PHYS 211A Special Topic Paper: Effects of Spatial Dispersion on the Optical Properties of Crystals

Chih-Chun Hsu

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1 Citation

1969 Oliver E. Buckley Condensed Matter Physics Prize Recipient: J. J. Hopfield and D. G. Thomas. ”For their joint work combining theory and experiment which has advanced the understanding of the interaction of light with solids”

2 Summary

One of their combined work is to resolve the problem of the non-local effect on the optical properties of crystals. A dielectric constant classical determined by the classical theory is only depending on frequency. They added the spatial dispersion based on the boundary condition to their new theory and tested the reflectivity of some crystals. The resulting non-local theory can explain the anomaly of sharp subsidiary reflectivity spikes in crystals (CdS and ZnTe in their work), which cannot be explained by any classical theories.

3 Classical dielectric theory of the optical properties

The classical theory considers the localized dielectric behavior, with a polarization **P** volume of radius r_0. The radius r_0 is much smaller than wavelengths. The resulting classical theory is that a dielectic constant is only dependent on the electric field **E** in the volume and therefore only dependent on frequency. The electromagnetic waves are the only factor considered in energy transport.

The classical theory of the optical properties did not include the spatial consideration, and there are some cases that the local approximation is no longer valid.

Hopfield and Thompson have been working on physics by excitons in crystals. Excitons are the first excited state given an insulating crystal in the conduction band, bound to a valence hole. The energy of such quantized particles are measured in the optical and near UV wavebands. They considered the effect on reflectivity of insulating crystals due to finite mass of excitons.

4 Theory

Hopfield and Thompson used a classical formulation of spatial dispersion effect on crystals.

Assume there is an electric field $\boldsymbol{E_0}\ e^{\boldsymbol{ik\cdot x}-i\omega t}$ exist in a crystal. The polarization wave can be written as:

$$\boldsymbol{P} = (\sum_{\boldsymbol{G}} \boldsymbol{\alpha}(\boldsymbol{k} + 2\pi\boldsymbol{G}, \omega)e^{2\pi i\boldsymbol{G\cdot x}})\boldsymbol{E_0}e^{\boldsymbol{ik\cdot x}-i\omega t}, \tag{1}$$

where $\boldsymbol{G}$ is a reciprocal lattice vector and $\boldsymbol{\alpha}(\boldsymbol{k}+2\pi\boldsymbol{G},\omega)$ is a second rank tensor function. Only low energy is considered ($\omega <<$ c/(lattice constant)). Then

$$\boldsymbol{P_k(\omega)} = \boldsymbol{\alpha}(k,\omega)\boldsymbol{E_k}(\omega), \tag{2}$$

Note that the polarizability $\boldsymbol{\alpha}$ is both frequency and wave-vector dependent. In insulating crystals,

$$\boldsymbol{\alpha}(k,\omega) = \sum_j \frac{\boldsymbol{\alpha_j(k)}\omega_j^2(k)}{\omega_j^2(k) - \omega^2 - i\omega\Gamma_j(\boldsymbol{k})}, \tag{3}$$

Obeying the Kramers-Kronig relation. To simplify the problem, consider only

(i) The frequency near a resonance

(ii) Ignore Γ (This is a good approximation)

(iii) Choose the wave vector $\boldsymbol{k}$ paralleled to one axis of $\boldsymbol{\alpha}$ and perpendicular to the remaining axes (e.g., $\boldsymbol{k}$ is in the direction $< 100 >$ in a cubic crystal)

(iv) Only the zeroth and the second order of $\boldsymbol{\alpha(k)}$ and $\omega_j(k)$ will be considered; the first order terms would vanish if the crystal has inversion symmetry

Therefore, we can obtain a rather simpler expression of $P_k(\omega)$

$$P_k(\omega) = \Big[\frac{\epsilon_0 - 1}{4\pi} + \frac{(\alpha_0 + \alpha_2 k^2)\omega_0^2}{\omega_0^2 + Bk^2 - \omega^2 - i\omega\Gamma}\Big] E_k(\omega), \tag{4}$$

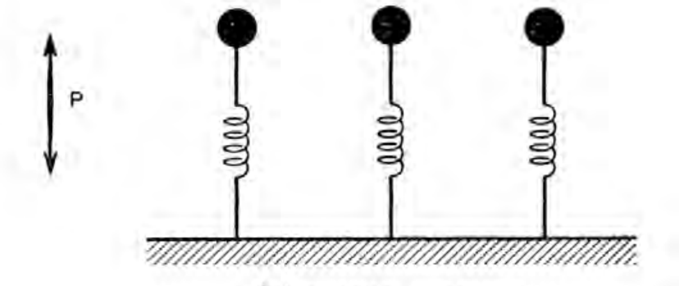
Put this equation into the Maxwell's equations, and we can get a transverse solution

$$n^2 \equiv \frac{c^2k^2}{\omega^2} = \epsilon_0 + \frac{4\pi(\alpha_0 + \alpha_2 k^2)\omega_0^2}{\omega_0^2 + Bk^2 - \omega^2 - i\omega\Gamma}, \tag{5}$$

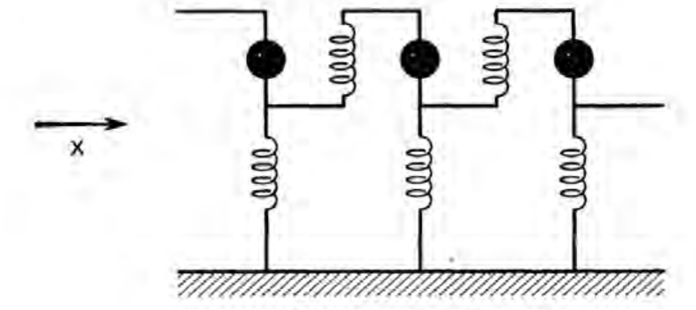
Consider several cases. In classical optics, $\alpha_2 = B = 0$, and the case $B = 0, \alpha_2 \neq 0$ is similar to the classical case. The case $B \neq 0, \alpha_2 = 0$ is more interesting. In this case, for a given ω, the equation 5 is in the order of k^4, so there are two transverse solutions propagating in two directions for a given α_0 and ω, one is electromagnectic and the other is mechanical based on the spatial boundary condition.

The term Bk^2 in the equation 5 can be interpreted as the contribution of excitons:

Figure 1: The classical model for a dielectric with charge-mass particles and springs (a) and with spatial dispersion (b). The polarization $\boldsymbol{P}$ and the direction $\boldsymbol{x}$ are indicated.



(a) CLASSICAL DIELECTRIC



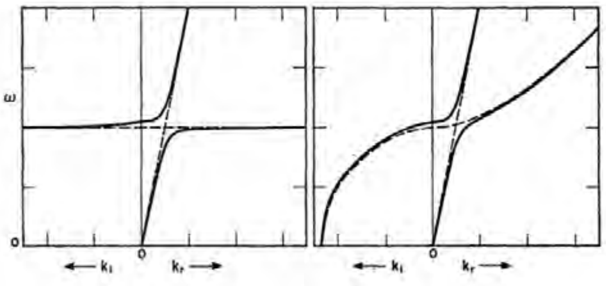
(b) SPATIAL DISPERSION

$$\omega^2 = \omega_0^2 + Bk^2 \text{ or } \hbar\omega \approx \hbar\omega_0 + \frac{1}{2}\frac{\hbar^2 k^2}{m^\star}, \tag{6}$$

where $m^\star$ is the exciton mass.

The figure 1 illustrates the comparison of the classical and the the model with spatial dispersion ($B \neq 0$). The polarizability contributed by excitons is determined by the equation 5 when $\alpha_2 = \Gamma = 0$. The figure 2 shows the frequency wave-vector dispersion relation between the two models.

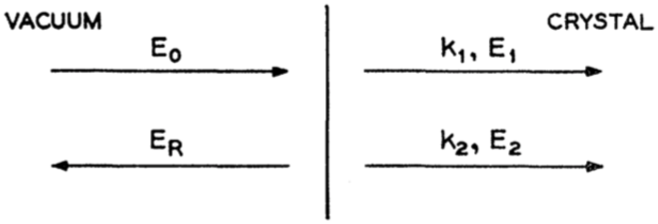
Figure 2: The frequency wave-vector dispersion for the transverse normal modes of light with a classical dielectric (left) and with a dielectric having spatial resonance dispersion (right). There is no damping and $\alpha_0 = 0$ for the dashed lines and $\alpha_0 \neq 0$ for the solid lines.



5 Boundary conditions

To make this effect experimentally attainable, Hopfield and Thompson considered the simplest case and therefore determined the boundary condition. The normal incidence in a principle direction is treated, shown in the figure 3. At normal incidence, the longitudinal mode does not occur; only the transverse mode exists. From the equation 5, consider $\alpha_2 = 0$ and a finite α_0, the dielectric constant can be described as

Figure 3: A diagram showing the case of the normal incidence reflectivity problem.



$$\epsilon(k,\omega) = \epsilon_0 + \frac{4\pi\alpha_0\omega_0^2}{\omega_0^2 - \omega^2 + (\hbar k^2\omega_0/m_\star - i\omega\Gamma)}, \tag{7}$$

near a frequency ω_0. In a uniaxial crystal, the electric field are parallel or perpendicular to the optical axis. The usual boundary conditions by Maxwell equations are

$$\begin{aligned} E_0 + E_R &= E_1 + E_2, \\ E_0 - E_R &= n_1 E_1 + n_2 E_2, \end{aligned} \tag{8}$$

where $n_1 = ck_1/\omega$, $n_2 = ck_2/\omega$, and k_1 and k_2 are the roots of the dispersion relation $c^2k^2/\omega^2 = \epsilon(k, \omega)$. Plugging the equation 7 back into the equation 5, we can obtain n_1^2 and n_2^2

$$\begin{aligned} n^2 = \frac{1}{2}[\epsilon_0 - (1 - \frac{\omega^2}{\omega_0^2} - i\frac{\Gamma\omega}{\omega_0^2})\frac{(mc^2)\omega_0}{\hbar\omega^2}] \\ \pm \{\frac{1}{4}[\epsilon_0 + (1 - \frac{\omega^2}{\omega_0^2} - i\frac{\Gamma\omega}{\omega_0^2})\frac{(mc^2)\omega_0}{\hbar\omega^2}]^2 + 4\pi\alpha_0\frac{mc^2\omega_0}{\hbar\omega^2}\}^{1/2}, \end{aligned} \tag{9}$$

Using the equation 9, the reflection coefficient R can be derived from the equation 7. However, there are two propagating modes, so another boundary condition is needed. For a perfect crystal, a free exciton will reflect back along the boundary, say for $x > 0$, and the exciton wave function should be in the form

$$\psi(x) \propto e^{ikx} + e^{-i\phi}e^{-ikx}, \tag{10}$$

where ψ is a real energy function. To determine ψ, two models are considered for the force turning the exciton around (without the coupling between the light and the exciton).

5.1 Tight-bonding model: Frenkel excitons with nearest-neighbor interactions

Consider the case of the tight-binding model. The crystal has a one-dimensional line with atoms that each have a single exciton state coupled to its nearest neighbors. Hopfield and Thompson formulated by setting a Hamiltonian with the ladder operators. The exciton wave function is

$$\psi(x_i) = e^{ik(x_j+a) - e^{-ik(x_j+a)}}, \tag{11}$$

This wave function satisfies the boundary condition that $\psi(x) = 0$ outside the crystal. For long wavelengths, the boundary condition can be simplified as

$$\psi(0) \approx a(\partial\psi/\partial x)(0), \tag{12}$$

or

$$\psi(0) \approx 0. \tag{13}$$

5.2 Weak-bonding model: Wannier-Mott excitons

The weak-binding approximation would be more applicable to real experiments. Consider a hydrogen-like exciton in the ground state (1S) state. The reflected surface is described by a potential $U(x)$. The polarization operator for excitons $P_e x(x)$ is proportional to $\psi(x) + \psi^\star(x)$. For the frequency near resonance,

$$[\frac{\partial^2}{\partial t^2} + \omega_0^2 - \frac{\hbar\omega_0}{m^\star}\frac{\partial^2}{\partial x^2} + 2\frac{\omega_0 U(x)}{h}]P_{ex}(x,t) = \alpha_0\omega_0^2 E(x,t) \tag{14}$$

where $E(x,t)$ is the electric field. If $U(x) = 0$, the polarizability determined by the equation 14 is the right term on the right hand side of the equation 7.

The boundary conditions can now be described. For $U(x) = 0$, the equation 13 says $P_{ex} = 0$. The additional boundary conditions are

$$P_{ex_1} + P_{ex_2} = 0 \text{ or } (n_1^2 - \epsilon_0)E_1 + (n_2^2 - \epsilon_0)E_2 = 0 \tag{15}$$

If $U(x) \neq 0$, then we need to solve the following equations

$$x < 0 : \frac{\partial^2 E}{\partial x^2} = +\frac{1}{c^2}\frac{\partial^2 E}{\partial t^2}, \tag{16}$$

$$x > 0 : \frac{\partial^2 E}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}(\epsilon_0 E + 4\pi P_{ex}), \tag{17}$$

subject to the boundary conditions

$$\begin{gathered} E(0_- = E(0_+), \\ \frac{\partial E}{\partial x}(0_-) = \frac{\partial E}{\partial x}(0_+), \\ P_{ex} = 0,\ x \leq 0, \end{gathered} \tag{18}$$

The reflectivity $R = E_R/E_0$ is derived as

$$R = (1 - n^\star/(1 + n^\star), \tag{19}$$

where $n^\star$ is the effective index of refraction. If the potential $U(x) = 0$ with the boundary condition 13,

$$n^\dagger = (n_1 n_2 + \epsilon_0)/(n_1 + n_2), n^\star = n^\dagger, \tag{20}$$

If the potential $U(x) \neq 0$,

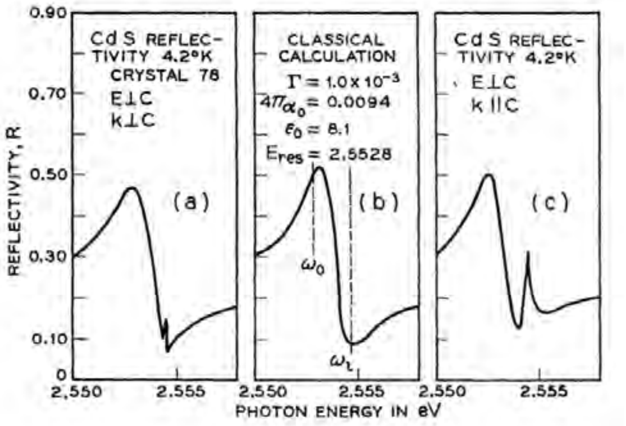
$$n^\dagger = (n_1 n_2 + \epsilon_0)/(n_1 + n_2), n^\star = n\Big[\frac{(n^\dagger + n)e^{-2iknl} - n + n^\dagger}{(n^\dagger + n)e^{-2iknl} + n - n^\dagger}\Big], \tag{21}$$

where l is required by $P(l) = 0$ in the crystal.

6 Experiments

Based on the boundary conditions derived above, the theory can explain the experiments of exciton absorption peaks. Thompson conducted the experiments using CdS (hexagonal) and ZnTe (cubic) to confirm the theories presented above at low temperature of 1.6-4.2 K.

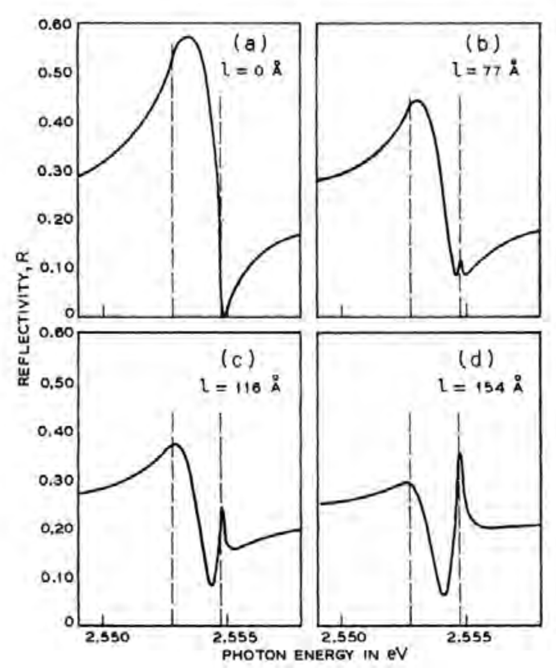
Figure 4: The CdS spectra at normal incidence. (a) and (c) are the measured spectra while (b) is the classical calculation. C is the hexagonal c axis.



The measured reflectivity of CdS of the lowest exciton state (exciton A) is shown in the figure 6 at normal incidence. The subplots (a) and (c) are the measured spectra with different geometry ((a) for $k \perp c$ and (c) $k \parallel c$), and (b) is the classical calculation. The classical calculation cannot explain the subsidiary peak near the absorption, and the classical theory predicts the cases (a) and (c) would be the same, which is not true in the experiment. Another difference is that the measured reflectivity is slightly larger and increases less rapidly than the classical calculation.

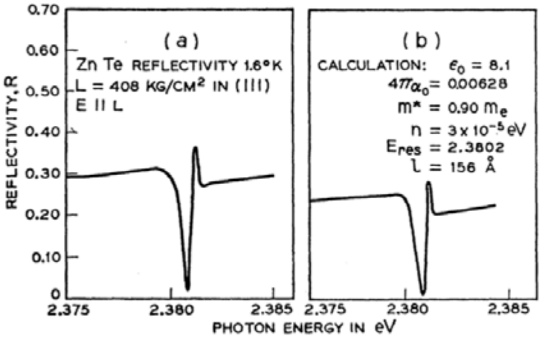
Some physical properties of the excitons in CdS are as follows. The exciton A in CdS is doubly degenerate. The figure 6 (a) is that when $\boldsymbol{k} \perp c$, exciton A splits into a longitudinal and a transverse exciton at frequency ω_l and ω_0. In the figure 6 (c), The exciton mode is not split, only transverse mode, but the subsidiary frequency ω_l is much enhanced.

Figure 5: The calculated spectra considering spatial dispersion as a function of l by Hopfield and Thompson.



If the spatial dispersion is considered with $l = 0$ and in the equations 19, 20, and 21, the calculated results are shown in the figure 6. A subsidiary peak followed by the absorption is compatible with the theory proposed by Hopfield and Thompson. To show that CdS is not the only example, they also used ZnTe in $< 111 >$ direction to confirm the theory. The figure 6 shows the measured and calculated reflctivity spectrum of ZnTe. They did not try to best fit the parameters, but just showed the theory is qualitatively consistent with the measured spectrum.

Figure 6: The measured and calculated reflectivity spectrum of ZnTe.



7 References

1. J. Frenkel, 1931 Phys. Rev. 37, 17
2. J. J. Hopfield, 1958 Phys. Rev. 112, 1555
3. J. J. Hopfield and D. G. Thomas, 1963 Phys. Rev. 132, 563