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Optical spectra of phonons bound to impurity centers

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A method proposed earlier for determining the energy spectrum of phonons bound to an electron impurity center is generalized to the calculation of the intensities of the lattice absorption and of the Raman scattering of light by bound phonons. Simple closed formulas are obtained for the intensities of both these processes. The behavior of the wavefunction of a bound phonon is also investigated. In conclusion, equations determining the vibrational spectrum of Jahn–Teller centers with an arbitrary structure of the electron spectrum are presented.

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1. INTRODUCTION

Under certain conditions, states which can be regarded as bound states of a phonon with a polaron, magnetopolaron, exciton or impurity electron arise in the energy spectrum of the electron-phonon system in semiconductors and ionic crystals. The spectrum of such states depends on the strength of the electron-phonon interaction and on a number of other parameters. A review of the experimental and theoretical work is contained in[1,2].

In the first theoretical papers[3–5] on the theory of bound states of phonons with electron centers (phonon-impurity complexes), the spectrum of the electron subsystem was described in a two-level approximation. This makes it possible to investigate the principal qualitative relationships sufficiently fully, but in the majority of cases—in particular, as applied to hydrogen-like centers of large radius—it cannot give a quantitative description.

It was shown previously by the author[6,7] that, when the dispersion of the phonons can be neglected and the electron-phonon coupling is weak in a certain sense, for an arbitrary spectrum of the electron subsystem the determination of the bound states of the phonons reduces to solving the equation1)

$$\lambda\{(\lambda+H-\varepsilon_0)^2-\omega_0^2\}\varphi=2(\lambda+H-\varepsilon_0)A\varphi, \tag{1}$$

where $\lambda=\omega_0-\omega$ are the eigenvalues defining the binding energy of the phonons and φ is related to the phonon wavefunction (see below). Here ω_0 is the phonon frequency in the ideal crystal, H is the Hamiltonian of the electron at the impurity center, and A is an integral operator with the kernel

$$A(\mathbf{r},\mathbf{r}')=\psi_0(\mathbf{r})V(\mathbf{r}-\mathbf{r}')\psi_0(\mathbf{r}'). \tag{2}$$

The operator

$$V(\mathbf{r})=\sum_{\mathbf{q}}\gamma_{\mathbf{q}}^2e^{i\mathbf{q}\mathbf{r}} \tag{3}$$

is entirely determined by the coefficients $\gamma_{\mathbf{q}}$ in the electron-phonon interaction Hamiltonian; ψ_0 and ε_0 are the wavefunction and energy corresponding to the lowest level (which is assumed to be nondegenerate) of the Hamiltonian H.

In[9] it was shown that the one-particle electron Green function can be expressed in terms of the functions φ,

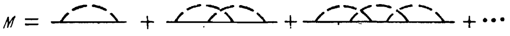

FIG. 1.

and in this way the intensities of the phonon satellites in the spectrum of the Frenkel impurity excitons were calculated. However, inasmuch as an expression for the two-particle Green function was not found, it was not possible to determine the intensities in the photon-emission spectrum of phonons bound to electron impurity centers.[2)]

In the present paper the intensities of optical transitions corresponding to the formation of bound states are expressed in terms of the phonon Green function, and this function is calculated. In the problem under consideration this way turns out to be the simplest. As a result, both the infrared-absorption probability and the probability of Raman scattering with formation of bound states of phonons can be expressed directly in terms of matrix elements containing the functions φ. Thus, Eq. (1) enables us to find not only the energy spectrum of the system but also the intensity distribution in the optical spectrum, i.e., it contains within itself the complete solution of the problem under consideration.

2. THE PHONON GREEN FUNCTION

Since bound states of a phonon with an electron impurity center are excited states of the interacting electron-phonon system, they correspond to poles of both the electron (G) and phonon (D) Green functions. In most cases the G-function has been analyzed. In the threshold approximation[11] for weak electron-phonon coupling the dominant contribution to the mass operator M is given by the sequence of diagrams of Fig. 1[1,2]; the averaging in G is performed over the no-electron state. Near the frequency $\varepsilon_0+\omega_0$ all the one-phonon sections are dangerous in the diagrams of Fig. 1; they correspond to a transition of the electron to the unoccupied ground state with emission of a phonon.

On the other hand, in the calculation of D the averaging should be performed over the state in which the ground level of the impurity center is occupied by an electron. With this choice of the vacuum, the singularity in M near $\varepsilon_0+\omega_0$ disappears (since the ground state is occupied!), and therefore, in the calculation of the phonon polarization operator P, the free G-functions can be taken in the electron loop.[3)] Thus, the problem consists in performing the summation over the whole electron spectrum of the impurity center; as shown below, this reduces to solving Eq. (1).

The diagrammatic equation for $D(\omega|\mathbf{qq}')$ is presented in Fig. 2. After integration over the frequency in the electron loop a nonzero contribution arises only if one of the quantum numbers (s or t) of the electron states is equal to zero (the ground state); in this case the other one differs from zero. Taking this circumstance into account, we can write the equation for D in the form

$$D(\lambda|\mathbf{qq}')=-\frac{\delta_{\mathbf{qq}'}}{\lambda}+\frac{1}{\lambda}\sum_{s\neq0}\sum_{\mathbf{q}_1}\gamma_{s0}(-\mathbf{q})\gamma_{0s}(\mathbf{q}_1)B_s(\lambda)D(\lambda|\mathbf{q}_1\mathbf{q}'). \tag{4}$$

Here we have introduced the phonon binding energy $\lambda=\omega_0-\omega$; in this case, $D_0\approx-1/\lambda$. The matrix elements are

$$\gamma_{st}(\mathbf{q})=(s|\gamma_\mathbf{q}(\mathbf{r})|t)=\gamma_\mathbf{q}(s|e^{i\mathbf{qr}}|t);$$

it is assumed that the electron functions ψ_s are chosen to be real. The operator $B(\lambda)$ is defined by the expression

$$B_s(\lambda)=(\lambda+\varepsilon_s-\varepsilon_0-\omega_0)^{-1}-(\lambda-\varepsilon_s+\varepsilon_0-\omega_0)^{-1}. \tag{5}$$

We define the vectors $\gamma(\mathbf{q})$ and $D(\lambda\mathbf{q})$ with components $\gamma_{s0}(\mathbf{q})$ and

$$D_s(\lambda\mathbf{q})=\sum_{\mathbf{q}_1}\gamma_{0s}(\mathbf{q}_1)D(\lambda|\mathbf{q}_1\mathbf{q}) \tag{6}$$

for $s\neq0$; we put their components with $s=0$ equal to zero. Then, premultiplying (4) by $\gamma_{r0}(\mathbf{q})$ and summing over $\mathbf{q}$, we obtain

$$(\lambda-AB(\lambda))D(\lambda\mathbf{q})=-\gamma(\mathbf{q}), \tag{7}$$

where the matrix A is defined by the formula

$$A_{st}=\sum_{\mathbf{q}}\gamma_{s0}(\mathbf{q})\gamma_{0t}(-\mathbf{q}),\ s,t\neq0, \tag{8}$$

and corresponds exactly to that part of the operator A (formula (2)) which acts in the subspace of functions φ orthogonal to ψ_0.

By defining the vectors φ_i as solutions of the equation

$$B(\lambda)A\varphi_i(\lambda)=\lambda_i(\lambda)\varphi_i(\lambda),\quad(\varphi_i,A\varphi_i)=1, \tag{9}$$

that depend parametrically on λ, and using the representation[4)]

$$(\lambda-AB)^{-1}=\sum_i\frac{1}{\lambda-\lambda_i(\lambda)}A\varphi_i\cdot\varphi_i^+, \tag{10}$$

where $A\varphi_i\cdot\varphi_i^+$ denotes the dyadic product of the vectors $A\varphi_i$ and φ_i^+, we obtain

$$D(\lambda\mathbf{q})=-\sum_i\frac{1}{\lambda-\lambda_i(\lambda)}(\varphi_i,\gamma(\mathbf{q}))A\varphi_i. \tag{11}$$

Substituting (11) into (4), we obtain finally

$$D(\lambda|\mathbf{qq}')=-\frac{\delta_{\mathbf{qq}'}}{\lambda}-\frac{1}{\lambda}\sum_i\frac{\lambda_i}{\lambda-\lambda_i}(\gamma(\mathbf{q}),\varphi_i)(\varphi_i,\gamma(\mathbf{q}'))\,. \tag{12}$$

Equation (9), taken together with the condition $\lambda=\lambda_i(\lambda)$ determining the pole of D, is completely equivalent to Eq. (1).

3. THE PHONON WAVEFUNCTIONS

The residues of the function $D(\lambda|qq)$, taken at its poles, determine the phonon wavefunction:

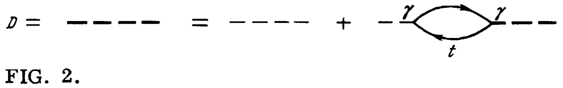

FIG. 2.

$$\Phi_i(\mathbf{q})=(1-d\lambda_i/d\lambda)^{-1/2}(\gamma(\mathbf{q}),\ \varphi_i)=(1-d\lambda_i/d\lambda)^{-1/2}\gamma_{\mathbf{q}}(\psi_0|e^{-i\mathbf{q}\mathbf{r}}|\varphi_i). \qquad (13)$$

Its physical meaning is simple enough. In the wavefunction of the electron-phonon system there are no-phonon, one- and two-phonon terms (cf. Fig. 1): $\Psi=\Psi_0+\Psi_1+\Psi_2$. The function Ψ_0 is directly determined from formula (19) of the paper.[9] The one-phonon function $\Psi_1=\psi_0(r)\Phi_i(\mathbf{q})$; the electron part of Ψ_1 is written here in the coordinate representation and the phonon part in the momentum representation. In (13) the term $d\lambda_i/d\lambda$ is comparable with unity only in the presence of a resonance, when one of the $|\varepsilon_s-\varepsilon_0|\approx\omega_0$,[9] and hybrid states arise.[1,2]

To go over to the coordinate representation we introduce the Fourier transform of the function $\gamma_{\mathbf{q}}$ separately for "polarization" ($\gamma_{\mathbf{q}}=\gamma/qV^{1/2}$) and "no-polarization" ($\gamma_{\mathbf{q}}=\gamma/V^{1/2}$) phonons:

$$\gamma(\mathbf{r})=\begin{cases}\gamma/2\pi r^2 - & \text{polarization interaction}\\ \gamma\delta(\mathbf{r}) - & \text{no-polarization interaction}\end{cases} \qquad (14)$$

Then,

$$\Phi_i(\mathbf{r})=\left(1-\frac{d\lambda_i}{d\lambda}\right)^{-1/2}\int d_3\mathbf{r}'\gamma(\mathbf{r}-\mathbf{r}')\psi_0(\mathbf{r}')\varphi_i(\mathbf{r}'). \qquad (15)$$

It can be seen that for a no-polarization interaction the relation of Φ_i to φ_i is especially simple.

As follows from (13), the analytic properties of Φ_i are entirely determined by the analytic behavior of $\varphi_i(\mathbf{r})$, to the analysis of which we now turn. We shall assume that the operators H and A have spherical symmetry; for application to the polarization interaction, restriction to cubic crystals is completely necessary, since in crystals with lower symmetry $\omega_0(\mathbf{q})$ depends nonanalytically on q at small q, i.e., there is inevitably dispersion of the phonons. In these conditions the functions φ can be classified by the angular momentum l ($\varphi=\rho Y_l$), and the equation for the radial parts ρ follows directly from (1):

$$\lambda\{(\lambda+H_l-\varepsilon_0)^2-\omega_0^2\}\rho=2(\lambda+H_l-\varepsilon_0)A_l\rho. \qquad (16)$$

As usual, H_l includes the centrifugal energy. The operator A_l is easily obtained from (2). Strictly speaking, it is necessary to take the part of A which acts in the subspace $(\varphi,\psi_0)=0$; but since the solutions of Eq. (1) satisfy this condition automatically,5) we can use the full operator A.

For the no-polarization interaction, putting $V(\mathbf{r})=v\delta(\mathbf{r})$, changing to atomic units and using the equations for ψ_0, we obtain the fourth-order differential equation

$$\lambda\left\{\left(-\frac{1}{2}\Delta_r+\frac{l(l+1)}{2r^2}-\frac{1}{r}+\frac{1}{2}\right)^2-\omega_0^2\right\}\rho$$
$$=2v\left\{\psi_0^2\left(-\frac{1}{2}\Delta_r+\frac{l(l+1)}{2r^2}+\frac{1}{r}-\frac{1}{2}\right)\rho-\left(\frac{d\psi_0}{dr}\right)^2\rho-\frac{d\psi_0^2}{dr}\frac{d\rho}{dr}\right\}. \qquad (17)$$

The characteristic equation determining the behavior of the solutions near the singular point $r=0$ is obtained entirely from the kinetic energy in the left-hand side of (17). Two of its roots ($\zeta=-l\pm1$) should be discarded, since they lead to divergences. The other roots $\zeta_1=l$ and $\zeta_2=l+2$ have physical meaning. Since $\zeta_2-\zeta_1=2$ is an integer, we encounter the situation, well-known from the theory of differential equations, in which the solution near the singular point has the form

$$\rho=r^l w_1(r)+r^{l+2}w_2(r)\ln r, \qquad (18)$$

where w_1 and w_2 are series in positive powers of r.

The situation with the polarization interaction is more complicated, since then Eq. (16) is an integro-differential equation. However, a simple investigation, which we shall not reproduce here, shows that in this case substitution of ρ from (18) into the right-hand side of (16) leads to an expression of the type $r^{l+1}\overline{w}_1(r)+r^{l+2}\overline{w}_2(r)\ln r$. Since the logarithmic terms are reproduced, there are no reasons to doubt that the solution will have the form (18), as before; however, the procedure for finding the series w_1 and w_2 becomes more complicated.

The right-hand side in (17) makes an exponentially small contribution to the asymptotic behavior at large r. As a result, $\rho\propto e^{-\beta r}$ with $\beta=(1\pm2\omega_0)^{1/2}$, i.e., there are two decay constants. Incidentally, it follows from this that for $\omega_0>\frac{1}{2}$ (in ordinary units, $\omega_0>|\varepsilon_0|$) stationary bound states do not exist. For a polarization interaction an inhomogeneous term proportional to $\psi_0(r)$ is contained in the asymptotic expansion of the right-hand side of (16) for $l\neq0$, and, therefore, yet a third decay constant $\beta=1$ appears.

According to (14) and (15), for a no-polarization interaction, $\Phi_i(\mathbf{r})\propto\psi_0(r)\varphi_i(\mathbf{r})$. For a polarization interaction, (15) makes it possible to find the asymptotic behavior of R ($\Phi=RY_l$). At large r we have $R\propto r^{-(l+2)}$ for states with angular momentum l. The s-states are an exception: here $R\propto r^{-4}$ because $(\varphi,\psi_0)=0$. At small r we obtain $R\propto r^{l+1}(1+cr^2\ln r)$; for s-states, however, the nonlogarithmic terms have a finite limit as $r\to0$.

We note also the behavior of $\Phi(\mathrm{q})$ at small q, which is important for the optical properties. It is obvious that $R(q)\propto q^l\gamma_{\mathbf{q}}$; for s-states, $R(q)\propto q^2\gamma_{\mathbf{q}}$.

In conclusion, it is instructive to write out the formula for φ and Φ as applied to a two-level scheme, when the presence of only one excited term (possibly degenerate) is taken into account. In this case, in B it is natural to keep only the resonance terms: $B_s(\lambda)\approx(\lambda+\varepsilon_s-\varepsilon_0-\omega_0)^{-1}$; the matrix A degenerates into a diagonal matrix acting in the subspace of the single excited term. Then $D(\lambda\mathrm{q})$ is determined directly from (7) and substitution of it into (4) leads immediately to

$$\Phi_s(q)=\gamma_{s0}(-q)/(\lambda^2+A_{ss})^{1/2},\quad \varphi_s=\psi_s A_{ss}^{-1/2},$$

where λ is determined from $A_{ss}B_s(\lambda)=1$. The index s labels the individual states belonging to the degenerate excited term. It was just such phonon wavefunctions that were used by Dean *et al.*[5] in a calculation of the Raman-scattering intensity.6)

4. OPTICAL ABSORPTION

We shall calculate now the intensity of the infrared absorption corresponding to the excitation of bound states

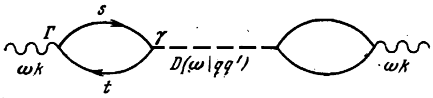

FIG. 3.

of phonons. This absorption is entirely described by the contribution (to the photon polarization operator Π) represented in Fig. 3. The photon and phonon lines are connected only through an impurity-electron loop. In fact, the no-polarization phonons do not interact directly with light at all. As regards the polarization phonons, it is only the transverse phonons that interact with light and almost exclusively the longitudinal phonons that interact with the electron; the contribution from the deformation interaction of the electron with the transverse-polarization phonons can usually be neglected. In this loop, for the reason already indicated in Sec. 2, we can use the free Green functions.

After integration over the frequencies the expression for $\mathrm{Im}\,\Pi_{\mathrm{imp}}$ is written in the form

$$\mathrm{Im}\,\Pi_{imp}(\omega)=\pi nV\sum_i\Big|\sum_{\mathbf{q}}\sum_{s\neq0}\Big\{\frac{\Gamma_{s0}(-\mathbf{k})\gamma_{0s}(\mathbf{q})}{\omega-(\varepsilon_s-\varepsilon_0)}-\frac{\Gamma_{0s}(-\mathbf{k})\gamma_{s0}(\mathbf{q})}{\omega+(\varepsilon_s-\varepsilon_0)}\Big\}\Phi_i(\mathbf{q})\Big|^2\delta(\omega-\omega_i). \tag{19}$$

Here n is the concentration of impurities and Γ is the vertex corresponding to the electron-photon interaction. For light polarized along the x axis, in the electric-dipole approximation $\Gamma=ep_x/mcV^{1/2}$.

Using the relation $(p_x)_{st}=im\omega_{st}x_{st}$ and the symmetry of γ_{st} and x_{st} with respect to interchange of the indices s and t, it is easy to transform the expression in curly brackets in (19) in such a way that the factor B_s is separated out. The summation over q in (19) can also be performed if we use (13) and (8). After this,

$$\mathrm{Im}\,\Pi_{imp}(\omega)=\pi n\left(\frac{e\omega}{c}\right)^2\sum_i\left(1-\frac{d\lambda_i}{d\lambda}\right)^{-1}\times\Big|\sum_{s\neq0}x_{s0}(BA\varphi_i)_s\Big|^2\delta(\omega-\omega_i). \tag{20}$$

Using also (9), it is easy to simplify the matrix element in (20). As a result, for the imaginary part of the dielectric permittivity we obtain

$$\varkappa''_{imp}(\omega)=\frac{4\pi c^2}{\omega^2}n\,\mathrm{Im}\,\Pi(\omega)=4\pi^2e^2n\sum_i\frac{\lambda_i^2}{1-d\lambda_i/d\lambda}|(\psi_0|x|\varphi_i)|^2\delta(\omega-\omega_i). \tag{21}$$

Formula (21) contains an important and interesting result: the intensity of the impurity absorption is completely determined in terms of the eigenfunctions φ_i and eigenvalues λ_i of the fundamental equation (9). Extremely unusual is the matrix element $(\psi_0|x|\varphi_i)$, which contains wavefunctions that are eigenfunctions of two completely different equations.[7)]

It is interesting to compare the impurity-absorption intensity described by the $\varkappa''(\omega)$ calculated here with the lattice-absorption intensity in the perfect crystal. The one-phonon absorption is nonzero only in polar crystals, and the corresponding contribution to $\varkappa''$ is equal to

$$\varkappa''_{intr}(\omega)={}^1/_2\pi\omega_0(\varkappa_0-\varkappa_\infty)\delta(\omega-\omega_0); \tag{22}$$

$\varkappa_0$ and $\varkappa_\infty$ are the low- and high-frequency values of $\varkappa$. It is natural to compare the impurity absorption calculated per impurity center with the lattice absorption calculated per unit cell:

$$K=\frac{\varkappa''_{imp}/n}{\varkappa''_{intr}d^3}\sim\frac{e^2\lambda_i^2|(\psi_0|x|\varphi_i)|^2}{\omega_0(\varkappa_0-\varkappa_\infty)}; \tag{23}$$

here d^3 is the volume of the unit cell. According to[7], $\lambda_i\sim\alpha\omega_0(\omega_0/R)^{1/2}$, where α is the usual electron-phonon coupling constant and R is the ionization potential of the impurity center. The functions ψ_0 and φ_i are concentrated in regions of size $\sim a^3$ (a is the Bohr radius of the impurity center) and, according to the normalization conditions, have order of magnitude $\psi_0^2\sim a^{-3}$, $\varphi_i^2\sim(R\lambda_i a^3)^{-1}$; therefore, $(\psi_0|x|\varphi_i)\sim a(R\lambda_i)^{1/2}$. If we also take $\varkappa_0\sim\varkappa_\infty$, we finally obtain $K\sim(a/d)^3$; for ordinary centers of large radius, $K\gg1$. The reason for the high intensity of the impurity absorption is exactly the same as that for the well-known giant oscillator strengths for impurity excitons—the appearance of coherent oscillations in a large volume $\sim a^3\gg d^3$; the distinctive feature of the situation is just that the magnitude of this volume is directly imposed on the phonon by the size of the region of localization of the impurity electron.

5. RAMAN SCATTERING

In this case there exist a large number of vertices connecting a photon with a phonon. Figure 4a shows the vertex $\mathcal{T}_i$ at which the coupling is effected via an impurity electron; in it the momentum, naturally, is not conserved. In addition there exists the vertex $\mathcal{T}_0$ (Fig. 4b) responsible for the Raman scattering in an ideal lattice. It incorporates both a purely ionic contribution and a contribution from the valence electrons, i.e., from diagrams of the type of Fig. 4a, in which, however, r, s, and t correspond to different states of the "intrinsic" electrons. It is known (cf., e.g.,[14] Sec. 20) that if the frequency of the scattered light is large ($\omega\gg\omega_0$) the electron contribution to $\mathcal{T}_0$ exceeds the purely lattice contribution by a factor $\sim(\omega/\omega_0)^{1/2}$.

For us, however, the relative magnitude of the vertices $\mathcal{T}_i$ and $\mathcal{T}_0$ is the most important thing. Inasmuch as a summation over the entire Brillouin zone appears in $\mathcal{T}_0$, the estimate is extremely crude and enables us only to extract the basic parameters that arise here. We give only the final result for the ratio of the effective values of the vertices in conditions of nonresonant scattering:

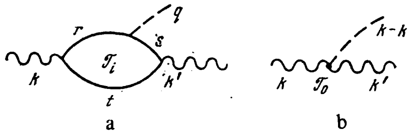

FIG. 4.

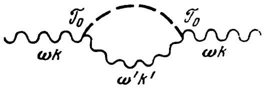

FIG. 5.

$$\left(\frac{\mathcal{T}_i}{\mathcal{T}_0}\right)_{\text{eff}} \sim \frac{d}{a}\left(\frac{R}{R_0}\right)^2\left(\frac{E_g}{\omega}\right)^2; \tag{24}$$

here $R_0 \sim 10$ eV and E_g is the effective value of the width of the gap (usually, $E_g \sim 1$ eV). For centers of large radius the first two factors in (24) are small and the third factor cannot compensate this. Therefore, the vertex $\mathcal{T}_0$ should make the dominant contribution. An analysis of the experimental data for GaP led Dean *et al.*[5] to precisely this conclusion.

If we confine ourselves to the vertex $\mathcal{T}_0$, the Raman scattering is described by the contribution to Π from the diagram of Fig. 5; from this it can be seen immediately that the intensity will be determined by the value of $\Phi_i(\mathbf{k}-\mathbf{k}')$:

$$\operatorname{Im}\Pi_{imp} = \pi n \Gamma \sum_i \sum_{\mathbf{k}'} \int \frac{d\omega'}{2\pi} |\mathcal{T}_0(\mathbf{k}\mathbf{e}|\mathbf{k}'\mathbf{e}')|^2 |\Phi_i(\mathbf{k}-\mathbf{k}')|^2 \delta(\omega-\omega'-\omega_i); \tag{25}$$

$\mathbf{e}$ and $\mathbf{e}'$ are the polarization vectors of the incident and scattered light. The contribution to the right-hand side from given values of ω, $\mathbf{k}'$ determines the intensity of the scattering into the corresponding states. Taking, as above, $ka \ll 1$, we obtain

$$|\Phi_i(\mathbf{k}-\mathbf{k}')|^2 \approx (1-d\lambda_i/d\lambda)^{-1}\gamma_{\mathbf{k}-\mathbf{k}'}^2 |(\psi_0|(\mathbf{k}-\mathbf{k}'.\mathbf{r})|\varphi_i)|^2. \tag{26}$$

i.e., the Raman scattering is determined by the same matrix element of the coordinate as the absorption.

It is convenient to exclude $\mathcal{T}_0$ by comparing the impurity scattering when a bound state with energy ω_i is formed (calculated per impurity center) with the lattice scattering in the same direction and with the same polarization (calculated per unit cell). The ratio of the effective cross-sections is

$$\frac{(\sigma_{imp})_i}{\sigma_{intr}} = \Gamma \frac{|(\mathbf{k}-\mathbf{k}')\gamma_{\mathbf{k}-\mathbf{k}'}|^2}{d^3(1-d\lambda_i/d\lambda)} \sum_{i'} |(\psi_0|x|\varphi_{i'})|^2, \tag{27}$$

where the summation over i' encompasses the states belonging to the level ω_i.

It can be seen from (27) that the impurity-scattering intensity is large only for polarization phonons, for which $\gamma_{\mathbf{q}} \propto q^{-1}$; for these,

$$\frac{(\sigma_{imp})_i}{\sigma_{intr}} = \left(1-\frac{d\lambda_i}{d\lambda}\right)^{-1} \frac{4\pi\alpha\omega_0^2}{d^3(2m\omega_0)^{3/2}} \sum_{i'} |(\psi_0|x|\varphi_{i'})|^2. \tag{28}$$

An estimate of the matrix element, analogous to the estimate used in Sec. 4, leads immediately to $(\sigma_{imp})_i/\sigma_{intr} \sim (a/d)^3$, i.e., the cross-section for impurity scattering, like that for impurity absorption, turns out to be huge. From (28) it follows also that p-type states should be dominant in Raman scattering. All these conclusions agree with the results obtained earlier from the two-level model of[5,13] and from analysis of the experimental data.[5] It is interesting to note that, according to[13], in front of the factor $(a/d)^3 \gg 1$ in the impurity-scattering cross-section there is also a large numerical coefficient ~400, which further increases the impurity-scattering intensity.

6. CONCLUDING REMARKS

The principal achievement of the method developed earlier[6,7,9] and above in the present article is the possibility of taking the whole spectrum of the excited electron states consistently into account in the determination of the frequencies of the dielectric modes and the intensities of the optical transitions associated with them. In this respect the method developed is more systematic and more general than the usual procedure, in which a restricted number of electron levels (usually two or three) is taken into account. The price which must be paid for this generality consists in the introduction of certain restrictions at other points. To conclude we shall discuss here to what extent these restrictions are essential and what possibilities exist for generalizing the results obtained.

Above, purely for the sake of simplicity, a single branch of the phonon spectrum was considered. If there are several degenerate branches (as in nonpolar cubic crystals near the point $\mathbf{k}=0$), the matter reduces to replacing $\gamma_{\mathbf{q}} \to \gamma_{\mathbf{q}\mu}$ and $\gamma(\mathbf{q}) \to \gamma(\mathbf{q}\mu)$; μ labels the branches. Then, in the calculation of A_{st} by formula (8), the summation is performed over $\mathbf{q}$ and μ, and for φ_i and the transition intensities we obtain exactly the same formulas (9), (21), and (25) as above. The individual components $\Phi_i(\mathbf{q}\mu)$ of the phonon wavefunction are obtained (13) by replacing $\gamma(\mathbf{q}) \to \gamma(\mathbf{q}\mu)$.

The assumption of weak electron-phonon coupling cannot be dropped. However, as was shown in[9], it can be substantially weakened. Essentially, it is required that $\alpha \ll (R/\omega_0)^{1/2}$; here the Franck-Condon energy is small compared with R (but can be of arbitrary size relative to ω_0).

The assumption of the absence of phonon dispersion is also essential for the whole scheme of the calculations. However, for centers of large radius it is not physically restrictive. Moreover, even in the framework of a two-level scheme, the phonon dispersion can be taken into account realistically only in the framework of numerical calculations.

From a physical point of view, the most severe restriction is associated with the assumption that the ground state of the center is nondegenerate. Jahn-Teller systems (including, e.g., acceptor centers in compounds of the type $A_{\text{III}}B_{\text{V}}$) have thereby been excluded from consideration. In these systems bound states of phonons already arise in the lowest approximation of the theory, when all the excited electron states are excluded from consideration.[15] At the same time, it is easy to see that for $R \sim \omega_0$ all electron states (both the excited states and the states belonging to the ground level) make a comparable contribution to the binding energy of the phonon. Therefore, for shallow impurity centers with $R \sim \omega_0$, the theory of the Jahn-Teller effect should necessarily take the contribution of all the excited states consistently into account. Without aiming at a detailed analysis of this problem, we nevertheless give in the Appendix equations which can be regarded as the generalization of (1) to the case of Jahn-Teller systems. Although the system obtained is more complicated than Eq. (1), its investigation and numerical solution are possible.

I take the opportunity to thank I. B. Levinson and V. I. Matsaev for valuable discussions and A. B. Zimin for collaboration in the initial stage of this work.

APPENDIX

Jahn-Teller systems

Here it is most convenient to write the Schrödinger equation directly for the electron-phonon wavefunction Ψ. Unlike in Sec. 3, only in the one-phonon part of Ψ is it necessary to take into account the contribution of all the electron functions $\psi_\sigma(\mathbf{r})$ belonging to the ground term:

$$\Psi_1 = \sum_{\mathbf{q}\mu\sigma} g_\sigma(\mathbf{q}\mu)\,\psi_\sigma b_{\mathbf{q}\mu}^+|0). \tag{A1}$$

Equating to zero the projections of the equation obtained on to the zero-, one-, and two-phonon subspaces, it is easy to obtain a system of equations for $g_\sigma(\mathbf{q}\mu)$. This system is conveniently rewritten by introducing the vectors $h_{\sigma\sigma'}$, with components

$$h_{\sigma\sigma',s} = \sum_{\mathbf{q}\mu} \gamma_{s\sigma}(\mathbf{q}\mu)\,g_{\sigma'}(\mathbf{q}\mu) \tag{A2}$$

and the operator A as

$$A^{\sigma\tau}_{st} = \sum_{\mathbf{q}\mu} \gamma_{s\sigma}(\mathbf{q}\mu)\,\gamma_{\tau t}(-\mathbf{q}\mu) \tag{A3}$$

or

$$A_{\sigma\tau}(\mathbf{r},\mathbf{r}') = \psi_\sigma(\mathbf{r})\,V(\mathbf{r}-\mathbf{r}')\,\psi_\tau(\mathbf{r}'), \quad V(\mathbf{r}) = \sum_{q\mu} \gamma_{q\mu}^2 e^{i\mathbf{q}\mathbf{r}}. \tag{A4}$$

Then

$$-\lambda h_{\sigma\sigma'} = \sum_{\tau} \{A_{\sigma\sigma'}(\varepsilon-H)^{-1}h_{\tau\tau} + A_{\sigma\tau}(\varepsilon-H-2\omega_0)^{-1}h_{\sigma'\tau}\}, \tag{A5}$$

where $\varepsilon = \varepsilon_0 + \omega_0 - \lambda$ is the energy of the system. At this stage it is easy to trace where the principal difference from the case of a nondegenerate ground level arises. In the latter case A does not carry a matrix index, and, as a result, the two Green functions in the right-hand side of (A5) are collected into the operator B (cf. (5)); therefore, introducing the function $\varphi = Bh$, we can reduce (A5) to (9). In the general case, on the other hand, the two Green functions appear separately, and therefore we must introduce the auxiliary function somewhat differently:

$$\chi_{\sigma\tau} = (\varepsilon-H)^{-1}(\varepsilon-H-2\omega_0)^{-1}h_{\sigma\tau}. \tag{A6}$$

In this case (A5) is transformed to the form

$$\lambda[(\lambda+H-\varepsilon_0)^2-\omega_0^2]\chi_{\sigma\sigma'} = \sum_{\tau} \{A_{\sigma\sigma'}(\lambda+H-\varepsilon_0-\omega_0)\chi_{\tau\tau} + A_{\sigma\tau}(\lambda+H-\varepsilon_0+\omega_0)\chi_{\sigma'\tau}\}. \tag{A7}$$

This system is the direct generalization of (1) to the case of Jahn-Teller systems. The number of independent equations in it can be reduced if we use the symmetry conditions.

[1)] A related equation was obtained in[8] for polaron-phonon complexes in conditions of strong coupling.

[2)] The related problem of the intensities in the spectrum for the formation of (magnetopolaron + phonon)-complexes has been solved with the aid of the two-particle electron-phonon function in a paper by Kaplan and Levinson.[10]

[3)] Ngai *et al.*[12] have already drawn attention to this fact.

[4)] Cf.,[9] Sec. 2. In cases when $B(\lambda)$ is not positive-definite, the arguments of[9] that use the operator $B^{1/2}$ become inapplicable; I am indebted to V. I. Matsaev for this remark. All the final formulas, however, are general.

[5)] This is accurate to within $|\lambda|/\omega_0 \ll 1$. But in the approximation taken we can drop λ altogether in the right-hand side of (1) and then the orthogonality condition will be satisfied exactly.

[6)] The two-level approximation has been analyzed in detail in the review article[13] by Klein. I am grateful to him for sending a preprint of this paper.

[7)] This result was first obtained jointly with A. B. Zimin by another route and was reported at the First Soviet-American Symposium on the Theory of Light Scattering in Solids (Moscow, May 1975).

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