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DYNAMICS OF COMPOSITE EXCITON-PHONON STATES IN DOPED MOLECULAR CRYSTALS

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Abstract - The transport properties of a composite exciton-phonon (CEP) is presented by calculating the rate of its trapping at impurities by emitting a phonon. It is demonstrated for the first time that a Debye-Waller type factor reduces the trapping probability in molecular crystals in the same way as that does in the electronic transport processes in atomic crystals.

I. INTRODUCTION

The transport of excitation energy and charge carriers in disordered solids has become an interesting topic /1-4/ because of its potential applications in electronic processes of industrial value. In crystals where disorder is created by substituting impurities studies about transport of excitations provide leads to the understanding of optical properties like quenching of fluorescence and phosphorescence. There are two approaches which may be followed theoretically to study disordered solids: (1) start with a crystalline material and introduce in it the effect of disorders at a later stage, or (2) start with the disordered system right from the beginning. Latter approach is usually followed for numerical calculations /4/. Here however we use the first approach which is more suitable for analytical work. First we study the properties of exciton states in pure crystalline solids and then the influence of substitution of impurities on the exciton states. Composite exciton-phonon (CEP) states arise in pure molecular crystals due to the coupling between Frenkel excitons and phonons /5/. We consider a crystal doped with isotopic impurities in low concentration so that the impurity-impurity interaction can be neglected. As a CEP excited in pure crystal region moves away it may encounter an impurity whose excited states energy is lower than that of host, and due to exciton, phonon and impurity interaction the CEP gets trapped. The excess energy of CEP is emitted as phonons. Emission of a phonon or a number of phonons would depend on the trap depth and lattice temperature. The transition rate from a free CEP to a trapped exciton can be calculated provided one has a suitable operator of exciton phonon and impurity interaction which was not derived for molecular excitons until recently /6/.

The purpose of this paper is to demonstrate for the first time that in deriving the exciton-phonon-impurity interaction operator for molecular crystals one gets a factor which is similar to the Debye-Waller factor known in the case of electron-phonon interaction in atomic crystals /7/. A similar factor is also shown by Mott and Davis /8/ to appear in relation with the transition between Anderson's localized

states in non-crystalline solids. We have calculated the rate of trapping of a CEP at impurities by emitting a phonon applying the zeroth order operator of exciton-phonon-impurity interaction. The effect of the above factor on the transition probability is discussed.

II. EXCITON-PHONON-IMPURITY INTERACTION

Consider a molecular crystal with an impurity molecule at one of the lattice sites at p , and the lattice is in equilibrium. Part of the exciton Hamiltonian involving the impurity site is written as /6/:

$$\hat{H}_p = \Delta_p B_p^\dagger B_p, \quad (1)$$

where Δ_p is the trap depth defined such that not only it accounts for the difference between the excitation energy of isolated host and impurity molecules but also that of their intermolecular interaction energies. Assuming that the impurity molecule occupies the lattice site such that no translational symmetry is destroyed (e.g. isotopic impurity) we can expand the exciton operator B_p^\dagger as /9/:

$$B_p^\dagger = N^{-\frac{1}{2}} \sum_{\underline{k}} \exp(-i\mathbf{k} \cdot \mathbf{p}) B_{\underline{k}}^\dagger, \quad (2)$$

where \underline{k} is the reciprocal lattice vector, and N is the number of molecules in the crystal. Here we consider a crystal with one molecule per unit cell.

Introducing the lattice vibrations and assuming that the displacement vectors from points of lattice equilibrium are small we may assume that the translational symmetry is preserved in a vibrating lattice. Thus one may take the lattice site at p to be instantaneously at $p + \underline{R}_p$ /7/ in a vibrating lattice. Using then (2) in (1), and in

there expanding lattice displacement vectors \underline{R}_p in terms of phonon modes /9/ we can derive \hat{H}_p in the following form:

$$\hat{H}_p = \Delta_p N^{-1} \sum_{\underline{k}, \underline{k}'} B_{\underline{k}}^\dagger B_{\underline{k}'} \exp [i(\underline{k}' - \underline{k}) \cdot \underline{p}] \prod_{\underline{q}} \exp \left[-\frac{1}{2} |(\underline{k}' - \underline{k}) \cdot \hat{\mathbf{e}}(\underline{q}) Z(\underline{q}, \underline{p})|^2 \right] \times$$

$$\prod_{\underline{q}} \sum_{\mu, \nu} (\mu! \nu!)^{-1} \left[i(\underline{k}' - \underline{k}) \cdot \hat{\mathbf{e}}^*(\underline{q}) Z^*(\underline{q}, \underline{p}) b_{\underline{q}}^{\dagger \mu} \right]^\mu \left[i(\underline{k}' - \underline{k}) \cdot \hat{\mathbf{e}}(\underline{q}) Z(\underline{q}, \underline{p}) b_{\underline{q}}^\nu \right]^\nu \quad (3)$$

where $b_{\underline{q}}^\dagger$ is the creation operator of a phonon with wavevector \underline{q} , unit polarization vector $\hat{\mathbf{e}}(\underline{q})$ and frequency $\omega(\underline{q})$. μ and ν index the order of the interaction operator e.g. $\mu=\nu=0$ is zeroth order, $\mu=0, \nu=1$ and $\mu=1, \nu=0$ first order etc. $Z(\underline{q}, \underline{p})$ is given by:

$$Z(\underline{q}, \underline{p}) = \left[\frac{\hbar}{2I_p N \omega(\underline{q})} \right]^{\frac{1}{2}} \exp(i\mathbf{q} \cdot \underline{p}). \quad (4)$$

I_p is the mass coefficient of the impurity molecule. It is to be noted that the second exponential factor in (3) does not depend on the location of the impurity molecule in the crystal.

III. RATE OF TRAPPING

The calculation of a general trapping rate in which any number of phonons can be emitted is very complicated therefore it will be published elsewhere. Here however we will focus our attention to calculate the trapping rate of a CEP at an impurity by emitting a phonon. The trapping probability R is given by:

$$R = \frac{2\pi}{\hbar} |\langle p; n | \hat{H}_p^0 | K; n \rangle|^2 \rho(\omega), \quad (5)$$

where \hat{H}_p^0 is the zeroth order term ($\mu=\nu=0$) of (3) and $\rho(\omega)$ is the density of phonon states. Here we consider emission of only low energy phonons. $|K; n\rangle$ is the state vector of a CEP with wavevector \underline{K} created initially in the pure crystal region; n representing the initial scheme of phonons occupation ($|n\rangle = |n_1, n_2, \dots, n_q, \dots\rangle$). The initial state vector $|K; n\rangle$ is written as /5/:

$$|K; n\rangle = \left[C_0(\underline{K}, 0; n) B_{\underline{K}}^{\dagger} + \sum_{\underline{k}} \{ C_1(\underline{k}, \underline{K}-\underline{k}; n+1) B_{\underline{k}}^{\dagger} b_{\underline{K}-\underline{k}}^{\dagger} + C_1(\underline{k}, \underline{k}-\underline{K}; n-1) B_{\underline{k}}^{\dagger} b_{\underline{k}-\underline{K}} \} \right] |0; n\rangle, \quad (6)$$

where C_0 and C_1 are respectively the probability amplitude coefficients of creating a pure exciton state accompanied by no phonons, and creating an exciton state accompanied by the creation or annihilation of a single phonon.

Finally when the CEP is trapped at the impurity and a phonon of wavevector \underline{q} is emitted the final state vector can be written as /10/:

$$|p; n\rangle = G_{\underline{q}} B_{\underline{p}}^{\dagger} b_{\underline{q}}^{\dagger} |0; n\rangle \delta_{\underline{q}, \underline{K}}, \quad (7)$$

where $G_{\underline{q}} = (1 + \bar{n}_{\underline{q}})^{-\frac{1}{2}}$ is a normalization constant and $\delta_{\underline{q}, \underline{K}}$ conserves the momentum of the system.

Using (3), (6) and (7) we get the transition matrix element $\langle p; n | \hat{H}_p^0 | K; n \rangle$ as:

$$\langle p; n | \hat{H}_p^0 | K; n \rangle = \Delta_p N^{-\frac{1}{2}} C_1(0, \underline{K}; n+1) (1 + \bar{n}_{\underline{q}})^{-\frac{1}{2}} \sum_{\underline{k}} f(\underline{k}) \quad (8)$$

where $\bar{n}_{\underline{q}}$ is the average phonon population in the initial state. The function $f(\underline{k})$ is obtained as:

$$f(\underline{k}) = \exp \left[- \frac{\frac{1}{2} \hbar^2 k^2}{4 I_p N} \sum_{\underline{q}'} \frac{1}{\hbar \omega(\underline{q}')} \right] \quad (9)$$

In (9) $f(\underline{k})$ has the same form as the Debye-Waller factor /7/ known in the electronic transport processes mediated by phonons in crystalline solids. Also a similar function is shown by Mott and Davis /8/ to appear in the transition matrix element

between Anderson's localized states in non-crystalline solids. Following /7/ we can derive $f(k)$ for low frequency phonons as:

$$f(k) = \exp \left[- \frac{3\hbar^2 k^2}{4I_p k_B \Theta_D} \right], \quad (10)$$

where k_B is the Boltzmann constant and Θ_D is the Debye temperature. For electronic transport in atomic solids /7/ one obtains a factor of $\frac{3}{8}$ instead of $\frac{3}{4}$ in the exponential of (10). It is because there are six vibrational (intermolecular) degrees of freedom for a molecule and only three for atoms in a crystal lattice.

Using (8) in (5) we obtain R as (details of the derivation can be seen in /10/ and (Singh, to be published):

$$R = R_0 \left| N^{-1} \sum_k f(k) \right|^2 \quad (11)$$

where

$$R_0 = \frac{6\pi \Delta_p^5 E(0) C_p}{\hbar B^2 k_B^3 \Theta_D^3} \quad (12)$$

$E(0)$ is the energy of an exciton at $k=0$ and it is measured from the centre of the exciton band, C_p is the impurity concentration and B is half of the unperturbed exciton band width. It is to be noted that the exponent of $f(k)$ (10) is not zero and therefore $R < R_0$ in (11).

IV. DISCUSSION

The motion of a CEP in mixed or doped molecular crystals with low impurity concentration is presented here. It is invoked for the first time that in the transport of CEP also a Debye-Waller type factor occurs which reduces the transition probability of CEP hopping from one state to another. It is difficult to calculate $f(k)$ accurately. However, as the molecular mass coefficients I occurs in the denominator which e.g. for naphthalene is ~ 20 times greater than the atomic mass, $f(k)$ is expected to be relatively higher than the Debye-Waller factor for electronic processes in atomic crystals. The exponent of $f(k)$ (10) is the mean square displacement of impurity molecules from equilibrium. According to our assumption of small lattice displacement vectors it is expected that at low temperatures the factor of R_0 in (11) might only be equal to a fraction. In naphthalene for example R_0 is calculated of the order of $10^7 - 10^9$ at $C_p \sim 10^{-3}$ /10/. The effect of $f(k)$ might only reduce R_0 at the most by an order of magnitude at lower temperature ($\sim 4.2^\circ\text{K}$). At higher temperature however the effect would be more prominent. A more accurate calculation of the factor $\sum_k f(k)$ (11) can be done using numerical methods.

For multiphonon processes, the calculation of $f(k)$ is much more complicated. For very deep traps i.e. with trap depth equal to energy of several phonons one can express the final phonon states as coherent states. The trapping rate thus obtained

is more general and it is expected that one can calculate such rates for any number of phonons emitted (usually greater than 3) after the trapping of a CEP. Results are however lengthy therefore they will be published elsewhere.

We have presented here the rate of transition using only \hat{H}_p^0 but calculations are done using \hat{H}_p^1 (Singh, to be published), \hat{H}_p^2 (Singh and Thilagam, to be published) and \hat{H}_p^m (Singh, to be published) as well. This leads to the probability of a CEP transition from one state to another dependent on several variables particularly in multiphonon processes. However for shallow traps the probability of single phonon emission is usually larger than that of multiphonon emission.

The substitution of impurities is known to create localized states in a crystalline materials. The form of the transition matrix element with the exponential factor suggests that CEP states can also be localized /8/.

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