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Theoretical simulation of V_K -centre migration in KCl: I. A quantum-chemical study

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Abstract. Using embedded quantum cluster models, we have studied the mechanism of V_K -centre 60° reorientation in KCl and LiCl, and have considered the possibility that both one-centre 'dielectric' polarons and 'molecular' polarons (V_K centres) coexist in KCl. These studies have shown that lattice polarization lowers the activation energy for V_K reorientation since the V_K centre strongly polarizes near the barrier point. The calculated adiabatic barrier for V_K reorientation is 0.63 eV, in reasonable agreement with the available experimental data. From the self-trapping energy calculations and the analysis of the structure and mechanism of the diffusion of the one-centre 'dielectric' polaron, it is apparent that it transforms adiabatically into a V_K centre without an energy barrier.

1. Introduction

The possibility of the coexistence of 'dielectric' and 'molecular' polarons in ionic solids has been discussed in several studies [1-3]. The self-trapping of 'dielectric' polarons is caused solely by the electron or hole interaction with a polar lattice, whereas in the case of 'molecular' polarons a decisive role is also played by the formation of a chemical bond between the ions that carry the net polaron charge. However, clear experimental evidence for the coexistence of these two types of polarons still does not exist. In this paper we shall consider this problem as related to alkali halide crystals, and in particular to KCl, where trapping and diffusion of electrons and holes has been studied most extensively. It is well established that the 'molecular' polaron (V_K centre) is energetically the most favourable self-trapped form of the hole in these crystals [4]. Since both types of polarons must be separated by an energy barrier [1-3], a transformation between 'molecular' and 'dielectric' forms requires thermal activation. Therefore, one way of observing this effect is to study the process of 'molecular' polaron diffusion. We consider this process from the point of view of both the mechanism of V_K centre diffusion and the kinetics of its recombination with electronic centres.

Experimental investigations of the dynamical properties of V_K centres in alkali halides were initially mainly concerned with a determination of the activation energy E_a for thermally activated hopping [5]. From optical dichroism studies [6] it was

concluded that V_K motion in FCC alkali halides occurs predominantly through 60° rotations. In particular, from these polarization experiments, the relevant activation energies for reorientations and frequency factors for KCl were determined to be $E_a = 0.54$ eV and $S_r = 4 \times 10^{13}$ s $^{-1}$. The same value of E_a was obtained by means of the fractional glow technique (which is a generalization of the standard thermostimulated luminescence (TSL) method) applied to mobile V_K recombination with Tl^0 centres in activated alkali halides [7].

On the other hand, pulse studies of V_K trapping by Tl impurities in KI:Tl, NaI:Tl and KCl:Tl performed over a wide temperature interval [8, 9] have resulted in the conclusion that the standard theory of continuous diffusion-controlled reactions [10] fails to describe these experiments: the measured V_K centre lifetimes appeared to be more than one order of magnitude less than would be expected theoretically using the value of S_r obtained from the polarization experiments and the reorientational hop length l . This observation was interpreted by the authors in terms of an occasional breaking of the X_2^- ($X =$ halogen ion) chemical bond during V_K reorientation with a further long-range rapid motion of the hole, which ends with a new self-trapping [8, 9, 11]. The effective activation energy for such 'hot' hole creation in all alkali halides under study turned out to be the same as for the V_K centre reorientational hops [8]. As such, the formation and fast resonant motion of 'dielectric' small-radius polarons (SRP) or even free holes during V_K -centre reorientation seems a possibility. The problem as we wish to address it is therefore: do relaxed 'dielectric' fast hole polarons exist in the alkali halide crystals, at least as kinetic particles?

As an initial step towards answering this question we have performed adiabatic calculations of 60° reorientations of V_K centres in KCl and LiCl, and analysed the redistribution of the hole density accompanying this process. These studies have demonstrated three points. First, the lattice polarization contributes strongly to the activation energy for V_K reorientation. Secondly, the V_K centre is strongly polarized near the barrier point such that the hole is almost totally localized on one of the chlorine ions that formed the Cl_2^- molecule. However, the chemical bond between the two chlorine ions of the Cl_2^- molecule is maintained at all points of the adiabatic potential energy surface and only switches at the barrier point. The height of the potential barrier calculated for KCl (0.63 eV) is in reasonable agreement with the experimental value (0.54 eV [6]). Thirdly, we find that the energy of the saddle point for the reorientation between two V_K -centre configurations is close to the energy of the relaxed one-centre 'dielectric' polaron state. Consequently there is a small probability that the system will tunnel into this state. However, the present analysis of the structure and the mechanism of diffusion of this polaron has shown that it adiabatically transforms into the V_K centre without any barrier.

In the second part of this work, we report a careful analysis of the experimentally observed kinetics for V_K -centre recombination with electronic centres [12]. This latter study was stimulated by experiments on V_K recombination with electron centres at moderate temperatures below the TSL peak (208 K in KCl) [7]. In order to detect hole centre migration in these studies, after the moment when the recombination intensity reached its steady-state magnitude (at temperatures close to those at which V_K centres become mobile), a small (3–5 K) stepwise increase in temperature (and hence mobility) was used. It resulted in a very delayed (~ 300 s) increase of the recombination luminescence intensity I , which was interpreted [7] as an additional argument for the slow motion of V_K centres via short hops (reorientations), but excluded the rare long hops discussed above.

A qualitative theoretical basis of these delayed reactions was presented quite recently [13] and lent support to the model of only reorientational motion of the V_K centre. However, the agreement between the theory and the experiment was only satisfactory due to the continuous diffusion approximation used. Therefore, in the second part of the present work [12], a more appropriate theory is developed, which takes into account finite hop lengths of V_K centres through the crystalline lattice.

The plan of this first paper is as follows. We first discuss, in section 2, the method of calculation, which is based on the embedded molecular cluster quantum-chemical approach. In sections 3.1 and 3.2 the V_K -centre structure, vibration and reorientation are simulated with particular reference to the associated polarization of the Cl_2^- molecular ion. The calculations discussed in section 3.3 concern the one-centre dielectric polaron and its stability as an intermediate in V_K -centre migration. In section 4 we summarize the main results of the study.

2. Method of calculation

Of the several theoretical studies aimed at estimating the activation energy of V_K -centre reorientations in cubic lattices [14, 17], the most comprehensive were concerned with the mechanism of this process in CaF_2 [16] and caesium halides [17]. Being based on atom-atom potentials, these calculations resulted in E_a values that are rather far from experimental data; the predominant reorientation through experimentally known angles is also not confidently reproduced. On the other hand, since the same technique was very successfully used to study the static properties of hole defects in alkali halide crystals [18], one is tempted to suppose that electron density redistribution plays a decisive role in determining E_a for V_K reorientation, and, as such, a quantum-chemical approach is more suitable to tackle the problem. It is certainly the only way to determine whether the V_K centre could be transformed into a mobile hole during reorientation.

In calculations on hole states we need to reproduce reliably both the chemical interactions of ions near the hole centres and the long-range polarization of the crystal. For this purpose the embedded molecular cluster (EMC) [19–21] model was implemented, which has been successfully used to study the static properties of V_K centres in alkali halides [22, 23] and, in addition, impurity-induced hole trapping in MgO [19, 21, 24].

In the EMC approximation, two different problems are solved in a self-consistent manner, namely the electronic structure of the quantum cluster embedded in the field of the polarized lattice, and the distortion of the lattice surrounding a defect, the polarization induced by the defect [19–21].

Two computer codes based on the EMC approximation, but employing different calculation techniques, are available for the study of point defects in ionic crystals: the ICECAP code [21, 25] and the CLUSTER code [19, 26]. Both codes combine the unrestricted Hartree-Fock-Roothaan (UHF) method [27] of calculating the electronic structure of the molecular cluster with the classical Mott-Littleton approach [28], which accounts for the polarization of the rest of the crystal. One of the basic ideas of the Mott-Littleton approach is to divide the crystal into two regions: an inner region (I), containing the defect and its immediate surrounds, and an outer region (II), which responds as a dielectric continuum [28]. The molecular cluster is placed at the centre of region I. There are the following basic differences between the two codes: (i)

the ICECAP code employs the *ab initio* UHF method whereas the CLUSTER code is based on the semi-empirical version of the UHF method implementing the approximation of intermediate neglect of differential overlap (INDO) [27]; (ii) the lattice ions in region I outside the cluster are treated in the ICECAP code within the shell-model approximation [28] and in the CLUSTER code using the non-point polarizable ion approximation [20, 26, 29]. Most of the present calculations were made employing the CLUSTER code. Calculations using the computationally more expensive ICECAP code were used where necessary for comparison. Despite certain discrepancies, we shall demonstrate that both methods yield similar results for the atomistic and electronic structures of the V_K centre. Let us discuss first some important details of the calculations.

The CLUSTER code allows us to determine the electronic structure of a quantum cluster containing several tens of ions. The parameters of the INDO method were first optimized to reproduce both the principal features of the electronic structure of the perfect crystals under study as well as the equilibrium distances and dissociation energies of relevant diatomic molecules (including K_2^+ , KCl, Cl_2 , Cl_2^-) [26]. Such a parametrization improves the reliability of the defect calculations especially for the quasi-molecular V_K centres whose properties are closer to those of the free Cl_2^- molecules than to the bulk halide [4]. The basis sets contained 3s, 3p Slater-type atomic orbitals (AO) for Cl^- , 4s, 4p for K^+ , 2s for Li^+ . The ionic polarizabilities were taken from [30].

The lattice outside the cluster is constructed from ions carrying the same basis of AO as inside the cluster, but with the Löwdin populations [27] of these AO frozen to those AO populations of the perfect lattice. The crystal lattice constant a (calculated to be 3.116 Å in KCl) and the populations of AO were obtained in a previous study of the perfect crystals using the periodic large unit cell (LUC) model [31]. In the present version of the EMC method only the Coulomb and charge-dipole interactions between the cluster and the remaining crystal are included in the calculation of elements of the Fock matrix. In the CLUSTER code the Coulomb interaction between ions inside and outside the cluster is calculated explicitly as between quantum-mechanical ions, although the angular dependence of the AO in the Coulomb integrals is neglected [27]. The potential of the lattice of non-point spherical ions is summed to infinity using the Ewald method [26].

The difference between the charge-density distributions in the cluster, containing the defect, and the perfect lattice produces an electric field, which acts on the rest of the crystal. This is calculated on each of the several iterations of the UHF self-consistency procedure. Two types of dipoles are created in the lattice as a response to this field: point dipoles on the polarized ions and ion-vacancy dipoles, which correspond to ions being displaced from their lattice sites due to the lattice distortion. The potential produced by the dipoles located in region I as well as the potential produced by region II (treated in the Mott-Littleton approximation [28]) is included in the calculation of the diagonal elements of the Fock matrix. Particular details of the calculation scheme and the self-consistency procedure are presented in [19].

Electronic excitation energies were calculated as the differences between the total self-consistent energies of a crystal in its ground and excited states (the Δ SCF method). For paramagnetic defects such as V_K centres it is also of interest to calculate, along with their migration energies and optical absorption spectra, the g -tensor. For these purposes the Stone equation [32], derived from second-order perturbation theory (PT2) applied to the spin-orbit and Zeeman interactions of an unpaired electron or-

bital momenta with the magnetic field, is widely used in quantum chemistry. However, for high-symmetry defects, such as V_K or H centres in alkali halides, PT2 yields zero shifts of the longitudinal components of a tensor, $\Delta g_{\parallel} = g_{\parallel} - g_0$ ($g_0 = 2.0023$), owing to the zero value of the relevant matrix elements between ground and all excited states. As is shown in [33–35], in this case a much better agreement with experimental data can be achieved by taking into account third-order perturbation corrections (PT3). We have recently derived a novel technique [36] permitting us to calculate g -factors by means of quantum-chemical methods based on PT2 and PT3 corrections for an arbitrary total electron spin of the paramagnetic defect. In the particular case $S = \frac{1}{2}$ our equations are reduced to those derived by Moreno [33].

3. V_K -centre structure and reorientation

3.1. Structure and spectroscopic properties of the V_K centre in KCl

V_K centres in alkali halides have been intensively investigated both experimentally [4] and theoretically [4, 22, 23, 37, 38]. Traditionally they are treated as a negatively charged diatomic halide molecule X_2^- occupying two anion sites and oriented along a $\langle 110 \rangle$ crystalline axis [4].

Displacements of ions surrounding the V_K centre in KCl calculated in this paper using the semi-empirical CLUSTER code and obtained in ICECAP calculations [23] agree quite well with one another as well as with the results of earlier pair-potential Mott–Littleton calculations [37]. The V_K -centre absorption energies calculated by both semi-empirical and Hartree–Fock codes and the g -tensor, calculated semi-empirically, using second- and third-order perturbation theory, are summarized in table 1. Along with the generally good agreement with experiment achieved with both methods, it should be noted that, as expected, PT3 gives much better results for the longitudinal component of the g -tensor. Agreement between the results of the different methods for the V_K geometry, absorption and g -tensors proves the reliability of the semi-empirical INDO scheme, which was used exclusively for the following computer simulations of V_K -centre reorientation.

Table 1. Spectroscopic properties of V_K centre (a) Excitation energies. (b) Principal values of g -tensor.

(a) Transition	Code		Experiment
	ICECAP	CLUSTER	
$b_{3u} \rightarrow b_{1g}$	1.85	1.39	1.65
$b_{3u} \rightarrow b_{2g}$	1.87	1.40	1.65
$b_{3u} \rightarrow b_{1u}$	2.67	2.53	2.75
$b_{3u} \rightarrow b_{2u}$	2.88	2.98	2.75
$b_{3u} \rightarrow a_{1g}$	3.40	3.40	3.40
(b)	PT2	PT3	Experiment
g_z	2.0023	2.0016	2.0014
g_x	2.0561	2.0562	2.0473
g_y	2.0474	2.0473	2.0424

3.2. 60° reorientations of V_K centres: computer simulations

All calculations presented in this section are carried out using the CLUSTER code with a $[K_{24}Cl_{24}]$ molecular cluster. Before investigating the adiabatic surface for V_K -centre reorientation, we studied different modes of the Cl_2^- local vibrations in the vicinity of the V_K equilibrium configuration. The calculated frequency of the valence mode (see figure 1(a)), $\sim 330\text{ cm}^{-1}$, is in satisfactory agreement with experimental data [39] and the result from the ICECAP calculation [23] (both $\sim 240\text{ cm}^{-1}$). The study of the other modes was more qualitative and aimed towards analysing the distortion and polarization of the Cl_2^- molecular ion caused by the vibration. These calculations have confirmed the 'softness' of the translational mode when the quasi-molecule shifts as a whole along the $\langle 110 \rangle$ axis (see figure 1(b)) [39]. Thus, the relatively large displacement of the Cl_2^- molecule of 0.3 \AA , or $0.1a$, requires the expenditure of only $\sim 0.1\text{ eV}$. We should note that this vibration does not lead to noticeable V_K polarization even at larger displacements. The adiabatic potential energy surface for rotation of the Cl_2^- molecule around the axis aligned through the nearest cations (figure 1(c)) is also quite soft. For example, a 30° rotation of Cl_2^- with respect to the $\langle 110 \rangle$ axis around the centre of mass (centre of V_K symmetry) requires only 0.3 eV . Another vibrational mode corresponds to Cl_2^- rotation as a whole around the axis going through its centre of mass parallel to the Z axis (figure 1(d)) and perpendicular to the molecular axis. Such vibrations are important for hole hopping since they transfer one of the Cl ions to another plane where it can approach a third anion and switch the chemical bond (see figure 1(e)). This vibration is also soft compared to the valence mode. All these vibrations taken separately are not accompanied by considerable distortion of the Cl-Cl chemical bond of the Cl_2^- molecule.

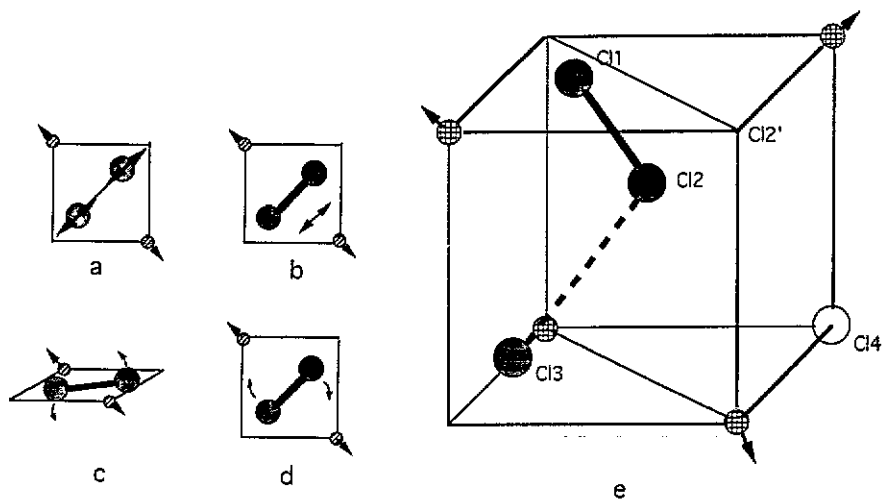


Figure 1. Schematic models of (a)–(d) different modes of the local vibrations of the Cl_2^- molecular ion in the V_K -centre and (e) the barrier point of the V_K centre 60° reorientation.

A study of the combined action of the four modes just described (taking into account the relaxation of the remaining crystal at any point on the potential energy curve) leads to the conclusion that, in the vicinity of the top of the reorientation barrier, the atomic configuration corresponds to those shown schematically in figure 1(e). The distances Cl1–Cl2 and Cl2–Cl3 are equivalent and correspond to about

an 8% stretching of the Cl_2^- bond compared with the V_K -centre equilibrium distance. Anions Cl1 and Cl3 are shifted from their regular sites by $0.28a$ (cf $0.19a$, the equilibrium shift within the V_K centre). Simultaneously, the hole spin density is localized by 75% on Cl2; with the remaining density equally shared by Cl1 and Cl3. The effective charge of Cl2 is about $-0.1e$, thereby confirming the strong V_K polarization during reorientation. Finally, the activation energy required for self-trapped hole (STH) reorientation, obtained in our calculations, is 0.63 eV. It is in reasonable agreement with the experimental value of 0.54 eV [6].

For the purposes of comparison we have studied the V_K reorientation process in LiCl. Applying the same procedure we find the activation energy to be about 0.47 eV. The lower energy value reflects the compactness of the LiCl crystalline lattice compared to that of KCl. Therefore the scale of the Cl_2^- molecular ion displacement necessary to reach the saddle point is proportionally smaller.

It should be stressed that, despite the V_K -centre polarization, mentioned above, the chemical bond between the Cl1 and Cl2 ions remains relatively rigid. Thus, V_K polarization is not accompanied by Cl1–Cl2 chemical bond breaking and V_K dissociation, with further displacements leading to its restoration of the form of (Cl2–Cl3). On the contrary, the chemical bond is switched from one pair of anions to another (with one anion remaining in common) within a narrow region of configurational coordinates near the top of the barrier. The Cl1–Cl2 bond cannot be appreciably stretched at any point of the potential energy surface without a considerable increase of the total energy. That is, the activation energy required for V_K -centre reorientation is defined by an excitation of translational and rotational modes as well as by a change in the crystal polarization energy. The latter, near the top of the barrier, is greater by 0.2 eV compared with an equilibrium V_K geometry, simply as a result of the localization of the hole. Thus, an important conclusion is that the repolarization energy (i.e. the difference of polarization energies in the saddle point and the equilibrium configurations) due to the essential change of both V_K configuration and its electronic structure reduces by about one-third the reorientation adiabatic barrier. This is in contrast to the case of the one-centre hole jumps in MgO [40]. In this case the saddle point for the hole diffusion corresponds to a state in which the hole is delocalized over two nearest oxygens. As such, the polarization of the crystal lattice at the saddle point is smaller compared with the equilibrium one-centre SRP state. Therefore, in MgO, the repolarization energy raises the barrier height.

3.3. The one-centre 'dielectric' polaron

As is clear from symmetry, the anions Cl3 and Cl4 may compete equivalently in making a chemical bond with Cl2 (see figure 1(e)). Therefore there has to be another reorientation saddle point between these two configurations, located in the $[1\ 1\ 0]$ plane. The energy of this more symmetrical point is ~ 0.05 eV higher than the energy of the barrier for the 60° reorientation. Apparently the most symmetrical saddle point corresponds to hole localization in the Cl2' site and symmetrical displacements of all 12 nearest-neighbour anions towards the central anion site. The energy of this configuration is calculated to be ~ 0.1 eV higher than the lowest barrier. However, it should be noted that the last energy is within the limit of the accuracy of our method since the calculated lattice distortion involves all the ions located on the border of the molecular cluster. Their displacements cannot be accurately reproduced in the EMC approximation because of neglect of the exchange and resonance interaction of these ions with even the nearest ions just across the cluster border. This may cause

an error in the calculation of the difference between total energies corresponding to strongly differing defect structures of the order of 0.1 eV. Therefore the possibility that the one-centre hole state in the anion site may have a close or equal energy to the reorientational barrier state cannot be absolutely excluded at this stage of our study. The localization of the hole on one anion in the course of the V_K -centre reorientation suggests that the hole could tunnel to this state. The one-centre 'dielectric' polaron could also be formed as a short-lived hole state immediately after the crystal is excited but before trapping by impurities or in the form of the V_K centre [8]. To study this point we have assumed that the one-centre 'dielectric' polaron can exist in a relaxed stationary state and have undertaken a more detailed study of its structure and transition into the V_K -centre configuration.

The most general energetic criteria for the existence of a self-trapped state are the sign and the value of the self-trapping energy [4, 41]. In particular, fast jumps of the 'dielectric' polaron (if they exist) should suggest that its state is close to the band of free hole states, i.e. the self-trapping energy is close to zero. In order to check this crucial point we used the method of calculation developed in [40]. The self-trapping energy may be approximately treated as a sum of the localization energy (E_{loc}) and the relaxation energy (E_{rel}).

E_{loc} may be calculated as the difference between the energy at the bottom of the band of free hole states (a completely delocalized state) and the energy corresponding to the Wannier-type localized state of the hole on one anion site (as in our case). The electronic polarization is assumed to be equal in both free and localized states and is neglected while estimating E_{loc} . If we assume that the dispersions of the valence and the hole bands are identical and employ the model Hamiltonian approach (the details of which are discussed fully in [40]), E_{loc} may be reliably estimated using matrix elements derived with the LUC method. E_{loc} for the hole is then calculated to be 0.8 eV. The width of the chlorine 3p valence band in KCL obtained from our LUC calculations is 2.1 eV. This value of E_{loc} may be a slight underestimate since the valence band width is smaller than the experimentally observed values of 2.3 eV [42] and 2.7 eV [43].

In the EMC approximation the 'dielectric' polaron relaxation energy may be determined as the energy difference between two states of the crystal with the hole localized on one of the molecular cluster anion sites: first, calculated including only the electronic part of the lattice polarization; secondly, corresponding to complete lattice relaxation about the hole. We performed the calculation of this energy using three different methods. In order to obtain the values of E_{loc} and E_{rel} within the same calculation scheme, the first calculation has been made using the CLUSTER code. The molecular cluster included three spheres of nearest-neighbour ions to the central chlorine atom, which carried the hole. To prevent the hole delocalizing into two anions and the formation of a V_K centre, the symmetry of the lattice distortion was restricted to be not lower than D_{4h} . In fact it appeared to be totally symmetrical. The value of E_{rel} , calculated with a self-consistent account of the crystal polarization, was determined to be -1.05 eV.

The second calculation was carried out using the CASCADE code, implementing the classical Mott-Littleton simulation technique [28]. The shell-model and pair-potential parameters for the interactions between the lattice ions were taken from [44]. The interactions of the central chlorine atom, Cl^0 , with the lattice ions were calculated using parameters derived for a study of hole centres in alkali halide crystals [18]. All potential parameters are reproduced in table 2. The value of E_{rel} obtained with this

Table 2. Potential parameters used in CASCADE calculations. (a) Pair-potential parameters. (b) Shell-model parameters.

(a) Interaction	A eV	ρ (Å)	C_6 (eV Å ⁶)
Cl ⁻ -Cl ⁻	1227.2	0.3214	124.9
Cl ⁻ -Cl ⁰	1205.0	0.3358	0.0
Cl ⁻ -K ⁺	4117.9	0.3048	0.0
K ⁺ -K ⁺	3796.9	0.2603	124.9
K ⁺ -Cl ⁰	1873.8	0.3048	0.0

(b)	Y (e)	k (eV Å ⁻²)
Cl ⁺	-2.485	29.38
Cl ⁰	-2.485	29.38
K ⁺	83.55	86 032.0

technique was -1.15 eV.

Finally we performed the calculation of E_{rel} , using the ICECAP code. The molecular cluster included the central chlorine atom and six nearest cations. The basis sets for Cl⁻ and K⁺ were the same as those used in a previous study [23]. We employed the same shell-model and pair-potential parameters as in the CASCADE calculation. In contrast to the CLUSTER and CASCADE calculations the ICECAP code correctly reproduces a small Jahn-Teller lattice distortion around the hole, localizing it to one of the chlorine p AO and lowering the symmetry of the centre from O_h to D_{4h}. In particular, the displacements of two nearest cations along the crystalline axis are $\sim 0.02a$ greater than those of the other four. The hole relaxation energy is equal to -1.2 eV.

The displacements (see figure 2(a)) of the lattice ions obtained using the CASCADE and the ICECAP codes are very close (except for the difference in symmetry). The nearest cations are displaced outwards from the chlorine atom by $\sim 0.09a$ with the CASCADE and by $0.10a$ and $0.12a$ with the ICECAP calculations. The 12 nearest anions are displaced inwards by $\sim 0.02\sqrt{3}a$. The displacement of the nearest cations obtained with the CLUSTER calculation are $\sim 0.06a$, whereas the displacements of the anions are approximately the same.

Summing up the results of these calculations we can conclude that the hole self-trapping energy ($E_{\text{loc}} + E_{\text{rel}}$) in the one-centre state is approximately -0.2 eV. However, the calculation of the adiabatic lattice relaxation performed using the CLUSTER code has shown that there is no adiabatic barrier between the one-centre hole state and the V_K -centre state. In other words, any fluctuation that breaks the symmetry of the state and brings one of the nearest chlorine ions closer to the central anion, carrying the hole, will lower the crystal energy. Therefore, the one-centre relaxed hole state can exist only if the hole transitions between two equivalent anion sites take place faster than these anions are able to respond. The resonant state for the hole transfer may be facilitated by cation fluctuations (see figure 2(b)). However, such fluctuations lower the local symmetry of the hole and produce favourable conditions for two anions to form a chemical bond. If the hole transfer between two sites takes place adiabatically, that is, the hole follows the nuclei all the time, the transition state for the hole transfer corresponds to the state in which the hole is equally shared between two anions and it relaxes into the V_K -centre configuration. Whether or not

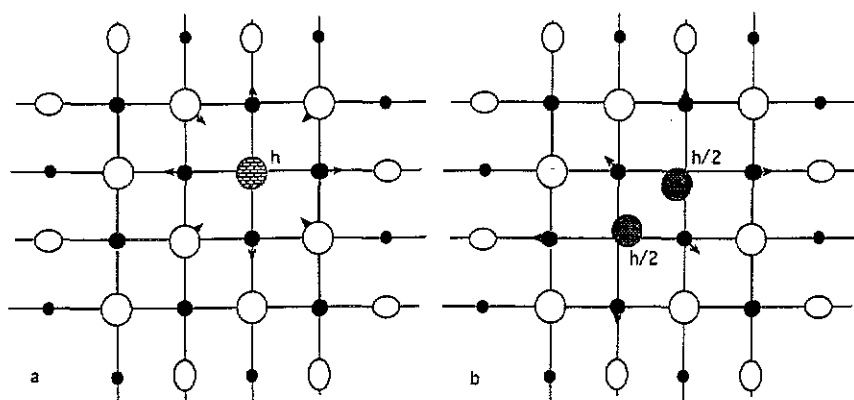


Figure 2. (a) The model of a symmetric lattice relaxation around the one-centre 'dielectric' polaron. (b) The adiabatic lattice relaxation corresponding to the resonant state of the hole jump between the nearest anion sites. The thick lines represent the border of the cluster used in the calculations (see text). The ion deformation outside the cluster schematically illustrates the polarization of the lattice.

the transition is adiabatic should be determined by the value of the transfer matrix element between two sites and the speed of the system motion through the Landau-Zener region [45]. The important point is that the gain in energy between the SRP state and the relaxed V_K -centre state is about 0.6 eV. Therefore, the effectiveness of the vibrational relaxation process plays a crucial role.

The approximate quantum-mechanical model of electron transfer in a polar medium, including the dynamics of the reaction coordinates relaxation, has been presented in [46]. It suggests an 'adiabaticity' parameter g , defined as

$$g = 2\pi|T|^2/\hbar\omega_c E_R$$

where T is the electron transition matrix element between the initial and final states; $1/\omega_c$ is the characteristic relaxation time of the reaction coordinate; and E_R is the system reorganization energy. The reaction is considered to be adiabatic or non-adiabatic depending on whether g is large or small. According to [45, 46], g may be qualitatively interpreted as the ratio between the time spent by the 'reaction coordinate' in the Landau-Zener region and the time taken by the one-electron transition between the initial and final states.

As has been noted above, the hole transfer process may be approximately considered as being driven by two main reaction coordinates: the breathing vibration of the cations surrounding both anion sites and the valence vibration of two anions involved in the hole transfer (see figure 2(b)). The relaxation of the same coordinates also takes place during the process of exciton self-trapping in alkali halide crystals [5]. Therefore, as an estimate for the value of $1/\omega_c$ we can use the relaxation time of the 'hot' luminescence that accompanies the exciton transition from a free into a self-trapped state [5]. According to the calculation made in [47] this time is greater than $3\omega_{LO}^{-1}$, where ω_{LO} is the frequency of the characteristic crystal optical vibrations. In KCl ω_{LO} is equal to $4.02 \times 10^{13} \text{ s}^{-1}$ [5]. Thus the value of $1/\omega_c$ may be estimated as $\sim 10^{-13} \text{ s}$.

In order to estimate the value of g we have calculated T and E_R for hole transfer between the nearest anion sites. Using the method suggested in [48] (see

also [40] for details) we have obtained a value of T equal to 0.07 eV. E_R is the energy difference between the relaxed initial state and the final state calculated with the same coordinates [46]. Its value was determined to be 0.72 eV.

Thus the value of g for the hole transition between the two nearest anion sites is greater than 7, suggesting that one resonant jump of the hole takes place much faster than the decay of the resonant state for hole transfer due to the relaxation process of the local vibrations. Hence the hole will be able to make many transitions between the two sites, and the loss of phase coherence between these states becomes an important question. As shown in [49], the reaction rate at this limit is similar to what one would obtain by assuming that the hole followed the nuclei adiabatically. Therefore, a hole relaxed into a one-centre state must convert into a V_K centre without preliminary long-range diffusion through the lattice.

4. Conclusions

Summing up the results of the present calculations we conclude that 'dielectric' small-radius polarons do not exist in KCl even as kinetic particles. This is in good agreement with the experimental observation that the hole does not exhibit an activation barrier for self-trapping in the 'molecular' (V_K -centre) form in KCl [5]. This result is mainly due to chemical bond formation between the two anions creating the V_K centre and to the relatively slow relaxation of the local lattice vibrations driving the self-trapping process, which makes it adiabatic. The strong dependence of the 'adiabaticity' parameter on the value of the electronic transfer matrix element suggests the possible existence of short-lived one-centre 'dielectric' polarons in alkali halide crystals with a larger anion-anion distance. We should also stress the importance of the 'adiabaticity' criteria for the calculation of the barriers for electron or hole transfer in solids. It may serve as an indicator of the validity of the adiabatic approximation for the calculation of the barrier point [50].

Finally we should note that our results do not support the possibility of free hole formation in the process of reorientational motion of the V_K centre in KCl. Analysis of the experimentally observed kinetics of delayed reactions between Tl^0 and V_K centres in KCl, presented in the second part of this paper [12], also reveals that V_K centres make only reorientational hops.

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