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A theory of hopping diffusion of the self-trapped exciton in alkali halide crystals

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Abstract. We propose a model for the hopping diffusion of the self-trapped exciton (STE) in alkali halide crystals. The STE was earlier shown to be equivalent to a primitive pair of F–H centres. The diffusion consists of a sequence of F–H centre permutation and rotation of the H centre in the lattice. It is shown that in NaCl and NaBr (and also probably in the iodides), the energy barrier for the permutation of the close F–H centres is small (about 0.2 eV), while in KCl and KBr (and also other alkali halides such as RbCl, RbBr and the fluorides), the same barrier is much higher (about 1 eV or larger). The rotation of the H centre in the STE requires very little energy. This prediction is in general agreement with the experimental observations so far available. The determining factor is the amount of the relaxation energy involved in the off-centre motion of the STE along the (110) axis. It is therefore also dependent on the magnitude of the off-centre shift of the STE. Correlation with other parameters of the STE is also discussed.

1. Introduction

The transfer of energy by exciton diffusion in alkali halide crystals was discovered in 1951 from the ionisation of F centres by excitons [1]. A similar process is shown to play an important role in photophysical phenomena in alkali halide crystals, such as sensitised luminescence [2–4], the scintillation process [5, 6], colour centre formation [4, 7, 8] and sputtering [9], and has been the subject of considerable interest for decades. It is well known that in most cases the excitons in alkali halide crystals become self-trapped soon after they are created. Compared with the hopping diffusion of the self-trapped hole (the V_k centre), for which direct observation is possible through optical or magnetic spectroscopy, no direct clear experimental evidence of the self-trapped exciton (STE) hopping diffusion has yet been presented. Vasil'chenko et al [10] for NaCl:Ag and Tanimura and Itoh [11] for NaCl:Li have given evidence of the hopping motion of the STE by observing that the quenching of the intrinsic luminescence and the growth of the impurity luminescence were due to the hopping diffusion of the STE. These workers observed that the thermal activation energy of the STE is smaller than that of the self-trapped hole (the V_k centre). Similar phenomena have also been observed in NaBr:Tl [12], KI:Tl [13] and others [14]. However, no such sensitisation was observed in KCl and RbCl doped with Tl and In up to a concentration of 10^{-3} mol [15].

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The STE in its lowest bound state has generally been accepted to be equivalent to a V_k centre that has captured an excited electron in a more or less diffuse s-like orbital, occupying the D_{2h} symmetry in NaCl structure alkali halides. Recent work [17, 18], however, has predicted that the STE in alkali halides is not stable in the D_{2h} symmetry and spontaneously undergoes an off-centre axial translation along the (110) axis and has C_{2v} symmetry. As a consequence, the STE should be regarded as a primitive F–H pair. After a period of some scepticism, recent analysis [19, 20] of earlier data and new experimental work on the π emission band shape [21], have brought more arguments in favour of the off-centre model of the STE in alkali halides. The STE in alkali halides is therefore very similar to that in the alkaline earth fluorides, where the EPR measurement clearly established this point at a very early stage [22].

In the light of this recent development, we face some interesting questions regarding the precise mechanism of the STE–(F–H) pair hopping motion. We should also explain why in some alkali halide crystals similar hopping diffusion of the STE is apparently not taking place. Earlier, Song [23] derived the expression and evaluated the activation energy of the STE ($V_k + e^-$) based on the small polaron theory. It was then shown that the activation energy for the STE would be smaller than that of the V_k centre by a factor of between two and three. This was attributed to the difference in the relaxation and polarisation of the surrounding lattice between the two defect systems occupying the same D_{2h} symmetry. With the new structure of the off-centre STE, in which the excited electron and self-trapped hole resemble a pair of perturbed F centres and H centres, one must find a more realistic model for the hopping diffusion. A tentative model has been suggested by Williams and Song [24] combining axial translation and rotation of the H centre.

In this paper we present a model for hopping motion of the off-centre STE. Using a method that we developed in the studies of the STE [17, 18], we show that there are two groups of STE in alkali halides. In the first group, which includes NaCl, NaBr and we believe also the iodides, the F centre electron and the nearby H centre can permutate sites with only a modest amount of energy. The H centre can also rotate with virtually no expense of energy. The hopping can thereby proceed by a succession of such steps. The evaluated activation energy is in the region of 0.2 eV which is in close agreement with the experimental data. In the second group, which includes KCl and KBr, and we believe RbCl, RbBr and the fluorides, the energy for the F–H pair permutation is much larger than in the first group. This is found to be about 1 eV for KCl and KBr. In section 2, we first describe briefly the method used in the calculation, followed by our model for the off-centre STE hopping motion. Section 3 represents the calculated energy barrier for the combined permutation and rotation. We also relate the two distinct hopping behaviours to other prominent characteristics of the STE in alkali halides from the point of view of the off-centre nature of the STE.

2. The model for the hopping motion of the off-centre STE

The theoretical approach used in this work has been described in earlier papers [17, 18, 19]. It treats the excited electron within the approximation of the extended-ion method, while the hole that is localised on two (or three) halogen atoms is represented by a CNDO code with a small cluster. The lattice and the polarisation energies are treated respectively by the conventional pair potential and the Mott–Littleton method in the lowest order. The entire package is interfaced in a self-consistent way, the structure of
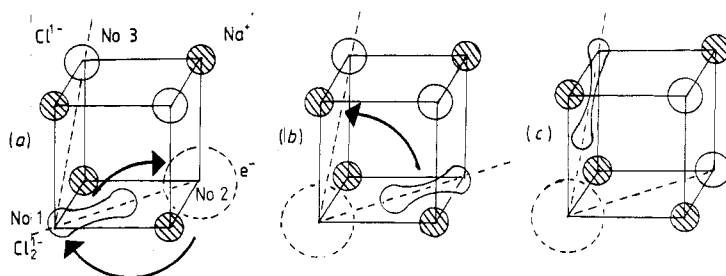
Figure 1. An illustration of the two steps proposed for the hopping motion of the off-centre STE in alkali halide crystals (the dumbell form represents the V_k core, in this case the Cl_2^- molecular ion). (*a*) The original configuration. (*b*) After a permutation of the F–H pair. (*c*) After a rotation of the H centre by 60°.

the system at equilibrium is determined by minimising the total energy. In determining the potential barrier during the permutation of the F and H centres, a designated halogen ion constituting the H centre is moved by a discrete amount and the other degrees of freedom are optimised. This method has proved to give results that are in good agreement with the experimental data of luminescence as reported in our recent works on luminescence [19]. We take the energy difference between the total energy at the off-centre equilibrium configuration and the highest energy on the pathway of the permutation and rotation of the STE as the thermal activation energy.

Our model for the hopping diffusion is illustrated in figure 1. As has been shown in a recent paper [18], the potential energy surface is fairly flat near the equilibrium with regard to the Q_2-mode of vibration (the translational motion of the H centre). For the first group of alkali halides, which includes NaCl and NaBr in particular, it does not require a significant amount of energy for the system to have the H centre pushed back to the mid-point of the original pair of anion sites [18]. When the H centre is pushed beyond the mid-point, the electron (the F centre) is found to jump to the opposite site along the [110] axis quite easily. This excited electron jump is studied most conveniently by our use of the floating Gaussian basis. Indeed, we have positioned two pairs of Gaussians on the two anion sites No 2 and No 1 (respectively the old and the new F centre sites). After the electron jumps to its new site, we have effectively a permutation of the F and H centres. Figure 1(*a*) and (*b*) describe respectively the defect configuration before and after the permutation. We find that for NaCl and NaBr, this permutation requires about 0.2 eV. By contrast, for KCl and KBr the same process requires more than 1 eV. The distinct behaviour of the two groups in this regard is probably not a coincidence. As we will discuss in more detail in the next section, they belong to two distinct groups in terms of the Stokes shift and the lifetime of the triplet emission bands [19]. They also belong to different groups in the Rabin–Klick diagram which shows the relative ease of creating F centres under ionising radiations at very low temperatures [18].

The second step consists of the rotation of the H centre to an adjacent ⟨110⟩ axis. During thermal fluctuations, anion No 1 could move away from the original partner No 2 and move closer to anion No 3. This will induce the hole to jump to the new axis 1–3 from the original 1–2 axis; see figure 1(*c*). We found this hole jump taking place with a minimal amount of energy for both groups of alkali halides. The main process that distinguishes the two groups therefore resides in the permutation of the F and H centres.

Table 1. The energy variation on the pathway to the F–H pair permutation, required for the hopping diffusion of the off-centre STE. Q_2 is the distance of the H centre along the [110] axis relative to the mid-point between No 1 and No 2 sites of figure 1(a). E is relative to the equilibrium configuration. In order to make the meaning of Q_2 more useful, the value of Q_2 at theoretical nearest neighbour (NN) separation of the F–H pair is also given beside the chemical symbol of the alkali halide.

Equilibrium point		Mid-point	Barrier top	ΔE_{calc}	ΔE_{exp}
NaCl ($Q_2^{NN} = 3.8$)					
Q_2 (au)	1.7	0.0	−0.3		
E (eV)	0.0	0.0	0.13	0.13	0.13† 0.21‡
NaBr ($Q_2^{NN} = 4.0$)					
Q_2 (au)	0.6	0.0	−0.9		
E (eV)	0.0	0.10	0.26	0.26	NA
KCl ($Q_2^{NN} = 4.2$)					
Q_2 (au)	8.2	0.0	−0.54		
E (eV)	0.0	0.40	1.18	1.18	NA
KBr ($Q_2^{NN} = 4.4$)					
Q_2 (au)	7.5	0.0	−0.74		
E (eV)	0.0	0.7	1.67	1.67	NA

† [11].
‡ [10].

To achieve a diffusion of the off-centre STE (a primitive F–H pair), we require a succession of the two motions in combination. This can be seen from the following observations. With only the permutation between the two centres, there is only an oscillation back and forth between the two configurations without a net diffusion. On the other hand, with the rotation of the H centre alone, the primitive F–H pair is rotating in space around the F centre site. The combination of the two steps will result in a net diffusion in the lattice away from the original site and orientation. It is to be noted that an axial diffusion of the centre alone will result in a more distant separation of the F–H pair, which also takes place in competition with the hopping diffusion of the STE we are interested in here.

3. Results and discussion

According to the off-centre theory of the STE [25], the trend of the excited electron to seek an anion vacancy and become an F centre is so pronounced that even when the V_k core is held at the mid-point along the [110] axis, the electron in its lowest bound state jumps to one side of the system. This trend was found to be universal for all alkali halides. In the present study, starting from the equilibrium off-centre STE configuration, the H centre (or the V_k core) is pushed backward toward the F centre beyond the mid-point along the [110] axis. Soon after passing the mid-point, the electron finds a more accommodating vacancy at the other end of the H centre and makes a jump, thereby realising a permutation of the F and H centres. The energy variation along this pathway is presented in table 1 for NaCl, NaBr, KCl and KBr. The system total energy obtained by calculation is given as a function of the position of the H centre (the centre of mass

of the two ions.) The distance of the H centre (in atomic units) as measured from the mid-point of the two ion sites No 1 and No 2 of figure 1(a), designated Q_2, is used to show the position of the H centre. Three points along the [110] axis are chosen. They are: the starting equilibrium configuration ($Q_2 > 0$); the mid-point ($Q_2 = 0$); and the barrier top on the pathway to F–H permutation (just before the electron jumps to the new F centre site: $Q_2 < 0$). In order to help visualise the position of the H centre inside the lattice along the [110] axis, table 1 also gives the value of Q_2 corresponding to the F–H pair in its ideal nearest neighbour configuration.

After the electron jumps to the new site, site No 1 of figure 1(a), the system energy drops by about 0.2 eV. The system can settle to another equilibrium configuration at this point. We have initiated the rotation at this point instead. By allowing the ion that is originally from site No 1 to approach the ion on site No 3, we can easily induce the hole to jump. The H centre rotates from the 1–2 axis to the 1–3 axis. The energy required to achieve this transformation is negligible for KCl and KBr, while it takes about 0.2 eV for NaCl and NaBr. After this rotation, the system can either settle into a new equilibrium off-centre configuration or continue further steps of hopping. We emphasise here that a separate permutation or reorientation alone will not lead to a net diffusion of the off-centre STE.

From this work, we conclude that the net activation energy for hopping diffusion is principally from the F–H permutation. As we stated above, the activation energy for the hopping is defined as the energy difference between the highest point on the pathway of permutation–rotation and the off-centre equilibrium configuration. This is compared with the experimental data available in table 1. The present work shows that in NaCl and NaBr, the activation energy of hopping is about 0.2 eV, and it is around 1 eV or more for KCl and KBr. The only available data are for NaCl: Ag [10] and NaCl: Li [11]. Our theoretical value of 0.2 eV is in qualitative agreement for both of them, as is seen in table 1. For others, no activation energies have been reported, except that impurity sensitisation has been observed in KI: Tl [13], NaBr: Tl [12]. On the other hand, no such sensitisation was observed in KCl: Tl, In and RbCl: Tl, In up to a concentration of 10^{-3} mol [15].

Although we have not examined it, it is quite possible that the hopping takes place in the reverse order: H centre rotation followed by permutation. In view of the small value of Q_2 at equilibrium in NaCl and NaBr, the two ways of achieving a diffusion would take about the same activation energies. In the other group, which includes KCl and KBr, in view of the large barrier energy involved, it does not seem to matter which way the hopping is attempted. The diffusion would be prohibitive.

It is well known that the H centres in alkali halides can axially diffuse and rotate with very small energies (37 meV and 90 meV respectively for rotation and translation in KBr [26]). Alternative models [24] of the off-centre STE hopping have been tried, but were not successful. The difficulty was not with the H centre motion, but was with the F centre motion. Other modes of F centre diffusion were met with stiff energy barriers, which is not altogether surprising since the F centre diffusion energy is about 1 eV in crystals that are otherwise pure [27]. The model presented in this work is the only one we found to be satisfactory for the STE.

In this work, various components of the system are treated by different but well tested methods. An important point is that the various parts are properly interfaced to ensure internal consistency. The extended-ion method contained in this work is very accurate within the approximation, because of our use of an accurate interpolation scheme based on the use of a floating 1s Gaussian basis. The CNDO code treats the hole

(the H centre) exclusively. Its parameters have been adjusted [19] to reproduce the molecular bond-length, vibrational frequency and the electron affinity. Our earlier work showed that the axial shift of the off-centre STE divides the alkali halides into two fairly well distinguished groups, and that the two groups behave differently in the triplet-state π-emission [19] and the Rabin–Klick diagram [18]. It is therefore significant that the hopping diffusion of the STE seems to divide the alkali halides into two groups along the same line.

From the results obtained for NaCl, NaBr, KCl and KBr, it appears fairly clear that the amount of relaxation energy involved in the off-centre shift of the STE (ΔE_2 of [18]), and therefore also the axial shift of the off-centre STE, is critical in the hopping motion of the STE in alkali halides. For the first group, which includes NaCl, NaBr and probably the iodides, although the excited electron in the STE has taken over one anion site and is therefore similar to an F centre, the V_k core (the primitive H centre) is quite close. For this group, it takes only a modest amount of energy (about 0.2 eV) to induce the electron to jump to the other site across the H centre, thereby accomplishing a permutation of the F and H centres. On the other hand, for the second group, which includes KCl, KBr and, we believe, RbCl, RbBr and the fluorides, it takes about 1 eV or more to achieve the permutation of the H and H centres. The present model is therefore in agreement with the relatively limited experimental data available. It also gives a fair estimate of the activation energy for the case of NaCl, the only case where the energy for hopping motion has been determined [10, 11]. In view of the novelty of the hopping mechanism proposed, the prediction that there are two groups of STE in hopping diffusion is of most interest.

We have reported earlier [18] that the low temperature F centre formation yield (the Rabin–Klick criterion) is governed by the degree of off-centre axial shift and the available relaxation energy of the off-centre STE. The two groups that we describe above belong to well distinguished groups in the Rabin–Klick diagram. A similar distinction is also reported in our recent paper regarding the triplet-state STE π-emission bands [19]. The first group generally shows a modest amount of Stokes shift compared to the second group, for which the Stokes shift may represent up to about 75% of the 1s free exciton absorption energy. Another remarkable parameter is the triplet-state lifetime which shows important variations inside a given halide family. For example, NaBr has a lifetime that is shorter than those of KBr and RbBr by a factor of about 300. These parameters can be correlated to the degree of axial shift of the off-centre STE in a simple way [20]. It seems, therefore, especially if more data becomes available in the future, that the hopping motion of the STE in alkali halide crystals, could add another interesting element to the clarification of the off-centre characteristics of the STE.

References

[1] Apker L and Taft E 1951 *Phys. Rev.* **81** 698
[2] Teegarden K 1966 *Luminescence of Inorganic Solids* ed P Goldberg (New York: Academic)
[3] Valbis Ya A 1966 *Opt. Spektrosc.* **21** 106

[4] Tanimura K and Okada T 1976 *Phys. Rev.* B **13** 1911
[5] Dietrich H B and Murray R B 1972 *J. Lumin.* **5** 155
[6] Dietrich H B, Purdy A E, Murray R B and Williams R T 1973 *Phys. Rev.* B **8** 5894
[7] Townsend P D 1976 *J. Phys. C: Solid State Phys.* **9** 1871
[8] Ortega J M 1979 *Phys. Rev.* B **19** 3222
[9] Jammal Y A L, Pooley D and Townsend P D 1973 *J. Phys. C: Solid State Phys.* **6** 247
[10] Vasil'chenko E A, Lushchik N E and Lushchik Ch B 1970 *Sov. Phys.–Solid State* **12** 167
[11] Tanimura K and Itoh N 1981 *J. Phys. Chem. Solids* **42** 901
[12] Kink R A 1968 Doctoral dissertation
[13] Teegarden K 1957 *Phys. Rev.* **105** 1222
[14] Lushchik N E and Kuketaev T A 1968 *Opt. Spectrosc.* **25** 890
[15] Il'mas E R, Lii'dya G G and Lushchik Ch B 1965 *Opt. Spectrosc.* **13** 453
[16] Kabler M N 1964 *Phys. Rev.* **136** A1296
[17] Leung C H, Brunet G and Song K S 1985 *J. Phys. C: Solid State Phys.* **18** 4459
[18] Song K S, Leung C H and Williams R T 1989 *J. Phys.: Condens. Matter* **1** 683
[19] Song K S and Leung C H 1989 *J. Phys.: Condens. Matter* **1** 8425
[20] Song K S and Chen L F 1989 *J. Phys. Soc. Japan* **58** 3022
[21] Suzuki S, Tanimura K, Itoh N and Song K S 1989 *J. Phys.: Condens. Matter* **1** 6993
[22] Call P J, Hayes W and Kabler M N 1975 *J. Phys. C: Solid State Phys.* **8** L60
[23] Song K S 1973 *J. Physique Coll.* **9** C34 495
[24] Williams R T and Song K S 1987 *Cryst. Latt. Defects Amorph. Mater.* **17** 151
[25] Song K S and Leung C H 1987 *J. Phys. Soc. Japan* **56** 2113
[26] Diens G J and Smolukowski R 1976 *J. Phys. Chem. Solids* **37** 95
[27] Fuller R G 1972 *Point Defects in Solids* vol 1, ed J H Crawford Jr and L M Slifkin (New York: Plenum)