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Theory of the absorption band shape and the fluorescence band shape of an impurity center in the Condon approximation

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We study the effect of the electron-phonon interaction $\hat{W}$, quadratic in the phonon operators, on the shape of the optical absorption and fluorescence bands of an impurity center. We do not assume that $\hat{W}$ is small. By solving an integral equation we obtain analytical expressions for the phonon functions which are responsible for the occurrence of phonon wings (PW) in the optical spectrum. We evaluate numerically on a computer the above-mentioned phonon functions. We analyze the breaking of the mirror symmetry of the absorption and fluorescence spectra, caused by the interaction $\hat{W}$, and also the effect of $\hat{W}$ on the integral intensity of the non-phonon line (NPL). We establish a simple analytical connection between the temperature broadening of the NPL and the above-mentioned lack of mirror symmetry of the phonon functions.

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INTRODUCTION

The intensity distribution, and also a number of important details of the optical band that corresponds to an allowed electron transition, can very often be explained in the Condon approximation. In that approximation the electron-phonon interaction is the difference $\hat{\Lambda}$ of the adiabatic potentials of the excited and the unexcited crystals. Expanding $\hat{\Lambda}$ in terms of the deviations of the molecules from their equilibrium positions we get the interaction $\hat{V}$ which is linear in the deviations and the interaction $\hat{W}$ which is quadratic in them.

So far the role of the linear interaction has been studied in great detail.[1–8] Appreciably less attention has been paid to the effect of the quadratic interaction $\hat{W}$ on the optical band shape. It is known that $\hat{W}$ may be responsible for the temperature broadening and the shift of the non-phonon lines (NPL)[9,10] and that it can also break down the mirror symmetry of the absorption and fluorescence bands.[11] The quadratic interaction therefore produces effects which are very often encountered experimentally. However, these effects may also be produced by other causes. It is therefore sometimes impossible to indicate exactly the cause of an observed effect without a quantitative comparison of theory and experiment. Unfortunately, it is difficult to compare quantitatively the formulae of[9–11] with experiments as perturbation theory was used in[9,10] to consider the quadratic interaction and the criteria for the applicability of the formulae given was not indicated, while in[11] such characteristics of the bands as the second moment which give little information were studied. It is true that Kubo and Toyazawa[6] took the effect of the linear and the quadratic interactions on the absorption band shape rigorously into account, but their formulae are very complicated and do not give a practical solution of the problem.

Recently, Levenson[12] and, independently, the present author[13] have proposed a different way to take the effect of $\hat{W}$ on the band shape into account. In their approach it is necessary for the evaluation of the band shape to find a function which is a solution of an integral equation. By solving this equation in various particular cases it was possible to get a number of new results referring to NPL and the phonon wing (PW).[13–15] However, a number of problems remained unanswered as we were not able to find an effective solution of the above-mentioned integral equation in the general case. We find such a solution in the present paper. Using it we obtain in Secs. 4 and 5 a few new physical results.

1. INTERACTION FUNCTION

The vibrational Hamiltonian $H^g(\mathbf{R})$ of a crystal with an unexcited ($g=0$) and with an excited ($g=e$) impurity can be written as follows:

$$H^g(\mathbf{R}+\mathbf{a}^g)={}^1/_2(\dot{\mathbf{R}}^2+(\mathbf{R}+\mathbf{a}^g)U^g(\mathbf{R}+\mathbf{a}^g)).$$

The coordinates R_q of the molecule are connected with the normal dimensionless coordinates $R_\varkappa^g$ of the crystal through the transformation1)

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$$R_q=\sum_\varkappa \frac{u^g(q,\varkappa)}{(2\nu_\varkappa^g)^{1/2}}R_\varkappa{}^g.$$

The dimensionless coefficients $u^g(q,\varkappa)$ and the frequencies $\nu_\varkappa^g$ of the normal vibrations can be found from the set of equations

$$\sum_q U_{qq'}{}^g u^g(q',\varkappa)=(\nu_\varkappa^g)^2 u^g(q,\varkappa).$$

We can investigate the case of a low impurity concentration by assuming that there is a single impurity molecule at the zero site. The function $J^g(\omega)$ which at $g=0$ describes the shape of the absorption band and at $g=e$ that of the fluorescence band can be written in the form

$$J^g(\omega)=\int_{-\infty}^{\infty} dt\,\exp(\pm i\omega t+h^g(t)). \tag{1}$$

The function $h^g(t)$ vanishes when there is no electron-phonon interaction and is completely determined by it. We shall therefore call it the interaction function. The electron-phonon interaction operator is the difference of the vibrational Hamiltonians which, writing $\mathbf{a}^0=0$, $\mathbf{a}^e=\mathbf{a}$, we can put in the following form:

$$\hat\Lambda=H^e(\mathbf{R}+\mathbf{a})-H^0(\mathbf{R})=\mathbf{a}U^e\mathbf{a}/2+\hat V+\hat W,$$

where $\hat V=\mathbf{a}U^e\mathbf{R}$ and $\hat W=\frac{1}{2}\mathbf{R}(E^e-U^0)\mathbf{R}$ are the linear and quadratic interactions which we mentioned in the Introduction. The interaction function was evaluated in[14,15]. The result of these calculations was

$$h^g(t)=-\frac{i}{2}\left(\mathbf{a}\mathbf{V}^g t+\int_0^t dx\int_0^t dy\,\mathbf{V}^g S^g(x,y|t)\mathbf{V}^g\right)$$

$$\pm\frac{1}{2}\int_0^t dx\,\mathrm{Sp}(WS^g(x,x|x)). \tag{2}$$

Here $W=U^e-U^0$, $\mathbf{V}^0=\mathbf{a}U^e$, $\mathbf{V}^e=\mathbf{a}U^0$, and $S^g(x,y|t)$ is the solution of the integral equation

$$S^g(x,y|t)=D^g(x-y)\pm\int_0^t dz\,D^g(x-z)WS^g(z,y|t). \tag{3}$$

In Eqs. (1) to (3) and everywhere else, unless we make a specific statement, one should take the upper sign for $g=0$ and the lower one for $g=e$. Equation (3) is a matrix equation as D^g is a matrix with the following elements:

$$D_{qq'}{}^g(x-y)=-i\langle \hat T R_q(x)R_{q'}(y)\rangle. \tag{4}$$

The averaging, and also the time-dependence of the operators R_q are determined by the Hamiltonian $H^g(\mathbf{R})$.

The aim of the present paper is to obtain equations and to use them to calculate the shape of the absorption and fluorescence bands without associating oneself with an assumption about the smallness of the displacements $\mathbf{a}$ of the equilibrium positions and the change W of the force matrix. One can only perform numerical calculations if one gives the model of the impurity center and a model for the interaction. It is expedient first to consider the simplest model for the interaction

$$W_{qq'}=W\delta_{q0}\delta_{q'0},\quad a_q=a\delta_{q0}. \tag{5}$$

It corresponds to the case when one takes into consideration for the excitation of the impurity only a single force constant which couples the impurity to some molecule in the crystal and also takes into account the change in their relative positions. The problem of the effect of the model for the interaction on the band shape is of independent interest but lies outside the framework of the present paper.

When using the model (5) it is expedient to introduce into the discussion together with (4) the causal Green functions

$$D_{VV}{}^g(x-y)=-i\langle \hat T\hat V(x)\hat V(y)\rangle,$$
$$D_{VR}{}^g(x-y)=-i\langle \hat T\hat V(x)R_0(y)\rangle,$$
$$D_{RR}{}^g(x-y)=-i\langle \hat T R_0(x)R_0(y)\rangle.$$

The interaction function $h^g(t)$ can then be written in the following form $(g'\neq g)$:

$$h^g(t)=-\frac{i}{2}\left(a^2U_{00}{}^{g'}t+\int_0^t d\tau\,Q_{VV}{}^g(\tau|t)\right)\pm\frac{W}{2}\int_0^t d\tau\,P^g(0|\tau), \tag{6}$$

where

$$Q_{VV}^g(\tau|t)=\int_0^t dx\,(D_{VV}^g(\tau-x)\pm WD_{VR}^g(\tau-x)Q_{RV}^g(x|t)), \tag{7}$$

while the functions Q_{RV}^g and P^g are solutions of the integral equations which differ only in the free terms:

$$Q_{RV}^g(x|t)=\int_0^t dy\,(D_{RV}^g(x-y)\pm WD_{RR}^g(x-y)Q_{RV}^g(y|t)), \tag{8}$$

$$P^g(x|t)=D_{RR}^g(x)\pm W\int_0^t dy\,D_{RR}^g(x-y)P^g(y|t). \tag{9}$$

In order to express the interaction function $h^g(t)$ in terms of the known functions D_{RR}^g, D_{RV}^g, and D_{VV}^g it is thus necessary to solve the integrals Eqs. (8) and (9). If we use an iteration method to solve them, i.e., use perturbation theory to evaluate the interaction function, we get an approximately correct intensity of the peaks in the phonon structure, but completely incorrect positions for them—they will be arranged at the vibrational frequencies of the initial electron state, while it is well known that they should be arranged at the frequencies of the final state. The problem of the break-down of mirror symmetry of the spectra in the framework of perturbation theory in terms of W can therefore not be discussed. An iteration procedure for solving Eqs. (8) and (9) leads us also to other incorrect conclusions, e.g., to the conclusion that the temperature broadening of the NPL is different in the absorption and the fluorescence spectra. If we take into account what we have said, it is clear that we must solve Eqs. (8) and (9) without using perturbation theory with respect to W. Such a solution is realized in the following sections.

2. SOLUTION OF EQS. (8) AND (9)

We transform Eqs. (8) and (9) into other ones. To do this we shall look for their solution in the form

$$Q_{RV}^{g}(x|t)=Q^{g}+\int_{0}^{\infty}\frac{d\nu}{\pi}Q^{g}(\nu,t)\,(e^{-i\nu x}+e^{i\nu(x-t)}),\tag{10}$$

$$P^{g}(x|t)=\int_{0}^{\infty}\frac{d\nu}{2\pi i}[P_{+}{}^{g}(\nu,t)\,(e^{-i\nu x}+e^{i\nu(x-t)})+P_{-}{}^{g}(\nu,t)\,(e^{-i\nu x}-e^{i\nu(x-t)})].\tag{11}$$

Substituting (10) and (11), respectively, into (8) and (9) we see that the last ones become identities, if the functions $Q^{g}(\nu,t)$, $P_{\pm}^{g}(\nu,t)$, and Q^{g} satisfy the following equations ($Q^{g}=-a$):

$$\begin{gathered}Q^{g}(\omega,t)\left(1\mp W\fint_{0}^{\infty}\frac{d\nu}{\pi}\frac{2\nu\Gamma^{g}(\nu)}{\omega^{2}-\nu^{2}}\right)\\ \mp W\Gamma^{g}(\omega)\left[(n(\omega)+1)\fint_{0}^{\infty}\frac{d\nu}{\pi}\left(\frac{1}{\omega-\nu}+\frac{e^{-i\nu t}}{\omega+\nu}\right)Q^{g}(\nu,t)\right.\\ \left.-e^{i\omega t}n(\omega)\fint_{0}^{\infty}\frac{d\nu}{\pi}\left(\frac{e^{-i\nu t}}{\omega-\nu}+\frac{1}{\omega+\nu}\right)Q^{g}(\nu,t)\right]=a\omega\Gamma^{g}(\omega)\,(n(\omega)+1-n(\omega)e^{i\omega t}),\end{gathered}\tag{12}$$

$$\begin{gathered}P_{\pm}{}^{g}(\omega,t)\left(1\mp W\fint_{0}^{\infty}\frac{d\nu}{\pi}\frac{2\nu\Gamma^{g}(\nu)}{\omega^{2}-\nu^{2}}\right)\\ \mp W\Gamma^{g}(\omega)\left[(n(\omega)+1)\fint_{0}^{\infty}\frac{d\nu}{\pi}\left(\frac{1}{\omega-\nu}\pm\frac{e^{-i\nu t}}{\omega+\nu}\right)P_{\pm}{}^{g}(\nu,t)\right.\\ \left.-e^{i\omega t}n(\omega)\fint_{0}^{\infty}\frac{d\nu}{\pi}\left(\frac{e^{-i\nu t}}{\omega-\nu}\pm\frac{1}{\omega+\nu}\right)P_{\pm}{}^{g}(\nu,t)\right]=\Gamma^{g}(\omega)\,(n(\omega)+1\pm n(\omega)e^{i\omega t}).\end{gathered}\tag{13}$$

The double sign in front of W in Eq. (13) refers to the index g and in the other cases we must take the plus sign when calculating P_{+}^{g} and the minus sign when evaluating P_{-}^{g}; $n(\omega)=[\exp(\omega/kT)-1]^{-1}$; the function $\Gamma^{g}(\nu)$ is the imaginary part of the function $D_{RR}^{g}(\nu)$ at zero temperature. It is described by the following expression:

$$\Gamma^{g}(\nu)=\frac{\pi}{2\nu}\sum_{\varkappa=1}^{N}(u^{g}(0,\varkappa))^{2}\,\delta(\nu-\nu_{\varkappa}{}^{g}).\tag{14}$$

Using Eqs. (7) and (12), we can express the function $Q_{VV}^{g}(\tau|t)$ directly in terms of $Q^{g}(\omega,t)$—the solution of Eq. (12):

$$Q_{VV}^{g}(\tau|t)=-a^{2}U_{00}{}^{g'}+a\int_{0}^{\infty}\frac{d\omega}{\pi}(e^{-i\omega\tau}+e^{i\omega(\tau-t)})\,\omega^{2}Q^{g}(\omega,t).\tag{15}$$

Substituting Eq. (15) into Eq. (6) which describes the interaction function and integrating over the time we get

$$h^{g}(t)=a\int_{0}^{\infty}\frac{d\omega}{\pi}(e^{-i\omega t}-1)\,\omega Q^{g}(\omega,t)\pm\frac{W}{2}\int_{0}^{t}d\tau\,P^{g}(0|\tau).\tag{16}$$

One might get the impression that changing from Eqs. (8) and (9) to the new Eqs. (12) and (13) did not make the problems any easier. However, this is not true. One can effectively solve Eqs. (12) and (13) both in the case when the number N of the modes interacting with the electron in the impurity is small, and also in the case where it is infinite.

We consider first the case where N is a small number. To fix the ideas we consider only the case of absorption, dropping in the remainder of this section the index $g=0$. We shall look for the solution of Eqs. (12) and (13) in the form

$$Q(\omega,t)=\pi\sum_{s=1}^{N}q(s,t)\,\delta(\omega-\omega_{s}),\tag{17}$$

$$P_{\pm}(\omega,t)=\pi\sum_{s=1}^{N}p_{\pm}(s,t)\,\delta(\omega-\omega_{s}),\tag{18}$$

where N of the frequencies ω_{s} are solutions of the following equation:

$$1-W\sum_{\varkappa=1}^{N}\frac{u^{2}(0,\varkappa)}{2\nu_{\varkappa}}\left(\frac{1}{\omega-\nu_{\varkappa}}-\frac{1}{\omega+\nu_{\varkappa}}\right)=0.$$

We first consider Eq. (13). Substituting (14) and (18) into (13) and using the fact that $x\delta(x)\equiv 0$ we get instead of (13)

$$\begin{gathered}\sum_{\varkappa=1}^{N}\left\{W\sum_{s=1}^{N}p_{\pm}(s,t)\left[\left(\frac{1}{\nu_{\varkappa}-\omega_{s}}\pm\frac{e^{-i\omega_{s}t}}{\nu_{\varkappa}+\omega}\right)(n_{\varkappa}+1)\right.\right.\\ \left.\left.-\left(\frac{e^{-i\omega_{s}t}}{\nu_{\varkappa}-\omega_{s}}\pm\frac{1}{\nu_{\varkappa}+\omega_{s}}\right)e^{i\nu_{\varkappa}t}n_{\varkappa}\right]+n_{\varkappa}+1\pm n_{\varkappa}e^{i\nu_{\varkappa}t}\right\}\frac{u^{2}(0,\varkappa)}{2\nu_{\varkappa}}\delta(\omega-\nu_{\varkappa})=0.\end{gathered}$$

This equation becomes an identity for any frequency ω if the coefficients of all delta-functions vanish. This requirement produces the following set of equations:

$$\begin{gathered}-W\sum_{s=1}^{N}p_{\pm}(s,t)\left[\left(\frac{1}{\nu_{\varkappa}-\omega_{s}}\pm\frac{e^{-i\omega_{s}t}}{\nu_{\varkappa}+\omega_{s}}\right)(n_{\varkappa}+1)\right.\\ \left.-\left(\frac{e^{-i\omega_{s}t}}{\nu_{\varkappa}-\omega_{s}}\pm\frac{1}{\nu_{\varkappa}+\omega_{s}}\right)e^{i\nu_{\varkappa}t}n_{\varkappa}\right]=n_{\varkappa}+1\pm n_{\varkappa}e^{i\nu_{\varkappa}t}\qquad(\varkappa=1,2,\ldots,N).\end{gathered}\tag{19}$$

If the number of modes is small one can easily determine the N functions $p_{\pm}(s,t)$ from the algebraic set of Eqs. (19). One can solve Eq. (12) in a similar way and thus determine the functions $q(s,t)$.

Knowing the functions $p_{\pm}(s,t)$ and $q(s,t)$ and using Eqs. (17), (18), (11), and (16), we can evaluate the interaction function. We compare the interaction function obtained from the formulae of the present paper with the interaction function obtained by Kubo and Toyazawa.[6] We consider the case of one mode as in that case the use of the equations from[6] does not cause any difficulties. Substituting (17) and (18) into Eq. (16) we get

$$h(t)=\frac{W}{4i}\int_{0}^{t}d\tau[p_{+}(\tau)+p_{-}(\tau)+(p_{+}(\tau)-p_{-}(\tau))e^{-i\omega\tau}]+a(e^{-i\omega t}-1)\,\omega q(t).\tag{20}$$

If we now use Eq. (19) and the anlogous equation for $q(t)$ to find the functions $p_{\pm}(\tau)$ and $q(t)$, we get, substituting them in (20), evaluating the integral over τ and after some algebraic transformations

$$\begin{gathered}h(t)=it\frac{\nu-\omega}{2}+a^{2}\frac{\nu\omega}{\nu+\omega}\left(1-\frac{n}{n+1}e^{i\nu t}\right)(e^{-i\omega t}-1)\\ \cdot\left[1+\frac{\nu-\omega}{\nu+\omega}e^{-i\omega t}-\frac{n}{n+1}\left(e^{-i\omega t}+\frac{\nu-\omega}{\nu+\omega}\right)e^{i\nu t}\right]^{-1}+\ln\frac{2(\nu\omega)^{1/2}}{(n+1)(\nu+\omega)}\\ -\ln\left[\left(1-\frac{n}{n+1}e^{i(\nu-\omega)t}\right)^{2}-\left(\frac{\nu-\omega}{\nu+\omega}\right)^{2}\left(e^{-i\omega t}-\frac{n}{n+1}e^{i\nu t}\right)^{2}\right]^{1/2}.\end{gathered}\tag{21}$$

where $n=[\exp(\nu/kT)-1]^{-1}$. If we now put $\lambda=it$, $\Delta=a$ into the formulae of[6] we get after some rather cumbersom trigonometric transformations of the functions $f_\Gamma(it)$ and $f_\Delta(it)$ of the cited paper

$$f_\Gamma(it)f_\Delta(it)=e^{h(t)},$$

i.e., complete agreement.2)

3. SOLUTION OF EQS. (12) AND (13) AT ZERO TEMPERATURE

If the number of modes is large, it has no sense to reduce the integral Eqs. (12) and (13) to an algebraic set. It is in that case better to solve the integral Eqs. (12) and (13) directly. The kernels of these equations together with the regular part also contain a singular part and therefore these equations belong to the class of singular equations. One can regularize such equations,[16] i.e., reduce them to Fredholm equations. It is most expedient to study the intensity distribution in the PW at zero temperature as then the PW structure is most clearly expressed. We therefore consider Eqs. (12) and (13) at that temperature. The two equations can then be written in the form:

$$\varphi^g(\omega,t)(1\mp W\Omega^g(\omega))\mp W\Gamma^g(\omega)\int_0^\infty\frac{d\nu}{\pi}\frac{\varphi^g(\nu,t)}{\omega-\nu}=\Gamma^g(\omega)\chi^g(\omega,t), \tag{22}$$

where

$$\Omega^g(\omega)=\int_0^\infty\frac{d\nu}{\pi}\Gamma^g(\nu)\left(\frac{1}{\omega-\nu}-\frac{1}{\omega+\nu}\right).$$

We have explicitly split off the singular part in (22) and included the regular part in $\chi^g(\omega,t)$. If $\varphi^g=P^g_\pm$, we have

$$\chi^0(\omega,t)=1\pm W\int_0^\infty\frac{d\nu}{\pi}\frac{e^{-i\nu t}}{\omega+\nu}P_\pm{}^0(\nu,t),$$

$$\chi^e(\omega,t)=1\mp W\int_0^\infty\frac{d\nu}{\pi}\frac{e^{-i\nu t}}{\omega+\nu}P_\pm{}^e(\nu,t);$$

if, however $\varphi^g=Q^g(\nu,t)$, we have

$$\chi^g(\omega,t)=a\omega\pm W\int_0^\infty\frac{d\nu}{\pi}\frac{e^{-i\nu t}}{\omega+\nu}Q^g(\nu,t).$$

We solve Eq. (22) in a similar way for $g=0$ and $g=e$ and it is therefore sufficient to consider in detail only the case with $g=0$, everywhere dropping the index, except at the functions $\Gamma^0(\omega)$ and $\Omega^0(\omega)$.

The integral Eq. (22) can be reduced to a Riemann boundary value problem for the functions $\Phi_+(\omega,t)$ and $\Phi_-(\omega,t)$ which are, respectively, analytical in the upper and lower half-planes of the complex variable ω. The required function $\varphi(\omega,t)$ is the jump in the function $\Phi(\omega,t)$ which occurs when going across the real axis:

$$\varphi(\omega,t)=\Phi_+(\omega,t)-\Phi_-(\omega,t). \tag{23}$$

The solution of the boundary value problem which vanishes at infinity looks like:

$$\Phi_\pm(\omega,t)=e^{-\psi_\pm(\omega)}\int_0^\infty\frac{d\nu}{-2\pi i}\frac{1}{\omega-\nu\pm i0^+}$$
$$\times\Gamma^0(\nu)\chi(\nu,t)e^{\psi(\nu)}[(1-W\Omega^0(\nu))^2+(W\Gamma^0(\nu))^2]^{-1/2}, \tag{24}$$

where

$$\psi_\pm(\omega)=\int_0^\infty\frac{d\nu}{-\pi}\frac{\Delta(\nu)}{\omega-\nu\pm i0^+}=\psi(\omega)\pm i\Delta(\omega),$$
$$\Delta(\nu)=\operatorname{arctg}\frac{W\Gamma^0(\nu)}{1-W\Omega^0(\nu)}.$$

If the function $\chi(\nu,t)$ were known, we would get the solution of Eq. (22) by substituting (24) into (23). In our case, however, after this substitution we get new, but already regular equations for the functions $P_\pm(\omega,t)$ and $Q(\omega,t)$:

$$Q(\omega,t)=Q(\omega)+W\int_0^\infty\frac{dE}{\pi}K(\omega,E)e^{-iEt}Q(E,t), \tag{25}$$

$$P_\pm(\omega,t)=P(\omega)\pm W\int_0^\infty\frac{dE}{\pi}K(\omega,E)e^{-iEt}P_\pm(E,t). \tag{26}$$

After a few transformations and an evaluation of the integrals we can write the kernel $K(\omega,E)$ and the function $Q(\omega)$ in the form

$$K(\omega,E)=\frac{P(\omega)e^{\psi(-E)}}{\omega+E}, \tag{27}$$
$$Q(\omega)=a(\omega+\Delta)P(\omega), \tag{28}$$

where

$$\Delta=\int_0^\infty\frac{d\nu}{-\pi}\Delta(\nu), \tag{29}$$

expressing them in terms of the function $P(\omega)$—the free term of Eq. (26). One can find the explicit form of this function, if we substitute Eq. (24) into (23) with $\chi=1$. Evaluating then the integral, we get

$$P(\omega)=\frac{1}{2iW}(e^{-\psi_-(\omega)}-e^{-\psi_+(\omega)}). \tag{30}$$

Although this formula is simple, it is difficult to work with if there are localized modes among the phonon modes. These modes correspond to discrete frequencies and in those points the functions $\psi_\pm(\omega)$ are singular. We can rid ourselves of this shortcoming. Using the identify

$$e^{-\psi(-\omega)}=\exp\int_0^\infty\frac{d\nu}{-\pi}\frac{\Delta(\nu)}{\omega+\nu}=e^{\psi(\omega)}[(1-W\Omega^0(\omega))^2+(W\Gamma^0(\omega))^2]^{-1/2},$$

we transform (30) to the form

$$P(\omega)=\Gamma^e(\omega)e^{\psi(-\omega)}, \tag{31}$$

where

$$\Gamma^e(\omega)=\frac{\Gamma^0(\omega)}{(1-W\Omega^0(\omega))^2+(W\Gamma^0(\omega))^2}.$$

The singularities caused by discrete frequencies are now only contained in the function $\Gamma^e(\omega)$ and do not cause trouble. For instance, we can use Eq. (31) to consider also the case of a single mode, studied in the preceding section. The results are the same. So far we have considered the case with $g=0$, i.e., we have looked for the functions determining the absorption band shape. We can find the analogous functions for the fluorescence band from Eqs. (25) and (26), and also Eqs. (27), (28), and (31) by the following formal substitution:

$$W\to -W,\quad \Delta(\omega)\to-\Delta(\omega),\quad \psi(\omega)\to-\psi(\omega),\quad \Gamma^e(\omega)\to\Gamma^0(\omega).$$

The functions $\Gamma^g(\omega)$ are the imaginary parts of the functions $D^g_{RR}(\omega)$ at zero temperature. They differ from zero only in the single-phonon region of frequencies L_1^g, by which we understand the segment occupied by the phonon frequencies and also separate points corresponding to localized modes. As the integration in Eqs. (25) and (26) is over a bounded region these equations are second-order Fredholm equations. We must draw attention to the fact that the functions $\Gamma^g(\omega)$ which have peaks at the frequencies of the final electron state occur in the kernel and the free terms of the regularizing Eqs. (25) and (26) and the PW structure therefore will also reflect the vibrational frequencies of the final electron state. This is a result of the regularization, i.e., of taking the most important part of the quadratic electron-phonon interaction rigorously into account. The problem of the possibility of splitting the quadratic interaction into two parts was considered before.[14]

We now turn to the interaction function $h^g(t)$. We can write it in the form

$$h^g(t)=\mp it\Delta-\frac{\gamma}{2}|t|-f(0)+f^g(t),\tag{32}$$

where $f^g(t)$ tends to zero when the time of the function increases, and $f(0)$ is its value at $t=0$. Each term in (32) is important for definite details of the optical band. Indeed, substituting (32) into (1) and integrating over the time we get

$$J^g(\omega)=\Psi_0(\omega)+\sum_{m=1}^{\infty}\Psi_m{}^g(\omega),\tag{33}$$

where

$$\Psi_0(\omega)=e^{-f(0)}\frac{\gamma/2}{(\omega+\Delta)^2+(\gamma/2)^2}\tag{34}$$

describes the NPL and the sum over m the PW;

$$\Psi_m{}^g(\omega)=\frac{1}{m!}\int\limits_{-\infty}^{\infty}\frac{d\nu_1}{\pi}\dots\int\limits_{-\infty}^{\infty}\frac{d\nu_m}{\pi}f^g(\nu_1)\dots f^g(\nu_m)\Psi_0(\omega\mp\nu_1\mp\dots\mp\nu_m).\tag{35}$$

Equations (33) to (35) are valid at any temperature, but in the framework of the adiabatic approximation $\gamma=0$ at zero temperature.[15] As the PW shape is according to (35) completely determined by the Fourier component of the function $f^g(t)$, we shall call $f^g(\nu)$ the phonon function. This function can be "recovered" from the PW. This procedure has been realized in several papers, e.g., in[17]. We can write the phonon function as the sum of two terms:

$$f^g(\nu)=w^g(\nu)+v^g(\nu).$$

The first term here determines the contribution to the PW of only the quadratic electron-phonon interaction, and the second one a joint contribution from the linear and the quadratic interaction. Solving Eqs. (25) and (26) by the iteration method and substituting these solutions into Eq. (16) we get after some non-trivial transformations the following expressions for the phonon functions:

$$v^g(\nu)=v_1{}^g(\nu)+v_2{}^g(\nu)+v_3{}^g(\nu)+\dots,\tag{36}$$

$$w^g(\nu)=w_2{}^g(\nu)+w_4{}^g(\nu)+w_6{}^g(\nu)+\dots,\tag{37}$$

where

$$v_1{}^g(\nu)=a^2\int\limits_0^{\infty}\frac{d\nu_1}{\pi}(\nu_1\pm\Delta)F^g(\nu_1)(\nu_1\pm\Delta)\delta(\nu-\nu_1),\tag{38}$$

$$v_2{}^g(\nu)=\pm Wa^2\int\limits_0^{\infty}\frac{d\nu_1}{\pi}\frac{d\nu_2}{\pi}(\nu_1\pm\Delta)F^g(\nu_1)\frac{1}{\nu_1+\nu_2}F^g(\nu_2)(\nu_2\pm\Delta)\delta(\nu-\nu_1-\nu_2),$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\tag{39}$$

$$w_2{}^g(\nu)=\frac{W^2}{2\nu}\int\limits_0^{\infty}\frac{d\nu_1}{\pi}\frac{d\nu_2}{\pi}F^g(\nu_1)\frac{1}{\nu_1+\nu_2}F^g(\nu_2)\delta(\nu-\nu_1-\nu_2),\tag{40}$$

$$w_4{}^g(\nu)=\frac{W^4}{2\nu}\int\limits_0^{\infty}\frac{d\nu_1}{\pi}\dots\frac{d\nu_4}{\pi}F^g(\nu_1)\frac{1}{\nu_1+\nu_2}F^g(\nu_2)\frac{1}{\nu_2+\nu_3}\times F^g(\nu_3)\frac{1}{\nu_3+\nu_4}F^g(\nu_4)\delta(\nu-\nu_1-\nu_2-\nu_3-\nu_4),\tag{41}$$

Here, as in Eq. (34) the constant Δ is given by Eq. (29). The function

$$F^g(\nu)=\Gamma^{g'}(\nu)e^{\pm2\psi(-\nu)}\quad(g'\neq g)$$

is negative. This fact makes the analysis of the convergence of the series (36) and (37) easier.

4. PHONON FUNCTIONS

As the function $F^g(\nu)$ is non-vanishing on the single-phonon interval $L_1^{g'}$, the phonon functions $v_k^g(\nu)$ and $w_k^g(\nu)$ are non-vanishing on the k-phonon interval $L_k^{g'}$. We shall therefore call them the k-phonon functions. The single-phonon functions $v_1^g(\nu)$, multiplied by the Debye-Waller function, are equal to the probabilities for a photo-transition with production of one phonon. The other phonon functions have no simple physical meaning. We elucidate the integrated properties of the k-phonon functions. We integrate them over the frequency and denote the corresponding integrated values by v_k^g and w_k^g. We get

$$v_k{}^0\neq v_k{}^e,\quad w_k{}^0=w_k{}^e.$$

Summing all v_k^g we find the following expression for the integrated value of the function $v^g(\nu)$:

$$v^g=a\int\limits_0^{\infty}\frac{d\omega}{\pi}\omega Q^g(\omega)=\frac{a^2}{W}\left(\frac{\Delta^3}{3}+\int\limits_0^{\infty}\frac{d\nu}{\pi}\nu^2\Delta(\nu)\right)=v.\tag{42}$$

Therefore, notwithstanding the fact that the partial values v_k^g depend on the electron index g, their sum does not depend on it. This means that the contribution from the linear interaction to the Debye-Waller factor is the

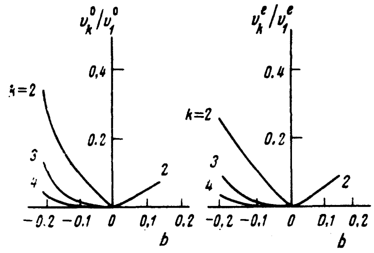

FIG. 1. Integrated values of the phonon functions v_k^0/v_1^0 and v_k^e/v_1^e.

same for the absorption and for the fluorescence spectrum.

Let us discuss the problem of the convergence of the series (36) and (37). Undoubtedly, the series converge for small W. If, however, $W=\infty$, the integral of the sum of series (36) is, according to (42), independent of W and equal to a finite value, while

$$w_2 : w_4 : w_6 : \ldots = 1 : \frac{1}{2} : \frac{1}{3} : \ldots,$$

i.e., even in this limiting case each successive term in (37) is less than the preceding one. For practically accessible changes in the force matrix the convergence of the series (36) and (37) will be rather fast. Let us elucidate what is the region where W is defined and what are the realistically accessible values of this parameter. As it describes the change in the force matrix in a photo-transition, the dimensionless parameter $b = W/\nu_D^2$, where ν_D is the boundary frequency of the phonon spectrum of the crystal, which is connected with it can change within the following range: $-|b_m| < b < \infty$. The left-hand limit of this range corresponds to the elastic constant being weakened to zero. It has been shown[18] that one can apply perturbation theory with respect to the parameter b, provided $|b| \lesssim 0.025$.[3] Practically attainable, apparently, is $|b| \lesssim 0.2$. If we take

$$\Gamma^0(x) = 13\pi x^3 (1-x)^{1/2} \quad (0 \leqslant x \leqslant 1), \tag{43}$$

where $x = \nu/\nu_D$, we have $-|b_m| = -0.25$. Using (43) and Eqs. (38) to (41) we have evaluated the phonon functions.[4] The results are shown in Figs. 1 to 4. According to Fig. 1 the convergence of the sequence v_k^g is very fast. The calculations show that the ratio w_4/w_2 is somewhat smaller than v_4/v_2. This means that we can practically everywhere put $f^g(\nu) \approx v_1^g(\nu) + v_2^g(\nu) + w_2^g(\nu)$. The effect of the quadratic interaction on the Debye-Waller factor $\alpha = \exp[-(v+w)]$ is, according to Fig. 2, small. We must note that for negative b the interference between the linear and the quadratic interactions can even somewhat increase the Debye-Waller factor. In Fig. 3 we show by full-drawn lines the single-phonon functions, calculated using the exact Eq. (38). In all cases the mirror symmetry is considerably broken. We show in Fig. 4 the two-phonon functions calculated using Eqs. (39) and (40). We draw attention to the fact that the two-phonon functions $v_2^g(\nu)$ are negative in one of the spectra. Hence, the total phonon function may also be negative outside the one-phonon region.

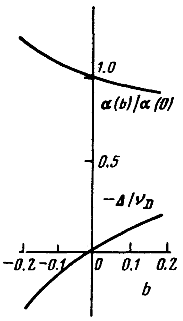

FIG. 2. Dependence on b of the NPL shift Δ and the Debye-Waller factor α.

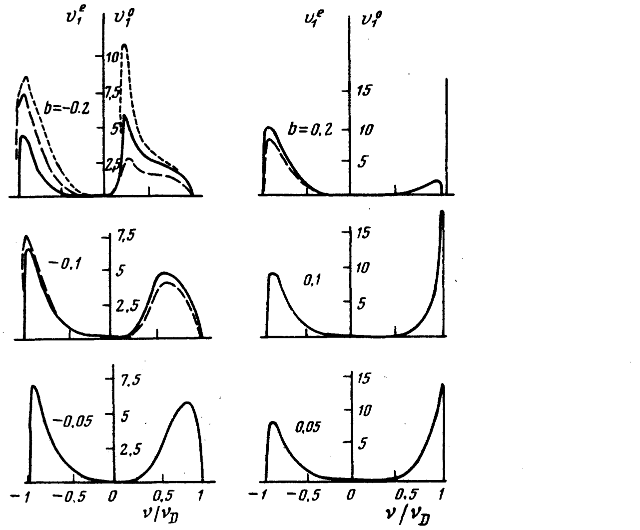

FIG. 3. Exact single-phonon functions $v_1^g(\nu)$ (full-drawn lines), and approximate ones v_1^{**g} (dashed) and v_1^{*g} (dotted) for $a^2\nu_D=1$ and various values of b ($g=0, e$).

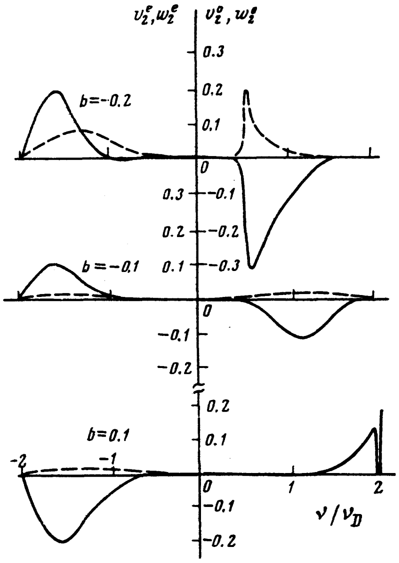

FIG. 4. Two-phonon functions $v_2^g(\nu)$ for $a^2\nu_D=1$ (full-drawn lines) and $w_2^g(\nu)$ (dashed lines) for various b ($g=0, e$).

5. CONNECTION BETWEEN LACK OF MIRROR SYMMETRY OF THE PW AND THE TEMPERATURE BROADENING OF NPL

If the lack of mirror symmetry of the PW is caused by the change in the force matrix there must exist a connection between the lack of mirror symmetry and the temperature broadening of the NPL as these two effects are produced by the same cause. The actual form of this connection depends, of course, on the model of the interaction. In the framework of the model described by Eq. (5) this connection has a rather simple form. Indeed, according to[15] the half-width of the NPL is described by the expression

$$\gamma(T)=\operatorname{Re}\int_0^\infty \frac{d\nu}{\pi}\ln\left(1+\frac{2iWn(\nu)\Gamma^0(\nu)}{1-W\Omega^0(\nu)+iW\Gamma^0(\nu)}\right), \tag{44}$$

i.e., it contains the parameter W and the function already encountered by us in Eq. (38) which describes the single-phonon function. Equations (44) and (38) establish a quantitative relation between the lack of mirror symmetry of the PW and the temperature broadening of the NPL. Unfortunately, the connection between the functions $v_1^0(x)$ and $v_1^e(x)$, obtained experimentally, and the temperature dependence $\gamma(T)$ is unclear as these quantities are expressed not in terms of one another, but in terms of $\Gamma^0(\nu)$ and W. However, if we use the fact that the form of the approximate single-phonon functions

$$v_1^{*g}(x)=a^2\nu_D x\Gamma^{g'}(x) \tag{45}$$

$$v_1^{**g}(x)=a^2\nu_D x^2\Gamma^{g'}(x)\quad (g'\neq g) \tag{46}$$

is close to the exact one (see Fig. 3) and use the connection between the functions $\Gamma^g(x)$ and the single-phonon functions which is, e.g., expressed by the approximate Eq. (25), we can explicitly connect the lack of mirror symmetry and the temperature broadening by means of the following formulae:

$$v_1^{*0}(x)=\frac{v_1^{*e}(x)}{(1-\varepsilon\Omega(x))^2+(\varepsilon v_1^{*e}(x)/x)^2}, \tag{47}$$

$$\frac{\gamma(T)}{\nu_D}=\operatorname{Re}\int_0^1\frac{dx}{\pi}\ln\left(1+\frac{2i\varepsilon n(x)v_1^{*e}(x)}{x(1-\varepsilon\Omega(x))+i\varepsilon v_1^{*e}(x)}\right), \tag{48}$$

where

$$\Omega(x)=\int_0^1\frac{dy}{\pi}\frac{2v_1^{*}(y)}{x^2-y^2}.$$

If we can select the only parameter ε so that we are able to describe the experimentally observed lack of mirror symmetry of the PW and the temperature broadening of NPL, this will serve as a clear proof of the fact that both effects are due to the same cause—the change W in the force matrix of the crystal when an impurity is excited.

The author is grateful to É. I. Rashba for discussing the results of this paper.

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[1] We use in this paper a system of units in which $\hbar=1$.

[2] It is clear that taking anharmonicity into account may lead to a change in the form of Eq. (21). Therefore, (21) is valid provided the anharmonic change in the frequency is appreciably smaller than $\nu-\omega$.

[3] The parameter b in the present paper is smaller by a factor 2 than the one used in[18].

[4] The author expresses his gratitude to S. A. Zhdanov who performed the computer calculations.

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