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1989 J. Phys.: Condens. Matter 1 8425

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A theoretical study of the π -luminescence from self-trapped excitons in alkali halide crystals

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Received 21 February 1989

Abstract. It is shown that the equilibrium axial shift of the V_k core of the self-trapped exciton (STE) in alkali halides is correlated with the lifetime and Stokes shift of the π -emission band and the binding energy of the STE. A configuration coordinate diagram for the STE in KCl is constructed which is consistent with existing data and accounts for the large Stokes shift and large binding energy of the STE. A detailed comparison is made between the configuration coordinate diagrams based on the off-centre (F–H pair) model and the on-centre ($V_k + e$) model of the STE. Using a previously developed extended-ion program package coupled with a CNDO code, the π -emission band peak energies and the binding energies of the STE are calculated for 12 alkali halides. The results are in general agreement with experiment.

1. Introduction

Band-gap excitation of an alkali halide crystal leads to the formation of self-trapped exciton (STE) states which originate most of the intrinsic recombination luminescence and figure prominently in radiation damage. In this paper, we are particularly interested in the π -emission band of the lowest triplet state of the STE, which exhibits some rather remarkable properties. First, there is a very large Stokes shift in most of them [1]. Typically, as in the fluorides, KCl, RbCl, KBr and RbBr, the emission-band peak energy is less than 40% of the 1s free-exciton absorption-band energy. In NaBr and NaI, it is about 70%. The proportion is intermediate between these two extremes for NaCl, KI and RbI. These large Stokes shifts have been attributed to the large lattice relaxation surrounding the STE although the precise nature of the relaxation has not been clarified.

The second feature concerns the long lifetime of the π -luminescence (or the lowest triplet STE state) which systematically increases as the halogen ion becomes lighter. Kabler and Patterson [2] have presented a fine analysis of the lifetime showing that it is the mixing with the spin singlet excited states which makes the emission from the spin triplet state becoming partially allowed. This mixing takes place through the spin-orbit coupling of the self-trapped hole, which therefore depends on the halogen ion. This analysis explains the overall trend of the lifetime between the different halide families. It is, however, still difficult to explain the large variation of the lifetime τ among the members of a given halide family. For example, τ for NaBr is shorter than that of KBr and RbBr by a factor of about 300.

The third interesting feature is the binding energies or the ionisation energy of the STE, which are found to be about two to four times larger than those of the corresponding 1s free excitons [3]. In addition, these binding energies are remarkably close to the binding energies of the F centres, except for NaBr and NaI where they are smaller.

The above three features of the STE are difficult to explain on the basis of the earlier 'on-centre' ($V_k + e$) model of the STE in which the excited electron is assumed to occupy a s-like orbital around the V_k centre in a configuration of D_{2h} symmetry. For example, the large Stokes shift (5–6 eV for some alkali halides) is difficult to be accounted for in terms of V_k -type relaxation alone [3, 4] unless an unreasonably large recombination ground-state energy (or a large ionisation energy at the V_k configuration) is assumed. Likewise, it is difficult to attribute the large variation of the triplet-state lifetime within a given halide family to the small variation of the equilibrium distance between the two ions of the V_k centre [2]. Finally, as will be explained later in § 2, the fact that the binding energies of the STE are much larger than those of the 1s free excitons is inconsistent with the prediction based on the 'on-centre' ($V_k + e$) model.

Our recent series of work on the structure of the STE in alkali halides [5, 6] has clearly shown that in the lowest triplet state the 'on-centre' ($V_k + e$) configuration is strongly unstable against axial (off-centre) displacement of the V_k core, and in equilibrium, the lowest triplet STE occupies an off-centre configuration of C_{2v} symmetry, nearly identical to a close (F–H) pair. This strong instability can be attributed to the fact that the pseudopotential of the V_k core is repulsive. The energy of the system can then be lowered by expulsion of the V_k core, with the electron settling in the nascent anion vacancy. This off-centre model of the STE has resolved a number of difficulties encountered earlier with the on-centre model [5]. In particular, the model has explained several puzzling aspects associated with F-centre formation at both low and high temperature [6, 7].

In this paper we are primarily concerned with the three aspects of the STE mentioned above. In § 2 we show that the three parameters, the Stokes shift, the lifetime and the binding energy of the STE, are correlated with the magnitude of the axial shift of the V_k core. In § 3 we construct a configuration coordinate diagram of the STE in a typical alkali halide, KCl, which shows that the off-centre STE model is consistent with various existing data. We present also, in the appendix, a critical comparison of the on-centre and off-centre models of the STE in terms of the configuration coordinate diagrams which the two models support. Finally, in § 4, we present the results of our calculations of the π -emission band peak energies and the binding energies of the STE for 12 alkali halides.

2. Stokes shift, lifetime and binding energy of the STE

In a recent paper [6] we have presented a theoretical basis for the Rabin–Klick criterion for low-temperature F-centre formation. We have shown that, according to the available relaxation energy for defect formation, there are two groups of alkali halides. Group I comprises NaF, KF, RbF, KCl, RbCl, KBr and RbBr, and group II NaCl, NaBr, NaI, KI and RbI. There is much more available energy in group I than in group II. For the present discussion, it is significant that the first group generally exhibits a larger axial shift of the V_k core and a fairly well formed F centre. On the other hand, group II is a generally characterised by a smaller axial shift, and the electron and hole of the STE are much close to each other. Although it is very hard, in some cases, to calculate the axial shift of the V_k core with great confidence, it remains very clear that the two groups are quite well defined and distinct.

There is a direct correlation between the axial shift and the various properties of the STE. A large Stokes shift generally indicates a strong lattice relaxation. Also the lifetime

Table 1. Parameters of the triplet STE (π -luminescence state).

	Free exciton ($n = 1$), E_0 (eV)	π -band peak, E_π (eV)	Stokes shift, $(E_0 - E_\pi)/E_0$	Ionisation limit, E_i (eV) ^a	Lifetime, τ (10^{-6} s) ^b	Axial shift, ΔQ_2 (au)
NaF	10.6	2.5	76%		670	≥ 4
KF	9.9	2.48	75%		37000	≥ 4
RbF						≥ 4
NaCl	8.05	3.47	57%	2.8	295	≤ 2
KCl	7.98	2.54	68%	2.6	5000	≥ 5
RbCl	7.65	2.41	69%	2.3	5500	≥ 5
NaBr	6.73	4.65	31%	≤ 1.1	0.49	≤ 2
KBr	6.93	2.44	65%	2.3	130	≥ 4
RbBr	6.86	2.36	66%	2.2	180	≥ 4
NaI	5.58	4.22	24%	≤ 1.2	0.09	≤ 2
KI	5.82	3.36	42%	1.7	4.4	≤ 2
RbI	5.8	3.09	47%	1.7	11	$= 3$

^a Reference [3].^b Reference [2].

of the emission band is closely related in the off-centre model to the spatial overlap between the excited electron and the hole wavefunctions: long lifetime implies smaller overlap and vice versa. In order to display the correlation, we have presented in table 1 a list of several parameters of the triplet state of the STE. These include the observed π -band peak energies, the Stokes shifts, the lifetimes, and the binding energies as deduced from experiment [3]. Following reference [3], only the higher-energy bands for the iodides are presented. Also shown are the axial shifts of the V_k core obtained in our calculations.

Table 1 shows a fairly clear correlation between the axial shift on the one hand, and the Stokes shift, the lifetime and the binding energy on the other. The large Stokes shifts (~ 5 – 6 eV) observed in group I could be attributed to the large axial shifts of the V_k core in this group. Likewise the relatively smaller Stokes shifts for group II are consistent with smaller axial shifts.

Kabler and Patterson [2] have explained the variation of lifetime among the different halide families. However, there is also a large variation in lifetime within a given halide family. For example, the lifetime for NaBr is shorter than those of KBr and RbBr by a factor of 250–300. In the analysis of Kabler and Patterson, the dipole moment of the transition probability remains almost a constant for a given halide family. By contrast, the fractional mixing coefficient of the $^1\pi_u$ (into the triplet π state) varies by a factor of about 15 from NaBr to KBr (and RbBr). (This is the parameter b^2 in reference [2]). This parameter is determined by the spin–orbit coupling constant and the energy separation between the two hole states which interact. The authors attributed the variation of b^2 to the variation of the bond length of the V_k core. In our opinion, it is not likely that a modest variation in the bond length can account for the observed variation of lifetime.

From the point of view of the off-centre model, the lifetime should depend sensitively on the axial shift, which is a measure of the distance of separation between the electron and the hole. In our model, therefore, the parameter b^2 is approximately constant for a given family of halides, while the dipole moment varies sensitively depending on the axial shift of the V_k core. We expect, therefore, that within a given halide family, the lifetime should be shorter for the materials with smaller axial shifts. This seems to explain the systematically shorter lifetime of NaCl compared with those of the other chlorides,

and of NaBr compared with the other bromides. According to the above classification, all fluorides belong to group I and all iodides belong to group II. NaF and NaI, however, are somewhat distinct among their respective halide families. Although we have not detected notable differences, we believe that their distinct features may be understood in view of the lattice constant difference within the respective halide families.

The binding energy (ionisation limit of reference [3]) of the STE is yet another interesting parameter which reveals information about the nature of the self-trapping. Williams and Kabler have shown that the binding energy of the STE is greater than that of the free exciton by a factor of roughly 2–4, and is very close to that of the F centre [3]. On the basis of the on-centre model in which the V_k centre has captured an electron in a s-like orbital, one would expect that the binding energy of the STE is smaller than that of the free exciton. This is the result contained in an earlier study [8] of the free exciton and the on-centre STE which shows the wavefunction of the electron of the on-centre STE is more diffuse and hence the binding energy of the on-centre STE is smaller. We present in the Appendix a detailed discussion on the binding energies of the on-centre and off-centre STE. The large binding energy of the STE, being also quite close to that of the F centre, provides further evidence of the off-centre structure of the STE. Indeed, the excited electron in the off-centre STE is basically a perturbed F centre. Although the authors have mentioned the difficulties in deducing the binding energies for NaBr and NaI [3], the smaller binding energies for these two materials are quite consistent with the fact that, especially for NaBr and NaI, the axial shifts are small and the V_k core is very close to the 'F-centre'.

The study of luminescence from alkali halides containing heavier halogen impurities reveals a wealth of information [9]. Variation of the triplet-state STE lifetime and Stokes shift of the impurity dimers (e.g. $I_2^- + e$ in KCl:I and RbCl:I) can also be understood in terms of the axial shift of the dimer and the lattice relaxation [10].

3. Configuration coordinate diagram of the STE in KCl

Construction of a configuration coordinate diagram of a crystal containing a STE will be useful, especially in view of its off-centre character. Wood [4] has constructed such a diagram and found that V_k -type relaxation as well as cubic relaxation must be included. The experimental data available then were much more limited, and the idea of an off-centre STE was not even contemplated.

In the following, we rely on both experimental data and theoretical calculations to construct a configuration coordinate diagram of KCl, which is a prototype of group I with large Stokes shift, long lifetime and large binding energy.

The parameters available from experiment are: (i) band-to-band absorption energy, 8.7 eV [11]; (ii) 1s exciton absorption energy, 7.98 eV [11]; (iii) π -emission band peak energy, 2.54 eV [1]; (iv) binding energy of the STE, 2.6 eV [3]. Theoretical calculations have provided the following: (i) stabilisation energy of the V_k centre, 0.5 eV [11] or 0.9 eV [12]; (ii) energy difference between the on-centre STE (D_{2h} symmetry) and the off-centre STE (C_{2v} symmetry), 1.5–2.0 eV; (iii) π -emission band peak energy, 2.4 eV; (iv) recombination ground-state energies, 4.3 eV for the off-centre STE and 2.2 eV for the on-centre exciton; (v) binding energy of the off-centre STE, 2.4 eV. Details of the calculations will be presented in § 4. Here we merely note that the calculated parameters for the off-centre STE are in good agreement with experiment.

The configuration coordinate diagram for KCl as constructed from the above values, after some slight adjustments, is presented in figure 1. The coordinates explicitly shown

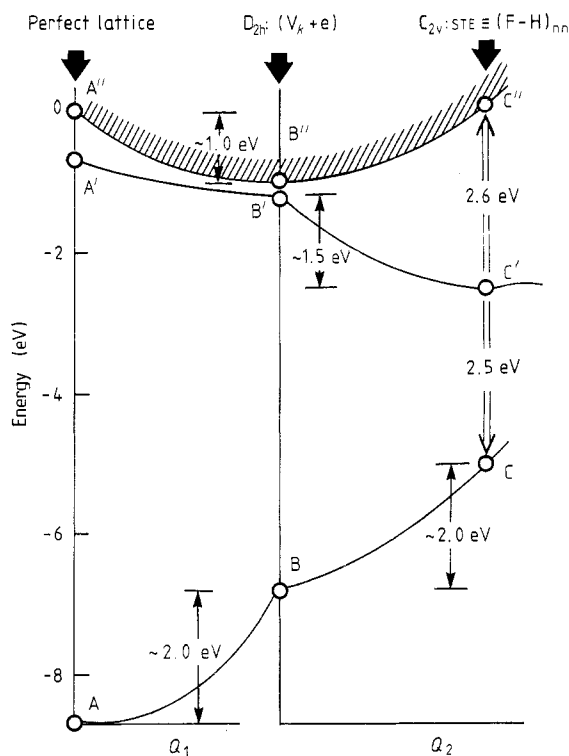


Figure 1. Configuration coordinate diagram of the STE in KCl. Q_1 represents the V_k -type relaxation, while Q_2 is for the off-centre axial distortion of the V_k core along the (110) axis leading to C_{2v} symmetry. The shaded part represents the ionised states. The diagram is based on available experimental data and theoretical work (see text).

are the internuclear distance (Q_1) of the Cl_2^- core, and the axial shift (Q_2) of the V_k core. Relaxations along other coordinates, such as the breathing mode or the odd-parity motion of the surrounding K^+ ions (called \tilde{Q}_2 in earlier papers [5, 7]) have been included, but are not explicitly shown.

We now comment on the various points of the diagram. The perfect crystal state is represented by A, and $A \rightarrow A'$ represents the formation of the $1s$ free exciton. Since the binding energy of the on-centre STE is very small as discussed in the last section, the energy of the on-centre STE at B' is taken to be close to the ionised limit at B'' . The on-centre STE at B' is unstable and relaxes to the off-centre STE at C' . $C' \rightarrow C$ represents the emission ending at the recombination ground state at C, followed by ground-state relaxation to A, after passing through B (of D_{2h} symmetry). The points A'' , B'' and C'' in the conduction band are determined respectively by the band-to-band absorption energy, the V_k centre stabilisation energy and the binding energy of the off-centre STE. Between the ionisation limits at C'' (of C_{2v} symmetry) and at B'' (of D_{2h} symmetry), there is an energy difference of about 1 eV.

We emphasise that the C_{2v} distortions (with coordinates Q_2 and \tilde{Q}_2) are essential to account for the large Stokes shift and large binding energy of the STE. There is no need to assume unreasonably large relaxation energy of the ground state along the Q_1 mode as in references and [3] and [4]. Recent work on the mechanism of electronic-transition-induced desorption [13] has also indicated the importance of the axial shift of the V_k core.

The large ionisation energy $C'C''$ of the off-centre STE compared with the small value $B'B''$ of the on-centre STE has an interesting consequence. It seems to suggest that the p-like excited states of the STE, which are about 0.7 eV below C'' , could merge into the continuum upon relaxation to the on-centre D_{2h} configuration. This could have quite significant implications. The efficient intersystem crossing between the triplet and singlet manifolds [14] could well have been caused by this effect [15].

We remark that the configuration coordinate diagram presented contains a few parameters which are rather difficult to calculate accurately. The binding energy of the on-centre STE ($V_k + e$) is one such example.

The configuration coordinate diagram of the STE differs considerably between the on-centre ($V_k + e$) model and off-centre (F–H pair) model. The principal point of the disagreement is regarding the optical binding energy of the STE at the ($V_k + e$) configuration. In the appendix, we argue on the basis of earlier and more recent work that the binding energy at this configuration is indeed very small, probably smaller than that of the free exciton (1s state). It seems unreasonable to attribute the observed binding energy of the STE (two to four times larger than that of the corresponding free exciton [3]) to the ($V_k + e$) configuration, as is reported recently [16]. As we argued above, there is no difficulty to explain why the binding energy is so close to that of the F centre in most alkali halides [3], with the possible exceptions of NaBr and NaI, from the standpoint of the off-centre (F–H pair) model. We believe that the off-centre model of the STE is able to account for the various experimental data, particularly the large Stokes shift and the large binding energy of the triplet STE in the most reasonable way.

4. Calculations of recombination luminescence energies and the binding energies

In this section we present the calculated results of the recombination luminescence energies of the π -band and ionisation energies of the STE for various alkali halides, and compare them with the observed data. A brief report of this work has been presented earlier [17].

The method employed is essentially the same as that used earlier [5, 17]. Only a brief account will be given here. The excited electron is treated by the extended-ion method within the framework of the one-electron Hartree–Fock approximation. The electron wavefunction is represented by a linear combination of floating 1s gaussians, which are individually orthogonalised to all the occupied electron states, including those of the V_k core as well as the ionic cores of other ions. Suitable orbitals were used for these cores [5]. For F_2^- and Cl_2^- , the published molecular orbitals [18] were used. Molecular orbitals for Br_2^- and I_2^- are not available and these were constructed from the Br and I atomic orbitals. The molecular energy levels were obtained by suitably scaling the free-atom and ion energy levels in the same way as they are related in F_2^- and Cl_2^- . The energy of an excited electron calculated in this way generally represents its energy relative to the absolute vacuum. The ionisation energies of alkali atoms calculated by this method were in good agreement with experiment [19]. For the hole state of the V_k core associated with the STE, we have employed a standard CNDO code. This is interfaced with the extended-ion program package for the excited electron in a consistent way. The CNDO part determines the hole-charge distribution on the two (or three) halogen ions, which is used in the extended-ion part to calculate the electron wavefunction and energy and the lattice displacements. On the other hand, the CNDO calculation requires the Madelung potentials at the V_k ion sites which depend on the electron wavefunction and the lattice configuration. Therefore, these two parts must be linked in an iterative and consistent way.

Table 2. CNDO parameters used in this work to represent the V_k core (X_2^- or X_3^{2-}).

Species	Orbital exponent (\AA^{-1})	Electronegativity, $\frac{1}{2}(1 + A)$		Bonding energy, β
F	2.11	37.43	8.66	-11.30
Cl	1.90	19.1	6.95	-7.80
Br	2.20	25.20	6.37	-6.90
I	2.33	19.10	5.67	-5.60

Table 3. Calculated π -emission band peak energy and optical binding energy^a.

	π -band peak (eV)		Optical binding energy (eV)	
	Experiment	Theory	Experiment	Theory
NaF	2.5	1.9-2.7	—	2.37
KF	2.48	2.04	—	1.60
RbF	—	1.64	—	1.98
NaCl	3.47	3.36	2.8	3.28
KCl	2.54	2.7-3.4	2.6	2.42
RbCl	2.41	2.3-3.1	2.3	2.24
NaBr	4.65	3.21	≤ 1.1	3.04
KBr	2.44	3.09	2.3	2.35
RbBr	2.36	2.56	2.2	2.44
NaI	4.22	2.98	≤ 1.2	4.32
KI	3.36	3.68	1.7	2.07
RbI	3.09	3.56	1.7	1.98

^a Experimental data for chlorides, bromides and iodides are from reference [3]; for fluorides, from reference [30].

The CNDO parameters for a halogen ion (X) employed in this work are slightly adjusted from the standard values to fit the observed bond length and vibration frequency of the X_2^- molecules, and the electron affinity of the halogen atom. This last adjustment was made in such a way that the total energies of X_2^{2-} and X_2^- , at large internuclear distance, differ by the known value of the electron affinity. This is necessary for the calculation of the luminescence energy. The CNDO parameters obtained in this way are listed in table 2.

The equilibrium state of the STE is obtained by minimisation of the total energy of the system with respect to the electron wavefunction, the hole wavefunction, the axial shift of the V_k core and the ionic positions of about 40 surrounding ions. This same ionic configuration is then used to determine the energy of the recombination ground state of the luminescence in accordance with the Franck-Condon principle.

To determine the ionisation threshold of the STE, we used a gradually more diffuse basis for the excited electron, and confirmed that the total energy converged to a limit. The limiting value was obtained when the excited electron was removed from the system. In this situation, there is a net charge in the defect region and the polarisation effect is more important. Our calculation, based on the lowest-order Mott and Littleton method, may lead to an overestimation of the polarisation energy.

The results of our calculations are presented in table 3. This includes the calculated emission energies, and the binding energies for 12 alkali halides, as well as the corresponding experimental values. As the equilibrium axial shift Q_2 is generally hard to determine with great reliability, we have listed a range of emission energies for some cases.

Table 4. Various terms in the excited and ground states of the STE in KCl. ΔE_L and ΔE_h are changes in the lattice and CNDO energies from the perfect lattice. All energies in eV. $\Delta Q_2 = 7.8$ au (axial shift of the V_k core); $E_{\text{emission}} = 2.9$ eV.

	ΔE_L		E_{el}	ΔE_h	E_{pol}	E_{tot}
	Coulomb	Short-range, repulsive				
ex)	10.88	2.20	-4.63	-0.91	-0.53	7.01
gr)	6.68	2.20	0	-0.20	-4.58	4.11

In general, our calculated values are in satisfactory agreement with experiment. The agreement is poor, however, for NaBr and NaI. We will comment on this later. The general acceptable agreement between theory and experiment provides further support for the off-centre model of the STE. A test run for the case of the on-centre STE in KCl gave the emission-band peak at 5.5 eV, much higher than the experimental value of 2.5 eV.

In order to analyse in some detail the recombination energy of the STE, we have listed in table 4 the various energy terms that contribute to the total energy of the system in both the excited and the ground states. The lattice energy E_L includes the Coulomb energy of the lattice ions and the repulsive short-range energy. The electron energy is denoted by E_{el} . The energy of the V_k core as obtained by the CNDO code is denoted by E_h . (The CNDO calculation for the ground state involves one more electron than for the excited state.) E_{pol} is the polarisation energy. Except for E_{pol} and E_{el} , all the energy terms presented in table 4 are the change of the respective energy terms relative to the perfect crystal. There is considerable cancellation among these terms. It is therefore clear that every term should be evaluated to a fair degree of reliability in order to produce a meaningful emission energy. E_h should be reliable because the CNDO parameters were adjusted to reproduce the observed parameters as discussed earlier. The polarisation energy is the hardest to calculate with great accuracy. It seems, however, that our present method of calculation of this term is acceptable.

The case of NaBr and NaI is difficult in several regards. Both represent the prototype of those alkali halides with very low efficiency of F-centre formation at low temperature. Calculation of the relaxation of ions around the STE for these materials is particularly difficult. As we discussed earlier, the excited electron sees a repulsive pseudopotential of the V_k core, and therefore tries to expel it along the [110] axis while it settles into the nascent anion vacancy. In the case of NaBr and NaI, it is the large ion size of Br^- and I^- , coupled with the relatively smaller lattice spacing of these materials, that seems to make the relaxation hard to determine. The calculated values of the binding energies and the emission energies are not in good agreement with experiment for both NaBr and NaI.

In an earlier work, Itoh *et al* [20] have studied the π -emission band of KCl using a CNDO code in conjunction with a lattice relaxation code (HADES). Their results are in general disagreement with ours. In particular, they found that the triplet state of the STE is stable in the D_{2h} symmetry configuration. They also found that there is a barrier of about 2 eV between the on-centre STE and the nearest-neighbour F-H pair. We believe that the difference is due to the fact that, in their work, the lattice relaxation is determined in the absence of the excited electron, thereby neglecting the strong interaction of the electron with the surrounding ions. A detailed comparison of their work with ours has therefore not been attempted. Shluger *et al* [21] have calculated the recombination

energy of ($V_k + e$) and (F–H) pairs of varying separation in LiF and KCl. Their method was the semi-empirical INDO code, and relied on the lattice configuration deduced from experiment or other independent calculation. Their recombination energy for the nearest-neighbour (F–H) pair is close to our result.

Acknowledgment

One of us (KSS) would like to acknowledge A M Stoneham for a useful discussion held about the way to calculate the recombination energy of the STE.

Appendix

In this appendix we present a detailed discussion on the principal point of disagreement between the on-centre ($V_k + e$) model and the off-centre (F–H pair) model of the STE with regard to the configuration coordinate diagrams that have been proposed. Both diagrams are constructed using essentially the same set of parameters (e.g., the π -emission band peak energy and the optical binding energy of the STE). Besides the fundamental disagreement concerning the role of the Q_2 mode (the axial translational mode of the V_k core), the most prominent difference between the two models is in the assignment of the ionisation limit (optical binding energy) of the excited electron ($B' \rightarrow B''$) in the D_{2h} symmetry of the STE. In reference [16], this is taken to be the same as the observed ionisation energy of the STE (2.7 eV in KCl [3]). As we argued in § 3, this energy ($B'B''$) is quite small, probably smaller than the ionisation energy of the 1s free exciton (about 0.7 eV in KCl).

In the following, we describe in some detail the difference of the excited electron state at the D_{2h} (on-centre) configuration (point B') and at the lowest-energy off-centre configuration (point C') on the basis of earlier works of ours and others as well as the results of our more recent calculations. Since the excited electron in the off-centre configuration is basically an F-centre according to our work (with their energies differing by only about 10%), we shall simply regard the excited electron of the off-centre STE as an F electron, thereby simplifying further comparison of our results with earlier work.

We consider first the point-ion approximation, where the structure of the ion core is neglected. In this case, both the F centre and on-centre STE are well binding. Indeed, we found good binding energies with single-optimised basis functions either of the Slater or the 1s gaussian types. For example, in KCl the ground-state energy of the F-centre electron is about -5.5 eV with the gaussian $\exp(-\beta r^2)$ of exponent $\beta = 0.09$ au. This can be compared with -5.8 eV obtained with a Slater basis ($\exp(-ar)$) for $\alpha = 0.34$ au [22]. For the on-centre STE the corresponding values are -3.1 eV with $\beta = 0.02$ au. We see here that the wavefunction of the F-centre electron (or the excited electron of the off-centre STE) is quite compact, well localised within the anion vacancy. The wavefunction of the on-centre STE electron, with its two half-vacancies, is much more diffuse. Use of a larger basis within the point-ion approximation improves the energy only slightly, for both the F-centre and the on-centre STE.

The inclusion of the effect of the ion-core structure in the calculation, either in the form of ion-size parameter or the more sophisticated extended-ion approach, produces a drastically different effect on the two systems. For the F centre (or the off-centre STE), the effect is rather modest and the energy is only slightly raised. A single-optimised gaussian ($\beta = 0.06$ au) gives -4.2 eV, using the extended-ion approach. It was reported

in reference [23] that the on-centre STE energy for the lowest a_{1g} state was very sensitive to the basis used as well as to the number of ion shells included in the calculation. Our search for the optimised single basis either of the Slater type or gaussian type with a large enough cluster of ions clearly showed that for both the ion-size or the extended-ion treatment, the optimised α for the Slater orbital, or β for the gaussian basis, are essentially zero. This indicates that the excited electron of the system ($V_k + e$) tends to be delocalised, and is very close to being ionised. It is well known that in such a situation, the size of the cluster should be large enough to avoid unphysical localisation of the wavefunction in the close vicinity of the point-ions [24].

In an earlier work [23], 15 basis Slater orbitals of various angular momenta were employed to obtain an energy of $-2.4 \sim -3.2$ eV for NaCl. The need for a very large basis set as well as the difficulty of obtaining stable energy are in sharp contrast with the F centre (or off-centre STE) treated with an identical method. Use of a large basis set may force the wavefunction to adapt itself too well to the rapidly varying pseudopotential, thereby contradicting the basic principle on which the ion-size theory was founded. Such a risk has been pointed out earlier by Mathew and Green [25].

Our past and recent work on this subject has led us to conclude that the electron in the off-centre STE (F-centre) and the on-centre STE configuration are greatly different both in the binding energy and in the spatial extent of the wavefunction. This is why we find it quite reasonable that the ionisation limit of the STE (in the off-centre model) is so close to that of the F-centre, as reported by Williams and Kabler [3]. At the same time, we have to conclude that the ionisation limit of the excited electron at the V_k configuration is very small, probably even smaller than that of the free exciton. In fact, this is also consistent with earlier work [8] on the exchange splitting of the free exciton and the STE, where it was shown that the smaller splitting of the on-centre STE is due to its more diffuse wavefunction. Further examples can also be seen in the ionisation energies of the diatomic molecular system such as H_2^+ which decreases with increasing distance between the two atoms.

It seems, from the above discussions, that the assignment of the observed ionisation limit (2.7 eV in KCl) of the excited electron to the V_k configuration is rather questionable. For example, one of the conclusions reported in reference [16] is that the lattice relaxation energy of the STE is appreciably larger than that of the self-trapped hole (the V_k centre). This is contrary to the common expectation that a neutral defect system generally has a smaller relaxation energy than a charged defect system occupying the same symmetry (D_{2h} in this case). It is to be noted, however, that a larger relaxation energy of the STE is expected in the off-centre model, because there is an extra relaxation associated with the symmetry-breaking axial shift of the V_k core.

Finally, we emphasise that the off-centre model is consistent with almost all of the existing experimental data, for example, excited-state EPR (which shows almost isotropic spin density), luminescence lifetime and polarisation, and absorption spectra (in particular the ordering of the excited p-like states: b_{1u} , b_{2u} , b_{3u}). The most direct experimental data published so far are to be found in the ENDOR experiment on KCl [26].

Recent experimental work by Suzuki *et al* [27] on the variation of the π -emission band shape as a function of temperature in NaCl seems to offer a decisive element regarding the structure of the triplet STE in alkali halide crystals. The initial state of the π -emission band is coupled to a very soft phonon mode (phonon energy of about 2 meV). Also, the analysis shows that the excited state minimum is shifted along this soft phonon mode by about 2 au relative to the ground state minimum. This seems to agree with the theoretical predictions which we made earlier [6, 7].

Where there is still some debate about the off-centre character of the STE in alkali halides, there is complete agreement between experimental observation [28] and theoretical prediction [29] regarding the fact that in alkaline-earth fluorides the STE is a close (F–H) pair.

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