# PROPRIÉTÉS GÉNÉRALES DES CENTRES COLORÉSTHEORETICAL STUDIES OF SOME ACTIVATION ENERGIES OF F- AND FΛ-CENTRES IN KCl

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# THEORETICAL STUDIES OF SOME ACTIVATION ENERGIES
# OF F- AND $F_A$-CENTRES IN KCl (*)

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**Résumé.** — Les énergies d'activation pour la diffusion par sauts du centre F et la réorientation des centres $F_A$(Na) et $F_A$(Li) dans KCl sont analysées théoriquement. Pour chaque défaut dans l'état fondamental et le premier état excité, l'énergie d'activation s'exprime par la somme des contributions de *a*) l'excès d'énergie cinétique de l'électron, *b*) son interaction avec le réseau, *c*) l'énergie de réseau du défaut et *d*) l'effet résultant de la distorsion élastique du réseau non comprise dans *a*) et *c*).

**Abstract.** — The activation energies for step-diffusion of the F-centre and reorientation of $F_A$(Na) and $F_A$(Li)-centres in KCl are analysed theoretically. For each defect in both ground and first excited states, the activation energy is expressed as a sum of contributions from *a*) the excess electron's kinetic energy, *b*) its interaction with the lattice (unpolarizable point ions with BSG ion-size correction), *c*) the lattice energy of the defect, and *d*) the net effect of harmonic lattice distortion, not included in *a*)-*c*). The method of lattice statics is applied, with the electronic state and lattice distortion determined self-consistently, using the variational method. When the activation energies are compared with experiment, we find the F-centre results about 0.5 eV too high, but qualitatively correct, the $F_A$(Na) and $F_A$(Li) ground state results in good agreement, and the $F_A$(Li), relaxed excited state (RES) result qualitatively correct. The excess electron's kinetic energy is dominant in lowering the RES activation energy relative to that in the ground state, and the effect of small impurities ($Na^+$ and $Li^+$) in lowering the activation energies in both states is about equally divided between lattice energy and Coulomb electron-lattice interaction.

**1. Introduction.** — Vacancy-type diffusion processes associated with colour centres are of importance in studies of formation, aggregation, and luminescence. The prototype process is vacancy diffusion. In figure 1 we illustrate anion vacancy diffusion in a NaCl-type alkali halide. In this process, a negative ion jumps into a nearest anion vacancy : the vacancy undergoes a diffusion « jump ». The activation energy is the difference between the activated configuration's energy and the initial (vacancy) configuration's energy. The activated configuration as illustrated in figure 1 is the so-called saddle-point configuration, in which the diffusing anion is in the plane of the diagram. This corresponds to the assumption on which the theoretical analysis of this process [1], [2] has been based, namely that the diffusing anion follows a straight-line

path, encountering a potential barrier whose height is the activation energy defined above. We shall report later an investigation of this assumption for related F-centre diffusion processes (Appendix).

An F-centre, which is an excess electron occupying an anion vacancy, may undergo the so-called « step-diffusion » process [3], analogous to vacancy diffusion, as in figure 2. In this process, the F-centre and a nearest anion exchange positions. The activation energy depends sensitively on the electronic state of the F-centre. Since both the ground and first excited states are quasi-stationary, either one of them may participate in a step-diffusion process, as illustrated in figures 2*a* and *b*. We have considered the possibility that the anion involved in F-centre step-diffusion may follow a path which carries it out of the plane of the diagram, because it may then encounter a slightly lower potential barrier than it would in passing through the strict saddle-point configuration of figure 1 (see Appendix). The diffusing anion is therefore indicated by a dashed circle in the activated configuration of figure 2.

7

initial (vacancy)
configuration

activated (saddle-point)
configuration

final ( vacancy )
configuration
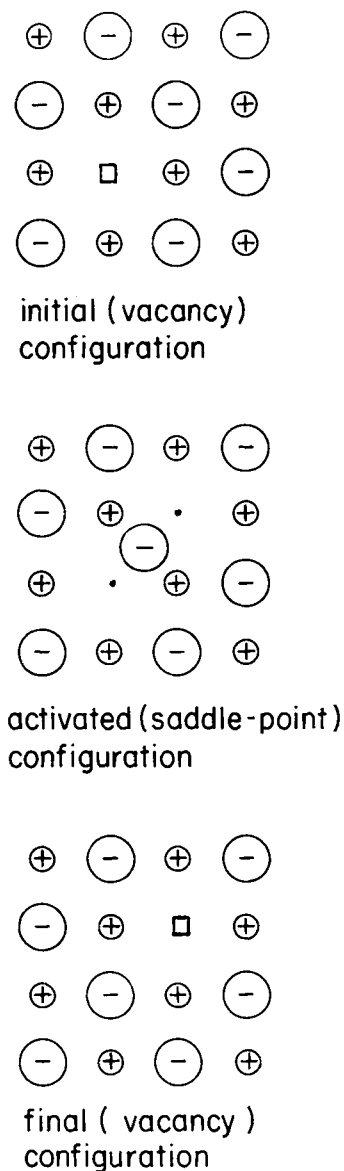
FIG. 1. — Anion vacancy diffusion process in KCl.



(a) Ground (even parity)
Electronic State

initial (vacancy)
configuration

activated (saddle-point)
configuration

final (vacancy)
configuration

(b) First Excited (odd parity)
Electronic State

initial ( vacancy )
configuration

activated (saddle-point)
configuration

final (vacancy )
configuration

FIG. 2. — F-centre step diffusion process in KCl. Crosshatched region represents the excess electron. Dashed circle for the saddle-point anion indicates asymmetrical position, out of the plane of the diagram.
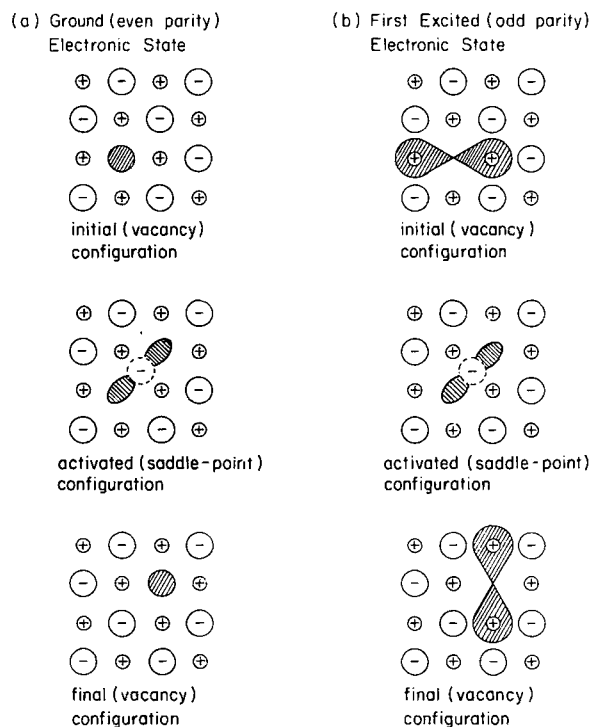
An $F_A$-centre has a substitutional impurity cation adjacent to an F-centre [4]. Consider the nearest neighbour $K^+$ ion lying immediately to the right of the F-centre in the initial configuration of figure 2. Now let it be replaced by a substitutional $Na^+$ or $Li^+$ ion. Then we have the so-called Type I $F_A(Na)$ or Type II $F_A(Li)$-centres respectively. The Type I $F_A(Na)$-centre behaves much like an F-centre, figure 2. However, an $F_A$-centre has an orientation in either electronic state. This orientation is given by the position of the excess electron relative to the substitutional impurity. Thus, for an $F_A$-centre as described above, the step diffusion process of figure 2 becomes a *reorientation* process. (For the F-centre in figure 2, there is no significance to the orientation shown for the odd-parity excited-state wave function. The figure is drawn in such a way that, for the corresponding $F_A$-centre described above, the odd-parity wave function would overlap the impurity cation in both initial

and final configurations of the reorientation process. However, the orientation of the $F_A$-centre refers only to the position of the anion vacancy relative to the impurity cation.)

The type II $F_A(Li)$-centre can undergo the reorientation process only in its electronic ground state. This is because its first excited state in the vacancy configuration is not even quasi-stationary, and therefore cannot serve as the initial configuration of a diffusion process. Instead, the excited state is stabilized in the saddle-point configuration [5]. Thus only figure 2a, but not figure 2b, modified by a substitutional $Li^+$ impurity, applies to the type II $F_A(Li)$-centre. The activation process of both types of $F_A$-centre in KCl has the diffusing anion following a straight-line path (see Appendix).

In figure 3 we display the experimental values for the activation energies of the processes described above. The sources of these data are : anion vacancy [6] : F-centre ground state [3] ; $F_A(Na)$ and $F_A(Li)$ ground states [7] ; F-centre excited state (empirical estimate) [8] ; $F_A(Na)$-centre excited state [9] ; $F_A(Li)$-centre excited state [5], where < 0 indicates stabilization in the saddle-point configuration. The data of figure 3 have two striking features :

1) The large splitting between the activation energies associated with ground and excited states, respectively, for a given colour centre ;

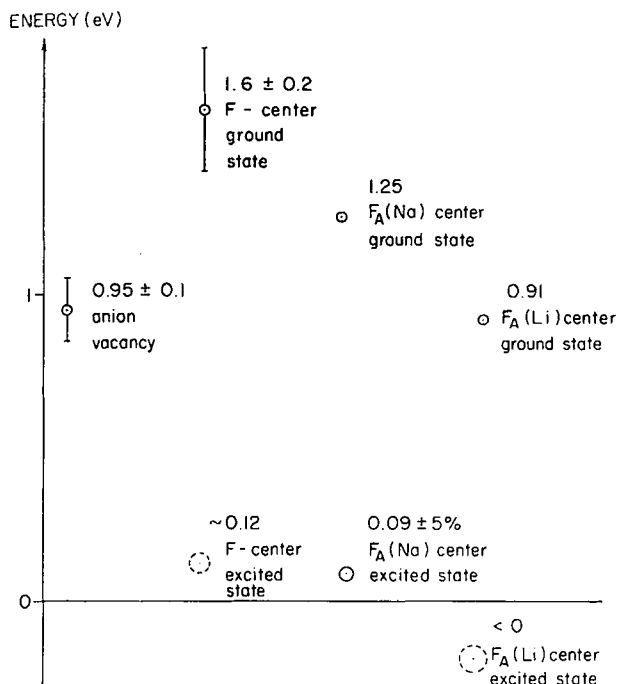2) The progressive lowering of both ground and excited state activation energies as one goes from F-

ENERGY (eV)



1.6 ± 0.2
φ F - center
  ground
  state

1.25
⊙ F$_A$(Na) center
  ground state

1- ⫶ 0.95 ± 0.1
   φ anion
     vacancy

0.91
⊙ F$_A$(Li) center
  ground state

~0.12
⟨⟩ F - center
   excited
   state

0.09 ± 5%
○ F$_A$(Na) center
  excited state

0-

< 0
⟨⟩ F$_A$(Li) center
  excited state

FIG. 3. — Experimental values, in eV, of the activation energies of defects in KCl.

centre to F$_A$(Na)-centre to F$_A$(Li)-centre, i. e. : as the associated cation is reduced in size from K$^+$ to Na$^+$ to Li$^+$.

It is the objective of this work to elucidate these two effects.

2. **Theoretical method.** — We have carried out analyses of the F-centre [[10] a), b)] and of the F$_A$-centres [11] in KCl, which provide estimates of the defect energy in both ground and first excited states, in both initial (vacancy) and activated (saddle-point) configurations. Our theoretical model, approximations, and methods, have been described in reference [10], and particularly in section II of reference [11]. We give only the simplest outline here. We assume a lattice of unpolarizable point ions with Coulomb forces, plus Born-Mayer repulsion between nearest neighbours. For the electron-lattice interaction, we include Coulomb forces plus the ion-size correction of Bartram *et al.* [12]. We use simple variational wave functions for the F-centre electron, with Gaussian localization in all cases, spherically symmetric for the vacancy configuration ground state, a first order Legendre polynomial for the angular dependence of the first excited state, and a linear combination of zeroth- and second-order Legendre polynomials for the saddle-point ground state. The Kanzaki method [13], [14], [15] is then applied to produce a rigorously self-consistent energy estimate, accurate to second-order small quantities, by minimization with respect to wave-function parameters and ionic displacements.

The estimated energy of a given defect in a given

electronic state with a given lattice configuration is expressible as a sum of five terms, as follows :

$$E = \overline{T} + \overline{V}_{PI} + \overline{V}_{IS} + V_L(0) + (d.e.).\qquad(1)$$

In eq. (1), the effect of the harmonic part of the lattice distortion field is omitted in the first four terms, and is fully included in the last. The terms have the following meanings :

$\overline{T}$ = electron's kinetic energy,

$\overline{V}_{PI}$ = interaction of electron with point-ion lattice,

$\overline{V}_{IS}$ = ion-size correction to electron-lattice interaction,

$V_L(0)$ = lattice energy of defect relative to the perfect lattice,

(d.e.) = *total* effect of including region II harmonic distortion self-consistently.

3. **Results.** — The F-centre calculation was first performed [[10] a), b)] on the assumption that, in the activated configuration, the diffusing anion lay in the strict saddle-point position, in the plane of the diagram of figure 2. The results of that analysis are summarized in table I of reference [[10] b)]. More recent analysis has shown that in zeroth-order the saddle-point ion has a slightly lower energy (~ 0.03 eV lower) in a position displaced out of the plane of figure 2 (Appendix). Whether this is the real activated configuration for our model depends on what happens to the relative energies of the strict saddle-point and displaced saddle-point configurations when the second order corrections from the Kanzaki method are included. As discussed in the Appendix, it is also necessary to include second neighbour repulsion for the displaced saddle-point Cl$^-$ ion. While the question of a displaced saddle-point for the activated configuration of the F-centre is extremely interesting, it appears from our work to date that its energy will not be much different from that of the strict (symmetrical) saddle-point analysed in reference [10], and accordingly the following discussion is based on the latter work.

Let us first examine the contribution from each term in eq. (1) to the splitting between the activation energies for a given colour centre in its ground state and in its excited state. If we let subscripts v and sp refer to vacancy and saddle-point lattice configurations respectively, and superscripts (e) and (o) refer to ground (even parity) and excited (odd parity) electronic states, then we have activation energies $E_{act}^{(e)}$ and $E_{act}^{(o)}$ as follows :

$$E_{act}^{(e)} = (E_{sp}^{(e)} - E_v^{(e)}),\qquad(2)$$

$$E_{act}^{(o)} = (E_{sp}^{(o)} - E_v^{(o)}),\qquad(3)$$

and the splitting $\Delta E_{act}$ between the activation energies is :

$$\Delta E_{act} = (E_{act}^{(e)} - E_{act}^{(o)}).\qquad(4)$$

We denote the contributions to $\Delta E_{\mathrm{act}}$, eq. (4), from the individual terms in eq. (1) by $\Delta \overline{T}$, etc. The relevant data for evaluating these contributions are found in table I of reference [[10] b)] and in table V of reference [11]. The results are given in table I for the F-centre, $F_A(Na)$ and $F_A(Li)$-centres. The experimental values obtainable from figure 3 are also given, for comparison.

## TABLE I

Contributions from eq. (1) to the splitting $\Delta E_{\mathrm{act}}$, eq. (4), between the activation energies of colour centres in their ground and excited states. Energies in eV.

| | F | $F_A(Na)$ | $F_A(Li)$ |
|---|---|---|---|
| $\Delta \overline{T}$ | 1.57 | 1.49 | 1.44 |
| $\Delta \overline{V}_{PI}$ | 0.10 | 0.22 | 0.23 |
| $\Delta \overline{V}_{IS}$ | 0.03 | 0.12 | 0.11 |
| $\Delta V_L(o)$ | -0.02 | -0.03 | -0.01 |
| $\Delta$(d.e.) | 0.04 | -0.29 | -0.33 |
| $\Delta E_{\mathrm{act.}}$ (theor.) | 1.72 | 1.51 | 1.44 |
| $\Delta E_{\mathrm{act.}}$ (exp't.) | ~1.5 | 1.16 | >0.91 |

The main qualitative feature of table I is that the electron's kinetic energy is mainly responsible for the splitting between ground and excited state activation energies. Examination of the data of references [10] and [11] reveals that this is because the electron's kinetic energy drops considerably in going from the vacancy to the activated (saddle-point) configuration in the excited state, but changes very little (rises only slightly) in the ground state process. The drop in excited-state kinetic energy between vacancy and saddle-point configurations is associated with a slight delocalization as the electron goes from binding to two nearest cations to binding in a rather weak two-well potential (Fig. 2b). We also note that the contributions $\Delta \overline{V}_{PI}$, $\Delta \overline{V}_{IS}$, $\Delta V_L(o)$, and $\Delta$(d. e.) in table I are very similar for $F_A(Na)$ and for $F_A(Li)$, and that they are larger than the corresponding contributions for the F-centre, but are almost exactly self-cancelling.

Next let us examine the effect of progressively smaller substitutional cations $Na^+$ and $Li^+$ on the F-centre's activation energy. For each type of $F_A$-centre in each electronic state, we evaluate the contribution from the terms in eq. (1) to the difference between F-centre and $F_A$-centre activation energies. The resultant data, obtained from references [10] and [11], are given in table II. The cumulative contributions are plotted in figure 4, and the experimental activation energies are shown for comparison.

The main qualitative features of figure 4 are as follows. First, for the ground (even parity) state, the

## TABLE II

Contributions (eq. (1)) to the difference between F-centre and $F_A$-centre activation energies. Energies in eV.

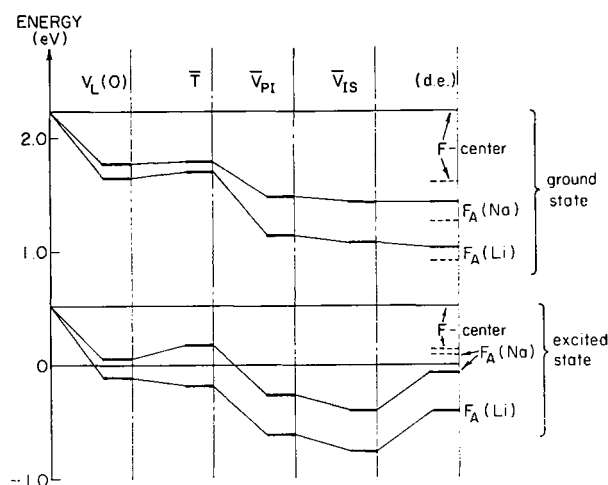| | F-$F_A$(Na) | | F-$F_A$(Li) | |
|---|---|---|---|---|
| | ground | excited | ground | excited |
| $V_L(o)$ | 0.46 | 0.45 | 0.61 | 0.62 |
| $\overline{T}$ | -0.03 | -0.11 | -0.05 | -0.17 |
| $\overline{V}_{PI}$ | 0.32 | 0.44 | 0.57 | 0.70 |
| $\overline{V}_{IS}$ | 0.05 | 0.14 | 0.06 | 0.14 |
| (d.e.) | 0.00 | -0.33 | 0.01 | -0.36 |
| Total | 0.80 | 0.59 | 1.20 | 0.93 |



FIG. 4. — Cummulative contributions (eq. (1)) to the difference between F- and $F_A$-center activation energies in KCl. The solid lines are theoretical and the dashed lines are experimental.

impurity ion depresses the F-centre's activation energy in two approximately equal steps, arising from (i) the non-harmonic lattice defect energy $V_L(o)$, and (ii) the point-ion interaction with the electron $\overline{V}_{PI}$, and each of these effects is greater for the $Li^+$ impurity than for the $Na^+$. The $V_L(o)$ effect probably arises because a small impurity in a KCl lattice is not as tightly pressed against its nearest neighbours as is a host $K^+$ ion, particularly in the saddle-point configuration. The $\overline{V}_{PI}$ effect is not easily understood intuitively, but it indicates that $\overline{V}_{PI}$ rises more during F-centre activation than during $F_A$-centre activation. For the excited (odd parity) state, relatively large effects again arise from $V_L(o)$ and $\overline{V}_{PI}$, but in addition there is a comparable effect in the opposite direction from the harmonic distortion (d. e.). Thus the excited state activation energies are lowered less than the ground state activation energies by the small impurity cation. If we compare the theoretical results with experiment in figure 4, we observe that (i) the theoretical ground state activation energies agree reasonably well with

experiment for both $F_A(Na)$ and $F_A(Li)$ centres ; (ii) both ground and excited state theoretical F-centre activation energies are about 0.5 eV above the experimental values ; and (iii) the theoretical excited state $F_A(Na)$ activation energy is slightly negative, whereas the experimental value is slightly positive. (Recall that a negative activation energy indicates a stabilized saddle-point configuration.)

4. **Discussion and conclusions.** — While the investigations reported here have been rather complicated to perform, they are still somewhat rudimentary in several aspects. The model and method have been critically discussed in section IV of reference [11]. There are several possible improvements that are in principle straightforward, but which would be quite time-consuming. They include more flexible trial wave-functions, less symmetric lattice configurations, and inclusion of ionic polarizability. We feel that the description of the relaxed excited state is inadequate, and that parity-mixing and possibly other lattice-dynamic effects are of importance. It may be that more precise characterization of interionic forces and of the ion-size effect are also required.

In spite of the above limitations, we have been able to theoretically demonstrate and analyse the splitting of the activation energies for different states of an F- or $F_A$-centre, the successive lowering of these activation energies by successively smaller substitutional cation impurities, and the stabilization of the Type II $F_A$-centre's relaxed excited state in the saddle-point configuration. We feel that these successes should encourage further work in a similar direction.

**Appendix.** — In this appendix we report an investigation of the following question : For F- and $F_A$-centres, is the activated configuration, figure 2, such that the diffusing anion lies in the plane of the diagram, or is it displaced out of the plane of the diagram ? We begin with a consideration of the relaxed excited state, figure 2b, and we evaluate the energy of the system for a succession of values of the displacement $x'$ of the saddle-point ion perpendicular to the plane of the diagram, under the following conditions : (i) the wave function remains centred at the saddle-point position, in the plane of the diagram ; (ii) all ions except the two positive ions nearest to the saddle-point remain fixed at their perfect lattice positions ; (iii) the energy is self-consistently minimized with respect to the trial wave function parameter and with respect to displacements of the two nearest positive ions in the plane of the diagram. (In the $F_A$-centres, one of these ions is $K^+$ and the other is either $Na^+$ or $Li^+$, so their displacements are different.) The results of this calculation are shown in figure 5. We see that the energy rises monotonically with $x'$ for the $F_A$-centres, but
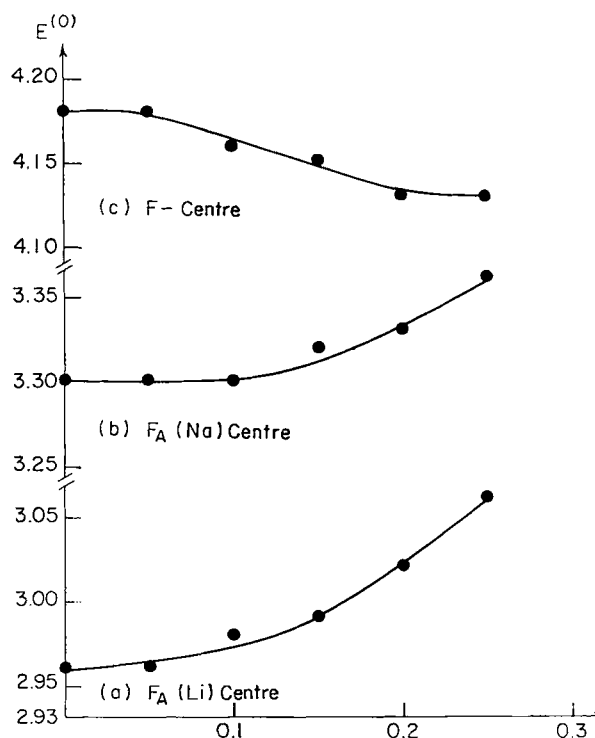


Fig. 5. — Zeroth order excited state energies of F and $F_A$-centres in KCl, as a function of displacement $x'$ of the Cl$^-$ ion from the saddle-point ($x'$ in units of nearest neighbour distance).

drops and then levels off for the F-centre at a value $x' \gtrsim 0.2\ a$, where $a$ is the nearest neighbour distance in the perfect KCl lattice. At this distance, $x' \sim 0.2\ a$, one expects the repulsive interaction between the diffusing Cl$^-$ ion and the nearest ions in the lattice plane above that of the diagram to become significant, and their ultimate displacements may also become non-harmonic, necessitating their inclusion in the zeroth-order calculation. In order to get some reasonable indication of what happens in F-centre step diffusion, we have performed the following calculation : (i) introduce Born-Mayer (Huggins-Mayer) repulsion between the saddle-point Cl$^-$ ion and its eight second Cl$^-$ neighbours, using the so-called WTF parameters of Tosi and Fumi for Cl$^-$-Cl$^-$ repulsion (ref. [16], Table I, column 1), which we denote $A'\exp(-r/\rho)$ where, from the data of reference [16], $A' = 2.51 \times 10^3$ eV and $\rho = 0.337$ Å, for KCl; (ii) evaluate the energy for successive values of $x'$ as before. The result is that the dip in figure 5c has been wiped out, and the new curve rises monotonically, rather steeply. We would not expect fuller treatment of the problem, including second neighbour interactions among all ions, a floating-centre wave function, and the lattice statics treatment of region II relaxation to alter the conclusion that the activated configuration of the F-centre involves a symmetrical saddle point.

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## DISCUSSION

I. Alsaffar. — From photoconductivity of additively coloured KCl we measured an activation energy for the excited state of F-centre of 0.18 eV. This value is higher that what has been stated. Could this be due to the increase of electron mobility as a result of thermally assisted tunneling from one excited state to a neighbouring F-centre ? The life-time of the excited state was prolonged since there was temporary formation of F' approximately $10^{-1}$ s.

J. M. Vail. — The experimental value of 0.12 eV for excited state F-centre activation, given in figure 3, is based on extrapolation of an empirical curve given in Lüty's 1968 review of $F_A$-centres. Our theoretical value is around 0.50 eV, which is probably too high. I cannot comment on the interpretation of your experimental results.