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## Temperature dependence of excitonic line shapes of disordered solids

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**Abstract.** The influence of weak exciton–phonon interaction in the presence of static disorder on the optical absorption line shape of Frenkel excitons has been investigated. It is shown that the presence of static disorder modifies the low temperature dependence of the excitonic linewidth from exponential to power law as a consequence of breaking the momentum conservation in disordered solids.

### 1. Introduction

Recently, many investigations considered the influence of static and dynamic disorder on optical absorption spectra of Frenkel excitons in molecular solids (see e.g. Ueta *et al* (1986), Port *et al* (1987) for further references). The theoretical study of the role of dynamic disorder was performed both for excitons interacting with a phonon bath (Toyozawa (1958); see also references in Winkler and Reineker (1987)) and for a stochastic modelling of the influence of the phonons by external noise (Haken and Strobl (1973), Haken and Reineker (1972); see also Reineker (1982) for additional references). The influence of static disorder (caused by impurities, defects or random site energies in mixed crystals) was investigated by means of both approximate analytical approaches, e.g. coherent potential approximation (CPA) (Velicky *et al* 1968, Sumi 1977, Klafter and Jortner 1978, Boukahil and Huber 1990) and numerical calculations (Schreiber and Toyozawa 1982, Huber and Cheng 1988). Very recently the optical absorption in a disordered one-dimensional excitonic solid in the presence of stochastic white noise has been studied numerically (Köhler *et al* 1989). However, the stochastic description does not allow one to consider temperature dependences because it corresponds formally to the case of infinite bath temperature, see e.g. Lindenberg and West (1983). In this paper we are interested in the temperature dependence of excitonic spectra caused by phonon induced dynamical disorder in the presence of a static disorder. Such a situation was considered in several studies (see e.g. Burland *et al* (1977), Port *et al* (1987), and references therein) both from the experimental and theoretical viewpoints. Usually it is assumed that static and dynamic disorder give additive contributions to the optical linewidth, the high temperature linewidth being

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determined by phonons and the low temperature one by static disorder. The temperature dependent part of the linewidth at  $T \ll T_D$  ( $T_D$  is the Debye temperature) decays exponentially with decreasing  $T$  for single-phonon processes and is proportional to  $(T/T_D)^7$  for two-phonon processes (Port *et al* 1979). The reason for such a drastic decrease of the single-phonon contribution at low temperatures is connected with momentum conservation and with the exponential decrease of the number of acoustic phonons with large momenta (and energy). However, in disordered solids exact momentum conservation no longer holds and phonons with all momenta contribute to the optical absorption linewidth. As a consequence, one should expect a modified low temperature behaviour of the excitonic linewidth. This behaviour is just the subject of this work.

## 2. Model Hamiltonian

Consider a molecular crystal with the Hamiltonian  $H = H_{\text{ex}} + H_{\text{ph}} + H_{\text{ex-ph}}$ , where the exciton Hamiltonian

$$H_{\text{ex}} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{n}} v_{\mathbf{n}} a_{\mathbf{n}}^{\dagger} a_{\mathbf{n}} \quad (1)$$

the phonon Hamiltonian

$$H_{\text{ph}} = \sum_{\mathbf{k}} \omega_{\mathbf{k}} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} \quad (2)$$

and the Hamiltonian of exciton-phonon interaction

$$H_{\text{ex-ph}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{n}} g(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{n}) a_{\mathbf{n}}^{\dagger} a_{\mathbf{n}} (b_{\mathbf{k}} + b_{-\mathbf{k}}^{\dagger}) \quad (3)$$

have the usual form. In these formulae  $N$  is the total number of lattice sites,  $a_{\mathbf{n}}$  ( $a_{\mathbf{k}}$ ) are the exciton operators in site (momentum) representation,  $b_{\mathbf{k}}$  is the phonon operator;  $\epsilon_{\mathbf{k}}$  and  $\omega_{\mathbf{k}}$  are the exciton and phonon energies in the ordered crystal, and  $v_{\mathbf{n}}$  are random site energies describing the static disorder.

A convenient tool for the description of kinetic problems is the Keldysh formalism (Keldysh 1964), which allows a systematic diagrammatic treatment. Here we restrict ourselves to the case of a weak external electromagnetic field. Considering the linear response problem we deal only with Keldysh single-particle Green's functions defined over the excitonic vacuum. In this case the non-diagonal component of the Keldysh excitonic Green's matrix function  $G_{12}$  vanishes and one has a closed formalism in terms of the diagonal component  $G_{11}$  (both arguments lying on the upper part of the Keldysh contour) coinciding in the case considered with the retarded excitonic Green's function

$$G(\mathbf{n}, t; \mathbf{m}, t') = -i\Theta(t - t') \langle\langle [a_{\mathbf{n}}(t), a_{\mathbf{m}}^{\dagger}(t')] \rangle\rangle \quad (4)$$

where  $\langle\langle \dots \rangle\rangle$  means thermal averaging over the crystal states in the absence of excitons. A second ingredient of the formalism is the causal phonon Green's function

$$D(\mathbf{k}, t; \mathbf{k}', t') = -i \langle\langle [T(\phi_{\mathbf{k}}(t), \phi_{\mathbf{k}'}(t')) \rangle\rangle \rangle \quad (5)$$

where  $\phi_{\mathbf{k}}(t) = b_{\mathbf{k}}(t) + b_{-\mathbf{k}}^{\dagger}(t)$ . For the usual interaction Hamiltonian of excitons with a plane electromagnetic wave  $\mathcal{E} \exp i(\mathbf{q} \cdot \mathbf{n} - \omega t) + \text{CC}$

$$H' = -\mu \sum_{\mathbf{n}} [a_{\mathbf{n}}^{\dagger} \mathcal{E} \exp i(\mathbf{q} \cdot \mathbf{n} - \omega t) + \text{HC}] \quad (6)$$

( $\mu$  is the transition dipole moment) we have the following expression for the optical absorption spectrum (up to a normalization factor):

$$\alpha(\omega) = -\text{Im} \bar{G}(\omega, \mathbf{q} \approx 0). \quad (7)$$

Here  $\bar{G}(\omega, \mathbf{q})$  is the frequency and momentum transform of the excitonic Green's function (4) averaged over random realizations of the static disorder; the frequency  $\omega$  is counted from the bottom of the free exciton band; the light wave vector  $\mathbf{q}$  will be neglected below.

### 3. Evaluation of excitonic self-energy

We restrict ourselves to the case of weak exciton-phonon interaction, assuming the following inequality between the inverse scattering times for excitons scattered by phonons and by static disorder:  $1/\tau_{\text{ph}} \ll 1/\tau \ll B$ ;  $B$  is the exciton bandwidth. In the lowest (Born) approximation in  $H_{\text{ex-ph}}$  we have the Dyson equation for the non-averaged excitonic Green's function  $G$ :

$$G = \mathcal{G} + \mathcal{G} \Sigma_{\text{ex-ph}}[\mathcal{G}]G. \quad (8)$$

Here  $\mathcal{G}$  is the excitonic Green's function (non-averaged) for the disordered crystal in the absence of exciton-phonon interaction, and the self-energy  $\Sigma_{\text{ex-ph}}[\mathcal{G}]$  is given by

$$\begin{aligned} \Sigma_{\text{ex-ph}}[\mathcal{G}] = \frac{i}{N} \sum_{\mathbf{k}} \int \frac{d\omega'}{2\pi} \exp(i\mathbf{k} \cdot (\mathbf{n} - \mathbf{n}')) |g(\mathbf{k})|^2 \\ \times D^{(0)}(\mathbf{k}, \omega') \mathcal{G}(\mathbf{n}, \mathbf{n}'; \omega - \omega'). \end{aligned} \quad (9)$$

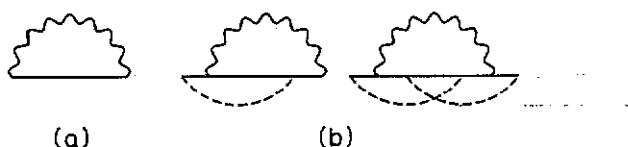
In this equation  $D^{(0)}(\mathbf{k}, \omega)$  is the reduced phonon Green's function (equation (5)) of zero order defined by  $D^{(0)}(\mathbf{k}, \mathbf{k}'; \omega) = D^{(0)}(\mathbf{k}, \omega) \delta_{\mathbf{k}, -\mathbf{k}'}$ . Explicitly, it is given by

$$D^{(0)}(\mathbf{k}, \omega) = \frac{2\omega_{\mathbf{k}}(n_{\mathbf{k}} + 1)}{\omega^2 - (\omega_{\mathbf{k}} - i0)^2} - \frac{2\omega_{\mathbf{k}}n_{\mathbf{k}}}{\omega^2 - (\omega_{\mathbf{k}} + i0)^2} \quad (10)$$

where  $n_{\mathbf{k}} = [\exp(\omega_{\mathbf{k}}/T) - 1]^{-1}$  is the equilibrium number of phonons in the  $k$ th mode.

We are interested in the excitonic Green's function averaged over the random site energies  $v_{\mathbf{n}}$ . In the absence of the exciton-phonon interaction the disorder averaged excitonic Green function  $\bar{G}$  could be represented in the form:

$$\bar{G}(\mathbf{k}, \omega) = \frac{1}{\omega - \epsilon_{\mathbf{k}} - u(\omega)} \quad (11)$$



**Figure 1.** The contribution to the excitonic self-energy given by a weak exciton-phonon interaction in a disordered medium (a) neglecting and (b) including disorder-induced corrections to exciton-phonon interaction vertices and higher order diagrams with crossing disorder lines. Straight and wavy lines represent, respectively, the excitonic Green's functions averaged over disorder and phonon Green's functions; dashed lines correspond to the correlation function of static disorder.

which differs from that for the ordered crystal  $G^{(0)}(\mathbf{k}, \omega) = (\omega - \epsilon_{\mathbf{k}} + i0)^{-1}$  by the complex self-energy  $u(\omega)$ . We neglect a possible dependence of  $u$  on the momentum which holds in the case of a weak disorder and also is the result of CPA treatments. To determine approximately the self-energy  $\Sigma$  of the disorder-averaged excitonic Green's function  $\bar{G}$  in the presence of the exciton-phonon interaction one could neglect the difference between  $\Sigma_{\text{ex-ph}}[\bar{G}]$  and  $\Sigma_{\text{ex-ph}}[\bar{G}]$ , which means taking into account the diagram shown in figure 1(a) and neglecting diagrams like those shown in figure 1(b), i.e. non-singular corrections to the interaction vertex and higher order diagrams with crossing disorder lines. In this approximation we have

$$\Sigma = u + \Sigma_{\text{ex-ph}}[\bar{G}]. \quad (12)$$

Here the first term is the disorder-induced part of the self-energy from (11) and could be found in a self-consistent way, e.g. by means of CPA. In the latter case it is determined from the equation (Velicky *et al* 1968)

$$\left\langle \frac{v_{\mathbf{n}} - u(\omega)}{1 - (v_{\mathbf{n}} - u(\omega))\bar{G}(\mathbf{n}, \mathbf{n}; \omega)} \right\rangle = 0. \quad (13)$$

The second term in (12), being small in comparison with the first one is, however, important because only this term determines temperature dependence of  $\Sigma$ . The optical absorption spectrum (equation (7)) has the form

$$\alpha(\omega) = - \frac{\text{Im } \Sigma(\omega)}{[\omega - \text{Re } \Sigma(\omega)]^2 + [\text{Im } \Sigma(\omega)]^2}. \quad (14)$$

Thus the excitonic linewidth  $\Gamma$  is given by  $\Gamma = -\text{Im } \Sigma(\omega_0)$ , where  $\omega_0$  describes a shift of the absorption line and is determined by the following equation:

$$0 = \omega_0 - \text{Re } \Sigma(\omega_0) \approx \omega_0 - \text{Re } u(\omega_0). \quad (15)$$

To extract the temperature dependent part of the linewidth we consider the temperature derivative of  $\text{Im } \Sigma(\omega)$  and obtain from equations (9) to (12)

$$\begin{aligned} \frac{\partial \text{Im } \Sigma(\omega)}{\partial T} = & \frac{1}{N} \sum_{\mathbf{k}} |g(\mathbf{k})|^2 \frac{\partial n_{\mathbf{k}}}{\partial T} \text{Im} \left( \frac{1}{\omega - \epsilon_{\mathbf{k}} - \omega_{\mathbf{k}} - u(\omega - \omega_{\mathbf{k}})} \right. \\ & \left. + \frac{1}{\omega - \epsilon_{\mathbf{k}} + \omega_{\mathbf{k}} - u(\omega + \omega_{\mathbf{k}})} \right) \end{aligned} \quad (16)$$

#### 4. Low temperature dependence of excitonic linewidth

The formulae (11), (13), (14), (16) describe the temperature dependence of the whole excitonic absorption spectrum. For low temperatures an analytical expression can be obtained for the width of the excitonic absorption peak at  $\omega_0$  (equation(15)). Due to the presence of the factor  $\partial n_{\mathbf{k}}/\partial T$  only acoustic phonons with frequencies  $\omega_{\mathbf{k}} \leq T$  give significant contribution to (17). Expanding  $u(\omega \pm \omega_{\mathbf{k}})$  at the vicinity of  $\omega \approx \omega_0$  we have

$$\frac{\partial \Gamma}{\partial T} = \frac{1}{N} \sum_{\mathbf{k}} |g(\mathbf{k})|^2 \frac{\partial n_{\mathbf{k}}}{\partial T} \operatorname{Im} \left( \frac{1}{\epsilon_{\mathbf{k}} - \tilde{\omega}_{\mathbf{k}} - i/2\tau} + \frac{1}{\epsilon_{\mathbf{k}} + \tilde{\omega}_{\mathbf{k}} - i/2\tau} \right) \quad (17)$$

where  $\tilde{\omega}_{\mathbf{k}} \equiv [1 - \partial \operatorname{Re} u(\omega_0)/\partial \omega_0] \omega_{\mathbf{k}}$ ,  $1/2\tau \equiv -\operatorname{Im} u(\omega_0)$ . Consider now the region  $T \ll 1/\tau$  which is absent for ordered crystals (elastic scattering rate  $1/\tau = 0$ ) and therefore is of particular interest in the disordered case. Assuming also  $T < T_0 = T_D^2/B$ , we could neglect in the denominators of equation (17) both quantities  $\epsilon_{\mathbf{k}}$  and  $\tilde{\omega}_{\mathbf{k}}$  as compared to  $1/\tau$ :

$$\frac{\partial \Gamma}{\partial T} = \frac{4\tau}{N} \sum_{\mathbf{k}} |g(\mathbf{k})|^2 \frac{\partial n_{\mathbf{k}}}{\partial T}. \quad (18)$$

Taking it that for small values of  $k$ ,  $\omega_{\mathbf{k}} \sim k^\mu$  ( $\mu \neq 0$ ) and  $|g(\mathbf{k})|^2 \sim k^\nu$  we have, from equation (18),  $\partial \Gamma/\partial T \sim T^{(3+\nu-\mu)/\mu}$ . In the important case of excitons interacting with long wavelength acoustic phonons, we have  $\omega_{\mathbf{k}} = sk$  and (Toyozawa 1958)  $|g_{\mathbf{k}}| = C\sqrt{(k/Ms)}$ , where  $C$  is a deformation energy,  $M$  is the molecular mass and  $s$  is a sound velocity. Integrating equation (18) we get the expression for the temperature dependent part  $\delta\Gamma(T)$  of the linewidth  $\Gamma(T) = \Gamma_0 + \delta\Gamma(T)$  (where  $\Gamma_0$  is the zero-temperature linewidth caused both by static disorder and zero-point lattice fluctuations) in the temperature region  $T \lesssim 1/2\tau$ :

$$\delta\Gamma(T) = \frac{4\pi^4 C^2 \tau T^4}{5 Ms^2 T_D^3}. \quad (19)$$

We stress once more that for ordered crystals ( $1/\tau = 0$ ) expression (19) has no range of applicability. In this case the value of  $\delta\Gamma(T)$  in the Born approximation considered would be exponentially small. Indeed, as is seen from equation (17), the only contribution to  $\delta\Gamma(T)$  is given by the  $k$ -region, where  $\epsilon_{\mathbf{k}} = \omega_{\mathbf{k}}$ , which means that  $\epsilon_{\mathbf{k}}$ ,  $\omega_{\mathbf{k}} \sim T_D^2/B \equiv T_0$ , and therefore  $\delta\Gamma(T) \sim \exp(-T/T_0)$ . Using (19) to estimate the value of  $\delta\Gamma(T)$  in the disordered case we take  $C \sim Ms^2 \sim T_D \sim 3 \times 10^2$  K,  $\tau^{-1} \sim (10^{-13} \text{ s})^{-1} \sim 60$  K. At  $T = 30$  K we get  $\delta\Gamma(T) \approx 12$  K. Note that the maximum value of  $\delta\Gamma(T)$  (equation (19)) in the temperature range considered,  $T \lesssim 1/2\tau$ , decays rapidly ( $\sim 1/\tau^3$ ) with decreasing static disorder.

#### 5. Conclusion

It has been shown that the presence of static disorder modifies the contribution of the exciton-phonon interaction in the optical absorption linewidth and changes its low temperature dependence. Being relatively small, this dependence could, however, be considered as a characteristic feature of disordered molecular crystals reflecting the breaking of momentum conservation in quasiparticle interaction processes.

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