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RESONANCE INTERACTION OF AN IMPURITY-CENTER ELECTRON WITH LATTICE OSCILLATIONS

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It is shown that interaction of an impurity-center electron with optical oscillations in semiconductors can lead to the appearance of local optical oscillations. The condition for splitting off of a local optical frequency is that the energy of transition of an electron from the ground state to an excited state shall be close to the phonon energy. Optical absorption by an impurity center is studied in the case of such a resonance interaction; it is shown that the appearance of a local optical oscillation results in an additional line in the optical absorption spectrum.

IN certain semiconductors with a comparatively narrow forbidden band (InSb, Ge, etc.), the excitation energy of a number of impurity centers is close to the energy of optical phonons. Transition of an electron from the ground state to an excited state on an impurity atom is usually spoken of as a "local exciton." If the energy of this excitation is close to the energy of optical phonons, then the interaction between them as a result of proximity to resonance becomes very appreciable. In the presence of such resonance interaction, there can occur local excitations of the crystal, constituting a superposition of "exciton" and phonon excitations. The occurrence of a local exciton-phonon excitation implies, in particular, the appearance of discrete oscillation frequencies of the lattice, which split off from the continuous phonon spectrum, and—under certain conditions—the appearance of an additional absorption line in the optical spectrum of the crystal.

We make a number of assumptions to simplify the exposition. We shall suppose that the excited state (as well as the ground state) of the impurity center is nondegenerate. That case occurs, it seems, quite rarely. But consideration of the more complicated case of degenerate levels leads to no essentially new results and only complicates the picture.

Since we are interested in the case quite close to resonance, we can restrict ourselves to consideration of a single transition in an impurity center, and not take into account the other excited states and the continuous spectrum. It is well known that the presence of an impurity center in the crystal evokes the appearance of local lattice oscillations because of the change in interatomic interaction and of the difference in mass between the impurity and the basic material.[1] For simplicity, we shall here disregard this circumstance, although taking it into account does not entail great labor. We shall also assume that the acoustical oscillations of the crystal are separated from the optical by a large enough gap so that it is permissible to ignore the acoustical branches. This assumption is justified in the case in which the splitting-off of the emerging local exciton-phonon level from the lower edge of the optical-oscillation band of the lattice is much smaller than the width of the gap between the optical and acoustic branches.

The energy operator of the system is

$$H = H_e + H_{ph} + H_i, \tag{1}$$

where

$$H_e = \sum_\mu \hbar\omega_\mu a_\mu^+ a_\mu \tag{2}$$

is the energy operator of an electron on the impurity center, a_μ^+ and a_μ are the creation and annihilation operators of an electron in state $|\mu\rangle$ with energy $\hbar\omega_\mu$,

$$H_{ph} = {}^1/_2 \sum_{\mathbf{f},j} (p_{\mathbf{f}j} p_{-\mathbf{f}j} + \omega_{\mathbf{f}j}^2 q_{\mathbf{f}j} q_{-\mathbf{f}j}) \tag{3}$$

is the energy operator of the lattice oscillations, $p_{\mathbf{f}j}$ and $q_{\mathbf{f}j}$ are the normal momenta and coordinates of the lattice oscillations, $\mathbf{f}$ and $\omega_{\mathbf{f}j}$ are the wave vector and frequency of the phonons, j is the number of the oscillation branch,

$$H_i = \hbar \sum_{\mu\nu\mathbf{f}j} C_{\mu\nu\mathbf{f}j} a_\mu^+ a_\nu q_{\mathbf{f}j} \tag{4}$$

is the energy operator of the electron-phonon interaction,

$$C_{\mu\nu\mathbf{f}j} = (2\omega_{\mathbf{f}j}/\hbar^3 V)^{1/2} c_{\mathbf{f}j} \langle \mu | e^{i\mathbf{f}\mathbf{x}} | \nu \rangle, \tag{5}$$

$V^{-1/2} c_{\mathbf{f}j}$ is the usual matrix element of electron-phonon interaction, and V is the normalized volume.

We introduce the retarded Green functions

$$D(\mathbf{f}j;\ t;\ \mathbf{k}l) = i\theta(t)\langle [q_{\mathbf{f}j}(t),\ q_{-\mathbf{k}l}(0)]\rangle, \tag{6}$$

$$G(\mu\nu;\ t;\ L) = i\theta(t)\langle [(a_\mu^+ a_\nu)_t,\ L(0)]\rangle, \tag{7}$$

where L is an arbitrary operator that commutes with $q_{\mathbf{f}j}$ and $p_{\mathbf{f}j}$.

On the assumption that the dispersion of the optical phonons is small and that the transition frequency ω_{10} is close to the frequency band of the phonons, we may leave in the polarization operator[2] only terms with a resonance denominator (cf. above). This leads to the following equations for the Fourier components of the Green functions:

$$d_{\mathbf{f}j}^{-1}(\omega) D(\mathbf{f}j;\ \omega;\ \mathbf{k}l) - \frac{2\omega_{10}(n_0 - n_1)}{\omega_{10}^2 - \omega^2} C^*_{10\mathbf{f}j} \sum_{\mathbf{f}'j'} C_{10\mathbf{f}'j'} D(\mathbf{f}'j';\ \omega;\ \mathbf{k}l) = \delta_{\mathbf{f},\mathbf{k}} \delta_{j,l}, \tag{8}$$

$$\Big\{1 - \frac{n_0 - n_1}{\omega_{10} - \omega} \sum_{\mathbf{f}j} |C_{10\mathbf{f}j}|^2 d_{\mathbf{f}j}(\omega)\Big\} G(0\,1;\ \omega;\ L) - \frac{n_0 - n_1}{\omega_{10} - \omega} \sum_{\mathbf{f}j} |C_{10\mathbf{f}j}|^2 d_{\mathbf{f}j}(\omega) G(10;\ \omega;\ L) = \frac{\langle [a_0^+ a_1,\ L]\rangle}{\omega_{10} - \omega}, \tag{9}$$

$$\Big\{1 - \frac{n_0 - n_1}{\omega_{10} + \omega} \sum_{\mathbf{f}j} |C_{10\mathbf{f}j}|^2 d_{\mathbf{f}j}(\omega)\Big\} G(10;\ \omega,\ L) - \frac{n_0 - n_1}{\omega_{10} + \omega} \sum_{\mathbf{f}j} |C_{10\mathbf{f}j}|^2 d_{\mathbf{f}j}(\omega) G(0\,1;\ \omega;\ L) = -\frac{\langle [a_1^+ a_0,\ L]\rangle}{\omega_{10} + \omega}, \tag{10}$$

where

$$d_{\mathbf{f}j}(\omega) = \hbar(\omega_{\mathbf{f}j}^2 - \omega^2)^{-1},$$

n_0 and n_1 are the probabilities of occupancy of the ground state and of the excited state, and $\hbar\omega_{10} = \hbar(\omega_1 - \omega_0)$ is the excitation energy of the impurity center in the absence of interaction with phonons. In the temperature range in which the impurity is still not ionized and our results have meaning, $n_1 \ll n_0$.

Equation (8) has the exact solution

$$D(\mathbf{f}j;\ \omega;\ \mathbf{k}l) = d_{\mathbf{f}j}(\omega)\delta_{\mathbf{f},\mathbf{k}}\delta_{j,l} + d_{\mathbf{f}j}(\omega) T_{\mathbf{f}j;\mathbf{k}l}(\omega) d_{\mathbf{k}l}(\omega). \tag{11}$$

Here we have introduced the scattering amplitude, equal to

$$T_{\mathbf{f}j;\mathbf{k}l} = \frac{(n_0 - n_1) 2\omega_{10} C^*_{10\mathbf{f}j} C_{10\mathbf{k}l}}{F(\omega^2) - (\omega^2 - \omega_{10}^2)}, \tag{12}$$

where

$$F(\omega^2) = -(n_0 - n_1) 2\omega_{10} \sum_{\mathbf{f}j} |C_{10\mathbf{f}j}|^2 d_{\mathbf{f}j}(\omega) = \sum_j \int \frac{d^3 f}{(2\pi)^3} \frac{\lambda_{\mathbf{f}j}}{\omega^2 - \omega_{\mathbf{f}j}^2}, \tag{13}$$

$$\lambda_{\mathbf{f}j} = \frac{4\omega_{10}\omega_{\mathbf{f}j}(n_0 - n_1)}{\hbar^2} |c_{\mathbf{f}j}|^2 |\langle 0 | e^{i\mathbf{f}\mathbf{x}} | 1 \rangle|^2. \tag{14}$$

The cross section for optical absorption by an impurity center is

$$\sigma(\omega) = \frac{2\pi\omega}{i\hbar cn} \lim_{\eta \to +0} \sum_{\mu\nu} d_{\nu\mu} \{G(\nu\mu;\ \omega + i\eta;\ L) - G(\nu\mu;\ -\omega + i\eta;\ L)\} \tag{15}$$

with the operator

$$L = \sum_{\varkappa\lambda} d_{\varkappa\lambda} a_\varkappa^+ a_\lambda, \tag{16}$$

$d_{\nu\mu}$ is the matrix element of the dipole moment for transition of the impurity center, and n is the refractive index of the crystal.

We shall consider the case of a nonpolar crystal, in which the optical oscillations of the lattice, in the dipole approximation, are nonactive. The generalization to the case of a polar crystal presents no difficulty.

On solving the system of equations (9), taking account of (16), and substituting the solution in (15), we get

$$\sigma(\omega) = \frac{8\pi|\omega|\omega_{10} d_{01}^2 (n_0 - n_1)}{\hbar cn} \times \Big\{\eta + \pi \sum_j \int \frac{d^3 f}{(2\pi)^3} \lambda_{\mathbf{f}j} \delta(\omega^2 - \omega_{\mathbf{f}j}^2)\Big\} \cdot \Big\{\Big[\omega^2 - \omega_{10}^2 - \sum_j \mathrm{P} \int \frac{d^3 f}{(2\pi)^3} \frac{\lambda_{\mathbf{f}j}}{\omega^2 - \omega_{\mathbf{f}j}^2}\Big]^2 + \Big[\eta + \pi \sum_j \int \frac{d^3 f}{(2\pi)^3} \lambda_{\mathbf{f}j} \delta(\omega^2 - \omega_{\mathbf{f}j}^2)\Big]^2\Big\}^{-1}. \tag{17}$$

We investigate the expressions obtained for $T_{\mathbf{f}j;\mathbf{k}l}(\omega)$ and $\sigma(\omega)$. As is known, the poles of the scattering amplitude determine the frequencies of local oscillations of the lattice. The equation for the poles of $T_{\mathbf{f}j;\mathbf{k}l}(\omega)$ has the form

$$F(z) = z - \omega_{10}^2, \tag{18}$$

where $z = \omega^2$. We designate by Ω_1 and Ω_2 the lowest and highest frequencies in the spectrum of optical oscillations of the lattice in the absence of the impurity. On the real axis, the function F(z) decreases monotonically with increase of z for $z < \Omega_1^2$ and for $z > \Omega_2^2$. We assume that the frequencies Ω_1 and Ω_2 are attained in isolated points of the Brillouin zone. Near these extrema, the density of oscillations is proportional to $(\omega^2 - \Omega_1^2)^{1/2}$ and $(\Omega_2^2 - \omega^2)^{1/2}$. In an investigation of the behavior of F(z) near Ω_1^2, for example, it can be expressed in the form

$$F(z) = -\int_0^{\Omega_2^2-\Omega_1^2} \frac{dx\, x^{1/2}\rho_1(x)}{x+\Omega_1^2-z}, \tag{19}$$

where $\rho_1(x) > 0$ has no singularities and does not vanish at $x = 0$.

When $z \to \Omega_1^2 - 0$ (and when $z \to \Omega_2^2 + 0$), the function F(z) approaches a definite finite value, and near Ω_1^2 and Ω_2^2 it has the respective forms

$$F(z) \approx F(\Omega_1^2) + \pi\rho_1(0)(\Omega_1^2 - z)^{1/2}, \tag{20}$$

$$F(z) \approx F(\Omega_2^2) - \pi\rho_2(0)(z - \Omega_2^2)^{1/2}. \tag{21}$$

When $|z| \ll \Omega_1^2$,

$$F(z) \approx -\sum_j \int \frac{d^3f}{(2\pi)^3} \frac{\lambda_{fj}}{\omega_{fj}^2},$$

when $z \gg \Omega_2^2$,

$$F(z) \approx z^{-1} \sum_j \int \frac{d^3f}{(2\pi)^3} \lambda_{fj}\,.$$

We go on to the (graphical) investigation of equation (18). Three cases are possible:

1) $\omega_{10} > \Omega_2$, 2) $\omega_{10} < \Omega_1$, 3) $\Omega_1 < \omega_{10} < \Omega_2$.

Figure 1 corresponds to the first case, in which the transition frequency is higher than the band of optical oscillations. Equation (18) can have either one or two solutions outside this band. One root (we designate it by z_2) exists for arbitrary coupling constants and for arbitrary $\omega_{10} > \Omega_2$; then $z_2 > \omega_{10}^2$. The other root z_1 and, consequently, the second local oscillation appear only in the case in which

$$|F(\Omega_1^2)| > \omega_{10}^2 - \Omega_1^2. \tag{22}$$

If z_1 is near Ω_1, so that the expression (20) applies,

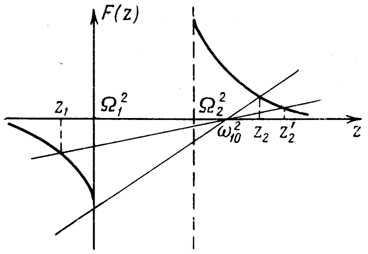

FIG. 1.

$$z_1 = \Omega_1^2 - \left\{\frac{|F(\Omega_1^2)| - (\omega_{10}^2 - \Omega_1^2)}{\pi\rho_1(0)}\right\}^2. \tag{23}$$

Investigation of the second case ($\omega_{10} < \Omega_1$) is carried out similarly.

When the transition frequency ω_{10} falls inside the band of optical phonons, i.e. $\Omega_1 < \omega_{10} < \Omega_2$, Eq. (18) may have no solution outside the lattice-oscillation band (cf. Fig. 2, straight line a), may have one solution (Fig. 2, straight line b), or may have two solutions (Fig. 2, straight line c). The conditions for realization of these possibilities are the following:

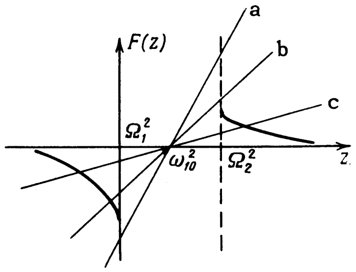

FIG. 2.

$$|F(\Omega_1^2)| + \Omega_1^2 < \omega_{10}^2 < \Omega_2^2 - F(\Omega_2^2); \tag{24a}$$

$$\omega_{10}^2 - \Omega_1^2 < |F(\Omega_1^2)|, \quad \Omega_2^2 - \omega_{10}^2 > F(\Omega_2^2), \tag{24b}$$

or

$$\Omega_2^2 - \omega_{10}^2 < F(\Omega_2^2), \quad \omega_{10}^2 - \Omega_1^2 > |F(\Omega_1^2)|;$$

$$\omega_{10}^2 - \Omega_1^2 < |F(\Omega_1^2)|, \quad \Omega_2^2 - \omega_{10}^2 < F(\Omega_2^2). \tag{24c}$$

It is evident that local oscillations with frequency $z_1^{1/2}$ in the first case (cf. (22)) and local oscillations in the third case (cf. (24b) and (24c)) occur only for sufficiently large values of the effective coupling constant λ_{fj}, which determines the values of $F(\Omega_1^2)$ and $F(\Omega_2^2)$. This coupling constant (cf. (14)) is proportional to the square of the matrix element of electron-phonon interaction.

We go on now to the investigation of optical absorption. We consider first absorption of radiation whose frequency lies outside the optical-phonon band. Since here

$$\sum_j \int \frac{d^3f}{(2\pi)^3} \lambda_{fj}\delta(\omega^2 - \omega_{fj}^2) = 0,$$

it follows from formula (17) that

$$\sigma(\omega) = \frac{8\pi^2 d_{01}^2 (n_0 - n_1)\omega_{10}|\omega|}{\hbar cn} \delta(\omega^2 - \omega_{10}^2 - F(\omega^2)). \tag{25}$$

If Eq. (18) has roots outside the band of optical oscillations, then

$$\sigma(\omega)=\frac{8\pi^2 d_{01}^2(n_0-n_1)\,\omega_{10}|\omega|}{\hbar cn}\times\left\{\frac{\delta(\omega^2-z_1)}{1+|(\partial F/\partial z)_{z_1}|}+\frac{\delta(\omega^2-z_2)}{1+|(\partial F/\partial z)_{z_2}|}\right\}. \qquad (26)$$

We examine the case in which Eq. (18) has only one root, near ω_{10}. Then

$$\sigma(\omega)=\frac{8\pi^2 d_{01}^2|\omega|\,\omega_{10}(n_0-n_1)}{\hbar cn}\,\frac{\delta(\omega^2-z_2)}{1+|(\partial F/\partial z)_{z_2}|}. \qquad (27)$$

This expression is close to the expression for the absorption cross section of an impurity in the absence of interaction with phonons. The difference consists in the fact that the resonance frequency is displaced, and the cross section is decreased by a factor $(1+|(\partial F/\partial z)_{z_2}|)^{-1}$.

With increase of the coupling constant, an additional root (z_1) appears, and in the absorption spectrum there appears a second resonance frequency, whose contribution to the cross section is[1)]

$$\frac{8\pi^2 d_{01}^2|\omega|\,\omega_{10}(n_0-n_1)}{\hbar cn}\,\frac{2(\Omega_1^2-z_1)^{1/2}}{\pi\rho_1(0)}\,\delta(\omega^2-z_1). \qquad (28)$$

From this it is clear that the expression for the absorption cross section at frequency $z_1^{1/2}$ cannot be obtained by means of simple perturbation theory.

When the frequency of the radiation lies within the frequency interval of optical oscillations ($\Omega_1 < \omega < \Omega_2$), it follows from (17) that

$$\sigma(\omega)=\frac{8\pi^2 d_{01}^2|\omega|\,\omega_{10}(n_0-n_1)}{\hbar cn}\times\frac{1}{\pi}\,\frac{\gamma(\omega^2)}{[\omega^2-\omega_{10}^2-\tilde{F}(\omega^2)]^2+\gamma^2(\omega^2)}, \qquad (29)$$

where

$$\gamma(\omega^2)\equiv\pi\sum_j\int\frac{d^3f}{(2\pi)^3}\lambda_{fj}\delta(\omega^2-\omega_{fj}^2),$$

$$\tilde{F}(\omega^2)\equiv\sum_j \mathrm{P}\int\frac{d^3f}{(2\pi)^3}\,\frac{\lambda_{fj}}{\omega^2-\omega_{fj}^2}. \qquad (30)$$

In this frequency interval, there is observed a smeared out absorption band, against whose background there are peaks located approximately at the frequencies ω_λ that are the roots of the equation

$$\omega_\lambda^2-\omega_{10}^2=\tilde{F}(\omega_\lambda^2). \qquad (31)$$

These peaks have a width of order

$$\frac{\gamma(\omega_\lambda^2)}{2\omega_\lambda}\left|1-\frac{\partial\tilde{F}(\omega_\lambda^2)}{\partial\omega_\lambda^2}\right|^{-1}. \qquad (32)$$

If we compare the expression for the scattering cross section of optical phonons on an impurity—which, as is known, is determined by the imaginary part of the scattering amplitude $T_{fj;kl}$—with the cross section (17) of absorption of radiation, it is easy to notice that both these quantities have the same denominator. Thus the resonances of optical absorption exactly correspond to the resonances of the scattering amplitude of phonons on an impurity. This circumstance is not accidental; it is connected with the fact that, as a result of the strong resonance interaction of the optical phonons with the electrons on an impurity, the crystal excitations that occur have a dipole moment and interact with light. The absorption of light is then proportional to the density of oscillations of the crystal, and this quantity has a maximum in the region of resonances of the scattering amplitude; this leads also to a "splash" in the optical absorption at frequencies near ω_λ.

If the transition frequency falls inside the frequency band of the phonons, then the resonance peak, for sufficiently small coupling constant, is simply the peak of impurity absorption, smeared out on account of interaction with the phonons. It is accompanied by a background, which, sufficiently far from the peak ($|\omega_{10}-\omega| \gg (\gamma(\omega_{10}^2)/2\omega_{10})$), is described by the expression

$$\sigma(\omega)=\frac{8\pi^2 d_{01}^2|\omega|\,\omega_{10}(n_0-n_1)}{\hbar cn}\,\frac{\gamma(\omega^2)}{(\omega^2-\omega_{10}^2)^2}. \qquad (33)$$

In closing, we remark that, because of the assumption that the system is close to resonance, the results obtained are valid, strictly speaking, only when the split-off frequencies of local oscillation lie sufficiently close to the frequency band of the optical phonons, i.e., when the dimensionless coupling constant is sufficiently small.

[1)] We assume that $\omega_{10} > \Omega_2$.

[1] I. M. Lifshitz, Nuovo Cimento Suppl. 3, 716 (1956).

[2] V. L. Bonch-Bruevich and S. V. Tyablikov, Metod funktsiĭ Grina v statisticheskoĭ mekhanike (The Green Function Method in Statistical Mechanics), Fizmatgiz, 1961; translation, Interscience Publishers (John Wiley & Sons, Inc.), 1962. A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike (Methods of Quantum Field Theory in Statistical Physics), Fizmatgiz, 1962; translation, Prentice-Hall, 1963.

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