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Wave-Number Dependent Oscillator Strength and Longitudinal-Transverse Splitting of Exciton in CuCl

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Wave-number dependence of exciton longitudinal-transverse splitting was considered in a previous paper, where a microscopic calculation of the electron-hole exchange interaction was shown to account for experiment on CuCl. In this paper, macroscopic approach, based on considerations on the dielectric function, is taken to the same problem. For exciton with finite wave number, it is necessary to distinguish between longitudinal and transverse oscillator strength; the former is proportional to the longitudinal-transverse splitting of exciton. Equivalence of the two approaches is proved.

§1. Introduction

Recent two-photon Raman scattering experiment permitted determination of exciton dispersion relation for wave number K up to as large as 1/10 of the Brillouin zone boundary. In CuCl, the observed dispersion relation revealed a strong wave-number dependence of the separation of longitudinal and transverse exciton energies.[1] The observed longitudinal-transverse splitting (L-T splitting) $\Delta_{LT}(K)$ can be put in the form

$$\Delta_{LT}(K)=\Delta_{LT}(0)+\alpha\frac{\hbar^2K^2}{2m}, \qquad (1.1)$$

with $\Delta_{LT}(0)=5.7$ meV and the non-dimensional parameter $\alpha=-0.12$. On account of negative α, the splitting decreases with increase in K. For example, it is reduced to 2.5 meV at $K=9\times10^6$ cm^{-1}. In a previous paper,[2] microscopic theory was developed to understand the above wave-number dependence. In this paper, we are going to approach the problem from another, macroscopic, point of view.

The L-T splitting can be investigated in two ways,[3] microscopic and macroscopic. In microscopic language, the L-T splitting is caused by the exchange interaction between electron and hole, as was first noted by Heller and Marcus[4] for Frenkel exciton. The formalism can be transcribed to the case of Wannier exciton[5] by substituting Wannier functions for the atomic wave functions. The exchange energy takes the form of the dipole lattice sum, as frequently met in lattice dynamics. The L-T splitting $\Delta_{LT}(K)$ computed from the fcc lattice sum gave[2] $\alpha=-0.00049$, which is far smaller than the experimental value. This disagreement means inadequacy of the Wannier-function formalism to exciton in CuCl. We have to use, instead, Bloch functions in construction of exciton states. In the Bloch-function representation, the exchange interaction consists of analytic and non-analytic parts.[3,6,7] It is this non-analytic part that gives rise to L-T splitting for small K.

We therefore calculated[2] the non-analytic exchange energy for finite wave vector K, using appropriate Bloch functions obtained by means of the $k\cdot p$ perturbation theory. To get the K^2 term in eq. (1.1), it was necessary to invoke the third-order $k\cdot p$ perturbation. In that perturbation process, mixing of the Γ_8 valence band—which lies below the top valence band Γ_7 by the spin-orbit splitting $\lambda=71$ meV—into the Γ_7 band turned out to be substantial because of small energy denominator λ. The resulting value of α was[2] -0.29, in order-of-magnitude agreement with experiment. In this way, non-analytic part of the electron-hole exchange interaction, combined with the $k\cdot p$ perturbed Bloch functions, could explain the observed L-T splitting.

The above calculation is direct and straightforward. Yet, it does not look simple on account of the high—third—order of perturbation. Hence, it seems desirable to consider the problem from another standpoint. We shall

investigate below the L-T splitting starting from macroscopic considerations. We can thus obtain further insight into the wave-number dependent L-T splitting.

When a crystal is regarded as a macroscopic continuum, its dielectric properties are described by the macroscopic dielectric function $\varepsilon(K, \omega)$. When we calculate $\varepsilon(K, \omega)$, we exclude the non-analytic exchange interaction from the Hamiltonian since it is a long-range interaction: the macroscopic electric field produced by this interaction is taken care of by the electric field $\boldsymbol{E}$ that obeys the Maxwell equation.

Now the energy of longitudinal-mode exciton is defined as the zero of the dielectric function $\varepsilon(K, \omega)$. As a result, the L-T splitting becomes proportional to the oscillator strength of exciton. The proportionality is established[3] for ordinary exciton with $K=0$. Its generalization to finite wave vector K, with which we shall begin §2 below, calls for a caution: For finite K, dielectric function and oscillator strength are no more isotropic tensors even in an isotropic medium. We shall have to distinguish between the longitudinal oscillator strength $f_{\mathrm{L}}(K)$ and transverse oscillator strength $f_{\mathrm{T}}(K)$. The L-T splitting $\Delta_{\mathrm{LT}}(K)$ is proportional to $f_{\mathrm{L}}(K)$, whereas $f_{\mathrm{T}}(K)$ should be used in the polariton dispersion equation.

Both $f_{\mathrm{L}}(K)$ and $f_{\mathrm{T}}(K)$ will be calculated up to the K^2 term, using the explicit forms of the $k\cdot p$ perturbed Bloch functions. To obtain the K^2 term in the oscillator strength, second-order $k\cdot p$ perturbation suffices, in contrast with the third-order perturbation necessitated by the calculation of exchange energy. $f_{\mathrm{L}}(K)$ and $f_{\mathrm{T}}(K)$ agree at $K=0$, as they should, but their K^2 terms have opposite sign. Therefore, it is essential to distinguish $f_{\mathrm{L}}(K)$ from $f_{\mathrm{T}}(K)$ to explain the observed K-dependent L-T splitting. The calculated $f_{\mathrm{L}}(K)$ immediately gives $\Delta_{\mathrm{LT}}(K)$. The result turns out to be the same as that obtained[2] from the non-analytic exchange interaction. Coincidence of the results of the two approaches is obtained only as a result of calculation at this stage (§2), but a proof will be given of the equivalence of the two approaches (§3).

We shall assume isotropy of the crystal throughout. This is permissible because both the conduction band Γ_6 and top valence band Γ_7 are spherical.

§2. Oscillator Strength and Longitudinal-Transverse Splitting of Exciton with Finite Wave Vector

In what follows, we consider the Z_3 exciton of CuCl with small but non-vanishing wave vector $\boldsymbol{K}$. Various quantities will be expanded up to second order in wave vector, when necessary.

The translational mass of exciton M_{T} is given by the sum of the electron mass m_{e} and hole mass m_{h}. The energy of exciton is written as

$$E_{\mathrm{T}}(K)=\hbar\omega(K)=E_{\mathrm{T}}(0)+\hbar^2K^2/2M_{\mathrm{T}}.$$

For vanishing wave vector $\boldsymbol{K}$, isotropic medium has an isotropic dielectric constant. However, for finite $\boldsymbol{K}$, we have dielectric tensor[8]

$$\varepsilon_{ij}(\boldsymbol{K}, \omega)=\varepsilon_{\mathrm{T}}(K, \omega)(\delta_{ij}-s_is_j)+\varepsilon_{\mathrm{L}}(K, \omega)s_is_j, \tag{2.1}$$

dependent on the direction of $\boldsymbol{K}$ vector $\boldsymbol{s}=\boldsymbol{K}/K$. The tensor ε_{ij} has two independent components, transverse and longitudinal. Linear terms in wave number (optical gyrotropy) vanish by symmetry.

Similarly, oscillator strength tensor $f_{ij}(\boldsymbol{K})$ can be expressed like eq. (2.1). It also has two independent components, transverse oscillator strength $f_{\mathrm{T}}(K)$ and longitudinal oscillator strength $f_{\mathrm{L}}(K)$. For frequencies ω near resonance with exciton, they are related to the dielectric function by[9]

$$\varepsilon_\lambda(K, \omega)=\varepsilon_{\mathrm{b}}+\frac{\omega_{\mathrm{P}}^2 f_\lambda(K)}{\omega(K)^2-\omega^2}, \quad (\lambda=\mathrm{L}, \text{ or } \mathrm{T}) \tag{2.2}$$

where ε_{b} is the background dielectric constant. The subscript λ specifies the direction of exciton polarization relative to the wave vector $\boldsymbol{K}$. "Plasma frequency" ω_{P} is defined by

$$\omega_{\mathrm{P}}^2=4\pi e^2/m\Omega, \tag{2.3}$$

where Ω is the volume of unit cell.

Electromagnetic normal modes in the crystal are determined by the Maxwell equation with use of the dielectric function (2.1). We have two kinds of solution.[10] Transverse mode satisfies

$$c^2K^2/\omega^2=\varepsilon_{\mathrm{T}}(K, \omega), \tag{2.4}$$

of which solution is called polariton. Longi-

tudinal mode satisfies

$$\varepsilon_{\mathrm{L}}(K,\omega)=0, \tag{2.5}$$

i.e., energy of longitudinal exciton is given by the zero of the longitudinal dielectric function. From eqs. (2.5) and (2.2), the L-T splitting is obtained

$$\Delta_{\mathrm{LT}}(K)=\frac{\hbar\omega_{\mathrm{P}}^2}{2\varepsilon_{\mathrm{b}}\omega(K)}f_{\mathrm{L}}(K), \tag{2.6}$$

under the good approximation $\Delta_{\mathrm{LT}}(K)\ll\hbar\omega(K)$.

For vanishingly small wave number K, we need place no distinction between f_{T} and f_{L}. For finite K, however, it becomes necessary to draw a distinction between them. Transverse oscillator strength $f_{\mathrm{T}}(K)$ should be used in the polariton dispersion equation (2.4). Longitudinal oscillator strength $f_{\mathrm{L}}(K)$ is proportional to the L-T splitting of exciton. Since the exciton energy $\hbar\omega(K)$, being on the order of a few electron volts, has only a weak K-dependence as a whole, the strong K-dependence of $\Delta_{\mathrm{LT}}(K)$ in CuCl is a consequence of the K dependence of $f_{\mathrm{L}}(K)$.

We now proceed to microscopic calculation of $f_{\mathrm{L}}(K)$ and $f_{\mathrm{T}}(K)$ up to the K^2 term. By definition,[11] oscillator strength is written as

$$f_\lambda(K)=\frac{2}{m\hbar\omega(K)}|M_\lambda(K)|^2, \qquad (\lambda=\mathrm{L},\ \text{or}\ \mathrm{T}) \tag{2.7}$$

in terms of the transition matrix element

$$\boldsymbol{M}_\lambda(\boldsymbol{K})=\langle\lambda\boldsymbol{K}|\hat{\boldsymbol{M}}|0\rangle, \tag{2.8}$$

$$\hat{\boldsymbol{M}}\equiv\frac{1}{2}(\boldsymbol{p}\,e^{i\boldsymbol{K}\cdot\boldsymbol{r}}+e^{i\boldsymbol{K}\cdot\boldsymbol{r}}\boldsymbol{p}). \tag{2.9}$$

The original, symmetric, expression is used for the excitation operator $\hat{\boldsymbol{M}}$. The ket $|0\rangle$ means the ground state, and $|\lambda\boldsymbol{K}\rangle$ the exciton state with wave vector $\boldsymbol{K}$ and polarization λ. The vector $\boldsymbol{M}_\lambda(\boldsymbol{K})$ has non-vanishing component only in the direction λ.

In the actual calculation, it is convenient to fix the exciton polarization, say, in the z direction, and choose the vector $\boldsymbol{K}$ either perpendicular or parallel to the z axis. Then we have

$$\begin{aligned}M_z(\boldsymbol{K})&=\langle z\boldsymbol{K}|\hat{M}_z|0\rangle\\&=\sqrt{\frac{2}{N}}\sum_{\boldsymbol{k}}A(\boldsymbol{k})\langle c_\uparrow\boldsymbol{k}|\hat{M}_z|v_\uparrow\boldsymbol{k}-\boldsymbol{K}\rangle.\end{aligned} \tag{2.10}$$

The factor $\sqrt{2}$ comes out of the spin-singlet construction of the exciton state. $A(\boldsymbol{k})$ denotes Fourier transform of the exciton envelope function $F(\boldsymbol{r})$, and N is the number of unit cells. The bra and ket in eq. (2.10) stand for the Bloch functions of conduction and valence bands. The dependence of $M_z(\boldsymbol{K})$ on $\boldsymbol{K}$ stems from the dependence of the above interband transition matrix element upon $\boldsymbol{k}$ and $\boldsymbol{k}-\boldsymbol{K}$. To get the K^2 term in the oscillator strength, we need to do second-order $\boldsymbol{k}\cdot\boldsymbol{p}$ perturbation. The resulting Bloch functions contain various terms. The dominant term possesses the spin-orbit splitting λ in the energy denominator. Other terms may be neglected since their energy denominators are on the order of the band gap energy E_{g}. In the notation of ref. 2, second-order mixing of the $|1/2\rangle$ state (belonging to Γ_8 band) into $|v_\uparrow\rangle$ prevails over the other terms. The above interband transition matrix element becomes then

$$\begin{aligned}&\langle c_\uparrow\boldsymbol{k}|\hat{M}_z|v_\uparrow\boldsymbol{k}-\boldsymbol{K}\rangle\\&=\frac{1}{\sqrt{3}}\langle s|p_z|z\rangle\left[1+\frac{P^2}{3\lambda E_{\mathrm{g}}}(k_x'^2+k_y'^2-2k_z'^2)\right],\end{aligned} \tag{2.11}$$

where $\boldsymbol{k}'=\boldsymbol{k}-\boldsymbol{K}$, and

$$P=i(\hbar/m)\langle s|p_z|z\rangle,$$

is the interband matrix element at $\boldsymbol{k}=0$, that appears in the perturbation process.

We use eq. (2.11) in eq. (2.10) and carry out the summation over $\boldsymbol{k}$, and then substitute the result into eq. (2.7). The transverse and longitudinal oscillator strengths thus obtained are

$$f_{\mathrm{T}}(K)=f(0)\left[1+\frac{2P^2}{3\lambda E_{\mathrm{g}}}\left(\frac{m_{\mathrm{h}}}{M_{\mathrm{T}}}\right)^2K^2\right], \tag{2.12}$$

$$f_{\mathrm{L}}(K)=f(0)\left[1-\frac{4P^2}{3\lambda E_{\mathrm{g}}}\left(\frac{m_{\mathrm{h}}}{M_{\mathrm{T}}}\right)^2K^2\right], \tag{2.13}$$

where

$$f(0)=\frac{4mP^2}{3\hbar^2E_{\mathrm{T}}(0)}|F(0)|^2,$$

neglecting the weak wave-number dependence of $E_{\mathrm{T}}(K)$. These two quantities agree at $K=0$, as they should in a cubic crystal, but they have different K^2 terms of opposite sign. When eq. (2.13) is used in eq. (2.6), we obtain explicit wave-number dependence of the L-T splitting. Putting the result in the form (1.1), we have

$$\alpha=-\Delta_{\mathrm{LT}}(0)\frac{8P^2m}{3\lambda E_{\mathrm{g}}\hbar^2}\left(\frac{m_{\mathrm{h}}}{M_{\mathrm{T}}}\right)^2. \tag{2.14}$$

This expression for α coincides with that obtained from an independent calculation of the non-analytic exchange energy (eq. (4.2) of ref. 2). Substitution of appropriate values for the parameters[2] in eq. (2.14) gives $\alpha=-0.29$. Equivalence of the two methods of calculating the L-T splitting will be investigated in the next section. In the present context, we should like to stress the distinction of transverse and longitudinal oscillator strength. If we erroneously use $f_{\mathrm{T}}(K)$ of eq. (2.12) in eq. (2.6) in place of $f_{\mathrm{L}}(K)$, we have positive α, contrary to experiment. The distinction is essential in understanding the observed wave-number dependent L-T splitting.

As for the transverse oscillator strength $f_{\mathrm{T}}(K)$, it appears in the polariton dispersion equation (2.4). Its wave-number dependence, however, does not significantly influence the polariton dispersion relation. At $K=1.5\times10^{6}$ cm^{-1}, the K^2 term in eq. (2.12) occupies 2% of the total $f_{\mathrm{T}}(K)$. Larger wave number raises $f_{\mathrm{T}}(K)$, but the increasing separation between the photon and transverse-exciton branches quenches their mixing. In fact, we analyzed the experimental data of ref. 1, using wave-number dependent $f_{\mathrm{T}}(K)$. We found no definite necessity of incorporating such wave-number dependence within the experimental accuracy.

§3. Equivalence of Macroscopic and Microscopic Approaches

In the preceding section, we calculated L-T splitting of exciton using the relation (2.6) derived on the basis of macroscopic considerations. On the other hand, in microscopic terms, L-T splitting is a consequence of the non-analytic exchange interaction between electron and hole. For $K=0$, equivalence of the two approaches is established.[3] We can generalize the equivalence to finite wave number K: we shall see below that the L-T splitting $\Delta_{\mathrm{LT}}(K)$ calculated from non-analytic exchange interaction can be written as eq. (2.6) for finite K.

The proof rests on the commutation relation

$$[\hat{H}, e^{i\boldsymbol{K}\cdot\boldsymbol{r}}]=(\hbar/m)\boldsymbol{K}\cdot\hat{\boldsymbol{M}}, \tag{3.1}$$

for one-electron Hamiltonian

$$\hat{H}=p^2/2m+V(\boldsymbol{r}).$$

The identity (3.1) is valid also for many-electron Hamiltonian that contains electron-electron interaction. Hence we have the relation

$$\hbar\omega(K)\langle\lambda\boldsymbol{K}|e^{i\boldsymbol{K}\cdot\boldsymbol{r}}|0\rangle=(\hbar/m)\boldsymbol{K}\cdot\langle\lambda\boldsymbol{K}|\hat{\boldsymbol{M}}|0\rangle, \tag{3.2}$$

for the matrix elements between the exciton state $|\lambda\boldsymbol{K}\rangle$ and the ground state $|0\rangle$.

Non-analytic part of the electron-hole exchange interaction is[7]

$$J^{\mathrm{NA}}_{\lambda\lambda'}(\boldsymbol{K})=\frac{4\pi e^2}{\varepsilon_{\mathrm{b}}\Omega}\frac{N_\lambda(\boldsymbol{K})^*N_{\lambda'}(\boldsymbol{K})}{K^2}, \tag{3.3}$$

where

$$N_\lambda(\boldsymbol{K})=\langle\lambda\boldsymbol{K}|e^{i\boldsymbol{K}\cdot\boldsymbol{r}}|0\rangle. \tag{3.4}$$

The interaction is screened by the background dielectric constant ε_{b}. When eq. (3.2) is used in eq. (3.4), we have

$$N_\lambda(\boldsymbol{K})=\frac{1}{m\omega(K)}\boldsymbol{K}\cdot\boldsymbol{M}_\lambda(\boldsymbol{K}). \tag{3.5}$$

Since the vector $\boldsymbol{M}_\lambda(\boldsymbol{K})$ lies in the direction of exciton polarization λ, the quantity $N_\lambda(\boldsymbol{K})$ vanishes for $\lambda=\mathrm{T}$ (transverse polarization),

$$N_{\mathrm{T}}(K)=0.$$

It is non-vanishing only for $\lambda=\mathrm{L}$ (longitudinal polarization),

$$N_{\mathrm{L}}(K)=\frac{K}{m\omega(K)}M_{\mathrm{L}}(K). \tag{3.6}$$

Consequently, the L-T splitting arising from the exchange interaction J^{NA} is given by

$$\Delta_{\mathrm{LT}}(K)=\frac{4\pi e^2}{\varepsilon_{\mathrm{b}}\Omega}\frac{N_{\mathrm{L}}(K)^2}{K^2}=\frac{4\pi e^2}{\varepsilon_{\mathrm{b}}\Omega}\frac{\hbar}{2m\omega(K)}f_{\mathrm{L}}(K), \tag{3.7}$$

where we used eqs. (3.6) and (2.7). The result (3.7) agrees with eq. (2.6).

The above proof shows that the L-T splitting is intimately related to the longitudinal oscillator strength. It has nothing to do with the transverse oscillator strength.

Equivalence of the two approaches tells us that the L-T splitting may be calculated in either way. In fact, in a previous paper, we carried out a calculation of eq. (3.4), which required third-order $k\cdot p$ perturbation. For the sake of computational simplicity, use of eq. (2.6) is favorable because the calculation of $f_{\mathrm{L}}(K)$ requires $k\cdot p$ perturbation of lower order.

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