Dislocation-state spectrum in semiconductors

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A model is proposed for the description of the energy spectrum of the electrons in the case of crystals with dislocations. In contrast to the Shockley-Read model [W. Shockley, Phys. Rev. **91**, 228 (1953); W. T. Read, Phil. Mag. **45**, 775 (1951)], the analysis includes the "indirect" exchange, i.e., the effect of quantum-mechanical mixing of the wave functions of the electrons localized in the dislocation core with the electrons of the nearest atoms that contain no broken bands. The calculation leads to an irregular dependence of the state density on the energy in the dislocation bands. The result is used to discuss experimental data on the microwave conductivity of semiconductors with dislocations.

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INTRODUCTION

Recent experiments show without any doubt that the presence of dislocations in semiconductor and insulator crystals leads to the onset of new electronic states in the forbidden band of the energy spectrum. A number of essential questions connected with the electronic dislocation spectrum itself, however, is still unclear: is this spectrum a system of local levels, a one-dimensional band, or a system of several bands? What are the widths of these bands and the degree of localization of the electrons in the dislocation states? All these questions are fundamental in the construction of a dislocation theory and for the understanding of the influence of dislocations on the physical properties of solids.

Experimental results on dislocations[3] electron paramagnetic resonance and on dislocation electric conductivity[4-7] give grounds for assuming that the dislocation spectrum consists of several bands. Other evidence in favor of a complex structure of the spectrum is provided by the data on the photoconductivity[8-10] and luminescence[11-14] of crystals with dislocations. There is no doubt that the choice of one model or another for a theoretical description of the spectrum involves the question of the degree of overlap of the wave functions of the electrons in the dislocation cores.

At the present time, the most widely accepted is the classical Shockley-Read (SR) theory, based on the model of a dislocation chain of broken chemical bonds along the core of the dislocation line. In the SR theory, account is taken of the interaction of the electrons only along the dislocation chain. In the present paper, on the contrary, we attempt to take into account the quantum-mechanical effect of mixing of wave functions of electrons localized along the dislocation line with the volume wave functions of the electrons of the atoms neighboring on the dislocations and having no broken bonds, i.e., to take into account the so-called "indirect" exchange phenomenon. The need for this procedure seems to us particularly important, because in the case of the simplest 60° dislocation in the diamond lattice the distance from an atom located in the dislocation core to the nearest neighbor inside the crystal is less than the distance between the nearest neighbors in the direction along the dislocation chain.

We use in the present calculations an approximation in which the width of the volume bands is assumed to be much larger than the width of the forbidden band. To describe the bottom of the conduction band and the top of the valence band we use the results of the calculation of the spectrum of the volume states.[15-17]

As will be seen from the results, allowance for the indirect exchange leads to irregularities in the dependence of the state density on the energy inside the dislocation bands. This result itself could cast light on some experimental data, especially on the microwave conductivity of crystals with dislocations. We recognize, however, that in the construction of the theoretical model itself we have made assumptions whose adequacy is difficult to estimate. In particular, a very serious problem in our model is that of a correct quantitative allowance for the Coulomb interaction energy of the electrons belonging to one site. This and a number of other considerations prompt us to assume that the theoretical result obtained in the present paper can so far be discussed only in connection with the available experimental data.

1. THE MODEL HAMILTONIAN

We write the Hamiltonian of a crystal with dislocations in the form

$$H=\sum_{nkl\sigma}\varepsilon_n(k,l)\,a^+_{nkl\sigma}a_{nkl\sigma}+\sum_{k\sigma}\varepsilon(k)\,b_{k\sigma}{}^+b_{k\sigma}+\sum_{nkl\sigma}(V_{nkl}a^+_{nkl\sigma}b_{k\sigma}+V^*_{nkl}b_{k\sigma}{}^+a_{nkl\sigma}). \quad (1)$$

The first term in (1) corresponds to volume states whose wave functions are smeared over the entire crystal; $\varepsilon_n(k,l)$ is the energy of the volume states; n is the number of the band, k is the projection of the quasimomentum on the dislocation direction; l is the set of quantum numbers describing the transverse motion; σ is the electron spin; $a^+_{nkl\sigma}$ and $a_{nkl\sigma}$ are respectively the electron creation and annihilation operators; the second term describes the dislocation states (DS) with wave functions $\psi_k(\mathrm{r})$ localized in the transverse direction at distances on the order of the interatomic distances, but delocalized along the dislocation; $b^+_{k\sigma}$ and $b_{k\sigma}$ are the

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operators of electron creation and annihilation in the DS. The energy $\varepsilon(k)$ of the dislocation electrons is

$$\varepsilon(k)=\varepsilon_d+2V_d\cos(ka)+Un+(2e^2/\varepsilon a)(n_0-1)\ln(R/R'). \quad (2)$$

The first two terms in this formula describe a one-dimensional dislocation band for non-interacting electrons; ε_d is the energy level of the state localized on an isolated dangling bond, i.e., a state with a wave function $\varphi_i(\mathbf{r})$ localized near the dangling bond i; V_d is the matrix element of the overlap of the states with wave functions $\varphi_i(\mathbf{r})$ and $\varphi_{i+1}(\mathbf{r})$; a is the distance between the dangling bonds.

The third and fourth terms in (2) take into account in the self-consistent field approximation the Coulomb energy of the electrons captured by the dislocation. The following initial charge distribution was postulated in their calculation: the total number of electrons bound by a dislocation on a single dangling bond is n_0, and the number of electrons localized on the bond i (i.e., in the state φ_i) is[1)] n. As will be seen from the solution, $n < n_0$ because not all the electrons bound by the dislocation are localized in the state φ_i. The difference $n_0 - n$ is distributed over a wider region than the φ_i localization region. This is in fact a direct consequence of allowance for the mixing of the DS with the volume states [third term in (1)].

The term Un (U is a constant that characterizes the Coulomb repulsion of the electron in the state φ_i) is obtained only in the quantum theory, while in the classical theory it corresponds to the self-energy of the electron and is therefore simply omitted; e is the electron charge; ε is the permittivity; R is the Read radius, i.e., the radius of the cylinder over which the positive charge of the ionizing minute donors that screen the dislocation is uniformly smeared out:

$$R^2=(n_0-1)/\pi a N_D,$$

where N_D is the donor density. We choose R' such that in a circle of radius a (this is approximately the dimension of the state φ_i) there are localized n of the n_0 particles, therefore

$$R'=a(n_0/n)^{1/2}.$$

The distribution parameters n and n_0 will be determined self-consistently.

The third term in (1) describes the mixing of the DS with the volume states. The coefficients V_{nkl} are the matrix elements of the overlap of the volume states with the wave functions $\psi_{nkl}(r)$ and of the DS with the functions $\psi_k(\mathbf{r})$. Generally speaking they are not small, since they do not contain terms corresponding to the overlap between nearest neighbors in the lattice. For example, they are even large compared with V_d, since V_d corresponds to overlap of nearest neighbors along the dislocation, but in the complete lattice they are the second-nearest neighbors (we have in mind here and below only 60° dislocations in a lattice of the diamond type).

An important characteristic of the model Hamiltonian are the functions $\varepsilon_{cl}(k)$ and $\varepsilon_{vu}(k)$, which describe respectively the dependences of the lower edge of the conduction band and of the upper edge of the valence band

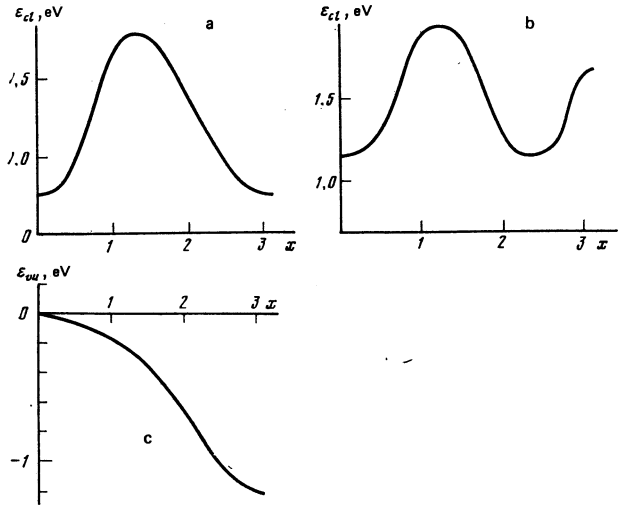

FIG. 1. Dependence of the energies of the conduction-band bottom ε_{cl} and of the valence-band top ε_{vu} on $x=ka$ (k is the projection of the quasimomentum along the [110] direction. a—$\varepsilon_{cl}(x)$ for Ge, b—$\varepsilon_{cl}(x)$ for Si, c—$\varepsilon_{vu}(x)$ for Ge and Si.

on the quasimomentum projection along the dislocation. According to this definition we can write

$$\varepsilon_{cl}(k)=\min_{(n_c,\mathbf{k}_\perp)}\varepsilon_{n_c}(k,\mathbf{k}_\perp), \quad (3)$$

$$\varepsilon_{vu}(k)=\max_{(n_v,\mathbf{k}_\perp)}\varepsilon_{n_v}(k,k_\perp). \quad (4)$$

The extrema in (3) and (4) are sought over the range of variation of n and $\mathbf{k}_\perp$. To find these functions it is necessary, for each fixed k, to draw in k-space planes perpendicular to the [110] direction at a distance k from the origin. The region of variation of $\mathbf{k}_\perp$ is that part of this plane which lies inside the Brillouin zone.

Thus, to determine $\varepsilon_{cl}(k)$ and $\varepsilon_{vu}(k)$ we must know $\varepsilon_n(k,\mathbf{k}_\perp)$ at all points of the Brillouin zone. No such information is available in the published calculations of the band structure. Only the function $\varepsilon_n(k,\mathbf{k}_\perp)$ along definite directions and the values of $\varepsilon_n(k,\mathbf{k}_\perp)$ at certain symmetry points are known.[15-17] Analysis of such numerical results makes it possible to establish qualitatively the form of the functions $\varepsilon_{cl}(k)$ and $\varepsilon_{vu}(k)$. As will be made clear below, the most important is the form of these functions at those points where they have extrema. Fortunately, the behavior of $\varepsilon_{cl}(k)$ and $\varepsilon_{vu}(k)$ at these points can be determined with sufficient accuracy. We confine ourselves hereafter to an investigation of the dislocation spectrum in Ge and Si. The functions $\varepsilon_{cl}(k)$ and $\varepsilon_{vu}(k)$ for them are shown in Fig. 1.

2. SELF-CONSISTENCY EQUATIONS

The operator equation for the single-particle Green's function is

$$[\varepsilon-H+i\delta\,\mathrm{sign}\,(\varepsilon-\varepsilon_F)]\hat{G}(\varepsilon)=1, \quad (5)$$

where ε_F is the Fermi energy.

Representing the Green's function in matrix form

$$G(\varepsilon)=\begin{pmatrix} G^{n'k'l'\sigma'}_{nkl\sigma} & G^{k'\sigma'}_{nkl\sigma} \\ G^{n'k'l'\sigma'}_{k\sigma} & G^{k'\sigma'}_{k\sigma}\end{pmatrix}, \quad (6)$$

and solving the system of equations that follows from (5) and (6) for the matrix elements of $\hat{G}$, we obtain

$$G_{k\sigma}^{k'\sigma'}(\varepsilon)=\frac{\delta_{kk'}\delta_{\sigma\sigma'}}{\varepsilon-\varepsilon(k)-\Sigma(\varepsilon,k)+i\delta\,\mathrm{sign}(\varepsilon-\varepsilon_F)},\tag{7}$$

where the self-energy part is

$$\Sigma(\varepsilon,k)=\sum_{nl}|V_{nkl}|^2[\varepsilon-\varepsilon_n(k,l)+i\delta\,\mathrm{sign}(\varepsilon-\varepsilon_F)]^{-1}.\tag{8}$$

We represent it in the form

$$\Sigma(\varepsilon,k)=\Lambda(\varepsilon,k)-i\Delta(\varepsilon,k)\,\mathrm{sign}\,(\varepsilon-\varepsilon_F),\tag{9}$$

where Λ and Δ are defined as

$$\Delta(\varepsilon,k)=\pi\sum_{nl}|V_{nkl}|^2\delta[\varepsilon-\varepsilon_n(k,l)],\tag{10}$$

$$\Lambda(\varepsilon,k)=\sum_{nl}\mathrm{P}\frac{|V_{nkl}|^2}{\varepsilon-\varepsilon_n(kl)}=\frac{\mathrm{P}}{\pi}\int_{-\infty}^{\infty}\frac{\Delta(\varepsilon',k)}{\varepsilon-\varepsilon'}d\varepsilon'.\tag{11}$$

In (11) use was already made of (10). All the information on the spectrum of the volume states and on the value of the matrix elements V_{nkl} is contained in the function $\Delta(\varepsilon,k)$. We assume henceforth that

$$\Delta(\varepsilon,k)=\begin{cases}\Delta & \text{if}\quad \varepsilon_{cl}(k)<\varepsilon<\varepsilon_{cl}(k)+\delta\varepsilon_c,\\ & \varepsilon_{vu}(k)-\delta\varepsilon_v<\varepsilon<\varepsilon_{vu}(k);\\ 0 & \text{if}\quad \varepsilon<\varepsilon_{vu}(k)-\delta\varepsilon_v,\ \varepsilon>\varepsilon_{cl}(k)+\delta\varepsilon_c,\\ & \varepsilon_{vu}(k)<\varepsilon<\varepsilon_{cl}(k).\end{cases}\tag{12}$$

Here $\delta\varepsilon_c$ and $\delta\varepsilon_v$ are the widths of the conduction and valence bands. This is the form chosen in Ref. 18. Its use in our case is justified by the following considerations. According to (10), $\Delta(\varepsilon,k)$ is determined, first, by the form of the two-dimensional state density $\rho(\varepsilon,k)$, and the second, by the values of V_{nkl}. Since the volume bands can be regarded as almost free, and for free electrons $\rho(\varepsilon,k)=\mathrm{const}$. The matrix element V_{nkl} is very difficult to calculate accurately. We assume that $V_{nkl}\sim\mathrm{const}$, since in the principle there are no grounds for assuming a strong dependence of V_{nkl} on n, k, or l.

From (10)–(12) we obtain

$$\Lambda(\varepsilon,k)=\frac{\Delta}{\pi}\ln\left|\frac{(\varepsilon_{vu}-\delta\varepsilon_v-\varepsilon)(\varepsilon_{cl}-\varepsilon)}{(\varepsilon_{vu}-\varepsilon)(\varepsilon_{cl}+\delta\varepsilon_c-\varepsilon)}\right|.\tag{13}$$

We shall consider states in the forbidden band, i.e., essentially $\varepsilon\sim\varepsilon_g$ (ε_g is the width of the forbidden band). Assuming that $\delta\varepsilon_c,\ \delta\varepsilon_v\gg\varepsilon_{cl},\varepsilon_{vu},\varepsilon_g$, we get from (13)

$$\Lambda(\varepsilon,k)=\frac{\Delta}{\pi}\ln\left|\frac{\varepsilon_{cl}(k)-\varepsilon}{\varepsilon_{vu}(k)-\varepsilon}\right|.\tag{14}$$

We proceed to derive the equations for the self-consistent determination of n, n_0, and ε_F. We obtain the first equation by putting

$$n=\sum_{\sigma}\langle b_{i\sigma}^{+}b_{i\sigma}\rangle\tag{15}$$

[here $b_{i\sigma}^{+}$ and $b_{i\sigma}$ are the operators of electron creation and annihilation in the state $\varphi_i(\mathbf{r})$] in terms of the Green's function

$$n=2a\int_{|k|<\pi/a}\frac{dk}{2\pi}n(k)=2a\int_{|k|<\pi/a}\frac{dk}{2\pi}\int_{-\infty}^{\varepsilon_F}\mathrm{Im}\,G_\sigma^{\sigma}(\varepsilon,k)\frac{d\varepsilon}{\pi}$$

$$=2a\int_{\substack{|k|<\pi/a\\ \varepsilon_0(k)<\varepsilon_F}}\frac{dk}{2\pi}\left(1-\frac{d\Lambda}{d\varepsilon}\right)^{-1}\Bigg|_{\varepsilon=\varepsilon_0(k)}+\frac{2a}{\pi}\int_{|k|<\pi/a}\frac{dk}{2\pi}\int_{-\infty}^{\varepsilon_F}\frac{\Delta d\varepsilon}{[\varepsilon-\varepsilon(k)-\Lambda]^2+\Delta^2}.\tag{16}$$

Here $\varepsilon_0(k)$ is the solution of the equation

TABLE I.

Constant	Values for Ge	Values for Si	Constant	Values for Ge	Values for Si
ε_D	0.73 eV	1.1 eV	$\beta=e^2/\varepsilon a$	0.23 eV	0.3 eV
ε_g	0.74 eV	1.15 eV	$\gamma=\pi a^3N_D$	$0.4\cdot10^{-8}$	$3.8\cdot10^{-8}$
Δ	1.0 eV	2.0 eV	V_d	0.025 eV	0.025 eV
U	5.0 eV	5.0 eV	N_D	$2\cdot10^{13}$ cm^{-3}	10^{14} cm^{-3}

$$\varepsilon-\varepsilon(k)-\Lambda(\varepsilon,k)=0.\tag{17}$$

In the derivation of (16) we used the formula

$$n(k)=\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\varepsilon_F}G_\sigma^{\sigma}(\varepsilon,k)d\varepsilon.\tag{18}$$

The first term in (16) is the contribution made to the density of the electrons on the dangling bonds from the localized DS with the functions φ_i. The second term is a contribution due to the mixing of the volume and dislocation states.

We obtain the second self-consistency equation by expressing the total number of the electrons bound by the dislocation per dangling bond, n_0, in terms of ε_F:

$$n_0=a\int_{\substack{|k|<\pi/a\\ \varepsilon_0(k)<\varepsilon_F}}dk/\pi.\tag{19}$$

The third equation can be written in the form

$$n_0=\min\{1+N_Da/n_d,\ \tilde{n}_0,\ 2\},\tag{20}$$

where $\tilde{n}_0$ is the solution of the equation $\varepsilon_F(\tilde{n}_0)=\varepsilon_D$, ε_D is the shallow-donor level, and n_d is the dislocation density.

Solution of the system (16), (19), and (20) yields self-consistent values of ε_F, n, and n_0 as well as various dependences of the type $\varepsilon_F(n_0)$ and $n(n_0)$.

3. NUMERICAL SOLUTION OF THE SELF-CONSISTENCY EQUATIONS AND PHYSICAL MEANINGS OF RESULTS

To obtain a numerical solution it is more convenient to modify the problem somewhat. We consider only the two equations (16) and (19), which make it possible to find the two unknowns n and n_0 if the third unknown ε_F is regarded as a specified parameter. The numerical values of the constants are indicated in the table. The constant ε_d is chosen from the condition that the Fermi level of a neutral dislocation coincide with the experimentally observed values:

$$\varepsilon_{F0}\equiv\mu_e=0{,}1\ \text{eV}\quad\text{for Ge},$$
$$\varepsilon_{F0}\equiv\mu_e=0{,}4\ \text{eV}\quad\text{for Si}.$$

Figures 2 and 3 show plots of $\varepsilon_F(n_0)$ and $n(n_0)$. Figure 4 shows the energy of the dislocation state of Ge as a function of $x=ka$. The solid horizontal line indicates the position of the Fermi level. From the functions $\varepsilon_F(n_0)$ and $n(n_0)$ we can obtain the values of n_0 and n. The corresponding results for Si are shown in Fig. 5. The dashed horizontal lines in Figs. 4 and 5 correspond to the forbidden-band width ε_g.

We now show how to obtain with the aid of the plotted results a numerical solution of the three equations (16), (19), and (20). To this end we draw on Fig. 2a the horizontal line $\varepsilon_F=\varepsilon_D$. The abscissa of the point of in-

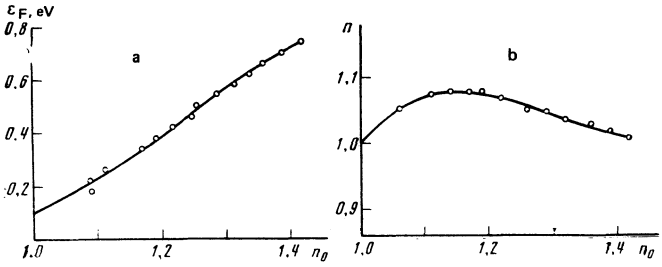

FIG. 2. Plots of $\varepsilon_F(n_0)$ (a) and $n(n_0)$ (b) for Ge.

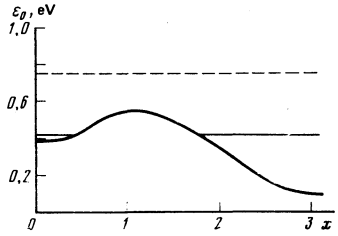

FIG. 4. DS energy ε_0 against x for Ge.

tersection of this line with the $\varepsilon_F(n_0)$ curve yields $\tilde{n}_0$. The self-consistent value of n_0 is determined by (20). Knowing n_0 we obtain ε_F and n from the plots of $\varepsilon_F(n_0)$ and $n(n_0)$.

We examine now the physical meaning of the results. It is seen from Fig, 2 and 3, first, that the maximum possible occupation numbers are ($f = n_0 - 1$)

$$f_{max} \approx 0.4 \quad \text{for Ge,} \qquad (21)$$
$$f_{max} \approx 0.5 \quad \text{for Si.}$$

This is much larger than in the SR theory, although somewhat smaller than in the preceding paper.[20] Nonetheless, comparing (21) with the earlier results,[20] we can draw the following conclusion: the maximum possible occupation numbers depend little on the structure of the spectrum of the volume states. What makes possible the existence of dislocations with occupation numbers $f \sim 1$ is the mixing of the DS with the volume states. The mixing leads to two effects. First, the wave function of the DS becomes more delocalized as the dislocations become filled with electrons, and this lowers the energy of the Coulomb interaction of the dislocation electrons. It is thus seen from the plot in Figs. 2b and 3b that with changing n_0 the number of electrons that are very strongly localized (in the region $r \sim a$ around the dislocation core), i.e., n, changes quite insignificantly, $\delta n < 0.1$. Second, mixing leads to a quantum-mechanical repulsion of the levels (see Ref. 20).

We note next that the DS form rather broad (~0.5 eV) one-dimensional bands. This result has two causes: allowance for the effect of the mixing of the states, and the strong dispersion of the edges of the dislocation band and of the conduction band. In fact, at $\Delta = 0$, the width of the band is $4V_d \approx 0.1$ eV (at the chosen values of the parameters). At $\Delta \neq 0$ the dislocation spectrum is determined by the solution of Eq. (17). The dispersion of the solution is determined not only by the function $\varepsilon(k)$ but also by the functions $\varepsilon_{cl}(k)$ and $\varepsilon_{vu}(k)$.

The physical meaning of this effect is that allowance for the mixing means in fact allowance for the overlap of the wave functions of the dangling bonds and the wave functions of the paired bonds. As a result, the electron acquires another opportunity of tunneling from one dangling band to another (besides the direct tunneling). The probability of the additional transitions is larger than that of the direct transitions, since the former are characterized by the matrix element of the overlap between nearest neighbors, whereas direct transitions correspond to overlap of second-nearest neighbors. As a result, the dislocation band becomes several times wider.

An important property of the DS spectrum is the nonmonotonic dependence of the energy ε_0 on the quasimomentum. As is seen from the numerical results, there are several values of k_i (and accordingly several values of ε_i) at which $d\varepsilon_0(k)/dk = 0$. Since the state density is inversely proportional to $d\varepsilon_0/dk$, the vanishing of $d\varepsilon_0/dk$ at certain values of ε_i means, in the one-dimensional case, that the state density has singularities at the point $\varepsilon = \varepsilon_i$. We define the half-width of the peak of the state density, with center at $\varepsilon = \varepsilon_i$, as the difference between ε_i and an energy value ε_i' such that the state density $\rho(\varepsilon_i')$ is larger than the minimum state density ρ_{min} by 10 times (by one order). The half-widths defined in this manner turn out to be ~0.002–0.006 eV, i.e., quite narrow.

At $\Delta = 0$ we have $d\varepsilon_0(k)/dk = 0$ only at $k = 0$ and $k = \pm\pi/a$. The physical cause of these extrema is the Bragg scattering of the one-dimensional electrons in a periodic one-dimensional structure with period $a \approx 4 \times 10^{-8}$ cm. Additional extrema appear at $\Delta \neq 0$. Taking into account the physical meaning of the mixing effect, it can be stated that they result from scattering of one-dimensional dislocation electrons by neighboring centers with dangling bonds. From the more formal point of view, the additional extrema are the consequences of the nonmonotonicity of the function $\varepsilon_{cl}(k)$, which in

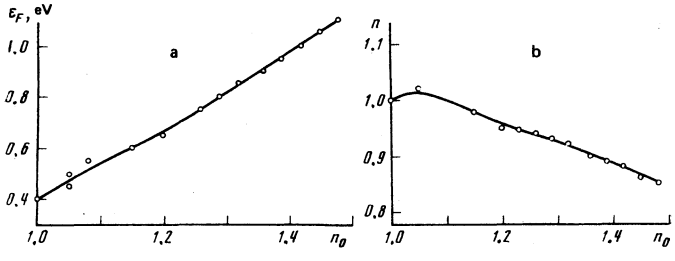

FIG. 3. Plots of $\varepsilon_F(n_0)$ (a) and $n(n_0)$ (b) for Si.

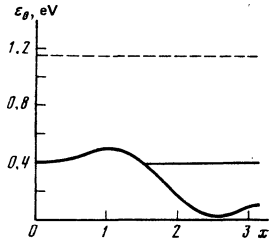

FIG. 5. DS energy ε_0 against x for Si.

turn is due to the presence of several equivalent minima of the conduction band at $k = k_{min} \neq 0$.

With changing Fermi level ε_F, the occupation numbers n and n_0 change and, according to (2) and (17), a change takes place in the structure of the dislocation spectrum, i.e., in the value of ε_i and in the character of the singularities of $\rho(\varepsilon)$ at ε_i. In concluding this section, we emphasize that only the numerical values of ε_i or the rate at which $\rho(\varepsilon)$ becomes infinite as $\varepsilon \to \varepsilon_i$ can depend on the values of the initial constants, but the very presence of singularities is a qualitative result and at a different choice of constants it does not depend on their numerical values.

4. COMPARISON WITH EXPERIMENTAL RESULTS

In the preceding section the numerical solution was obtained using the specific parameter values listed in the table. Some of them, for example Δ and U, were chosen quite arbitrarily. The numerical results must therefore be regarded as an illustration of the physical phenomena that are possible within the framework of the given model. On the other hand, to describe an actual experimental situation these parameters must be regarded as adjustable. It is more convenient to obtain a separate fit for each concrete case. In the present section we confine ourselves to an investigation of only several fundamental possibilities of using the model to explain the experimental results.

a. It follows from Sec. 3 that $f_{max} \approx 0.4$ for Ge and $f_{max} \approx 0.5$ for Si. Obviously, by changing the constants Δ and U, and also by changing the functions $\varepsilon_{cl}(k)$ and $\varepsilon_{vu}(k)$ (at those values of k for which the exact form of these functions is unknown) it is possible to obtain $f_{max} = 0.1-1.0$, in good agreement with the observed values.[21-23] No such agreement can be obtained within the framework of the SR theory.

b. We consider the microwave dislocation conductivity. Dislocation bands of width ~0.5 eV must of necessity contain energy sections on which $d\varepsilon_0/dk \sim 10^7$ cm/sec. Consequently, if the Fermi level falls on these sections, then $v_F \sim 10^7$ cm/sec. According to Ref. 24, this yields $\sigma_{mw} \sim 10^{-3}$ $(\Omega \cdot \text{cm})^{-1}$ (at a mean free path $l = 10^{-4}$ cm). This agrees in order of magnitude with the results of Ref. 4–7. At the same time, at certain values of the parameters (donor density, dislocation density) the Fermi level can land in a region where $d\varepsilon_0/dk \ll 10^7$ cm/sec. Taking into account the relation $\sigma_{mw} \propto v_F^4$ (see Ref. 24) we can expect a drastic decrease of σ_{mw}. It follows from the numerical results that v_F can decrease by dozens of times if the Fermi level lands in a vicinity of one of the singularities of the state density.

We note the following circumstance. Strictly speaking, the results of Ref. 24 are valid for the case when the equation $\varepsilon_0(k) = \varepsilon_F$ has two solutions, $k = \pm k_F$. In our problem, on the other hand, in addition to this case there is encountered also another, when there are four solutions: $k = \pm k_{F1}, k = \pm k_{F2}$. This problem was not considered theoretically, and we do not know definitely to what results the presence of the additional two solutions $\pm k_{F2}$ can lead. However, in one limiting case the qualitative result can be understood from the following reasoning. Assume that there are four solutions $k = \pm k_{F1}, k = \pm k_{F2}$, and the corresponding Fermi velocities satisfy the condition $|v_{F1}| \gg |v_{F2}|$. In this situation, in addition to the scattering processes $k_{F1} \to k_{F1}$, $k_{F1} \to -k_{F2}$, there are possible also the processes $k_{F1} \to k_{F2}, k_{F1} \to -k_{F2}$. The electron is then in a state with a small Fermi velocity. It is clear that in this case the presence of states with $k = \pm k_{F2}$ can only decrease the conductivity. The experimentally observed decrease of σ_{mw} of n-Ge with increasing dislocation density can be attributed to just this cause. In fact, it is seen from the numerical results that the smaller the dislocation charge (i.e., the higher the dislocation density) the closer we approach to the considered limiting situation. It is reached approximately at $\varepsilon_F \approx 0.2$ eV, whereas in experiment the decrease of σ_{mw} occurs for practically neutral dislocations, i.e., at $\varepsilon_F = 0.1$ eV. This discrepancy can be eliminated by changing the numerical values of $\varepsilon_{cl}(k)$ and $\varepsilon_{vu}(k)$ (we recall that the forms of these functions are known to use only qualitatively).

c. Observation of the EPR signal is direct proof of the existence of DS. From the point of view of our model, the observed signal comes from a one-dimensional metallic band. The magnitude of the signal is proportional to the static susceptibility, which in the case of a smooth $\rho(\varepsilon)$ function is proportional in turn to the state density on the Fermi level. In fact, we write down the static susceptibility in the form

$$\chi = \left(\frac{\partial M}{\partial H}\right)_{H \to 0} = -\beta^2 \int_{\varepsilon_1}^{\varepsilon_2} \rho(\varepsilon) \frac{\partial f}{\partial \varepsilon} d\varepsilon, \tag{22}$$

where M is the magnetization, H is the magnetic field, β is the Bohr magnetism, f is the Fermi function, and ε_1 and ε_2 are the end points of the one-dimensional band. At low temperatures T, the function $\partial f/\partial e$ is usually replaced by $-\delta(\varepsilon - \mu)$ (μ is the chemical potential), a procedure valid if $\rho(\varepsilon)$ changes little with changing $\varepsilon \sim k_B T$ (k_B is the Boltzmann constant). If $\rho(\varepsilon)$ has singularities, then the width of the peak of the function $\partial f/\partial \varepsilon$ must be kept constant. Representing $\partial f/\partial \varepsilon$ in the form

$$\frac{\partial f}{\partial \varepsilon} = -\frac{1}{\pi^{1/2} k_B T} \exp\left[-\left(\frac{\varepsilon - \mu}{k_B T}\right)^2\right],$$

we obtain for the susceptibility the expression

$$\chi = \beta^2 \int_{\varepsilon_1}^{\varepsilon_2} \frac{\rho(\varepsilon)}{\pi^{1/2} k_B T} \exp\left[-\left(\frac{\varepsilon - \mu}{k_B T}\right)^2\right] d\varepsilon. \tag{23}$$

If μ does not lie in the vicinity of the singularity of $\rho(\varepsilon)$, then we get from (23)

$$\chi_b = \beta^2 \rho(\mu) = \frac{\beta^2}{(2\pi d\varepsilon_0/dk)}\Big|_{\varepsilon_0(k) \to \mu} \sim \frac{\beta^2}{2a\delta\varepsilon_0}, \tag{24}$$

which is approximately smaller by a factor 10^3 (at $T = 10$ K and $\delta\varepsilon_0 \approx 1$ eV) then the Curie susceptibility

$$\chi_C = \beta^2/\pi^{1/2} a k_B T$$

from the discrete levels. This means that the EPR signal from the dislocation band is very weak compared with the signal from the discrete levels and is practically unobservable. In experiment[3] on the other hand an intense signal is observed with $\chi \propto T^{-1}$ at $T > 50$ K.

This phenomenon can be easily explained if it is recognized that μ can land in the vicinity of one of the singularities of $\rho(\varepsilon)$.

We assume for simplicity that $\mu = \varepsilon_i$ and let the singularity of $\rho(\varepsilon)$ at the point ε_i obey a power-law,

$$\rho(\varepsilon) = a^{-1}\Gamma^{\delta-1}|\varepsilon-\varepsilon_i|^{-\delta}. \tag{25}$$

Here δ is the exponent of the singularity, $\delta > 0$, and Γ is a constant with the dimension of energy. For $k_B T \ll |\varepsilon_2 - \varepsilon_1|$ but $k_B T \gg \gamma$ (γ is the width of the singularity) expression (23) yields

$$\chi = C_1\beta^2/\pi^{1/2}ak_BT; \qquad C_1 = \int_0^q dx/|x|^\delta \sim 1; \qquad q = \gamma/\Gamma. \tag{26}$$

It agrees with the result observed at $T > 50$ K both in magnitude and with respect to the temperature dependence. For $k_B T \ll \gamma$ we get

$$\chi = C_2\frac{\beta^2}{a\Gamma}\left(\frac{\Gamma}{k_BT}\right)^\delta, \qquad C_2 = \int_0^\infty \frac{dx\exp(-x^2)}{\pi^{1/2}|x|^\delta}. \tag{27}$$

The transition from the Curie law ($\chi \propto T^{-1}$) to the relation $\chi \propto T^{-\delta}$ takes place at $k_B T \approx \gamma$. From the numerical results it follows that $\gamma/k_B \sim 20$–60 K, in fair agreement with the observed deviation from the Curie law at $T \leq 50$ K.

Next, experiment has recently revealed a situation that is at first glance contradictory. Investigations of the influence of the annealing temperature on the EPR signal have shown that annealing at 700 °C leads already practically to a vanishing of the EPR signal. It has also been proved that the observed signal is connected with the dislocation level 0.44 eV (in Si).[25] At the same time, investigation of the electret state[26] indicate that the 0.44 eV level remains if the samples are annealed not only at 700 °C, but also at 1000 °C. In the SR theory these results contradict each other. In our model, on the other hand, there is a natural explanation.

Indeed, the EPR signal is observed only when μ lands in the region of a peak in the state density, otherwise the signal is weak. On the other hand, in an investigation of the electret state one actually measures μ independently of whether μ is in the region of the peak or not. The contradiction is resolved if it is assumed that in the course of annealing the spectrum becomes restructured in such a way that the state density at the Fermi level decreases. This is a very natural assumption, since annealing changes the screening of the dislocation by the impurities, and this changes the self-consistent Coulomb energy, leading in turn to a change in the form of the spectrum.

The numerical results provide also an answer to the question as to why EPR signals are observed in silicon and not in germanium. To this end we compare the dislocation spectra of almost neutral dislocations (EPR is investigated as a rule at high densities of the dislocations, when they are almost neutral) of silicon and germanium. It turns out that the chemical potential of silicon is equal to the energy at which $\rho(\varepsilon)$ has a singularity, whereas this is not the case for germanium.

d. We discuss now the investigations of the photoconductivity, electroluminescence, and photoluminescence spectra.[8-14] The electroluminescence and photoluminescence spectra are complicated. They can be represented as superpositions of peaks $\sim 5 \times 10^{-3}$ eV wide. As a result, several peaks are observed. Their width is practically independent of temperature, something difficult to reconcile with the notion of transitions from a band to a discrete level (in which the case the peak width is $\propto T$). It is interesting that the levels determined from the temperature dependence of the carrier density never manifest themselves in the luminescence spectra. In the photoconductivity spectra, deep levels correspond to "steps." In the case of dislocations, the positions and number of these steps depends noticeably on the experimental conditions. In addition, very frequently a decrease of the photoconductivity is observed after the start of the step, something that should not occur for transitions from bands to deep levels.

All these singularities can be qualitatively explained within the framework of our model. In fact, in place of deep discrete levels we have a system of state density peaks of width $\sim 8 \times 10^{-3}$ eV. Thus, the observed line width should be $\gtrsim 8 \times 10^{-3}$ eV. Consequently, if the measurements are made at $T < 8 \cdot 10^{-3}/k_B \approx 90$ K the line width should be independent of temperature. In addition, within the framework of this model, "intracenter" transitions are possible.[12] The electrons can tunnel through the electrostatic barrier to upper dislocation states that lie within the limits of the conduction band. They fall next to lower levels and emits photons. In these transitions the line width is also independent of temperature. A decrease of the photoconductivity should then be observed in the spectrum after the start of the step, as is in fact observed in experiment.

We note that between the peaks the state density is small but still finite. This in turn makes possible nonradiative transitions, in good agreement with the experimental fact that the presence of dislocations decreases strongly the intensity of the radiative recombination. Next, the levels determined from the temperature dependence of the carrier density correspond to the position of μ. If μ is in the region where the state density is low, no corresponding levels will appear in optical experiments. This apparently is the case with the 0.1 eV level in Ge.

When a change takes place in the occupation numbers and in the character of the dislocation screening, the distances between the singularities and their number can change. This can partially explain the difference between the experimental results obtained for the same substances.

We not also the following interesting circumstance. It is seen from the numerical results that under certain conditions the upper edge of the dislocation band touches the bottom of the conduction band. It appears that anomalies should then be observed in the carrier lifetimes and in the kinetic phenomena, owing to the resonant scattering by the dislocations, and nonlinear effects

connected with the transfer of dislocation electrons into the conduction band are also possible.

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[1)]We emphasize that to obtain self-consistent results it is necessary to introduce at least two parameters, n and n_0. By introducing only one parameter it is impossible to satisfy all the self-consistency conditions. The quantities n and n_0 have different physical meanings (a similar situation was encountered in Ref. 18). Failure to understand this difference is apparently the cause of the principal error of Ref. 19, in which the first attempt was made to study the influence of mixing on the DS.

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Theory of structural phase transitions in cyanides of alkali metals

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The thermodynamic properties of a structural phase transition model for alkali-metal cyanides are discussed in the molecular-field approximation. The temperature dependences of the transition parameters and of the specific heat are obtained. The jumps and changes of the transition entropies are calculated. The results of the calculation are compared with the experimental data for the crystals KCN, NaCN, CsCN, and RbCN.

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1. INTRODUCTION

Structural phase transitions (PT) in crystals of the type MeCN (Me = K, Na, Rb, Cs) have been the subject of many studies. It has been experimentally established that the transitions in these crystals are connected with the ordering of the cyanide groups. Potassium cyanide (KCN) has at room temperature an NaCl structure, and in this phase the cyanide groups CN are disordered relative to the orientations of their longitudinal axes. It was found that the CN groups do not rotate freely,[1] but move in a potential with a large number of minima. The published opinions concerning the form of this potential vary,[1-6] since it is impossible to distinguish in experiment with sufficient reliability the motion of the CN groups in an eight-minimum potential (equally probable orientation of the group axis relative to the body diagonals of the cube plus equally probable dispositions of the C and N atoms on the ends of the molecule) from that in a twelve-minimum potential (equally probable orientation of the group axis relative to the diagonals of the faces of the cube plus interchange of the positions of the C and N atoms in the molecule).

At atmospheric pressure KCN undergoes at 168 K, a first-order PT into a partially ordered phase with space group D_{2h}^{25} ($Z = 1$), in which the CN groups are oriented

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