Radiative decay of excitons in thin crystal films

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The radiative decay of excitons in thin films is studied. The exciton modes capable of radiating are found to be superradiant, in contrast to the case of excitons in a bulk crystal. It is estimated that this radiative decay mechanism will dominate over the other decay mechanisms such as those due to phonons or lattice imperfections.

The study of coherent radiation, superradiant states, etc., has attracted much attention lately.[1-7] In particular, the radiation from the bulk of a crystal with a small number of excited atoms was investigated by Lee, Lee, and Chang.[8] A considerable amount of photon trapping was found. It was concluded that the boundary effect should be of importance for the observation of the radiation. In a recent work[9] the spontaneous radiation from thin films is calculated by taking into account the transverse radiative coupling but neglecting the longitudinal Coulombic coupling between atoms. Correlated states of the film analogous to Dicke's superradiant states were found. However, it is known that the Coulombic interaction among atoms gives rise to the propagation of excitation energy in the form of excitons.[10] The interaction of photons with exciton leads, in a three-dimensional bulk crystal, to the formation of polariton, which undergoes no radiative decay.[11] This is no longer the case when the crystal symmetry is broken. In this paper, the radiative decay of excitons in thin films will be calculated.

We first consider a crystal film of one layer consisting of tightly bound atoms as in solid Ar, where the last filled band is separated from the conduction band by $\hbar\omega_0$. It can be shown that the transverse exciton annihilation operator $\beta_{\vec{q}\lambda}$ and the photon annihilation operator $a_{\vec{q}k_z\lambda}$ obey the equations

$$i\frac{d}{dt}\beta_{\vec{q}\lambda}(t) = \sum_{k_z} \mathcal{C}^*_{\vec{q}k_z\lambda} \exp(i\omega_{\vec{q}k_z\lambda}t) a_{\vec{q}k_z\lambda}(t), \tag{1}$$

$$i\frac{d}{dt}a_{\vec{q}k_z\lambda}(t) = \mathcal{C}_{\vec{q}k_z\lambda} \exp(-i\omega_{\vec{q}k_z\lambda}t)\beta_{\vec{q}\lambda}(t) + A^{(2)}_{\vec{q}k_z} a_{\vec{q}k_z\lambda}. \tag{2}$$

$\vec{q}$ is a two-dimensional momentum vector in the plane of the crystal film, whose normal is in the z direction

$$\omega_{\vec{q}k_z\lambda} = E_{\vec{q}\lambda} - c(q^2 + k_z^2)^{1/2}, \tag{3}$$

where $E_{\vec{q}\lambda}$ is the energy of the exciton in the $\vec{q}\lambda$ mode

$$\mathcal{C}_{\vec{q}k_z\lambda} = i\left(\frac{2\pi\hbar c}{(q^2+k_z^2)^{1/2}}\right)^{1/2}\left(\frac{e\omega_0}{c}\right)\vec{X}\cdot\hat{\epsilon}_{\vec{q}k_z\lambda}, \tag{4}$$

$$A^{(2)}_{\vec{q}k_z} = (4\pi e^2/c)(q^2+k_z^2)^{-1/2}(N/V)\omega_0|\vec{X}|^2, \tag{5}$$

where $\vec{X}$ is essentially the dipole-moment matrix element of the atomic states,[12] and $\hat{\epsilon}_{\vec{q}k_z\lambda}$ is the polarization unit vector.

Note that an exciton of momentum $\vec{q}$ can be coupled to a photon of momentum $\vec{q}+\hat{z}k_z$ since the crystal symmetry is broken in the z direction while the momentum in the xy plane is conserved owing to the neglect of all umklapp processes. The term involving $A^{(2)}_{\vec{q}k_z}$ in (2) arises from the $A^2\rho$ coupling of the atoms with the transverse radiation field while the other terms of Eqs. (1) and (2) come from the $\vec{A}\cdot\vec{j}$ coupling.

The solution to (1) and (2) can be obtained in a manner similar to that of Ref. 8.

$$\beta_{\vec{q}\lambda}(t) = \beta_{\vec{q}\lambda}(0)\exp\{i[E_{\vec{q}\lambda} - \Omega_s(\vec{q}\lambda)]t - \Gamma_s(\vec{q}\lambda)t\}, \tag{6}$$

where

$$\Omega_s(\vec{q}\lambda) = P\sum_{k_z}\frac{|\mathcal{C}_{\vec{q}k_z\lambda}|^2}{\omega_{\vec{q}k_z\lambda}}, \tag{7}$$

$$\Gamma_s(\vec{q}\lambda) = \Pi\sum_{k_z}|\mathcal{C}_{\vec{q}k_z\lambda}|^2\delta(\omega_{\vec{q}k_z\lambda}). \tag{8}$$

It can be shown that, for excitons in the optical region $[(\omega_0/c)d \ll 1]$,

$$\Gamma_s(\vec{q}\lambda) = \begin{cases} \dfrac{3\pi}{2k_0^3}\dfrac{N}{L^2}\gamma_s\dfrac{(k_0^2-q^2)|\hat{X}\times\hat{z}|^2 + |\vec{X}\times\vec{q}|^2}{(k_0^2-q^2)^{1/2}}, & \text{when } q < k_0, \\ 0, & \text{otherwise}, \end{cases} \tag{9}$$

where γ_s is the decay rate of an isolated atom, d is the lattice spacing, and L^2 is the area of the film. Also, the radiation intensity distribution is

$$\lim_{t\to\infty}|a_{\vec{q}k_z\lambda}(t)|^2 \sim \frac{|\mathcal{C}_{\vec{q}k_z\lambda}|^2}{[\omega_{\vec{q}k_z\lambda} + \Omega_s(\vec{q}\lambda) - A^{(2)}_{\vec{q}k_z}]^2 + \Gamma_s(\vec{q}\lambda)} \tag{10}$$

for $q < k_0$.

From (10) and (3) we observe that the interaction of the transverse radiation field with the exciton leads to a shift of the exciton frequency $(1/\hbar)E_{\vec{q}\lambda}$ by $\Omega_s(\vec{q}\lambda) - A^{(2)}_{\vec{q}k_z}$. In the limit of vanishing dipolar interaction, the exciton frequency reduces to ω_0. Thus, the consideration of Coulombic interaction among the atoms affects only the frequency of the exciton but not its radiative decay rate.

When we have a thin film of n layers, then as long as the thickness of the film is small compared with the radiation wavelength, the different layers will radiate coherently in the $\vec{q}\lambda$ exciton mode with a rate approximately equal to $n\Gamma_s(\vec{q}\lambda)$.

For an approximate evaluation of the decay rate it is easy to see from Eq. (9) that[13]

$$\Gamma_s(\vec{q}\lambda) \sim \frac{\gamma_s}{[(\omega_0/c)d]^2} \quad \text{for } q < k_0 . \tag{11}$$

Thus, only those exciton modes with $q < k_0$ can decay into photons, but with a very much enhanced rate characterized by an enhancement factor $(c/\omega_0 d)^2$. The number of such modes is $[(\omega_0/c)L]^2$. These modes are exactly analogous to the superradiant modes of Dicke's.[1] In order to compare the importance of the radiative decay mechanism with other mechanisms due to phonons or lattice imperfections etc. for a thin film, we use the absorption of the "yellow series" of exciton in CuO_2 as an example.[14] In this example of a bulk crystal, the usually dominating decay mechanisms yield a relative decay width

$$(\Delta\omega/\omega)_{\text{other}} \sim \tfrac{1}{2000},$$

while the radiative mechanism would give

$$(\Delta\omega/\omega)_{\text{radiative}} \sim \tfrac{1}{100}$$

for a thin film. This conclusion is based on the above completely quantum mechanical calculation. It is also consistent with the result of Sugakov[15] who studied the effect of surface exciton on a semi-infinite crystal in a semiclassical approximation.

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[13]Note that in Ref. 9 it was erroneously stated that the $\vec{q}$ vector for which $\Gamma_s(\vec{q}) \neq 0$ are those within the k_0 neighborhood of the four corners of the first Brillouin zone. The correct statement is made here in Eq. (9). The rest of the conclusions in Ref. 9 are still correct.
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