

## The lattice relaxation energy associated with self-trapping of a positive hole and an exciton in alkali halides

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**Abstract.** We have evaluated the upper and lower bounds to the lattice relaxation energy gained on the self-trapping of excitons, using experimental values of transition energies for free and self-trapped excitons and theoretical values for lattice relaxation energies and optical transition energies. The lattice relaxation energy upon self-trapping of an exciton in alkali halides proves to be appreciably larger than that of a self-trapped hole. We discuss the implications for a number of solid state processes including the production mechanism of F and H centres and the desorption of halogen atoms following valence electron excitation.

### 1. Introduction

The self-trapping of a particle in a solid is an important step in several solid state processes, including defect production and certain desorption mechanisms. Whether or not self-trapping will occur is determined mainly by the relative magnitudes of two energies [1, 2]. The first energy is the band width, which is a measure of the gain in kinetic energy on delocalising the particle; for a full band width  $\| 2B$ , this gain is  $B$ . The second energy is the gain in the relaxation energy  $S$  from lattice distortion and polarisation on localising the particle. The main aim in our present paper is the estimation of this self-trapping relaxation energy for self-trapped excitons in alkali halides, since this energy allows us to clarify several aspects of solid state processes. We do not consider here the dynamics of the self-trapping process [3, 4].

For a simple particle, like an electron, or a muon, or an electronic hole, the condition for self-trapping is simply  $S > B$ . For a composite particle, like an exciton, there will be contributions to  $S$  from both constituent particles, and these electron and hole components will be commented on later. The self-trapping of excitons is a very widespread phenomenon, and has been observed in alkali halides, alkaline-earth fluorides, silica (quartz) and alumina (see, e.g., [5]). Although positive holes are known to be self-

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<sup>||</sup> Strictly this applies for a solid with one atom per unit cell, for the energy gain is  $B$  on delocalising from a Wannier function associated with a single unit cell. For a compound, like a halide, there is no problem so long as the band is associated with one ion in the cell (e.g. the valence band of alkali halides is halogen-like). However, when the band involves several inequivalent ions,  $B$  must be defined more carefully.

trapped, holes have been sought in vain in  $\text{MgF}_2$  [6] and  $\text{SiO}_2$  [7]. Thus excitons are self-trapped in a rather wider range of substances than are positive holes. Partly this happens because the band width for holes (essentially the valence band width for the crystal) is much larger than that for excitons [8] and partly because, in some cases at least, the relaxation energy for excitons is larger than for holes.

Toyozawa [9] has discussed the criterion for the self-trapping of excitons, and especially the conditions for localisation of electron and hole on a single ion (on-site case) or of the electron on one site and the hole on another. For on-site localisation the effective relaxation energy is the sum of the electron contributions  $S_{\text{ex}}$ , the hole contribution  $S_{\text{hx}}$  and the on-site Coulomb interaction energy  $U$ . For separate sites, the Coulomb term will be much smaller. Localisation on a single site is favoured if the coupling coefficients for the electron and hole have the same sign, i.e. if the relaxation caused by the electron involves the same ionic motions as that driven by the hole. Whilst there are no direct measurements of the lattice relaxation energy for self-trapped excitons in alkali halides, nor are there calculations of the highest accuracy, both the range of cases for which self-trapping is seen and Toyozawa's description suggest that the relaxation energy for self-trapped excitons is bigger than that for self-trapped holes. This is confirmed by our later analysis.

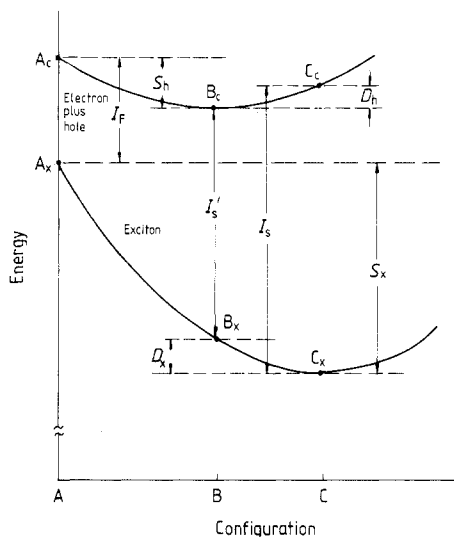
For some systems, the self-trapped exciton can be regarded as an electron localised by a self-trapped hole. This appears to be so in the alkali halides and in  $\text{AgCl}$ , for instance, and this would be an 'on-site' system in Toyozawa's classification. The separate-site case is typical of more open crystal structures, notably the alkaline-earth fluorides, where the electron and hole are localised at different sites and the self-trapped exciton is sometimes described as a close F- and H-centre pair. Usually for the alkali halides, the self-trapped excitons have been taken to be of the on-site type, i.e.  $[\text{V}_k\text{e}]$ , or an electron trapped by a self-trapped hole. This picture is consistent with a wide range of data, although ENDOR data for  $\text{KCl}$  [10, 11] suggest a separate-site model and the idea of an off-centre self-trapped exciton has been followed up with some success [12, 13]. In our present analysis we shall leave the question of one or two sites [4, 14] open, although our results do put some limits on the models. In particular, we shall allow the geometry for the self-trapped hole to differ from that for the self-trapped exciton.

The aim of the present paper is to derive information on the energies of excitons. We shall compare the lattice relaxation energies of self-trapped excitons and positive holes using available experimental and theoretical data. This shows that the exciton has a significantly larger relaxation energy. The same approach allows us to make a reasonable estimate of this relaxation energy, and hence to relate the various energies of excited states of the self-trapped exciton to the unrelaxed exciton energy. These relative energies are critical in a number of important solid state processes, notably the production mechanisms of F and H centres [15], the question of the possible inverse conversion from an F-H pair to a self-trapped exciton [16] and the desorption of halogen atoms following valence electron excitation [17].

## 2. Evaluation of the lattice relaxation energy of self-trapped excitons

### 2.1. Energy cycles giving bounds on the relaxation energy

We have taken two different energy cycles to obtain upper and lower bounds for the relaxation energy  $S_x$  for the self-trapped exciton. To describe these energy cycles we



**Figure 1.** A configuration coordinate curve for excitons in KCl. The energies for the perfect lattice configuration are based on experimental results. For the self-trapped configuration the energy differences within the configuration are based on experimental data but the energies relative to the ground state give only the lower bound.

make use of the adiabatic energy surfaces shown in figure 1. These curves describe the energy of the exciton in its lowest-energy state and that of the ionised exciton (i.e. a hole plus a free electron) as a function of a relaxation coordinate. For clarity we have assumed it is adequate to draw a single coordinate, although this assumption is not used in the energy cycles. The configuration A corresponds to the perfect crystal geometry, so  $A_x$  corresponds to a 1s free exciton and  $A_c$  to a free-electron–free-hole pair. Relaxation takes the free exciton to its self-trapped form  $C_x$  at configuration C; similarly, the electron–hole pair relaxes to a free electron and self-trapped hole  $B_c$  at configuration B. As noted earlier we shall not assume configurations B and C are the same. In approaches that assume a  $[V_k e]$  model for the self-trapped exciton the configurations differ primarily in the relaxations around the  $V_k$  centre because of the localised electron charge, while in approaches that assume the  $[F-H]$  model, the differences are primarily in the position of the halogen molecular ion.

The energy cycle that gives the upper bound is as follows. Starting from a free-electron–hole pair ( $A_c$ ), let the hole be self-trapped, gaining energy  $S_h$ . The self-trapped hole is further distorted to the self-trapped-exciton configuration, costing energy  $D_h$ . The distortion energy is a positive quantity. Recombination of the electron with the self-trapped hole at the self-trapped-exciton configuration C leads to the self-trapped exciton  $C_x$  at the lowest state. The energy emitted by the recombination equals the ionisation energy  $I_s$  of a self-trapped exciton. Restoring the perfect lattice configuration costs the relaxation energy  $S_x$  of the self-trapped exciton, and the ionisation of a 1s exciton costs ionisation energy  $I_F$ . Thus we obtain

$$S_x = S_h + I_s - D_h - I_F \quad (1)$$

or, since  $D_h \geq 0$ , the upper bound  $S_x^u$  of  $S_x$  is given by

$$S_x^u = S_h + I_s - I_F. \quad (2)$$

In evaluating the lower bound  $S_x^l$  of  $S_x$ , we start from  $C_x$  and distort the lattice to the

self-trapped-hole configuration, costing energy  $D_x$ .  $D_x$ , like  $D_h$ , is a positive quantity. We now ionise the  $1s$  exciton at the self-trapped-hole configuration costing  $I'_s$ , and this is followed by restoration of the perfect lattice configuration (costing energy  $S_h$ ). Recombination of the electron-hole pair (gaining energy  $I_F$ ) and lattice relaxation to the self-trapped-exciton configuration (gaining energy  $S_x$ ) leads to the self-trapped exciton. Thus we obtain

$$S_x = S_h + I'_s + D_x - I_F. \quad (3)$$

Since  $D_x \geq 0$ , the lower bound  $S_x^l$  of  $S_x$  is given by

$$S_x^l = S_h + I'_s - I_F. \quad (4)$$

Comparing equations (2) and (4), we see that the difference between the bounds on the relaxation energy ( $S_x^u - S_x^l$ ) is simply  $I_s - I'_s$ , i.e. the change in ionisation energy of the self-trapped exciton on going from configuration B to configuration C. If we use equations (1) and (2), we note that  $I_s - I'_s$  is also equal to  $D_x + D_h$ . The bounds will be especially close when the ionic configurations of the self-trapped exciton and of the self-trapped hole are close. Equations (1) and (3) can also be rewritten to display the difference between the relaxation energies of the exciton and the hole:

$$S_x - S_h = (I_s - I_F) - D_h = (I_s - I_F) + D_x - (I_s - I'_s). \quad (5)$$

The first term, the difference between the ionisation energies of the self-trapped ( $I_s$ ) and free ( $I_F$ ) excitons, can be obtained directly from experiment and is certainly large, and this proves critical.

## 2.2. Estimates of relaxation energies for self-trapped excitons

We now evaluate the various terms in equations (1)–(5), starting with an estimate of the difference between the self-trapped-exciton ionisation energies for the self-trapped-hole geometry  $I'_s$  and for its actual geometry  $I_s$ . Experimentally, only  $I_s$  can be obtained directly. However, there have been several calculations of self-trapped excitons for the  $V_k$ -centre geometry, and we can use a comparison between these theoretical predictions and observed spectra to estimate  $I'_s - I_s$ . The comparison is made most easily for bound-bound transitions (table 1 shows results from a variety of methods), rather than for ionisation energies, since there has been less theoretical work on ionisation. The energies of the excited states will be less sensitive to local geometry than the lower-lying states, so this approach should give reasonable insight into the ionisation energy differences. With the exception of the  $1s - 2p\sigma$  transition energies, the agreement of the predicted and observed energies is good, consistent with small differences between  $I'_s$  and  $I_s$ . In the case of the  $1s - 2p\sigma$  transition, the spread of values surely reflects the strong interactions between the electron and the halogen molecular ion; if so, this is not relevant for the ionisation transition, where the final state has a delocalised electron. Overall, it seems unlikely that  $I'_s$  and  $I_s$  differ by more than about 0.5 eV. The upper and lower bounds (equations (1), (3)) will thus be rather close, and we shall concentrate on  $S_x^u$ . A corollary is that  $D_x + D_h$  is also unlikely to exceed 0.5 eV, so both the distortion energies  $D_x$  and  $D_h$  will be small.

In table 2 we show the results of calculations of  $S_x^u$  for NaCl, KCl, KBr and RbCl. The values of  $S_h$  were taken by combining the calculations of Cade and co-workers [18]

**Table 1.** A comparison of 1s–2p transition energies of the self-trapped exciton obtained experimentally and obtained theoretically using the  $[V_k e]$  model.

Substance	Transition	Experiment	Theory ( $V_k$ -centre geometry)		
NaCl	1s–2p $\sigma$	2.02	1.8 <sup>a</sup>	1.49 <sup>b</sup>	0.7–1.1 <sup>c</sup>
	1s–2p $\pi$	2.25	1.7 <sup>a</sup>	1.95 <sup>b</sup>	2.3–2.4 <sup>c</sup>
KCl				1.79 <sup>b</sup>	2.3–2.4
	1s–2p $\sigma$	2.19		2.0 <sup>a</sup>	0.7 <sup>d</sup>
	1s–2p $\pi$	1.87		2.0 <sup>a</sup>	2.56 <sup>d</sup>
KBr		2.10			2.73 <sup>d</sup>
	1s–2p $\sigma$	1.70		1.5 <sup>a</sup>	0.94 <sup>d</sup>
	1s–2p $\pi$	1.57		1.4 <sup>a</sup>	1.69 <sup>d</sup>
RbCl		1.77			2.47 <sup>d</sup>
	1s–2p $\sigma$	1.99		2.0 <sup>a</sup>	
	1s–2p $\pi$	1.71		2.0 <sup>a</sup>	
		1.89			

<sup>a</sup> [23].<sup>b</sup> [24].<sup>c</sup> [25].<sup>d</sup> [26].<sup>e</sup> [20].**Table 2.** Energies in electron volts of the lattice relaxation ( $S_h$ ) of a positive hole, ionisation ( $I_s$ ) of a self-trapped exciton, ionisation ( $I_F$ ) of a free exciton, and upper bound on the lattice relaxation ( $S_x^u$ ) of a 1s exciton.

	$S_h^a$	$I_s$	$I_F^b$	$S_x^u$
NaCl	1.69	3.16 <sup>c</sup> 2.8 <sup>d</sup>	0.81	4.04
KCl	1.61	2.73 <sup>e</sup>	0.93	3.41
KBr	1.53	2.24 <sup>e</sup>	0.70	3.07
RbCl	1.32	2.48 <sup>e</sup>	0.69	3.11

<sup>a</sup> [18] and present work.<sup>b</sup> [19].<sup>c</sup> [24].<sup>d</sup> [27].<sup>e</sup> [15].

with new estimates of the hole relaxation energy (i.e.  $Cl^0 \rightarrow Cl_2^-$ ) using the same potentials. The values of  $I_s$  and  $I_F$  were taken from the experimental results given in [15] and [19], respectively. The fact that  $I_s > I_F$  indicates that the lattice relaxation of the 1s exciton lowers its ionisation energy more significantly than the ionised exciton. We note further that, taking into account the possible differences between  $S_x^l$  and  $S_x^u$ , the value of  $S_x$  is significantly larger than  $S_h$ . The relaxation energy for the self-trapped exciton is larger than that for the self-trapped holes by 1.5–2.5 eV:  $S_x$  is typically 3–4 eV, whereas  $S_h$  is only about 1.5 eV.

### 2.3. Self-trapped exciton structure: the role of the electron

We discuss here what information  $S_x - S_h$  gives on the geometry of the self-trapped exciton. The result  $S_x > S_h$  certainly indicates that the electron associated with an exciton

plays an important role in the lattice relaxation energy. According to Toyozawa, the difference  $S_x - S_h$  can be ascribed to the on-site Coulomb energy if the self-trapped exciton has the  $[V_k e]$  structure. However, if the [F–H] model of the self-trapped exciton is valid, Toyozawa's argument suggests  $S_x \approx S_h$ . Because of the proximity of the sites of trapped electron and hole, however, their interaction cannot be ignored and it is likely that  $S_x > S_h$  even in this case. No firm conclusion can be drawn on the model of the self-trapped exciton in alkali halides on the basis of the result  $S_x > S_h$  although, since the interaction is unlikely to exceed a few tenths of an eV, it is likely that a one-site form is favoured.

The result that  $D_h + D_x = I_s - I'_s \leq 0.5$  eV, i.e. that the two distortion energies are small, does, however, appear to favour the  $[V_k e]$  model. This can be seen from estimates of the two separate terms  $D_h$  and  $D_x$ . Leung and co-workers [12] estimate that  $D_x$  is about 1 eV, already larger than seems likely from the inequality. For consistency, this would certainly need a very small value of  $D_h$ , i.e. a negligible energy to shift the molecular ion of the self-trapped hole along its axis. Yet some idea of  $D_h$  can be obtained using the HADES code alone here, this being a well tested and accurate approach, since no explicit solution of the Schrödinger equation is needed in this particular calculation. Rough estimates, following [18] and [20], suggest  $D_h$  cannot be negligible unless the  $[V_k e]$  model holds. In all, therefore, the large value of  $D_x$  of [12] leads to an apparent inconsistency unless the degree of off-centring, if any, is small.

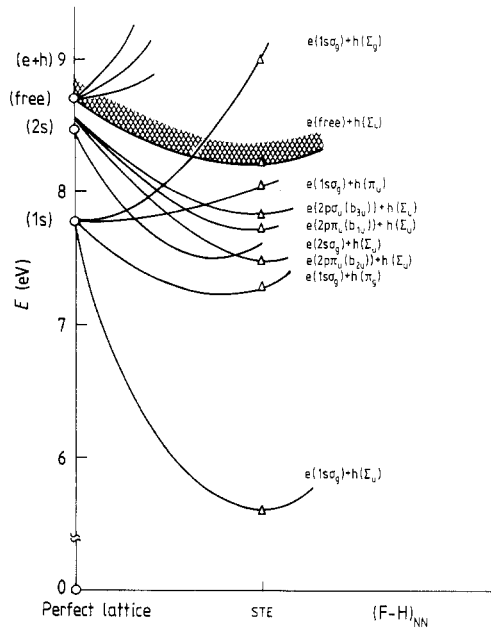
### 3. Implications of the large exciton self-trapping energy

#### 3.1. Relative energies of free and self-trapped exciton states

Using the value of  $S_x^u$  obtained above we have evaluated the energy of excited states of free excitons and self-trapped excitons for KCl and the result is shown in figure 2. In this calculation, we assume that the hole transition energies in the self-trapped exciton are the same as those of the self-trapped hole [21]. The curves are drawn to show merely the correlation between the states at the perfect lattice and the self-trapped-exciton configurations. The adiabatic potential curves are schematic: that for the lowest self-trapped exciton is a parabola which has a minimum at the self-trapped-exciton configuration, and the other curves are similar parabolae with the correct energies at the two configurations indicated. We now turn to some of the implications of these curves and the large difference between  $S_h$  and  $S_x$ .

#### 3.2. Implications for solid state processes

The relative energies shown in figure 2 are important in several solid state processes, as now discussed. First, several of the excited states of the self-trapped exciton (both hole and electron excitations) are lower in energy than the ground state of the free exciton. In particular we note that the 1s self-trapped exciton with the hole in a  $\pi_g$  excited state is lower in energy than the 1s free exciton, and hence is bonding with respect to the halogen–halogen separation. According to the suggestion by Itoh and Saidoh [22], the transformation to F–H pairs occurs from this excited state of the self-trapped excitons. The bonding nature of this excited state favours the shift of the whole halogen molecular ion to form the F–H pair configuration.



**Figure 2.** The energy levels for the free exciton ( $\circ$ , the perfect lattice geometry) and the self-trapped exciton ( $\triangle$ ) geometries. The lowest curve for the exciton is a parabola with its minimum for the STE configuration; the other curves are schematic. Note the way in which the  $[e(1s\sigma_g) + h(\pi_g)]$  state relaxes from the free-exciton state. The abscissa represents a relaxation coordinate which includes both  $V_k$ -like relaxation and translational halogen motion along the (110) axis, as in [20].

Secondly, the energy of the lowest state of the self-trapped exciton is even higher than that of an isolated pair of an F centre and an H centre [20]. Thus it is unlikely that recombination of an F centre and an H centre forms a self-trapped exciton.

Thirdly, the lower bound for the energy of the self-trapped exciton in its lowest state has been shown to be slightly smaller than the energy required to desorb a halogen atom from the surface [17]. Thus it is likely that the desorption of halogen atoms is induced from the *next* excited state (i.e. the  $\pi_g$  hole and its  $\sigma_g$  electron), which is about 2 eV above the lowest state of the self-trapped exciton, similarly to the formation of a pair of an F centre and H centre.

#### 4. Conclusion

We find that energy cycles obtained using experimental and theoretical data provide useful upper and lower bounds on the energies of self-trapped excitons and on processes involving self-trapped excitons. All available data appear consistent with the conclusions that the self-trapping energy  $S_x$  for the exciton is appreciably larger than that ( $S_h$ ) for the hole, and that the distortion energies ( $D_x$  and  $D_h$ ) are both small.

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