Urbach tail for ferroelectric materials with an order-disorder-type phase transition

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We present a model describing the Urbach tail of exciton absorption spectra in ferroelectric materials with order-disorder-type phase transition. In addition to the thermal effect of exciton-lattice interactions, the internal Stark effect by the local electric field due to the displacement of protons is taken into account. The random distribution of the direction of local electric field induces a random polarization of the lowest exciton state. This results in an additional randomness of the exciton band in the disordered phase. The anomalous temperature dependence of the steepness parameter for the Urbach tail observed in $PbHPO_4$ is reproduced by a numerical simulation within the present model. [S0163-1829(99)03128-8]

In many insulators, the low-energy tail of fundamental absorption edge depends exponentially on the energy of photons. Since the first report by Urbach,[1] this rule has been widely observed in many kinds of materials. The tail of the spectra called the Urbach tail is empirically given as a function of photon energy E,

$$F(E) = A \exp\left(-\sigma \frac{E_0 - E}{k_B T}\right), \qquad (1)$$

where the convergence energy E_0 and the steepness parameter σ are almost constant at sufficiently high temperatures.[2]

In order to explain the origin of the Urbach tail, a number of theoretical studies have been carried out.[3–12] Among them, two types of theories seem to be worth mentioning at present. One is the theory based on the model of the internal Stark effect.[4,7,11] In this theory, it is asserted that the Franz-Keldysh effect by the microfield due to lattice vibrations is responsible for the appearance of the exponential tail in the absorption edge. Dow and Redfield[11] have made a comprehensive survey of Urbach's rule from the viewpoint of this microfield model. On the other hand, Toyozawa and co-workers[3,8–10] developed a theory of Urbach's rule on the basis of the model of short-range interaction of phonons with the center-of-mass motion of excitons. According to the theory of Sumi and Toyozawa,[9] thermal fluctuations of lattice systems result in an adiabatic modulation of site energies, which can be described by a Gaussian distribution of random potentials. It was shown that the optical transitions to the exciton state momentarily trapped by this local potential gives rise to the exponential tail at the absorption edge. By applying Einstein's relation to the absorption and emission spectra, they succeeded in deriving a criterion described in terms of the steepness parameter σ, which determines whether the exciton is self-trapped or not. Furthermore, numerical simulations by Schreiber and Toyozawa[13] have clearly demonstrated that the model of momentarily trapped exciton reproduces well the line shape given by Eq. (1), including its temperature dependence. At least for insulating materials with relatively strong electron-phonon coupling, this model gives the most reasonable explanation of the Urbach tail. It should be noted that the Urbach tail is widely observed also in the absorption spectra of amorphous

materials:[14–16] The steepness of the exponential tail is essentially independent of temperatures in this case. It can be said, therefore, that we detect various kinds of randomness of crystals through the measurement of the Urbach tail.

$PbHPO_4$ is a ferroelectric material containing hydrogen bonds. The ferroelectric transition occurs at $T_c = 310$ K. This transition is a second-order one, and the spontaneous polarization P_s slowly rises below T_c.[17–19] It is known that the one-dimensional ordering of protons between the two stable configurations of O—H—O bonds is a primary cause of this phase transition.[18] Although displacements of heavy ions are also observed, its temperature dependence is not directly correlated with that of P_s. Recently, Kida *et al.*[20] studied experimentally the optical-absorption spectra of $PbHPO_4$. The first exciton peak has been assigned as due to the cationic excitation of $6s \rightarrow 6p$ in Pb^{2+} ions. They found that the Urbach tail of the absorption spectra exhibits an anomalous temperature dependence. It was pointed out that, as the temperature is lowered below T_c, the steepness parameter σ increases from the value above T_c, and this increment behaves similarly to P_s as a function of temperature. This result strongly suggests that the ordering of protons has a close relation with the anomalous behavior of σ.

In the present study, we propose a simple model for the Urbach tail of exciton absorption in ferroelectric materials with order-disorder-type phase transition. Our theory is essentially based on the model of the internal Stark effect. It is quite natural to expect that strong electric fields are acting on the internal motion of excitons in ferroelectric materials. Generally it is difficult to make a precise evaluation of the strength of microscopic fields in crystals. As a very rough estimation for $PbHPO_4$, we take the electric field $E = 2.4 \times 10^7$ V cm^{-1} at low temperatures, which is calculated from the saturated value of $P_s = 2.1$ μC cm^{-2}.[17] This is an order of magnitude larger than those estimated in Ref. 11 for the field strength induced by the LO phonons in alkali halides at room temperature. Such an electric field will strongly polarize the excitons as shown in Ref. 11. It should be noted, however, that the conventional microfield model of the Urbach tail will lead to the prediction that the steepness parameter σ becomes *smaller* below T_c since the effective-field strength increases below T_c. This is in contradiction with the experimental observation, in which σ becomes *larger* below

T_c. We would like to point out that it is not the change of averaged field strength but the change of degree of randomness in the local field that is the main cause of the anomaly in σ.

We assume there is a microscopic polarization accompanied with the displacement of protons for each unit cell; This polarization itself will be simply called ''proton'' hereafter. It is assumed that a proton has two degrees of freedom ρ_j at the jth unit cell, $\rho_j = +1$ and -1, corresponding to its stable positions. In completely ordered phase, ρ_j takes an identical value $+1$ or -1 at every unit cell; while in completely disordered phase, ρ_j takes the values $+1$ and -1 randomly with the expectation value of 0. In order to explicitly describe the Stark effect of excitons, we consider the internal degrees of freedom of the exciton, namely, an s state and a p state of the relative motion. The electric field associated with the proton displacement will mix these two states. This is nothing but the field-induced polarization of excitons. The point is that the phase of s-p mixing depends on the sign of ρ_j. Therefore, in the disordered phase, the lowest exciton state has a random orientation of polarization at each unit cell. Then, the exciton must travel the crystal with a random flip-flop motion of its polarization orientation. It should be noted that, if we adopt the tight-binding picture, the transfer integral of the exciton depends on the relative phase between the state vectors of the nearest-neighbor cells. Therefore, the randomness of the orientation of polarization will affect the effective transfer integrals, and the exciton motion will be modulated randomly.

The Hamiltonian is given by

$$H = \sum_j (\varepsilon_s |s_j\rangle\langle s_j| + \varepsilon_p |p_j\rangle\langle p_j|)$$
$$- t \sum_{\langle i,j \rangle} (|s_j\rangle\langle s_i| + |s_i\rangle\langle s_j| + |p_j\rangle\langle p_i| + |p_i\rangle\langle p_j|)$$
$$+ \sum_j \Delta_j(|p_j\rangle\langle s_j| + |s_j\rangle\langle p_j|)$$
$$- c \sum_j q_j(|s_j\rangle\langle s_j| + |p_j\rangle\langle p_j|), \tag{2}$$

$$\Delta_j \equiv \Delta \rho_j. \tag{3}$$

Here $|s_j\rangle$ and $|p_j\rangle$ represent the s and p states of the exciton with the energy ε_s and ε_p at the jth unit cell. The transfer integral between nearest-neighbor unit cells is denoted by t. Δ represents the intensity of the hybridization of the exciton states caused by the local electric field. The last term in Eq. (2) represents the thermal effect of lattice vibrations, which has been introduced in the theory of momentarily trapped excitons.[9,10,13] It is assumed that the local potentials by lattice distortion act on the center-of-mass motion of the exciton with the coupling constant c. The transition dipole operator M is simply given by

$$M = \sum_j (|s_j\rangle\langle g| + |g\rangle\langle s_j|), \tag{4}$$

aside from constant factors, where $|g\rangle$ is the ground state of the crystal.

At temperature T, the amplitude of the lattice distortion q_j at the jth unit cell has the thermal distribution given by the probability

$$P(q_j) \propto \exp\left(-\frac{q_j^2}{2k_B T^*}\right).$$

Here T^* is the effective temperature, which incorporates the effect of zero-point vibration of phonons and is given by

$$k_B T^* = \frac{1}{2}\hbar\omega\coth\left(\frac{\hbar\omega}{2k_B T}\right), \tag{5}$$

where $\hbar\omega$ is the effective energy of phonons. It has been shown both analytically[9] and numerically[13] that this Gaussian distribution of the local potential gives rise to the exponential tail of the absorption edge. Mahr[21] pointed out that, by taking into account the zero-point vibration, σ in the formula (1) is written as

$$\sigma = \frac{2k_B T}{\hbar\omega}\tanh\left(\frac{\hbar\omega}{2k_B T}\right)\sigma_0, \tag{6}$$

where σ_0 is a constant that agrees with σ at high temperature. Usually, experimental data of the temperature dependence of the Urbach tail are fitted well by this equation. It is known that σ_0 is related with the dimensionless coupling constant g through the steepness index s as $\sigma_0 = s/g$,[9,13] where g is given by $g = c^2/2\nu t$ in which ν is the configuration number.

We do not go into details of the theoretical treatment of order-disorder transition in the proton system[22] here. In the present study, we fix the expectation value $\langle\rho_j\rangle$ proportional to the observed value of $P_s(T)$ as a function of temperature. The random variables $\rho_j(=\pm1)$ are generated numerically under the condition $\langle\rho_j\rangle = P_s(T)/P_s(0)$, where $P_s(0)$ is the saturated value. This procedure entirely neglects the clustering effect and probably overestimates the disordered nature near T_c. However, it will be sufficient for our purpose here.

Actual calculations of the absorption spectra have been done for a simple cubic lattice system with $21 \times 21 \times 21$ lattice points. The absorption spectra have been calculated as an average over 20 000 samplings of the two types of random variables $\{q_j\}$ and $\{\rho_j\}$. Since little is known about the parameter values of excitons in PbHPO$_4$, we have tentatively chosen $\varepsilon_p - \varepsilon_s = 0.1$ eV, $\Delta = 0.5$ eV with the bandwidth of the exciton ($=12t$) 1 eV. These values correspond to a strong hybridization between the s and p states. From the fitting of the experimental data below 180 K, we set $\hbar\omega = 11.3$ meV and $\sigma_0 = 0.79$.[20] The steepness index s was determined to be 1.10 by our separate calculation of the Urbach tail for the same lattice system. This value is a little smaller than the value determined by Schreiber and Toyozawa.[13]

In order to display the effect of disorder in the proton system, we show in Fig. 1 the absorption spectra calculated for two fictitious cases where (a) the proton system is fixed to be completely ordered and (b) completely disordered, irrespective of temperatures. The temperature effect is only included in thermal fluctuations of the lattice distortion q_j. In Fig. 1(a), ρ_j is fixed to be $+1$ for every unit cell. Because of the Stark shift, the absorption edge is lowered from the band edge ($= -0.5$ eV) of the system without protons. It can
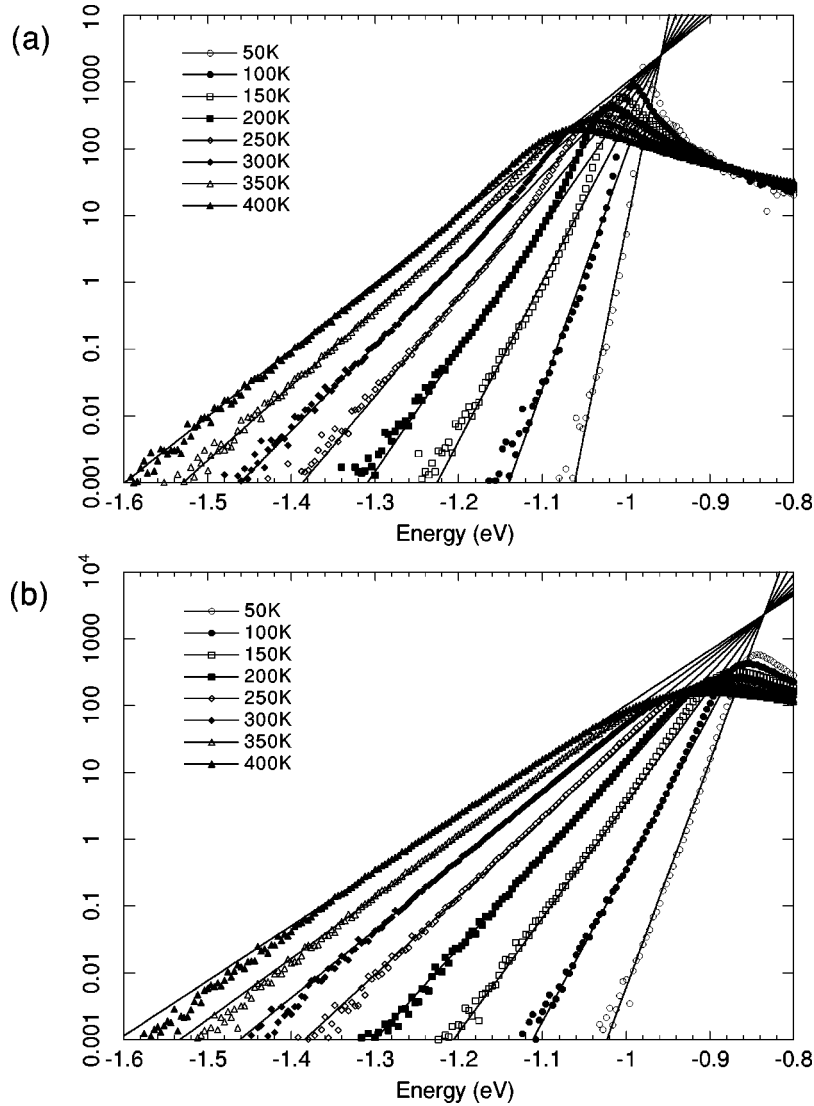
FIG. 1. Calculated absorption spectra in the low-energy tail for (a) completely ordered proton system, $\langle \rho_j \rangle = 1.0$ and (b) completely disordered proton system, $\langle \rho_j \rangle = 0.0$, irrespective of temperatures. The effect of temperature is included only in the lattice vibration through exciton-lattice interaction.

be easily shown that the absorption spectra in this case should be identical with those given by the model by Schreiber and Toyozawa[13] except for the Stark shift of E_0. In fact, our numerical results agree well with those given in Ref. 13. The fitting by the straight lines in logarithmic plot is good, but the low-energy part of the spectra deviates from the straight line and shows a concave shape at low temperatures. This tendency has already been pointed out in Ref. 13.

In the calculation of Fig. 1(b), ρ_j is assumed to take the values $+1$ and -1 randomly irrespective of temperatures with the expectation value $\langle \rho_j \rangle = 0$. As can be seen from the figure, the absorption spectra still exhibit exponential decays, but the steepness is obviously diminished as compared with the spectra at the same temperatures in Fig. 1(a). This means that the additional randomness in the proton system works cooperatively with the Gaussian randomness of the local potential by the lattice distortion. We have also calculated the absorption spectra in the case where only the interaction with protons exists. In this case, the absorption spectra exhibit a broadening, but the tail part cannot be fitted by exponential functions.

In order to analyze the experimental data of $PbHPO_4$, we have carried out numerical calculations by taking into account the temperature dependence of ρ_j as mentioned earlier, in addition to the Gaussian randomness of q_j. The absorption spectra were plotted in a logarithmic scale, and the steepness parameter σ was determined as a function of temperature. In Fig. 2, the obtained temperature dependence of σ is shown by the open diamonds connected by the solid line. We have also plotted the values of σ for the case in which the proton system is in completely ordered state by solid circles and in completely disordered state by solid squares. In the inset of Fig. 2, the experimentally obtained values of σ for $PbHPO_4$ (Ref. 20) are also shown. It can be seen from the figure that, if one chooses this set of parameter values, the theoretical result reproduces the characteristic features of the observed data fairly well. Thus, the anomalous increase of σ below T_c can be explained in this model as a result of decrease of randomness due to ordering of protons. Experimentally, it has been observed that the convergence energy E_0 shifts to the low-energy side as the tem-
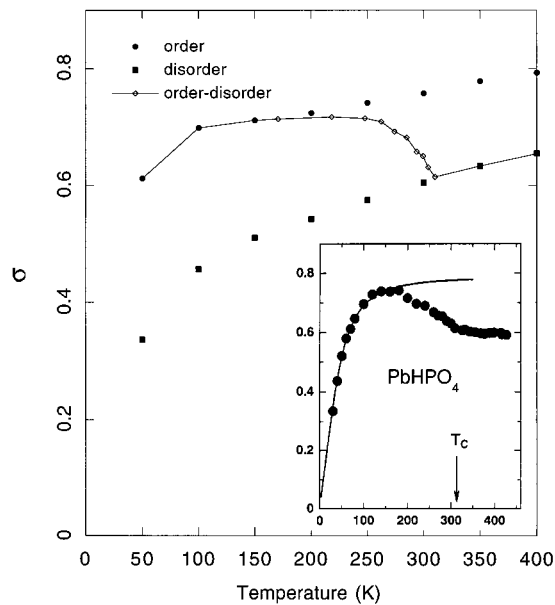
FIG. 2. The temperature dependence of the steepness parameter σ for the completely ordered proton system (solid circles) and the completely disordered proton system (solid squares) and the realistic system where $\langle \rho_j \rangle$ is assumed to vary in accordance with the temperature dependence of P_s (solid line). The inset shows the experimental data for PbHPO$_4$, which is reproduced from Ref. 20.

perature is lowered across T_c.[20] This is also consistent with our model as shown in Figs. 1(a) and 1(b).

Although the present model can explain the experimental tendency qualitatively, there still remain some problems. In order to describe the internal Stark effect of excitons, we have adopted a two-level model. This is a crude approximation of real systems because, for Wannier excitons, there is a quasicontinuous spectrum of excited states above $2p$ state. A more realistic treatment of the internal degrees of freedom of

excitons will affect the estimations of the parameter values. Secondly, the temperature dependence of σ in the case of exciton-lattice interaction alone does not exactly agree with the formula (6). At low temperatures, it is difficult to fit the log plot of calculated results definitely by straight lines because of the concave nature of the calculated spectra, which becomes salient in the low-temperature limit. Even at high temperatures, the calculated value of σ increases gradually with temperature instead of approaching a constant value, as shown in Fig. 2. This is not in agreement with the experimental data obtained in many materials. We have confirmed that this discrepancy is not resolved by increasing the system size. This indicates some refinement is needed in the theory of the Urbach tail by the model of momentarily trapped exciton.

In conclusion, we would like to point out the possibility to use the exciton absorption or emission spectra as a probe of ferroelectric phase transitions. Above T_c, the internal field-induced polarization of exciton is smeared out because of randomization. Below T_c, however, it is expected that a net polarization appears, implying that the inversion symmetry of the exciton is broken. This may be confirmed by some nonlinear optical techniques.[23] The coupling constant g is estimated as $g = 1.4$ for PbHPO$_4$. This value indicates that the self-trapped state is stabilized for the excitons in this material. Bausá et $al.$ observed a broad luminescence band around 450 nm under band-to-band excitation.[24] Recently, Ohno investigated this luminescence spectrum in detail and assigned it to the transition from the self-trapped exciton state.[25] This is in agreement with the above estimation. The investigation of the effect of interaction of self-trapped excitons with the surrounding proton system at around T_c is also an interesting subject.

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