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Polaritons associated with nearly degenerate excitons: Their dispersion and the resulting reflectivity for the 1*s* exciton in CuBr

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We propose a method to calculate the dispersion of polaritons associated with nonparabolic excitons. It gives directly the polariton wave vectors versus the photon energy, as required for a reflectivity calculation. For CuBr, we determine the normal reflectivity of the 1*s* exciton and find a good agreement with the experimental results. The existence of $\vec{k}$-linear terms explains the reflectance spike due to the triplet exciton. In most cases, an exciton state corresponds to a reflectivity structure. Sometimes, however, a given state is associated with none or with two singularities.

I. INTRODUCTION

Exciton properties are often studied in reflectivity measurements, which are, however, quite difficult to interpret in terms of exciton parameters. In order to do it properly, a polariton model has been developed[1,2] which considers the special exciton properties as well as the strong exciton-photon coupling. This model is, however, difficult to handle. Consequently it has been used only for relatively simple cases, involving only one or two exciton states with simple analytic spatial dispersion. In many cases, however, one is confronted with a set of degenerate or nearly degenerate exciton states,[3-8] interacting with each other and having, therefore, a complex dispersion. Then the usual method to determine the polariton dispersion, in order to calculate the reflectivity, is no longer applicable. The polariton formalism itself remains, however, still valid, and we recall in Sec. II different analytic solutions for the polariton dispersion, which correspond to different approximations frequently encountered in the literature. We propose also an original and rigorous method for the numerical calculation of the dispersion curves, which is *a priori* adapted to any kind of practical problem.

After a discussion of the method used to calculate the normal reflectivity for a given set of polariton branches, we give in Sec. III some results obtained in the vicinity of the 1*s* exciton of CuBr. In this zinc-blende-type material, the existence of $\vec{k}$-linear terms,[6] inducing different exciton interactions, explains some particular features of the reflectivity spectrum. It will be shown that the polariton model is not only useful to derive quantitative information from the experiment, but explains also an important behavior: A dipole active exciton "branch" does not necessarily correspond to a reflectivity singularity; we found examples where a given branch may be associated with none or with two reflectivity singularities. Simple arguments show that these features are not due to a particular choice of additional boundary conditions (ABC).

II. THE DISPERSION OF EXCITONIC POLARITONS

A method to obtain the polariton dispersion in presence of a set of excitons with a complicated spatial dispersion has been developed in the semiclassical approximation.[7] We prefer to use here a purely quantum-mechanical approach which is more rigorous and generally gives the best picture of the physical phenomena. It also gives a better starting point for eventual studies of phenomena such as light scattering or nonlinear optics. Moreover, we will propose a mathematical method which, for practical applications, makes the dispersion calculation much easier than using the method of Ref. 7.

A. Excitonic aspect

We are mainly interested here in "nonparabolic" excitons, constructed with electrons and holes belonging to nonspherical or degenerate band extrema, but for simplicity we consider only transitions at the center of the Brillouin zone (BZ). It has been proposed[9] to use an adapted $\vec{k}\cdot\vec{p}$ method to find the excitonic dispersion in the small part of the BZ involved in direct transitions. We therefore start with the effective-mass Hamiltonian as defined by Dresselhaus[9]:

$$H_e(\vec{p}_e)+H_h(\vec{p}_h)-\frac{e^2}{|\vec{r}_e-\vec{r}_h|}\ , \tag{1}$$

where H_e and H_h are $r\times r$ and $s\times s$ matrix operators, r (s) being the degeneracy of the conduction (valence) band. In a first step, only the spherical part of (1) is considered. A center-of-mass transformation[9-11]

$$\vec r = \vec r_e - \vec r_h\,,\qquad \vec R = \alpha \vec r_e + \beta \vec r_h\,, \tag{2}$$

where $\alpha + \beta = 1$, enables to express the eigenfunctions of the spherical part of (1) as

$$\varphi_n(\vec k, \vec r) = e^{i\vec k\cdot\vec r}\varphi_n(0, \vec r)\,, \tag{3}$$

where $\vec k$, the total exciton wave vector, is an eigenvalue of the operator $-i(\alpha+\beta)\vec\nabla_k$. The envelope function $\varphi_n(0, \vec r)$ is obtained by solving a set of $r \times s$ identical equations and is a simple hydrogenoid function. The total excitonic wave functions can be written[10] as

$$\phi_l^{\vec k} = \phi_{ij}^{n,\vec k} = e^{i\vec k\cdot\vec r}\varphi_n(0, \vec r)u_{ci}u_{vj}\,, \tag{4}$$

where u_{ci} and u_{vj} are the Bloch functions of the conduction and valence bands taken for $\vec k = 0$. The three indices n, i, and j appearing in (4) have been condensed into the index l for simplicity. We call $\mathcal{E}_l(\vec k)$ the eigenvalues corresponding to $\phi_l^{\vec k}$.

The nonspherical part of the Hamiltonian (1) is considered as a small perturbation.[3,10] Using the wave functions $\phi_l^{\vec k}$ as a basis, an interaction matrix can be constructed, eigenvalues and eigenfunctions of which are those of the "perturbed" system. In practice, however, we are interested only in the behavior of a finite set of n excitonic states $\phi_l^{\vec k}$. Consequently the interactions of these n exciton states with all the other ones (which are supposed to be far enough in energy) are treated in second-order perturbation theory.[3,10] Then the interactions between the n excitons are treated exactly. The same method is used in the $\vec k\cdot\vec p$ theory for the calculation of the band dispersion.[12] We therefore arrive at an $n \times n$ interaction matrix H_x, constructed on the basis $\phi_l^{\vec k}$. The solution of

$$H_x\psi = EI\psi\,, \tag{5}$$

where I is the $n \times n$ unity matrix, gives the required eigenvalues $E_i(\vec k)$ and eigenfunctions $\psi_i(\vec k)$. The general form of H_x can be obtained by group-theoretical considerations or by the invariant method.[13] It is known that H_x may contain $\vec k$-linear terms in materials without center of inversion. If the bands are nonspherical or degenerate, H_x contains quadratic terms like k_x^2, $k_xk_y, \ldots$. We do not consider terms of higher order in $\vec k$, although the method developed in the following does not impose any restriction. Owing to the nondiagonal k-dependent terms in H_x, the excitonic dispersion is anisotropic and difficult to expand into a series.

For practical purposes, it is often necessary to consider various effects related, for example, to the spin-orbit coupling, the electron-hole exchange interaction, an external perturbation, etc. In some cases they can be taken into account by a perturbation theory and H_x must be modified as a consequence. This, however, does not change the formal aspect of the exciton problem nor the conclusions we obtain in the following.

B. Polariton dispersion

To study the polariton problem, we follow Hopfield[1] and Bendow[14] and write H_x in the second quantization formalism

$$H_x = \sum_{i,j} H_x^{ij}(\vec k)b^+_{i,\vec k}b^-_{j,\vec k}\,, \tag{6}$$

where $b^\pm_{i,\vec k}$ are the creation and destruction operators of the excitons $(\mathcal{E}_i(\vec k),\ \phi_i^{\vec k})$ of our basis. We define the photon field by its vector potential $\vec A$ in the Coulomb gauge $(\vec\nabla\cdot\vec A = 0)$ and fix the light wave vector and polarization directions. The photon Hamiltonian reads

$$H_P = \sum_{\vec k} \hbar ck(a^+_{\vec k}a^-_{\vec k}) + \sum_{\vec k} D(k)(a^+_{\vec k}a^-_{\vec k} + a^-_{\vec k}a^+_{\vec k} + a^+_{\vec k}a^+_{-\vec k} + a^-_{-\vec k}a^-_{+\vec k})\,, \tag{7}$$

where $a^\pm_{\vec k}$ are the creation and destruction operators of the photon of wave vector $\vec k$. The exciton-photon interaction is considered in the electric-dipole approximation. As we use the exciton basis $\phi_i^{\vec k}$, the interaction Hamiltonian H_{xP} can be written as in Refs. 1 and 14:

$$H_{xP} = i\sum_{\vec k, j} |C_j(k)|\,(a^+_{\vec k}b^-_{j,\vec k} - a^-_{\vec k}b^+_{j,\vec k} + a^-_{-\vec k}b^-_{j,\vec k} - a^+_{-\vec k}b^+_{j,\vec k})\,, \tag{8}$$

where $C_j(k)$ is related to the dimensionless parameter β_j and to g_j by

$$C_j(k) = \frac{\mathcal{E}_j^{3/2}(0)(\pi\beta_j)^{1/2}}{(\hbar ck)^{1/2}} = \frac{g_j}{(\hbar ck)^{1/2}}\,. \tag{9}$$

Fermi's golden rule enables us to define $D(k)$ in Eq. (7) by[14]

$$D(k) = \frac{1}{\hbar ck}\sum_j \frac{|g_j|^2}{\mathcal{E}_j(0)} = \frac{\omega_p^2}{\hbar ck}\,. \tag{10}$$

With the definition given here, we consider simultaneously the absorption and emission processes as well as the nonlinear effects related to A^2. Following again Refs. 1 and 14 we obtain the eigenenergies E of the Hamiltonian $H_T = H_x + H_P + H_{xP}$, which are just the energies of the so-called polaritons, by solving $\det A = 0$, where

$$A=\begin{pmatrix} \hbar ck+2D-E & [iC_j] & 2D & [-iC_j^*] \\ \{-iC_j^*\} & (H_x-EI) & \{-iC_j^*\} & (0) \\ -2D & [-iC_j] & -\hbar ck-2D-E & [iC_j^*] \\ \{-iC_j\} & (0) & \{-iC_j\} & (-H_x-EI) \end{pmatrix}, \tag{11}$$

where the symbol ( ) indicates a $n\times n$ matrix, [ ] and { } indicate row and column vectors. The matrices H_x and I are defined in Eq. (5). For simplicity we have not indicated the k dependence of D and C_j.

Though the solution of Eq. (11) gives the polariton energies, it has not been used for practical purposes. To find the usual dispersion equation, we will rewrite Eq. (11) in the exciton basis, $[E_j(\vec{k}), \psi_j(\vec{k})]$ which is obtained by solving Eq. (5). Let us call $T(\vec{k})$ the unitary matrix which transforms the basis ϕ_i^k into $\psi_j(\vec{k})$. Consequently, we transform the matrix A of relation (11) by changing H_x into $\tilde{H}_x=T(\vec{k})H_xT^{-1}(\vec{k})$ and redefining constants $G_i(\vec{k})$ by

$$G_i(\vec{k})=\sum_j T_{ij}(\vec{k})g_j\,. \tag{12}$$

$\tilde{H}_x$ being diagonal, it is easy to derive an analytical expression, equivalent to Eq. (11):

$$\left(\frac{\hbar ck}{E}\right)^2=1+\sum_j\frac{4\,|G_j(\vec{k})|^2}{E_j(\vec{k})[E_j^2(\vec{k})-E^2]}\,. \tag{13}$$

For a given value of $\vec{k}$, it is possible to find $T(\vec{k})$ and compute $E_j(\vec{k})$ and $G_j(\vec{k})$. Using Eq. (13) one then finds $E(\vec{k})$. This enables us to obtain the polariton dispersion, even if the exciton dispersion is complicated.[6,15] In the reflectivity problem, however, we must fix the energy E and calculate the wave vector $\vec{k}$ of the various corresponding polaritons. Equation (13) is only useful if $E_j(\vec{k})$ and $G_j(\vec{k})$ have simple analytical development, as in Refs. 16 and 17, for example. In our case, such developments are too complicated or inaccurate. In addition, the anisotropic dispersion of the excitons complicates the problem of the non-normal reflectivity. In this case, it is known that several polaritons may propagate in the crystal in different directions. In the presence of "isotropic excitons" the polariton energies depend only on $k=|\vec{k}|$, and the eigenstates of the crystal are easily found. In the present anisotropic case, it is necessary to determine both the modulus and the direction of $\vec{k}$ (in a given plane). To avoid this complication, we restrict ourselves to the normal incidence case. Then all the polaritons propagate in the direction $\vec{\eta}$ of the incoming light. $\vec{\eta}$ being fixed, we will write $k_\eta=\vec{k}\cdot\vec{\eta}$, which is just a scalar, instead of $\vec{k}$ in H_x. In the matrix A defined in relation (11), once E has been fixed, there are constants and quantities depending on k_η and on k. In the most general case, the relation $E_j(\vec{k})=E_j(-\vec{k})$ being unfulfilled, the two cases $k_\eta>0$ and $k_\eta<0$ have to be considered separately by solving, for example, Eq. (11) twice. To avoid this complication we multiply the first and third lines and columns of A by $(\hbar ck)^{1/2}$ and then transform k into k_η. We obtain

$$A'=\begin{pmatrix} (\hbar ck_\eta)^2-\hbar ck_\eta E+2\omega_p^2 & [ig_j] & 2\omega_p^2 & [-ig_j^*] \\ \{-ig_j^*\} & (H_x(k_\eta)-EI) & \{-ig_j^*\} & (0) \\ -2\omega_p^2 & [-ig_j] & -(\hbar ck_\eta)^2-\hbar ck_\eta E-2\omega_p^2 & [ig_j^*] \\ \{-ig_j\} & 0 & \{-ig_j\} & (-H_x(k_\eta)-EI) \end{pmatrix}, \tag{14}$$

where g_j and ω_p^2 are constants defined in Eqs. (9) and (10). One verifies easily that the solutions of $\det A'=0$ are the sum of the two sets of solutions of $\det A=0$ obtained for $k_\eta>0$ and $k_\eta<0$.

All the matrix elements in A' are polynomials of k_η: $A'_{lm}=a_{lm}k_\eta^2+b_{lm}k_\eta+c_{lm}$. Consequently $\det A'$ can be developed into a polynomial $F(k_\eta)$, the poles of which can be obtained by a numerical method. This method of solving the polariton problem has been indicated first in Ref. 7 and has been used for practical applications in Ref. 8. The derivation of $F(k_\eta)$, however, can be very tedious in the presence of a complex set of excitons. We therefore develop

$$A'=A_0k_\eta^2+A_1k_\eta+A_2\,, \tag{15}$$

where the A_i are $2(n+1)\times 2(n+1)$ matrices. The eigenvalues k_η of (15) are obtained following Wayland[18] by solving

$$\det M = \det\begin{pmatrix} A_0^{-1}A_1 + k_\eta I & A_0^{-1}A_2 \\ -I & k_\eta I \end{pmatrix} = 0\,, \tag{16}$$

when I is the $(2n+1)\times(2n+1)$ unity matrix. The eigenvectors V_M of M can be written as

$$(V_M) = \begin{pmatrix} k_\eta x \\ x \end{pmatrix},$$

where x are the eigenvectors of A'. Generally, A_0^{-1} exists. If not, we can define $\lambda = 1/k_\eta$ which can be calculated because A_2^{-1} is defined for almost all values of E.

With the present method, the determination of the polariton wave vectors reduces to a simple eigenvalue problem [Eq. (16)] and is therefore not more complicated than in the case of excitons with simple dispersion. However, the dimension of M, in relation (16), may be important in some practical cases. To save computer time it will be necessary to simplify the matrix A' by making the following approximations, justified if the photon energy E and the various exciton energies $\mathcal{E}_i(0)$ hold true simultaneously for $|E - \mathcal{E}_i(0)|/E \ll 1$. One can first neglect the nonlinear effects, i.e., write $\omega_p = 0$ in (14). This is equivalent to transforming Eq. (13) into

$$\left(\frac{\hbar c k}{E}\right)^2 = 1 + \sum_j \frac{4|G_j(\vec{k})|^2 E_j(\vec{k})}{E^2[E_j^2(\vec{k}) - E^2]}$$

$$\simeq 1 + \sum_j \frac{4|G_j(\vec{k})|^2}{E_j(\vec{k})[E_j^2(\vec{k}) - E^2]}\,. \tag{17}$$

Furthermore, the fourth line and column in (14) can also be neglected. This is equivalent to writing

$$\left(\frac{\hbar c k}{E}\right)^2 = 1 + \sum_j \frac{2|G_j(\vec{k})|^2}{E_j^2(\vec{k})[E_j(\vec{k}) - E]}\,. \tag{18}$$

Both approximations are generally used in the literature.

In practical applications, one considers in detail only a given set of "resonant" oscillators. The influence of all the others is taken into account by a background dielectric constant ϵ_b. Then the above definitions must be modified by multiplying c, C_j, $\beta_j^{1/2} g_j$, and ω_p by $\epsilon_b^{-1/2}$.

III. APPLICATION TO THE 1s EXCITON OF CuBr

A. Excitonic dispersion

CuBr has the zinc-blende structure. The 1s exciton (Z_{12}) is constructed with Γ_8 holes and Γ_6 electrons. The exchange interaction splits the exciton ground state for $k \simeq 0$ into the triplet states $\Gamma_3 + \Gamma_4$ (forbidden in dipole approximation), the transverse Γ_{5T} states (dipole allowed), and the longitudinal Γ_{5L} state.[6] We call Δ_1 and Δ_{TL} the $(\Gamma_3+\Gamma_4) - \Gamma_{5T}$ and the $\Gamma_{5T} - \Gamma_{5L}$ separation. As Δ_{TL} is large in our case (12 meV), the longitudinal state can be neglected in the following examples. We neglect also all other exciton states of the present series ($2s, 2p, \ldots$) and all other series; this is justified here because the 1s binding energy and the spin-orbit splitting are large[19] (110 and 170 meV). To construct the matrix interaction H_x we choose an exciton basis for which the exchange interaction, characterized by Δ_1 and Δ_{TL}, is diagonalized. We then take into account the diagonal term $\hbar^2k^2/2M_{\text{ex}}$ and the $\vec{k}$-linear terms which already split the Γ_8 band for $k \neq 0$.[20] They are proportional to the spin-orbit splitting and are presumably important in CuBr. We neglect for the moment the influence of the Γ_8 warping, which will be discussed later.

We consider the case of the normal reflectivity of a semi-infinite crystal in the [110] direction. Following Ref. 4, we construct the matrix H_{x1} for the excitons playing a role in the [001] polarization:

$$H_{x1} = \begin{pmatrix} -\sqrt{3}Ck_\eta & 0 & \sqrt{2}iCk_\eta \\ 0 & \sqrt{3}Ck_\eta & -\sqrt{2}iCk_\eta \\ -\sqrt{2}iCk_\eta & \sqrt{2}iCk_\eta & \Delta_1 \end{pmatrix}, \tag{19}$$

where the zero of energy corresponds with the $(\Gamma_3+\Gamma_4)$ levels for $k=0$. C is the excitonic constant of the $\vec{k}$-linear terms, related to the Γ_8 band parameter C_k by

$$C = \frac{\sqrt{3}}{4}\, C_k m_h^*/(m_e^* + m_h^*)\,.$$

In H_{x1}, we omit the diagonal term $\hbar^2k^2/2M_{\text{ex}}$ and we have chosen the basis wave functions of the $(\Gamma_3+\Gamma_4)$ states in order to diagonalize partially H_{x1}. For the polarization $[1\bar{1}0]$ we obtain, with the same conventions,

$$H_{x2} = \begin{bmatrix} -Ck_\eta & 0 & 0 & (3/2)^{1/2}Ck_\eta \\ 0 & 0 & 0 & -2iCk_\eta \\ 0 & 0 & Ck_\eta & (3/2)^{1/2}Ck_\eta \\ (3/2)^{1/2}Ck_\eta & 2iCk_\eta & (3/2)^{1/2}Ck_\eta & \Delta_1 \end{bmatrix}. \tag{20}$$

In each of the exciton bases used to derive H_{x1} and H_{x2}, there is only one allowed state for $k=0$, at the energy Δ_1.

B. Polariton dispersion

Using H_{x1} and H_{x2}, we are able to calculate the polariton dispersion, using the results of Sec. II. This is done here with the approximations used to obtain Eq. (18). The unique coupling constant C_j of the problem is calculated from (9) and from the relation $2\pi\beta = \epsilon_b \Delta_{TL}/E(\Gamma_{5T})$,

Starting with a set of n excitons, we find, for a given energy, $2(n+1)$ solutions in the k_η space. We shall indicate them with $\hat{k}$. Without magnetic field, they exist as pairs $(+\hat{k}, -\hat{k})$ and are real, purely imaginary, or complex. The complex solutions are due to the existence of the $\vec{k}$-linear terms as in the present case or in the case studied by Mahan and Hopfield.[16] If a complex solution $\hat{k}$ is found, then one shows that $-\hat{k}$, $\hat{k}^*$, and $-\hat{k}^*$ are also solutions. In the reflectivity problem one must eliminate one of the solutions of the pairs $(\hat{k}, -\hat{k})$. This is done with the following criteria:

(i) If $\hat{k}$ is real it must satisfy $dE(\hat{k})/d\hat{k} > 0$, the energy transport being allowed in only one direction.

(ii) If $\hat{k}$ is purely imaginary we take $\hat{k} = +i|\hat{k}|$ to obtain a maximum wave amplitude at the surface.

(iii) If $\hat{k}$ is complex, $\hat{k} = \hat{k}_r + i\hat{k}_i$, it gives rise to a wave like

$$a\exp(i\hat{k}_r r)\exp(-\hat{k}_i r)$$

which cannot exist because we have actually no scattering processes in the crystal. However, we can combine the two solutions $\hat{k}$ and $-\hat{k}^*$ to construct a wave like

$$[a\exp(i\hat{k}_r r) + a^*\exp(-i\hat{k}_r r)]\exp(-\hat{k}_i r),$$

with the condition $\hat{k}_i > 0$. This corresponds to a "stationary-damped" wave, which does not transport any energy. It occurs only if the two amplitudes a and a^* are complex conjugate. We have verified that in the following examples, this occurs effectively within a good approximation.

We report in Figs. 1 and 2 the polaritons we obtain for the two systems of excitons (19) and (20). The branches which do not play a role in the reflectivity have not been reported. We use the following parameters: $\Delta_{TL} = 12$ meV, $M_{ex} = 1.7m_0$, $C = 3.2\ 10^{-7}$ meV cm, $\Delta_1 \simeq 1.1$ meV, and $\epsilon_b \simeq 5.7$, which are generally in good agreement with the values recently determined by the hyper-Raman-scattering method[21] and the values reported in Ref. 6. We note in Figs. 1 and 2 that all polariton curves are continuous. There are, however, singularities with zero slopes when k changes from a complex to a real value.

C. Calculation of the reflectivity

In order to calculate the reflectivity we use the ABC defined by Cho,[7] which are just Pekar conditions[2] modified to take into account the existence of forbidden excitons for $k = 0$.[22] We do not introduce any "dead layer"[23] near the surface, because we are dealing with small-radius excitons, and because the experimental spectra obtained on cleaved samples are easily reproduced. We define damping parameters Γ_j and transform the matrix H_x in (14) into $H_x + i(\Gamma_j \delta_{jk})$. At very low temperature the Γ_j are probably mainly related to scattering by defects and by acoustic phonons. The latter process introduces a dependence of Γ_j with $\vec{k}$, which appears in the calculation of the density of the final states of the scattering. In the present problem, the excitonic dispersion being nonspherical, the $\vec{k}$ dependence of Γ_j cannot be easily derived. We therefore use constants, which are *a priori* larger for an exciton of high energy than for an exciton of small energy, because of the possible interband scatterings and the thermalization.

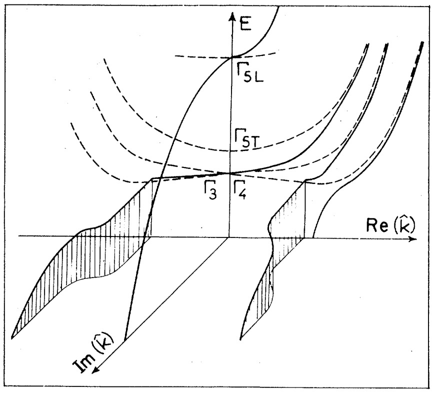

FIG. 1. Schematic representation of the exciton (dashed lines) and polariton (full line) disperion for $\vec{k}\parallel[110]$ and the polarization $\vec{\epsilon}\parallel[001]$. Re($\hat{k}$) and Im($\hat{k}$) are the real and imaginary part of $\hat{k}$.

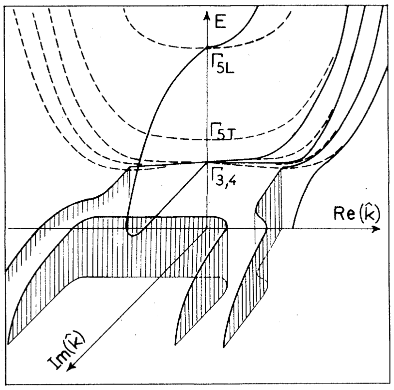

FIG. 2. Schematic representation of the exciton and polariton dispersion for $\vec{k}\parallel[110]$ and the polarization $\vec{\epsilon}\parallel[1\bar{1}0]$.

A comparison of the experimental and calculated reflectivity curves (using the parameters given above) is shown in Fig. 3. The agreement is satisfactory and will be probably enhanced by a fitting procedure and a better definition of the damping parameters.

We will now focus our attention on the small structures appearing in the reflectivity curves and which are related to the $(\Gamma_3+\Gamma_4)$ excitons. Let us recall that the reflectivity depends on all polariton branches of the crystal, and that they are all considered in the Maxwell equations and the ABC. However, the branches with a real $\hat{k}$ have a predominant role because they are the only ones for which an energy transport occurs. Hopfield[24] gives as a rule that a singularity in such "real branches" gives a singularity of the reflectivity. This is true, however, if the polariton at this $\hat{k}$ value has a mixed exciton-photon character and is not purely excitonic. This rule is well illustrated by the strong singularity occurring at the energy E_L where the "upper polariton" crosses the $\hat{k}=0$ axis with a zero slope.

We report in Figs. 4 and 5 the real branches of Figs. 1 and 2 and the corresponding calculated reflectivities. We note that for small $\hat{k}$ various exciton and polariton curves are identical; this is due to the fact that forbidden excitons are good eigenstates of the crystal. For larger $\hat{k}$ all excitons are allowed and their dispersion differs from that of the polariton. For still greater $\hat{k}$ the polaritons are mainly "excitons" or "photons."

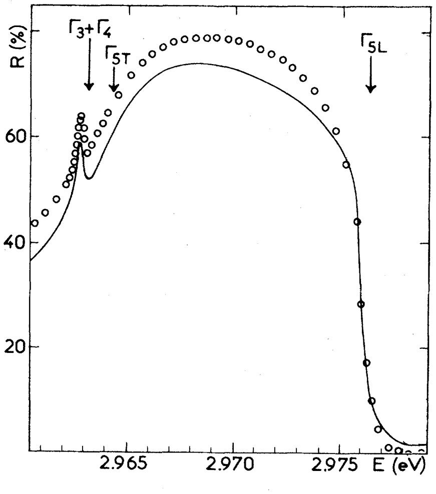

FIG. 3. Experimental (——) and calculated (O) reflectivity of CuBr for $\vec{k} \parallel [110]$ and the polarization $\vec{\epsilon} \parallel [001]$. The experiment is done at 1.8 K. The parameters used in the calculation are given in the text. The arrows indicate the exciton positions for $k=0$. The excitonic dampings are 0.01 meV for the $(\Gamma_3+\Gamma_4)$ states and 0.2 meV for the Γ_5 state.

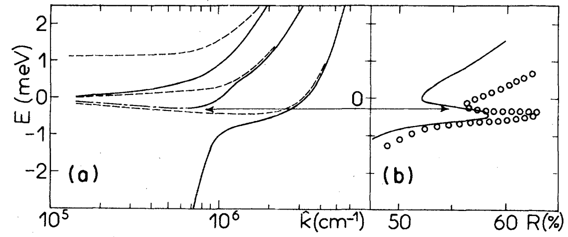

FIG. 4. (a) Excitons (----) and polaritons (——) for $\vec{k} \parallel [110]$ and $\vec{\epsilon} \parallel [001]$. The curve (·-·-) corresponds to a polariton branch $E(\hat{k})$ with negative $\hat{k}$ values for which we have done the substitution $\hat{k} \rightarrow -\hat{k}$. (b) Calculated (O) and observed (——) reflectivity in the same geometry as in (a).

In each of the figures we note the existence of a polariton singularity (with a zero group velocity) which just corresponds to the singularity of the calculated reflectivity. For the two geometries considered in Figs. 4 and 5, the singularities occur for different energies depending on M_{ex} and C. Experimentally, the reflectivity differs also, as reported in Figs. 4 and 5. This has been observed for many crystals and gives, in particular, a strong differential signal in polarization modulated experiments. This dichroism is explained by the polariton model, and the calculated reflectivity in Figs. 4 and 5 reproduces the experimental one well. Different dampings are, however, used for the $(\Gamma_3+\Gamma_4)$ states: 0.1 meV for $\vec{\epsilon} \parallel [1\bar{1}0]$ and 0.01 meV for $\vec{\epsilon} \parallel [001]$. The reason for such a difference is not clear to us.

In Figs. 4 and 5, we note also the existence of two or three exciton branches, converging at small $\hat{k}$, to the $(\Gamma_3+\Gamma_4)$ state. For $\hat{k}$ values of the order of 10^6 cm^{-1}, all are appreciably mixed with the strongly dipole active Γ_5 state. In the [001] polarization, for example, and for $\hat{k}=10^6$ cm^{-1}, the relative transition probabilities for the three excitons in Fig. 4, classified from low to high energy, are 0.07, 0.17, and 0.76. Adopting an ex-

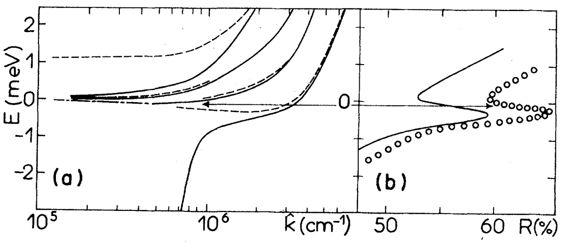

FIG. 5. (a) Excitons (-----) and polaritons (——) for $\vec{k} \parallel [110]$ and $\vec{\epsilon} \parallel [1\bar{1}0]$. For the curve (·-·-) we use the same convention as in Fig. 4(a). (b) Calculated (O) and observed (——) reflectivity in the same geometry as in (a).

citon point of view, as for example in Refs. 6 and 25, we expect the appearance of a doublet (Fig. 4) or a triplet (Fig. 5) in the $\Gamma_3 - \Gamma_4$ region, rather than the single structures observed experimentally or calculated in the polariton model.

We shall note also that in spite of the weakness of the $\Gamma_3 - \Gamma_4$ reflectivity spikes, the $\vec{k}$ linear terms produce relatively strong effects in the crystal. For example, in the case of Fig. 5, the transition probabilities for the lowest exciton are of the order of 10% of the overall transition probabilities for $\hat{k} \simeq 6.10^5\ \text{cm}^{-1}$, i.e., in the region of the polariton singularity. Thus the presence of the weak $\Gamma_3 - \Gamma_4$ structure cannot be associated with the existence of "weakly allowed states." Other examples in the literature[1,17] show that in presence of various oscillators, it is difficult to relate the oscillator strengths to the shape of the reflectivity structures.

D. Effects related to k^2 terms

In the above discussion, we have not taken into account all the valence-band properties and neglected terms proportional to $\gamma_2 k^2$ and $\gamma_3 k^2$ in the matrices (19) and (20) (γ_2 and γ_3 are the Luttinger parameters). Such terms, which are easily calculated by the method of Refs. 10 or 4, modify the exciton dispersion and, like the $\vec{k}$-linear terms, mix the singlet and triplet states.

We have first tried to calculate their effect, in the absence of $\vec{k}$-linear terms, but in the presence of a nonzero Δ_1. In such a case we do not reproduce the experimental $\Gamma_3 - \Gamma_4$ spike. The reason is that all the exciton singularities occur for $k = 0$ —a situation found by other authors for different compounds.[10,11,15] Then the polariton singularities occur also for $\hat{k} = 0$, where they have an entirely excitonic character and do not influence the reflectivity. The only situation for which a $\Gamma_3 - \Gamma_4$ spike is found is for values of γ_2 and γ_3 which give a very flat excitonic curve. This is, however, an unphysical situation and furthermore the experimental results of Figs. 4 and 5 cannot be reproduced with a unique set of values of γ_2 and γ_3.

We have then calculated the reflectivity by considering the $\vec{k}$-linear terms and the warping effects together with the parameters $\gamma_2 = 0.19$, $\gamma_3 = 0.17$, and $m_e^*/m_h^* = 0.14$ calculated by Khan.[26] This modifies only slightly the curves of Figs. 4 and 5 and does not introduce any new effect. Thus it is probably reasonable to neglect the effects related to γ_2 and γ_3 in CuBr. The same conclusion is obtained in Ref. 21.

E. Extra structures in the reflectivity

We have seen in Sec. III C that the existence of an excitonic branch does not mean automatically a reflectivity structure. In the analysis of experimental results obtained on CuBr in presence of external perturbations[27] (magnetic field and uniaxial stress) we have observed another unexpected effect: The number of reflectivity structures is, in some cases, bigger than the number of excitonic branches. To illustrate this effect we show in Fig. 6 the dispersion of the excitons and polaritons calculated in the presence of a magnetic field of 70 kG, for $\vec{k} \parallel [110]$, $\vec{H} \parallel [\bar{1}10]$, and the π polarization. In this case there are four active excitons which, for $k = 0$, can be labeled $|1.0\rangle$, $|2.0\rangle$, and $|2 \pm 2\rangle$. Under the influence of the magnetic field[5] plus the $\vec{k}$-linear terms,[4] we found that the $|2.0\rangle - |1.0\rangle$ mixings are much stronger than the $|2 \pm 2\rangle - |1.0\rangle$ ones. We neglect, therefore, the $|2 \pm 2\rangle$ states, and the excitonic matrix interaction becomes

$$H_x = \begin{array}{cc} \begin{pmatrix} 0 & g_3\mu_B H + \dfrac{3\sqrt{3}}{2}\, Ck_\eta \\ g_3\mu_B H + \dfrac{3\sqrt{3}}{2}\, Ck_\eta & \Delta_1 \end{pmatrix} & \begin{array}{l} |2.0\rangle \\ \\ |1.0\rangle \end{array} \end{array}, \tag{21}$$

where μ_B is the Bohr magneton and g_3 a constant related to the band g values. A preliminary analysis of magneto-optical experiments on CuBr (Ref. 25) gives the value $g_3 \simeq 0.8 \pm 0.2$. The exciton and polariton curves in correspondance with the matrix (21) are given in Fig. 6. We observe that the lowest polariton branch becomes very flat in a given region. The calculated reflectivity presents two structures in the $|2.0\rangle$ region. The first corresponds to the acute maximum of the density of state of the lowest polariton; the second corresponds to the singularity of the other polariton branch. These two structures are clearly related to only one exciton branch, and the polariton model gives here a result which is unexpected in the exciton model. This result is in agreement with the experiments, where two well-resolved structures are observed, at the same energies as the calculated ones.

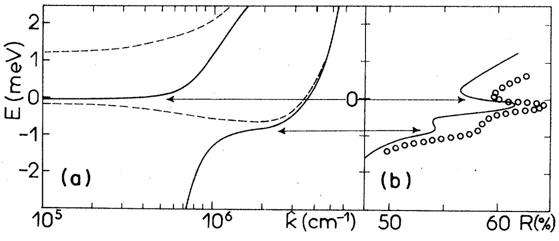

FIG. 6. (a) Simplified model of the exciton (---) and polariton (——) dispersion in CuBr for $\vec{k} \parallel [110]$, $\vec{\epsilon} \parallel [\bar{1}10]$, in the presence of a magnetic field of 70 kG directed along $[\bar{1}10]$. (b) Corresponding calculated (O) and observed (——) reflectivities.

To close this section, we shall note that the analysis of the experimental reflectivity, as done here, does not enable an accurate determination of the excitonic parameters ($M_{ex}, C, \gamma_2, \gamma_3, \Delta_1, \Delta_{TL}, \ldots$). This comes from several facts. First, the experiment gives information on the energies but not on the wave vector of the polariton singularities. Second, there are too many parameters to be considered simultaneously. Third, as noted in Sec. III C the damping parameters probably have a complicated k dependence which has not been taken into account. For all these reasons, a quantitative comparison (by a best-fitting procedure, for example) between the experimental and calculated spectra cannot be done. Such a comparison will need, at most, too long a computation time.

The same kind of difficulties are also encountered by the authors of Ref. 8, who perform a line-shape analysis of the 1s exciton of CuI in the presence of a magnetic field. In Ref. 8, the polariton dispersion is calculated following the classical approach of Ref. 7, which, as expected, gives the same results as the second quantization formalism. With the experimental situation being comparable in CuBr and CuI, the same approximations are used in both cases and the excitonic parameters which are estimated in the two cases are comparable, as expected for these two similar materials.

IV. CONCLUSION

The formalism we have developed to find the polariton dispersion in the presence of a set of interacting excitons is simple to use and does not require more approximations than in the case of isolated excitons having a simple dispersion. It can be used when the exciton behavior is well described by a perturbation theory. It can be easily adapted to more complicated cases than those considered here if, for example, the excitonic interaction matrix contains terms proportional to $k^3, k^4, \ldots$ or if the exciton-photon interaction is not restricted to the electric-dipole approximation only.

The analysis of the reflectivity of CuBr shows clearly the necessity to use the polariton model. As is well known, this model enables us to relate the spectral singularities to the position of the excitons and explains quantitatively the spectra related to several oscillators. However, the role of spatial dispersion has been previously studied in a restricted number of simple cases where it essentially lowers the reflection coefficient in the reststrahlen region. In the CuBr case, the spatial dispersion plays a more essential role and explains why a close correspondence does not exist between the number of active excitonic branches and the number of reflectivity singularities. To our knowledge, this fact is reported here for the first time. The spatial dispersion is also responsible for some line splittings which are not understood in a simple excitonic level.[25,27]

Thus, even for a qualitative reflectance analysis, the polariton model must be used in the presence of a complex set of excitons. To perform a quantitative analysis, difficulties still remain, such as the influence of the broadening effects and the choice of ABC. However, we have been able here to calculate reflection spectra which reproduce well the experimental ones and we have verified that the calculated singularities are not introduced by some artifact depending, for example, upon our particular ABC. It is therefore expected that the method we have used will permit us to analyze many other experimental results.

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