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The calculation of the self-trapping energy in crystals with mixed valence band

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Abstract. We present a method of calculation of the localization energy of the hole in the crystal in which the density of states in the valence band has comparable contributions from both cation and anion states. The method is applied to the study of hole self-trapping in AgCl. The quantum-chemical simulations of the different hole structures revealed that the V_K -type form of hole self-trapping in AgCl is unstable. The calculated self-trapping energy for the hole on one silver site is equal to -0.1 eV.

1. Introduction

Although the possibility of small electron polaron formation in a perfect deformable lattice was predicted by Landau almost 60 years ago [1], theoretical studies of small polarons in different crystals still cause interest [2, 3]. Since then the words 'self-trapped state', 'small radius polaron' and 'strongly localized state' in the perfect lattice have become close synonyms. As has been noted by Toyozawa in his pioneering paper [4] the word 'self-trapping' or 'localization' should not be taken so literally, and the problem of the possibility of self-trapping should be replaced by a discussion of the magnitude of the effective mass of the self-trapping quasi-particle interacting and the lattice distortion. Among various theoretical approaches [5, 6] developed for an understanding of this phenomenon, a static quantum-chemical approach has the advantage of being specific and applicable to particular crystals. It has recently been used in KCl [7], MgO [8] and Al_2O_3 [9] and has provided satisfactory microscopic models of the self-trapped holes in these crystals. In this paper we present its further development. In particular, we will focus on the method of calculation of the localization energy of the hole in the crystal in which the density of states in the valence band has comparable contributions from both cation and anion states. The method is applied to the study of hole self-trapping in AgCl.

The structure of the self-trapped hole in AgCl has been studied using various experimental techniques and reliably established [10-12]. However, the question still remains as to why the holes in the alkali halides and AgCl have such different structures. Both crystals have the same type of crystalline structure, but different valence band electronic structure. Is the latter the main reason that in the alkali halides the holes are self-trapped in the anion sublattice and form the X_2^- molecular

ions occupying two anion sites (V_K centres [14]) whereas in AgCl the hole is localized on one cation? To address this question we performed quantum-chemical simulations of the different hole structures which revealed that the V_K -type form of hole self-trapping in AgCl is indeed unstable.

2. Method of calculation

2.1. Static approach

The key characteristic, which is usually calculated using the static approach is the self-trapping energy (E_{st}) [4]. It may be considered as the energy which is required in order to produce the self-trapped state from the lowest delocalized (band) state of the quasi-particle. (Henceforth the hole will be used as the example of a quasi-particle, although the same approach with minor changes may be applied to electrons and excitons). If the calculated value of E_{st} is negative the localized state is considered to be stable with respect to the band of the delocalized states. If E_{st} is found to be positive the localized state is certainly unstable and the hole can exist only in the delocalized state. As was noted in [7,8] the kinetic behaviour of the localized hole is determined not only by the value of E_{st} but also by the character (adiabatic/non-adiabatic) and the barriers for its diffusion between different localized states.

Within the static approach it is convenient to divide E_{st} into two terms: the localization energy, E_{loc} , and the relaxation energy, E_{rel} . E_{loc} may be considered as the energy which is required in order to localize the hole on one or several lattice sites where the ions are in their sites and only the electrons follow the presence of the hole, whereas the E_{rel} is the energy gain due to the lattice relaxation from this state. The self-trapping energy is hence the difference:

$$E_{st} = E_{loc} - E_{rel}. \quad (1)$$

In order to clarify this point let us present the Hamiltonian of the crystal with the hole as a sum of three terms:

$$H = H_{ee} + H_{vibr} + H_{e-vibr} \quad (2)$$

where H_{ee} is the Hamiltonian of the electrons when the nuclei are fixed in their site positions, H_{vibr} is the Hamiltonian of the lattice vibrations and H_{e-vibr} describes the interaction between the electrons and the lattice vibrations. In this case the self-trapping energy according to our definition is equal to:

$$E_{st} = \langle \Phi_{st} | H | \Phi_{st} \rangle - \langle \Phi_{del} | H | \Phi_{del} \rangle \quad (3)$$

where $|\Phi_{st}\rangle$ and $|\Phi_{del}\rangle$ denote the wavefunctions of the self-trapped and the lowest delocalized state, respectively. If we use the Landau-Pekar approximation in which the total wavefunction of the system is treated as a simple product of the electronic $|\varphi\rangle$ and vibrational $|\chi\rangle$ wavefunctions:

$$|\Phi\rangle = |\varphi\rangle|\chi\rangle \quad (4)$$

the self-trapping energy may be presented in the form

$$E_{st} = (\langle \varphi_{st} | H_{ee} | \varphi_{st} \rangle - \langle \varphi_{del} | H_{ee} | \varphi_{del} \rangle) - (\langle \Phi_{del} | H_{vibr} + H_{e-vibr} | \Phi_{del} \rangle - \langle \Phi_{st} | H_{vibr} + H_{e-vibr} | \Phi_{st} \rangle). \quad (5)$$

Hence E_{loc} and E_{rel} are equal to the following differences of matrix elements:

$$E_{loc} = \langle \varphi_{st} | H_{ee} | \varphi_{st} \rangle - \langle \varphi_{del} | H_{ee} | \varphi_{del} \rangle$$

$$E_{rel} = \langle \Phi_{del} | H_{vibr} + H_{e-vibr} | \Phi_{del} \rangle - \langle \Phi_{st} | H_{vibr} + H_{e-vibr} | \Phi_{st} \rangle.$$

In order to use a standard stationary quantum-chemical technique an artificial intermediate state, $|\Phi_i\rangle$, should be introduced to provide a common reference point for the calculation of the E_{loc} and E_{rel} . Therefore the actual approach, which is often used in order to find a stable configuration of the polaron, is somewhat different. It assumes that the polaron may be localized within the crystal area which coincides with some finite atomic cluster. Plausible models of the localized polaron are then simulated making use of the Mott-Littleton or some quantum-chemical technique. These models may be chosen on the basis of experimental data and preliminary assumptions. If the minimization of the total energy of the system predicts a stable configuration of the polaron with respect to the variation of positions of the ions in the cluster, the relaxation and localization energies are then calculated for this configuration.

For these purposes one needs to construct in the perfect lattice qualitatively the same electronic state $|\Phi_i\rangle$ as was obtained for the localized configuration, and to assume the equivalence of the magnitudes of the electronic polarization produced by this state and the completely delocalized hole state. The validity of the latter approximation was analysed by Fowler in [24]. In this case, using the above procedure, the self-trapping energy may be written in the form:

$$E_{st} = (\langle \varphi_i | H_{ee} | \varphi_i \rangle - \langle \varphi_{del} | H_{ee} | \varphi_{del} \rangle) + (\langle \Phi_i | H_{vibr} + H_{e-vibr} | \Phi_i \rangle - \langle \Phi_{del} | H_{vibr} + H_{e-vibr} | \Phi_{del} \rangle) - (\langle \Phi_i | H | \Phi_i \rangle - \langle \Phi_{st} | H | \Phi_{st} \rangle). \quad (6)$$

The second term is equal to zero because of our assumption that in both delocalized and intermediate states the lattice ions are located in their sites. Hence the localization and relaxation energies correspond to the following combinations of the matrix elements:

$$E'_{loc} = \langle \varphi_i | H_{ee} | \varphi_i \rangle - \langle \varphi_{del} | H_{ee} | \varphi_{del} \rangle$$

$$E'_{rel} = \langle \Phi_i | H | \Phi_i \rangle - \langle \Phi_{st} | H | \Phi_{st} \rangle \quad (7)$$

having a quite transparent physical sense.

In the majority of the approximate microscopic approaches employed so far in the theory of self-trapping and in the calculations of the structure of the self-trapped particles in particular systems, the electron-phonon coupling is treated in the linear approximation [4,5]. The electronic Hamiltonian is often presented in

the tight-binding approximation, taking into account only the largest matrix elements of the Hamiltonian between the nearest sites. Since all these matrix elements are equivalent, the density of states of the valence band has a symmetric form. As a consequence of the latter assumption, the localization energy of the particle on one lattice site appears to be equal to the half-width of the band of its delocalized states. The structure of the band of the delocalized states may be correctly described in this approximation if the basis of *s* atomic orbitals centred on the sites provides an appropriate representation of the hole states. However in many crystals the wavefunction of the hole has *p* or *d* orbital characteristics. In these cases the simple approach described above leads to the substantial overestimation of the localization energy [7, 8].

Since the localization and relaxation energies are usually similar and their difference is much smaller than the width of the band of the delocalized states, the accuracy of the calculation of E_{loc} is a crucial point in the estimation of the E_{st} . As has been shown in [8], accounting for the angular dependence of the matrix elements of the tight-binding Hamiltonian improves the accuracy of the calculation of E_{loc} . Another problem concerns the details of the electronic structure of the crystal under study. In particular, if the hole is created in the valence band, the nature and characteristics of the density of states in the band play an important role in the self-trapping process. The situation becomes particularly complicated when the valence band is a mixture of the states originating from two or more sublattices. This takes place in AgCl, alumina and other crystals, where the self-trapping of holes is the topic of discussion [3, 9–12].

2.2. Quantum-chemical method

The important peculiarity of the method suggested for the study of self-trapped holes in [7, 8] is that both the localization and relaxation energies of the hole are calculated using the same quantum-chemical technique and set of parameters. This is achieved employing the CLUSTER computer code which combines both the possibility to make calculations of charged defects within the embedded molecular cluster (EMC) model [15] and to study the band structure of perfect crystals using the periodic large unit cell method [16]. It is based on the semi-empirical version of the unrestricted Hartree–Fock–Roothaan method implementing the approximation of intermediate neglect of differential overlap (INDO) [17] which allows us to obtain with reasonable accuracy the electronic structure of quantum clusters and LUC containing several tens of ions. The latter is important in order to study different possible configurations of the localized hole. The polarization of the crystal is treated in the polarizable ion approximation [18].

The CLUSTER code is described in a previous paper [19]. The basis set of present calculations includes 3*s* and 3*p* Slater-type atomic orbitals (AOs) on chlorine ions and 4*d*, 5*s* and 5*p* AOs on silver ions. The INDO parameters were optimized with reference to a series of molecular species including all the different bonding possibilities that will be important in our study of hole self-trapping (Ag_2 , Ag_2^+ , Cl_2^- , AgCl), the crystal lattice constant and the electronic structure of the valence band. We calculate the electronic structure and the lattice constant of the bulk material within the LUC method applying the periodic boundary conditions to the cell $[\text{Ag}_{32}\text{Cl}_{32}]$. This allows us to effectively take into account eight non-equivalent *k*-points of the Brillouin zone (BZ) [16]. The lattice constant finally determined from the LUC calculations after the optimization of the parameters was 5.18 au (the experimental value is 5.25 au).

The valence band has an electronic structure close to that calculated using the *ab initio* band structure technique [20]. In the projected density of states in the valence band, the most significant contributions are from the 4d states of Ag ions and the 3p states of Cl ions. The top of the band is located in the L point of the BZ and is mainly determined by the d states of the Ag ion. The one-electronic wavefunction of the state corresponding to the Γ point of the BZ is mainly determined by the 3p states of the Cl ion. The electronic energy of this point is 2.1 eV lower than that of the L point, which is in good agreement with the experimental value of 1.9 eV [10]. Lowdin population analysis was used to calculate the effective ion charges; their modulus for silver and chlorine ions in the perfect lattice is $0.69 e$ (e is the electron charge) in agreement with the experimental estimation 0.66 – $0.69 e$ [21].

The lattice outside the cluster is constructed from non-point polarizable ions carrying the same basis of AOs as ions inside the cluster. The Lowdin populations of these AOs are frozen to those AO populations of the perfect lattice. Only the Coulomb and charge–dipole interactions between the cluster ions and remaining crystal are included in the calculation of elements of the Fock matrix. The Coulomb interaction between ions inside and outside the cluster is calculated explicitly as between quantum-mechanical ions, although the angular dependence of the AOs in the Coulomb integrals is neglected according to the INDO approximation. The potential of the lattice of non-point spherical ions is summed to infinity using the Ewald method [19].

To simulate the self-trapping of a hole the polarization of the remaining crystal, not included in the quantum cluster, is accounted for in a self-consistent manner [15, 18]. The potential of the polarization field generated as a consequence of the response of the polarizable lattice to the hole is incorporated directly into the Fock matrix. It is recalculated after every few steps of the UHF self-consistency procedure until the consistency is finally achieved.

3. Hole self-trapping in AgCl

In order to find a possible stable configuration of the hole we use the following approach. First we suppose that the hole may be localized within the crystal area which coincides with the molecular cluster. The largest cluster used in these calculations is comprised of 48 ions [$\text{Ag}_{24}\text{Cl}_{24}$]. According to the experimental data regarding the hole self-trapping in the crystals with close structure, like alkali halides, cubic oxides or alkali earth fluorides and to the results of theoretical calculations for these crystals [2, 7, 8, 14, 22], one can assume three plausible models for the self-trapped hole in AgCl: the one-centre and V_K -like localization in the anion sublattice and the one-centre localization in the cation sublattice.

First we simulated the V_K -like configuration of the hole using the molecular cluster [$\text{Ag}_{24}\text{Cl}_{24}$]. By the symmetrical displacement of two central chlorine ions from their sites towards each other it is possible to localize the hole predominantly on these ions. To minimize the total energy of the system keeping the D_{2h} symmetry of the defect, it appears that at the energy minimum the hole is only slightly localized on two displaced chlorines. In fact about 60% of the spin density is localized on the two nearest Ag ions which are slightly displaced from their sites

(see figure 1(a)). The analysis of this configuration has shown that this antibonding state is located about 0.25 eV higher than the bonding state of the same symmetry (see figure 1(b)). Hence in this model the hole prefers to localize in the state determined by the silver atomic orbitals. The further minimization of the system's total energy without additional symmetry restrictions indicates that the two-centre hole localization on silver ions is unstable and much lower energy corresponds to the one-centre state depicted in figure 1(c). If we start from the state corresponding to the localization of the hole upon one chlorine ion, which may be prepared by a strong symmetrical displacement of the six nearest cations outwards, by minimizing the total energy we end up with the same one-centre state localized on one silver ion.

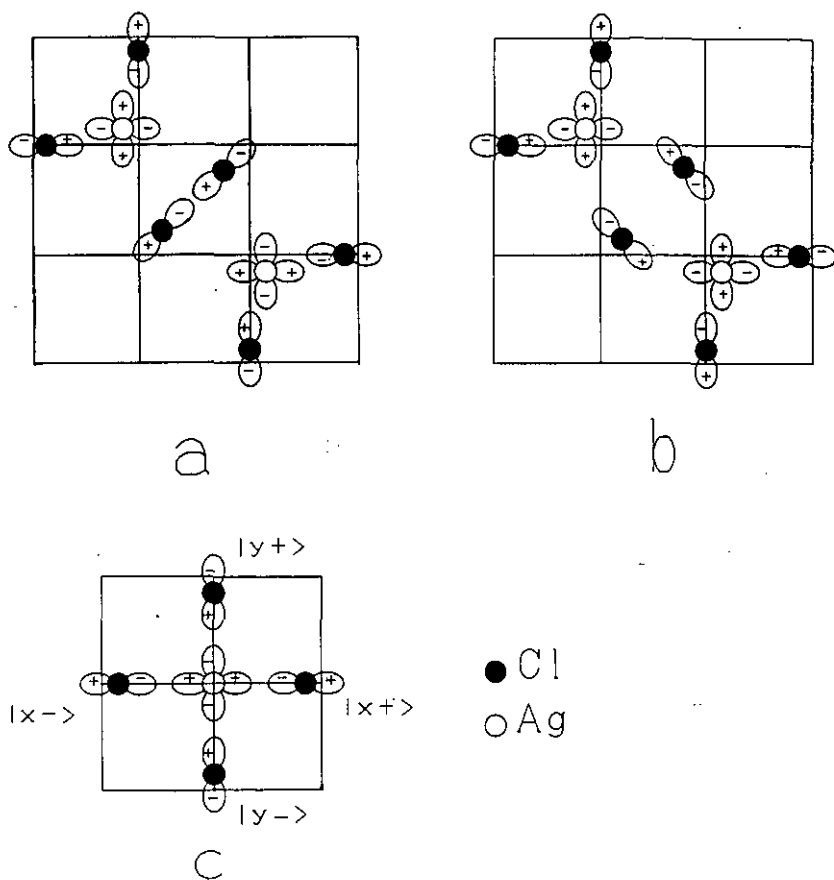


Figure 1. Molecular orbitals of the self-trapped hole: (a) the antibonding two-centre hole state; (b) the bonding hole state at the same ionic displacements as (a), which is analogous to the hole wavefunction in the V_K centre; (c) the 'one-centre' hole state on the silver ion.

Further analysis of the one-centre hole configuration on the silver ion was performed using the molecular cluster $[Ag_{13}Cl_{14}]$. It has revealed that about 67% of the hole is localized on the $d_{x^2-y^2}$ atomic orbital of the central silver ion. The remaining 33% of the spin density of the hole is delocalized by the $3p_{x,y}$ orbitals of the four chlorine ions located in the Oxy plane of the cluster. The displacements of

the nearest ions surrounding the central silver ion are summarized in table 1. The symmetry of the centre is in fact D_{4h} because the four nearest anions in the Oxy plane are attracted to the hole a bit more strongly than those located by the z -axis. This is a consequence of the Jahn-Teller interaction of the hole with E_g vibrations of the nearest anions. The symmetry of the hole predicted by our calculation coincides with that observed in the ESR experiment [12]. Therefore the one-centre state on the silver ion may be considered as a good candidate for the model of the self-trapped hole in AgCl. However, a more confident conclusion may be made only after a calculation of the self-trapping energy.

Table 1. The displacements of two nearest-neighbour spheres of ions of the self-trapped hole in AgCl (in units of internuclear distance).

Ions	Types of sites	Displacements		
		x	y	z
Ag	1 0 0	0.050	0.000	0.000
Ag	0 0 1	0.000	0.000	0.025
Cl	1 1 0	0.025	0.025	0.000
Cl	1 0 1	0.015	0.000	0.025

In order to calculate the localization energy of the hole on one silver ion let us present its Hamiltonian in the tight-binding approximation

$$H_h = - \sum_{L,\mu} \epsilon_p a_{Lp\mu}^\dagger a_{Lp\mu} - \sum_{L,\mu} \epsilon_{d\mu} a_{Ld\mu}^\dagger a_{Ld\mu} - \sum_{L,L'} \sum_{\lambda,\sigma} V(L-L', \lambda, \sigma) a_{L\lambda}^\dagger a_{L'\sigma}$$

$$\epsilon_{d_{xy}} = \epsilon_{d_{xz}} = \epsilon_{d_{yz}} = \epsilon_d - \frac{2}{5} \Delta$$

$$\epsilon_{d_{x^2-y^2}} = \epsilon_{d_{z^2}} = \epsilon_d + \frac{3}{5} \Delta. \quad (8)$$

Here μ are different symmetry projections of 3p and 4d orbitals of chlorine and silver, respectively; $-\epsilon_p$ and $-\epsilon_{d\mu}$ are the energies of the hole localized on the chlorine 3p orbitals or the silver 4d orbitals; V denotes the non-diagonal matrix elements, where L and L' are the vectors of the direct lattice and λ, σ refer to all the symmetry projections of chlorine 3p orbitals and silver 4d orbitals; Δ characterizes the splitting of the silver 4d states in the crystalline field. According to the results of our calculations, the wavefunction of the localized hole may be presented in the form of the linear combination

$$|\varphi_h\rangle = \alpha|x^2 - y^2\rangle - (\beta/2)(|x-\rangle - |x+\rangle + |y+\rangle - |y-\rangle) \quad (9)$$

where the $|x^2 - y^2\rangle$ denotes the $d_{x^2-y^2}$ atomic orbital of the silver ion and the $|\lambda\pm\rangle$ are the 3p orbitals of the chlorine ions in the Oxy plane, \pm refers to the relative positions of the chlorine ions with respect to the central silver ion (see figure 1(c)), and α, β are the real coefficients, which are determined from the Hartree-Fock calculation of the hole. According to our definition (7) we have to calculate the

energy difference between the lowest delocalized state and the intermediate state corresponding to the hole localized in the perfect lattice with the wavefunction (9). The latter is equal to

$$\begin{aligned}
 E_h &= \langle \varphi_h | H | \varphi_h \rangle \\
 &= -\alpha^2 \varepsilon_{d_{x^2-y^2}} - \beta^2 \{ \varepsilon_p + V([2a, 0, 0], p_x, p_x) \\
 &\quad + 2V([-a, a, 0], p_x, p_y) \} \\
 &\quad + 4\alpha\beta V([a, 0, -a], d_{x^2-y^2}, p_x).
 \end{aligned} \tag{10}$$

Two usual approximations were employed in order to calculate the energy of the delocalized state. Firstly, in our calculations the band of free holes coincides with the valence band taken with the opposite sign [23], i.e. the bottom of the hole band corresponds to the top of the valence band. Secondly, we assume the equivalence of magnitudes of the electronic polarization produced by the delocalized and localized holes [24]. Using these approximations, the matrix elements of the hole Hamiltonian in both delocalized and intermediate states may be derived from the matrix elements of the Fock operator in the site representation obtained at the last iteration of the self-consistency procedure of the band structure calculation of the perfect crystal. This calculation was performed using the LUC method and the cell $[\text{Ag}_{32}\text{Cl}_{32}]$. The localization energy calculated in this manner is equal to 0.8 eV.

In order to find the relaxation energy, the total energy of the molecular cluster simulating the perfect lattice was calculated for the electronic density distribution corresponding to the hole wavefunction (9). Only the electronic part of the lattice polarization by the hole has been taken into account since, in the intermediate state, all ions are assumed to be in their sites. The value of E_{rel} is approximately equal to the difference between this energy and the energy of the completely relaxed state. In our calculation this value is equal to 0.9 eV.

According to (1) the self-trapping energy is equal $0.8-0.9 = -0.1$ eV. The negative value of the E_{st} supports the conclusion that the hole in AgCl may be self-trapped on one silver ion. The magnitude of the E_{st} is close to the experimentally obtained activation energy of the thermo-activated ionization of the self-trapped hole in AgCl which is equal to 0.12 eV [25].

4. Discussion

The results of these calculations agree with the experimental observation that the hole in AgCl is localized on the silver ion. They also exclude the possibility of hole localization in the chlorine sublattice in the bulk of the perfect crystal. The latter result is not absolutely evident despite the fact that the top of the valence band in AgCl is determined by the d states of silver ions. The estimation of the hole (V_K centre) self-trapping energy in KCl [7] gives the value of -1.7 eV which is close to the splitting (1.9 eV) between L (silver-like) and Γ (chlorine-like) points in the valence band of AgCl. Therefore one could expect that hole self-trapping on chlorines is due to a delicate balance of different contributions to the self-trapping energy. However, the fact that the silver states have higher energy causes a hole

density redistribution from the chlorine ions to silver. Consequently the chemical bond between two chlorines sharing the hole does not form, whereas the lattice polarization cannot prevent the hole transfer onto silver ions.

Finally we should note that the alternative estimate of the localization energy could be made as a half-width of the silver subband in the valence band of AgCl. In order to compare with the E_{rel} obtained in our calculations we should get the value of E_{loc} from the band structure calculation made by the same quantum-chemical method. In our LUC calculations the width of the silver subband is found to be equal to 2.1 eV. Therefore the value of E_{loc} may be estimated as 1.05 eV. Thus the E_{st} obtained in this manner is $1.05 - 0.9 = 0.25$ eV and hence, according to this estimation, the holes cannot be self-trapped in AgCl. This paradoxical result supports the conclusion made in previous calculations [7,8] that the real electronic structure of the valence band has to be taken into account in the calculations of the hole localization energy.

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