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Theoretical simulation of localized holes in MgO

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Abstract. We propose a consistent approach to the study of hole self-trapping and diffusion in ionic crystals based on the static quantum-chemical calculation of the self-trapping energy and adiabatic barriers for hole diffusion. The calculations made for MgO revealed the possibility that the hole is localized on one anion site in the perfect lattice and predict its high mobility.

1. Introduction

Despite its long history, the theory of small polarons is still incomplete. Detailed discussions of its present status have been presented in [1, 2]. There have been only a few theoretical studies combining a many-electron treatment of the electronic structure of the localizing polaron with the Mott-Littleton approach for the calculation of the accompanying polarization of the rest of the crystal [3-6]. Such studies have the advantage of being specific and applicable to particular crystals. In this paper we shall study the various possibilities for hole self-trapping and mechanisms of their mobility in the bulk of the crystal; we calculate the key energetic terms using static quantum-chemical methods which we apply to MgO—one of the simplest crystalline oxides.

There are at least two different ways in which to approach the problem of particle localization or self-trapping in a material.

(i) Calculate the self-trapping energy, which is the difference between the energies of the bottom of the free particle band and the localized stable state.

(ii) Study the barriers for the particle transitions between equivalent localized states or for their release from the localized state to the nearby impurity.

In the present paper, which focuses on the question of hole localization in MgO, we employ both approaches, starting from the well established state of the hole localized near the Li^+ ion substituted for Mg^{2+} on a lattice site.

In cubic oxides and in particular in MgO, the localization of the small polarons near impurities is a well established phenomenon [7]. One of the best studied is the $[\text{Li}]^0$ centre in MgO, which plays an important role in the catalytic activity of this crystal [8]. It is known that the $[\text{Li}]^0$ centre is destroyed by optical excitation in its absorption band or thermally at relatively low temperatures (about 200 K) [7]. However, the products resulting from its decay have not been observed. This result

distinguishes the $[\text{Li}]^0$ centre from analogous impurity hole centres (Ag^{2+} , Tl^{2+} [9, 10] and Mg^+ [11]) in alkali halides, in which their optical and thermal destruction produces the self-trapped holes (V_k centres).

The self-trapping of holes has not been spectroscopically observed in MgO, although experiments employing various types of crystal excitation have been carried out. One of the most plausible reasons for such behaviour for holes in MgO may be high mobility, which makes it difficult to observe them experimentally by spectroscopic techniques, although we should note that the only evidence favouring the existence of highly mobile holes concerns their behaviour on the surface of MgO at high temperatures [12]. Recent theoretical calculations of self-trapping energies indicated that small-polaron formation is not favoured [13, 14]. It was suggested that, despite the large lattice relaxation energy (1.7 eV [13] and 2.4 eV [14]), the holes cannot self-trap in the bulk of MgO because the localization energy has almost the same magnitude, but with the opposite sign. However, an estimate of the localization energy was made using a crude approximation, allowing only qualitative conclusions to be drawn. Therefore a more sophisticated treatment is clearly needed; in particular we require a consistent calculation scheme for both relaxation and localization energies. This would be of value for studies not only of MgO but also of other insulators, e.g. SiO_2 or Al_2O_3 , where the self-trapping of the holes is still a subject for discussion [15, 16].

Two different approaches are used in this paper. First, we consider the hole localized on the $[\text{Li}]^0$ centre and calculate the adiabatic barriers both for its jump from the axial into the equatorial position within the centre and for its jump out of the centre. The heights of these barriers are both about 0.9 eV, which seems to be unreasonably large. To investigate the factors that might decrease the barrier height we calculate the adiabatic barriers for the hole diffusion in the perfect lattice and include the effects of interatomic electron correlation, which we find considerably decrease the barrier for hole migration. Therefore it seems plausible to conclude that the thermal destruction of impurity hole centres in MgO leads to the creation of rapidly moving small-radius polarons (SRPs).

In order to check this conclusion we calculate the energy for the self-trapping of the hole from the free delocalized state into the state in which it is localized on one site of the perfect lattice. This energy may serve as an indicator of how far the localized state (if it exists) is from the band of delocalized states, and together with the value of the barrier for the hole jumps between localized states this may give a more reliable picture of the behaviour of the holes in the lattice. For this purpose, we introduce a new technique for the calculation of the localization energy. The self-trapping energy is calculated to be negative but small, confirming that the holes may localize but will be very mobile.

The plan of the paper is as follows. First we shall discuss (in section 2) the method of calculation based on the embedded-molecular-cluster (EMC) quantum-chemical approach, with the results of the calculations for the hole centres in MgO given in section 3. Further discussion and conclusions are given in section 4.

2. Method of calculation

In the study of the positively charged hole states we need to reproduce reliably the chemical interactions of ions near the hole centres, the long-range interaction usually described as crystal polarization, and the band structure of the perfect crystal. For

this purpose we use the EMC [3, 4, 17] model and the large-unit-cell (LUC) method [18], both of which are combined in the CLUSTER code [3, 19], which was employed in most of the present calculations.

The CLUSTER code is based on the semi-empirical version of the UHF method implementing the approximation of intermediate neglect of differential overlap (INDO) [20], which allows us to obtain (with reasonable accuracy) the electronic structure of a quantum cluster or LUC containing several tens of ions. The polarization of the crystal is treated in the polarizable-ion approximation [3, 17, 21]. It is calculated consistently with the electronic structure calculation at each point of the adiabatic potential energy surface as a response to the electric field produced by the difference between the charge-density distributions $\Delta\rho(\mathbf{R}_i)$ in the perfect lattice and in the molecular cluster containing the defect [3]. The values of $\Delta\rho(\mathbf{R}_i)$ are treated in the ionic approximation as the difference between the effective charges (calculated according to the Löwdin population analysis [20]) of the cations and anions in the perfect lattice, calculated by the LUC method, and ions with the coordinates \mathbf{R}_i in the molecular cluster. The lattice polarization is recalculated for each of the several iterations of the UHF self-consistency procedure. The matrix elements of the potential produced by the polarized lattice are included in the diagonal elements of the Fock matrix.

The parameters of the INDO method were 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 MgO, LiO, O_2^- , Mg_2^+ , etc [19]. Such a parametrization improves the reliability of the defect calculations. The basis sets contained 2s Slater-type atomic orbitals for Li^+ , 3s for Mg^{2+} and 2s, 2p for O^{2-} . The lattice constant and the electronic structure of the perfect MgO were obtained in a previous study of the perfect crystals using the LUC model [19], and their values were also used in defect calculations. Finally, the ionic polarizabilities were taken from [22].

The electronic excitation energies were calculated as the difference between the total self-consistent energies of a crystal in its ground and excited states (the ΔSCF method). The g -tensor for the paramagnetic $[\text{Li}]^0$ centre was calculated employing the Stone [23] equation, derived using second-order perturbation theory to describe the spin-orbit and Zeeman interactions of the unpaired electron orbital momenta with the magnetic field, as is widely used in quantum-chemical studies.

3. $[\text{Li}]^0$ centre and SRP in MgO

3.1. Atomic and electronic structure of the $[\text{Li}]^0$ centre

The $[\text{Li}]^0$ centre in MgO has been much investigated both experimentally and theoretically [3, 7, 13]. Our calculations focus on the question of hole jumps around the Li^+ ion, and of the thermal decomposition of the centre. The structural model of the centre is shown in figure 1. The displacements of ions surrounding the centre are given in the figure; they are close to those obtained in the previous calculation [28]. The hole is localized mainly on one of the oxygen ions, which appears to be strongly displaced from the regular lattice site. The calculated position for the maximum of the optical absorption band is $E_{\text{max}} = 1.8$ eV and the components of the g -tensor

are $g_{\parallel} = 2.0043$ and $g_{\perp} = 2.038$. They agree quite satisfactorily with the corresponding experimental values: $E_{\max} = 1.83$ eV [17]; $g_{\parallel} = 2.0049$ and $g_{\perp} = 2.0545$ [7].

The optical absorption of the $[\text{Li}]^0$ and related impurity hole centres has been established as being determined by transitions from resonant states in the valence band into the local hole state in the gap [24]. The present calculations add quantitative details to this qualitative model. In particular, there are two sources for perturbations which give rise to the resonant states in the valence band: first, the strong perturbation of the surrounding nearest-neighbour anions by the Li^+ ion; second, the much weaker perturbation of the next-nearest-neighbour anions by the hole localized on one oxygen anion. The first perturbation produces the resonant states near the top of the valence band, whereas the second perturbation produces resonant states near the bottom of the valence band. The maximum of the optical absorption band of the centre corresponds to the transitions from the resonant states near the top of the valence band. The energies of all such transitions depend very much on the values of the ion displacements [11]. The good agreement of our optical transition energy and g -tensor with the experimental results shows that the geometry of the centre is also determined reliably.

3.2. Hole jumps near the $[\text{Li}]^0$ centre and SRP in MgO

All six anions surrounding the Li^+ ion are equivalent. According to the EPR data the hole localized in the $[\text{Li}]^0$ centre jumps between them, even at liquid-helium temperature [7, 25]. The estimate of the activation energy of these jumps made in [25] by fitting to the experimental kinetics gives a value of 0.2 eV. A much higher value of 0.8 eV was obtained in recent Mott-Littleton calculations [13]. It is also well established that individual $[\text{Li}]^0$ centres are thermally decomposed at about 200 K [7]. This relatively low temperature also seems to contradict the results of [13], in which a value of 0.77 eV was calculated for the barrier of the first step of the Li^+ ion-hole separation (see figure 1). These calculations were made on the assumption that the hole transfer process takes place adiabatically, i.e. the relaxation of the reaction coordinate is much slower than hole exchange between trapping sites.

The way in which the transition between sites occurs plays a key role in the calculations and has to be addressed for each system individually, as discussed recently in [1, 2]. A useful 'adiabaticity' parameter G , has been introduced in [26]. It is determined by the ratio of the 'time spent' by the reaction coordinate in the Landau-Zener region [27] to the time taken by a one-electron (or a one-hole) transition between trapping sites. A large value of this ratio means that the barrier state may be approximately treated as stationary and calculated, taking into account both the electronic and the ionic relaxation of the lattice. The parameter G is defined as [26]

$$G = 2\pi|T|^2/h\Omega_c E_R \quad (1)$$

where T is the electron transfer matrix element, E_R is the so-called reorganization energy and $1/\Omega_c$ is the relaxation time of the reaction coordinate. In order to estimate the value of G we have calculated the reorganization energy and the transfer matrix element for the case of hole transfer between the nearest sites around the Li^+ ion in the $[\text{Li}]^0$ centre.

According to the conventional definition [26], E_R may be calculated as the difference between the energy at the adiabatic potential energy minima, corresponding to

the hole localization at one of the oxygen anions, and the state when the hole is localized at a nearest-neighbour oxygen anion but with the crystal relaxation remaining the same as in the first case. The calculation of T is much less straightforward [28, 29]. As shown in [29], for the case of electron transfer between strongly interacting resonant states, a good estimate of T may be obtained in terms of the charge-delocalized solution, using the following expression:

$$T = (E_- - E_+)/2.$$

Here E_- and E_+ are the system total energies at the top of the adiabatic barrier, corresponding respectively to the many-electron states Ψ_- and Ψ_+ , obtained from the configurational mixing between the non-orthogonal diabatic states Ψ_1 and Ψ_2 , localized at each diabatic minimum. The Ψ_{\pm} wavefunctions may be written as

$$\Psi_{\pm} = (\Psi_1 \pm \Psi_2)/[2(1 \pm S_{12})]^{1/2}$$

where the S_{12} is the overlap integral between Ψ_1 and Ψ_2 . To a good approximation, E_+ may be calculated as the crystal total energy, corresponding to the barrier-type relaxation and the wavefunction equally delocalized by two oxygen ions, whereas E_- is the crystal total energy, corresponding to the one-electron excitation from this state to the Ψ_- anti-bonding-type state, differing mainly by the sign in the linear combination of atomic orbitals, localized on the two oxygen anions.

The resulting values of T and E_R , calculated for the hole jumps between two nearest oxygen anions in the $[\text{Li}]^0$ centre are 0.25 eV and 2.0 eV. Assuming that the value of Ω_c is between 10^{13} and 10^{14}s^{-1} , we obtain for G an estimate of 3–30, i.e. larger than unity. This supports the ability to use the adiabatic approximation in the barrier height calculation for the hole jump between nearest sites.

The calculated values of the adiabatic barriers for the hole transfer between two nearest oxygen anions in the $[\text{Li}]^0$ centre and for the hole jump into the next-nearest-neighbour position appeared to be very close to each other and equal to about 0.9 eV, i.e. even larger than those obtained in the Mott-Littleton calculations [13]. This is most surprising for hole jumps around the Li^+ ion. The large barrier for the first jump of the hole out of the $[\text{Li}]^0$ centre may be partly caused by the large Coulomb interaction between the Li^+ ion and the hole. It should also be noted that the extent of the hole localization does not change in the next-nearest-neighbour position relative to the Li^+ ion; it is still almost completely localized on one oxygen anion. One of the reasons for the large barrier for the hole jump from the axial into the equatorial position might be the large axial lattice relaxation around the $[\text{Li}]^0$ centre. However, both results contradict experimental observations. Moreover, if the interaction between the hole and the impurity centre is so important, one can assume that the barrier for the unperturbed hole jumps between nearest sites of the perfect lattice has to be much lower.

To investigate this assumption and possible reasons for such large values of the barrier heights, we have simplified the system by performing the calculations for the localized hole transfer between nearest sites in the perfect lattice. The previous calculations [13, 14] suggested that the holes could not self-trap in MgO because of the large value of the localization energy. Therefore one could expect that the barrier for their intersite transfer has to be low, reflecting a high mobility. Surprisingly we obtain a value for the adiabatic barrier of 0.66 eV. This result reveals clearly that the

perturbation by the defect is not the main reason for the high barriers also in the previous case. Analysing the contributions of different factors to the barrier value, we find that about 30% of it is due to a repolarization energy, i.e. the difference between the energies of the polarization of the lattice by the hole localized on one site and delocalized by two sites. That is, in the delocalized case the polarization energy is about 0.2 eV smaller than in the localized case, contributing this value to the barrier height.

It is well known that electron correlation is especially important at reaction barrier regions and usually considerably affects their height. In our calculations the intra-ionic part of the electron correlation is effectively included in a semi-empirical manner through the electronic part of the lattice polarization and the experimental values of the ionic polarizabilities used in the calculation. In order to estimate the possible role of the interionic part of electron correlation we have performed *ab initio* cluster calculations of the localized and delocalized hole states.

3.3. Role of the electron correlation in the calculation of the adiabatic barrier of the SRP jumps

In calculating the magnitude of the differential electron correlation between the localized state situated on a given oxygen anion and the adiabatic barrier state for the hole transfer between nearest oxygen sites we have employed an embedded-cluster model. This comprises two explicitly treated oxygen anions surrounded by a point ion array chosen to reproduce the Madelung potential of the infinite crystal at the oxygen site. *Ab initio* all-electron calculations were performed using the program GAMESS [30], within the GVB formalism [31] to treat the open shell hole states at the Hartree-Fock level. The basis set utilized was 8-411G*, optimized for bulk magnesium oxide within the program CRYSTAL [32].

Post-Hartree-Fock treatment of the electron correlation was incorporated by configurational interaction involving single and double excitations (CISD) [33], with an active space that includes all valence electron orbitals and their corresponding virtual states.

Because of their point charge nature, it is not possible to perform geometry optimization of the surrounding ions. Hence, the positions of the nearest-neighbour embedding ions were taken to be the same as those calculated by the CLUSTER method. For the localized hole state the nearest magnesium cations are displaced $0.06a$ away from the oxygen anion on which the hole is situated, while the surrounding 12 oxygen anions relax towards the central oxygen anion by $0.03a$. At the transition state for hole migration, both oxygen anions are predicted by the semi-empirical method to relax by approximately 0.2 \AA away from each lattice site towards each other, with the magnesium cations now displaced $0.03a$ away from both oxygen sites.

The adiabatic barrier to hole transfer is given by the energy difference between the state in which the hole is completely localized on one oxygen centre and that in which it is equally distributed over the two adjacent oxygen sites, with the geometries of surrounding ions as described above. This barrier is found to be 1.05 eV at the *ab initio* Hartree-Fock level, while inclusion of CISD for the valence electrons greatly reduces this value to 0.23 eV. The correlation energies for the one-centre and two-centre localized states at these particular geometries are calculated to be 9.8 eV and 10.6 eV, respectively. Therefore the reduction in barrier height is due to the difference Δ between these two correlation energies. We have further examined the variation in Δ as a function of the separation between the two explicitly considered

oxygen anions in the hole migration transition state. The magnitude of Δ is found to be approximately invariant at 0.8 eV over a range of 0.8 Å in the inter-oxygen distance.

To explain the difference between the correlation energies of the localized and delocalized states it is necessary to examine the nature of the dominant excitations. At the transition state, the symmetry of the system is D_{2h} and the main excitation involves the promotion of an electron from the doubly occupied σ_g orbital to the singly occupied σ_u , and of a second electron to an unoccupied orbital. In the case of the localized hole state the electronic configurations with the largest coefficients in the CI expression do not involve excitations to or from the singly occupied orbital. Hence the majority of the correlation energy is due to electrons in the doubly filled valence orbitals. Consequently, at the barrier point to hole migration, the hole is distributed over several orbitals in the CI expression, giving rise to an extra contribution to the correlation energy.

While the above *ab initio* calculations can only be considered as a preliminary study, the importance of inclusion of correlation is apparent. Although the value of Δ , equal to -0.8 eV, cannot be treated directly as an additive correction to the barrier height of 0.66 eV obtained semi-empirically, the magnitude of the term is sufficiently large to suggest that the barrier for hole migration between nearest perfect lattice sites will be greatly reduced. The same arguments may be used to understand the high barrier values for the hole jumps near the defect. Since physically the processes are identical, it is quite plausible that the calculated barriers will be reduced if electron correlation were to be taken into account.

The correlation included in the *ab initio* calculations comprises both intra-ionic and inter-ionic contributions; however, the polarization energy calculated semi-empirically already includes intra-ionic polarization of oxygen anions sharing the hole. Consequently the value of Δ obtained here does not allow us to reach a more definite quantitative conclusion without performing more extensive *ab initio* calculations including both polarization of the surrounding lattice and electron correlation inside the cluster.

3.4. Self-trapping from the free hole state

Now, let us compare the results of the above calculations with the calculation of the self-trapping energy from the free hole state. Strictly speaking, in order to do this we need to use a method suitable for both localized and completely delocalized hole states. In principle the best candidate is the model Hamiltonian (MH) approach developed by Toyozawa [34]. However, at present such methods do not allow us to take into account the microscopic structure of the hole (i.e. the hole electronic density distribution and large displacements of surrounding ions). On the other hand, quantum-chemical methods are well suited to describing local chemical interactions of ions near a point defect treated in terms of the molecular cluster but fail to consider hole states delocalized through a whole crystal. Our idea is therefore to combine both methods.

The assumptions used in such an approach are as follows.

- (i) The valence and free hole bands have equivalent dispersions.
- (ii) The electronic polarization of the crystal produced by the delocalized hole and the hole localized on one site are equal.
- (iii) The hole state artificially localized in the molecular cluster, simulating the

perfect lattice, can be used as the initial state for the stationary quantum-chemical relaxation energy calculation.

In these assumptions we can find the bottom of the free hole band and the energy of the state in the band, corresponding to the certain degree of localization (one, two, etc, sites). The difference between these two energies will give us the so-called localization energy E_{loc} . Now, starting from the same localized state in the cluster calculation, one can find the relaxation energy E_{rel} , as a difference between crystal energies in that state without ionic displacements and the completely relaxed localized state. The sum of E_{loc} and E_{rel} is believed to be the self-trapping energy. In the simplest approximation the value of E_{loc} may be taken as half the valence band width [35–37]. In this approximation, the localization energy has been found to be close to or larger than the E_{rel} in MgO [13, 14].

In the present paper we used the more accurate MH method to calculate the hole localization energy on one or two anions. When constructing the MH, one has to take into account the fact that, since the upper valence bands of the alkali halides and oxides are formed by the p states of anions, the off-diagonal (in lattice sites) matrix elements of the MH differ from each other even for anions entering the same anion sphere. Neglect of these differences leads to an overestimate of the hole localization energy, as is the case for earlier studies [36, 37]. Let us write down the Hamiltonian of a perfect crystal in the tight-binding approximation incorporating two anion spheres of nearest neighbours. First, the free-hole Hamiltonian in site representation reads

$$H_h = - \sum_{L\mu} \epsilon_0 a_{L\mu}^\dagger a_{L\mu} - \sum_{L,L'} \sum_{\mu,\nu} t_{0\mu,L'\nu} a_{L\mu}^\dagger a_{L+L',\nu} \quad (2)$$

where L and L' are lattice translational vectors, $\mu, \nu = x, y, z, \binom{L}{\mu}$ is the Wannier function of p kind localized at the site L . (Coordinate axes are oriented along (100), (010) and (001) crystal axes.) $a_{L\mu}^\dagger$ and $a_{L\mu}$ are hole creation and annihilation operators at the p_μ orbital $\binom{L}{\mu}$ placed at the site L . An additional restriction in equation (2) is that $|L'| < 2a$, where a is the interanion distance. It follows from the lattice symmetry that the matrix elements $t_{0\mu,L'\nu}$ for anions L' in the first sphere could be described by three parameters: T_σ (interaction of two p orbitals which lie along the vector L' (figure 2) and oriented in the same manner), $T_{\pi 1}$ (p orbitals perpendicular to the vector L' and oriented in the direction of nearest anions) and $T_{\pi 2}$ (p orbitals perpendicular to L' and directed to the nearest cations). Thus, we find for an arbitrary vector L that the matrix $t_{0L'} = \|t_{0\mu,L'\nu}\| = \mathbf{C}_{L'}^\dagger \mathbf{t}_{L'} \mathbf{C}_{L'}$, where $\mathbf{C}_{L'}$ is the three-dimensional rotation matrix orienting sites 0 and L' along the z axis, $\mathbf{t}_{L'}$ diagonal matrix of elements $T_\sigma, T_{\pi 1}$ and $T_{\pi 2}$. For example, for $L' = (1, 1, 0)$ the matrix $\mathbf{C}_{L'}$ is an anti-clockwise rotation by an angle $\pi/4$, $t_{11} = T_\sigma, t_{22} = T_{\pi 1}, t_{33} = T_{\pi 2}$. We proceed in a similar way for anions L' from the second coordination sphere; in this case $\mathbf{t}_{L'}$ is diagonal for all L' , these diagonal elements are either T'_σ or $T'_\pi = T'_{\pi 1} = T'_{\pi 2}$. (Their meaning is the same for those in the first sphere.)

Diagonalization of equation (2) permits us to calculate the dispersion of all three hole bands $\epsilon_j(k)$, $j = 1, 2, 3$. Thus, the hole energies at Γ, X and L points of the Brillouin zone (BZ) are

$$\begin{aligned} \epsilon_\Gamma &= -\epsilon_0 - 8\alpha - 4\gamma - 2\delta \\ \epsilon_X^\parallel &= -\epsilon_0 + 8\alpha - 4\gamma - 2\delta & \epsilon_X^\perp &= -\epsilon_0 + 4\gamma - 2\delta \\ \epsilon_L^\parallel &= -\epsilon_0 + 8\beta + 2\delta & \epsilon_L^\perp &= -\epsilon_0 - 4\beta + 2\delta. \end{aligned} \quad (3)$$

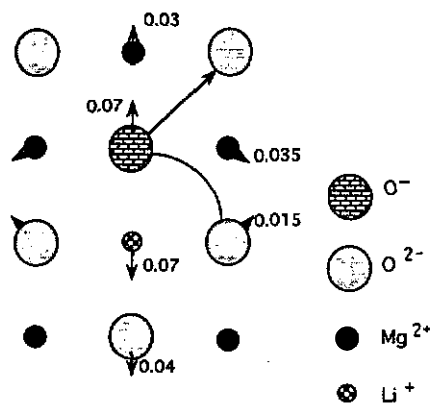


Figure 1. The schematic structure of the $[\text{Li}]^0$ centre in MgO. Long arrows show the hole transitions into the equatorial position and out of the centre. Small arrows indicate the directions of the ion displacements around the centre from their site position. The numbers near the ends of the small arrows are the values of the ion displacements in the units of MgO lattice interionic distance.

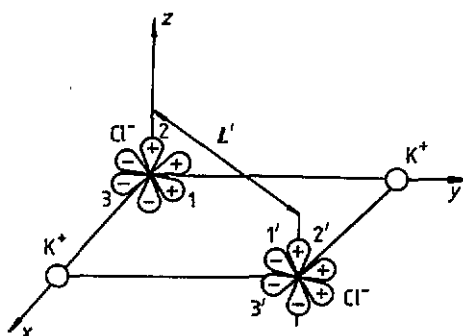


Figure 2. The schematic illustration of the notations used in the calculation of the matrix elements of the MH.

where the superscripts \parallel and \perp denote energy branches whose eigenvectors are parallel and perpendicular to the direction of the wavevector k . Also, $\alpha = \frac{1}{2}(T_\sigma + T_{\pi 1})$, $\beta = \frac{1}{2}(T_\sigma - T_{\pi 1})$, $\gamma = T_{\pi 2}$ and $\delta = T'_\sigma + 2T'_\pi$.

In the state corresponding to hole localization on one centre, the hole wavefunction may be written as

$$\Phi_1 = a_{0x}^+ |0\rangle$$

whereas in the two-centre case it takes the form

$$\Phi_2 = \frac{1}{4}(a_{0x}^+ + a_{0y}^+ + a_{1x}^+ + a_{1y}^+) |0\rangle.$$

The site 0 is placed at the coordinate origin, and site 1 lies on the σ (110) axis (anions 0 and 1 forming the V_k centre). The hole self-energy in these states appears to be equal to (cf [38])

$$E_1 = \langle \Phi_1 | H_h | \Phi_1 \rangle = -\epsilon_0 \quad E_2 = \langle \Phi_2 | H_h | \Phi_2 \rangle = -\epsilon_0 - T_\sigma.$$

Band-structure calculation by means of any quantum-chemical method allows us to obtain all the parameters of the Hamiltonian (2). In the present paper these calculations were done with the aid of the LUC method in the INDO approximation, employing the CLUSTER code [18, 19]. (Note that the same code was also used for the EMC $[\text{Li}]^0$ centre calculations.) We employed the LUCS $[\text{Mg}_8\text{O}_8]$ and $[\text{Mg}_{32}\text{O}_{32}]$, allowing us to obtain energies at correspondingly three and eight symmetry points of the BZ [18]. The calculation at only Γ , X and L k -points already satisfactorily reproduces the main features of the band structure and electron density distribution in ionic crystals [18]. In particular, the widths of the valence band obtained for the

small LUC (5.8 eV) and for the large LUC (5.9 eV) are very close. In the three- k -points approximation the centre of mass of the hole band may be written as

$$\epsilon_0 = -\frac{1}{24}(3\epsilon_{\Gamma} + 3\epsilon_{X}^{\parallel} + 6\epsilon_{X}^{\perp} + 4\epsilon_{L}^{\parallel} + 8\epsilon_{L}^{\perp}).$$

Other parameters of the MH can be easily obtained from equation (3).

The results of our LUC calculations have demonstrated that the localization energy depends only slightly on the number of k -points included and appears to be much smaller than half the valence band width, used as E_{loc} in the previous studies. Its value for the three k -points is calculated to be 1.9 eV and for eight k -points 2.0 eV. The present results concerning E_{loc} , however, should be considered as estimates, consistent with the method of calculation of the relaxation energy, since there are still discrepancies between the theoretical and the experimental values of E_{ν} for MgO. In particular, our value of $E_{\nu} = 5.9$ eV is larger than the total valence band width of 5.1 eV obtained in the CRYSTAL calculation [32] and 4.8 ± 0.3 eV obtained in recent experiments [39]. For comparison the calculations [40] by the tight-binding method gave for E_{ν} the value of 8.5 eV. More detailed discussion of the present status of the studies of MgO electronic structure is presented in [13, 32, 40].

With the present value of E_{loc} and the relaxation energy $E_{\text{rel}} = -2.4$ eV obtained in [14] by the same method, we obtain a self-trapping energy of about -0.4 eV. Its small value shows that the localized state of the hole is close to the bottom of the band of free hole states. This is consistent with the conclusion of the previous section that the SRPs in MgO should have small barriers for their jumps and therefore move very rapidly, which in other words means a strong interaction with the band of delocalized states.

4. Discussion and conclusions

Although the self-trapping of holes and excitons is a well established phenomenon, its understanding in particular cases is a difficult problem. Most of the theoretical attempts in this field are based on the calculation of the self-trapping energy, where a negative value indicates trapping. The evaluation of the self-trapping energy is based on an uncertain procedure, which assumes that for the relaxation energy calculation one can completely localize the particle in the molecular cluster, where it is considered to be in a stationary state. The lattice relaxation energy for such a state of the charged hole is usually large (greater than 1.5 eV). As shown in the present paper, for the case of the pure anion valence band, one can calculate the localization energy using the same calculation scheme as for the relaxation energy. This approach may be generalized for the more complicated case of mixed bands and makes the estimate of the self-trapping energy more reliable. Our calculations for both the hole relaxation and the localization energies have shown that the resulting hole self-trapping energy in MgO is small, i.e. about -0.4 eV.

However, even the negative value of the self-trapping energy does not prove that the hole will be really self-trapped in the sense of being localized on one ion or several ions long enough to be observed by spectroscopic methods. If the barrier for diffusion is small, its behaviour may be difficult to distinguish from that of the free hole. Therefore, calculation of the barrier for the hole diffusion is a necessary part of the total study of hole self-trapping.

To avoid the problem of the non-stationary wavefunction for the hypothetical localized hole state in the perfect lattice, one can start from the states of the holes that are trapped by impurities. These hole states are usually stable and therefore may be successfully treated by stationary quantum-chemical methods. The thermally activated site jumps of the holes away from these defects in the first stage may be accompanied by the formation of localized SRPs and can be treated adiabatically. Present semi-empirical and *ab initio* quantum-chemical calculations of the height of the barrier for the localized hole jumps between the nearest sites in the perfect MgO lattice have emphasized the importance of the electron correlation at the barrier point. In particular, the difference between the crystalline lattice polarization energies for the one-site hole localization and the barrier point for its diffusion, corresponding to the hole delocalization by two nearest anion sites, increases the barrier height. Simultaneously the electron correlation treated explicitly for the two-site hole state appears to be larger than that for the one-site state and considerably decreases the barrier. Although we were unable to apportion accurately both of these effects, we believe that real adiabatic barriers for the hole diffusion in MgO are much less than the values of about 0.7–0.8 eV predicted by the previous pair-potential calculations [13] and present quantum-chemical CLUSTER calculations. This result is in qualitative agreement with the small value of the self-trapping energy. Both of them reveal that the state of the one-site localized hole is close to the band of free hole states and strongly interacts with it.

Finally we would emphasize that the static many-electron quantum-chemical approach proposed in the present paper may be useful for studies of holes and excitons self-trapping in a wide range of materials.

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