[3] W. Tobocman, Nuovo Cimento 3, 1213 (1956).

[4] D. I. Candlin, Nuovo Cimento 4, 231 (1956).

[5] P. A. M. Dirac, Revs. Mod. Phys. 17, 195 (1945).

[6] P. A. M. Dirac, The Principles of Quantum Mechanics (Russ. Transl.), Second Edition, Sec. 33, GITL, Moscow 1937.

NONRADIATIVE RECOMBINATION OF ELECTRONS AT IMPURITY CENTERS IN N-TYPE GERMANIUM

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Nonradiative ("phonon") recombination of a current carrier at a Coulomb impurity center in n-type germanium is investigated at helium temperatures. Interaction between an electron and acoustic vibrations of the lattice is taken into account by successive diagonalization of the original Hamiltonian by a unitary transformation. The tensor nature of the effective carrier mass and also the general expression for the deformation potential are taken into account in the calculations.

1. FORMULATION OF THE PROBLEM

The complex character of the energy bands in germanium and silicon, which has been revealed in cyclotron ("diamagnetic") resonance experiments and in certain other experiments, again raises the problem of calculating the energy levels and wave functions of the electron in an impurity center in these crystals. For n-type samples there exist experimental data concerning the existence of a "longitudinal" effective mass, μ_ℓ, and a "transverse" effective mass, μ_t, of the electron. The tensor character of the effective mass has made it necessary to reexamine the old "scalar" model of impurity centers.[1,2] In these investigations, however, the interaction between the electron and the lattice vibration has not been taken into account. On the other hand, Deigen's[3] work has shown, that when one takes account of such interactions (deformation potential) for impurities in homopolar crystals, there appear in some cases comparatively deep levels, located below the bottom of the conduction band. Apparently, with respect to this so called "condenson" effect,[4] one encounters in Ge a case of weak binding. General expressions for the deformation potential in n-type germanium were obtained by Dumke,[5] who calculated, in the same paper, the scattering of current carriers in an ideal crystal by interaction with the lattice vibrations.

The purpose of the present work is to take into account the deformation potential for an electron in an impurity center by means of the weak-coupling approximation, and also to construct a corresponding theory for non-radiative recombination. It must be emphasized, that within the framework of the proposed method of calculation, the discrete and continuous spectra of electrons in impurity centers are considered together and thus the well known difficulties in this question[6] can be avoided.

2. ENERGY LEVELS AND QUANTUM STATES OF THE SYSTEM

It is known, that the conduction band in n-type germanium has eight degenerate energy minima or energy valleys, oriented along the [111] direction of the first Brilliouin zone. In the vicinity of each of these minima, the constant energy surfaces have the form of elongated ellipsoids, whose major axis is oriented along the [111] direction. Lampert[1] has shown, following the analysis of Koster and Slater, that the ground state of the electron in an impurity center can be found by the method of effective masses, by considering only the wave function belonging to a given energy valley. Such a treatment remains valid when one sets out to construct a theory of thermal transitions, if the thermal dissociation of the impurity center gives rise to electrons with a wave vector k, which does not exceed the bounds of the given valley. For the inverse process of thermal recombination, this essentially presupposes that the probability for capture of an electron with a vector k, associated with a particular valley, by a bound state associated with another energy valley, is small. Such "intervalley" capture can occur in principle, but will not be considered in this paper.

In what follows, it is convenient to choose a coordinate system such that the Z-axis coincides with the major axis of the ellipsoid associated with the given valley. If one takes into account the interaction of the electron with the potential due to the strain and shear deformations,[5] then the generalized Hamiltonian of the system, after transformation to the second quantization representation, can be written in the form

$$\hat{H} = \frac{\hat{p}_X^2 + \hat{p}_Y^2}{2\mu_t} + \frac{\hat{p}_Z^2}{2\mu_l} + V(R) + \sum_{j=1}^{3} \sum_{q} \hbar\omega_{qj} \hat{B}_{qj}^+ \hat{B}_{qj} + \hat{H}_i. \tag{1}$$

Here

$$V(R) = -ze^2/\varepsilon R \tag{2}$$

is the Coulomb energy of the electron; ε is the dielectric constant; $\hat{B}_{qj}^+$ and $\hat{B}_{qj}$ are Bose operators, and H_i is the operator for the interaction of the electron with the free phonon field:

$$\hat{H}_i = G_1 \sum_{j=1}^{3} \sum_{q} (\hbar\omega_{qj}/2C_{qj}L^3)^{1/2} f_j(\theta)(\hat{B}_{qj}e^{iqR} + e^{-iqR}\hat{B}_{qj}^+), \quad f_1(\theta) = 1 + (G_2/G_1)(3\cos^2\theta - 1),$$

$$f_2(\theta) = (3G_2/G_1)\cos\theta\sin\theta\cos\chi, \quad f_3(\theta) = (3G_2/G_1)\cos\theta\sin\theta\sin\chi. \tag{3}$$

Summation over j in Eq. (1) and (3) includes one longitudinal and two transverse waves for every acoustic-wave vector[1] q. In Eqs. (3), θ is the angle between q and the Z axis for the given energy valley; χ is the angle between the direction of polarization e_{q_2} of the acoustic wave and the plane passing through the Z axis and the normal to q; the energy constants G_1 and G_2 are chosen to give the best fit between the theoretical calculations of the mobility of current carriers in germanium and experimental measurements.[5] The elastic constants G_{qj}, as shown in Ref. (5), can be considered independent of the wave vector q and for germanium crystals one can substitute certain average values corresponding to longitudinal and transverse waves; L^3 is the volume of the fundamental cell of the crystal.

In what follows, we shall change for convenience from the variables X, Y, and Z in Eqs. (1) and (3) to the variables x, y, and z defined thus:

$$x = X; \quad y = Y; \quad z = Z/\gamma; \quad \gamma = \sqrt{\mu_t/\mu_l}. \tag{4}$$

We take advantage of the method of successive diagonalizations of the Hamiltonian by unitary transformations[8] in the form proposed by Bohm and Pines and employed subsequently by Toyazawa[9] in his investigation of the "electron polaron." Such a method allows us to take into account the interaction of the electron with the phonon field with an accuracy to second-order terms.

The transformed Hamiltonian Eq. (1) has the form

$$\hat{\Lambda} = \hat{U}^{-1}\hat{H}U. \tag{5}$$

The unitary operator $\hat{U}$ is chosen to have the form

$$\hat{U} = \exp(i\hat{S}/\hbar), \tag{6}$$

where the Hermitian operator $\hat{S}$ is defined below.

Omitting the details of the calculations, we arrive at

$$\hat{H} = \hat{p}^2/2\mu_t + V\,(\sqrt{x^2+y^2+\gamma^2 z^2}) + \sum_{q,\,j}\hbar\omega_{qj}\hat{b}^+_{qj}\hat{b}_{qj} + \hat{H}' + \hat{H}''. \tag{7}$$

Here

$$\hat{b}_{qj} = e^{i\hat{S}/\hbar}B_{qj}e^{-i\hat{S}/\hbar}; \quad \hat{b}^+_{qj} = e^{-i\hat{S}/\hbar}\hat{B}^+_{qj}e^{i\hat{S}/\hbar}, \tag{8}$$

$\hat{H}'$ and $\hat{H}''$ are second-order operators.

$$\hat{H}' = -\frac{i}{2\hbar}[\hat{S},\ \hat{\Lambda}_i], \quad \hat{H}'' = -\frac{i}{\hbar}[\hat{S},\ V\,(\sqrt{x^2+y^2+\gamma^2 z^2})], \tag{9}$$

$$\hat{\Lambda}_i = e^{i\hat{S}/\hbar}\,\hat{H}_i\,e^{-i\hat{S}/\hbar} = G_1\sum_{q,\,j}\sqrt{\frac{\hbar\omega_{qj}}{2C_{qj}L^3}}f_i\,(\theta)\,[\hat{b}_{qj}\exp\{i\,(xq_x+yq_y+\gamma z q_z)\} + \exp\{-i\,(xq_x+yq_y+\gamma z q_z)\}\hat{b}^+_{qj}]. \tag{10}$$

The operator $\hat{S}$ is defined by equating the sum of first order terms to zero, thus;

$$\hat{\Lambda}_i - \frac{i}{\hbar}\Big[\hat{S},\ \frac{\hat{p}^2}{2\mu_t}\Big] - \frac{i}{\hbar}\Big[\hat{S},\ \Big(\sum_{q,\,j}\hbar\omega_{qj}\hat{b}^+_{qj}\,\hat{b}_{qj}\Big)\Big] = 0. \tag{11}$$

It can be put into a more convenient form as follows:

$$\hat{S} = \sum_{q,\,j}(\hat{\alpha}_{qj}\,\hat{b}_{qj}\exp\{i\,(xq_x+yq_y+\gamma z q_z)\} - \exp\{-i\,(xq_x+yq_y+\gamma z q_z)\}\hat{\alpha}^+_{qj}\,\hat{b}^+_{qj}). \tag{12}$$

After evaluating the commutators in Eq. (11), we arrive at:

$$\hat{S} = -i\hbar\,G_1\sum_{q,\,j}\sqrt{\frac{\hbar\omega_{qj}}{2C_{qj}L^3}}f_j\,(\theta)\,(\hat{b}_{qj}\,\hat{L}^{-1}e^{i\,(xq_x+yq_y+\gamma z q_z)} - \hat{b}^+_{qj}\,e^{-i\,(xq_x+yq_y+\gamma z q_z)}\,\hat{L}^{-1}), \tag{13}$$

$$\hat{L} = \frac{\hbar^2}{2\mu_t}(q_x^2 + q_y^2 + \gamma^2 q_z^2) - \frac{\hbar}{\mu_t}(q_x\hat{p}_x + q_y\hat{p}_y + \gamma q_z\hat{p}_z) + \hbar\omega_{qj}. \tag{14}$$

Using the given value of $\hat{S}$, it is possible to arrive at explicit expressions for $\hat{H}'$ and $\hat{H}''$.

The calculations are greatly simplified if the operator L^{-1} is expanded into a series in the ratio of the electron momentum to the phonon momentum, which is a small quantity. Such an expansion can be made for all q, which satisfy the relation:

$$q \gg p/\hbar \approx \sqrt{\mu_t E_{\text{ion}}/\hbar^2} \approx 10^6\ \text{cm}^{-1}. \tag{15}$$

Since $q_{\text{max}} = (6\pi^2/a^3)^{\frac{1}{3}} \approx 10^8\,\text{cm}^{-1}$ (a is the lattice constant), the inequality (15) embraces, as will be evident from Eq. (20), the region of the largest most important values of (q).

Calculation of $\hat{H}''$ yields:

$$\hat{H}'' = -\frac{ie^2\hbar^2 G_1}{\mu_t\varepsilon}\sum_{q,\,j}\sqrt{\frac{\hbar\omega_{qj}}{2C_{qj}L^3}}f_j\,(\theta)\,\frac{xq_x+yq_y+\gamma^3 z q_z}{(x^2+y^2+\gamma^2 z^2)^{3/2}}\,\frac{\hat{b}_{qj}\exp\{i\,(xq_x+yq_y+\gamma z q_z)\} - \hat{b}^+_{qj}\exp\{-i\,(xq_x+yq_y+\gamma z q_z)\}}{[(\hbar^2/2\mu_t)\,(q_x^2+q_y^2+\gamma^2 q_z^2) + \hbar\omega_{qj}]^2}. \tag{16}$$

To determine $\hat{H}'$, note the following. The eigenvalues of the energy operator $\hat{H}$ can be obtained if Eq. (7) is first averaged over oscillations of the field. Then, in the energy of the electron there appear additional terms only for the averaged operator $\hat{H}'$. They have the form

$$\langle\hat{H}'\rangle = \mathscr{E}_0 - (\hat{p}_x^2 + \hat{p}_y^2)/2M_t - \hat{p}_z^2/2M_l. \tag{17}$$

Here $\langle\ldots\rangle$ signifies an averaging over the virtual phonon field. To simplify the calculation, we consider the case of low temperatures, when we can with great accuracy say that

$$\langle\hat{b}^+_{qj}\,\hat{b}_{qj}\rangle = O\,(L^{-3}); \quad \langle\hat{b}_{qj}\hat{b}^+_{qj}\rangle = 1 + O\,(L^{-3}). \tag{18}$$

The expression for $\mathcal{E}_0$ has the form

$$\mathcal{E}_0 = -\frac{\hbar G_1^2}{2L^3} \sum_{q,j} f_j^2(\theta)\, \omega_{qj} / C_{qj}\, [\cdots], \quad [\cdots] = [(\hbar^2/2\mu_t)\,(q_x^2 + q_y^2 + \gamma^2 q_z^2) + \hbar\omega_{qj}].$$

(19)

The quantities $1/M_t$ and $1/M_\ell$ are respectively given by

$$1/M_t = (G_1^2\hbar^3/\mu_t^2 L^3) \sum_{q,j} f_j^2(\theta)\, \omega_{qj} q q_x^2 / C_{qj}\, [\cdots]^3 = (G_1^2\hbar^3/\mu_t^2 L^3) \sum_{q,j} f_j^2(\theta)\, \omega_{qj} q q_y^2 / C_{qj}\, [\cdots]^3,$$

$$1/M_l = (\gamma^2 G_1^2\hbar^3/\mu_t^2 L^3) \sum_{q,j} f_j^2(\theta)\, \omega_{qj} q q_z^2 / C_{qj}\, [\cdots]^3.$$

(20)

Thus, one can speak of an equivalent Hamiltonian $\widetilde{H}$, in which $\hat{H}'$ is included:

$$\widetilde{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2}{2\mu'_{\text{eff}}} + \frac{\hat{p}_z^2}{2\mu''_{\text{eff}}} + V(\sqrt{x^2 + y^2 + \gamma^2 z^2}) + \sum_{q,j} \hbar\omega_{qj}\, \hat{b}_{qj}^+ \hat{b}_{qj} + \mathcal{E}_0 + \hat{H}''$$

$$1/\mu'_{\text{eff}} = 1/\mu_t - 1/M_t; \quad 1/\mu''_{\text{eff}} = 1/\mu_t - 1/M_l.$$

(21)

The Hamiltonian $\widetilde{H}$ describes a motion of a condenson, similar to that of a quasi-particle in the Coulomb field of the impurity center.

In the approximation of an isotropic crystal, μ_{eff} and $\mathcal{E}_0$ are readily determined. If one assumes $\gamma = 1$; $G_2 = 0$, $\omega_q = w_\ell q$ (w_ℓ is the "longitudinal" velocity of sound), then changing the summation in Eqs. (19) and (20) into an integration in spherical coordinates, we find:

$$\mathcal{E}_0 = -\frac{1}{4\pi^2}\frac{\hbar G_1^2}{\rho w_l} \int_0^{q_{\max}} \frac{q^2 dq}{\hbar w_l + \hbar^2 q/2\mu}, \quad \mu_{\text{eff}} = \mu\left[1 + \frac{4\mu^2 G_1^2}{3\pi^2 \rho w_l \hbar^3}\int_0^{q_{\max}} \frac{q^2 dq}{(q + 2\mu w_l/\hbar)^3}\right],$$

(22)

where ρ is the density of the crystal. This result agrees exactly with the calculation (by Pekar and Krivoglaz) of the ground-state energy and the effective mass of the condeson in a homopolar crystal; they used a different method.[10]

If we take into account the tensor character of the effective mass and neglect for simplicity the shear deformation in describing the deformation potential, we obtain the following result:

$$\mathcal{E}_0 = -\frac{w_l G_1^2 \mu_t^3}{\pi^2 \rho \hbar^3 \sqrt{1-\gamma^2}} \int_0^{\hbar q_{\max}/2\mu_t\, w_l} \frac{x^2}{\sqrt{x(x+1)}} \ln\left|\frac{\sqrt{x(1-\gamma^2)} + \sqrt{x+1}}{\sqrt{x(1-\gamma^2)} - \sqrt{x+1}}\right| dx,$$

(23)

$$\frac{\mu'_{\text{eff}}}{\mu_t} \approx 1 + \frac{\mu_t}{M_t} = 1 + \frac{\mu_t^2 G_1^2}{4\pi^2 \rho w_l \hbar^3 \sqrt{1-\gamma^2}} \int_0^{\hbar q_{\max}/2\mu_t\, w_l} \frac{x\,dx}{(1+x)^2}\left(3 + \frac{1+x+|\gamma^2-1|x}{\sqrt{(1-\gamma^2)(1+x)x}}\ln\frac{\sqrt{x(1-\gamma^2)} - \sqrt{1+x}}{\sqrt{x(1-\gamma^2)} + \sqrt{1+x}}\right),$$

$$\mu''_{\text{eff}}/\mu_t \approx 1 + \mu_t/M_l; \quad M_l \approx M_t/100\gamma^2.$$

(24)

Including the shear deformation in Eqs. (19) and (20) complicates the mathematical description of the final results somewhat, but does not change their numerical value very much.

The fact, that in the approximation adopted in this analysis, the binding energy of the condenson $\mathcal{E}_0$ does not depend on the quantum number of the electronic state in the Coulomb field of the impurity, becomes understandable if one notes that the radius of the electronic state is very large even for the ground state (the ionization energy of the impurity center is about 0.01 ev).

In what follows, the operator $\hat{H}''$ plays the role of a small perturbation that induces quantum transitions between stationary states of the system, obtained from solutions of Schrödinger's equation

$$(\widetilde{H} - \hat{H}'')\Psi = E\Psi.$$

(25)

The wave function in the zeroth approximation assumes the form.

$$\Psi_{s\ldots n_{qj}\ldots} = \psi_s(x, y, z)\prod_{q,j} \Delta(n_{qj} - n_{qj}^0)$$

(26)

where $\psi_S (x, y, z)$ is defined by the equation

$$\frac{p_x^2 + p_y^2}{2\mu'_{\text{eff}}} \psi_s + \frac{p_z^2}{2\mu''_{\text{eff}}} \psi_s - \frac{ze^2}{\varepsilon \sqrt{x^2 + y^2 + \gamma^2 z^2}} \psi_s = E_s \psi_s.$$

(27)

The second term in Eq. (26) is the wave function of the oscillators of the field in the second-quantization representation (Δ is the Kronecker function).

The ground state can be obtained from Eq. (27) by the variational method. Let us neglect the differences in the effective masses of the "longitudinal" condensons and adopt the approximation:

$$\mu'_{\text{eff}} \approx \mu''_{\text{eff}} \approx \mu_t,$$

(28)

We can then take advantage, for example, of Lampert's results.[1] We must take it into account here that the energy level of an electron in an impurity center is always shifted by an amount $\mathcal{E}_0$, which equals for Ge crystals amounts to $8 - 10\%$ of the theoretically calculated ionization energy of the center.

3. NONRADIATIVE RECOMBINATION OF A CONDENSON AT A COULOMB CENTER

The problem of non-radiative recombination in Ge crystals has been treated in Refs. (11) through (13). These investigations are not satisfactory from our viewpoint, because of the way that the interaction with the lattice vibrations is handled. Thus some of these authors completely neglect the lattice vibrations in the zeroth approximation; others consider it in the tight-coupling approximation. The use of the adiabatic method in Ge cannot really be justified, in view of the exceedingly small value of the thermal-dissociation energy of the impurity. Besides, the calculations mentioned above are based on the "scalar" model of the center, which therefore reduces the theoretical significance of the results.

Let us consider one of the problems of the theory of nonradiative transitions, namely, the thermal transition of a condenson from the ground state of the Coulomb center to the conduction band under the action of the perturbation operator $\hat{H}''$. Furthermore, let us assume that the condition described by Eq. (28) is satisfied, thus allowing us, in effect, to change the word "condenson" to "electron." The uniqueness of the diagonalization of the Hamiltonian manifests itself above all in the theory of thermal transitions, principally because the form of the perturbation operator is changed substantially. Let us choose for simplicity the following initial form for the electron wave function ψ_S

$$\psi_s = A \exp \{- \alpha^2 (x^2 + y^2) - \beta^2 z^2\}.$$

(29)

Here α^2 and β^2 are variable parameters, determined by the condition that the energy E in Eq. (27) is a minimum.

The wave function of the final state of the electron in a crystal with a large dielectric constant is usually assumed to have the form of a plane wave.[11,13] However, as has been correctly pointed out by Gummel and Lax, the replacement of the Coulomb function by the continuous spectrum of a plane wave leads to a lowering of the transition probability by one or two orders of magnitude.

Solutions of Eq. (27) for electronic states in the continuous spectrum cannot be obtained directly. One can hardly expect success from the generalized variational method for this case. On the other hand, in crystals like Ge, the large effective-mass anisotropy allows one to introduce the following approximation into the potential-energy terms of the Hamiltonian for large distances from the center:

$$\gamma^2 = \mu_t/\mu_l \approx 0.$$

(30)

Transforming Eq. (27) into cylindrical coordinates and making use of Eq. (30), one can arrive at an approximate expression for the wave function of the continuous spectrum

$$\psi_{k_0, m, k_z} = C_{k_0} e^{ik_z z} e^{im\varphi} (2ik_0\rho)^m e^{-ik_0\rho} F \left(m + \frac{i\alpha_0}{k} + \frac{1}{2}; 2m + 1; 2ik_0\rho \right),$$

$$\rho = \sqrt{x^2 + y^2}; \ k_0 = \sqrt{k_x^2 + k_y^2}; \ \alpha_0 = \mu e^2/\varepsilon\hbar^2,$$

(31)

F (a, b, c) is the confluent hypergeometric function and C_{k_0} is a normalization constant.

Calculation of the matrix element from such a function is an extremely complicated mathematical problem, whose solution can be obtained only by numerical methods. To illustrate some of the characteristics

of the theory of thermal transitions which follow from the theory described here, we should try to obtain the final equations for the transition probabilities by analytic methods. In view of this, let us limit ourselves to considering functions of the form

$$\psi_{k_x, k_y, k_z} = L^{-3/2} \exp\{i(k_x x + k_y y + k_z z)\}.$$ (32)

The transition probability of the system from the state $(s \ldots n_{qj} \ldots)$ to all states $(k_x, k_y, k_z \ldots n'_{qj} \ldots)$ should be averaged over all initial vibrational states of the lattice and summed over all final states of the electron and the lattice. Utilizing the method of summing probabilities given by Lax,[14] one can obtain the following expression for the transition probability:

$$W_{\text{ion}} = \frac{1}{\hbar^2} \sum_{k} \sum_{q, j} \int_{-\infty}^{+\infty} |(s|H''|k)|^2 [(\bar{n}_{qj} + 1) e^{i\omega_{qj} t} + \bar{n}_{qj} e^{-i\omega_{qj} t}] \exp\left\{\frac{i}{\hbar}(\mathscr{E}_k - E_s) t\right\} dt.$$ (33)

Here $\bar{n}_{qj}$ is the average value of the quantum number:

$$\bar{n}_{qj} = [\exp(\hbar\omega_{qj}/k_0 T) - 1]^{-1} \approx \exp(-\hbar\omega_{qj}/k_0 T)$$ (34)

and $\mathscr{E}_k$ is defined as

$$\mathscr{E}_k = \hbar^2 k^2/2\mu_t.$$

The matrix element that enters into Eq. (33) has the following form in cylindrical coordinates:

$$(s|H''|k) = \sqrt{\frac{AB_{qj}}{L^3}} \int_0^\infty e^{-\alpha^2\rho^2} \rho \, d\rho \int_{-\infty}^{+\infty} \frac{e^{-\beta^2 z^2 + i\gamma z(q_z - k_z/\gamma)}}{(\rho^2 + \gamma^2 z^2)^{3/2}} dz$$

$$\int_0^{2\pi} \exp\{i\rho[(q_x - k_x)\cos\varphi + (q_y - k_y)\sin\varphi]\} (\rho q_x \cos\varphi + \rho q_y \sin\varphi + \gamma^3 z q_z) d\varphi,$$

$$A = (2/\pi)^{3/2}\beta\alpha^2, \quad B_{qj} = \omega_{qj} e^{4\hbar^5} f_j^2(\theta) G_1^2/2L^3 C_{qj}\varepsilon^2\mu_t^2 [\ldots]^4.$$ (35)

Let us change the summation over q in Eq. (33) to an integration in spherical coordinates, with the polar axis chosen to coincide with the original Z axis. To do this we must bear in mind that there are $(L/2\pi)^3 d\tau_q$ acoustic vibrations in an element of volume in q-space, associated with a given direction of polarization. Integration over the variable t yields a δ-function, with which one can immediately calculate the integral over q:

$$W_{\text{ion}} = \frac{L^3}{4\pi^2\hbar^2} \sum_{k} \sum_{j=1}^{3} \frac{q_{0j}^2}{w_j} \int_0^{2\pi} d\varphi \int_0^{\pi} |(s|H''|k)|^2 \exp\left(-\frac{\hbar w_j q_{0j}}{k_0 T}\right) \sin\theta \, d\theta.$$ (36)

In the above the dispersion law we used $\omega_{qj} = w_j q_{0j}$, where q_{0j} is the wave number, determined from the conservation of energy:

$$\hbar w_j q_{0j} = \hbar^2 k^2/2\mu_t + |E_s|.$$ (37)

At low temperatures, the quantity q_{0j} that enters into the matrix element of Eq. (36) can be written

$$q_{0j} \approx |E_s|/\hbar w_j.$$ (38)

It is assumed that in crystals like Ge and Si the anisotropy does not alter the inequalities, which are valid at helium temperatures for isotropic crystals,[12] namely

$$\mathscr{E}_k \approx k_0 T \ll k\Theta_D - |E_s|,$$ (39)

where Θ_D is the Debye temperature.

The integrals in the matrix element of Eq. (35) can be evaluated by expanding the integrand in a series in terms of the small-valued parameter γ^2 ($\gamma_{\text{Ge}}^2 = 0.059$, cf. Ref. 1). Furthermore, in accordance with Eq. (39), the quantities k_x, k_y, and k_z/γ can be neglected compared with the wave vector of the lattice, q_{0j}. Integration over φ in Eq. (35) leads to Bessel functions, and subsequent integrations proceed in a straightforward way. Finally, we obtain

$$\langle s \,|\, H'' \,|\, k \rangle = \frac{i\pi^2}{2\alpha\beta} \sqrt{\frac{ABq_{0j}}{L^3}} \, q_{0j}^2 \sin^2\theta \exp\left(-\frac{q_{0j}^2 \sin^2\theta}{4\alpha^2}\right) F\left(\frac{3}{2}; 2; \frac{q_{0j}^2 \sin^2\theta}{4\alpha^2}\right) \left\{1 + \frac{\gamma^2}{2\beta^2}\left[-\frac{q_{0j}^2 \cos^2\theta}{2} + 3\alpha^2 \frac{F\,(5/2;\, 2;\, q_{0j}^2 \sin^2\theta/4\alpha^2)}{F\,(3/2;\, 2;\, q_{0j}^2 \sin^2\theta/4\alpha^2)}\right]\right\} \quad (40)$$

(θ is the angle between the vector q and the z axis, and F (a, b, c) is the confluent hypergeometric function). Further, substituting Eq. (40) into Eq. (36), we replace summation over q by integration in spherical coordintes, with the polar axis chosen as before to coincide with the original z axis. The integrand in the integral with respect to the variable $\cos\theta = x$ has a sharp maximum near the point $x_m = 1 - \gamma^2$; the functions that change very little with increasing x can be taken outside the integral and replaced by their values at $x = x_m$. Omitting the details of the calculation, we arrive at the result:

$$W_{\text{ion}} = \frac{16\alpha^2 G_1^2 e^4 \mu_t^{7/2} (k_0 T)^{5/2} \exp\{-|E_s|/k_0 T\}}{3\pi\beta\varepsilon^2 \gamma^4 \hbar^8} \sum_{j=1}^{3} \frac{f_j^2(x_m)}{C_j q_{0j}^3} \left[1 - \frac{\gamma^2 q_{0j}^2}{2\beta^2}(1 - 12\gamma^2 \Phi(\gamma))\right], \quad (41)$$

$$\Phi(\gamma) = \int_0^1 \frac{(1-x^2)^3}{[1-(1-\gamma^2)x^2]^4} \, dx \approx \frac{1+3\gamma^2}{4}\left[\frac{11}{3}(\gamma^2 - 1) + (2 + \gamma^2)\ln\left|\frac{4-\gamma^2}{\gamma^2}\right|\right]. \quad (42)$$

The hypergeometric functions are replaced by their asymptotic values.[15]
Summation over j in Eq. (41) yields,

$$W_{\text{ion}} = \frac{16\alpha^2 G_1^2 w_l^3 e^4 \mu_t^{7/2} (k_0 T)^{5/2} \exp\left(-|E_s|/k_0 T\right)}{3\pi\beta C_L \varepsilon^2 \gamma^4 \hbar^5 E_s^3} \left\{\left(1 + \frac{2G_2}{G_1}\right)^2 \left[1 - \frac{\gamma^2 E_s^2}{2\hbar^2\beta^2 w_l^2}(1 - 12\gamma^2\Phi)\right] + \frac{18\gamma^2 C_L G_2^2}{C_T G_1^2}\left(\frac{w_t}{w_l}\right)^3 \left[1 - \frac{\gamma^2 E_s^2 (1 - 12\gamma^2\Phi)}{2\hbar^2\beta^2 w_t^2}\right]\right\}.$$

Following Ref. 5, we use for the elastic constants C_L and C_T the arithmetic means of the elastic constants corresponding to the directions of propagation [110], [100] and [111] for longitudinal and transverse waves. Note that the expression that is subtracted from unity in the brackets of Eq. (41) is the second term in the expansion of the matrix element in terms of the small parameter γ^2. For Ge it amounts to only several percent of the first term in the series.

In a manner similar to that presented above one can calculate the probability for capture of a current carrier by the ground state of the impurity center.

The corresponding calculation leads to:

$$w_{\text{rec}} \approx \frac{32\sqrt{2\pi}\alpha^2\mu_t^2 e^4}{3^3\varepsilon^2\hbar^2 E_s^3 \gamma^4 L^3}\left[\frac{(G_1 + 2G_2)^2 \, w_l^3}{C_L} + \frac{18\gamma^2 G_2^2 w_t^3}{C_T}\right] \quad (44)$$

The same result is obtained directly by applying the principle of detailed balancing.

One can evaluate α^2, β^2, and E_s in Eq. (44) with the help of the variational method, and obtain the following:

$$\beta^2 = \gamma\sqrt{2}\alpha^2; \quad \alpha^2 = \left(\frac{ze^2\mu_t}{2\varepsilon\hbar^2}\right)^2 \frac{2\pi}{(1-\gamma/\sqrt{2})^3}; \quad E_s = \frac{\hbar^2}{2\mu_t}(\beta^2 + 2\alpha^2) - \frac{ze^2\sqrt{2\pi}\alpha\beta}{\varepsilon\,(\beta^2 - \alpha^2\gamma^2)^{1/2}}. \quad (45)$$

Using the following values[16] for the parameters of Ge:

$\rho = 5.4$ g/cm^3; $\mu_t = 0.083$ m; $\gamma^2 = 0.059$; $\varepsilon = 16$; $w_l = 5.16 \times 10^5$ cm/sec; $w_t = 3.2 \times 10^5$ cm/sec;

$C_L = 14.2 \times 10^{11}$ dynes/cm^2; $C_T = 5.8 \times 10^{11}$ dynes/cm^2; $G_1 \approx -G_2$; $G_2 = 5.84$ ev.

We obtain:

$\alpha^2 = 2.62 \times 10^{12}$ cm^{-2}; $\beta^2 = 0.905 \times 10^{12}$ cm^{-2}; $E = 0.0115$ ev

Equation (44) yields

$$w_{\text{rec}} = 1.48 \cdot 10^{-8} L^{-3} \text{ sec}^{-1}. \quad (46)$$

Replacement of the plane wave by the more accurate function, Eq. (31), should increase the calculated transition probability by one or two orders of magnitude. For low temperatures this, apparently, is a general result.[9,12]

Note, that the value of W_{rec} calculated by Sclar and Burstein,[17] who used the equations of Gummel and Lax[12] and took into account the Coulomb function for the electron in the continuous spectrum, is $3.5 \times 10^{-9} L^{-3}$ sec^{-1}. This is three orders of magnitude smaller than the value determined from data[17]

on the photoconductivity of Ge and Si. It follows directly from Eq. (46) that, within the framework of the theory presented here, we have succeeded qualitatively in eliminating the above discrepancy with experiment. We have also indicated what must be done for an accurate quantitative calculation. The question of competing mechanisms of recombination[18] will be investigated separately.

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[1] M. A. Lampert, Phys. Rev. **97**, 352 (1955).

[2] A. N. Anselm and L. I. Korovich, J. Tech. Phys. (U.S.S.R.) **25**, 2044 (1955).

[3] M. F. Deigen, J. Exptl. Theoret. Phys. (U.S.S.R.) **31**, 504 (1956), Soviet Phys. JETP **4**, 424 (1957).

[4] M. F. Deigen, and S. I. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) **21**, 80 (1951).

[5] W. P. Dumke, Phys. Rev. **101**, 531 (1956).

[6] Io. E. Perlin, J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 105 (1957), Soviet Phys. JETP **5**, 71 (1957); H. D. Vasileff, Phys. Rev. **96**, 603 (1954).

[7] G. Koster and J. Slater, Phys. Rev. **95**, 1167 (1954).

[8] S. V. Tiablikov, J. Exptl. Theoret. Phys. (U.S.S.R.) **21**, 16 (1951).

[9] R. Kubo and I. Toyozawa, Prog. Theor. Phys. (Japan) **13**, 160 (1955).

[10] M. A. Krivoglaz and S. I. Pekar, Izv. Akad. Nauk SSSR, Ser. Fiz., **21**, 3 (1957).

[11] Goodman, Lawson, and Schiff, Phys. Rev. **71**, 191 (1947).

[12] H. Gummel and M. Lax, Phys. Rev. **97**, 1469 (1955).

[13] R. Kubo and I. Toyozawa, Prog. Theor. Phys. (Japan) **13**, 160 (1955).

[14] M. Lax, Jour. Chem. Phys. **20**, 1752 (1953).

[15] L. L. Landau and E. M. Lifshitz, Квантовая механика (Quantum Mechanics) Gostekhizdat, Moscow, 1948.

[16] Bond, Mason, McScimin, and Olsen, Phys. Rev. **78**, 176 (1950).

[17] N. Sclar and E. Burstein, Phys. Rev. **98**, 1757 (1955).

[18] V. L. Bonch-Bruevich, Izv. Akad. Nauk SSSR, Ser. Fiz., **21**, 87 (1957); L. Sosnowskii, Izv. Akad. Nauk SSSR, Ser. Phys. **21**, 70 (1957).

THE MAGNETIC STRUCTURE OF FLUORIDES OF THE TRANSITION METALS

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The method of Ref. 1 is applied to the problem of the magnetic structure of the antiferromagnetic crystals MnF_2, CoF_2, FeF_2, and NiF_2. It is shown that crystals with such symmetry may possess a weak ferromagnetism.

IN Ref. 1 the problem of the weak ferromagnetism of certain antiferromagnetic substances was treated on the basis of Landau's theory of phase transitions of the second kind. In the present work the same method is used to study the magnetic structure of MnF_2, CoF_2, FeF_2, and NiF_2.