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Mutual influence of the composite exciton-phonon states and impurity states on the spectra of doped molecular crystals

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We have calculated the energy eigenvalues of the localized energy states arising from the interaction between the composite exciton-phonon states and isotopic impurity states for 0-0 and 0-1 phonon transitions in molecular crystals. The exciton-phonon—impurity state interaction Hamiltonian is derived, and the results are obtained at low temperatures where the participation of the low-energy acoustic phonons is assumed to be dominant. A condition on the localized energy states as a function of the trap depth is obtained. The results are found to be in good agreement with experiments on doped naphthalene crystals, and with the theoretical results already established.

I. INTRODUCTION

Lattice vibrations always exist in crystalline solids, and most solids contain some impurities. Studies of the electronic and spectral properties of doped crystalline solids thus provide information very useful in several applications. In molecular crystals which are mostly insulators or poor semiconductors, the exciton-phonon interaction is an important area of investigation. In doped crystals or crystals with defects, however, in addition to the exciton-phonon interaction, the effect of impurities and defects on excitons and phonons, and vice versa, must also be taken into consideration. In other words, one has to study the interactions among excitons, phonons, and defects or impurities in solids.

The problem of exciton-phonon interaction in pure molecular crystals is usually approached through the use of an interaction operator[1–4] linear in lattice displacement vectors, i.e., within the single-phonon-approximation limit. In crystals with defects[5] or structural disorders,[6] the theory of exciton, phonon, and defect interactions has been worked out, including only the exciton-phonon and exciton-defect interactions. However, the defect-phonon interaction has usually been omitted. It is done through diagonalization of the exciton-defect interaction Hamiltonian first, and then in the approximately diagonalized Hamiltonian thus obtained the exciton-phonon interaction is introduced.[5,6] One obvious inconsistency in this approach is that the introduction of lattice defects or structural disorders destroys the translational symmetry of the crystal. As a result the wave vector $\vec{k}$ does not remain a good quantum number which is so otherwise for excitons, phonons, and exciton-phonon interactions in pure crystals. Therefore, by diagonalizing the exciton-defect Hamiltonian first one moves from the translationally symmetric situation to non-translationally-symmetric situation, but in that one again considers the exciton-phonon interaction which is translationally symmetric, as the defect-phonon interaction is omitted. In order to avoid this problem of going back and forth from translationally symmetric to non-translationally-symmetric situations it may be considered more appropriate to diagonalize the exciton-phonon interaction first and then introduce the structural disorders or lattice defects. The diagonalization of the exciton-phonon interaction gives rise to the composite exciton-phonon states[7,8] which are different from the exciton states interacting with the localized intramolecular vibrations as done by Klafter and Jortner.[9]

In the present paper we study the mutual effects of the composite exciton-phonon states and isolated impurities (impurity-impurity interaction is omitted) in doped molecular crystals. It is done by assuming that the impurity concentration is so less that one impurity is infinitely apart from the others and their mutual interactions can be neglected. It is also assumed that the impurity molecules differ from the host only in their energy of excitation, otherwise they have the same molecular structure, i.e., the impurities are like isotopic impurities. The Hamiltonian for a molecular crystal with excitons, phonons, and an impurity is presented in Sec. II. From this Hamiltonian then the energy eigenvalues of the doped crystal are calculated for (1) 0-0 phonon and (2) 0-1 phonon transitions in Secs. III and IV, respectively. The diagonalized Hamilton[8] of the composite exciton-phonon states for 0-0 and 0-1 phonon transitions are used, and in these the exciton-impurity and impurity-phonon interactions are introduced. The energy eigenvalues of the two transitions are then obtained as functions of the Debye cutoff frequency, trap depth (difference between the excited-state energies of the impurity and host molecules), and the unperturbed exciton bandwidth of the molecular crystal. In Sec. V the results are calculated for doped naphthalene crystals with four types of isotopic impurities. The results derived here are valid in the low-temperature limit in which the acoustic phonons are anticipated to play the dominant role. From the results obtained two very important features emerge: (a) the actual trap depth is reduced due to the interaction with phonons and (b) the structure of phonon spectra changes with the change in trap depth in 0-0 phonon transitions but not in 0-1 phonon transitions. These two characteristics agree remarkably well with the previous theory, and experimental results obtained in doped molecular crystals. Although the theory presented here is essentially worked out in the presence of acoustic phonons, the method can easily be extended to the optical phonons as well.

II. THEORY

For a molecular crystal with an isotopic impurity the exciton-phonon—impurity Hamiltonian is derived in Appendix A. With the use of (A7) and (A8), the Hamiltonian may preferably be written in the following form:

$$\hat{H}(\vec{R})=\hat{H}_0+\hat{H}_{\mathrm{IP}}\;, \tag{1}$$

where

$$\hat{H}_0=\hat{H}_{\mathrm{ex}}+\hat{H}_{\mathrm{ph}}+\hat{H}_{\mathrm{ex\text{-}ph}} \tag{2}$$

and

$$\hat{H}_{\mathrm{IP}}=\hat{H}_{\mathrm{ex}\text{-}D}+\hat{H}_{D\text{-}\mathrm{ph}}\;. \tag{3}$$

The right-hand side terms of (2) and (3) are given in (A8).

It is to be noted that the problem of lattice defects[5] and structural disorders[6] in molecular crystals has so far been solved only with the exciton-defect interaction operator similar to $\hat{H}_{\mathrm{ex}\text{-}D}$ in (3), and the exciton-defect-phonon operator $\hat{H}_{D\text{-}\mathrm{ph}}$ has been neglected. The importance of $\hat{H}_{D\text{-}\mathrm{ph}}$ is that it represents the interaction between exciton and impurity in a vibrating lattice where as $\hat{H}_{\mathrm{ex}\text{-}D}$ represents the interaction only in a rigid lattice (at the lattice equilibrium). In a vibrating lattice, therefore, $\hat{H}_{D\text{-}\mathrm{ph}}$ has to be included. One should also note that in the interaction operators $\hat{H}_{\mathrm{ex}\text{-}D}$ (A8c) and $\hat{H}_{D\text{-}\mathrm{ph}}$ (A8f) of $\hat{H}_{\mathrm{IP}}$ (3), the wave vectors are not conserved, whereas in all the interaction operators of $\hat{H}_0$ (2) the exciton and phonon wave vectors remain conserved. This is a consequence of the translational symmetry being preserved in $\hat{H}_0$ (2) but not in $\hat{H}_{\mathrm{IP}}$ (3), which is obtained only due to the impurity that destroys the translational symmetry of the crystal. In what follows we will use the Hamiltonian (1) to solve the eigenvalue problems for 0-0 and 0-1 phonon transitions in doped molecular crystals.

III. 0-0 PHONON TRANSITION

The operator $\hat{H}_0$ in the Hamiltonian (1) represents the unperturbed Hamiltonian and this has been diagonalized[8] in a form that represents the composite exciton-phonon Hamiltonian $\hat{H}_{0\text{-}0}$ for 0-0 phonon transition:

$$\hat{H}_{0\text{-}0}=\sum_{\vec{K}}\lambda_0(\vec{K})A^{\dagger}_{\vec{K}}A_{\vec{K}}\;, \tag{4}$$

where $\lambda_0(\vec{K})$ is the energy eigenvalue of a composite exciton-phonon state with wave vector $\vec{K}$, and $A^{\dagger}_{\vec{K}}$ represents the creation operator of a composite exciton-phonon:

$$A^{\dagger}_{\vec{K}}=\Bigg\{C_0(\vec{K},\vec{0};n)B^{\dagger}_{\vec{K}}+\sum_{\vec{k}}\big[C_1(\vec{k},\vec{K}-\vec{k};n+1)B^{\dagger}_{\vec{k}}b^{\dagger}_{\vec{K}-\vec{k}}$$
$$+C_1(\vec{k},\vec{k}-\vec{K};n-1)B^{\dagger}_{\vec{k}}b_{\vec{k}-\vec{K}}\big]\Bigg\}\,|\,0;n\,\rangle\langle 0_{\mathrm{ex\text{-}ph}}\,|\;. \tag{5}$$

The annihilation operator[10] $A_{\vec{K}}$ is the conjugate of (5) and $|\,0_{\mathrm{ex\text{-}ph}}\rangle$ represents the vacuum state of the composite exciton-phonon particles. The eigenvalue $\lambda_0(\vec{K})$ is obtained by solving the secular equation:[8,10]

$$W(\vec{K})-\lambda_0(\vec{K})=N^{-1}\sum_{\vec{k}}S^2(\vec{k},\vec{K}-\vec{k})$$
$$\times\left\{\frac{1+\bar{n}_{\vec{K}-\vec{k}}}{W(\vec{k})+\hbar\omega(\vec{K}-\vec{k})-\lambda_0}+\frac{\bar{n}_{\vec{k}-\vec{K}}}{W(\vec{k})-\hbar\omega(\vec{k}-\vec{K})-\lambda_0}\right\}, \tag{6}$$

where the phonon branch index s has been omitted.

We aim at solving the eigenvalue equation:

$$(\hat{H}_{0\text{-}0}+\hat{H}_{\mathrm{IP}})\,|\,\Psi\rangle_{0\text{-}0}=W_D^0\,|\,\Psi\rangle_{0\text{-}0}\;, \tag{7}$$

and we have already solved:[8]

$$\hat{H}_{0\text{-}0}\,|\,\vec{K};n\,\rangle=\lambda_0(\vec{K})\,|\,\vec{K};n\,\rangle\;, \tag{8}$$

where

$$|\,\vec{K};n\,\rangle=A^{\dagger}_{\vec{K}}\,|\,0_{\mathrm{ex\text{-}ph}}\rangle\;. \tag{9}$$

Therefore, we expand $|\,\Psi\rangle_{0\text{-}0}$ in terms of $|\,K;n\,\rangle$ as

$$|\,\psi\rangle_{0\text{-}0}=\sum_{\vec{K}}D_0(\vec{K})\,|\,\vec{K};n\,\rangle\;, \tag{10}$$

where $D_0(\vec{K})$ is the probability amplitude coefficient whose Fourier transform is assumed to be[11,5]

$$D_0(\vec{m})=N^{-1/2}\sum_{\vec{K}}D_0(\vec{K})\exp(-i\vec{K}\cdot\vec{m})\;. \tag{11}$$

$D_0(\vec{m})$ is localized at the lattice site $\vec{m}$. Using (8), (9), and (10) in (7) and then multiplying (7) from the left-hand side by an eigenvector $|\,K;n\,\rangle^*$, we obtain the following secular equation:

$$[\lambda_0(\vec{K})-W_D^0]D_0(\vec{K})+\Delta_p N^{-1}\sum_{\vec{K}_1}D_0(\vec{K}_1)C_0^*(\vec{K},\vec{0};n)C_0(\vec{K}_1,\vec{0};n)\exp[i(\vec{K}_1-\vec{K})\cdot\vec{p}\,]$$
$$\times[Z_0(\vec{K}_1,\vec{K},\lambda_0)+Z_1(\vec{K}_1,\vec{K},\lambda_0)+Z_2(\vec{K}_1,\vec{K},\lambda_0)]=0\;. \tag{12}$$

where

$$Z_0(\vec{K}_1,\vec{K},\lambda_0)=N^{-1}\sum_{\vec{k}}\left\{1+\frac{S^2(\vec{k},\vec{K}-\vec{k})(1+\bar{n}_{\vec{K}-\vec{k}})}{[W(\vec{k})+\hbar\omega(\vec{K}-\vec{k})-\lambda_0(\vec{K})][W(\vec{k}+\vec{K}_1-\vec{K})+\hbar\omega(\vec{K}-\vec{k})-\lambda_0(\vec{K}_1)]}\right.$$
$$\left.+\frac{S^2(\vec{k},\vec{K}-\vec{k})\bar{n}_{\vec{k}-\vec{K}}}{[W(\vec{k})-\hbar\omega(\vec{k}-\vec{K})-\lambda_0(\vec{K})][W(\vec{k}+\vec{K}_1-\vec{K})-\hbar\omega(\vec{k}-\vec{K})-\lambda_0(\vec{K}_1)]}\right\}, \tag{13}$$

$$Z_1(\vec{K}_1,\vec{K},\lambda_0)=-\sum_{\vec{k}}P(\vec{K},\vec{k},\vec{K}_1-\vec{k})\left[\frac{S^*(\vec{k},\vec{K}_1-\vec{k})(1+\bar{n}_{\vec{K}_1-\vec{k}})}{W(\vec{k})+\hbar\omega(\vec{K}_1-\vec{k})-\lambda_0}+\frac{S^*(\vec{k},\vec{k}-\vec{K}_1)\bar{n}_{\vec{k}-\vec{K}_1}}{W(\vec{k})-\hbar\omega(\vec{k}-\vec{K}_1)-\lambda_0}\right], \tag{14}$$

$$Z_2(\vec{K}_1,\vec{K},\lambda_0)=-\sum_{\vec{k}}P(\vec{k},\vec{K}_1,\vec{k}-\vec{K})\left[\frac{S^*(\vec{k},\vec{K}-\vec{k})(1+\bar{n}_{\vec{K}-\vec{k}})}{W(\vec{k})+\hbar\omega(\vec{K}-\vec{k})-\lambda_0}+\frac{S^*(\vec{k},\vec{k}-\vec{K})\bar{n}_{\vec{k}-\vec{K}}}{W(\vec{k})-\hbar\omega(\vec{k}-\vec{K})-\lambda_0}\right]. \tag{15}$$

In order to solve the secular equation (12) analytically we have to make certain simplifying assumptions. We assume that Z_0, Z_1, and Z_2 are not very sensitive to $\vec{K}_1-\vec{K}$, and this enables us to obtain

$$Z_0(\vec{K}_1,\vec{K},\lambda_0)\sim Z_0(\vec{K},\vec{K},\lambda_0)=[C_0(\vec{K},\vec{0};n)]^{-2}, \tag{16}$$

$$Z_1(\vec{K}_1,\vec{K},\lambda_0)\sim Z_1(\vec{K},\vec{K},\lambda_0)=Z(\vec{K},\lambda_0), \tag{17}$$

$$Z_2(\vec{K}_1,\vec{K},\lambda_0)\sim Z_2(\vec{K},\vec{K},\lambda_0)=Z(\vec{K},\lambda_0). \tag{18}$$

We use (16)—(18) in (12), multiply (12) by $N^{-1}C_0(\vec{K},\vec{0};n)\exp[i\vec{K}\cdot\vec{m}]$, and then sum it over $\vec{K}$ to obtain

$$F_0(\vec{m})+\Delta_p N^{-1}\sum_{\vec{K}}\frac{\exp[i\vec{K}\cdot(\vec{m}-\vec{p})]F_0(\vec{p})}{\lambda_0(\vec{K})-W_D^0}+2N^{-1}\sum_{\vec{K}}\frac{C_0(\vec{K},\vec{0};n)^2Z(\vec{K},\lambda_0)\exp[i\vec{K}\cdot(\vec{m}-\vec{p})]Z(\vec{K},\lambda_0)}{\lambda_0(\vec{K})-W_D^0}=0, \tag{19}$$

where

$$F_0(\vec{m})=N^{-1}\sum_{\vec{K}}C_0(\vec{K},\vec{0};n)D_0(\vec{K})\exp(i\vec{K}\cdot\vec{m}). \tag{20}$$

For $\vec{m}=\vec{p}$ the secular equation (19) becomes

$$1+\Delta_p N^{-1}\sum_{\vec{K}}\frac{1}{\lambda_0(\vec{K})-W_D^0}+2N^{-1}\sum_{\vec{K}}\frac{|C_0(\vec{K},\vec{0};n)|^2Z(\vec{K},\lambda_0)}{\lambda_0(\vec{K})-W_D^0}=0. \tag{21}$$

Equation (21) is still very complicated to solve; one has to evaluate first $C_0(\vec{K},\vec{0};n)$ and $Z(\vec{K},\lambda_0)$ as explicit functions of $\vec{K}$ and λ_0. For this we define a low-temperature limit in which one can assume that the phonon population $\bar{n}_{\vec{k}}=\bar{n}_{-\vec{k}}=0$, and only the low-energy acoustic phonons can take an active part.[8] By using these assumptions, $Z(\vec{K},\lambda_0)$ and $C_0(\vec{K},\vec{0};n)$ are evaluated in Appendices B and C, respectively, and it is found that $C_0(\vec{K},\vec{0};n)^2$. Using (B8) in (21), we obtain the secular equation as

$$1+\Delta_p\left[T_1+\frac{3\hbar\omega_{\text{Debye}}}{8(II_p)^{1/2}v^2}(T_1+T_2)\right]+\frac{(5W_D^0-4\hbar\omega_{\text{Debye}})}{5}T_3=0, \tag{22}$$

where I and I_p are, respectively, the mass of host and impurity molecules. v is the velocity of sound in the crystal and

$$T_1=N^{-1}\sum_{\vec{K}}\frac{1}{\lambda_0(\vec{K})-W_D^0}, \tag{23a}$$

$$T_2=N^{-1}\sum_{\vec{K}}\frac{1}{[E_0(\vec{K})-\lambda_0(\vec{K})]}, \tag{23b}$$

$$T_3=N^{-1}\sum_{\vec{K}}\frac{1}{[E_0(\vec{K})-\lambda_0(\vec{K})][\lambda_0(\vec{K})-W_D^0]}. \tag{23c}$$

The secular equation (22) gives W_D^0 as the energy eigenvalue obtained due to the interaction between the composite exciton-phonon states and impurity or the trap with depth Δ_p. The composite exciton-phonon wave vector $\vec{K}$ sums over all possible values. However, before one can calculate W_D^0 from (22) one need to evaluate T_1, T_2, and T_3. Here we present the evaluation of T_1, and only mention the results for T_2 and T_3 which can also be evaluated following the same procedure.

A. Evaluation of T_1 (23a)

We convert the sum over $\vec{K}$ in (23a) into an integration[12] over the composite exciton-phonon energies as

$$T_1=\int\frac{\rho^0_{\text{ex-ph}}d\lambda_0}{\lambda_0-W_D^0}, \tag{24}$$

where $\rho^0_{\text{ex-ph}}$ represents the density of the composite exciton-phonon states in 0-0 phonon transition. $\rho^{0}_{\text{ex-ph}}$ is obtained from the product of the density of exciton states ρ_{ex} and that of phonon states $D(\hbar\omega)$ as

$$\rho^{0}_{\text{ex-ph}}=\int_{E_0'-B}^{E_0'+B}\int_{0}^{\hbar\omega_{\text{Debye}}}\rho_{\text{ex}}(E)D(\hbar\omega)\delta(W_0-W-\hbar\omega)\times dE\,d(\hbar\omega)\,. \tag{25}$$

In evaluating the integral (25) we set the initial phonon population $\sum_{\vec{q}}\hbar\omega_{\vec{q}}(\bar{n}_{\vec{q}}+\frac{1}{2})=0$, so that

$$W=E+\sum_{\vec{q}}\hbar\omega(\vec{q})(\bar{n}_{\vec{q}}+\tfrac{1}{2})=E\,.$$

However, this is done only to avoid the superficial complications without the loss of any generality. The exciton energy limits of integration is taken within the unperturbed exciton band ranging in energy from $E_0'-B$ to $E_0'+B$; E_0' being the center and $2B$ the width of the unperturbed exciton band. Using the Debye model for the density of acoustic-phonon states given in (B5), we obtain from (25)

$$\rho^{0}_{\text{ex-ph}}=\frac{3[(E_0-E_0')^2+B^2/2]}{(\hbar\omega_{\text{Debye}})^3}\,, \tag{26}$$

where E_0 represents the energy variable of the pure excitonic state corresponding to

$$W_0=E_0+\sum_{\vec{q}}\hbar\omega(\vec{q})(\bar{n}_{\vec{q}}+\tfrac{1}{2})\,.$$

In order to evaluate T_1 (24), we also need to know the eigenvalue λ_0 of the composite exciton-phonon state and it is obtained[8] as

$$\lambda_0=E_0\pm[E_0'^2(E_0-E_0')+B^2(E_0/2-E_0')]^{1/2}t^{-1/2}\,, \tag{27}$$

where $t=Iv^2=m\Omega_0v^2$ with m being the mass density and Ω_0 the volume per unit cell of the crystal.

Using $\rho^{0}_{\text{ex-ph}}$ (26) and λ_0 (27) in (24) we obtain T_1 in the following form:

$$T_1=\frac{3}{(\hbar\omega_{\text{Debye}})^3}\left[\left[\frac{B^4}{8t^2}+\frac{B^2W_D^0}{t}+W_D^{02}+\frac{B^2}{2}\right]\ln\left|\frac{1+u}{1-u}\right|\mp\frac{2B^{5/2}}{3\sqrt{2t}}\mp\frac{2B^{3/2}}{\sqrt{2t}}\left[\frac{B^2}{2t}+3W_D^0\right]+\frac{B}{2t}(B^2+4W_D^0t)\right]\,, \tag{28}$$

where

$$u=\frac{B^{3/2}}{\sqrt{2t}\,(B-W_D^0)}\,. \tag{29}$$

T_1 (28) is derived taking the center of the unperturbed exciton band, $E_0'=0$, and within the limit such that

$$\frac{(B^2+8W_D^0t)^{1/2}}{\sqrt{2t}\,(2\sqrt{2tB}+B)}\sim 1\,.$$

Likewise, T_2 (23b) and T_3 (23c) can be evaluated, and the expressions obtained are

$$T_2=\pm\frac{42\sqrt{2t}\,B^{3/2}}{5(\hbar\omega_{\text{Debye}})^3}\,, \tag{30}$$

$$T_3=\frac{3}{(\hbar\omega_{\text{Debye}})^3}\left[\mp\frac{4\sqrt{2tB}}{B}\left[\frac{B}{3}+W_D^0\right]+\left[\frac{B^2}{4t}+\frac{3}{2}W_d^0-\frac{B^2}{2W_D^0}\right]\ln\left|\frac{1+u}{1-u}\right|+B\mp\frac{2B^{3/2}}{\sqrt{2t}}\right]\,. \tag{31}$$

B. Solution of the secular equation (22)

Usually it is expected that $t \gg B$ and $|W_D^0-B|$ is not very small. This gives $|U| \ll 1$ leading to

$$\ln\left|\frac{1+u}{1-u}\right|\sim 0\,.$$

In this limit we substitute T_1 (28), T_2 (30), and T_3 (31) in the secular equation (22) which then becomes a quadratic in W_D^0, and the possible solutions are given by

$$W_D^{0\pm}=[-b\pm(b^2-4ac)^{1/2}]/2a\,, \tag{32}$$

where

$$a=\pm 180\Delta_p(\hbar\omega_{\text{Debye}})\sqrt{2t}\,, \tag{33}$$

$$b=30\Delta_p(8t+3\hbar\omega_{\text{Debye}})(\pm 3tB^2-Bt\sqrt{2tB})/t\sqrt{2t}-15\Delta_p\hbar\omega_{\text{Debye}}(\mp 4B\sqrt{2t}+3B^{3/2}\mp 6B^2/\sqrt{2t})\mp 144\sqrt{2t}\,\Delta_p(\hbar\omega_{\text{Debye}})^2\,, \tag{34}$$

$$c=-40t(\hbar\omega_{\text{Debye}})^3\sqrt{B}-5\Delta_p(8t+3\hbar\omega_{\text{Debye}})(\mp 2B^3t\mp 3B^4+\tfrac{3}{2}B^3\sqrt{2tB})\pm 126\Delta_p(\hbar\omega_{\text{Debye}})B^2\sqrt{2t}+12\Delta_p(\hbar\omega_{\text{Debye}})^2(\mp 4B\sqrt{2t}+3B^{3/2}\mp 6B^2/\sqrt{2t})\,. \tag{35}$$

The eigenvalue W_D^0 thus derived in (32) represents the possible solutions for 0-0 phonon transition energy states as explicit function of the trap depth Δ_p, Debye frequency $\hbar\omega_{\text{Debye}}$, and the bandwidth $(2B)$ of the unperturbed exciton band.

IV. 0-1 PHONON TRANSITION

We follow the same procedure as for 0-0 phonon transition. The unperturbed Hamiltonian (2) is obtained in a diagonal form[8] as

$$\hat{H}_{0\text{-}1}=\sum_{\vec{K},\vec{k}} \lambda_1(\vec{K},\vec{k})A^{\dagger}_{\vec{K},\vec{k}}A_{\vec{K},\vec{k}} , \tag{36}$$

where

$$\lambda_1(\vec{K},\vec{k})=W(\vec{K}-\vec{k})+\hbar\omega(\vec{k})\pm N^{-1/2}\,|S(\vec{K}-\vec{k},\vec{k})| , \tag{37}$$

represents the energy eigenvalue of a composite exciton-phonon state with wave vector $\vec{K}$ created by an exciton with wave vector $(\vec{K}-\vec{k})$ and a phonon with $\vec{k}$. The composite exciton-phonon creation operator $A^{\dagger}_{\vec{K},\vec{k}}$ is obtained[8] as

$$A^{\dagger}_{\vec{K},\vec{k}}=[C_1(\vec{K}-\vec{k},\vec{k};n+1)B^{\dagger}_{\vec{K}-\vec{k}}b^{\dagger}_{\vec{k}}+C_0(\vec{K},\vec{0};n)B^{\dagger}_{\vec{K}}]\times|0;n\rangle\langle 0_{\text{ex-ph}}| . \tag{38}$$

In (36)—(38) it is assumed that in a 0-1 phonon transition only the interaction between a pure exciton state and a state with one exciton and one particular phonon is important within the single-phonon approximation. Interaction with multiphonon states[8] is neglected here.

The eigenvector of the Hamiltonian $\hat{H}_{0\text{-}1}$ (36) plus $\hat{H}_{\text{IP}}$(3) can be constructed as

$$|\Psi\rangle_{0\text{-}1}=\sum_{\vec{K}} D_1(\vec{K},\vec{k})\,|\vec{K},\vec{K}-\vec{k},\vec{k};n\rangle , \tag{39}$$

where $D_1(\vec{K},\vec{k})$ are the probability amplitude coefficient, and $|\vec{K},\vec{K}-\vec{q};\vec{q};\vec{n}\rangle$ are the eigenvectors of $\hat{H}_{0\text{-}1}$:

$$\hat{H}_{0\text{-}1}\,|\vec{K},\vec{K}-\vec{q},\vec{q};n\rangle=\lambda_1(\vec{K},\vec{q})\,|\vec{K},\vec{K}-\vec{q},\vec{q};\vec{n}\rangle , \tag{40}$$

and

$$|\vec{K},\vec{K}-\vec{k},\vec{k};n\rangle=A^{\dagger}_{\vec{K},\vec{k}}\,|0_{\text{ex-ph}}\rangle . \tag{41}$$

Using (36), (3), and (38)—(41), we solve the following Schrödinger equation for the 0-1 phonon transition as we did for 0-0 phonon transition in the preceding section:

$$(\hat{H}_{0\text{-}1}+\hat{H}_{\text{IP}})\,|\Psi\rangle_{0\text{-}1}=W_D^1\,|\Psi\rangle_{0\text{-}1} . \tag{42}$$

The secular equation thus obtained is

$$[\lambda_1(\vec{K},\vec{k})-W_D^1]D_1(\vec{K},\vec{k})+\Delta_p N^{-1}\sum_{\vec{K}'} D_1(\vec{K}',\vec{k})C_1^*(\vec{K}-\vec{k},\vec{k};n+1)C_1(\vec{K}'-\vec{k},\vec{k};n+1)\exp[i(\vec{K}'-\vec{K})\cdot\vec{p}]$$
$$\times[Z_{11}(\vec{K}',\vec{K},\vec{k},\vec{k})+Z_{12}(\vec{K}',\vec{K},\vec{k},\vec{k})+Z_{13}(\vec{K}',\vec{K},\vec{k},\vec{k})]=0 , \tag{43}$$

where

$$Z_{11}(\vec{K}',\vec{K},\vec{k},\vec{k})=(1+\bar{n}_{\vec{k}})\left[1+\frac{S^*(\vec{K}'-\vec{k},\vec{k})S(\vec{K}-\vec{k},\vec{k})}{[W_1(\vec{K}'-\vec{k})+\hbar\omega(\vec{k})-\lambda_1][W(\vec{K}-\vec{k})+\hbar\omega(\vec{k})-\lambda_1]}\right] , \tag{44a}$$

$$Z_{12}(\vec{K}',\vec{K},\vec{k},\vec{q})=-\frac{P(\vec{K},\vec{K}'-\vec{q},\vec{q})S(\vec{K}-\vec{k},\vec{k})(1+\bar{n}_{\vec{k}})(1+\bar{n}_{\vec{q}})}{W_1(\vec{K}-\vec{k})+\hbar\omega(\vec{k})-\lambda_1} , \tag{44b}$$

$$Z_{13}(\vec{K},\vec{K},\vec{k},\vec{q})=-\frac{P_s(\vec{K}-\vec{k},\vec{K}',-\vec{k})S(\vec{K}'-\vec{q},\vec{q})(1+\bar{n}_{\vec{k}})(1+\bar{n}_{\vec{q}})}{W_1(\vec{K}'-\vec{q})+\hbar\omega(\vec{q})-\lambda_1} . \tag{44c}$$

In order to solve (43) we assume that $Z_{11}(\vec{K}',\vec{K},\vec{k},\vec{k})$, $Z_{12}(\vec{K}',\vec{K},\vec{k},\vec{k})$, and $Z_{13}(\vec{K}',\vec{K},\vec{k},\vec{k})$ are not very sensitive to $\vec{K}'-\vec{K}$. Applying, then, the low-temperature limit $(\bar{n}_{\vec{k}}=\bar{n}_{-\vec{k}}=0)$, we obtain from (44) the following simplified forms:

$$Z_{11}(\vec{K},\vec{K},\vec{k},\vec{k})=[C_1(\vec{K}-\vec{k},\vec{k};n+1)]^{-2} , \tag{45a}$$

$$Z_{12}(\vec{K}',\vec{K},\vec{k},\vec{k})=Z_{13}(\vec{K}',\vec{K},\vec{k},\vec{k})\sim Z(\vec{K},\vec{k})=\frac{\hbar\vec{k}^{2}[W_1(\vec{K}-\vec{k})+\hbar\omega(\vec{k})-\lambda_1]^{-1}}{2N(II_p)^{1/2}\omega(\vec{k})} . \tag{45b}$$

Using (45) in (43), we obtain the secular equation:

$$[\lambda_1(\vec{\mathrm{K}},\vec{\mathrm{k}})-W_D^1]D_1(\vec{\mathrm{K}},\vec{\mathrm{k}})+\Delta_p N^{-1}\sum_{K} D_1(\vec{\mathrm{K}}',\vec{\mathrm{k}})C_1^*(\vec{\mathrm{K}}-\vec{\mathrm{k}},\vec{\mathrm{k}};n+1)C_1(\vec{\mathrm{K}}'-\vec{\mathrm{k}},\vec{\mathrm{k}};n+1)\exp[i(\vec{\mathrm{K}}'-\vec{\mathrm{K}})\cdot\vec{\mathrm{p}}]$$
$$\times[C_1(\vec{\mathrm{K}}-\vec{\mathrm{k}},\vec{\mathrm{k}};n+1)^{-2}+2Z(\vec{\mathrm{K}},\vec{\mathrm{k}})]=0\;. \tag{46}$$

As N is usually very large one can expect $Z(\vec{\mathrm{K}},\vec{\mathrm{k}})\ll 1$, and this gives a very simplified secular equation from (46) as

$$[\lambda_1(\vec{\mathrm{K}},\vec{\mathrm{k}})-W_D^1]D_1(\vec{\mathrm{K}},\vec{\mathrm{k}})C_1(\vec{\mathrm{K}}-\vec{\mathrm{k}},\vec{\mathrm{k}};n+1)+\Delta_p N^{-1}\sum_{\vec{\mathrm{K}}'} D_1(\vec{\mathrm{K}}',\vec{\mathrm{k}})C_1(\vec{\mathrm{K}}'-\vec{\mathrm{k}},\vec{\mathrm{k}};n+1)\exp[i(\vec{\mathrm{K}}'-\vec{\mathrm{K}}')\cdot p]=0\;. \tag{47}$$

As in the 0-0 phonon transition, we define here a $F_1(\vec{\mathrm{m}},\vec{\mathrm{k}})$ as

$$F_1(\vec{\mathrm{m}},\vec{\mathrm{k}})=N^{-1/2}\sum_{\vec{\mathrm{K}}} D_1(\vec{\mathrm{K}},\vec{\mathrm{k}})C_1(\vec{\mathrm{K}},\vec{\mathrm{k}};n+1)\exp[i\vec{\mathrm{K}}\cdot\vec{\mathrm{m}}]\;, \tag{48}$$

and (48) enables us to write (47) as

$$F_1(\vec{\mathrm{m}},\vec{\mathrm{k}})+\Delta_p N^{-1}\sum_{\vec{\mathrm{K}}}\frac{F_1(\vec{\mathrm{p}},\vec{\mathrm{k}})\exp[i\vec{\mathrm{K}}\cdot(\vec{\mathrm{m}}-\vec{\mathrm{p}})]}{\lambda_1(\vec{\mathrm{K}},\vec{\mathrm{k}})-W_D^1}=0\;. \tag{49}$$

For $m=p$, we obtain from (49)

$$1+\Delta_p N^{-1}\sum_{\vec{\mathrm{K}}}\frac{1}{\lambda_1(\vec{\mathrm{K}},\vec{\mathrm{k}})-W_D^1}\;. \tag{50}$$

We convert the sum into an integration over the energy variables in (50) to give

$$1+\Delta_p\int\frac{\rho_{\text{ex-ph}}^1 d\lambda_1}{\lambda_1-W_D^1}=0\;, \tag{51}$$

where $\rho_{\text{ex-ph}}^1$ is the density of the composite exciton-phonon states in the 0-1 phonon transition.

$\rho_{\text{ex-ph}}^1$ is obtained, as shown in the preceding section, from the product of exciton's density of states, ρ_{ex} and phonon density of states $D(\hbar\omega)$. In the 0-1 phonon transition, however, as we consider the excitation of only one phonon of a particular mode, the composite exciton-phonon density of states would be the same as the exciton density of states:

$$\rho_{\text{ex-ph}}^1=\frac{1}{\pi}[B^2-(E-E_0')^2]^{-1/2}\;. \tag{52}$$

Using (52) in (51) and taking the center of the unperturbed exciton band at zero ($E_0'=0$), one obtains the energy eigenvalue W_D^1 from (51) as

$$W_D^1=-B(1+\Delta_p^2/B^2)^{1/2}+\hbar\omega\;. \tag{53}$$

The energy eigenvalues W_D^0 (32) for 0-0 phonon transitions and W_D^1 (53) for 0-1 phonon transitions both are calculated within the low-temperature limit. Obviously at higher temperatures the spectra will be much more complicated as will a solution to be the corresponding secular equations.

V. RESULTS AND DISCUSSION

The eigenvalues $W_D^{0\pm}$ (32) for the 0-0 phonon transition are obtained as roots of a quadratic equation, and therefore they become imaginary for $b^2-4ac<0$. On the other hand, the eigenvalue W_D^1 (53) for 0-1 phonon transition does not show such a behavior. This is a very interesting difference between the eigenvalues W_D^0 and W_D^1 and the meaning of this will carefully be presented in what follows. However, before doing this one may like to see some numerical values for W_D^0 and W_D^1 in order to get a deeper insight of the problem.

Consider naphthalene crystals doped with four types of isotopic impurities[13] (1) $C_{10}D_8$, (2) 2α-$C_{10}H_6D_2$, (3) 2α-$C_{10}H_2D_6$, and (4) 4-$C_{10}H_4D_4$. The corresponding trap depths (Δ_p) of the impurity levels,[13] measured from the bottom edge of the unperturbed exciton band of the host crystal, are (1) $\Delta_p=50$ cm^{-1}, (2) $\Delta_p=30$ cm^{-1}, (3) $\Delta_p=18$ cm^{-1}, and (4) $\Delta_p=8$ cm^{-1}. We consider a typical value for the unperturbed exciton bandwidth in the pure naphthalene crystal as 200 cm^{-1}, so that $B=100$ cm^{-1}. The eigenvalues W_D^0(32) and W_D^1 (53) are calculated taking the center of the unperturbed band as the origin ($E_0'=0$); therefore, we measure the impurity energy levels also from the center of the unperturbed band. The above four impurities then would appear at energies E_p such that (1) $E_p=-150$ cm^{-1}, (2) $E_p=-130$ cm^{-1}, (3) $E_p=-118$ cm^{-1}, and (4) $E_p=-108$ cm^{-1}. The bottom edge of the unperturbed exciton band would then be at an energy $=-100$ cm^{-1}. With the use of the above values, in Table I $W_{0\text{-}0}^{\pm}=W_D^{0\pm}-E_p$ and $W_{0\text{-}1}=W_D^1-E_p$, where $W_{0\text{-}0}^{\pm}$ gives the position of the energy eigenvalue for 0-0 phonon transition measured from the energy E_p of impurities. One can calculate the energy eigenvalue due to the interaction of exciton-defect interaction[5,15] (no phonons) as

$$W_{d-x}=-B(1+\Delta_p^2/B^2)^{1/2}\;. \tag{54}$$

The position of W_{d-x} measured from E_p, and given as $E_{D\text{-ex}}=W_{D\text{-ex}}-E_p$ is also calculated and given in the Table I for above four doped crystals. The composite exciton-phonon energy eigenvalue for the 0-0 phonon transition λ_0's (27) relative position from E_p, defined by $\lambda_{0\text{-}0}=\lambda_0-E_p$, is also given in Table I. $\lambda_{0\text{-}0}$ does not depend on the impurity. For results given in Table I the positive sign in λ_0 (27) is used.

TABLE I. Eigenvalues $W^{+}_{0\text{-}0}$ and $W^{0}_{0\text{-}0}$ of 0-0 phonon transition, and the corresponding energy eigenvalue of the composite exciton-phonon states ($\lambda_{0\text{-}0}$) are calculated for naphthalene crystals doped with isotopic impurities of trap depths $\Delta_p=50$, 30, 18, and 8 cm^{-1}. The parameters used in the calculations are the sound velocity $v=1.3\times10^{4}$ cm/s, unit-cell volume $\Omega_0=4.74\times10^{-22}$ cm^3, and mass density $m=1.283$ g/cm^3. Debye frequency $\hbar\omega_{\text{Debye}}=90$ cm^{-1}. The energy eigenvalue $E_{\text{ex-}D}$, and $W_{0\text{-}1}$ are also calculated.

E_p (cm^{-1})	$E_{\text{ex-}D}=W_{D\text{-ex}}-E_p$ (cm^{-1})	$W^{+}_{0\text{-}0}=(W_D^{+})^0-E_p$ (cm^{-1})	$W^{-}_{0\text{-}0}=(W_D^{0})^0-E_p$ (cm^{-1})	$\lambda_{0\text{-}0}=\lambda_0-E_p$ (cm^{-1})	$W_{0\text{-}1}=W_D^{1}-E_p$ (cm^{-1})
−150	38	22	75	281[a]	$38+\hbar\omega$
−130	26	8	49	261[a]	$26+\hbar\omega$
−118	16	3	20	249[a]	$16+\hbar\omega$
−108	6	not possible	not possible	239	$6+\hbar\omega$
−100 (pure crystal)	0			231	

[a] Not prominently effective.

A. Comparison with experiments

In the fluorescence spectra of 0-0 phonon transition in naphthalene crystals doped with the above four impurities, Meletov *et al.*[13,14] have observed at temperature ≤ 4.2 K that as the trap depth Δ_p changes from 50 to 8 cm^{-1} the fluorescence spectra changes significantly. For $\Delta_p=8$ cm^{-1} some emission occurs at about 120 cm^{-1} away from the impurity transition line at E_p, and this emission is identically close to the intrinsic spectra of pure naphthalene crystal.

From Table I it is clear that we get localized energy states (do not depend on $\vec{k}$) with two distinct ($W^{+}_{0\text{-}0}$ and $W^{-}_{0\text{-}0}$) eigenvalues due to interaction between the composite exciton-phonon states and impurity levels for trap depths 50, 30, and 18 cm^{-1}. The transition can, therefore, be expected to take place at these energies in the 0-0 phonon fluorescence spectra. This agrees very well with spectra by Meletov *et al.*,[13,14] where they observe double peaks between 40 and 80 cm^{-1} range from phononless impurity transition for trap depths 50, 30, and 18 cm^{-1}. According to the present calculation these lines are due to the localized energy states arising from the interaction between the composite exciton-phonon states and the impurity.

For the trap depth 8 cm^{-1}, however, Meletov *et al.*[13,14] have observed a change in the spectra such that one of the peaks of the doublet changes into another peak that appears at about 120 cm^{-1} away from the peak at E_p.

From Table I we see that the trap depth 8 cm^{-1} satisfies the condition of $b^2<4ac$ in (32) as result the eigenvalues due to the interaction of the impurity and composite exciton-phonons are not possible. That means the localized energy states due to the interaction between the composite exciton-phonon states and impurity states do not arise when trap $\Delta_p<8$ cm^{-1}. However, the eigenvalue λ_0 of the composite exciton-phonon states are still possible, hence a composite exciton-phonon line can be expected to appear at λ_0. According to the result of Table I this line appears at 239 cm^{-1} away from the phononless line. It is, therefore, conclusively convincing that the line observed by Meletove *et al.* at 120 cm^{-1} for the trap depth 8 cm^{-1} is due to transitions into the composite exciton-phonon states. It is also observed by Meletov *et al.* that the features of the 0-0 phonon spectra corresponding to the trap depth 8 cm^{-1} is very close to those observed in a pure crystal. This is what one can expect from our calculations as well because the composite exciton-phonon states are the intrinsic characteristic of a pure crystal. Therefore, in pure crystals the transitions correspond to energy states at λ_0. In Table I, $\lambda_{0\text{-}0}=231$ cm^{-1}, away from the bottom edge of the unperturbed exciton band in pure crystal is very close to $\lambda_{0\text{-}0}=239$ cm^{-1} corresponding to the trap depth 8 cm^{-1}.

Although in Table I we give the eigenvalue ($\lambda_{0\text{-}0}$) of the composite exciton-phonon states in crystals with $\Delta_p=50$, 30, and 18 cm^{-1} as well, it is expected that for these trap depths the interaction between the impurity and composite exciton-phonon is relatively much more prominent to give rise to the localized energy states at $W^{\pm}_{0\text{-}0}$. Therefore, the pure crystal's energy states $\lambda_{0\text{-}0}$ of the composite exciton-phonon would not play significant role in crystals with deep trap depths, i.e., $\Delta_p=50$, 30, or 18 cm^{-1}.

In view of the results obtained here and those observed by Meletov *et al.*, the mechanism of interaction of the composite exciton-phonon with an impurity can be described as follows: If the trap depth Δ_p is appreciably large so that $b^2-4ac\geq0$ is satisfied the composite exciton-phonon and impurity states interact to give rise to new localized energy states different from the pure crystal spectra. However, if the trap depth Δ_p is small such that $b^2-4ac<0$, the interaction between the impurity and composite exciton-phonon states does not remain so prominent. The localized energy states do not arise then. In this case, one would observe the impurity spectral lines and composite exciton-phonon peaks separately, as it appears in the crystal of naphthalene with trap depth 8 cm^{-1}.

Meletov *et al.*[13,14] have observed the occurrence of no emission lines in the 0-1 phonon transition as it appears in the 0-0 phonon transition at $\Delta_p=8$ cm^{-1}. It is obvious from Table I as well as from (53) that W_D^1 exists for every value of Δ_p, i.e., the presence of an impurity, no matter how small its trap depth might be, does seem to change the intrinsic spectra of 0-1 phonon transition. Therefore, the recurrence of the intrinsic composite exciton-phonon lines as it happens in the 0-0 phonon transition is not possible in 0-1 phonon transition at small Δ_p. Thus, here again the present theory is in perfect agreement with the observed result.

B. Comparison with previous theory

Craig and Singh[15] have suggested that the participation of phonons masks the true trap depths of impurities in molecular crystals. From Table I one can see that the impurity line appearing at E_p changes to W_D^{0+} or W_D^{0-} due to interaction with the composite exciton-phonon states. Both W_D^{0+} and W_D^{0-} are shallower than W_D by $W_{0\text{-}0}^{+}$ and $W_{0\text{-}0}^{-}$, respectively. For example, the impurity spectral line that should occur at an energy $-150\ \mathrm{cm}^{-1}$ (for 50 cm^{-1} trap depth) occurs due to the interaction with the composite exciton-phonon states, at -128 or $-75\ \mathrm{cm}^{-1}$ from the center of the unperturbed exciton band. Thus, the masking effect[15] of impurities is demonstrated more clearly through the present calculations.

The results obtained here are in excellent agreement with the experimental as well as theoretical results; however, it should still be considered only as a qualitative agreement: firstly, because the results are calculated for crystals with one molecule per unit cell, secondly, because the parameters such as B and $\hbar\omega_D$ are not known exactly for naphthalene crystals, and finally, because of the approximations and assumptions involved in arriving at the final results.

The results derived here are valid only at low temperature where one can neglect the phonon population ($\bar{n}_{\vec{q}} \sim 0$). This is why all the energy eigenvalues are obtained independent of the temperature as

$$\bar{n}_{\vec{q}} = [\exp(\hbar\omega_{\vec{q}}\beta) - 1]^{-1}$$

($\beta = 1/k_B T$, k_B is the Boltzmann constant) is neglected. It is, however, obvious from the secular equations (12) for 0-0, and (43) for 0-1 phonon transitions, that their solutions are extremely difficult to find otherwise. This also means in other words that the spectral analysis would be very complicated at higher temperatures for both 0-0 and 0-1 phonon transitions. Meletov *et al.*[13,14] have observed such complicated spectra in doped naphthalene at higher temperatures.

The theory developed here is essentially applicable for crystals with very low isotopic impurity concentration so that the isolated impurity approximation can be applied. For higher concentration, however, one has to include the impurity-impurity interaction which has been neglected here in the Hamiltonian (1). The problem then becomes severely complicated, as is well known.

APPENDIX A: EXCITON-PHONON-IMPURITY HAMILTONIAN

Consider a molecular crystal with an impurity occupying one of its lattice sites at $\vec{p}$. The impurity molecule is assumed to be such that only its energy of excitation is different from the host molecules, an isotopic impurity. The exciton Hamiltonian of such a crystal without any lattice vibrations can be written in the real crystal space as[1]

$$\hat{H} = \sum_{\vec{l} \neq \vec{p}} \left[\Delta E + \sum_{\vec{l} \neq \vec{m}} D_{\vec{l},\vec{m}} \right] B_{\vec{l}}^{\dagger} B_{\vec{l}} + \sum_{\vec{l} \neq \vec{m}} M_{\vec{l},\vec{m}} B_l^{\dagger} B_{\vec{m}} + \Delta E_{\vec{p}} B_{\vec{p}}^{\dagger} B_{\vec{p}} \ , \tag{A1}$$

where ΔE is the excitation energy of host and ΔE_p is that of the impurity molecules. It is assumed in writing the the Hamiltonian (A1) that the intermolecular interaction terms $D_{\vec{n},\vec{l}}$ and $M_{\vec{l},\vec{m}}$ between impurity and host are equal to those between host and host molecules. This assumption may be considered fully justified for isotopic impurities which have similar molecular structures. One does not have to use this assumption, but then one must write these different intermolecular interaction terms separately, which only complicates the form of (A1) without any significant change in the final results particularly for isotopic impurities.

The Hamiltonian (A1) can be rearranged as

$$\hat{H} = \sum_{\vec{l}} \left[\Delta E + \sum_{\vec{m} \neq \vec{l}} D_{\vec{l},\vec{m}} \right] B_{\vec{l}}^{\dagger} B_{\vec{l}} + \sum_{\vec{l} \neq \vec{m}} M_{\vec{l},\vec{m}} B_{\vec{l}}^{\dagger} B_{\vec{m}} + \Delta_p B_{\vec{p}}^{\dagger} B_{\vec{p}} \ , \tag{A2}$$

where $\Delta_p = \Delta E_p - \Delta E$ is usually known as the trap depth. The first part of the Hamiltonian (A2), without the term Δ_p, is the same as that for a pure crystal, and the impurity term can be considered as a perturbation operator. For a pure crystal with one molecule per unit cell the exciton operators transform as

$$B_{\vec{l}}^{\dagger} = N^{-1/2} \sum_{\vec{k}} B_{\vec{k}}^{\dagger} \exp(-i\vec{k} \cdot \vec{l}) \ . \tag{A3}$$

The transformation (A3) can be considered as the zeroth-order correct basis for the crystal with isotopic impurity, whose excitonic Hamiltonian is given in (A2), because the operators $B_{\vec{l}}^{\dagger}$ are originally obtained as the product[1,16] of electronic wave functions localized at individual molecules. Therefore, the operator $B_{\vec{p}}^{\dagger}$ in (A2) as well can be expressed as (A3) up to the zeroth order.

Using (A3) in (A2), we obtain

$$\hat{H} = N^{-1} \sum_{\vec{l}} \sum_{\vec{k},\vec{k}'} \left[\Delta E + \sum_{m \neq \vec{l}} D_{\vec{l},\vec{m}} \right] B_{\vec{k}}^{\dagger} B_{\vec{k}'} \exp[i(\vec{k}' - \vec{k}) \cdot \vec{l}] + N^{-1} \sum_{\vec{l} \neq \vec{m}} \sum_{\vec{k},\vec{k}'} M_{\vec{l},\vec{m}} B_{\vec{k}}^{\dagger} B'_{\vec{k}} \exp[i(\vec{k}' \cdot \vec{m} - \vec{k} \cdot \vec{l})] + \Delta_p N^{-1} \sum_{\vec{k},\vec{k}'} B_{\vec{k}}^{\dagger} B_{\vec{k}'} \exp[i(\vec{k}' - \vec{k}) \cdot \vec{p}] \ . \tag{A4}$$

The lattice vibrations can be introduced now in (A4) by considering $\vec{l},\vec{m}$ as the instantaneous positions of the molecules during the lattice vibrations. For clarity, however, we will replace in (A4) $\vec{l},\vec{m}$ by $\vec{l}',\vec{m}'$ such that $\vec{l}'=\vec{l}+\vec{R}_{\vec{l}}$ and $\vec{m}'=\vec{m}+\vec{R}_{\vec{m}}$, where $\vec{l},\vec{m}$ represent the equilibrium positions and $\vec{R}_{\vec{l}},\vec{R}_{\vec{m}}$ the lattice displacement vectors due to vibrations. We will denote the Hamiltonian thus obtained from (A4) as $\hat{H}(\vec{R})$, meaning that the Hamiltonian now depends on the lattice displacement vectors $\vec{R}$. We expand $\hat{H}(\vec{R})$ in Taylor's series about the lattice equilibrium to obtain

$$\hat{H}(R)=\hat{H}(\vec{0})+\hat{H}'(\vec{R}) , \tag{A5}$$

where $\hat{H}(\vec{0})$ is the Hamiltonian at the lattice equilibrium and it is identical to (A4). $\hat{H}'(\vec{R})$ is the first-order term of the Taylor's series and it is linear in lattice displacement vectors $\vec{R}_{\vec{l}}$ as

$$\hat{H}'(\vec{R})=\sum_{\vec{l}} \vec{R}_{\vec{l}}\cdot \left[\frac{\partial \hat{H}(\vec{R})}{\partial \vec{R}_{\vec{l}}} \right]_{\vec{R}_{\vec{l}}=\vec{0}} . \tag{A6}$$

Expressing[1,7] $\vec{R}_{\vec{l}}$ in terms of phonon wave vectors $\vec{q}$, and then using the translational symmetry in the unperturbed part of the Hamiltonian $H(\vec{R})$, we obtain from (A5)

$$\hat{H}(\vec{R})=\hat{H}_{\text{ex}}+\hat{H}_{\text{ex-}D}+\hat{H}_{\text{ex-ph}}+\hat{H}_{D\text{-ph}}+\hat{H}_{\text{ph}} , \tag{A7}$$

where

$$\hat{H}_{\text{ex}}=\sum_{\vec{k}} E(\vec{k})B^{\dagger}_{\vec{k}}B_{\vec{k}} , \tag{A8a}$$

is the unperturbed exciton Hamiltonian with the unperturbed exciton energy,

$$E(\vec{k})=\Delta E+\sum_{m\neq 0}[D_{\vec{0},\vec{m}}(\vec{R}=\vec{0}) +M_{\vec{0},\vec{m}}(\vec{R}=\vec{0})\exp(i\vec{k}\cdot\vec{m})] . \tag{A8b}$$

Also,

$$\hat{H}_{\text{ex-}D}=\Delta_p N^{-1}\sum_{\vec{k},\vec{k}'}\exp[i(\vec{k}'-\vec{k})\cdot\vec{p}]B^{\dagger}_{\vec{k}}B_{\vec{k}'} , \tag{A8c}$$

is the exciton-defect interaction at the lattice equilibrium,

$$\hat{H}_{\text{ex-ph}}=N^{-1/2}\sum_{\vec{k},\vec{q},s} S_s(\vec{k},\vec{q})B^{\dagger}_{\vec{k}+\vec{q}}B_{\vec{k}}(b^{\dagger}_{-\vec{q},s}+b_{\vec{q},s}) , \tag{A8d}$$

is the usual exciton-phonon interaction obtained from the unperturbed part of $\hat{H}(\vec{R})$,

$$S_s(\vec{k},\vec{q})=F_s(\vec{k},\vec{q})+X_s(\vec{q})+I_s(\vec{k},\vec{q})+J_s(\vec{k},\vec{q}) , \tag{A8e}$$

is the exciton-phonon coupling function[7,16,17] with s denoting the phonon branch, and

$$\hat{H}_{D\text{-ph}}=\Delta_p N^{-1}\sum_{\vec{k},\vec{k}',\vec{q},s} P_s(\vec{k},\vec{k}',\vec{q}) \times\exp[i(\vec{k}'-\vec{k}+\vec{q})\cdot\vec{p}] \times B^{\dagger}_{\vec{k}}B_{\vec{k}'}(b^{\dagger}_{-\vec{q},s}+b_{\vec{q},s}) , \tag{A8f}$$

is the exciton-defect-phonon interaction due to the perturbation term. $P_s(\vec{k},\vec{k}',\vec{q})$ represents the coupling function of interaction between excitons and phonons in the presence of an impurity, and is given by

$$P_s(\vec{k},\vec{k}',\vec{q})=-i\left[\frac{\hbar}{2I_pN\omega_s(\vec{q})}\right]^{1/2}(\vec{k}-\vec{k}')\cdot\hat{e}_s(\vec{q}) , \tag{A9}$$

with I_p as the mass coefficient of the impurity, $\omega_s(\vec{q})$ is the frequency of phonons with vector $\vec{q}$, and $\hat{e}_s(\vec{q})$ is the unit polarization wave vector.

$\hat{H}_{\text{ph}}$ is the usual phonon Hamiltonian as

$$\hat{H}_{\text{ph}}=\sum_{\vec{q},s}\hbar\omega_s(\vec{q})(b^{\dagger}_{\vec{q},s}b_{\vec{q},s}+\tfrac{1}{2}) . \tag{A10}$$

It is to be noted that $\hat{H}_{\text{ph}}$ is added in (A7) and it is not derived from (A6).

APPENDIX B: EVALUATION OF $Z(\vec{K},\lambda_0)$
[in Eq. (21)]

From (14) or (15), and (17) and (18), we find

$$Z(\vec{K},\lambda_0)=-\sum_{\vec{k}}P(\vec{K},\vec{k},\vec{K}-\vec{k}) \times\left[\frac{S^*(\vec{k},\vec{K}-\vec{k})(1+\bar{n}_{\vec{K}-\vec{k}})}{W(\vec{k})+\hbar\omega(\vec{K}-\vec{k})-\lambda_0} +\frac{S^*(\vec{k},\vec{k}-\vec{K})\bar{n}_{\vec{k}-\vec{K}}}{W(\vec{k})-\hbar\omega(\vec{k}-\vec{K})-\lambda_0}\right] . \tag{B1}$$

We evaluate $Z(\vec{K},\lambda_0)$ at low temperatures with $\bar{n}_{\vec{K}-\vec{k}}=\bar{n}_{\vec{k}-\vec{K}}=0$. Also, we consider only the term $I_s(\vec{k},\vec{K}-\vec{k})$ contributing dominantly to the coupling function $S(\vec{k},\vec{K}-\vec{k})$ in (B1). $I_s(\vec{k},\vec{q})$ is given by[17]

$$I_s(\vec{k},\vec{q})=-i\left[\frac{\hbar}{2I\omega_s(q)}\right]^{1/2}E(\vec{k})\hat{e}_s(\vec{q})\cdot\vec{q} . \tag{B2}$$

Using (A9) and (B1) in (B2), we obtain $Z(K,\lambda_0)$ in the low-temperature limit as

$$\begin{aligned} Z(\vec{K},\lambda_0)&=\frac{N^{-2}}{2(II_p)^{1/2}}\sum_{\vec{k}}\frac{\hbar E(\vec{k})(\vec{K}-\vec{k})^2}{\omega_s(\vec{K}-\vec{k})[W(\vec{k})+\hbar\omega(\vec{K}-\vec{k})-\lambda_0]}\\ &=\frac{N^{-2}}{2(II_p)^{1/2}}\sum_{\vec{k},\vec{k}'}\frac{\hbar E(\vec{k})k'^2\delta(\vec{K}-\vec{k}-\vec{k}')}{\omega_s(\vec{k}')[W(\vec{k})+\hbar\omega_s(\vec{k}')-\lambda_0]} . \end{aligned} \tag{B3}$$

Converting the summation into integration over the energy variables we obtain

$$Z(\vec{K},\lambda_0)=\frac{1}{(II_p)^{1/2}v^2}\int_{E_0'-B}^{E_0'+B}\int_0^{\hbar\omega_{\text{Debye}}}\frac{E\hbar\omega(W_0-W-\hbar\omega)D(\hbar\omega)}{W+\hbar\omega-\lambda_0}dE\,d(\hbar\omega) \tag{B4}$$

when v is the sound velocity in the crystal, and $D(\hbar\omega)$ is the phonon density of states given by

$$D(\hbar\omega)=3(\hbar\omega)^2/(\hbar\omega_{\text{Debye}})^3\ . \tag{B5}$$

ω_{Debye} is the Debye cutoff frequency and E_0' is the center of the unperturbed exciton band. For

$$W(\vec{k})=E(\vec{k})+\sum_{\vec{q}}\hbar\omega_s(\vec{q})(\bar{n}_{\vec{q}}+\tfrac{1}{2}) \tag{B6}$$

we can set the initial phonon energy to zero without any loss of the generality, and then

$$W(\vec{k})=E(\vec{k})\ . \tag{B7}$$

Using (B5) and (B7) in (B4), we find that

$$Z(\vec{K},\lambda_0)=\frac{3(\hbar\omega_{\text{Debye}})(5E_0(\vec{K})-4\hbar\omega_{\text{Debye}})}{20(II_p)^{1/2}v^2[E_0(\vec{K})-\lambda_0(\vec{K})]}\ . \tag{B8}$$

APPENDIX C: EVALUATION OF THE COEFFICIENT $C_0(\vec{K},\vec{0};n)$

$C_0(\vec{K},\vec{0};n)$ is obtained as[8]

$$|C_0(\vec{K},\vec{0};n)|^{-2}=N^{-1}\sum_{\vec{k}}\left[1+\frac{S^2(\vec{k},\vec{K}-\vec{k})(1+\bar{n}_{\vec{K}-\vec{k}})}{[W(\vec{k})+\hbar\omega(\vec{K}-\vec{k})-\lambda_0]^2}+\frac{n_{\vec{K}-\vec{k}}}{[W(\vec{k})-\hbar\omega(\vec{K}-\vec{k})-\lambda_0]^2}\right]. \tag{C1}$$

We intend to evaluate $C_0(\vec{K},\vec{0};n)$ at low temperatures, where only the involvement of low-frequency acoustic phonons can be considered significant; optical phonons can be neglected:

$$|C_0(K,0;n)|^{-2}=N^{-1}\sum_{\vec{k}}\left[1+\frac{S^2(\vec{k},\vec{K}-\vec{k})}{[W(\vec{k})+\hbar\omega(\vec{K}-\vec{k})-\lambda_0]^2}\right]. \tag{C2}$$

The coupling function of exciton and phonon consists of four terms as given in (A8e).

$F_s(\vec{k},\vec{q})$ and $X_s(\vec{q})$ are dominant for phonons with zero wave vectors, $I_s(\vec{k},\vec{q})$ is dominant for phonons with nonzero wave vectors, and $J_s(\vec{k},\vec{q})$ is usually very small and can be neglected. One can therefore write (A8e) as

$$S_s(\vec{k},\vec{q})=|F_s(\vec{k},\vec{q})+X_s(\vec{q})|\delta_{\vec{q},\vec{0}}+I_s(\vec{k},\vec{q})\ . \tag{C3}$$

Using (C3) in (C2) we obtain

$$|C_0(K,0;n)|^{-2}=N^{-1}\sum_{k}\left[1+\frac{|F_s(\vec{K},\vec{0})+X_s(0)|^2\delta_{\vec{k},\vec{K}}+|I_s(\vec{k},\vec{K}-\vec{k})|^2}{[W(\vec{k})+\hbar\omega(\vec{K}-\vec{k})-\lambda_0]^2}\right]. \tag{C4}$$

In (C4) the term with coupling functions F and X for acoustic phonons will become

$$N^{-1}\frac{|F_s(\vec{K},\vec{0})+X_s(\vec{0})|^2}{[W(\vec{K})-\lambda_0]}\ . \tag{C5}$$

N is usually large and therefore this term can easily be neglected from (C4); we then obtain the resulting $C_0(\vec{K},\vec{0};n)$ as

$$|C_0(\vec{K},\vec{0};n)|^{-2}=1+N^{-1}\sum_{\vec{k}}\frac{|I_s(\vec{k},\vec{K}-\vec{k})|^2}{W(\vec{K})+\hbar\omega(\vec{K}-\vec{k})-\lambda_0}\ . \tag{C6}$$

The coupling function $I_s(\vec{k},\vec{K}-\vec{k})$ is given by

$$|I_s(\vec{k},\vec{K}-\vec{k})|^2=\frac{\hbar E^2(\vec{k})(\vec{K}-\vec{k})^2}{2I\omega_s(\vec{K}-\vec{k})}\ . \tag{C7}$$

Substituting (C7) in (C6), we obtain

$$
\begin{aligned}
|C_0(\vec{\mathrm{K}},\vec{0};n)|^2 &= 1+N^{-1}\sum_{k}\frac{\hbar E^2(\vec{\mathrm{k}})(\vec{\mathrm{K}}-\vec{\mathrm{k}})^2}{2I\omega(\vec{\mathrm{K}}-\vec{\mathrm{k}})[W(\vec{\mathrm{k}})+h\omega(\vec{\mathrm{K}}-\vec{\mathrm{k}})-\lambda_0]^2}\\
&= 1+\frac{(2\pi)^3N^{-2}}{2Iv}\sum_{\vec{\mathrm{k}},\vec{\mathrm{k}}'}\frac{\hbar E^2(\vec{\mathrm{k}})\vec{\mathrm{k}}'^2\delta_{\vec{\mathrm{k}}',\vec{\mathrm{K}}-\vec{\mathrm{k}}}}{W(\vec{\mathrm{k}}')[W(\vec{\mathrm{k}})+h\omega(\vec{\mathrm{k}}')-\lambda_0]^2}\ .
\end{aligned}
\tag{C8}
$$

We now convert the summation over $\vec{\mathrm{k}}$ into an integration over the energy variables and then following the steps used in solving (B3), we obtain from (C8):

$$
|C_0(\vec{\mathrm{K}},\vec{0};n)|^{-2}=1+\frac{\hbar}{Iv^2}\int_{E_0'-B}^{E_0'+B}\int_0^{\hbar\omega_{\mathrm{Debye}}}\frac{E^2\omega\delta(W_0-W-\hbar\omega)\rho_{\mathrm{ex}}dE\,d(\hbar\omega)}{(W+\hbar\omega-\lambda_0)^2}\ . \tag{C9}
$$

One can set the initial phonon population to zero, i.e., $\sum_{\vec{\mathrm{q}}}\hbar\omega(\vec{\mathrm{q}})(\bar{n}_{\vec{\mathrm{q}}}+\frac{1}{2})=0$. $|C_0(\vec{\mathrm{K}},\vec{0};n)|^2$ is then obtained as

$$
|C_0(\vec{\mathrm{K}},\vec{0};n)|^{-2}=1+\frac{E_0'^2\,|E_0(\vec{\mathrm{K}})-E_0'|+B^2\,|E_0(\vec{\mathrm{K}})/2-E_0'|}{Iv^2(E_0(\vec{\mathrm{K}})-\lambda_0)^2}\ . \tag{C10}
$$

Using (27) in (C10), we obtain

$$
C_0(\vec{\mathrm{K}},\vec{0};n)=1/\sqrt{2}\ . \tag{C11}
$$

Therefore, at very low temperatures, the probability ($|C_0(\vec{\mathrm{K}},\vec{0};n)|^2$) of exciting a pure excitonic state is $\frac{1}{2}$. That is what one may expect anyway as there are only two possibilities in exciting a pure excitonic state at low temperatures.

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