

## The self-trapped hole in caesium halides

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**Abstract.** The equilibrium lattice configuration, electronic excitation energies and activation energies for hopping motion are calculated for a self-trapped hole in simple cubic CsCl, CsBr and CsI. The defect is regarded as a  $X_2^-$  molecular ion ( $X = \text{Cl, Br, I}$ ) whose bond-length has been modified by the crystalline environment. Agreement with the experimental ultraviolet transition energies is good. Excitation energies deduced from measurement of  $g$  shifts in CsBr and CsI are too low, a feature common to all alkali bromides and iodides, and attributed to the approximations involved in their derivation. The initial calculations predict lower activation energies for  $90^\circ$  jumps than for  $180^\circ$  jumps, in contrast with what is observed in CsI. An alternative model is presented, which reproduces the correct trend. Comparison of the actual numbers with experiment is hampered by the fact that the latter are done at low temperature (60–90K), the calculations being done in the high-temperature limit.

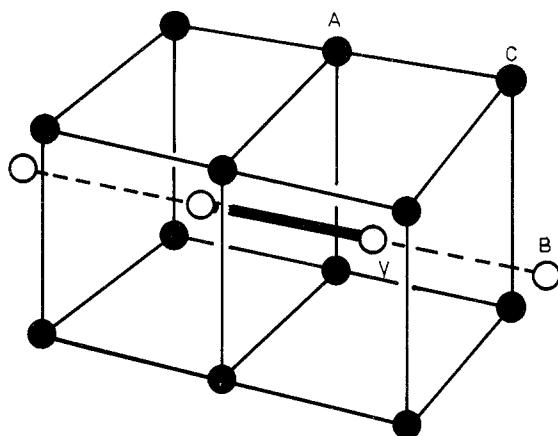
### 1. Introduction

Spin resonance data (Pilloud and Jaccard 1975, and private communication) indicate that the hole in simple cubic caesium halides is localised on two neighbouring halide ions, with the axis of the centre pointing in the  $[100]$  direction, as illustrated in figure 1. This sharing of the hole between two adjacent anions (the  $V_k$  centre) is typical of all alkali halides and alkaline earth fluorides and has been observed in more complicated compounds like e.g.  $\text{KMgF}_3$ ,  $\text{RbCaF}_3$  and the ammonium halides. It has led to the development of a theoretical model for the hole centre known as the ‘molecule in the crystal’ model (see e.g. Stoneham 1975). Its basis assumption is that the electronic (i.e. optical and spin resonance) properties of the centre are those of an  $X_2^-$  molecular ion, the crystal environment only affecting the interatomic spacing within the molecule. It has been applied successfully to the alkali fluorides and chlorides (Jette *et al* 1969, Adrian and Jette 1974) as well as the alkaline earth fluorides (Jette and Das 1969, Norgett and Stoneham 1973). It should be particularly adequate for simple caesium halides, where the high symmetry of the  $V_k$  centre ( $D_{4h}$  as opposed to  $D_{2h}$  in the other cases mentioned) ensures that certain electronic states of the molecular ion will not be split by the crystal field.

Only very recently did potential curves for the heavier molecular ions  $\text{Br}_2^-$  and  $\text{I}_2^-$  become available (Tasker *et al* 1976), and previous treatments of the self-trapped hole in the corresponding caesium halides had to resort to an alternative small polaron approach

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**Figure 1.** Geometry of the  $V_k$  centre in the CsCl lattice. The open circles are halide ions, the full circles are caesium ions.

(Iida and Monnier 1976a, b). These calculations further supported the 'molecule in the crystal' hypothesis by explicitly showing that two-site self-trapping is energetically more favourable than trapping on a single site or complete delocalisation.

The purpose of this paper is to take advantage of the newly published results on  $\text{Br}_2^-$  and  $\text{I}_2^-$ , and to present a unified treatment of the static and dynamical properties of the self-trapped hole in all simple cubic caesium halides based on the 'molecule in the crystal' model. Specifically, we shall be concerned with the lattice distortion around the  $V_k$  centre and the corresponding relaxation energy, as well as with the evaluation of activation energies for the hole's hopping motion.

## 2. Model potentials

Our calculations follow many of the ideas of Mott and Littleton (1938). Ions in an inner region were relaxed explicitly until they experienced no net resulting force, while ions in the remainder of the lattice were displaced until the polarisation of the crystal was the same as that of the material regarded as a dielectric continuum.

To describe the interaction between ions of the perfect lattice we used a shell model, which gives a realistic description of both elastic and dielectric properties, and guarantees a continuous behaviour of the latter between the inner and outer Mott-Littleton region. The model parameters were obtained from Müller and Norgett 1973 for CsCl; exactly equivalent results for CsBr and CsI were obtained from M J Norgett (private communication), who fitted the interionic potentials to the lattice constants and shear constants  $c_{11}$ – $c_{12}$  and  $c_{44}$  at 0 K, and calculated the shell parameters from the transverse optic frequencies, dielectric constants and ionic polarisabilities. The choice of Van der Waals parameters follows the full discussion by Catlow *et al* (1977). The results are collected in Appendix 1.

Tasker *et al* (1976) obtained potentials for  $\text{Cl}_2^-$ ,  $\text{Br}_2^-$  and  $\text{I}_2^-$  using the orthogonalised Moffit method. Their results for  $\text{Cl}_2^-$  are in good agreement with the self-consistent field molecular orbital calculation of Gilbert and Wahl (1971). They have fitted their ground

state ( ${}^2\Sigma_u^+$ ) potential curves to sixth-degree polynomials in the internuclear distance†. This form is appropriate for separations close to the equilibrium bond-length. At large distances, which are important when the hole is in a thermally activated state, it breaks down and we have used the following Buckingham form:

$$V(r) = A \exp(-r/\rho) - c/r^6 \quad (2.1)$$

where the three constants were fixed by asking that the equilibrium bond-lengths, dissociation energies and harmonic frequencies be the ones given by Tasker *et al* (1976). The parameters are again listed in Appendix 1. In order to check (2.1) we have computed the lattice distortion and relaxation energy for the ground state of the  $V_k$  centre in all three caesium halides, using both Tasker *et al*'s parameterisation and ours, and found no significant differences.

Finally we have to specify the interactions between the defect and the lattice. In our model the hole is spread evenly between the two ions forming the  $V_k$  centre giving each of them a net charge of  $-\frac{1}{2}|e|$ . Due to the contraction of the electron cloud upon formation of the molecule, the defect ions should be less polarisable than ordinary lattice anions. Following Diller (1976) we take this effect into account by assuming that the two ions of the centre have the same polarisability as the isoelectronic rare gas atoms. The resulting spring constants and shell charges are also listed in Appendix 1. (Calculations done with unpolarisable  $V_k$  ions showed that the results are insensitive to the choice of polarisabilities, the maximum difference in relaxation energy being less than 0.1 eV, with a negligible change in lattice distortion). The last problem is to define the short-range (i.e. non-electrostatic) interactions between lattice and defect. In our first calculations, we regard the  $V_k$  ions as ordinary lattice anions in that respect. A second model in which some anisotropy is built into the  $X^{-1/2}$ -anion interaction is briefly discussed in the last section.

### 3. Hopping motion

The hole's motion through the crystal is a hopping process. The simple cubic anion lattice allows for two types of jumps: those in which the orientation of the centre is not altered ( $180^\circ$  jump) and those in which the initial and final configuration are at right angles ( $90^\circ$  jump). Both have been observed in CsI and their respective activation energies measured (Pellaux 1976) and a lower energy found for the  $180^\circ$  jumps. In a previous theoretical treatment of the problem, Iida and Monnier (1976a, b) predicted that the  $90^\circ$  energy should be lower, most of the difference between the calculated activation energies being due to the interaction of the hole with the longitudinal optic modes of the lattice. They worked in the harmonic approximation, expanding the ionic displacements in phonon coordinates of the perfect lattice in the long-wavelength limit, and treated the hole-lattice coupling to linear order, using a point-ion model. Our approach differs from theirs in that we work in real space, use better interatomic potentials and go beyond the harmonic approximation. A concise exposition of the theory of hopping within the small polaron model as well as useful references can be found in the paper of Norgett and Stoneham (1973). Here we shall content ourselves with quoting the main results.

Our activation energies are calculated as differences between two energies:

$$E_a = E_r(\text{activated}) - E_r(\text{ground}) \quad (3.1)$$

† Their coefficient  $f$  for  $I_2^-$  should read  $-0.95324356$  instead of  $-0.95824356$ .

where  $E_r$  (ground) is the relaxation energy for the equilibrium configuration of the  $V_k$  centre, and  $E_r$  (activated) is the relaxation energy of the hybrid defect configuration which minimises the potential energy in a force field equal to the average of the fields in the initial and final equilibrium configurations (Norgett and Stoneham 1973, pp 240–1).  $E_a$  is the activation energy in the high-temperature limit. Experiments are usually done at temperatures well below this limit and the jump probability is fitted to an expression:

$$W_{\text{obs}} = W_0 \exp(-U_{\text{obs}}/kT). \quad (3.2)$$

In order to compare our calculated activation energies with the experimental ones, we have to assume a form like (3.2) at any temperature, which leads to an effective activation energy:

$$U = kT^2 \frac{d}{dT} \ln [W_{\text{th}}(T)]. \quad (3.3)$$

The problem of relating  $E_a$  to  $U$  for an arbitrary phonon spectrum is still open. From the work of Yamashita and Kurosawa (1958) who treated the simplest possible case, i.e. the coupling to phonons of a single frequency  $\omega$ , we can extract the following relation:

$$U = E_a 2 \operatorname{cosech}^2(y) \left( \frac{I_1[S \operatorname{cosech}(y)]}{I_0[S \operatorname{cosech}(y)]} \cosh(y) - 1 \right) \quad (3.4)$$

where  $I_0$  and  $I_1$  are modified Bessel functions,  $y \equiv \hbar\omega/2kT$  and  $S \equiv 4E_a/\hbar\omega$  is the Huang–Rhys factor (see e.g. Stoneham 1975). We shall use (3.4), with  $\omega$  equal to the longitudinal optic frequency to relate our data with experiment, although the procedure is extremely unsatisfactory, in view of the important role played by the acoustic phonons in the self-trapping process.

#### 4. Calculations and results

We have calculated the ionic configuration and relaxation energy of the  $V_k$  centre in its equilibrium and thermally activated state in the Mott–Littleton approximation, using the HADES (Harwell Automatic Defect Evaluation System) program (see e.g. Lidiard and Norgett 1972). In our final computations the number of explicitly relaxed ions was typically of the order of one hundred.

##### 4.1. Equilibrium properties

In table 1 we present the  $V_k$  formation energies. They correspond to the work required to move two  $X^-$  ions separately to infinity and then to introduce an  $X_2^-$  molecule, originally with the atoms separated, into the crystal. For comparison, the energy of a hole at the top

**Table 1.** Energy of  $V_k$  centre, compared with that of a hole at the top of the valence band in an undistorted crystal.

	CsCl	CsBr	CsI
$E_{V_k}$ (eV)	3.64	3.55	3.43
$E_T$ (eV)	6.0	5.6	5.4

**Table 2.** Displacements of a few selected ions. The coordinates refer to the cores. The origin is at the midpoint between the two  $V_k$  ions. The labels refer to figure 1.

Undisplaced site	Displaced site			
$V(\frac{1}{2}, 0, 0)$	0.334	0	0	CsCl
	0.343	0	0	CsBr
	0.362	0	0	CsI
$V(0, \frac{1}{2}, \frac{1}{2})$	0	0.557	0.557	
	0	0.557	0.557	
	0	0.554	0.554	
$B(\frac{3}{2}, 0, 0)$	1.467	0	0	
	1.467	0	0	
	1.467	0	0	
$C(1, \frac{1}{2}, \frac{1}{2})$	1.013	0.515	0.515	
	1.013	0.515	0.515	
	1.013	0.515	0.515	

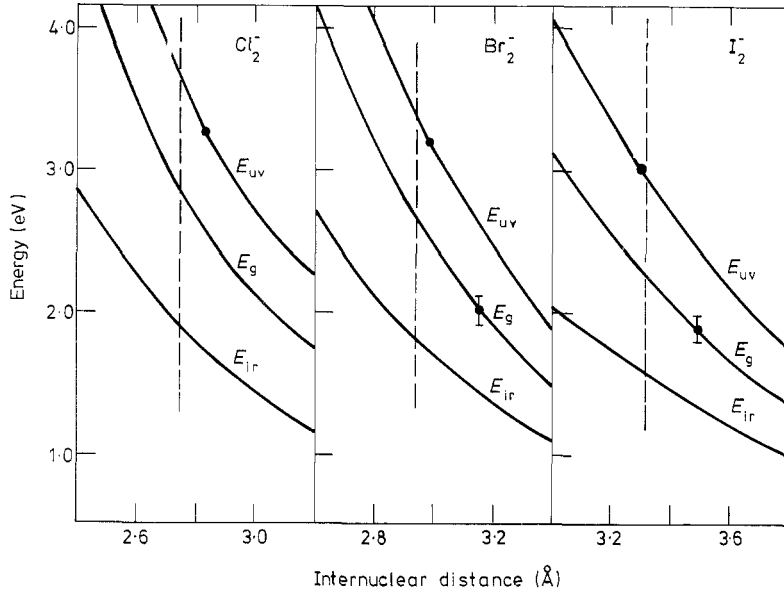
of the valence band of an undistorted crystal is roughly equal to:

$$E_{\Gamma} = E_{\text{M}} - \frac{1}{2} E_{\text{v}} \quad (4.1)$$

where  $E_{\text{M}}$  is the Madelung potential at the anion ( $29.31 \text{ eV}/a$ , where  $a$  is the lattice constant in  $\text{\AA}$ ), and  $E_{\text{v}}$  is the width of the valence band in the undistorted crystal with the spin-orbit contribution subtracted. Table 1 also contains estimates of  $E_{\Gamma}$  based on bandwidths deduced from photoelectron spectra (Poole *et al* 1975). As expected, the self-trapped configuration is more stable in all cases. In table 2 we show the displacements of a few ions in and around the  $X_2^-$  molecule. They are very similar for all three substances, their amplitude decreasing slightly with increasing anion size. Finally, in table 3, we list the separations between the two ions of the  $V_k$  centres and compare them with the equilibrium bond lengths for the free molecular ions. Once these separations are known, the transition energies to electronically excited states of the centre can be read off Tasker *et al*'s potential curves, which we reproduce in reduced form in figure 2. The calculations which led to these curves did not include the spin-orbit interaction. This should be kept in mind when comparing the results for the infrared excitation ( ${}^2\Sigma_{\mu}^+ \rightarrow {}^2\Pi_{\text{g}}$  in the standard notation) with experiment: the  ${}^2\Pi_{\text{g}}$  state is spin-orbit split, and almost all the intensity goes into the transition to the  ${}^2\Pi_{\frac{3}{2}\text{g}}$  component, which lies higher in energy than its  ${}^2\Pi_{\frac{1}{2}\text{g}}$  counterpart. The computed curves represent an average between the two transition energies. This last remark also applies to the energy  $E_{\text{g}}$  deduced from spin resonance data, and corresponding to the transition  ${}^2\Sigma_{\mu}^+ \rightarrow {}^2\Pi_{\mu}$ .

**Table 3.** Atomic separation of  $V_k$  centre (shell-shell distance), compared with the equilibrium bond-length for the free molecular ion computed by Tasker *et al*.

	CsCl	CsBr	CsI
$d_{\text{crystal}}(\text{\AA})$	2.73	2.93	3.31
$d_{\text{free}}(\text{\AA})$	2.71	2.90	3.28



**Figure 2.** Excitation energies as a function of internuclear distance in the 'molecule in the crystal' model. Shown are the ultraviolet ( $E_{UV}$ ) and infrared ( $E_{IR}$ ) optical transition energies, and the energy  $E_g$  derived from the  $g$  factor. The vertical broken lines correspond to the calculated equilibrium separations. The full circles are experimental results ( $E_{UV}$  from Sidler 1976,  $E_g$  from Pilloud and Jaccard 1975 and private communication).

#### 4.2. Hopping motion

Our calculated activation energies are collected in table 4. In all cases the  $90^\circ$  jump has a lower value of  $E_a$  than the  $180^\circ$  jump. By fitting to (3.2) thermoluminescence data for CsI doped with F centres and submitted to a 30 min  $\beta$  irradiation, Pelloux (1976) obtains the following values for the observed activation energies:

$$\text{Linear motion } (55 \text{ K} \leq T_{\text{fit}} \leq 66 \text{ K}): U_{\text{obs}}^{180^\circ} = 0.13 \pm 0.01 \text{ eV}$$

$$90^\circ \text{ jump } (84 \text{ K} \leq T_{\text{fit}} \leq 90 \text{ K}): U_{\text{obs}}^{90^\circ} = 0.20 \pm 0.01 \text{ eV}.$$

A crude estimate of the corresponding values for  $E_a$  can be found by inverting equation (3.4), and the result is:

$$E_a[180^\circ \text{ jump}] = 0.17 \pm 0.02 \text{ eV} \quad E_a[90^\circ \text{ jump}] = 0.23 \pm 0.01 \text{ eV}$$

**Table 4.** Activation energies for the two types of allowed jumps in a simple cubic structure.

	CsCl	CsBr	CsI
$E_a$ (eV) ( $09^\circ$ jump)	0.76	0.73	0.64
$E_a$ (eV) ( $180^\circ$ jump)	0.98	0.90	0.74

where the errors allow for both quoted experimental errors and for uncertainties in the choice of effective frequency. In view of the oversimplified form of (3.4) and the ambiguities connected with the determination of activation energies from glow curves, the discrepancies in magnitudes between the experimental and computed results are not surprising. Of more concern is the fact that our calculations predict a lower activation energy for  $90^\circ$  jumps. A remedy to this situation is presented below.

## 5. Discussion

The good agreement between the calculated separations of the two ions forming the  $V_k$  centre and those obtained from ultraviolet transition energies supports the 'molecule in the crystal' picture. The excitation energies deduced from spin resonance data are too low (see figure 2), a feature common to all alkali bromides and iodides (Tasker and Stoneham 1976). This is certainly due to the approximate derivation of  $E_g$  from the shift in  $g_{\parallel}$ , the  $g$  component parallel to the axis of the centre (Schoemaker 1973), which involves a perturbation expansion to second order in  $(\lambda/E_g)$  where  $\lambda$  is the spin-orbit parameter. (For  $\text{Br}_2^-$  and  $\text{I}_2^-$  the expansion parameter is respectively equal to  $\sim 0.15$  and  $\sim 0.33$ , as opposed to  $\sim 0.03$  for  $\text{Cl}_2^-$ .)

We also considered the hole's hopping motion and our results, which predict a lower activation energy for  $90^\circ$  jumps than for  $180^\circ$  jumps, are in contradiction with what is observed in CsI. Faced with the same situation in the case of the alkaline earth fluorides Norgett and Stoneham argued that, upon formation of the molecular bond the contraction of the electronic cloud should be much larger in the direction parallel to the axis of the molecule than in the direction perpendicular to it. Accordingly, they suggested a model in which the short-range repulsion between the  $V_k$  ions and the nearest-neighbour anions along the molecular axis was reduced by one half, and which predicted the correct trend. Their argument should *a fortiori* apply to the larger anions considered here, and we have performed calculations along these lines. In all three cases we find that a decrease in the short-range repulsion between ions V and B (see figure 1) by 50% brings the activation energy for linear motion below the one for  $90^\circ$  jumps, without introducing any significant change in the latter and in the equilibrium properties.

## Acknowledgments

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## Appendix 1. Model parameters

### A1.1. Perfect lattice

Repulsive and Van der Waals potential  $V_{ij}(r) = A_{ij} \exp(-r/\rho) - c_{ij}/r^6 - D_{ij}/r^8$ .

Shell charges

$Y_+$        $Y_-$

Spring constants

$k_+$        $k_-$

	CsCl	CsBr	CsI
$A_{++}$ (eV)	8908.0	5815.0	3599.0
$A_{+-}$	5602.0	5815.0	6563.0
$A_{--}$	3523.0	5815.0	11965.0
$C_{++}$ (eVÅ <sup>6</sup> )	411.0	390.0	359.0
$C_{+-}$	0.0	0.0	0.0
$C_{--}$	349.0	550.0	1002.0
$D_{++}$ (eVÅ <sup>8</sup> )	751.0	714.0	657.0
$D_{+-}$	0.0	0.0	0.0
$D_{--}$	702.5	1258.0	2813.0
$\rho$ (Å)	0.3234	0.3348	0.3496
$Y_+$ ( e )	-6.25	-6.08	-6.13
$Y_-$	-1.64	-1.69	-1.87
$k_+$ (eVÅ <sup>-2</sup> )	220.0	198.0	187.0
$k_-$	11.5	8.90	7.25

### A1.2. $X_2^-$ molecule potential and shell parameter

$V(r) = A \exp(-r/\rho) - C/r^6$ , shell charge  $Y_{1/2}$ , spring constant  $k_{1/2}$

	Cl <sub>2</sub> <sup>-</sup>	Br <sub>2</sub> <sup>-</sup>	I <sub>2</sub> <sup>-</sup>
$A$ (eV)	11956.7	11640.7	11554.0
$\rho$ (Å)	0.3339	0.3554	0.3936
$C$ (eVÅ <sup>6</sup> )	1913.7	2693.5	4803.0
$Y_{1/2}$ ( e )	-2.485	-2.705	-4.087
$k_{1/2}$ (eVÅ <sup>-2</sup> )	54.216	42.485	59.532

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