

## EXCITON POLARONS AND PLASMA-EXCITON WAVES

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The interaction between carriers in magnetoactive crystals and Frenkel excitons, which are excited d-shell states, is investigated. The electron-exciton interaction Hamiltonian consists of polarization and exchange parts. If the first is predominant, then exciton polarons will be the carriers in such substances. Owing to the non-Bose nature of the exciton operators, the temperature dependence of the polaron effect differs from that of ordinary polarons. If, however, exchange electron-exciton interaction is predominant, then excitation of d-shells of one or several atoms may be energetically advantageous. Enhancement of the exchange between magnetic atoms and conduction electrons compensates for the energy spent in exciton formation, provided the electron is localized near the excited atoms. Plasma-exciton resonance is possible in magnetoactive metals or semimetals. In this case longitudinal electric oscillations may be mixed with magnetic-moment waves. Under some conditions, longitudinal waves with the same frequencies but different wave vectors may move in the same direction. Resonance between volume excitons and surface plasmons leads to the formation of a new branch of surface excitons that do not go over to the usual branch when the carrier concentration tends to zero.

THE energy spectrum of compounds of transition and rare-earth metals include exciton branches corresponding to excited states of internal partially-filled electron shells. These excitons have a typically Frenkel character, since the excitation of the shell is not accompanied by a transition of the electron to neighboring atoms. They differ from Frenkel excitons in molecular crystals in their low energy (tenths of an eV or even less). We investigate in the present paper the interaction between Frenkel excitons and carriers in conducting magnetic crystals. We consider two aspects of this problem: the states of the conduction electrons that are "dressed" as a result of interaction with low-energy excitons, and plasma-exciton resonance. The former is of interest for semiconductors with low carrier densities, and the latter for large densities.

The conduction electrons that are "dressed" by virtual excitons ("exciton polarons") are similar in many respects to polarons in ionic crystals, which were first investigated by Pekar<sup>[1]</sup>. There are, however, essential differences, which become most strongly manifest in the temperature dependence of the polaron effects. These differences are connected with the "non-Bose" character of the excitons: in each atom it is possible to excite only one low-energy exciton. Therefore, with increasing temperature, the occupation numbers of such exciton states tend to a limiting value that does not exceed unity. On the other hand, in the case of phonons these numbers can be large compared with unity.

The possibility of plasma-exciton resonance was already noted in<sup>[2]</sup>. The appearance of this resonance can be expected in semi-metallic compounds of transition and rare-earth elements, which frequently have "degenerate" carrier densities on the order of  $10^{19}$ – $10^{20}$  cm<sup>-3</sup>, and they can be varied in a sufficiently wide range by doping. Materials with low carrier mobilities, in which plasmons are not clearly defined elementary excitations, are excluded from consideration. Quasiparticles that are in a certain sense analogs of optical excitons are produced as a result of the reson-

ant shift of the electrons and plasmons. In the case when the excitons can be subdivided into longitudinal and transverse ones, the plasmons mix in only with the former, and the photons with the latter.

Besides volume plasma-exciton resonance, we consider in this paper also the resonance between volume excitons and surface plasmons. We show that it gives rise to a new branch of surface excitons, different from the usual branch and not going over into it when the carrier density tends to zero. The resonant mechanism of formation of surface levels is of the same type as the resonant mechanism producing local levels, a mechanism first considered in<sup>[3]</sup> in the investigation of the interaction between an impurity center and optical phonons.

As is well known, the energy spectrum of semiconducting crystals contains, besides low-frequency plasma oscillations of carriers, a branch of high-frequency plasma oscillations of the electrons of the atomic valence shells. Such plasmons can resonate with high-frequency Frenkel excitons corresponding to a transition to a partly filled electron shell from the deeper shells. High-frequency plasma-exciton resonance is possible also in magnetic metals if such excitons are realized there. The results obtained in the paper remain valid also in these cases.

## 1. EXCITON POLARONS

In this section we shall investigate the interaction between the conduction electrons and excitons in a semiconductor having such a low carrier density that the interaction between them can be disregarded. We disregard likewise the electron-phonon interaction. Besides, we assume that the carrier is neither in the magneto-polaron nor in the quasi-oscillator states that can be realized in an antiferromagnetic semiconductor<sup>[4-6]</sup>.

In the calculation presented below we assume for simplicity that the occurrence of excitons is not accom-

panied by a change in the spins of the magnetic atoms. We consider only the interaction between the carriers and the lowest-lying exciton branches. Such excitons arise as a result of a transition of an unpaired electron of a magnetic atom from a state with index zero into one of the degenerate atomic states with index  $n$ . The field potential  $\Phi(r)$  produced by the electrons of the partially-filled shells can be determined from the Poisson quantum equation

$$\Delta\Phi(r) = -\frac{4\pi e}{\epsilon_\infty} \sum_{fmm'\sigma} \Psi_{fm}^*(r) \Psi_{f'm'}(r) a_{fms}^* a_{f'm'\sigma}. \quad (1.1)$$

Here  $\epsilon_\infty$  is the dielectric constant of the crystal at frequencies greatly exceeding the exciton frequency  $\omega$ , but small compared with the frequencies of the other electronic transitions. Further,  $a_{fms}^*$  and  $a_{fms}$  are the operators of creation and annihilation of an electron of a partially filled shell of an atom numbered  $f$  in the state  $m$  and spin projection  $\sigma$ , and  $\Psi_{fm}(r)$  are the corresponding single-electron wave functions. The index  $m$  can assume values  $n$  or  $0$ . The exciton operators are expressed in terms of the electron operators with the aid of the relations

$$b_{fn}^* = \sum_{\sigma} a_{fns}^* a_{f0\sigma}, \quad b_{fn} = \sum_{\sigma} a_{f0\sigma} a_{fn\sigma}. \quad (1.2)$$

Obviously, the exciton operators pertaining to different atoms commute with one another. On the other hand, operators pertaining to the same atom satisfy relations of the Fermi type

$$b_{fn}^* b_{fn'} = b_{fn} b_{fn'} = 0, \quad (1.3)$$

which follow from the fact that in the model assumed here all the exciton states are realized as a result of excitation of only one electron from each magnetic atom.

On the basis of relations (1.1)–(1.3), the polarization part of the electron-exciton interaction Hamiltonian can be represented in the dipole approximation in the following form:

$$\mathcal{H}_p = -\sum u_{kn} (b_{kn} + b_{-kn}^*) a_{p\sigma}^* a_{p-k\sigma},$$

$$u_{kn} = \frac{4\pi e^2 k g_{0n}}{\sqrt{N} \epsilon_\infty v_0 k^2}, \quad g_{0n} = \int \Psi_{f0}^* r \Psi_{fn} d^3r. \quad (1.4)$$

Here  $a_{p\sigma}^*$  and  $a_{p\sigma}$  are the operators of the conduction electron with momentum  $p$ , while  $v_0$  is the volume of the unit cell.

If the excitons can be subdivided into longitudinal and transverse ones, then it follows from (1.4) that the conduction electrons interact only with the former. The dependence of the quantities  $u_{kn}$  on  $k$ , as expected, has exactly the same character as in the case of optical phonons. An analog of the electron-phonon coupling constant is the quantity

$$\alpha = \frac{4\pi e^2 g^2}{v_0 \epsilon_\infty^2 (\hbar\omega)^2} \sqrt{\frac{2m^* \omega}{\hbar}}$$

(the dispersion in the exciton spectrum is not taken into account). If the bare effective mass  $m^*$  of the electron is equal to the true mass,  $\epsilon_\infty = 10$ ,  $v_0^{1/3} = 3 \times 10^{-8}$  cm,  $\hbar\omega = 0.3$  eV,  $g = 5 \times 10^{-9}$  cm, then the electron-exciton coupling constant  $\alpha$  is approximately equal to 4. Thus, under real conditions the electron-exciton coupling can

be sufficiently strong to increase greatly the effective carrier mass.

Estimates similar to those given in<sup>[1]</sup> show that at effective masses  $m^*$  comparable with the free-electron mass, and at reasonable values of  $\alpha$ , the radius of the polarization well is large compared with the lattice constant. Therefore the number of excitons per atom at  $T = 0$  is small compared with unity, and the excitons can be regarded as Bose quasiparticles. This makes it possible to apply immediately to the exciton polarons, at  $T = 0$ , the well known results of the theory of polarons in ionic crystals. The non-Bose character of the exciton is manifest here only at sufficiently high temperatures. On the other hand, if the bare effective mass of the electron is large, then the non-Bose character is significant also at  $T = 0$ .

In order to illustrate the foregoing, we shall consider two limiting cases: the weak-coupling approximation and the small-radius-polaron approximation. The exciton band is assumed to be nondegenerate, so that in accordance with expression (1.3) the commutation relations for the exciton operators reduce to the Pauli relations. The dispersion in the exciton spectrum is assumed to be negligibly small.

In the former case we set up a chain of equations of motion for the two-time Green's functions

$$\langle\langle a_{p\sigma} | a_{p\sigma}^* \rangle\rangle = -i\theta(t) \langle [a_{p\sigma}(t) a_{p\sigma}^* + a_{p\sigma}^* a_{p\sigma}(t)] \rangle$$

and for the functions associated with them (the angle brackets represent temperature averaging, and  $\theta(t)$  is the step function). In the fundamental approximation in  $\alpha$ , it is sufficient to confine oneself to the following equations:

$$\left( i \frac{\partial}{\partial t} - E_p \right) \langle\langle a_{p\sigma} | a_{p\sigma}^* \rangle\rangle = \delta(t) + \frac{1}{\sqrt{N}} \sum_{kf} u_k e^{ikf} [ \langle\langle b_f a_{p-k\sigma} | a_{p\sigma}^* \rangle\rangle + \langle\langle b_f^* a_{p-k\sigma} | a_{p\sigma}^* \rangle\rangle ],$$

$$\left( i \frac{\partial}{\partial t} - \omega - E_{p-k} \right) \langle\langle b_f a_{p-k\sigma} | a_{p\sigma}^* \rangle\rangle = \frac{1}{\sqrt{N}} \sum_{k'f'} e^{ik'f'} u_{k'} [ \langle\langle b_{f'} b_{f'} a_{p-k-h\sigma} | a_{p\sigma}^* \rangle\rangle + \langle\langle b_{f'} b_{f'}^* a_{p-k-h\sigma} | a_{p\sigma}^* \rangle\rangle ] \quad (E_p = p^2/2m^*, \hbar = 1) \quad (1.5)$$

and to an analogous equation for the Green's function  $\langle\langle b_f^* a_{p-k\sigma} | a_{p\sigma}^* \rangle\rangle$ . We took into account here the single-electron character of the problem. To describe the excitons, we use the nodal representation in lieu of the momentum representation. In the principal approximation in  $\alpha$ , we can have the following decouplings of the higher Green's functions of the type

$$\langle\langle b_f b_{f'} a_{p\sigma} | a_{p\sigma}^* \rangle\rangle = 0,$$

$$\langle\langle b_f b_{f'}^* a_{p\sigma} | a_{p\sigma}^* \rangle\rangle = (1 - \bar{n}) \langle\langle a_{p\sigma} | a_{p\sigma}^* \rangle\rangle \delta_{ff'}, \quad (1.6)$$

where  $\bar{n}$  is the average number of electrons per atom. In (1.6), account is taken of the fact that, owing to neglect of dispersion in the exciton spectrum, the Hamiltonian of the free excitons is diagonal in the nodal representation.

Relations (1.5) and (1.6) make it possible to obtain the following expression for the exciton-polaron energy:

$$E_p = E_p + (1 - \bar{n}) \sum_k \frac{|u_k|^2}{E_p - E_{p-k} - \omega} + \bar{n} \sum_k \frac{|u_k|^2}{E_p - E_{p-k} + \omega}. \quad (1.7)$$

Expression (1.7) differs from the well known expression

for the energy of the ordinary polaron in that the Bose temperature factors are replaced by Fermi factors. With increasing temperature, the value of  $\bar{n}$  tends in this case to  $1/2$ , i.e., the polaron level shift turns out to be limited. In the case of an ordinary polaron, the level shift at high temperatures is proportional to the temperature.

The analysis of the small-radius exciton polaron at  $T = 0$  is analogous to that of the small-radius polaron in an ionic crystal<sup>[7]</sup>. The Hamiltonian of the system is broken up into the zeroth-approximation Hamiltonian  $\mathcal{H}_0$  and the perturbation Hamiltonian  $\mathcal{H}_1$  in the following manner:

$$\begin{aligned} \mathcal{H}_0 &= \omega \sum_h b_h^* b_h + \sum_{h,f} U(h-f) (b_h^* + b_h) a_{f\sigma}^* a_{f\sigma}, \\ \mathcal{H}_1 &= \sum_{\delta, \Delta} B(\Delta) a_{g\sigma}^* a_{g+\Delta\sigma}, \quad U(f) = \frac{1}{\sqrt{N}} \sum_h u_h e^{ihf}. \end{aligned} \quad (1.8)$$

Instead of the momentum representation we use here the nodal representation. In accord with the condition that the electron band is narrow, we take into account only electron transitions between nearest neighbors. The index  $\Delta$  numbers the nearest neighbors of the atom under consideration.

The zeroth-approximation Hamiltonian  $\mathcal{H}_0$  can be diagonalized exactly. The normalized eigenfunction of the ground state of the atom  $h$  depends on the number  $f$  of the atom at which the conduction electron is situated, and is expressed in terms of the vacuum function by relation of the type

$$\begin{aligned} [c_1(f-h) + c_2(f-h) b_h^*] |0\rangle, \\ c_2(f) / c_1(f) = 2U(f) / [\omega - \sqrt{\omega^2 + 4U^2(f)}]. \end{aligned}$$

For the depth of the polaron well  $E_p$  and the width of the polaron band  $E_z$  we obtain the following expressions:

$$E_p = E_{pB} + \sum_f \left\{ \left[ \frac{\omega}{2} - \sqrt{\frac{\omega^2}{4} + U^2(f)} \right] + \frac{U^2(f)}{\omega} \right\}, \quad (1.9)$$

$$\begin{aligned} E_z = 2 \sum_{\Delta} B(\Delta) \exp \left\{ -\frac{1}{2} \sum_f \{ [c_1(f) - c_1(f+\Delta)]^2 \right. \\ \left. + [c_2(f) - c_2(f+\Delta)]^2 \right\}. \end{aligned} \quad (1.10)$$

Here  $E_{pB}$  is the energy that would be possessed by the polaron if the exciton operators were Bose operators.

As seen from (1.9), the non-Bose character of the excitons leads to a decrease in the depth of the polaron well, and at typical values of the parameters it can amount to several tenths of an eV. The exponential factor in (1.10) describes the narrowing of the carrier band due to the polaron effect. Unfortunately, it is impossible to establish a simple relation between the Bose and Pauli narrowings. It was shown in<sup>[8]</sup> that when dispersion is neglected in the optical-phonon spectrum, the width of the small-radius polaron band increases exponentially with temperature. Since the occupation numbers of the exciton states are limited, there can be no strong temperature dependence of the bandwidth for a small-radius exciton polaron.

So far we did not take into account the fact that when the partly filled shell of the atom is excited a change takes place in its exchange integral with the conduction electron. Yet this change can lead to an occurrence of an autolocalized state different from the polaron state.

Let us assume that in the zeroth approximation we can neglect the polarization part of the electron-exciton interaction energy (1.4), so that the number of electrons is an integral of the motion. It then can turn out that in the ground state the number of excitons is different from zero. The energy required to create them is offset by the gain in the energy of exchange between the excited atoms and the conduction electron compared with the energy of exchange between the electron and the non-excited atoms. For this purpose, the electron must be localized in the region where the excited atoms are situated. Of course, it is necessary that the excitation of the atom increase the absolute value of the energy of its exchange with the conduction electron  $A$  by more than the exciton frequency  $\omega$ . Such a state differs from a polaron not only in the short-range character of the forces producing it, but also in the fact that it is connected with the presence of real and not virtual excitations (the Hamiltonian of the exchange electron-exciton interaction is quadratic in the exciton operators). In the particular case when a state of this type, with one excited exciton, can be produced in a ferromagnet at  $T = 0$ , its energy can be readily determined in the zeroth approximation with the aid of the theory of regular perturbation<sup>[9]</sup>. For its realizability, it is necessary that the width of the bare electron band be small compared with  $A$ . The motion of the quasiparticle over the crystal is connected with fluctuations of the number of excitons and is described by the Hamiltonian (1.4). It is easy to show that the width of its band is of the order of  $U(0)U(\Delta)/A(A-\omega)$  or  $U^2(\Delta)/A(2\omega-A)$  of the width of the electron band, i.e., unlike the exciton polarons, it increases rather than decrease with increasing coupling constant  $\alpha$ .

## 2. PLASMA-EXCITON WAVES

In this section we consider the electron-exciton interaction at such large carrier densities, that the frequency of their plasma oscillations is close to the exciton frequency. It is assumed that this interaction can be taken into account with the aid of perturbation theory. The procedure employed here is a special variant of perturbation theory, in which the self-energy part of the exciton can be immediately expressed in terms of the penetrability  $\epsilon(r, r', \omega)$  of the electron gas, assumed to be known both form an infinite and for a semi-infinite crystal.

It is assumed as before that the exciton band is non-degenerate and that dipole exciton transitions are allowed. Then, according to expressions (1.1) and (1.2), in the absence of conduction electrons, the excitons produce in the crystal a potential

$$\Phi_0(r) = -eg \sum_f \nabla \frac{1}{|r-f|} (b_f^* + b_f), \quad (2.1)$$

where  $f$  stands for the coordinate of the corresponding atom. In the case of a semi-infinite crystal it is necessary to introduce in (2.1) also a term proportional to the difference between  $\epsilon_\infty$  and the dielectric constant  $\epsilon_e$  of the medium outside the crystal. However, this is irrelevant for the effect under consideration and will no longer be taken into account. The quantity  $\epsilon_\infty$  and (2.1) is not written out explicitly in (2.1), since it is assumed to be included in the charge  $e$  ( $e \rightarrow e/\sqrt{\epsilon_\infty}$ ).

Owing to the dynamic screening of the excitons by the conduction electrons, the potential  $\Phi_0$  goes over into the potential  $\Phi$ , which is connected with it by the relation

$$\Phi(r) = \hat{\epsilon}^{-1}(\omega)\Phi_0(r),$$

where  $\hat{\epsilon}^{-1}(\omega)$  is the operator of the reciprocal dielectric constant of the electrons at frequency  $\omega$ . Thus, the potential of the field of the electrons polarized by excitons is given by the difference between the quantities  $\Phi$  and  $\Phi_0$ . The energy of the electrons of partly filled shells in this field is obviously given by the expression

$$\hat{\mathcal{H}}_{ex} = \frac{e}{2} \int d^3r \sum_{\sigma} \hat{\psi}_{\sigma}^* (\Phi - \Phi_0) \hat{\psi}_{\sigma}, \quad (2.2)$$

where  $\hat{\psi}_{\sigma}(r)$  is the field operator of these electrons:

$$\hat{\psi}_{\sigma}(r) = \sum_f [\varphi_{f0}(r) a_{f0\sigma} + \varphi_{fn}(r) a_{fn\sigma}]$$

(the factor 1/2 in front of the integral in (2.2) is connected with the fact that this expression describes in essence an interaction of a definite type between d-electrons of different atoms, and thus each pair of atoms should enter only once).

At low temperatures, the exciton operators can be regarded as Bose operators. Using their definition (1.2) and expanding the potential in a series about the centers of the atoms, we obtain finally

$$\hat{\mathcal{H}}_{ex} = -e^2 \sum_{jh} g \nabla \left\{ [\hat{\epsilon}^{-1}(\omega) - 1] g \nabla \frac{1}{|r-h|} \right\}_{r=f} b_j^* b_h. \quad (2.3)$$

Since in the derivation of expression (2.3) we use the operator  $\hat{\epsilon}^{-1}$  for the "bare electrons," this expression is valid in the principal approximation in  $g^2$ .

The transition to the momentum representation in the Hamiltonian (2.3) yields immediately the dispersion equation for the volume crystals, coinciding with that obtained in<sup>[2]</sup> by the Green's-function method. An analysis of this expression shows that at sufficiently high dispersion in the spectra of the excitons in plasmons, and at a small difference in the positions of the centers of the corresponding bands, two waves are possible with identical frequencies but with different wave vectors, the polarization vectors of which are not orthogonal to each other. If one uses a model with transverse and longitudinal excitons, then one can speak of an additional longitudinal wave analogous to Pekar's additional transverse wave<sup>[10]</sup>.

In certain situations, the mixing of the plasmons with excitons whose occurrence is accompanied by a change in the spins of the magnetic atoms, may be important. The coupling between the plasmons and such excitons is via the spin-orbit interaction. The relativistic smallness of this interaction turns out to be compensated to a considerable degree, if besides the considered exciton state, the frequency of which is close to the plasmon frequency, there exists also an exciton state having the same spin but much lower frequency, and if a dipole transition between these exciton states is allowed. Thus, the longitudinal electric wave turns out to be connected with the wave of variation of the magnetic moment. This makes excitation of plasma waves by neutrons possible.

We proceed now to consider the resonance between

surface plasmons and volume excitons. Such a resonance leads to the formation of a new branch of surface excitons, differing from the usual branch and not pending to the latter when the carrier density is decreased. It is assumed that the crystal fills the half-space  $x > 0$ , and we use the continuous-medium approximation. If it is assumed that the boundary condition on the surface for long-wave excitons requires that their wave function be extremal, then the exciton operators can be represented in the form

$$b(r) = \sqrt{\frac{2}{V}} \sum e^{i\rho\rho} \cos(kx) b_{k\rho} \quad (b_f \rightarrow b(r)/\sqrt{V_0}), \\ r = (x, \rho), \quad \rho = (y, z). \quad (2.4)$$

It should be noted that if dispersion is neglected in the exciton spectrum, the form of the boundary conditions is not reflected at all in the final result, for in this case the excitons can be assumed to be not collectivized but localized on individual atoms.

By changing over in (2.3) to the Fourier representation with respect to  $\rho$ , we can write down the effective Hamiltonian of the excitons interacting with the electrons in the following form:

$$\mathcal{H}_{eff}(p\omega) = \sum_k \omega_{pk} b_{pk}^* b_{pk} + \sum_{hk'} G_{phk'} b_{pk}^* b_{pk'}, \\ G_{phk'} = \frac{4\pi(pg)^2 e^2}{Lv_0} \int_0^{\infty} dx dx' \frac{\cos kx'}{p^2 + k^2} \\ \times [e^{-1}(x, x'|p\omega) - \delta(x-x')] [2 \cos kx' - e^{-px}], \quad (2.5)$$

where  $L$  is the normalization length. To simplify the notation, it is assumed that the dipole moment  $g$  is parallel to the surface of the crystal.

Besides the exact form of the operator  $\hat{\epsilon}$ , we assume also that the eigenfunctions and the eigenvalues are known:

$$\int_{-\infty}^{\infty} dx' \epsilon(x, x'|p\omega) \varphi_{\lambda}(x'|p\omega) = \epsilon_{\lambda}(p\omega) \varphi_{\lambda}(x|p\omega).$$

The frequencies  $\omega_{\lambda}$  of the plasma oscillations are determined from the condition that the eigenvalues of the operator of the dielectric constant  $\epsilon_{\lambda}(\omega_{\lambda})$  vanish. The corresponding eigenfunction  $\varphi_{\lambda}(\omega_{\lambda})$  is none other than the plasma wave that is possible in the system under consideration. We shall henceforth consider only frequencies that are close to the frequency of the surface plasmon  $\omega_S$ , which, as is well known, is separated from the volume frequencies by a gap. In accordance with<sup>[11]</sup>, the normalized surface eigenfunction can be written in the form

$$\varphi_s(x|p\omega_s) = \sqrt{p} \exp(-|p||x|). \quad (2.6)$$

If we neglect the spatial dispersion of the electrons far from the surface, then the surface eigenvalue of the dielectric constant  $\epsilon_s(\omega)$  is equal to half the sum of the volume dielectric constant of the crystal and the dielectric constant of the medium outside the crystal. This follows, in particular, from the symmetry of the function  $\varphi_s(x)$  (2.6) relative to the surface of the crystal.

The result of the action of the operator  $\hat{\epsilon}^{-1}$  on an arbitrary function can be readily obtained by expanding the latter in the eigenfunctions of this operator. At frequencies close to  $\omega_S$ , it is sufficient to retain in this

expansion only the resonant term. By the same token, the coefficient  $G_{pkk'}$  in (2.5) turns out to be factorized:

$$G_{pkk'} = \frac{e^2}{v_0} (pg)^2 [\epsilon_s^{-1}(p\omega) - 1] A_{k'p} B_{kp},$$

$$A_{kp} = \sqrt{\frac{2}{Lp}} \frac{\pi(3p^2 - k^2)}{(p^2 + k^2)^2}, \quad B_{kp} = \sqrt{\frac{2}{L}} \frac{p^{3/2}}{(p^2 + k^2)}. \quad (2.7)$$

The expressions for the quantities  $A_{kp}$  and  $B_{kp}$  were obtained with allowance for formula (2.6). The Hamiltonian (2.5) with allowance for (2.7) can be diagonalized by linearly transforming the exciton operators  $b_{kp} = \sum_{\nu} c_{k\nu} b_{\nu p}$ . This leads to the following eigenvalue problem:

$$(\omega - \omega_{pk^0}) c_k = \frac{e^2 (pg)^2}{v_0} [\epsilon_s^{-1}(p\omega) - 1] B_{kp} \sum_{k'} A_{k'p} c_{k'}. \quad (2.8)$$

The solution of the integral equation (2.8) leads to the following transcendental equation for the determination of the frequencies of the elementary surface excitations:

$$1 = \frac{e^2 (pg)^2}{v_0} [\epsilon_s^{-1}(p\omega) - 1] \sum_k \frac{A_{kp} B_{kp}}{\omega - \omega_{kp^0}}. \quad (2.9)$$

If the dispersion in the exciton spectrum can be neglected and all the exciton frequencies can be assumed equal to  $\omega^0$ , then the solution of Eq. (2.9) takes the form

$$\omega(p) = \frac{\omega^0 + \omega_s(p)}{2} \pm \sqrt{[\omega^0 - \omega_s(p)]^2 + \frac{2\pi e^2 (pg)^2}{v_0 p^2} \left[ \frac{\partial \epsilon_s(p\omega_s)}{\partial \omega} \right]^{-1}}. \quad (2.10)$$

Expression (2.10) shows that at fixed  $p$  there exist two surface levels, the first of which is genetically connected with the surface plasmon, and the second with the volume excitons. Thus, the resonant interaction of the excitons with surface plasmons leads to a splitting of surface exciton levels from the exciton band. Owing to the damping of the bare plasmon states, the surface excitons also have finite damping. Allowance for dispersion in the exciton spectrum can lead to certain limita-

tions on the possible existence of surface excitons.

It can be shown that neglecting dispersion in the exciton spectrum Eq. (2.10) remains valid also in the case of arbitrary orientation of the dipole moment  $g$  relative to the surface of the crystal (by  $p$  is meant, as before, the quasimomentum component along the surface). In particular, it follows from this that at a dipole moment perpendicular to the surface, no surface excitons of the type considered here occur.

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