Multiexciton complexes in semiconductors

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Estimates were made of the binding energies of complexes consisting of several excitons. It was assumed that the excitons retain their individuality in the complexes and are not transformed into an electron-hole system. It is shown that the free complexes are made unstable by zero-point oscillations (a similar result was obtained for clusters consisting of several helium atoms). The stable complexes were those produced on an immobile impurity center. The obtained values of the binding energy agree with the available experimental data.

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A high-density exciton system in a semiconductor condenses at helium temperatures into an electron-hole liquid (EHL).[1] The condensation centers can be various crystal inhomogeneities, impurity atoms, etc. Introduction of an impurity can thus contribute to the formation of complexes—nuclei of a new phase—in an exciton vapor close to saturation. Pokrovskiĭ and co-workers[2] were the first to observe a series of lines in doped silicon at $T = 4$ K. These lines were observed between the free-exciton line and the EHL line, and the hypothesis was advanced that the lines are the results of radiative recombination of excitons bound by the impurity atoms into a complex (cluster); each line corresponds to a definite number N of excitons in the complex, $N = 1, 2, 3$, etc.

The results of[2] were repeated and expanded later,[3–8]; up to 10 lines were resolved in the series; analogous lines were observed in germanium,[9,10] cadmium sulfide,[11] and silicon carbide.[12] Favoring the multiexciton origin of these lines are the following: a) they are situated in the spectrum between the free-exciton and EHL lines; b) they are observed only in doped semiconductors; c) with increasing pump level they appear in the following order: first for $N = 1$ (bound exciton), then for $N = 2$, and so on, the intensity of the entire series then increases, and finally the EHL line appears and gradually overwhelms the entire series. Zhurkin and co-workers[10] observed interesting regularities in the lines following the cessation of the excitation. Doubts concerning the multiexciton origin of these lines were expressed only in[7,8].

The study of multiexciton complexes is important not only for the understanding of exciton condensation, but for the problem of condensation in an ordinary vapor–liquid phase transition. The exciton gas is analogous in many respects to the atom gas, and the two may condense in similar manner. An experimental observation of condensation nuclei of an ordinary liquid, however, can be difficult while the EHL nuclei produce in the spectrum lines that are distinct for each value of N.

The theoretical studies were heretofore devoted only to clusters of atoms and molecules, but not to exciton clusters. The molecular-dynamics method was applied to the investigation of clusters,[13–17], the Monte Carlo method was also used,[18 19] and the main configuration of the atoms was calculated by a variational method.[20] Clusters of argon and water were considered (see also the review[21]).

In this paper we use the molecular-dynamics method to calculate the binding energy of exciton clusters. In contrast to the heavy-atom clusters considered in[13–20], an important role in the calculation of the binding energy of exciton clusters is played by the contribution of the zero-point oscillations. We have determined the cluster oscillation spectrum by the method proposed in[13], namely, from the velocity autocorrelator. Besides free clusters that consist of excitons only, we consider clusters formed on impurity centers. We studied clusters on neutral as well as on charged centers. The results are compared with the experimental data.[2–11]

THE CLUSTER MODEL

When the EHL is formed, the excitons lose their individuality: the liquid consists not of excitons but of collectivized electrons and holes. In a complex with small N, such a collectivization is not obligatory, since the average distances between the particles in the complex can be larger than in the EHL.

The Zeeman effect for lines corresponding to $N = 1–5$ was investigated in[7,12] and it was observed that the line splitting is practically independent of N. Sauer and Weber[7] have concluded that this is precisely why the lines are not of the multiexciton type. This conclusion might be correct if the complexes were to consist of electrons and holes.[1)] However, the results of the measurements in[7,12] can be interpreted as evidence that at the values $N = 1–5$ the complexes still consist of individual excitons. The interaction between the excitons leads to a dependence of the width of the Zeeman components on N, and this may possibly explain also the N-dependence of the relative intensities. Both dependences were observed in[7,12].

Sauer and Weber[8] investigated the splitting and shift of the same line as a result of deformation along different crystal axes (similar investigations were initiated by Alkeev, Kaminskiĭ, and Pokrovskiĭ[6]). The results of[6,8] show that in the considered cases $N = 1–5$ all lines behave in like fashion. These observations also indicate that at these values of N the excitons in the complex are

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not collectivized. Arguments that the excitons preserve their individuality in the complex at small N are advanced also in[11]. Pokrovskiĭ[3] has shown that the appearance of new lines can likewise not be attributed to the presence of many valleys.

In this paper we assume a model wherein the complex consists of individual excitons. The exciton–exciton interaction potential is chosen in the Lennard-Jones form:

$$\Phi(r)=\varepsilon_0[(\sigma/r)^{12}-2(\sigma/r)^6]. \tag{1}$$

The exciton-cluster model is therefore similar to the atomic cluster, but with different parameters ε_0 and σ for the excitons. The potential (1) permits all the calculations to be performed in relative units. The energy, length, and mass units are chosen to be ε_0, σ, and m (m is the exciton mass); the frequency unit is then $(\varepsilon_0/\sigma^2 m)^{1/2}$, the velocity unit $(\varepsilon_0/m)^{1/2}$, and so on. This makes it possible to recalculate some of the results of[13–20] and apply them to exciton clusters. The total energy of the clusters is assumed to be pairwise additive:

$$E=\sum_{j>i}\Phi(r_{ij}), \tag{2}$$

where i and j are the numbers of the excitons in the cluster.

The main difference between an exciton system and a heavy-atom cluster is that the smallness of the exciton mass makes the contribution of the zero-point oscillations to the binding energy ε_N significant. To estimate ε_N we use the formula[2)]

$$N\varepsilon_N=N\varepsilon_0\varepsilon_N^*-\frac{1}{2}\hbar\left(\frac{\varepsilon_0}{\sigma^2 m}\right)^{1/2}\sum_{s=1}^{3N-6}\omega_{sN}^*, \tag{3}$$

where the first term is the value of the minimum of the energy (2); ω_{sN}^* are the cluster frequencies in units of $(\varepsilon_0/\sigma^2 m)^{1/2}$. We note that ε_N^* and ω_{sN}^* are independent of ε_0, σ, and m.

To determine the values of ε_0 and σ of the exciton interaction we require that formula (3) yield the correct biexciton binding energy $2\varepsilon_2=1.5$ K[22]:

$$2\varepsilon_2=\varepsilon_0-{}^1/{}_2\hbar(\varepsilon_0/\sigma^2 m')^{1/2}\omega_2^*, \tag{4}$$

where $m'=m/2$, $\omega_2^*=6\cdot 2^{1/3}$. Formula (3), with (4) taken into account, can be rewritten as

$$\varepsilon_N/\varepsilon_0=\varepsilon_N^*-(\varepsilon_0-2\varepsilon_2)\sum_s\omega_{sN}^*/N\varepsilon_0\omega_2^*, \tag{5}$$

from which it is seen that if $\varepsilon_0\gg 2\varepsilon_2$ then the relative binding energy is independent not only of σ but also of ε_0.

It follows from the results of[22] that $\varepsilon_0\approx 12$ K (to satisfy the condition $2\varepsilon_2=1.5$ K it is then necessary to have $\sigma=450$ Å). Moskalenko *et al.*[23] have proposed for the exciton–exciton interaction potential another model, a generalization of the Morse potential. This potential depends on several parameters, but it can be approximated roughly by (1) with $\varepsilon_0=6$ K ($\sigma=740$ Å).

We shall consider also clusters bound to a neutral impurity atom. The exciton–impurity interaction is also chosen in the form (1). The connection between the corresponding values of ε_0' and σ' can also be found from an expression similar to (4). For germanium, the binding energy of an exciton on a phosphorus atom is $\varepsilon_1'=11.5$ K.[9] Nothing is known concerning the depth of ε_0'. We shall assume $\varepsilon_0'/\varepsilon_1'\approx\varepsilon_0/2\varepsilon_2\approx 8$ (then $\sigma'=185$ Å).

As a third variant of the system we consider a cluster bound to an immobile charge. It was assumed that the charge interacts with the exciton via a potential that goes over into the polarization at large distances and into a constant (< 0) at short distances:

$$U(r)=\begin{cases}-e^2\alpha/2r^4, & \text{if } r\geqslant R_0\\ -U_0, & \text{if } r\leqslant R_0\end{cases}, \tag{6}$$

where r is the distance from the charge to the exciton $\alpha=4.5\,a_0^3$ is the exciton polarizability chosen by analogy with the hydrogen atom, $U_0\approx 3\varepsilon_0$, and $R_0\approx\sigma$. The values of U_0 and R_0 can be made more prceise by using the results of[24].

THE MOLECULAR-DYNAMICS METHOD

The quantities ε_N^* and ω_{sN}^* in (2) can be calculated by the molecular-dynamics method, in which the equations of motion of N interacting particles are solved numerically. The initial particle coordinates in the free clusters are assumed to have the equilibrium values of[19]. The initial velocities were chosen to be Maxwellian and low enough (corresponding to an initial temperature $kT/\varepsilon_0<0.01$). This choice of the initial coordinates and velocities greatly shortened the time required for the system to reach the equilibrium state. The motion of the mass center and the rotation of the cluster were excluded. The equations of motion were solved by using the numerical scheme

$$\mathbf{v}_i^{k+1}=\mathbf{v}_i^k+\mathbf{f}_i^k\Delta t/m,$$

$$\mathbf{r}_i^{k+1}=\mathbf{r}_i^k+\mathbf{v}_i^{k+1}\Delta t,\quad i=1,\ldots,N,$$

where k is the number of the time interval, $\Delta T^*\approx 10^{-2}$ is the length of the interval; the resultant $\mathbf{f}_i$ of all the forces applied to the i-th particle is obtained by differentiating (2). The correctness of the calculation was monitored by ensuring conservation of the total energy of the cluster.

The cluster binding energy was obtained on the equilibrium section, and the corresponding temperature was determined from the equation

$$\langle K\rangle=(3N-6)kT/2,$$

where K is the kinetic energy and $\langle\ldots\rangle$ denotes averaging over the ensemble. The frequency spectrum can be obtained via a Fourier transformation of the velocity autocorrelation function:

$$\gamma(t)=\left\langle\sum_i\mathbf{v}_i(t)\mathbf{v}_i(0)\Big/\sum_i\mathbf{v}_i^2(0)\right\rangle, \tag{7}$$

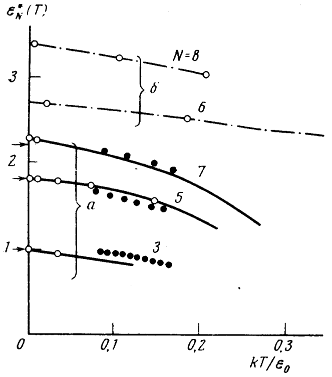

FIG. 1. Temperature dependences of the binding energy for free (a) and impurity (b) classical clusters: o—present results, ●—[16], solid curves—[19], arrows—[20], the dash-dot curve is drawn through the calculated points.

where $\mathbf{v}_i(t)$ is the velocity of the i-th atom at the instant t. We replace the averaging over the ensemble by averaging over time, and then

$$\gamma(t)=\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau dt'\sum_i \mathbf{v}_i(t+t')\mathbf{v}_i(t')\Big/\sum \mathbf{v}_i^2(t'). \tag{8}$$

The frequency spectrum is obtained from the formula (see[13])

$$D(\omega)=\int_0^\infty \gamma(t)\cos\omega t\,dt. \tag{9}$$

The total number of the frequencies should be $3N-6$, and $D(\omega)$ is normalized to unity.

BINDING ENERGY OF FREE CLUSTERS

Figure 1 shows plots of $\varepsilon_N^*(T)=\langle E\rangle/N\varepsilon_0$ against temperature for clusters made up of identical particles, with N equal to 3, 5, and 7. The value of $\langle E\rangle$ is obtained by averaging the energy (2). It is seen from Fig. 1a that the data obtained by different workers are in agreement. The energy $\varepsilon_N^*\equiv\varepsilon_N^*(0)$ in (3) is determined by extrapolation to $T\to 0$.

Figure 2a shows the time dependence of the velocity autocorrelation function, calculated by us for a cluster of five particles. This figure corresponds to low temperatures, when the cluster oscillations are close to harmonic. To check on the independence of the autocorrelator at low T, the calculations were performed for $kT/\varepsilon_0=7.4\cdot10^{-4}$; $4.2\cdot10^{-4}$; $5.8\cdot10^{-5}$. Figure 2b covers a larger time interval than Fig. 2a, and the high-frequency oscillations are smoothed out. The autocorrelator attenuates weakly with time, which again attests to the harmonic character of the oscillations. The approximately obtained autocorrelator by the multiply modulated wave

$$\gamma(t)\approx\cos 0.038t^*\cos 0.35t^*\cos 1.4t^*\cos 16.9t^*, \tag{10}$$

from which we can obtain a spectrum containing eight frequencies: 15.1, 15.19, 15.81, 15.9, 17.9, 17.99, 18.61, and 18.7. The last, ninth frequency could not be determined for our calculation. It can therefore be assumed that this frequency is low enough.

Figure 3 shows plots of the cluster binding energy against $N^{-1.3}$. This scale was chosen because the difference between the cluster binding energy and the binding energy of the macroscopic system varies in proportion to the ratio of the surface energy of the cluster to the volume energy, i.e., in proportion to $N^{-1/3}$. Therefore, by extrapolating linearly the results for the cluster binding energy in this scale into the region $N\to\infty$ we can obtain the characteristics of a macroscopic system. Line 1 is plotted from the results of[15,16,19] for ε_N^*. The point 7 corresponds to the experimental binding energy of solids comprised of atoms of heavy inert gases.

The values plotted for the exciton clusters take into account the zero-point oscillations. For the frequencies of the 5-particle cluster we used our own data. The frequencies of the clusters of 55, 135, and 429 particles were obtained from the spectra calculated in[15] for $kT/\varepsilon_0=0.15$. The lines 2 and 3 correspond to two aforementioned variants of the choice of ε_0 and σ. It is seen that extrapolation of lines 2 and 3 to $N=\infty$ yields binding energies of the same order as the experimental ones (arrows 8 and 9). One cannot expect good agreement here, for when N is increased the exciton is converted into an electron-hole cluster, and extrapolation to $N=\infty$ would be valid only for the latter.$^{3)}$

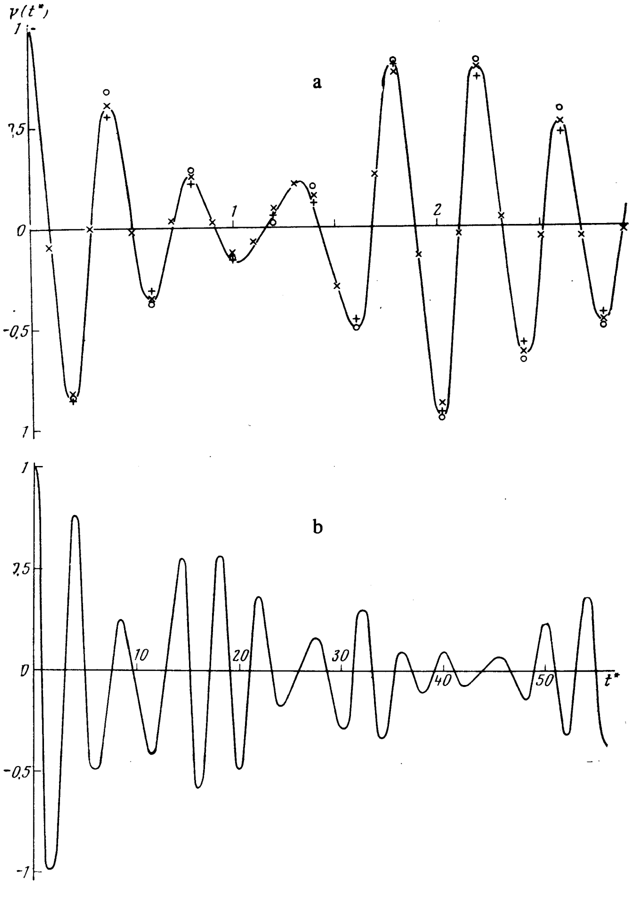

FIG. 2. Autocorrelation functions of the velocity for $N=5$; a—initial section, the points correspond to calculations at various temperatures kT/ε_0: o—5.8×10^{-5}, ×—4.2×10^{-4}, +—7.4×10^{-4}, the smooth curve is drawn through the calculated points; b—autocorrelator with smoothed high frequency, drawn through the calculated points.

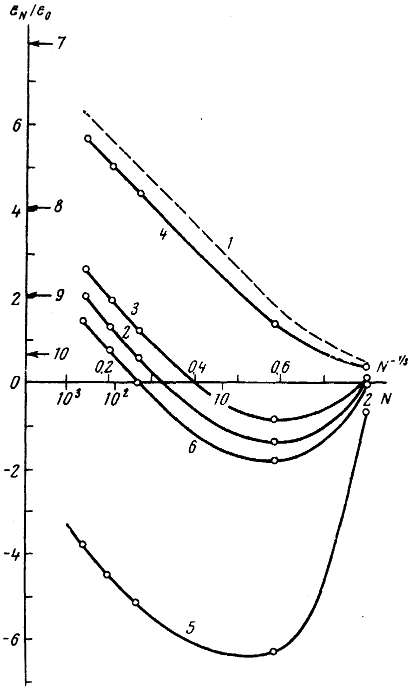

FIG. 3. Binding energies of free clusters. 1) Curve for classical heavy-atom clusters, plotted in accordance with the data of[15,16,19,20]. Curves 2–6 are drawn through the calculated points for excitions—2 ($\varepsilon_0 = 12$ K, $2\varepsilon_2 = 1.5$ K), 3 ($\varepsilon_0 = 6$ K; $2\varepsilon_2 = 1.5$ K), argon—4 ($\varepsilon_0 = 119$ K, $\sigma = 3.82$ Å), and helium—5 ($\varepsilon_0 = 10$ K, $\sigma = 2.87$ Å), 6 ($\varepsilon_2 = 0$). The experimental values of the relative binding energies of macroscopic systems are plotted for argon—7, EHL—8 ($\varepsilon_0 = 6$ K), 9 ($\varepsilon_0 = 12$ K), and helium—10.

Formula (3) and the potentials (1) and (2) are approximate. To verify the reliability of the estimates within the framework of this model, the corresponding energies were calculated for He^4-atom clusters. Line 5 was obtained from (3) using the known values of ε_0 and σ, and line 6 was obtained from (5) under the assumption that $\varepsilon_2 = 0$. In the latter case we took into account the fact that the He$_2$ molecule binding energy is close to zero.[25] It is seen from Fig. 3 that line 6, normalized against the He$_2$ molecule, results in better agreement with experiment than line 5 when the extrapolation $N \to \infty$ is made. Thus, one can expect that the errors in the exciton-cluster binding energies calculated by us, likewise normalized to a two-atom system, are not too large.

The results obtained for exciton and helium clusters allow us to conclude that neutral quantum clusters have an intrinsic instability that covers the ranges $N \approx 3-10^1$ for excitons and $N \cong 3-10^2$ for He^4. This result is worthy of investigation by more rigorous method. A system of three helium atoms was considered in[26]. With increasing atom mass, the instability interval falls and, e.g., argon-atom clusters are stable for all N (line 4 on Fig. 3).

CLUSTERS ON IMPURITIES

Figure 1b shows the dependence of the binding energy (without allowance for the zero-point oscillations) of clusters of six and eight particles bound by neutral centers. High temperatures were not investigated. The autocorrelator was calculated only up to 10^5 steps in time and corresponded to a temperature $kT/\varepsilon_0 = 0.2$. For a cluster bound by an impurity, the oscillation frequencies turned out to be lower than for free clusters. The binding energy was also calculated for clusters bound to immobile charges. The oscillation spectrum was not calculated. It appears that the role of the zero-point oscillations in this case will be even less.

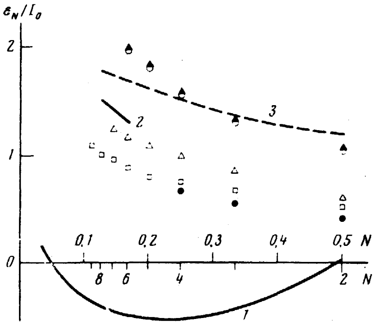

FIG. 4. Binding energies of complexes. Calculation results: 1—free cluster, 2—cluster on neutral impurity, 3—cluster on charged impurity, Measurement results: ●—[2,3], △—[4,7,8], □—[5], ○—[9], ▲—[10].

The results of the calculations are compared in Fig. 4 with measurements[2–10]. Since only clusters with small numbers of particles were considered, the binding energy is plotted in Fig. 4 as a function of N^{-1}, and there is no extrapolation to $N \to \infty$. The ordinates of Fig. 4 are the ratios of the cluster binding energies to the binding energies I_0 per pair of particles in the EHL, so that the figure shows the results of experiments performed both on germanium and on silicon. These results agree with one another and reveal a monotonic growth of the binding energy with increasing number of particles in the cluster.1) The cluster binding energies turned out to be higher than the binding energies per particle pair in the EHL, so that with further increase of N one should expect this dependence to have a maximum, so as to ensure that $\lim(\varepsilon_N/I_0) \to 1$ as $N \to \infty$. The energy of negative clusters of alkali metals behaves similarly.[21]

Taking into account the approximate character of the calculation, one can speak of an agreement of curves 2 and 3 with the experimental data. We note that the calculations were made within the framework of an isotropic model. Anisotropy increases the binding energy of both the biexciton[22] and the EHL.[1]

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1) An attempt to retain the multiexciton interpretation for this case, too, was made in[12].

2) The asterisk labels relative quantities.

3) For exciton clusters we can expect a dielectric–metal transition of a type of its own with increasing N.

4) The results of[11] for CdS are similar, but are not marked on Fig. 4, inasmuch as in this case the lines for different N overlap and the interval of N to which the binding energies measured in[11] pertain remains unclear.

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Theory of tunneling in crystals at arbitrary ratios of the widths of the forbidden and allowed bands

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A quasiclassical theory of tunneling in crystals in an electric field is developed. The theory takes into account the finite widths of the allowed energy bands. The two-band Slater-Koster model is used to calculate the tunneling probability. It is shown that for crystals with narrow allowed bands, the customarily employed Kane model yields an erroneous estimate of the tunneling probability. Criteria are obtained for the applicability of the Kane model, and a correct tunnel probability is calculated for the case when these criteria do not hold. Tunneling accompanied by photon absorption in a crystal is investigated with account taken of the finite widths of the allowed bands. The dependence of the tunneling probability on the angles between the electric-field intensity vector and the symmetry axes of the crystal is investigated; this dependence does not appear in Kane's model. It is demonstrated that this dependence can yield additional information on the crystal symmetry and crystal structure.

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The investigation of tunneling in crystals in an external electric field is of considerable interest for solid-state electronics. Interband tunneling in a constant electric field determines, for example, the current flow in Esaki diodes.[1,2] Theoretical descriptions of the tunneling process in crystal are contained in many papers for the case of constant[3-6] and time-alternating (laser emission)[7,8] electric field. In most cited papers they used Kane's two-band model,[9] which corresponds to the following dispersion law (the dependence of the energy ε on the quasimomentum $\hbar\mathbf{k}$):

$$\varepsilon(\mathbf{k})=(\Delta^2+\Delta\hbar^2k^2/\mu)^{1/2}. \tag{1}$$

Here Δ is the half-width of the forbidden band and μ is the reduced effective mass of the electron and hole. The results of expression (1) are greatly limited in scope. In Kane's model (1), the allowed energy bands are assumed to be infinitely broad in comparison with the forbidden band. This assumption can be justified for tunneling processes only for the special class of narrow-band crystals (e.g., of the InSb type).

The decisive circumstance for the quasiclassical tun-

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