

Dynamics and instabilities of an exciton in the phonon field and the correlated absorption–emission spectra

Yutaka Toyozawa

Department of Physics, Chuo University, Kasuga, Bunkyo-ku, Tokyo 112, Japan

Abstract: Dynamics of an exciton in the phonon field is studied with particular attention to the varying feature of the optical spectra with increasing exciton-phonon coupling. The absorption lineshape varies gradually from a Lorentzian broadened by the scattering rate of the delocalized exciton to a Gaussian broadened by the energy fluctuation of the localized excitation; the latter broadening is narrowed into the former by the motional effect of the exciton. The luminescence is subject to abrupt change from the resonant sharp line of the free exciton to the Stokes-shifted broad band of the self-trapped exciton as coupling constant exceeds a critical value. The steepness constant characterizing the low energy tail of the absorption is inversely proportional to the coupling constant, allowing the prediction on the types of luminescence from the absorption spectrum. Depending on the lattice relaxation energy coping with the optical excitation energy, one can consider three different situations with high, low and no luminescence. As the ultimate instability, one can conceive spontaneous generation and condensation of self-trapped excitons which amounts to the electronic-structural phase transition. A few examples of this catastrophic situation are presented.

INTRODUCTION

The exciton is an elementary electronic excitation in nonmetallic solid, and plays a fundamental role in the optical spectra. Being a composite particle of an electron and a hole, it has two degrees of freedom besides spin. One is the relative motion, with its eigenstates consisting of discrete bound states and continuous ionized states, which manifest themselves directly in the optical spectra. The other is the center of mass motion, with its energy eigenvalues forming a continuous exciton band in the case of a bound state. However, each exciton band shows up only its particular K-point as an exciton line in the spectra due to the momentum conservation between the incident photon and the excited electron.

The real lattice is undergoing thermal vibrations which act as scatterer for the moving exciton, resulting in the shift and broadening of the exciton line. This means that the spectral shape of an exciton line provides us with the most direct information on the dynamics of the exciton interacting with the phonon field. Since the interaction is mutual, the optically created exciton will make the surrounding lattice to deform so as to stabilize itself, resulting in self-trapping if the interaction is large enough. The relaxed lattice configuration is reflected in the Stokes-shift and the broadening of the optical emission therefrom. The spectral correlation between the absorption and emission spectra, or more generally speaking, the spectral and temporal dependence of the second order optical processes, reveals the dynamics of the optically created exciton in the phonon field throughout its radiative lifetime. The relaxed exciton may also result in nonradiative annihilation and defect formation. The study of these exciton instabilities across the band gap leads to the ultimate catastrophic situation in which the self-trapped exciton (STE) is destabilized against spontaneous generation and condensation, resulting in the electronic-structural phase transition of the entire lattice.

The purpose of the present paper is to describe dynamical behaviors and possible instabilities of an exciton in the phonon field and to compare theoretical predictions with experimental results on the optical spectra and the phase transitions. To make the statements as general and useful as possible, we will introduce a few important parameters characterizing the material, in terms of which one can classify different situations realized in different materials without going into the individual detail.

A MODEL HAMILTONIAN FOR THE EXCITON-PHONON SYSTEM

The exciton is a mobile entity, with electronic excitation propagating from site to site through the intersite transfer energy. With the use of the tight binding model, one can write the Hamiltonian for an exciton in the site representation as (ref. 1)

$$H(q) = \sum_n |n\rangle E_n(q) \langle n| + \sum_{n \neq m} \sum_m |n\rangle t_{nm}(q) \langle m|. \quad (1)$$

where the dependence of the site excitation energy E_n and the intersite energy t_{nm} on the atomic displacements (q) from equilibrium positions are to be taken into account. In $E_n(q)$, we consider up to the linear terms whose sum will be written by a single coordinate Q_n , namely we put $E_n(q) = E_a - cQ_n$. The intra-site (atomic or molecular) excitation energy E_a at the equilibrium position of atoms is common to all sites due to the translational symmetry. The new coordinate Q_n thus introduced is called the "interaction mode" at the site n . Being a superposition of infinite number of sinusoidally vibrating normal modes with continuously distributed frequencies, Q_n relaxes to the new equilibrium position as the result of dephasing. It is a localized mode in the sense that the atomic displacement pattern associated with Q_n is confined to the region which is affected by the electronic excitation at the site n . This pattern around the site n is the same as that of Q_m around the site m due to the translational symmetry. One can visualize Q_n e.g. as an intramolecular mode or as a breathing mode around the site. It is to be noted that (Q_n) are neither normal modes nor orthogonal, nor complete. For simplicity, however, we will treat them as normal modes. Then the Hamiltonian for the atomic motion in the ground electronic state of the crystal can be written as

$$H_p = \sum_n (1/2)(\omega^2 P_n^2 + Q_n^2) = K(P) + U(Q), \quad (2)$$

where Q_n is so normalized that the vibrational frequency appears in the kinetic energy term. This choice is more natural for the adiabatic approximation whose validity is assured by the smallness of ω . Neglecting the q -dependence of transfer energies, one can now write down the total Hamiltonian for the exciton phonon system as

$$H_{\text{tot}} = H + H_p = H_e + H_{ep} + H_p, \quad (3)$$

$$H_e = \sum_n |n\rangle E_a \langle n| + \sum_{n \neq m} \sum_m |n\rangle t_{nm} \langle m|, \quad (4)$$

$$H_{ep} = \sum_n |n\rangle (-cQ_n) \langle n|. \quad (5)$$

LOCALIZED VERSUS DELOCALIZED EXCITATION

Let us consider the limit of vanishing t 's which corresponds to the case of intra-site or "localized excitation". Confining the excitation to the site n , one can write the adiabatic energy for this excited state as

$$W^{(\text{en})}(Q) = (E_a - E_{\text{LR}}) + (1/2)(Q_n - c)^2 + \sum_{m(\neq n)} (1/2)Q_m^2, \quad (6)$$

where $E_{\text{LR}} = c^2/2$. In the configuration coordinate (C.C.) space (Q), the lattice relaxation after the Franck-Condon excitation of the site n takes place in such a way that only Q_n approach the new

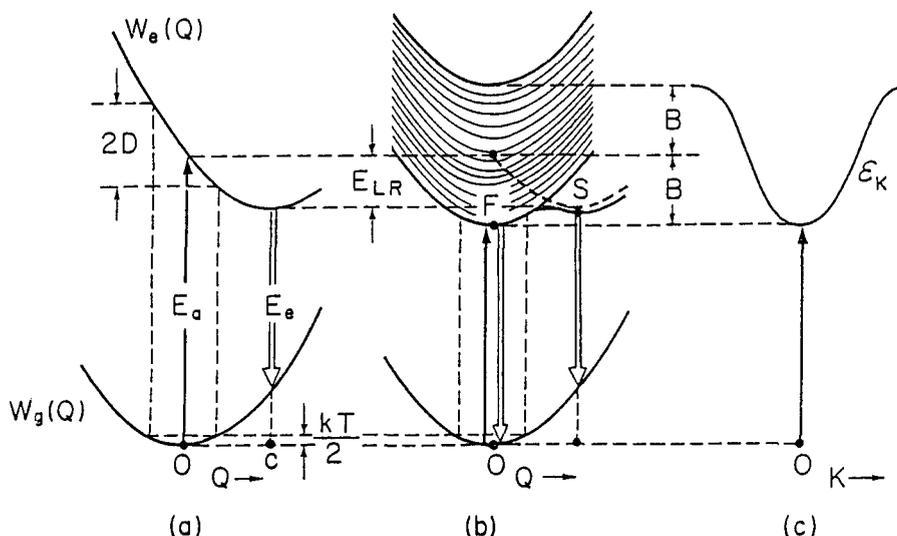


Fig. 1: Configuration coordinate models for localized excitation (a) and exciton (b), and excitonic band in rigid lattice (c)

equilibrium position c , with the corresponding energy decrease by E_{LR} which will hereafter be called "lattice relaxation energy". Other modes $Q_m (m \neq n)$ are not affected by this localized excitation: $(g) \rightarrow (e_n)$. Since the adiabatic energy difference between these states is given by $W^{(en)}(Q) - U(Q) = E_n(Q) = E_a - cQ_n$, the lineshape calculation of the absorption spectrum in the Franck-Condon approximation also reduces to the problem of one-dimensional C.C. model which is schematically shown in Fig. 1(a). The normalized lineshape at high temperature, as given by

$$F(E) = \int dQ_n (2\pi k_B T)^{-1/2} \exp\{-Q_n^2 / (2k_B T)\} \delta[E_a - cQ_n - E] \\ = (2\pi D^2)^{-1/2} \exp\{-(E - E_a)^2 / 2D^2\}, \quad (7)$$

$$\text{with } D^2 = \langle\langle (-cQ_n)^2 \rangle\rangle = 2E_{LR} k_B T, \quad (8)$$

is a Gaussian, with its width D representing the mean amplitude of the fluctuation of local excitation energy.

Let us then consider the opposite limit of vanishing exciton-phonon interaction. The eigenstates are given by the Bloch type exciton states: $|\mathbf{K}\rangle = N^{-1/2} \sum_n \exp(i\mathbf{K} \cdot \mathbf{R}_n) |n\rangle$. For a simple d -dimensional lattice with only the nearest neighbor transfer energy t , the eigenenergy is given by $E(\mathbf{K}) = E_a + 2t \sum_{i=1}^d \cos(K_i a_0)$ where a_0 is the lattice constant. As shown in Fig. 1(c), the exciton band extends from $E_a - B$ to $E_a + B$ where the half band width $B = 2d|t|$ represents how mobile the exciton is: the time needed for an exciton to move to any of the nearest neighbor is given by $\sim B^{-1}$ (the unit with $\hbar = 1$ will be used throughout the paper), as is also obvious from the uncertainty principle. If $t < 0$, the optically allowed exciton state with $\mathbf{K} = 0$ is at the bottom of the exciton band—the "direct gap" case which will mainly be considered hereafter unless otherwise stated.

The effect of the exciton-phonon interaction H_{ep} on the line width can be described by the following exact expression for the lineshape (ref. 1). Denoting the eigenvalues and eigenstates of $H(Q) = H_e + H_{ep}(Q)$ by $E_\nu(Q)$ and $|\nu(Q)\rangle$, respectively, and the optically allowed eigenstate $|\mathbf{K} = 0\rangle$ of H_e simply by $|0\rangle$, one can write the normalized lineshape as

$$F(E) = \langle\langle \sum_\nu |\langle 0 | \nu(Q) \rangle|^2 \delta(E_\nu(Q) - E) \rangle\rangle$$

$$\begin{aligned}
&= -\pi^{-1} \left\langle \left\langle \lim_{\eta \rightarrow +0} \langle 0 | (H(Q) - E + i\eta)^{-1} | 0 \rangle \right\rangle \right\rangle = -\pi^{-1} \text{Im} (E_0 + \Sigma_0(E) - E)^{-1} \\
&= \pi^{-1} \Gamma_0(E) \left[\{E - E_0 - \Delta_0(E)\}^2 + \{\Gamma_0(E)\}^2 \right]^{-1}, \quad (9)
\end{aligned}$$

where the complex self-energy of the exciton: $\Sigma_K(E) = \Delta_K(E) + i\Gamma_K(E)$ due to the scattering by fluctuating potential H_{ep} is to be determined self-consistently from

$$\Sigma_K(E) = \sum_{K'} \left\langle \left\langle | (H_{ep}(Q))_{KK'}|^2 \right\rangle \right\rangle [E - E_{K'} - \Sigma_{K'}(E)]^{-1} + (\text{higher order terms}). \quad (10)$$

In the lowest order perturbation theory, one obtains the golden rule for the transition rate:

$$\Gamma_K(E) = \pi D^2 \rho^{(0)}(E) \quad (11)$$

with the use of the statistical average of fluctuation as given by eq. (8). Here, $\rho^{(0)}(E) = N^{-1} \sum_k \delta(E - E_K)$ is the normalized density of states (DOS) of the unperturbed H_e , which amounts to $(2B)^{-1}$ if it is assumed for simplicity to be constant within the band $(E_a - B, E_a + B)$. Then one obtains a Lorentzian lineshape, with energy independent half-width $\Gamma_0 = (\pi/2)D^2/B$ ($\propto T$) which represents the scattering rate.

The above result based on the perturbation theory holds in the weak scattering regime ($D \ll B$), whereas we already obtained a Gaussian lineshape in the strong scattering regime ($D \gg B$). The nature of exciton changes gradually from localized to delocalized type as B , the energy transfer to nearest neighbors, increases and overcomes the potential fluctuation D . Physical meaning of the line width also changes from the local energy fluctuation D to the scattering rate Γ . The fact that the latter is smaller than D by a factor D/B ($\ll 1$ in this weak scattering regime) is due to the motional narrowing effect, as is also well known in the ESR study. The exciton stays on each site for a time of the order of B^{-1} , which is shorter than the time needed for it to perceive the local energy fluctuation D according to the uncertainty principle. As the result, the spatial fluctuation perceived by the moving exciton is reduced by this time ratio, D/B , which is called "narrowing factor".

Theoretical predictions are in satisfactory agreement with observations of the absorption lineshapes in a variety of inorganic and organic materials which in fact are widely distributed from weak to strong scattering regime. However, the low energy tails of the exciton absorption spectra of the weak scattering materials have been found to decay exponentially with a decay constant being proportional to reciprocal temperature (at high temperature):

$$F(E) = A \exp[-\sigma(E'_0 - E)/k_B T] \quad (12)$$

where E' is close to the absorption peak and the steepness constant σ is a dimensionless material constant. The universality and simplicity of this empirical rule—now called "Urbach rule"—evoked a number of theoretical and experimental studies to explain it on a microscopic basis.

According to the weak scattering expression (11) for $\Gamma(E)$, the absorption spectrum given by eq. (9) vanishes below the bottom of the exciton band. In fact, there should be localized states below the band bottom originating from the spatial fluctuation of the potential $V_n = -cQ_n$ at each instant which is also temporally fluctuating following the Gaussian distribution $\exp(-Q_n^2/2k_B T)$ of the Boltzmann statistics (see eq. (7)). Suppose the Urbach rule (12) is derivable from the exact expression (9) with the use of the Hamiltonian (3) under the above mentioned statistical distribution of Q_n 's at high temperature where ω can be neglected. If the energy is measured in unit of B , the only parameter governing the lineshape is the scattering strength D/B as mentioned before. The exponent in eq. (12) should then be of the form: $[(E'_0 - E)/B][B/D]^2$ (times a dimensionless constant) in order to give the factor: T^{-1} (see eq. (8)). The material constant σ in the empirical rule (12) should then be related with the exciton-phonon coupling constant g defined by

$$g = E_{\text{LR}}/B \quad (13)$$

through

$$\sigma = s/g \quad (14)$$

where s , called "steepness index", is a dimensionless parameter which may depend on the geometrical factor such as lattice structure and dimensionality but no more on the individual material.

Various method beyond the perturbation theory, such as the t -matrix approximation (ref. 2) and the coherent potential approximation (CPA) (ref. 3), were applied to incorporate the localized states into the self-energy so as to derive (12). As the most straightforward method free from any sophistication, the Monte-Carlo calculation was performed for 1-, 2- and 3-dimensional simple lattices by direct diagonalization of the energy matrix: $H(Q)$ for each configuration (Q_1, Q_2, \dots) with the Boltzmann statistics (ref. 4). The Urbach rule (12) for the tail part (as well as the Lorentzian shape of the main part) was in fact reproduced, and the steepness indices s were obtained for each dimensionality and for direct and indirect gap cases. The analysis of wave functions not only confirmed the conjecture that the exponential tail originates from the localized states, but also endorsed the CPA to be a good approximation. The exciton-phonon coupling constant (13) had in fact been introduced in the study of relaxed exciton before the explanation of the Urbach rule, as will be described in the next section.

THE RELAXED EXCITON IN DEFORMABLE LATTICE

So far we studied the optical excitation energy, the eigenvalues $E(Q)$ of $H(Q)$, as functions of the atomic configuration (Q) which is regarded as external variable governed by the Boltzmann statistics: $\exp[-U(Q)/k_{\text{B}}T]$. In other words, we were concerned with the Franck-Condon states. Let us now study what happens with the atomic configurations under the existence of an exciton as time goes on after the optical transition. In order to describe the dynamics of this relaxation, we have to include $U(Q)$ so as to deal with the adiabatic potential: $W^{(e\nu)}(Q) = E_{\nu}(Q) + U(Q)$.

The situation is obvious in the two limiting cases. Under the absence of exciton-phonon interaction ($c = 0$), the optically created exciton will stay at the bottom of the exciton band with energy $E_0 = E_{\text{a}} - B$. Under the absence of transfer t , the exciton will stay localized at some site n , with Q_n relaxing to c so as to minimize $W^{(e\nu)}(Q)$ to $E_{\text{a}} - E_{\text{LR}}$ (see eq. (6)). What will happen under the coexistence of t and c ? The question is to be answered most properly by studying the adiabatic potential $W^{(e\nu_0)}(Q) = E_{\nu_0}(Q) + U(Q)$ for the lowest eigenstate $E_{\nu_0}(Q)$ of $H(Q)$ and by looking for its minima, as is done elsewhere (ref. 1). However, if one is interested only in the minimum points of the adiabatic potential $W^{(e\nu_0)}(Q)$, all one has to do is to minimize the expectation value of $H(Q) + U(Q)$ with respect to both the wave function ψ and the atomic configuration (Q) . A simpler way to perform this is first to minimize with respect to (Q) for fixed ψ and then to minimize with respect to ψ , since the practically intractable work of looking for the minima in the multidimensional (Q) -space is thereby reduced to an appropriate choice of the trial wave function ψ (inverse adiabatic approximation! which is justified only for this purpose).

We choose the trial wave function localized around a site with orbital radius a as the only variable parameter, since we are particularly concerned with the intermediate situation between the completely delocalized ($a = \infty$) and completely localized ($a = a_0$ since ψ is an envelope wave function for the center-of-mass motion) states. The expectation value of $H + U(Q)$, after minimization with respect to (Q) , is then given by

$$E(a) = E_{\text{a}} - B + B(a_0/a)^2 - E_{\text{LR}}(a_0/a)^d. \quad (15)$$

To derive or confirm this formula, one first note that it reduces to $E_{\text{a}} - B$ and $E_{\text{a}} - E_{\text{LR}}$ in the limits of delocalization and localization, in accordance with what was mentioned above. Secondly, the

first three terms of (15) is the expectation value of H_e in the effective mass approximation, the third term representing the kinetic energy for localization (the uncertainty principle). The fourth term is the result of minimizing the expectation value $\langle \psi | H_{ep}(Q) | \psi \rangle + U(Q)$ with respect to (Q) . In fact, the minimization gives $Q_n = -c|\psi(n)|^2$, and putting this value in, one obtains $-(c^2/2) \sum_n |\psi(n)|^4$. Considering that $|\psi(n)|^2$ has significant values of the order of M^{-1} within the region of volume a^d containing $M \sim (a/a_0)^d$ sites, one obtains the power d for this fourth term.

The minima of eq. (15) with respect to $\lambda = a_0/a$ ($0 < \lambda < 1$), the degree of localization, correspond to the minima of the adiabatic potential, namely the relaxed excited states (RES). The situation depends on the dimensionality of the lattice. For $d = 3$, one has two RES's: the free state F ($\lambda = 0$) and the self-trapped state S ($\lambda = 1$) when the coupling constant g defined by eq. (13) is greater than $2/3$. When g exceeds unity, the stable state changes abruptly from F to S, but F remains to exist as a metastable state. The maximum at $\lambda = 2/3g$ corresponds to the adiabatic potential barrier (saddle point in (Q) -space) of height $E_b = 4B/27g^2$ above F which must be surmounted for the free exciton to become self-trapped. The adiabatic picture for this activation process is shown schematically in Fig. 1(b) by a solid curve connecting F and S (assumed to be metastable here). Note that two different aspects of our problem are incorporated in this Fig. (b): namely the adiabatic picture for localized excitation shown in Fig. (a) and the band picture for delocalized excitation shown in Fig. (c). One can expect from this Figure that the exciton luminescence in the coexistent case ($2/3 < g < \infty$) consists of two components: a sharp resonant line from the F state and a Stokes-shifted broad band from the S state.

With $d = 1$, one has the only minimum at $\lambda = \text{Min.}\{(g/2), 1\}$. This means that the nature of RES changes gradually from F-like to S-like as g increases. The optically created free exciton will straightforwardly relax to this RES without surmounting any potential barrier. This RES may better be called "polaron state" since the situation resembles the electron interacting with polar mode of lattice vibrations in 3-dimensional lattice.

We are now in a position to correlate absorption and luminescence spectra. The latter is subject to the abrupt change as g exceeds unity, while the former is not subject to such an abrupt change. Moreover, the gradual change from weak to strong scattering is governed by the ratio $D/B = (2gk_B T/B)^{1/2}$. Except in molecular crystals with small B , there is a wide range with "weak scattering but strong coupling" ($B/k_B T > g > 1$). In this case, the optically created exciton behaves as a nearly free particle until it finally surmounts the potential barrier to become self-trapped, as is the case in many materials inclusive of alkali halides. However, the steepness constant of the low energy tail of the absorption spectrum is directly related with g through eq. (14), as it should since the tail part originates from localized states (not from the scattering states which are responsible for the main part of the absorption peak).

These predictions are in satisfactory agreement with observations on a variety of materials (ref. 1). Abrupt change of low temperature luminescence from F to S type has been observed in mixed crystal $\text{AgCl}_x\text{Br}_{1-x}$ when x exceeds $x_c = 0.45$ and in some aromatic molecular crystals under the change of applied pressure. The prediction on the absorption-luminescence correlation through eq. (14) is in excellent agreement with observations. It gives a criterion that F or S is more stable according as σ is greater or smaller than σ_c (1.64 for direct and 0.93 for indirect gap in 3-dimensional crystal). Almost all materials (organic and inorganic) of which σ has been measured (ranging from 3.0 of CdTe to 0.76 of NaCl) and F-S relative stability has been confirmed are in conformity with this criterion. Of particular interest is the indirect exciton absorption edge in $\text{AgCl}_x\text{Br}_{1-x}$, of which the measured σ decreases from 0.98 for $x = 0$ to 0.78 for $x = 1$, taking the value 0.89 at the abrupt change of luminescence, in excellent agreement with the predicted σ_c .

COMPETITION BETWEEN RADIATIVE AND NONRADIATIVE ANNIHILATIONS

Let us now consider the situation where the crossing of the adiabatic potentials of the relaxing exciton and the ground state comes into play, and apply the Dexter-Klick-Russel criterion on the competition of radiative and nonradiative recombination processes. Making use of the model shown in Fig. 1 but confining ourselves to the case in which S is more stable than F, one can consider the three possible cases (ref. 5) in the increasing order of E_{LR} against E_0 , as shown in Fig. 2 where E_0 is varied against E_{LR} .

In case (i) in which the crossing point is situated higher than F, the nonradiative transition is improbable except at high temperature. The quantum yield for luminescence is nearly unity. Because of long radiative lifetime, quasi-thermal equilibrium in population may be established between F and S excitons, which allows the estimation of the F-S energy difference from the temperature dependent intensity ratio of F- and S-type emission bands, as was done for some aromatic crystals.

In case (ii) in which the crossing point is situated lower than F but its abscissa is still beyond the minimum point Q_m , it is energetically possible for the relaxing exciton to reach this point (after overshooting Q_m) where it will make nonradiative transition to the ground state with significant probability. The opening of this nonradiative channel affects most directly the steady state population of STE's, making the quantum yield of luminescence much lower than in case (i). The temperature dependence of the intensity of the F-type emission in the steady state allows one to estimate the height of potential barrier for self-trapping. The STE's in alkali halides which have been most extensively studied belong to this case.

In case (iii) of Fig. 2 realized when $E_a/2 < E_{LR} < E_a$, the RES cannot emit a photon since there is no lower electronic state at Q_m . It may not be appropriate to call such state as a relaxed exciton. The formation of a pair of F and H centers in irradiated alkali halides, and probably some of the photo-structural changes in amorphous semiconductors belong to this case.

The case U is a fictitious situation where the RES has lower energy than the ground state ($E_a - E_{LR} < 0$); namely the ground state from which we started is unstable. However, there is an instructive

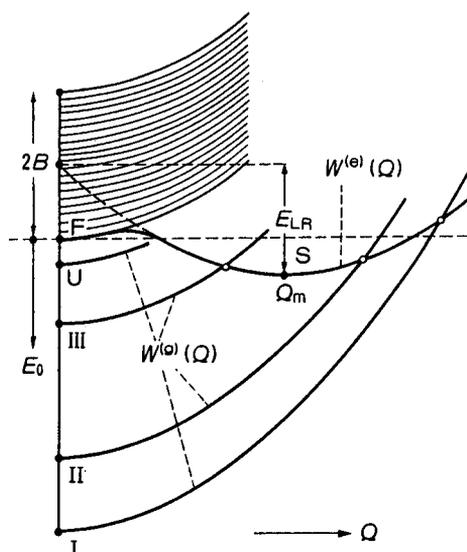


Fig. 2: Adiabatic potentials for the groundstate and the free and self-trapped excitation for various values of E_0 , the energy of the optical exciton.

example of material of which one can start from a conceptually simple but actually false ground state and get to a real but complicated ground state (ref. 6). That is the Wolfram's reds, a quasi-one dimensional material of which the skeleton consists of an alternate array: $(\text{Cl}^- - \text{Pt}^{3+} -)^{2n}$, which is a simple (and metallic) but false ground state. The real ground state is an insulator with a complicated structure of doubled period: $(\text{Cl}^- - \text{Pt}^{4+} - \text{Cl}^- - \text{Pt}^{2+} -)^n$, which can be reached from the former through the Peierls transition with charge density wave of large amplitude.

CONDENSATION OF SELF-TRAPPED EXCITONS AND THE PHASE TRANSITION

In the context of our argument, the example of phase transition mentioned in the last section can be described in terms of spontaneous generation, at all unit cells, of self-decomposed electron-hole pairs—the parity-broken STE's. The self-decomposition takes place as the result of phonon-mediated electron-hole repulsion (due to different signs of deformation potentials) counterbalancing the direct coulomb attraction, and in fact, the majority of STE's in alkali halides are known to belong to this type. If such STE's were formed at all lattice sites, there should be significant interaction among them. Assuming them to be attractive, one could define the cohesive energy per one STE which will be denoted by E_c . If the energy of the condensed state of STE's per unit cell, given by $E_a - E_{\text{LR}} - E_c$, is negative, the new phase become more stable than the ground state from which we started (ref. 7) (even if $E_a - E_{\text{LR}}$ is still positive).

Such a dramatic phase transition can be seen among quasi-one dimensional charge transfer compounds with mixed stacking of donor (D) and acceptor (A) molecules. They undergo the neutral-ionic (NI) transition, approximately described as $(\text{D}^0\text{A}^0)^n$ to $(\text{D}^+\text{A}^-)^n$, under decrease in temperature or by applying pressure. It is considered that the contraction of D-A distance a results in the increase of Madelung energy $1.2e^2/a$ so as to overcome the redox potential Δ of D and A. We will present here a qualitative argument supporting our condensation model. A localized charge transfer (CT) exciton, after self-decomposition, consists of a D^+A^- pair in N-phase matrix with dipole moment $\mu = ae\delta\rho$, where $\delta\rho$ denotes for the actual fraction of charge transfer. The cohesive energy for such STE solid is then given by the sum of dipole-dipole interactions which amounts to $E_c = 1.2 \cdot 2\mu^2 / (2a)^3 \sim 0.37$ eV in the case of TTF-chloranil if we tentatively assume $\delta\rho \sim 0.6$. At the NI transition point, $E_a - E_{\text{LR}} - E_c$ vanishes. From the CT exciton peak observed at 0.76 eV, one obtains $E_{\text{LR}} \sim 0.39$ eV, satisfying the criterion for the absence of luminescence: $E_{\text{LR}} > E_a/2$. The half-width of the exciton band, given by the second order expression: $B \sim 2t^2/\Delta$ (ref. 8) for the nearly N phase, turns out to be ~ 0.04 eV if D-A transfer energy $|t|$ is assumed to be 0.3 eV. This assures our assumption of strong scattering: $D = (2k_{\text{B}}T \cdot E_{\text{LR}})^{1/2} \gg B$. On the other hand, with a microscopic model that D^+A^- distance gets shorter due to their coulomb attraction, E_{LR} can be estimated to be $0.8(e\delta\rho)^4 / (M_r\omega_N^2 a^4) \sim 0.34$ eV where M_r denotes for the reduced mass of D-A pair and ω_N for the observed angular frequency of the optical mode of lattice vibration in the N phase. This value of E_{LR} is not far from the above value, in spite of the independent ways of estimation. Thus we can construct a physically reasonable and consistent description of the NI transition in terms of spontaneous generation and condensation of STE's.

REFERENCES

1. Y. Toyozawa. in *Organic Molecular Aggregates* (P. Reineker, H. Haken and H. C. Wolf, ed.) pp. 90-106. Springer-Verlag, Berlin Heidelberg New York Tokyo (1983).
2. H. Sumi and Y. Toyozawa. *J. Phys. Soc. Jpn.* **31**, 342 (1971).
3. H. Sumi. *J. Phys. Soc. Jpn.* **32**, 616 (1972); H. Sumi and A. Sumi. *J. Phys. Soc. Jpn.* **56**, 2211 (1987).
4. M. Schreiber and Y. Toyozawa. *J. Phys. Soc. Jpn.* **51**, 1528 (1982); **52**, 318 (1983).
5. Y. Toyozawa. *J. Phys. Soc. Jpn.* **58**, 2629 (1989).
6. H. Tanino and K. Kobayashi. *J. Phys. Soc. Jpn.* **52**, 1446 (1983).
7. Y. Toyozawa. *Acta Phys. Pol.* **87**, 47 (1995).
8. T. Iizuka-Sakano and Y. Toyozawa. *J. Phys. Soc. Jpn.* **65**, 671 (1996).