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Relation between the Stokes shift of excitons in alkali halides and the energy of diffusion of V_K centers*

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The application of polaron theory to the Stokes shift observed in the luminescence of alkali halides predicts an activation energy of diffusion of V_K centers that is in excellent agreement with the experimental results. This is to be largely expected and implies that in most alkali halides there is a very small overlap of the polarizations associated with the electron and with the hole.

In color-center physics Fowler and Dexter[1] emphasized that the state reached as a result of optical absorption is not necessarily the same as the initial state for optical emission plus a relatively large number of phonons; in general the lattice relaxation changes the potential experienced by the electron so that a completely new problem must be solved. The same point of view is expected to apply to exciton absorption,[2] particularly when the electron phonon coupling is strong, so that the resulting Stokes shift is important. In this case the state reached in optical absorption may be expected to be a free exciton, while the initial state for optical emission is a self-trapped exciton (STE). A difficulty (common to color centers) of this assumption is that a free-exciton state would not be an eigenstate of the crystal in which the lattice polarization is consistent with the electronic distribution.

In direct-gap materials like the alkali halides it is difficult to experimentally distinguish, on the basis of optical-absorption data, between an excited state of the STE and a free exciton: Both will give rise to an absorption that resembles a broadened δ function.

In a given crystal, if the polarization associated with the electron does not overlap that associated with the hole, we may expect that the relaxed exciton will have a binding energy that is equal to the energy of a free exciton plus the energies associated with the polarization of both the electron and the hole. The total polarization energy is half the observed Stokes shift between absorption and emission. The interpretation of cyclotron-resonance results in the light of polaron theory permits the determination of the polarization energy associated with the electron. This result and the Stokes shift observed between absorption and emission of intrinsic excitons permit the calculation of the self-energy of the hole. As will be seen in this paper, this self-energy is related to the activation energy of diffusion. The calculated energy of diffusion is in excellent agreement with experimental results obtained in a variety of alkali halides.

The STE in alkali halides can be described as a V_K center on which an electron is trapped.[3] In this model the orbit of the electron around the self-trapped hole has the σ_g (or Γ_1^+) symmetry of the group appropriate to the self-trapped hole, D_{2h} in the case of crystals of the NaCl structure. Although such a description is not used to calculate[4] the energy levels of the STE, it is an instructive model for its qualitative description. It is also helpful in determining some relations between energy levels of the relaxed and free exciton states.

Spin-resonance measurements[5–7] of STE in a triplet state indicate that the overlap of the electron and hole charge distribution is small. Although there are no corresponding measurements for the singlet STE state, we shall assume that the same conclusion can be applied to this case. A justification for this assumption will be found in the agreement between the calculated and the experimental results.

Pekar[8] has shown that in the adiabatic approximation the energy necessary to optically release a strongly coupled polaron from its polarization well is equal to three times the energy Δ that would be measured if the same result were obtained by thermal excitation. Lemmens and Devreese[9] have reached the same conclusion without the limitations imposed by the adiabatic approximation, provided that the electron-phonon interaction does not depend on the mass of the carrier.

Labeling E_0 the energy of the ground state of the perfect crystal, E_1 the energy of the free-exciton state reached by optical absorption, E_2 the initial state from which optical emission takes place, and E_3 the state reached in the emission process, the Stokes shift is

$$(E_1 - E_0) - (E_2 - E_3) = h(\nu_{\text{abs}} - \nu_{\text{em}}). \qquad (1)$$

The quantity $E_1 - E_2$ is, however, the energy one should provide optically in order to excite a STE outside its polarization well; $E_3 - E_0$ is the energy we should provide optically in order to localize the recombined exciton (i.e., to create the polarization characteristic of the STE). According to Pekar's theorem,[8,9] $(E_1 - E_2) = 3\Delta_{\text{ex}}$. We shall assume without further justification that $E_3 - E_0 = E_1 - E_2$, so that we would expect $6\Delta_{\text{ex}} = h(\nu_{\text{abs}} - \nu_{\text{em}})$.

Fowler *et al.*[4] stressed the fact that the molecular-orbital basis function that describes a singlet STE is symmetric in the interchange of the spatial coordinates of the electron and the hole and antisymmetric in their spin coordinates. The reverse is the case for the triplet STE. As a consequence, the polarization energies associated with the singlet and the triplet STE states are completely different. Support for this conclusion is the observation that the energy difference between the singlet and triplet STE states calculated on the basis of EPR data[4] (i.e., when the polarization around the STE corresponds to the triplet) is ~300 times larger than the difference of the energies of the recombination of the singlet and triplet states.

The Stokes shift to be calculated from polaron theory measures the polarization associated with lattice relaxation without a corresponding change of the symmetry of the spatial charge distribution. It is therefore appropriate to consider the Stokes shift associated with singlet excitons because a free singlet exciton is created in optical absorption. Unfortunately, in many alkali halides the σ-polarized luminescence assigned to the recombination of a singlet STE is absent[3,10,11]; we must therefore estimate the position of the unobserved singlet level on the basis of the observed luminescence assigned to the triplet.

As seen above the difference of energy between the luminescence assigned to the singlet and triplet STE recombination is primarily due to the different lattice polarizations. As in the case of the V_K centers,[12] these energy levels are expected to depend primarily on the two negative ions that are pulled towards each other when either a V_K or a STE is formed. Support for this conclusion is obtained on the one hand from the measured triplet STE hyperfine interaction, which is in excellent agreement with what would be expected from V_K centers,[5,6] and on the other from the near-independence of the spin Hamiltonian of the V_K center of the properties of the host lattice, as opposed to its strong dependence on the properties of the two nearest-neighbor halogen ions.[12] A final supporting argument is given by the data in Table I, where it is seen that the energy difference between singlet and triplet STE $(E_s - E_t)$ is independent of the halogen ions in the few cases when all the fluorescence emission spectra have been observed (KBr, RbBr, KI, RbI). The energy of the largest photon arising from recombination of the triplet STE must be taken in the case when more than one π-polarized emission is observed.

We shall estimate the recombination energy $(E_s)_A$ of an unobserved singlet STE in a crystal A in which the recombination energy of a triplet STE

TABLE I. Relation between the measured and calculated activation energies of diffusion (Δ) of the V_K center in alkali halides. For the remaining symbols see text.

Crystal	E_s (eV)	E_t (eV)	E_{abs} (eV)	$\frac{1}{6}(E_{\text{abs}} - E_s)$	$\frac{1}{3}\alpha_e\hbar\omega$ (eV)	Δ_{calc} (eV)	Δ_{expt} (eV)
KBr	4.42[a]	2.27[a]	6.77[a]	0.39	0.021[b]	0.41	0.45[c]
RbBr	4.20[a]	2.10[a]	6.60[a]	0.40	(0.020)[b]	0.42	<0.53[c]
CsBr	(5.69)	3.49[d]	6.80[e]	(0.18)	(0.018)[b]	(0.20)	0.17*[d]
NaBr	(6.70)	4.60[f]	6.68[a]	(0)	0.026	(0.026)	<0.36[c]
KI	4.15[f]	3.34[a]	5.80[a]	0.275	0.015[b]	0.29	0.27*[g] 0.29[c]
RbI	3.95[f]	3.15[f] 2.30[a]	5.70[a]	0.29	0.014[b]	0.30	0.28*[h] 0.31[c]
CsI	(5.08)	3.65[i] 4.27[i]	5.81[i]	(0.12)	0.014[b]	(0.13)	0.16[i]
NaI	(5.0)	4.20[f,a]	5.56[a]	(0.09)	(0.02)[b]	(0.11)	0.18*[h] 0.16[c]
NaCl	5.6[a]	3.49[f]	7.96[a]	0.39	(0.033)[b]	0.42	0.42[c]
KCl	(4.43)	2.32[a]	7.76[a]	(0.55)	0.03	(0.58)	0.54*[j]
RbCl	(4.49)	2.27[f,a]	7.51[a]	(0.50)	0.009	(0.51)	0.59[c]

[a] Reference 11.
[b] Reference 17.
[c] Reference 8.
[d] Reference 16.
[e] J. H. Shulman and W. D. Compton, *Color Centers in Solids* (Pergamon, New York, 1963).
[f] Reference 10.
[g] Reference 13.
[h] Reference 14.
[i] H. Lamatsch, J. Rossel, and E. Saurer, Phys. Status Solidi B <u>48</u>, 311 (1971).
[j] Reference 15.

$(E_t)_A$ has been measured by writing

$$(E_s)_A = (E_t)_A + (E_s - E_t)_B \ , \tag{2}$$

where $(E_s - E_t)_B$ is the difference of energy between the photons emitted in the recombination of a singlet and triplet exciton in a crystal B where both have been observed. The halogen in crystal A is the same as in crystal B.

The numbers in parentheses in the column labeled E_s in Table I have been obtained by the use of Eq. (2) applied to the largest triplet STE recombination peak.

The activation energy for diffusion V_K centers has not been measured directly in most alkali halides. In the case of KI,[13] RbI,[14] KCl,[15] NaI,[14] and CsBr,[16] this activation energy has been obtained from the temperature dependence of the time necessary to randomize an initially oriented population of V_K centers. The corresponding values are accompanied by an asterisk in the column labeled Δ of Table I. The remaining values of Δ are obtained by observing the temperature at which the V_K centers begin to reorient, assuming that the preexponential factor in the diffusion constant is the same for all alkali halides.[12] A simple proportionality between the measured temperature of reorientation and the activation energy for KCl has been assumed.[12]

The column labeled $\frac{1}{3}\ \alpha\hbar\omega$ gives one-third of the self-energy of the electron in the different crystals[17] calculated on the basis of Fröhlich's Hamiltonian to first order in the polaron coupling constant α. The band (undressed) electron effective mass is unknown in the case of crystals for which the electron self-energy is in parentheses. In all alkali-halide crystals where cyclotron resonance was carried out the electron band mass is near $0.4 m_0$. The same value has been assumed in the case of the unknown masses; this determines $\alpha\hbar\omega$.

The calculated energy of diffusion of the V_K centers is equal to one-sixth of the Stokes shift of the singlet exciton plus $\frac{1}{3}\ \alpha\hbar\omega$. The results shown in the last two columns of Table I indicate an embarrassingly good agreement between experiment and this simple-minded calculation. Notable exceptions are NaI, possibly NaBr, and CsI. The first two also have an anomalously low binding energy of the triplet STE.[18]

In order to explore qualitatively the possible reasons for this apparent agreement it appears fruitful to study the relation between the molecular orbital description of the STE and the corresponding Wannier exciton model.[19] The symmetry of both representations must be the same, although one may be much more precise than the other for the purpose of calculation of the actual energy levels.

Both the singlet and triplet STE are described by a wave function[3,4] whose axis points along $\langle 110\rangle$, in the case of crystals with the NaCl structure, and along $\langle 100\rangle$ in cases of crystals with the CsCl structure. Corresponding to a given axis there are four different spin states. In a crystal with the NaCl structure there are six equivalent $\langle 110\rangle$ directions and therefore 24 exciton states (six singlets and 18 triplets). The corresponding number in the case of the CsCl structure is 12.

The unrelaxed exciton in alkali halides has a hole in a triply degenerate valence band (Γ_4^-) (in the absence of spin), and an electron in a nondegenerate band Γ_1^+. The wave function describing the relative motion has Γ_i symmetry. After inclusion of the four spin states corresponding to each orbital state the total number of levels is equal to 12 times the multiplicity of the wave function describing the relative motion of the electron and the hole. Upon lattice relaxation this exciton must give rise to all the equivalent singlet and triplet states of the STE.

From the above considerations it is clear that in the case of the NaCl structure Γ_i must be doubly degenerate. The only possible even representations[20] of O_h are Γ_3^+ (in the case of NaCl structure) and Γ_1^+ (in the case of the CsCl structure), i.e., respectively, d- and s-like. Upon lattice relaxation the symmetry of the STE is either D_{2h} (NaCl structure) or D_{4h} (CsCl structure) and both Γ_3^+ and Γ_1^+ of O_h reduce, respectively, to Γ_1^+ of D_{2h} and Γ_1^+ of D_{4h}, in accordance with the model initially proposed by Kabler.[3]

The conclusions that the STE states arise from a d-like unrelaxed state (i.e., $n \geq 3$ for a hydrogenic model) in the case of crystals with the NaCl structure does not imply that the lowest exciton peaks observed in optical absorption must also be assigned to d-like excitons.

The conclusion that the STE states might be traced to an unrelaxed exciton in a state with $n > 1$ is not new. Wood[21] made a model calculation of the lattice relaxation of an exciton. A significant result of that study is that the curve that describes the variation of $n > 1$ free-exciton states as a function of ionic motion extrapolates to near the minimum energy expected for a STE; the curve that describes the variation of the $n = 1$ free-exciton state extrapolates instead to a much higher energy. Spin was neglected in Wood's calculation. We can expect, therefore, that the wave function that describes the electron density around the self-trapped hole is doughnut-like with a minimum charge density at the position of the hole. We believe that this feature is the primary reason for the excellent agreement displayed for the different estimates of the depth of the polarization well given in Table I for most crystals with the NaCl structure.

The poor agreement observed in Table I in the case of NaI would then indicate a less concentrated

V_K center and a much larger overlap of the electron and hole polarization. Another possible indication of an anomalous behavior might be discerned in the deviation of the g tensor and hyperfine interaction (A_z) of V_K centers in NaI from those of other iodides.[12] Similar explanations appear appropriate for NaBr.

In the case of both CsI and CsBr we might expect that the activation energy of diffusion of V_K centers will be larger than what is calculated from the Stokes shifts because, on account of the s-like charge distribution of the electron, the polarizations created by the electron and the hole will overlap appreciably. Contrary to our expectations, the energy of diffusion of V_K centers calculated from the Stokes shift of the exciton in CsBr does not disagree with the measured result. We must therefore conclude that the overlap of the polarizations of the electron and the hole remains small; this is only compatible with an extended electron wave function and a small binding energy of the singlet STE. This might be a reason why σ-polarized emission of STE has not been observed in the Cs salts.

In conclusion, we have shown that the polarization energy that can be calculated from the Stokes shift of the exciton compares favorably with the activation energy of diffusion of V_K centers. This agreement implies that the orbit of the electron that is bound to the hole corresponds to a doughnut-like charge density in the case of crystals with the NaCl structure and a more extended orbit in the case of the salts with the CsCl structure.

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[1] W. Beall Fowler and D. L. Dexter, Phys. Rev. 128, 2154 (1962).

[2] F. Seitz, *Modern Theory of Solids* (McGraw-Hill, New York, 1940), Sec. 108.

[3] M. N. Kabler, in ***Point Defects in Solids***, edited by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York, 1972), p. 327.

[4] W. Beall Fowler, M. J. Marrone, and M. N. Kabler, Phys. Rev. B 8, 5903 (1973).

[5] A. Wasiela, G. Ascarelli, and Y. Merle d'Aubigné, Phys. Rev. Lett. 31, 993 (1973).

[6] M. J. Marrone, F. W. Patten, and M. N. Kabler, Phys. Rev. Lett. 31, 467 (1973).

[7] M. J. Marrone and F. W. Patten, Bull. APS Series II 19, 282 (1974).

[8] S. I. Pekar, *Untersuchungen uber die Elektronentheorie der Kristalle* (Academie Verlag, Berlin, 1954).

[9] L. F. Lemmens and J. T. Devreese, Solid State Commun. 12, 1067 (1973).

[10] R. S. Knox and K. J. Teegarden, in *Physics of Color Centers*, edited by W. Beall Fowler (Academic, New York, 1968), p. 1.

[11] M. N. Kabler and D. A. Patterson, Phys. Rev. Lett. 19, 652 (1967).

[12] D. Schoemaker, Phys. Rev. B 7, 786 (1973).

[13] F. J. Keller and R. B. Murray, Phys. Rev. 150, 670 (1966).

[14] H. B. Dietrich and R. B. Murray, J. Luminescence 5, 155 (1972).

[15] F. J. Keller, R. B. Murray, M. M. Abraham, and R. A. Weeks, Phys. Rev. 154, 812 (1967).

[16] E. Vasil'chenko, N. Lushik, and Ch. Lushik, J. Luminescence 5, 117 (1972).

[17] E. Kartheurser, in *Polarons in Ionic Crystals and Polar Semiconductors*, edited by J. T. Devreese (North-Holland, Amsterdam, 1972).

[18] R. T. Williams and M. N. Kabler, Phys. Rev. B 9, 1897 (1974).

[19] R. S. Knox, *Theory of Excitons* (Academic, New York, 1963).

[20] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, Mass., 1963).

[21] R. F. Wood, Phys. Rev. 151, 623 (1966).