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Further Contribution to the Theory of the Line-Shape of the Exciton Absorption Band

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The line-shape of the exciton absorption band, in the case that $k=0$ is at the bottom (or the top) of the exciton energy band and that there are no states with the same energy in other exciton bands, is investigated in the limit of weak exciton-phonon coupling, with the use of the damping theory. The equations for the energy dependent shift and broadening are solved with the aid of graphic calculation.

Except for the low temperature region, one can assume the exciton-phonon scattering to be elastic, and the line-shape in the main part of the absorption band is determined essentially by the properties of long wavelength excitons and phonons. The half-value width is rather small, and is proportional to $(gT)^2$ where g is the exciton-phonon coupling constant and T is the absolute temperature.

The line-shape is strongly asymmetric, with a tail which is due to the indirect transition, on the high or low energy side according as $k=0$ is the bottom or the top of the exciton band.

§ 1. Introduction

The line-shape of the exciton absorption band in insulating crystal was investigated in a previous paper,[1] with the method of the generating function. The absorption corresponds to the electronic transition from the ground state of the crystal to that excited state in which a bound pair of an electron and a hole propagates through the crystal with translational pseudo-momentum $\hbar k$ transferred to the electron system from the incident photon. Since the wave number k of the photon is much smaller than the reciprocal of lattice constant, we can put $k\approx 0$ for usual purposes. The absorption spectrum should consist of a series of sharp lines corresponding to various quantum states of the relative motion of the electron and the hole (ground and excited states of the exciton), if there were no perturbing effects such as lattice vibrations and lattice imperfections which scatter the exciton, and the (spontaneous) radiation field which may annihilate the exciton.[2]

The effects of lattice vibrations and lattice imperfections on the width of the absorption line were discussed in the previous paper, which will be referred to as I in the present paper. The following conclusions were obtained in I, as regards the effect of lattice vibration. When the coupling constant g between the exciton and lattice vibration is sufficiently weak, the absorption line-shape

is Lorentzian, with the half-value width W equal to $\hbar\Gamma(0)$ where $\Gamma(\boldsymbol{k})$ is the reciprocal of the lifetime of the exciton with wave number $\boldsymbol{k}$ due to the scattering by lattice vibration. The situation is similar to the natural line-width of the atomic spectra. The width W is proportional to gT at high temperatures where T is the absolute temperature. On the other hand, when g is very large, it can be shown that the line-shape is Gaussian, with the width W proportional to $(gT)^{1/2}$. This is due to the fact that the picture of a localized exciton is better than that of a running exciton, in other words, that we can take the adiabatic approximation and apply the Franck-Condon principle to the transition.

These conclusions were derived by, first, expanding the generating function in power series of g, and then rewriting it in closed forms in the two limiting cases mentioned above, thereby dropping the contributions which become unimportant in the limits. There was, however, another condition for the validity of the conclusion for the weak coupling case. This is analogous to the Landau-Peierls condition as regards the validity of the Boltzmann-Bloch equation for the transport processes in metals.[3] In the present case, the condition is that $\Gamma(\boldsymbol{k})$, the scattering probability of the $\boldsymbol{k}$-exciton, should be well-defined in the neighborhood of $\boldsymbol{k}=0$. In other words, successive scatterings should be well separated elementary processes so that

$$\Gamma(\boldsymbol{k})\,\tau_c(\boldsymbol{k}) \ll 1, \tag{1·1}$$

where τ_c is the duration of a collision (see Eq. (4·8) of I). τ_c is of the order of de Broglie wavelength divided by the velocity of the exciton, which amounts to

$$\tau_c(\boldsymbol{k}) \sim (2\pi/k)/(\hbar k/m^*), \tag{1·2}$$

if a simple exciton band with effective mass m^* is assumed.

In the case of the acoustical mode of lattice vibration, we have

$$\Gamma(\boldsymbol{k}) = \text{const. } gTk, \tag{1·3}$$

under the assumption of a simple band, if we neglect the energies of the acoustical phonons in the exciton-phonon scattering (see Eq. (7·1′) of I). This means that the relation (1·1) is not valid in the neighborhood of $\boldsymbol{k}=0$, however small g may be.

If we put $W=\hbar\Gamma(0)$ in the case of the simple band, we have an absurd result that the width vanishes if we neglect the phonon energy. The real situation, however, may be as follows. To each exciton level belongs a level broadening $\hbar\Gamma(\boldsymbol{k})$, in other words, the neighboring levels within the energy interval $\hbar\Gamma(\boldsymbol{k})$ are mixed virtually in the real state $\boldsymbol{k}$. This way of description is not correct for those states with small k such that $\Gamma(\boldsymbol{k})\tau_c(\boldsymbol{k}) \gtrsim 1$. Since the successive scatterings are inseparable, these states intermingle with each other in a complicated way all the time. The creation of an exciton by a photon means the excitation of one of these intermingling states. Then we may infer, qualitatively at least, that the line-width would be of the order of

$$W\sim\hbar^2\tilde{k}^2/2m^*\sim\hbar\Gamma'(\tilde{k})\propto(gT)^2, \tag{1·4}$$

where $\tilde{k}$ is to be determined by $\Gamma'(k)\tau_c(k)\sim 1$.

On the other hand, the exciton absorption band is expected to have a tail decreasing with $(-3/2)$ power of the energy difference from the absorption peak due to the indirect transition,[4] on the high energy side if a positive effective mass is assumed for the exciton band. This situation is necessarily reflected upon the strong asymmetry of the line-shape even in the main part of the absorption band.*)

The difficulty arising from the singular behaviors of $\hbar\Gamma'(\boldsymbol{k})$ and $\tau_c(\boldsymbol{k})$ as $k\to 0$ does not take place when $\boldsymbol{k}=0$ is neither the bottom nor the top of the band, or when there is finite density of levels in other exciton bands at the energy value of the $\boldsymbol{k}=0$ exciton we are now considering. The $\boldsymbol{k}=0$ exciton will be scattered into these states with finite probability, even when the phonon energy is neglected. In the previous paper we had to confine the discussion of the weak coupling limit to these cases.

In this paper we investigate the case of the simple exciton band where $\boldsymbol{k}=0$ is the *bottom* (or the *top*) of the band, and where there are no levels in the other exciton bands which have the same energy. This case, in spite of its standard nature, prevented us from quantitative discussion in I, due to the singular situation stated above. In order to dissolve this singularity, we make use of the damping theory in the present work. Special classes of graphs among all the irreducible graphs appearing in the expansion of the resolvent are summed up to infinite order in the exciton-phonon coupling, in such a way that the result is exact up to the sixth order. We find that the higher order processes such as the two and three phonon processes are important in determining the line-width, in conformity with the above statement that the single phonon scatterings are inseparable from each other for the excitons with small wave numbers. The dependence of the width upon g and T is just what is implied by the relation (1·4).

§ 2. Formulation of the problem in terms of the damping theory

Assuming only one exciton band with energy ε_k, the normalized line-shape of the exciton absorption band is given by (see Eq. (3·10) of I)

$$F(\hbar\omega)=(2\pi\hbar)^{-1}\int_{-\infty}^{+\infty}\langle(0|\exp(iHt/\hbar)|0)\exp(-iH_Lt/\hbar)\rangle_L\exp(-i\omega t)\,dt, \tag{2·1}$$

where $\hbar\omega$ is the photon energy, $|\boldsymbol{k})$ means the excited electronic state of the crystal with the $\boldsymbol{k}$-exciton, and $\langle\cdots\rangle_L$ means the average on the lattice vibrational

*) We mean by the "main part" the parts of the absorption band which are not very far from the peak compared with the half-value width.

states in the absence of an exciton. H_L is the Hamiltonian for this vibrational motion, while H is that for the composite system of an exciton and lattice vibration with the interaction V:

$$H=H_e+H_L+V. \tag{2·2}$$

It might be more satisfactory to say that H and H_L are the projections of the Hamiltonian operator for the total system of crystal electrons plus phonons upon the sub-spaces of one and no exciton respectively.

Introducing the operators defined by

$$\begin{aligned} G(E)&=\delta(E-H),\\ G_L(E)&=\delta(E-H_L), \end{aligned} \tag{2·3}$$

where $\delta(E)$ is the Dirac's δ-function, we can write Eq. (2·1) as

$$F(\hbar\omega)=\int_{-\infty}^{+\infty} dE\langle (0|G(E+\hbar\omega)|0)\, G_L(E)\rangle_L, \tag{2·4}$$

or in the representation in which H_L is diagonal with the energy eigenvalues E_{Ln}, we have an alternative form

$$F(\hbar\omega)=\sum_n \rho_n (0|G(E_{Ln}+\hbar\omega)|0)_{nn}, \tag{2·5}$$

where $\rho_n=\exp(-\beta E_{Ln})/\sum_n \exp(-\beta E_{Ln})$ is the statistical weight for the vibrational state n in the ground electronic state of the crystal.

Defining the resolvent by

$$R^{(\pm)}(E)=(H-E\mp i\eta)^{-1} \quad (\eta\to+0), \tag{2·6}$$

we can rewrite Eq. (2·3) as

$$G(E)=(2\pi i)^{-1}\{R^{(+)}(E)-R^{(-)}(E)\}. \tag{2·7}$$

The diagonal part of the resolvent, which is necessary for the calculation of the line-shape (2·5), can be written as

$$D^{(\pm)}(E)=R^{(\pm)}(E)_{diag.}=\{H_e+H_L-\mathcal{G}^{(\pm)}(E)-E\}^{-1}, \tag{2·8}$$

$$\mathcal{G}^{(\pm)}(E)=-\Delta(E)\pm i\Gamma(E) \quad (\Delta,\ \Gamma\text{: real operators}), \tag{2·9}$$

exactly, if the interaction V has the diagonal singularity, as van Hove showed in his work on the damping theory.[5] The diagonal operator $\mathcal{G}^{(\pm)}$ satisfies the integral equation

$$\mathcal{G}^{(\pm)}(E)=\{VD^{(\pm)}(E)\,V+VD^{(\pm)}(E)\,VD^{(\pm)}(E)\,V+\cdots\}_{id.} \tag{2·10}$$

where $\{\cdots\}_{id}$, the abbreviation for the "irreducible diagonal", means that one has only to take those intermediate states which are different from each other and from the initial state.

Since the (k, n') element of Eq. (2·8) can be written, for $E=E_{Ln}+\hbar\omega$, as

$$D^{(\pm)}(E_{Ln}+\hbar\omega)_{k,n'}=\{\varepsilon_k+E_{Ln'}-\mathcal{G}^{(\pm)}(E_{Ln}+\hbar\omega)_{kn'}-E_{Ln}-\hbar\omega\}^{-1}, \quad (2\cdot11)$$

we can write the line-shape function (2·5) as

$$F(\hbar\omega)=\pi^{-1}\sum_n \rho_n \frac{\Gamma(\hbar\omega+E_{Ln})_{0n}}{\{\varepsilon_0+\Delta(\hbar\omega+E_{Ln})_{0n}-\hbar\omega\}^2+\Gamma(\hbar\omega+E_{Ln})_{0n}^2}. \quad (2\cdot12)$$

As is well known, $\Delta_{kn}(E)$ and $\Gamma_{kn}(E)$ are the so-called shift (self-energy) and broadening of the state (k, n), if the appropriate energy value is inserted in E. They consist of an infinite number of infinitesimal contributions from each mode (specified by the wave number w) of lattice vibrations, or from the combinations of finite number of modes if we take into account the higher order terms in Eq. (2·10). Although the number of phonons for each w has a finite fluctuation, we see that the quantity which follows $\sum_l \rho_n$ in Eq. (2·12) has negligible fluctuation as regards the distribution (n). This follows from the central limit theorem. Within the relative error of the order of $N^{-1/2}$ where N is the total number of unit cells and may be made as large as one desires, we can put

$$F(\hbar\omega)=\frac{1}{\pi}\frac{\Gamma(\hbar\omega+E_{Ln})_{0n}}{\{\varepsilon_0+\Delta(\hbar\omega+E_{Ln})_{0n}-\hbar\omega\}^2+\Gamma(\hbar\omega+E_{Ln})_{0n}^2}. \quad (2\cdot13)$$

In the case which we dealt with in I in the weak coupling limit, $\bar{\Gamma}$ and $\bar{\Delta}$ can be taken to be more or less constant while ω changes within the range in which the absorption $F(\hbar\omega)$ is not small (see § 4 of I). Eq. (2·13) is then of Lorentzian shape. What we are going to investigate in this paper is the case in which $\bar{\Gamma}$ vanishes at $\hbar\omega=\varepsilon_0$ in the first approximation. The line shape is expected to differ very much from Lorentzian with strong asymmetry such that $F(\hbar\omega)$ has a tail on the high frequency side (provided that $m^*>0$) where $\Gamma(\hbar\omega+E_{Ln})$ increases with ω. In order to determine the line-shape (2·13), we have to solve the integral equation (2·10) for $\Delta(\hbar\omega+E_{Ln})_{kn}$ and $\Gamma(\hbar\omega+E_{Ln})_{kn}$ with variables k and a parameter ω.

Making use of the creation and annihilation operators a_k^* and a_k for the exciton, and b_w^* and b_w for the phonon, and taking the deformation potential model for the exciton-phonon interaction, we can write

$$\begin{aligned} H_e&=\sum_k \varepsilon_k a_k^* a_k, \\ H_L&=\sum_w \hbar\omega_w b_w^* b_w, \qquad (2\cdot14) \\ V&=\sum_k\sum_w \gamma_w a_{k+w}^* a_k (b_w+b_{-w}^*), \\ \gamma_w&=(\hbar/2NMu)^{1/2} E_d w^{1/2}, \quad \omega_w=uw, \qquad (2\cdot15) \end{aligned}$$

where M is the mass of a unit cell, u the sound velocity and E_d is the deformation potential constant.

Eq. (2·10) is now written down explicitly as

$$\overline{\mathcal{G}^{(\pm)}(E_{Ln}+\hbar\omega)_{kn}}=\sum_{w}\gamma_{w}^{2}\left\{\frac{\bar{n}_{w}}{\varepsilon_{k+w}-\overline{\mathcal{G}^{(\pm)}(E_{Ln}+\hbar\omega)_{k+w,n-1}}-\hbar\omega_{w}-\hbar\omega}\right.$$

$$\left.+\frac{\bar{n}_{w}+1}{\varepsilon_{k+w}-\overline{\mathcal{G}^{(\pm)}(E_{Ln}+\hbar\omega)_{k+w,n+1}}+\hbar\omega_{w}-\hbar\omega}\right\}$$

$$+(\text{higher order terms}), \tag{2·16}$$

where we have taken an average on the phonon numbers. To take the average independently in the numerator and the denominator on the right-hand side is justified on the same ground as was stated above.

Now we assume that the following three conditions are satisfied, putting off the thorough examination of them to § 4.

(1) *Elastic scattering.* For those w-values which make important contributions to the right hand side of Eq. (2·16), and for those $\hbar\omega$-values for which the absorption $F(\hbar\omega)$ is appreciable, we can neglect the phonon energy $\hbar\omega_{w}$ in the denominator of Eq. (2·16). With this assumption we can put n for $n\pm1$ which are suffixes to $\mathcal{G}^{(\pm)}$, as is easily seen from Eq. (2·11).

(2) *High temperature.* For the same w-values as are specified in (1), we can take the high temperature approximation for the phonon numbers. We can then put

$$\gamma_{w}^{2}\bar{n}_{w}=\gamma_{w}^{2}(\bar{n}_{w}+1)=E_{d}^{2}\kappa T/2NMu^{2}. \tag{2·17}$$

(3) *k-dependence of the solution.* As for the k-dependence of the solution $\overline{\mathcal{G}^{(\pm)}(\hbar\omega+E_{Ln})_{kn}}$, it is assumed that one can put

$$\overline{\Delta(\hbar\omega+E_{Ln})_{kn}}=\Delta_{0}+\delta\hbar^{2}k^{2}/2m^{*}+\Delta(\hbar\omega), \tag{2·18}$$

$$\overline{\Gamma(\hbar\omega+E_{Ln})_{kn}}=\Gamma(\hbar\omega), \tag{2·19}$$

for the above ranges of k and $\hbar\omega$. Here $\Delta(\hbar\omega)$ and $\Gamma(\hbar\omega)$ are independent of k, whereas Δ_{0} and δ is independent of k and $\hbar\omega$, although these quantities may of course depend on the temperature. As will be seen later, the leading terms in Δ_{0} and δ are of the first order in the coupling constant g, while $\Delta(\hbar\omega)$ and $\Gamma(\hbar\omega)$ are of the second order.*) We can now put the unrenormalized and the renormalized energy as

$$\varepsilon_{k}=\varepsilon_{0}+\hbar^{2}k^{2}/2m^{*}, \tag{2·20}$$

$$\tilde{\varepsilon}_{k}=(\varepsilon_{0}+\Delta_{0})+(1+\delta)\hbar^{2}k^{2}/2m^{*}=\tilde{\varepsilon}_{0}+\hbar^{2}k^{2}/2\tilde{m}^{*}. \tag{2·21}$$**)

With these assumptions, Eq. (2·16) is greatly simplified if we introduce the dimensionless quantities

*) The division into Δ_{0} and $\Delta(\hbar\omega)$ is not unique but only for the sake of convenience.

**) $\tilde{m}^{*}$ defined by Eq. (2·21) is different from the conventional renormalized mass. Roughly speaking, the latter is obtained by taking the second derivative of $\overline{\Delta(\varepsilon_{k}+E_{Ln})_{kn}}$ as regards k.

$$\{\hbar\omega-\tilde{\varepsilon}_0-\Delta(\hbar\omega)\}/\Gamma_0=x,\quad \Delta(\hbar\omega)/\Gamma_0=s,$$
$$\{\hbar\omega-\tilde{\varepsilon}_0\}/\Gamma_0=x+s=z,\quad \Delta_0/\Gamma_0=s_0, \tag{2·22}$$
$$\Gamma(\hbar\omega)/\Gamma_0=y>0,$$
$$(x+iy)^{1/2}=\zeta=ir\exp(-i\psi)\quad (0\leq\psi\leq\pi/2),$$
$$\{\hbar^2/2\tilde{m}^*\Gamma_0\}^{1/2}w=p, \tag{2·23}$$
$$Q(\boldsymbol{p})=(p^2-\zeta^2)^{-1}, \tag{2·24}$$

in terms of the energy unit

$$\Gamma_0=(8\pi^2)^{-1}\{v_0\tilde{m}^{*3/2}E_d^{\,2}\kappa T/\hbar^3Mu^2\}^2=g^2(\kappa T)^2/8\pi^2\tilde{m}^*u^2. \tag{2·25}$$

g is the demensionless coupling constant defined by

$$g=v_0\tilde{m}^{*2}E_d^{\,2}/\hbar^3Mu, \tag{2·26}$$

and v_0 is the volume of a unit cell.

Eq. (2·16) is now written, for $\boldsymbol{k}=0$, in a very simple form:

$$-s_0-s+iy=\pi^{-2}\int Q(\boldsymbol{p})\,d\boldsymbol{p}+\pi^{-4}\iint Q(\boldsymbol{p}_1)\,Q(\boldsymbol{p}_1+\boldsymbol{p}_2)\,Q(\boldsymbol{p}_2)\,d\boldsymbol{p}_1\,d\boldsymbol{p}_2$$
$$+(\text{higher order terms}). \tag{2·27}$$

In general, the $2n$-th order term as regards V in Eq.(2·10), or as regards γ in Eq. (2·16), includes $(2n-1)Q$'s, n-fold integration over $\boldsymbol{p}$'s and a factor π^{-2n}.

§ 3. Graphic calculation of damping

Our problem is now to solve Eq. (2·27) for the energy dependent damping y and shift (s_0+s) as functions of x and finally as functions of the energy $z=x+s$. The unknown y is also included in Q's. It is interesting to note that Eq. (2·27) includes no parameter except for the Debye cutoff w_0 of the phonon wave-number whose effect can be made included in s_0 as will be seen later. This means that the line-shape (2·13), or

$$F(\hbar\omega)=\frac{1}{\pi\Gamma_0}\frac{y(x)}{x^2+y(x)^2}=\frac{1}{\pi\Gamma_0}\frac{\sin 2\psi}{r^2}, \tag{3·1}$$

is similar for any temperatures when the width W, which is of the order of $\Gamma_0(\propto g^2T^2)$, is normalized, so far as the three conditions mentioned in § 2 are satisfied.

To begin with, let us solve Eq. (2·27) in the lowest order by taking into account only the first term on the right-hand side, in order to get a rough idea on the form of the solution. In calculating

$$\int Q(\boldsymbol{p})\,d\boldsymbol{p}=4\pi\int_0^{p_0}dp+4\pi\zeta^2\int_0^{p_0}(p^2-\zeta^2)^{-1}\,dp,$$

we note that the Debye cutoff w_0, or

$$p_0=\{\hbar^2/2\widetilde{m}^* I'_0\}^{1/2} w_0=2\pi g^{-1}(\hbar u w_0/\kappa T) \tag{3·2}$$

in reduced unit, can be replaced by ∞ in the second integral, if

$$p_0 \gg |\zeta|, \quad \text{or} \quad \hbar^2 w_0^2/2m^* \gg I'_0|\zeta|^2, \tag{3·3}$$

that is, if the width of the absorption peak is much smaller than the exciton band width. This condition is satisfied so far as the exciton-phonon coupling is small, with which case we are concerned here. On the other hand, the finiteness of w_0 or p_0 is essential for the first term, which makes energy-independent real contribution.

The first approximation for Eq. (2·27) then gives

$$-s_0=(4/\pi)p_0, \quad -s=-2r\cos\psi, \tag{3·4}$$

$$r^2\sin 2\psi=2r\sin\psi, \tag{3·5}$$

with the line-shape function

$$\begin{aligned} F(\hbar\omega) &= (\pi I'_0)^{-1} 2z^{-2}(z-1)^{1/2} \quad (z>1), \\ &= 0 \qquad\qquad\qquad\quad (z<1), \end{aligned} \tag{3·6}$$

which satisfies the normalization condition

$$\int F(\hbar\omega)\, d\hbar\omega = 1, \tag{3·7}$$

in spite of the approximation we have made.

On the high frequency side such that $\hbar\omega-\varepsilon_0 \gg I'_0$, or $z \gg 1$, we have $F(\hbar\omega) \propto z^{-3/2}$, which is nothing but the tail of the exciton absorption band due to the indirect transition. For these z-values, the higher order terms in Eq. (2·27) are very small, the $2n$-th order (as regards the interaction V) term being of the order of $z^{-(n/2-1)}$ as is easily verified by recalling the definition (2·24) and that $\int dp$ contributes a factor of the order of $|\zeta| \sim z^{1/2}$. However, to the line-shape of the main part such that $|z|$ is of the order of unity contribute all the higher order terms with the same order of magnitude; we have therefore to sum up important terms if not all.

Recalling that we have to take only the irreducible diagonal part in Eq. (2·10), and that the absorption and the emission of a phonon contribute the same magnitude of quantities due to the conditions (1) and (2) of § 2, we can write down the terms in Eq. (2·27) by Feynman graphs, as shown in Fig. 1 for the lowest order terms. For instance, the fourth order term corresponds to successive emissions (or emission and absorption, or absorptions) of two phonons followed by successive absorptions (or absorption and emission, or emissions) of them in the same order. The terms such as shown in Fig. 2 are to be omitted according to the definition of the irreducibility, because their effects are already taken into

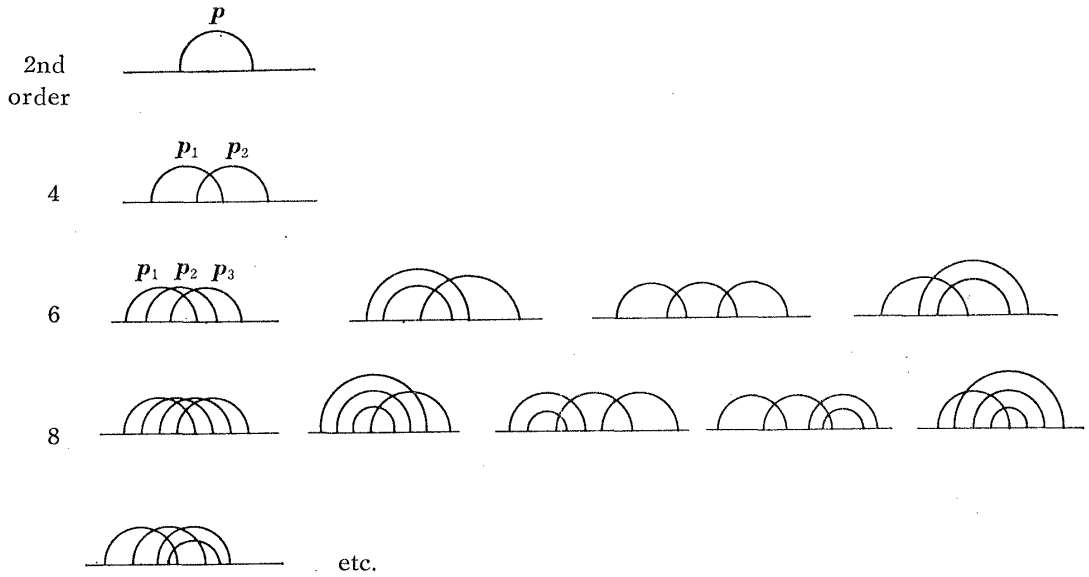

Fig. 1. Graphic representation of the terms appearing in Eq. (2·27).

Fig. 2. Typical graphs which are not to be included in Eq. (2·27).

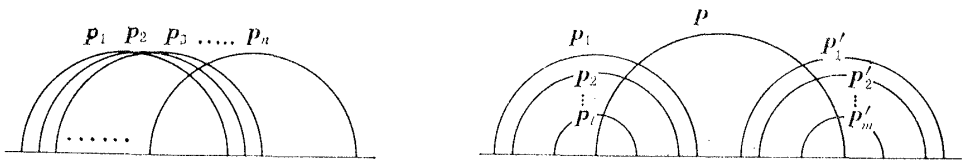

Fig. 3. The two classes of graphs which have been taken into account in calculating the damping.

account in the shift and broadening of each level.

Among the graphs shown in Fig. 1, we have two series of graphs, represented by Fig. 3a and b. Though they are rather special types of graphs, all terms up to the sixth order, and some of the higher order terms, belong to one of them. The second and fourth order terms can be taken to belong to any of the two, while for the sixth and higher order terms the classification is unique. Assuming that the convergence is not too slow, we take into account only those graphs given in Fig. 3.

The first graph of Fig. 3, which is of the $2n$-th order, contributes

$$(-s_0-s+iy)^{(a)}_{2n}=\pi^{-2n}\int\int\cdots\int d\boldsymbol{p}_1\,d\boldsymbol{p}_2\cdots d\boldsymbol{p}_n$$

$$\times Q(\boldsymbol{p}_1)\,Q(\boldsymbol{p}_1+\boldsymbol{p}_2)\cdots Q(\boldsymbol{p}_1+\boldsymbol{p}_2+\cdots+\boldsymbol{p}_n)\,Q(\boldsymbol{p}_2+\cdots+\boldsymbol{p}_n)\cdots Q(\boldsymbol{p}_n), \qquad (3\cdot8)$$

while the second graph, of the $2(l+m+1)$-th order, contributes

$$(-s_0-s+iy)^{(b)}_{2l,2m}=\pi^{-2(l+m+1)}\int\cdots\int dp_1\,dp_2\cdots dp_l\,dp\,dp_1'\,dp_2'\cdots dp_m'$$
$$\times Q(p_1)\cdots Q(p_1+\cdots+p_l)\,Q(p_1+\cdots+p_l+p)\,Q(p_1+\cdots+p_{l-1}+p)\cdots Q(p)$$
$$\times Q(p+p_1')\cdots Q(p+p_1'+\cdots+p_m')\,Q(p_1'+\cdots+p_m')\,Q(p_1'+\cdots+p_{m-1}')\cdots Q(p_1'). \tag{3·9}$$

Introducing the convolution

$$Q^{(2)}(p)=\int Q(-p')\,Q(p'+p)\,dp'=\frac{\pi^2}{ip}\ln\frac{1-(p/2\zeta)}{1+(p/2\zeta)}, \tag{3·10}$$

where the branch of the logarithmic function is such that it tends to zero as $p\to 0$, we can easily calculate Eq. (3·9) as

$$(-s_0-s+iy)^{(b)}_{2l,2m}=\int dp\,\pi^{-2}Q(p)\,\{\pi^{-2}Q^{(2)}(p)\}^{l+m}\,dp. \tag{3·11}$$

Eq. (3·8) can also be brought into the same form. If we put $p_1+p_2+\cdots+p_n=p$, the last $(n-1)Q$'s can be written as

$$Q(p-p_1)\,Q(p-(p_1+p_2))\cdots Q(p-(p_1+\cdots+p_{n-1})),$$

each of which can be combined with the corresponding factor among the first $(n-1)Q$'s in Eq. (3·8), resulting in $Q^{(2)}(p)$. We have, therefore,

$$(-s_0-s+iy)^{(a)}_{2n}=\int\pi^{-2}Q(p)\,\{\pi^{-2}Q^{(2)}(p)\}^{n-1}\,dp. \tag{3·12}$$

Among the $2n$-th order terms, there are n different graphs of the type (b) corresponding to $l=0, 1, \cdots, n-1$, whereas there is only one of the type (a). Taking care of the exceptional cases of $n=1$ and $n=2$, we can write

$$-s_0-s+iy=\int dp\,\pi^{-2}Q(p)[1+\pi^{-2}Q^{(2)}(p)+\sum_{n=3}^{\infty}(n+1)\,\{\pi^{-2}Q^{(2)}(p)\}^{n-1}]. \tag{3·13}$$

The integration path along the real axis p can be replaced by the radial path with phase angle $-\psi$. Transforming the variable p into ϕ by

$$p=-2i\zeta\tan\phi\quad(0<\phi<\pi/2), \tag{3·14}$$

we have

$$\int dp\,\pi^{-2}Q(p)\,\{\pi^{-2}Q^{(2)}(p)\}^{n-1}=(32/\pi)\,r^{-(n-2)}\exp\{i(n-2)\psi\}$$
$$\times\int_0^{\pi/2}(\phi/\tan\phi)^{n-3}\phi^2(1+3\sin^2\phi)^{-1}\,d\phi. \tag{3·15}$$

For $n=2$, we have to be a little more careful since we have a contribution $4i\psi$ when we change the integration path in the manner stated above. At the

same time, the Debye cutoff p_0, which corresponds to the upper limit $\phi=\pi/2-2|\zeta|/p_0$ (see Eq. (3·14)), must be taken into account in the ϕ-integration of Eq. (3·15), since otherwise the integral diverges logarithmically. Thus we have

$$\int d\boldsymbol{p}\,\pi^{-2}Q(\boldsymbol{p})\,\{\pi^{-2}Q^{(2)}(\boldsymbol{p})\}=4i\psi+(32/\pi)\int_0^{\frac{\pi}{2}-\frac{2|\zeta|}{p_0}}\frac{\phi\tan\phi}{1+3\sin^2\phi}\,d\phi$$

$$=4i\psi+\int_0^{\pi/2}\left\{\frac{32}{\pi}\,\frac{\phi\tan\phi}{1+3\sin^2\phi}-\frac{4}{\pi/2-\phi}\right\}d\phi+4\ln(\pi p_0/4)-4\ln r. \qquad (3\cdot16)$$

Making use of Eqs.(2·22), we can write Eq. (3·13) as follows.

$$s_0=-4p_0/\pi-4\ln(\pi p_0/4)+\int_0^{\pi/2}d\phi\left\{\frac{4}{\pi/2-\phi}-\frac{32}{\pi}\,\frac{\phi\tan\phi}{1+3\sin^2\phi}\right\}, \qquad (3\cdot17)$$

$$s=2r\cos\psi+4\ln r-\sum_{n=3}^{\infty}2c_n r^{-(n-2)}\cos(n-2)\psi, \qquad (3\cdot18)$$

$$\frac{\sin2\psi}{2\psi}=r^{-1}\frac{\sin\psi}{\psi}+2r^{-2}+\sum_{n=3}^{\infty}c_n r^{-n}\frac{\sin(n-2)\psi}{\psi}, \qquad (3\cdot19)$$

$$c_n=16(n+1)\pi^{-1}\int_0^{\pi/2}d\phi\,(\phi/\tan\phi)^{n-3}\phi^2(1+3\sin^2\phi)^{-1}. \qquad (3\cdot20)$$

As is evident from Eqs. (2·25) and (3·2), the energy independent shift $\Delta_0=\Gamma_0 s_0$ which is renormalized in $\tilde{\varepsilon}_0$, is expressed as $0(g)+0(g^2\ln(1/g))+0(g^2)+$ higher order terms which would have been obtained if we had taken into account the

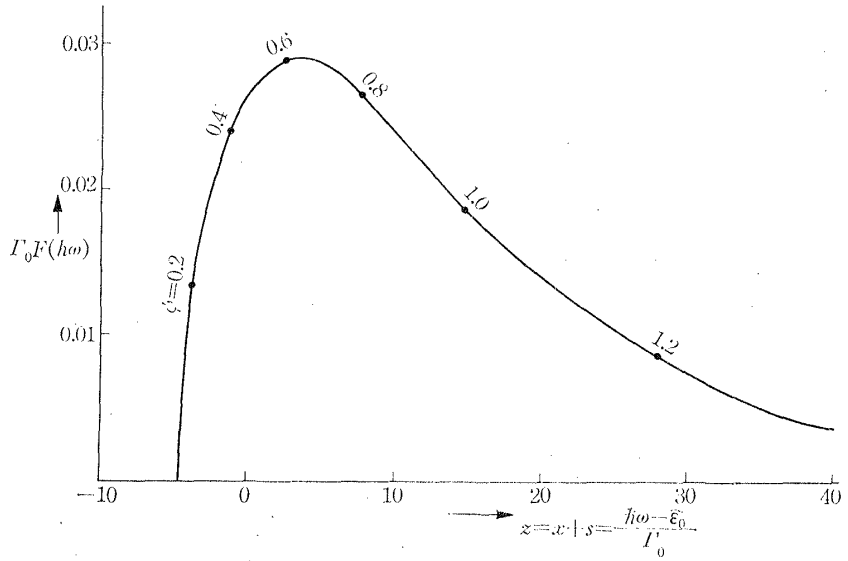

Fig. 4. The line-shape of the exciton absorption band in the case that $\boldsymbol{k}=0$ is the bottom of the exciton energy band. The unit of energy, Γ_0, is given by Eq. (2·25).

Debye cutoff in Eq. (3·15) for $n>2$. On the other hand, the energy dependent shift $\Delta(\hbar\omega)=s\Gamma_0$ as well as the broadening $\Gamma(\hbar\omega)=y\Gamma_0$ consists of a number of terms whose relative magnitudes do not depend upon the coupling constant, so far as the main part of the absorption band is concerned.

After calculating the integral (3·20) by numerical integration, we have solved the equation (3·19) for r as a function of ψ. With the help of Eq. (3·18) we have obtained the line-shape (3·1) as a function of the energy $z=x+s$. The result is shown in Fig. 4. It is remarkable that the half-width $z_2-z_1=19.2-(-3.6)=22.8$ is twelve times as large as the value $z_2-z_1=2.91-1.03=1.88$ which is obtained in the lowest approximation (3·6). Comparing the numerical values of the various terms in Eqs. (3·18) and (3·19), we find that the two and three phonon processes make contributions as large as the one phonon process does. Since the peak is at $z_0=4.0$, the asymmetry A of the line-shape, which was defined by Eq .(4·14) of I, is given by $(z_1+z_2-2z_0)/(z_2-z_1)=0.33$. The total area is calculated to be 0.95, while it should be unity if we could solve Eq. (2·27) exactly.

§ 4. Discussion

We must now examine whether and under what conditions the assumptions made in §§ 2 and 3 are valid. We begin with the assumption (3) of § 2. Confining ourselves to the lowest order approximation, we put Eqs. (2·18) and (2·19) in the denominator on the right-hand side of Eq. (2·16), and calculate the $\boldsymbol{k}$-dependent $\overline{\mathcal{G}^{(\pm)}(E_{Ln}+\hbar\omega)_{kn}}$. With the use of Eqs. (2·22) and (2·23), we can write

$$\overline{\mathcal{G}_{\boldsymbol{k}}^{(+)}}-\overline{\mathcal{G}_{0}^{(+)}}=\pi^{-2}\Gamma_0\int d\boldsymbol{p}[\{(\boldsymbol{p}+\boldsymbol{q})^2-\zeta^2\}^{-1}-\{\boldsymbol{p}^2-\zeta^2\}^{-1}], \tag{4·1}$$

where we have put

$$q=\{\hbar^2/2\tilde{m}^*\Gamma_0\}^{1/2}k. \tag{4·2}$$

Making use of the assumption (3·3), we get

$$\begin{aligned}\overline{\mathcal{G}_{\boldsymbol{k}}^{(+)}}-\overline{\mathcal{G}_{0}^{(+)}}=&-(4/3\pi)(\hbar^2w_0^2\Gamma_0/2\tilde{m}^*)^{1/2}(k/w_0)^2\{1+2(\zeta/p_0)^2+\cdots\}\\&-(4/15\pi)(\hbar^2w_0^2\Gamma_0/2\tilde{m}^*)^{1/2}(k/w_0)^4\{1+9(\zeta/p_0)^2+\cdots\}+\cdots.\end{aligned} \tag{4·3}$$

The ratio of the second term to the first term on the right-hand side of Eq. (4·3) is of the order of $(k/w_0)^2\sim(\zeta/p_0)^2$ for those $\boldsymbol{k}$-values which make important contributions to the line-shape of the main part, as is seen from Eqs. (2·23) and (2·24). Neglecting $(\zeta/p_0)^2$ in view of the assumption (3·3), we see that only the real part of $\overline{\mathcal{G}_{\boldsymbol{k}}^{(+)}}$ is $\boldsymbol{k}$-dependent, in the form given by Eq. (2·18), and

$$\delta=(4/3\pi)(2\tilde{m}^*\Gamma_0/\hbar^2w_0^2)^{1/2}=(2/3\pi^2)(\kappa T/\hbar uw_0)\,g \tag{4·4}$$

is in fact energy independent as was assumed there. It is not difficult to see

that this conclusion is not modified even when we take into account the higher order terms in Eq. (2·16).

Since the values of those $\boldsymbol{w}$'s which make important contributions to Eq. (2·16) is of the order of $(2\tilde{m}^*\Gamma_0/\hbar^2)^{1/2}|\zeta|$ because of Eqs. (2·23) and (2·24), we see that the assumptions (1) and (2) of § 2 can be written as

$$\hbar u(2\tilde{m}^*\Gamma_0/\hbar^2)^{1/2}|\zeta| \ll \Gamma_0|\zeta|^2, \tag{4·5}$$

and

$$\hbar u(2\tilde{m}^*\Gamma_0/\hbar^2)^{1/2}|\zeta| \ll \kappa T. \tag{4·6}$$

As $\Gamma_0|\zeta|^2$ is of the order of the half-value width

$$W=23\,\Gamma_0=0.3\,g^2(\kappa T)^2/m^*u^2, \tag{4·7}$$

the conditions (4·5) and (4·6) can be written as

$$2\tilde{m}^*u^2 \ll W \ll (\kappa T)^2/2\tilde{m}^*u^2, \tag{4·5′ and 6′}$$

or

$$T \gg T_0=2.6\,\tilde{m}^*u^2/\kappa g, \tag{4·5″}$$

and

$$g \ll 1. \tag{4·6″}$$

When the temperature is lower than T_0 defined by Eq. (4·5″), we must take into account the phonon energy in the exciton-phonon scattering. In this case, the width W' is given by Eq. (7·1) of I, which can be written as

$$W'=(2/\pi)\,g\kappa T \quad (2\tilde{m}^*u^2 \ll \kappa T \ll \kappa T_0), \tag{4·8}$$

$$=(4/\pi)\,g\tilde{m}^*u^2 \quad (\kappa T \lesssim 2\tilde{m}^*u^2), \tag{4·9}$$

with the use of Eqs. (7·2) and (7·3) of I. It is interesting to note that the value (4·7) is larger or smaller than the value (4·8) according as $T \gtrless T_0'=2.1\,\tilde{m}^*u^2/\kappa g$. Since the larger half value width is more effective, this condition is in qualitative accordance with the condition (4·5″). That is, the present theory is consistent with the result obtained in the previous paper, as regards the region of validity, although they deal with different regions by different methods. As for the line-shape, however, a more quantitative discussion might be necessary for the inelastic region $T \lesssim T_0$.

Now the condition (3·3) for the weak coupling is written as

$$T \ll \hbar u w_0/\kappa g. \tag{4·10}$$

The conditions (4·6″) and (4·10) can be combined into a single condition

$$\left(1+\frac{\kappa T}{\hbar u w_0}\right) g \ll 1. \tag{4·11}$$

We see, from Eq. (4·4), that $\delta \ll 1/10$ as far as the condition (4·11) is satisfied.

When the left-hand side of the condition (4·11) is much larger than unity, either due to high temperature or due to a strong coupling constant, the line-shape is Gaussian, as we have shown in I (see Eqs. (5·7) and (7·8) of I). Systematic investigations on the effect of the exciton-phonon interaction on the exciton states, for the whole range of the coupling constant, have been carried out by Haken.[6]

Since $\hbar u w_0/\tilde{m}^* u^2 = (\hbar^2 w_0^2/\tilde{m}^*)/(\hbar u w_0)$ is usually of the order of 100 in real crystals, there is a fairly large range of the temperature which satisfies the conditions (4·5″) and (4·10) simultaneously.

Putting $M/v_0 = 3$ gr/c.c., $E_d = 6$ ev, $u = 0.5 \cdot 10^6$ cm/sec and $m^* =$ true electron mass, we have $g = 0.05$ and the condition (4·5″) for elastic scattering becomes $T \gg 70$°K. The half-value width is given by $0.5 \cdot 10^{-2}$ ev at $T = 300$°K.

Since the exciton wave-numbers which make appreciable contribution to the line-shape in the main part of the absorption band are very small, the Ansatz (2·15) for the coupling coefficient γ_w with constant E_d, and the Ansatz (2·20) of the parabolic band structure are fairly good approximations.*) For those w-values which are comparable to or larger than the reciprocal α of the exciton radius, the coefficient should be multiplied by the screening factor (2·18) of I. It is easy to show that such w-values do not contribute to the main part of the absorption band if the half-value width W is small compared with $\hbar^2\alpha^2/2m^*$, that is, if the exciton absorption peak is well separated from other exciton peaks or the continuum absorption.**) On the other hand, the screening factor should have been taken account of in the calculation of the energy independent shift $\Delta_0 = \Gamma_0 s_0$. While this effect is reflected on the temperature *shift* of the peak, it does not affect the line-*shape* in the main part.

Another remark should be made here concerning the line-shape of the low energy tail. In Fig. 4, we see that the absorption curve has a clear-cut threshold on the low energy side. That might seem somewhat embarrassing in view of the existing theories on the line-shape. Dexter[7] discussed the line-shape in the tail part in connection with the Urbach-Martienssen rule,[8] essentially on the basis of the adiabatic approximation which seems to be appropriate for this part. According to his result, the tail never shows such threshold, though it decays rapidly with decreasing energy. It is to be noted that the damping theory, though suitable for the main part of the absorption peak (and also for the high energy tail as has been shown above), is not very powerful for the (low energy) tail. If we could have included all the terms appearing in Eq. (2·27), the low energy tail without threshold would have been obtained, but it would not be a

*) Even in the case in which m^* is a tensor, or the energy surface is warped, the main conclusion will not be changed.

**) Note that the binding energy of the electron and the hole in the exciton is given by $\hbar^2\alpha^2/2\mu$ if one takes the hydrogen model. μ is the reduced mass for the pair, and is of the same order of magnitude with the translational effective mass m^*.

practical way of treating this part. As is well known, the adiabatic approximation and the damping theory are usually complementary to each other in the general theory of line-shape.

As for the low energy tail of the exciton absorption band, which seems to be due to the strongly deformed parts of the crystal, the quadratic term of the exciton-phonon interaction is expected to play an important rôle,[9] especially in view of the Urbach-Martienssen rule. The comparison of our results with experiments will be deferred until we discuss the effect of the quadratic term on the tail part more fully.

§ 5. Conclusion

We have investigated the line-shape of the exciton absorption band in such case that $\boldsymbol{k}=0$ is the bottom (or the top) of the exciton energy band, and that there are no levels (with $\boldsymbol{k}\neq 0$) in the other exciton bands or in the ionization continuum which have the same energy as the $\boldsymbol{k}=0$ exciton with which we are concerned.

When the exciton-lattice coupling is small as is specified by the condition (4·11), and the temperature is not too low (Eq. (4·5″)), the line shape of the main part of the absorption band is expected to be given by the curve of Fig. 4,*) which is shown in terms of the energy unit Γ'_0(Eq. (2·25)). The asymmetry is very strong ($A=0.33$), and the half-value width is given by Eq. (4·7). The dependence of the latter on the coupling constant and on the temperature are rather strong. The high energy tail of the absorption curve coincides with the result obtained by the second order perturbation theory (the indirect transition).

Since the wave-numbers of the exciton and the phonon which make important contributions to the line-shape of the main part are very small, we can use the high temperature approximation for the expectation value of the phonon number, and at the same time we can neglect the phonon energy in the exciton-phonon scattering. In the same reason, the exciton band structure in the neighborhood of $\boldsymbol{k}=0$ only is important in determining the line-shape.

The conclusions stated above are subject to no essential change even when the effective mass is tensor, or the energy surface is warped in the neighborhood of $\boldsymbol{k}=0$, if the appropriate value of m^* (averaged for all directions) is inserted. When $\boldsymbol{k}=0$ is the top of the exciton energy band, the line-shape is the mirror image of Fig. 4 with the sign reversal of the abscissa—the energy measured from the renormalized energy $\tilde{\varepsilon}_0$.

However, the above conclusions fail completely when the exciton energy ε_k increases in some directions but decreases in other directions as k increases from zero. Such a case was investigated in I.

The comparison with experiment will be left to the future when we investi-

*) Except for the low energy edge. See the discussion towards the end of § 4.

gate more fully the effect of the quadratic term of the exciton-phonon interaction on the low energy tail part, in connection with the Urbach-Martienssen rule.

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