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Mollwo-Ivey relation for the electron transition energy of the self-trapped excitons in alkali halides

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We investigate the dependence on the interionic distance R of the transition energy ΔE of the electron from $1s$ to $2p$ states of the self-trapped exciton (STE) for alkali halides. It is found that the ΔE-vs-R plots, except for NaBr and NaI, fall in two distinctive straight lines, showing that the STE in alkali halides can be divided into two groups. This grouping is found to be in accordance with the grouping in terms of the Stokes shift presented by Kan'no, Tanaka, and Hayashi. The relaxed configuration of excitons in alkali halides has been discussed on the basis of these results.

I. INTRODUCTION

Exciton self-trapping, caused by strong electron-lattice interaction, is a phenomenon observed in many solids with different crystal structures and bonding nature.[1,2] The configuration of the self-trapped excitons (STE's) depends strongly on materials,[2,3] and consequently the STE-related phenomena, such as transport of excitation energy, luminescence, and formation of lattice defects, show a wide variety of features from material to material.[2,4,5] However, the relation between the resulting configuration of the STE in a given crystal and its basic properties has not yet been clarified, and it still remains an interesting question.

The alkali halide is the material for which most extensive and systematic studies on the STE have been carried out both experimentally and theoretically. It has been shown that the STE consists of an X_2^- molecular ion (X denotes a halogen atom), on which a hole is localized, and a bound electron.[6,7] The luminescence bands emitted by STE recombination have been characterized by the orientation of the optical dipole moment with respect to the axis of the X_2^-: the σ luminescence, σ polarized and having a short lifetime of a few ns, and the π luminescence, π polarized and having a long lifetime ranging between μs and ms.[6,8] Magnetic circular dichroism[9] and magnetic-resonance studies[10-13] have clearly shown that the initial state of the π luminescence is triplet in nature, and hence it has been identified to be the lowest triplet state of the STE, while the σ luminescence has been ascribed to emission from the singlet state.[14]

Recently Kan'no, Tanaka, and Hayashi have classified the STE-luminescence bands in alkali halide crystals into three groups in terms of the Stokes shift.[15] One of them (described as type I) is characterized by a relatively small Stokes shift of about $0.3E_{\mathrm{ex}}$, where E_{ex} denotes the exciton energy. The π bands in NaBr and NaI and the σ bands in many alkali halides belong to this group. Another group (described as type III) is characterized by a large Stokes shift more than $0.6E_{\mathrm{ex}}$. The π bands in alkali halides with large S/D (where S is the space between two neighboring halogen ions and D is the radius of halogen atoms), such as KCl, RbCl, KBr, and RbBr, and the 2.27-eV band of RbI belong to this group. The rest (described as type II) are intermediate between type I and type III in terms of the Stokes shift. The π bands of alkali halides with small S/D, such as NaCl and KI, and the 3.07-eV band of RbI,[16-18] belong to this group.

Earlier it was suggested that the lowest triplet STE has D_{2h} point-group symmetry with the X_2^- oriented along a $\langle 110 \rangle$ direction. The model is called an on-center model. Later Song *et al.*[19-23] pointed out theoretically that the on-center configuration of the STE at the lowest triplet state is unstable, leading to spontaneous symmetry-breaking displacement of the X_2^- along its axial direction into an off-center configuration having C_{2v} point-group symmetry. Some existing experimental results can be explained more satisfactorily using the off-center model.[2] Kan'no, Tanaka, and Hayashi[15] and Kayanuma[24] have suggested the configurations of the three luminescent states in terms of the off-center model: type-I luminescence is emitted from the on-center configuration; type-II luminescence is emitted from a relaxed configuration with X_2^- slightly off centered and with symmetry-breaking distortion of the surrounding alkali skeleton; and type-III luminescence is emitted from a relaxed configuration with X_2^- off centered to the nearest halogen site forming a nearest F- and H-center pair. No experimental evidence that supports the model has been reported yet.

The STE is essentially a pair comprising a localized electron and a localized hole, the latter in the form of X_2^-. Since the electron is bound in a Coulomb potential arising from the presence of the hole, the nature of the potential reflects the configuration of the pair. Thus any information on the nature of the Coulomb potential is useful to determine the configuration of the STE's. The optical-absorption spectrum due to the electron transitions from the lowest triplet STE's in typical alkali halides has been measured first by Williams and Kabler.[25] They showed that the so-called Mollwo-Ivey relation holds between the energy ΔE due to the electron transition of the STE's and the interionic distance R in the lattice as for isolated F centers. Recently optical-absorption spectra for fluorides[26] and Li^+ halides[27] have been obtained. Furthermore, Tanimura and Itoh have carried out dichroic measurements and revealed optical-absorption bands corresponding to the electron transitions from the lowest 1s-type level to each symmetry-split 2p-type sublevel.[28] Thus it is now possible to examine the Mollwo-Ivey plot within higher accuracy.

II. MOLLWO-IVEY RELATION OF THE ELECTRON TRANSITION ENERGY OF THE STE

Among the optical-absorption bands due to the electron transitions of the STE's, the peak energy ΔE of that located at the lowest in energy was plotted as a function of R in Fig. 1. It is evident from Fig. 1 that the ΔE vs R relation falls in two straight lines L_1 and L_2: L_1 for LiF, NaF, KCl, RbCl, KBr, and RbBr and L_2 for LiCl, LiBr, NaCl, and KI. Among two emission bands in RbI, the optical-absorption band from the initial state of the type-III emission falls on the upper straight line, while that of the type-II emission falls on the lower straight line. The absorption bands for NaBr and NaI are shown to be located below 0.5 eV. Thus the STE's in these two materials appear to form another group different from those plotted in Fig. 1. According to the classification due to the Stokes shift, the luminescence bands in these crystals belong not to type II or type III but to type I.

Compared with the classification of the luminescence band, it is clear that the relaxed configuration emitting type-III luminescence and that emitting type-II luminescence show optical-absorption bands of different nature falling in two different Mollwo-Ivey relations. LiF, LiCl, and LiBr were not included in the classification according to the Stokes shift. The Stokes shift of the π band in LiF is $0.73E_{\text{ex}}$, while those in LiCl and LiBr are $0.52E_{\text{ex}}$ and $0.46E_{\text{ex}}$, respectively.[28] Therefore, the π band in LiF belongs to type III, while those in LiCl and LiBr belong to type II. Thus the two Mollwo-Ivey relations shown in Fig. 1 substantiate the classification of the luminescent states according to the Stokes shift and suggest strongly that the STE's in alkali halides except NaBr and NaI can take two structures, either type II or III (only RbI can take two structures). The difference between the properties of the two types of STE's may be substantiated also by the spectroscopic features of the optical-absorption band: type-III STE exhibits well-resolved three-peak structures, while only a broad band is observed for type-II STE.

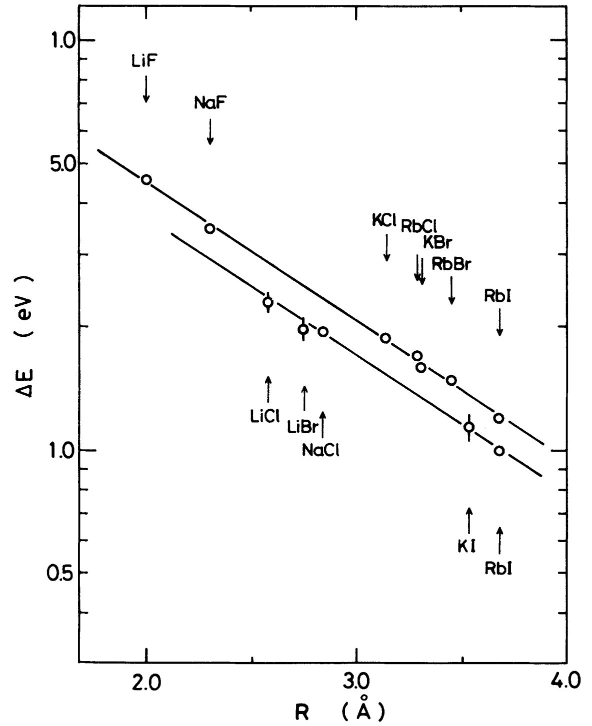

FIG. 1. Relation between the peak energy ΔE of the electron transition band of the STE and the interionic distance R in alkali halides. The energy of the lowest transition was collected so far as it is determined experimentally.

The physical basis of the Mollwo-Ivey relation has been discussed by Wood.[29] Using the point-ion model, he showed that the energy of each state of an electron localized by a potential well of ionic crystals can be described by a series in inverse powers of R. Assuming that the potential-energy term primarily proportional to R^{-1} and the kinetic-energy term proportional to R^{-2} dominate other higher-order terms, the energy of the state i is expressed as

$$E_i=\frac{c_i}{R}+\frac{c_i'}{R^2}\,, \tag{1}$$

where c_i and c_i' are constants. Thus the transition energy ΔE from state to i to j is given similar to Eq. (1), of which coefficient we denote for the R^{-1} term by $A=c_j-c_i$ and for R^{-2} term by $B=c_j'-c_i'$. Then the value at $1/R=0$ of the straight line pertaining the plots for $\Delta E\,R$ and $1/R$ gives the coefficient A, and its slope gives B. In Fig. 2, such a plot is made for the STE's and F centers. The $\Delta E\,R$ vs $1/R$ plots for the two straight lines in Fig. 1 have the same slope, but have the different intersects of negative values, while the plots for the F centers (shown by dashed lines) have smaller slope and a positive intersect.

According to Wood, the slope B of the ΔER vs $1/R$ curve indicates the difference in the kinetic energy for the lowest and excited states, and hence depends on the size of the potential well; the smaller the size, the larger B is. Thus the results suggest that the sizes of the potential well for the STE's of type II and III are nearly the same but smaller than that of the F centers. Furthermore, if both the ground and excited states are within the potential well, $A=0$, giving $\Delta=R^{-2}$, as pointed out by Fröhlich.[30] Thus the positive value for the F center has been ascribed to further delocalization of the excited state than the ground state. The negative value for the STE may arise from its complex structure, for which the application of the point-ion model may not be appropriate. Although any conclusion on the types of potential well from the Mollwo-Ivey relation cannot be derived, it is clear that the main part of the potential well for the electron is of simple structure; similar to that for the F center but with perturbation due to the presence of the X_2^-

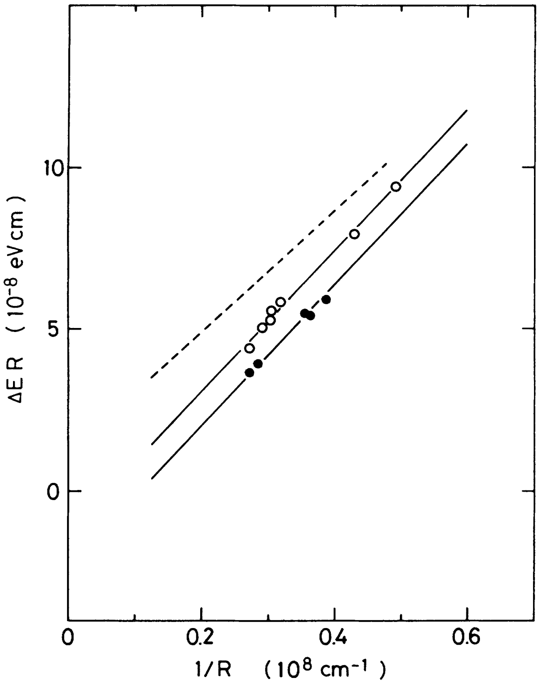

FIG. 2. Plots of the product of the energy ΔE of the electron transition of the STE and the interionic distance R with respect to R for type-II (solid circles) and type-III (open circles) STE's and F centers (dashed line).

molecular ion.

Theoretical attempts to obtain the minima of the adiabatic potential surfaces for the lowest STE's have been made. Song *et al.* used the pseudopotential and obtained a minimum for axial displacements of the X_2^- molecular ion to the nearest-neighbor position for alkali halides with large S/D, typically for KCl (Refs. 19–23), while Shluger *et al.* obtained a minimum at a much smaller displacement for KCl.[31] Thus it appears that the theoretical calculation has not yielded any definite atomic structure for the STE's. Another difficulty of the theory is that it usually gives at most two minima; thus all three configurations of STE's cannot be explained, unless the presence of a minimum at the on-center configuration is assumed, as by Kan'no, Tanaka, and Hayashi[15] and Kayanuma.[24]

The result that the optical transition energy of the STE's of type II and III are scaled by R indicates that the electron for each type of the STE is trapped in a well-defined potential, of which the magnitude is scaled by R. The scaling factor for the potential energy formed by the off-centered X_2^--molecular ion with displacement different from material to material appears to be more complicated. Thus the assignment that the type-II STE's are of off-centered configuration with different displacements may need further consideration.

One way of interpreting the result that the ΔE is scaled by R and that STE in alkali halides can take three types of configurations is to consider the configurations of the X_2^- molecular ion with respect to the trapped electron other than off-center displacement; for instance, a pair of an F center and a reoriented X_2^- molecular ion (the H center). We can expect that ΔE can be scaled by R for the F-H pairs at the nearest neighbor with the X_2^- molecular ion oriented both by 90° and 60° with respect to the direction connecting the F-H centers. Further details of the reoriented F-H pair model for the STE's are described elsewhere.

In conclusion, we have shown that the electron of the STE's in alkali halides is trapped in a potential well scaled by R. Furthermore, the same classification of the STE's as that made in terms of the Stokes shift can be made in terms of the transition energy of the electron. We note further that the Stokes shift for the STE's is scaled better by S/D. Since the luminescence involves both the electron and hole, it appears that the configuration of the hole of a STE is sensitive to S/D, while the electron is localized in a well-defined potential well.

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