_Z$ is fulfilled, T_M is also determined from Eq. (24 in those cases when it is comparable with ω/k. It is possible that the mechanism described can explain the insulator-metal transition in SmB_6. An insulator-metal transition is also possible in those cases when there are bound electron-exciton states at low temperatures. At high enough temperatures, when the exciton concentration is great, the concept of bound electron-exciton states loses its meaning and the situation becomes analogous to that considered earlier. We can expect the transition temperature in this case to be of order ω/k. In principle, this can explain the transition from conduction of the semiconductive type with small carrier mobility to metallic conduction in $LaCoO_3$ crystals. For agreement with the experimental values of T_M, the excitation energy of a triplet exciton must be 0.05-0.1 eV.

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[1] G. H. Jonker, Philips Res. Rep. **24**, 1 (1969).

[2] A. Menth, E. Buehler, and T. H. Geballe, Phys. Rev. Lett. **22**, 295 (1969).

[3] É. L. Nagaev, Zh. Eksp. Teor. Fiz. **57**, 469 (1969) [Sov. Phys.-JETP **30**, 257 (1970)].

[4] T. Holstein, Ann. Phys. **8**, 325, 343 (1959); É. L. Nagaev, Fiz. Tverd. Tela **4**, 2201 (1962) [Sov. Phys.-

Solid State 4, 1611 (1962)].

[5] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **17**, 1017, 1076 (1947).

[6] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Gostekhizdat, M., 1963 (Eng. transl. published by Pergamon Press, Oxford, 1965).

[7] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[8] É. L. Nagaev, ZhETF Pis. Red. **6**, 484 (1967) [JETP Lett. **6**, 18 (1967)].

[9] É. L. Nagaev, Zh. Eksp. Teor. Fiz. **54**, 228 (1968) [Sov. Phys.-JETP **27**, 122 (1968)].

[10] F. Holtzberg, T. R. McGuire, S. Methfessel, and J. Suits, Phys. Rev. Lett. **13**, 18 (1964).

[11] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

[12] I. M. Lifshitz, Advan. Phys. **13**, 483 (1964).

[13] É. L. Nagaev, Fiz. Tverd. Tela **9**, 2469 (1967) [Sov. Phys.-Solid State **9**, 1942 (1968)].

[14] R. A. Smith, Semiconductors, Cambridge University Press, 1959 (Russ. Transl., IIL, M., 1962).

[15] G. Busch, P. Junod, and P. Wachter, Phys. Lett. **12**, 11 (1964).

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