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Interference of an Exciton with the Continuum Absorption Caused by the Electron-Hole Exchange Interaction

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When an exciton absorption overlaps a continuum background absorption, the exciton line is broadened and interferes with the background. The interference effect is investigated for an exciton superposed on the continuum absorption of its spin-orbit partner channel. For that case it is shown that the electron-hole exchange interaction is the important factor for the interference. A line-shape formula is derived which properly takes account of the interference caused by the exchange interaction, and the result is compared with experiment for NaBr with reasonable agreement.

I. INTRODUCTION

When a discrete level is embedded in a continuum in excitation spectra, the discrete state can decay into ionized states of the background continuum, and as a consequence, the line shape gets a characteristic asymmetric peak.

This interference effect (Fano effect) was first considered by Fano[1] for the atomic excitation spectra; it was shown that the interference causes a rather drastic change of the line shape from a simple superposition of the discrete and continuous spectra.

As for the optical spectra of solids, a similar situation occurs for excitons overlapping with a continuous band-to-band transition spectrum. Phillips and co-workers stressed the importance of the Fano effect in the fundamental spectra of rare-gas solids.[2,3] Toyozawa *et al.*[4] discussed the interference effect from a somewhat different approach on the basis of their general formalism for the fundamental optical spectra. Several model calculations[5-7] have also been done for exciton resonance embedded in a continuum. In these theoretical calculations, only a single conduction band and a single valence band are considered explicitly; in other words, they consider a single-channel problem, when we understand the term "channel" to mean collectively electron-hole pairs generated by the same conduction and valence bands. Since the continuum and the exciton superposed on it belong to the same channel, the interference occurs through the intrachannel interaction. Coulomb interaction between electron and hole is responsible for such an intrachannel interaction.

In the actual optical-absorption spectra of insulating crystals, however, we observe usually more than one channel. A typical example is the two channels corresponding to the two valence bands split by the spin-orbit interaction, as encountered, for example, in alkali halides. Interference of such spin-orbit-split two channels is the subject of the present paper.

The most conspicuous effect of such an interchannel interaction can already be seen in the exciton doublet absorption of alkali halides. The intensity ratio of the doublet deviates considerably from 2:1, a normally expected value in the absence of the interchannel mixing. The topic was previously discussed by Toyozawa and the present author,[8] and the exchange interaction between electron and hole is known to be responsible for such an interchannel mixing. Recent experiments for CuBr-CuCl solid solutions presented a good demonstration of the theory.[9]

In this paper, we generalize the theory so as to include the continuum absorption as well, and see the effect of the electron-hole exchange interaction on the whole line shape. We are particularly interested in the case where the binding energy of the exciton is a little smaller than the spin-orbit splitting of the valence band, so that the exciton of the second channel is superposed on the continuum of the first channel. The exchange interaction then gives rise to an interference of the exciton line with the continuum. Such a situation is certainly realized in alkali bromides, and we can compare our results with experiment.

In Sec. II, we consider the interchannel interaction between the spin-orbit-split two channels, having in mind simple insulating crystals with an s-like conduction band and a p-like valence band split by the spin-orbit interaction. In the usual theory of the Wannier exciton, both the Coulomb and the exchange interactions between electron and hole can cause interchannel mixing, but in the present specific case, it is shown that only the exchange interaction gives rise to mixing of the two channels. A line-shape formula is then obtained using a Green's-function technique to describe the interference effects caused by the exchange interaction. The result is used in Sec. III to analyze the fundamental optical spectra of NaBr. In Sec. IV, conclusions are summarized.

We shall entirely rely upon the Wannier exciton theory[10–12] and use the Elliott hydrogenic model.[13]

II. INTERFERENCE OF SPIN-ORBIT-SPLIT TWO CHANNELS

We consider a simple band structure commonly found in many ionic crystals and rare-gas solids: The conduction band has a minimum at $\vec{k}=0$ of the standard shape and of s symmetry. It is twofold degenerate. The two states will be specified by an index n. The p-like valence band, possessing its top at $k=0$, is split by the spin-orbit interaction into a fourfold degenerate $p_{3/2}$ band and a twofold $p_{1/2}$ band. We distinguish these six valence-band states by an index m. We assume that the $p_{3/2}$ and $p_{1/2}$ valence bands can be characterized by a common spherical mass, neglecting fluting of the constant energy surface. This assumption is permissible since the reduced mass of exciton is primarily determined by the spherical electron mass, which is much lighter than the hole mass in alkali halides. We shall hereafter refer to the electron-hole pairs with a $p_{3/2}$ hole and a $p_{1/2}$ hole as belonging to the A and B channels, respectively.

We aim at taking into account mixing of the two channels, but for the moment we neglect it and regard the two channels as independent. The effective-mass equation for the exciton is then written

$$\sum_{\vec{\beta}'} H_0(\vec{\beta},\vec{\beta}')F_\nu(\vec{\beta}')=E_\nu F_\nu(\vec{\beta}) \;, \tag{1}$$

$$H_0(\vec{\beta},\vec{\beta}')=\frac{1}{N}\sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{\beta}-\vec{\beta}')}W(\vec{k})+\delta_{\vec{\beta}\vec{\beta}'}v(\vec{\beta})$$

$$+\begin{cases} +\frac{2}{3}\lambda & \text{for the } p_{1/2} \text{ hole } (B \text{ channel}) \\ -\frac{1}{3}\lambda & \text{for the } p_{3/2} \text{ hole } (A \text{ channel}) \end{cases}$$

We have $W(\vec{k})=\hbar^2k^2/2\mu$, μ being the reduced mass, and $v(\vec{\beta})$ is an appropriate attractive Coulomb interaction. The index ν refers to the quantum number of exciton states. The total wave vector $\vec{K}$ is taken to be infinitesimal, since we consider direct excitons. As we forget for the moment the interchannel effects, the Hamiltonian H_0 is diagonal with respect to the band indices m and n, and the envelope function F_ν is common to all the band pairs (m,n).

The conventional method of Wannier for solving Eq. (1) is to transform it into a differential equation. When the potential $v(\vec{\beta})$ is taken to be hydrogenic, then the problem reduces to that of a hydrogen atom. By using that solution, the optical-absorption spectrum

$$I(\hbar\omega)=\sum_\nu |F_\nu(0)|^2\delta(\hbar\omega-E_\nu) \tag{2}$$

can be calculated.[13,14] Only s-like envelope functions can contribute to it. The index ν refers to discrete as well as continuum states. Figure 1 shows schematically the optical spectra according to the Elliott theory.[13] The intensity of the A channel is twice as large as that of the B, because of the difference of the degeneracy of the valence $p_{3/2}$ and $p_{1/2}$ levels.

Two cases can occur according to the relative magnitudes of the spin-orbit splitting λ and the exciton binding energy E_B. When $\lambda \ll E_B$ as in Fig. 1(a), the doublet exciton absorption is well separated from the continuum absorption, whereas if $\lambda \gtrsim E_B$ as in Fig. 1(b) the B exciton is embedded in the continuum of the A channel. In any case, the spectra are simple so long as we ignore the interchannel interaction; the intensity of the A exciton is twice as strong as that of the B exciton, and besides, the B exciton overlapping with the continuum remains a sharp δ function. This situation changes however when we take account of the interchannel interaction. In fact, in our previous paper, we have considered the case (a) and investigated the variation of the intensity ratio of the A and B excitons due to the electron-hole exchange interaction.[8] The purpose of the present section is to generalize the theory so as to include the continuum states as well and thereby to consider broadening of the B exciton due to the interchannel interaction.

The plan of the remainder of this section is as follows: We first consider the origin of the interchannel interaction. The residual electron-hole interaction not included in the Hamiltonian H_0 is the exchange interaction

$$\langle mn\vec{\beta}\,|\,V_x\,|\,m'n'\vec{\beta}'\rangle=\delta_{\vec{\beta}\vec{0}}\delta_{\vec{\beta}'\vec{0}} \times\sum_{\vec{R}} e^{i\vec{K}\cdot\vec{R}}(n\vec{0},m'\vec{R}\,|\,g\,|\,m\vec{0},n'\vec{R}) \tag{3}$$

and off-diagonal parts of the Coulomb interaction

$$\langle mn\vec{\beta}\,|\,V_C\,|\,m'n'\vec{\beta}'\rangle=-\,\delta_{\vec{\beta}\vec{\beta}'}(n\vec{\beta},m'\vec{0}\,|\,g\,|\,n'\vec{\beta},m\vec{0}) \;, \tag{4}$$

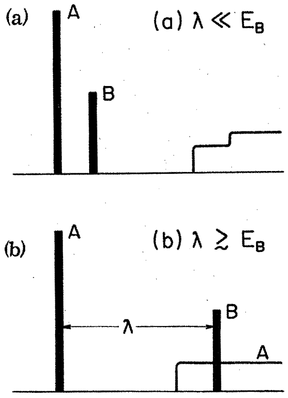

FIG. 1. Optical-absorption spectra due to the independent A and B channels for (a) $\lambda \ll E_B$ and (b) $\lambda \gtrsim E_B$ cases.

whose diagonal ($m=m', n=n'$) terms are already included in H_0. Expressions (3) and (4) are obtained in the standard theory of Wannier exciton under the assumption that the Wannier functions are sufficiently well localized so that their overlap can be neglected. The basis ket $|mn\vec{\beta}\rangle$ stands for a state in which the valence electron m is excited to a conduction band n and the electron-hole relative separation is $\vec{\beta}$. The two-electron integrals with respect to the Wannier functions

$$(n\vec{0}, m'\vec{\mathrm{R}}\,|g|\,m\vec{0}, n'\vec{\mathrm{R}}) = \int d\vec{\mathrm{r}}_1 \int d\vec{\mathrm{r}}_2$$

$$\times a^*_{n\vec{0}}(\vec{\mathrm{r}}_1) a^*_{m'\vec{\mathrm{R}}}(\vec{\mathrm{r}}_2)(e^2/|\vec{\mathrm{r}}_1 - \vec{\mathrm{r}}_2|) a_{m\vec{0}}(\vec{\mathrm{r}}_1) a_{n'\vec{\mathrm{R}}}(\vec{\mathrm{r}}_2)$$

are understood to include spin inner products. We first evaluate the matrix elements of these interactions for our problem. It will be seen that the Coulomb interaction does not couple the two channels split by the spin-orbit interaction. Therefore, we are left only with the exchange interaction as the origin of the interchannel mixing. Having established this, we proceed to compute the line shape of the optical-absorption spectra. The result will be compared with experiment for NaBr in Sec. III.

Let us first prove that the interchannel matrix elements of the Coulomb interaction vanish. Consider the states

$$\textstyle\sum_{\vec{\beta}} F_\nu(\vec{\beta})\,|mn\vec{\beta}\rangle \quad \text{and} \quad \sum_{\vec{\beta}'} F_{\nu'}(\vec{\beta}')\,|m'n'\vec{\beta}'\rangle$$

belonging to different channels. Since we are considering optically allowed states, we understand both F_ν and $F_{\nu'}$ to be s-like. Matrix element of the direct Coulomb interaction between these two states becomes

$$-\int\int \Big[\textstyle\sum_{\vec{\beta}} F_\nu(\vec{\beta}) F_{\nu'}(\vec{\beta}) a^*_n(\vec{\mathrm{r}}_1 - \vec{\beta}) a_{n'}(\vec{\mathrm{r}}_1 - \vec{\beta})\Big]$$

$$\times g(|\vec{\mathrm{r}}_1 - \vec{\mathrm{r}}_2|) a^*_{m'}(\vec{\mathrm{r}}_2) a_m(\vec{\mathrm{r}}_2) d\vec{\mathrm{r}}_1 d\vec{\mathrm{r}}_2, \qquad (5)$$

using the expression (4) for the Coulomb interaction. We first take the spin inner product for $\vec{\mathrm{r}}_1$. Since the conduction-band indices n and n' should be either $s\alpha$ or $s\beta$ in the present problem, n and n' must be the same in order that the integral may not vanish. Next, in view of the s symmetry of the conduction-band Wannier function and of the envelope functions, the quantity in the bracket is totally symmetric with respect to $\vec{\mathrm{r}}_1$. Therefore, in order that the integral may remain nonvanishing, a_m and $a_{m'}$ must be of the same symmetry. That is, however, impossible since they belong to valence bands of different symmetry ($p_{3/2}$ and $p_{1/2}$), which means that the integral (5) itself should vanish. In this way, we have shown that the Coulomb interaction does not couple the two spin-orbit-split channels, under the assumption that the Wannier functions are sufficiently well localized that their overlap can be neglected.

Having thus known that interchannel matrix elements of the Coulomb interaction vanish, we now see that the interchannel interaction arises from the electron-hole exchange interaction alone. In considering the exchange interaction, it is convenient to use symmetrized electron-hole pair states as the basis states. From the $p_{3/2}$ hole and the $s_{1/2}$ electron (A channel), one gets exciton states with total angular momentum $J=1$ and 2. Similarly the $p_{1/2}$ hole and the $s_{1/2}$ electron produce $J=0$ and $J=1$ states (B channel). Among these states we are interested solely in the $J=1$ states since only they are optically allowed. We shall denote these states by $|A\vec{\beta}\rangle$ and $|B\vec{\beta}\rangle$, respectively, in the exciton representation. Their explicit expressions are given in Ref. 8, and we do not repeat it here. The spin singlet components in these wave functions are $\frac{2}{3}$ and $\frac{1}{3}$, respectively, and the dipole moments associated with them are proportional to $\sqrt{\frac{2}{3}}$ and $\sqrt{\frac{1}{3}}$, respectively.[8] The matrix elements of the exchange interaction in this representation can be computed using (3) and the explicit form of the exciton wave functions, to get the result

$$\begin{aligned}
\langle A\vec{\beta}\,|V_x|\,A\vec{\beta}'\rangle &= \tfrac{4}{3} J \delta_{\vec{\beta}\vec{0}} \delta_{\vec{\beta}'\vec{0}}\,,\\
\langle B\vec{\beta}\,|V_x|\,B\vec{\beta}'\rangle &= \tfrac{2}{3} J \delta_{\vec{\beta}\vec{0}} \delta_{\vec{\beta}'0'}\,, \qquad (6)\\
\langle A\vec{\beta}\,|V_x|\,B\vec{\beta}'\rangle = \langle B\vec{\beta}\,|V_x|\,A\vec{\beta}'\rangle &= \tfrac{2}{3} 2^{1/2} J \delta_{\vec{\beta}\vec{0}} \delta_{\vec{\beta}'\vec{0}}\,,
\end{aligned}$$

where

$$J = \int\int a_x(\vec{\mathrm{r}}_1) a_s(\vec{\mathrm{r}}_1) g(|\vec{\mathrm{r}}_1 - \vec{\mathrm{r}}_2|) a_x(\vec{\mathrm{r}}_2) a_s(\vec{\mathrm{r}}_2) d\vec{\mathrm{r}}_1 d\vec{\mathrm{r}}_2$$

$$-\tfrac{4}{3}\pi(\mu^2/\Omega), \qquad (7)$$

$$\mu = \int a_x(\vec{\mathrm{r}})\, ex\, a_s(\vec{\mathrm{r}}) d\vec{\mathrm{r}},$$

for transverse-wave excitation. The integrals in the above expression include no more spin inner products. a_x and a_s are the spatial parts of the Wannier functions for the valence and conduction bands, respectively, and Ω is the volume of the unit cell. The matrix elements (6) indicate that the exchange interaction gives rise to interchannel as well as intrachannel interaction. The Kronecker δ's in (6) reflect the short-ranged nature of the exchange interaction, which works only when the electron and hole come on the same lattice site.

Now that the matrix elements of the exchange interaction are known, we proceed to calculate the optical-absorption spectra in the presence of the exchange interaction. If we ignore the exchange interaction, the line shape becomes the one given by Elliott[13]; but introduction of the exchange interaction causes a rather drastic change in the optical spectra unexpected in the simple Elliott theory.

The line shape of the optical-absorption spectrum is given, apart from some unessential factors, by

$$I(\hbar\omega)=\textstyle\sum_j|\langle g|M|j\rangle|^2\,\delta(\hbar\omega-E_j), \tag{8}$$

where $|g\rangle$ is the ground state of the crystal, $|j\rangle$ is an excited eigenstate of the total Hamiltonian $H=H_0+V_x$, with energy eigenvalue E_j, and M is the dipole moment operator. As is known from the Elliott theory,[13,14] M is nonvanishing only (i) for states with $\vec{K}=0$, (ii) for singlet spin states, and (iii) when the electron and hole are on the same lattice site.

Equation (8) can be rewritten

$$\begin{aligned}I(\hbar\omega)&=\pi^{-1}\,\mathrm{Im}\langle g|M(z-H)^{-1}M|g\rangle\\&=\pi^{-1}\,\mathrm{Im}\left(\tfrac{2}{3}G_{00}^{AA}+\tfrac{1}{3}G_{00}^{BB}+\tfrac{1}{3}2^{1/2}G_{00}^{AB}+\tfrac{1}{3}2^{1/2}G_{00}^{BA}\right)\end{aligned} \tag{9}$$

using the Green's function

$$G_{\vec{\beta}\vec{\beta}'}^{AB}(z)=\langle A\vec{\beta}|\,(z-H)^{-1}\,|B\vec{\beta}'\rangle,$$

$$z=\hbar\omega-i0^{+}.$$

Let us define the Green's function in the absence of the exchange interaction by

$$R_{\vec{\beta}\vec{\beta}'}^{AA}(z)=\langle A\vec{\beta}|\,(z-H_0)^{-1}\,|A\vec{\beta}'\rangle\ .$$

Since H_0 does not couple the A and B channels, $R^{AB}(z)$ vanishes. The line shape in the absence of the exchange interaction is therefore given by

$$I_0(\hbar\omega)=\pi^{-1}\,\mathrm{Im}\left[\tfrac{2}{3}R_{00}^{AA}(z)+\tfrac{1}{3}R_{00}^{BB}(z)\right]\ . \tag{10}$$

This line-shape spectrum is just what is shown schematically in Fig. 1. It is simply a superposition of the spectra of independent two channels, each of which can be calculated according to the Elliott theory.[13]

In the presence of the exchange interaction, we take matrix elements of the operator identity

$$\frac{1}{z-H}=\frac{1}{z-H_0}+\frac{1}{z-H_0}V_x\frac{1}{z-H}\ .$$

Since the electron-hole exchange interaction V_x has nonvanishing matrix elements only for $\beta=\beta'=0$, the resulting equations can be written simply in matrix form as

$$\begin{pmatrix}G_{00}^{AA}&G_{00}^{AB}\\G_{00}^{BA}&G_{00}^{BB}\end{pmatrix}=\begin{pmatrix}R_{00}^{AA}&0\\0&R_{00}^{BB}\end{pmatrix}+\frac{2}{3}J\begin{pmatrix}R_{00}^{AA}&0\\0&R_{00}^{BB}\end{pmatrix}\times\begin{pmatrix}2&\sqrt{2}\\\sqrt{2}&1\end{pmatrix}\begin{pmatrix}G_{00}^{AA}&G_{00}^{AB}\\G_{00}^{BA}&G_{00}^{BB}\end{pmatrix},$$

which can be easily solved for G_{00}^{AA}, G_{00}^{AB}, G_{00}^{BA}, and G_{00}^{BB}. Substitution of them into Eq. (9) yields

$$I(\hbar\omega)=\frac{1}{\pi}\,\mathrm{Im}\,\frac{\frac{2}{3}R_{00}^{AA}(z)+\frac{1}{3}R_{00}^{BB}(z)}{1-2J\left[\frac{2}{3}R_{00}^{AA}(z)+\frac{1}{3}R_{00}^{BB}(z)\right]}\ . \tag{11}$$

This gives the line-shape formula including the interchannel as well as intrachannel effects of the exchange interaction.

Our line-shape formula (11) is seen to include the following special cases.

(a) When we neglect the exchange interaction, it reduces to the simple expression (10), a superposition of the absorption due to the noninteracting two channels. There is no interference between the two. In particular, the B exciton remains unbroadened even when it overlaps with the continuum absorption of the A channel.

(b) When $\lambda\ll E_B$, the doublet exciton absorption is well separated from the continuum, as shown in Fig. 1(a). In the exciton region, we can approximate

$$R_{00}^{AA}(z)=\frac{|F_{1s}(0)|^2}{z}\quad\text{and}\quad R_{00}^{BB}(z)=\frac{|F_{1s}(0)|^2}{z-\lambda}\ ,$$

where the energy z is measured from the energy level of the $n=1$ exciton of the A channel, and F_{1s} is the envelope function for that state. Since we assumed the same effective mass for the A and B excitons, the envelope function is common to the two channels. Then our expression (11) has simple poles at energies which satisfy

$$1-\Delta\left(\frac{\frac{2}{3}}{E}+\frac{\frac{1}{3}}{E-\lambda}\right)=0\ ,$$

where the exchange energy Δ is defined by

$$\Delta=2J\,|F_{1s}(0)|^2\ . \tag{12}$$

These poles

$$E=\tfrac{1}{2}\left[\Delta+\lambda\pm(\Delta^2+\lambda^2-\tfrac{1}{3}2\lambda\Delta)^{1/2}\right]$$

give the energies of the exciton states in the presence of the exchange interaction. Intensities of the absorptions are given by the residues. One can thus investigate the relative intensity of the A and B excitons as a function of the exchange energy Δ and the spin-orbit splitting λ. The result can be shown to be the same as was previously obtained by means of a more direct calculation.[8]

The above two cases are the special cases included in our line-shape formula (11). To see the effects of the exchange interaction in more detail, in particular, its effect on the interference, we assume for simplicity that the absorption spectra of the A channel consist of a single discrete exciton line and a flat continuum starting from the $n=2$ exciton level. We therefore take

$$\frac{1}{\pi}\,\mathrm{Im}R_{00}^{AA}(z)=|F_{1s}(0)|^2\,\delta(\hbar\omega)+\frac{\Omega}{2\pi E_B a_B^3}\,\theta(\hbar\omega-\tfrac{3}{4}E_B)\ , \tag{13}$$

where a_B is the exciton Bohr radius, and the constant before the step function θ is the height of the Elliott step at the beginning of the continuum absorption.[13] The origin of the photon energy $\hbar\omega$ is placed at the $n=1$ exciton level of the A channel.

The analytic function which realizes (13) is

$$R_{00}^{AA}(z)=\frac{|F_{1s}(0)|^2}{z}+\frac{\Omega}{2\pi E_B a_B^3}\ln\frac{\frac{3}{4}E_B-z}{E_c}\;, \tag{14}$$

with an appropriate cutoff constant E_c, which is on the order of the width of the conduction band. For the B-channel Green's function, we consider only the exciton absorption

$$R_{00}^{BB}(z)=|F_{1s}(0)|^2/(z-\lambda)\;, \tag{15}$$

since we are most interested in the interference of this exciton line with the continuum absorption.

Substituting Eqs. (14) and (15) into Eq. (11), and using $|F_{1s}(0)|^2=\Omega/\pi a_B^3$, we get the line-shape formula

$$I(\hbar\omega)=\frac{|F_{1s}(0)|^2}{\pi\Delta}\operatorname{Im}\frac{1}{f(z)}\;, \tag{16}$$

$$f(z)=1-\frac{\Delta}{3}\left(\frac{1}{z-\lambda}+\frac{2}{z}+\frac{1}{E_B}\ln\frac{\frac{3}{4}E_B-z}{E_c}\right).$$

The A exciton is shifted to an energy E, a root of $f(E)=0$, after the exchange interaction has been switched on. It appears as a δ function with the integrated intensity

$$\frac{|F_{1s}(0)|^2}{\Delta}\left(\frac{\partial f(z)}{\partial z}\right)^{-1}_{z=E}. \tag{17}$$

Our line-shape formula (16) includes also the interference of the B exciton with the A continuum when the former is superposed on the latter, which can be seen, for example, in that the spectral intensity drops to zero at the photon energy $\hbar\omega=\lambda$, the original energy position of the B exciton. Such a situation is characteristic of a case where there exists only a single continuum; if the background continuum absorption on which a discrete level is superposed consists of more than one channel, then the intensity does not drop to zero.[1]

Another feature of the line shape (16) arises from the positive sign of the exchange energy Δ. Although not transparent in our expression for the exchange energy (12) and (7), Takeuti[11] has shown that it is absolutely positive, in terms of another representation for it. Now the positive sign of Δ guarantees the shift of the B exciton to higher energy by the exchange interaction. We can, therefore, in general expect positive asymmetry, i.e., a dip (down to zero) on the low-energy side and a peak on the high-energy side, as a result of the interference caused by the exchange interaction.

Besides, the broadening of the B exciton can be computed from Eq. (16) in the limit of weak interchannel coupling. The half-height full width becomes

$$W=2\pi\Delta^2/9E_B \tag{18}$$

in that limit.

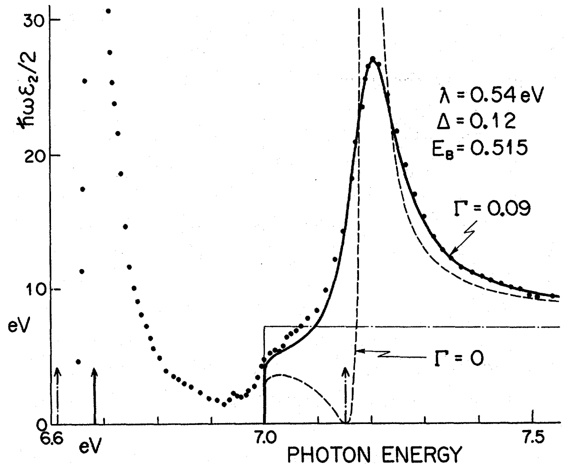

FIG. 2. Optical-conductivity spectra of NaBr. The dots are the experimental values obtained by Miyata through Kramers-Kronig analysis of his reflectivity data at 85 °K (Ref. 17). The dot-dashed line represents the step absorption assumed in the absence of the electron-hole exchange interaction. The solid and dashed lines are the theoretical curves with the exchange interaction taken into account. The former includes incoherent broadening of the B exciton ($\Gamma=0.09$ eV). The scale of the theoretical curves is normalized so that the integrated intensity of the first exciton at 6.68 eV agrees with the experimental value (Ref. 17) 5.23 eV^2. The dot-dashed arrows indicate the energy positions of the excitons in the absence of the exchange interaction.

These are the qualitative features expected from our line-shape formula (16). In Sec. III, it is used to analyze the fundamental optical spectra of NaBr.

III. COMPARISON WITH EXPERIMENT AND DISCUSSION

In Sec. II we considered interference of spin-orbit-split two channels for a simple, but realistic, band structure frequently encountered in many insulating crystals. The interchannel coupling has been shown to arise from the electron-hole exchange interaction. A line-shape formula has been obtained which takes into account such an interference effect.

We are especially concerned with the interference of the exciton line with continuum absorption when the former is overlapping with the latter. Such a situation can occur if $\lambda \gtrsim E_B$, as seen in Fig. 1(b). NaBr is the best example in which the above situation is realized, as confirmed by two-photon absorption experiments.[15,16] We therefore try in this section to analyze the optical spectra of NaBr observed very recently by Miyata,[17] on the basis of the theory developed in Sec. II.

The dots in Fig. 2 show the spectra of optical conductivity—a quantity proportional to oscillator strength density—of NaBr at 85 °K. The first peak located at 6.68 eV is the A exciton broadened by exciton-phonon interaction. It has quite a narrow width, 0.02 eV.[17] Above the tail absorption on the high-energy side, which is mostly due to the optic-phonon sideband, the spectral intensity starts to rise at ≈ 7.0 eV, where we consider the continuum absorption of the A channel to set in. The value 7.0 eV is consistent with the onset of the two-photon absorption,[16] which should begin with the $n=2$ exciton. Upon this continuum is superposed the B exciton at 7.2 eV broadened by interchannel interaction with the continuum absorption. We are going to analyze this line shape using the formula (16) obtained in Sec. II.

In doing that, the ordinate of the theoretical curves will be normalized in such a way that the integrated intensity of the A exciton given by (17) may agree with the experimental value. That is to say, we consider not only the line shape of the B exciton resonance but also its intensity relative to the A exciton.

The line-shape expression (16) includes four parameters: E_C, λ, E_B, and Δ. Among them, the cutoff constant E_C, introduced to prevent the real part of the Green's function from diverging, is taken to be 1.0 eV. The calculated spectrum is insensitive to the choice of this parameter. The spin-orbit splitting λ and the binding energy of the $n=1$ exciton E_B are almost determined; we take $\lambda = 0.54$ eV and $E_B = 0.515$ eV. The broken line in Fig. 2 represents the line shape (16) for the exchange energy $\Delta = 0.12$ eV. The broken arrows indicate the energy positions of the A and B exciton levels in the absence of the exchange interaction. One can see that the excitons are shifted to higher energy by the exchange interaction on account of the positive sign of Δ. The most interesting feature of the calculated spectrum is the antiresonance at 7.15 eV, the original energy position of the B exciton. Such a drop of the spectral intensity to zero is specific to the case where the background continuum consists of a single channel[1] as in the present problem. The width of the B exciton resonance can be calculated from (18) to be $W = 0.02$ eV.

This value is however far too small compared with the observed width. Furthermore, the observed spectrum has no characteristic antiresonance. These discrepancies are due to the fact that the spectra are broadened by electron-phonon interaction, whose effects we have not yet taken into account. The B exciton can decay into free electron-hole pairs of the A channel through the electron-phonon interaction as well as through the exchange interaction. In the absence of a theory on the interference effects caused by the electron-phonon interaction, we make an *ad hoc* assumption that the B exciton is incoherently broadened by electron-phonon interaction with the background, and we replace $(z-\lambda)^{-1}$ in Eq. (16) by $(z-\lambda-i\Gamma/2)^{-1}$, introducing an incoherent broadening Γ of the B exciton. The resulting line shape is shown in solid line for $\Gamma = 0.09$ eV. The overall agreement with experiment is very good, though a little discrepancy remains in the starting region. The positive asymmetry of the line shape is still maintained in the solid curve, in agreement with the observed asymmetry. This is due to the positive sign of the exchange energy, as mentioned above.

The agreement is good indeed, but one may well feel that many parameters have been used in the fit. In actual fact, however, we have not much liberty in the choice of the values of the parameters. The broadening Γ, the spin-orbit splitting λ, and the binding energy E_B are almost determined; there is left little room for adjusting their values. The only disposable parameter is the exchange energy Δ, to which the overall line shape is quite sensitive. By adjusting this parameter, we have made the fit so as to reproduce the line shape as well as the intensity relative to the A exciton. For this reason, the fit is a rather severe test. It is therefore believed that the agreement supports our theory of the interference effects caused by the exchange interaction.

As for the magnitude of the spin-orbit splitting λ, our value 0.54 eV is appreciably larger than the free-atom splitting 0.47 eV. The splitting is known to be enhanced in the solid state because of the overlap of the halogen p orbitals,[18] and our value is in good agreement with the value 0.53 eV computed by Kunz.[18]

Before closing this section we make a remark on the antiresonance. The calculated line shape for $\Gamma = 0$ has a pronounced antiresonance on the low energy side of the peak. But it is smeared out in the 85 °K spectra on account of the broadening due to the electron-phonon interaction. Since the phonon effects diminish at low temperatures, it is hoped to extend the experiments down to liquid-helium temperatures to observe possible antiresonance. In fact, such a dip has been observed for RbI by Fischer and Hilsch.[19] More recently Tomiki and co-workers observed a similar dip in KI, which becomes progressively pronounced with lowering of the temperature.[20] Although the exciton structure of these iodides are somewhat complex because of the presence of higher conduction bands, the underlying physics is believed to be similar.

IV. SUMMARY

We have investigated interference of an exciton with a continuum absorption for the case where the two belong to spin-orbit-split channels. The interchannel interaction has been shown to arise from the exchange interaction between electron and hole.

A line-shape formula has then been derived to take account of the effects caused by the exchange interaction. An analysis of the observed optical spectra of NaBr based on that formula supports our theory of the interference. The most striking feature in the spectra is a possible antiresonance on the low energy side, which is in general expected from the positive sign of the exchange energy. It has also been found that the interchannel interaction through the electron-phonon interaction is important, so the author hopes to do a theoretical study on the interference of a discrete exciton state with a continuum absorption caused by electron-phonon interaction.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 8 15 OCTOBER 1971

Theory for the Non-Devonshire Lines Observed in the Hydroxyl-Ion-Doped Alkali Halide Matrices

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The isotope effect of the non-Devonshire lines can be well understood if one takes the origin of these as transitions corresponding to the quantized translational motion of the impurity in the matrix cage and considers the various perturbing mechanisms. The present model in which rotation-translation coupling and coupling through the anisotropic part of crystalline field are considered as the chief perturbing mechanisms proves to be good in explaining the isotope effect of the near-infrared lines in the KCl and KBr matrices. It provides a good explanation of the multiplet line structure observed in the KCl-OH^- system and absence of such a structure in the KCl-OD^- system. The more complex case of the NaCl matrix is also explained in a satisfactory way. There has not been an attempt to explain the RbCl-OH^- system because of the lack of sufficient experimental data.

I. INTRODUCTION

Recent experiments on the near-[1-3] and far-infrared spectroscopy[4] and the thermal-conductivity measurements[5] on the hydroxyl-ion-doped alkali halide systems have established the presence of a 30–35 cm^{-1} energy level for this impurity. This level could not be explained by the Devonshire model, and hence was named the non-Devonshire level. Different workers tried to explain the origin of this level, but without significant success. In the KCl matrix, the OH^- to OD^- frequency ratio for the non-Devonshire line has been found to be very close to the square root of the moments of inertia of the two ions. This is the expected isotope effect for the energy levels associated with the torsional-harmonic-oscillation model of the impurity.[1] However, the simple torsional-harmonic-oscillator