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Ab initio and semiempirical calculations of H^- centers in MgO crystals

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The atomic and electronic structure of H^- ions substituting for O^{2-} ions in regular sites in MgO crystals are calculated using an *ab initio* Hartree-Fock (HF) cluster approach and its semiempirical version, intermediate neglect of the differential overlap. The theoretical optical absorption energy is predicted to be 10 eV, which is supported by analysis of experimental data for the H^- centers in a series of ionic crystals. The HF simulations of H^- ion diffusion via direct interstitial hops along the [100] axis predict an activation energy of about 3 eV. [S0163-1829(99)05303-5]

I. INTRODUCTION

Hydrogen-related defects are very common in ionic crystals[1] including oxides.[2] They have a profound effect on the electronic and optical properties of many oxide materials including MgO,[3–12] CaO,[12–14] Al_2O_3,[15,16] $MgAl_2O_4$,[17] TiO_2,[18] $LiNbO_3$,[19,20] and $LiTaO_3$.[21] Studies of hydrogen substituting for oxygen in thermochemically reduced MgO crystals have evoked considerable interest during the past 15 years.[3–12] These centers consist of a proton surrounded by either two or three electrons (H^- and H^{2-} centers), which occupy an oxygen vacancy. H^- ions play an important role in the *F* center long-lived luminescence through electron trapping by H^- ions and formation of H^{2-} ions.[11,12] The presence of the H^{2-} ion has been verified by EPR spectroscopy of deuterium-enriched MgO crystals.[7] H^- ions have been identified by local vibrational modes at 1053, 1032 and 1024 cm^{-1}.[3,6] However, all attempts to observe the optical absorption of the H^- centers in the wide energy range of $0.5-6$ eV were unsuccessful.[12]

H^- and H^{2-} centers in MgO have been a subject of several theoretical studies.[22–24] Pandey and Vail[22] have carried out embedded-cluster calculations of these defects, treating 19-atom clusters within the unrestricted Hartree-Fock approximation as implemented into the ICECAP computer code. However, neither information on the defect level position in the band energy gap nor absorption energies have been presented. Wang and Holzwarth studied the electronic structure of both H^- and H^{2-} substitutional defects, within the local-density theory, using the self-consistent mixed-basis pseudopotential techniques.[23] The use of a small supercell in this study resulted in wide defect bands which made determination of the hydride energy level in the gap quite problematic.

The presence of hydrogen as a transmutation product is important to understand the modifications of the electronic, mechanical and optical properties of ceramics subjected to irradiations with energetic neutrons. In the past two decades much effort has been devoted to studying proton diffusion in prospective ceramics (see Refs. 15 and 16 and references therein). The motivation for these studies was the potential use of ceramics for hydrogen-storage applications due to their low permeability to hydrogen. However, the mechanism of hydrogen diffusion is still unknown. Shell-model calculations assuming a vacancy diffusion mechanism predict a very high energy barrier of 4.85 eV.[22]

In the present paper, we have performed a theoretical study of the electronic structure, absorption energy, and diffusion of H^- defects in MgO using two different methods and large quantum clusters.

II. THEORY

We have used the embedded molecular cluster model in the framework of two types of calculations (*ab initio* and semiempirical) based on the Hartree-Fock (HF) molecular orbital theory. Our *ab initio* embedded cluster method is similar to the DICAP code which was found very useful in studies of defects in alkali halides.[25] Our approach and its application to defects in MgO are described in detail in Ref. 26. For calculations of the static (both atomic and electronic) properties of the hydride center, a 27-atom quantum cluster $[\mathrm{Mg_{12}O_{14}H}]^{-1}$ of O_h symmetry was used in *ab initio* calculations. This cube-shaped cluster consists of a single, negatively charged H^- ion in its center and three spheres of surrounding ions. The wave function for the excited state of the substitutional H^- ion is expected to be rather diffuse (similar to the H^{2-} ion[22]). This is in agreement with the fact that the ground state energy level of the H^{2-} ion is known experimentally to lie close to the bottom of the conduction band; the same is to be expected for the H^- excited state. Therefore we have augmented the standard 31 G basis set for the H^- ion with an additional diffuse orbital with an exponent of 0.08 a.u. Six nearest neighbor (NN) Mg^{2+} cations and another eight Mg^{2+} cations from the third sphere were treated in the valence approximation using the 21/21 G basis set.[27] Their cores were represented by effective core pseudopotentials.[28] Twelve O^{2-} anions, which are the 2NNs of the defect, were considered as all-electron atoms with 721/41 G basis set[27] The Madelung potential of the crystalline lattice field was simulated by 200 point charges surrounding the quantum cluster. To improve the cluster boundary conditions, Mg^{2+} ions nearest to the cluster were simulated by bare core pseudopotentials without basis functions attached. In order to allow geometry optimization for ions in a quantum cluster, short-range interactions between O^{2-} ions outside the cluster and Mg^{2+} ions inside the cluster have been described by atom-atom potentials (see more in Refs. 25 and 26):

$$\phi_{ij}(r_{ij}) = A_{ij}\exp(-r_{ij}/\rho_{ij}). \tag{1}$$

The parameters of these potentials ($A_{ij}=46.8624$ a.u. and $\rho_{ij}=1.7569$ a.u.) were taken from Ref. 29.

The total energy gradient optimization technique was employed to find the equilibrium ground-state configuration of the cluster. In *ab initio* studies we used the GAUSSIAN-92 computer code[27] which was modified to include classical contributions, Eq. (1), to the total energy and energy gradients[25] as well as energy derivatives for the cluster in the field of point charges.[26] A similar method was also applied in defect diffusion simulations using 81-atom quantum clusters (see below). In these calculations we have optimized the equilibrium and saddle point geometry for the jumping interstitial ion at the beginning and in the middle of its path, respectively. The activation energy for a diffusion jump is the difference between the corresponding total energies, calculated for the relaxed lattice around the defect.

Another computational technique used was the semiempirical intermediate neglect of the differential overlap[30] (INDO) version of the HF method. Recently, this formalism was modified for calculations of ionic solids and defects therein.[31] The Fock matrix elements in the modified INDO approximation contains several semiempirical parameters. The *orbital exponent* ζ enters the radial part of Slater-type atomic orbitals:

$$R_{nl}(r) = (2\zeta)^{n+1/2}[(2n)!]^{-1/2}r^{n-1}\exp(-\zeta r), \tag{2}$$

where n is the principal quantum number of the valence shell. The diagonal matrix elements of the interaction of an electron in the μth valence atomic orbital (AO) on atom A with its own core are written as

$$U^A_{\mu\mu} = -E^A_{\mathrm{neg}}(\mu) - \sum_{\nu\in A}\left(P^{(0)A}_{\nu\nu}\gamma_{\mu\nu} - 1/2P^{(0)A}_{\nu\nu}K_{\mu\nu}\right), \tag{3}$$

where $P^{(0)A}_{\mu\mu}$ is the diagonal elements (initial guess) of the density matrix, $\gamma_{\mu\nu}$ and $K_{\mu\nu}$ are one-center Coulomb and exchange integrals, respectively, and $E^A_{\mathrm{neg}}(\mu)$ is the initial guess of the μth AO energy. The interaction of an electron in the μth AO on atom A with the core of another atom B reads as

$$V^B_\mu = Z_B\{1/R_{AB} + [\langle\mu\mu|\nu\nu\rangle - 1/R_{AB}]\exp(-\alpha_{AB}R_{AB})\}, \tag{4}$$

where R_{AB} is the distance between the cores of atoms A and B, Z_B is the core charge of atom B, and the parameter α_{AB} describes the non-point character of this interaction. The resonance-integral parameter $\beta_{\mu\nu}$ enters the off-diagonal Fock matrix elements for the spin component u:

$$F^u_{\mu\nu} = \beta_{\mu\nu}S_{\mu\nu} - P^u_{\mu\nu}\langle\mu\mu|\nu\nu\rangle, \tag{5}$$

where the μth and νth AO are centered at different atoms, $S_{\mu\nu}$ is the overlap matrix between them, and $\langle|\rangle$ are two-electron integrals. Thus, the modified INDO parametrization scheme contains the following set of parameters per atom: $\zeta, E_{neg}, P^{(0)}, \alpha$, and β.

This method has been successfully applied to the study of defects in many metal oxides, including MgO, $Li_2O, ZrO_2, Al_2O_3, KNbO_3, KTaO_3$ (see Ref. 32 and references therein). In these calculations quantum clusters consisting of 125 atoms (nine spheres of atoms surrounding a defect in a fcc lattice) were typically used. In the present study we found that $[\mathrm{Mg_{62}O_{62}H}]^{-1}$ clusters are sufficient. This semiempirical embedded cluster model provides an accurate Madelung potential on cluster atoms via the Ewald summation technique and accounts for the nonpoint-charge distribution of ions near the quantum cluster. The INDO parameters for Mg and O were taken from previous studies.[32] The standard INDO parametrization scheme[30] reproduces reasonably well the properties of a neutral hydrogen atom and a proton. However, these parameters obviously cannot be explored in our study which focuses on a negatively charged H^- ion. We readjusted the hydrogen parameters to the experimental properties of a series of H-containing ions and molecules, including MgH_2, LiH, H_2, etc. In particular, we reproduced the experimental dissociation energies and equilibrium interatomic distances (geometry) of these molecules with an accuracy of 1%–2%.

We also checked these parameters by calculating the band structure and lattice parameters of LiH and MgH_2 crystals; the results are close to the relevant experimental data. The optimized INDO parameters are given in Table. I. We have used the INDO SYM-SYM code[33] which permits a complete treatment of the point symmetry of defects and automated geometry optimization.

TABLE I. Optimized parameters of the INDO method for H^- ions. The diagonal element of the β matrix for hydrogen ion interaction is $\beta_{\nu\nu}(H)=9.0$, off-diagonal elements are $\beta_{\mu\nu}(H-Mg)=\beta_{\mu\nu}(H-O)=3.5$.

	AO	(a.u.)	Energy (eV)	
	1*s*	0.60	6.8	
	2*p*	0.40	1.0	
		α_{AB} matrix		
A (core)	*B*		(s,p,d orbitals)	
Mg	H	0.25	0.0	0.0
O	H	0.20	0.0	0.0
H	Mg	0.25	0.0	0.0
H	O	0.25	0.25	0.0
H	H	0.24	0.0	0.0

A. Results and discussion

1. Optical absorption energy

The optimized ionic displacements for the three NN spheres of ions and the effective charges on the ions surrounding the H^- center are given in Table II. In our *ab initio* calculations, the Mg ions are displaced outwards from the defect by 1% of the interatomic Mg-O distance in a perfect crystal due to the Coulomb repulsion from the H^- ion, whereas the 2NN O ions are displaced inwards by 4%. A similar relaxation was also found in our semiempirical INDO calculations presented in Table II. Similar O ion displacements but larger Mg displacements were obtained in the *ab initio* ICECAP calculations.[22]

The effective charges of Mg and O ions are close to those expected for purely ionic bonding (± 2 e). (Note that the Mulliken population analysis was used in *ab initio* calculations and the Löwdin analysis was used in the semiempirical calculations.) *Ab initio* calculations predict half an electron of the H^- defect to be delocalized, mainly over the NN Mg ions. In the INDO calculations H^- electrons are much more strongly localized, perhaps due to the absence of diffuse functions in the basis for H.

TABLE II. Results of *ab initio* and semiempirical calculations of the ionic displacements (in units of the interatomic Mg-O distance, $a_0=2.1$ Å) and effective charges (in $|e|$) on ions surrounding the H^- ion in MgO crystals.

		Coordinates of atom		
Atom	*x*	*y*	*z*	Charge on atom
		ab initio		
H	0.00	0.00	0.00	−0.458
Mg	1.01	0.00	0.00	1.608
O	0.97	0.97	0.00	−1.803
Mg	1.00	1.00	1.00	1.899
		ICECAP Ref. 22		
Mg	1.03	0.00	0.00	-
O	0.97	0.97	0.0	-
Mg	1.03	1.03	1.03	-
		INDO		
Mg	1.02	0.00	0.00	1.805
O	0.98	0.98	0.00	−1.814
Mg	1.01	1.01	1.01	1.813

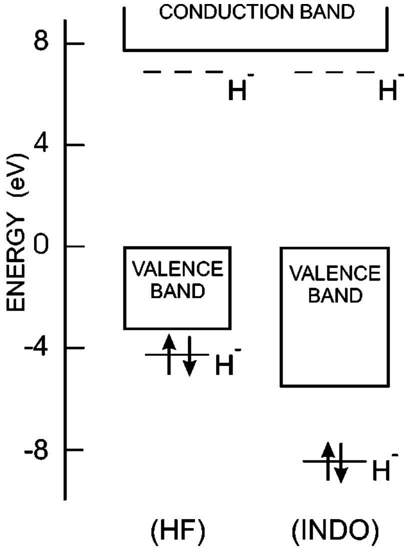

FIG. 1. Positions of the one-electron levels of the H^- defect with respect to the perfect MgO bands calculated by means of the (a) *ab initio* HF and (b) semiempirical INDO. Dashed lines denote the empty levels below the conduction band. The width of the valence band in the HF calculation (3.3 eV) is narrower than in the INDO calculation (5.5 eV) because the quantum cluster used in HF is much smaller than in INDO. The experimental width of the valence band is ≈6 eV.

As follows from both *ab initio* and semiempirical results, the H^- impurity has two local states. One of them, occupied by two electrons, lies *below* the bottom of the O 2*p* upper valence band (Fig. 1). The energy separation is about 1 eV in *ab initio* calculations and 3 eV in INDO. Another, empty energy level is located by both methods 7 eV above the top of the valence band. These results are in qualitative agreement with those obtained in the local density approximation (LDA) calculations.[23] The fact that a virtual state (vacant energy level) of the H^- center lies very close to the bottom of the conduction band makes this center a shallow acceptor for electrons. Thus, the H^- ion acts as an efficient trap for electrons released from the *F* centers as was discussed in Ref. 12.

It is often stated in the literature that HF calculations overestimate transition energies. This conclusion typically refers to the energy of the optical gap in insulators, estimated roughly as the difference of one-electron energies for the top of the outmost occupied valence band and virtual states at the bottom of the empty conduction band. However, much better results are obtained with the self-consistent field (ΔSCF) method based on the calculation between the difference of the two *total* energies — for the ground and excited states. According to the Frank-Condon principle, the absorption energy is the difference between these two total energies calculated for the vertical transition, e.g., with the atomic

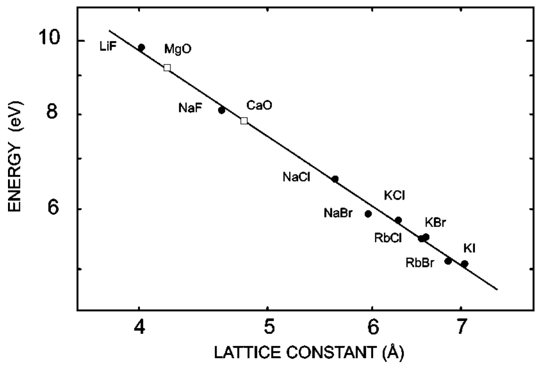

FIG. 2. Mollwo-Ivey plot of H^- ion absorption energy vs lattice constant in ionic crystals. The extrapolated values for MgO and CaO crystals are represented by square symbols.

geometry fixed at the equilibrium ground state. This is well illustrated by our INDO calculations. The difference between the one-electron energies for the optical gap is as much as 18.5 eV (with the experimental value of 7.8 eV). ΔSCF greatly reduces this value, to 10.2 eV. It is also well known that for delocalized band states, the polarization effects caused by an electron in the conduction band and a hole in the valence band are quite important. Indeed, the incorporation of these effects using the restricted configuration interaction (RCI) method[34,35] matches the theoretical and experimental optical gaps. In Fig. 1 we have used the RCI gap value for the perfect MgO lattice.

The H^- optical absorption energy calculated by the ΔSCF method yields 10 eV, far inside the absorption edge. This explains the failure of attempts to observe the H^- absorption experimentally in the wide range of energy between 0.5 and 6 eV.[11,12] Recent numerical defect calculations in MgO demonstrate that the ΔSCF method gives good results for optical transition energies (absorption/luminescence) for localized states due to point defects, with an accuracy of $0.2-0.3$ eV.[32] This accuracy is sufficient for the semi-qualitative conclusions we draw in this paper.

Studies (both theoretical and experimental) of the so-called *U* centers in alkali halides and alkaline-earth fluorides have long been a subject of interest.[36–40] The *U* center is an H^- impurity substituting for an anion. The optical properties of the *U* centers in the near UV region have been extensively investigated and reveal a close analogy between *F* (anion vacancy which has trapped an electron) and *U* centers. The latter can be thought of as an *F* center perturbed by a neighbor hydrogen atom. In fact, both *F* and *U* absorption band peaks obey the Mollwo-Ivey relation.[36] To estimate the optical absorption transition in MgO and CaO oxides, we have plotted, in Fig. 2, the *U* center absorption energy as a function of the lattice constant. (Data for KI, RbBr, KBr, NaBr, NaCl, KCl, and RbCl are taken from Ref. 36, whereas data for LiF and NaF are taken from Refs. 37 and 41, respectively). From this plot, the H^- absorption energies in MgO and CaO would occur at about 9.2 and 7.8-7.9 eV, respectively, far inside the corresponding absorption edges. The extrapolated value for MgO agrees very well with our calculated value. A smaller predicted absorption energy for CaO is also in agreement with the calculations.[14]

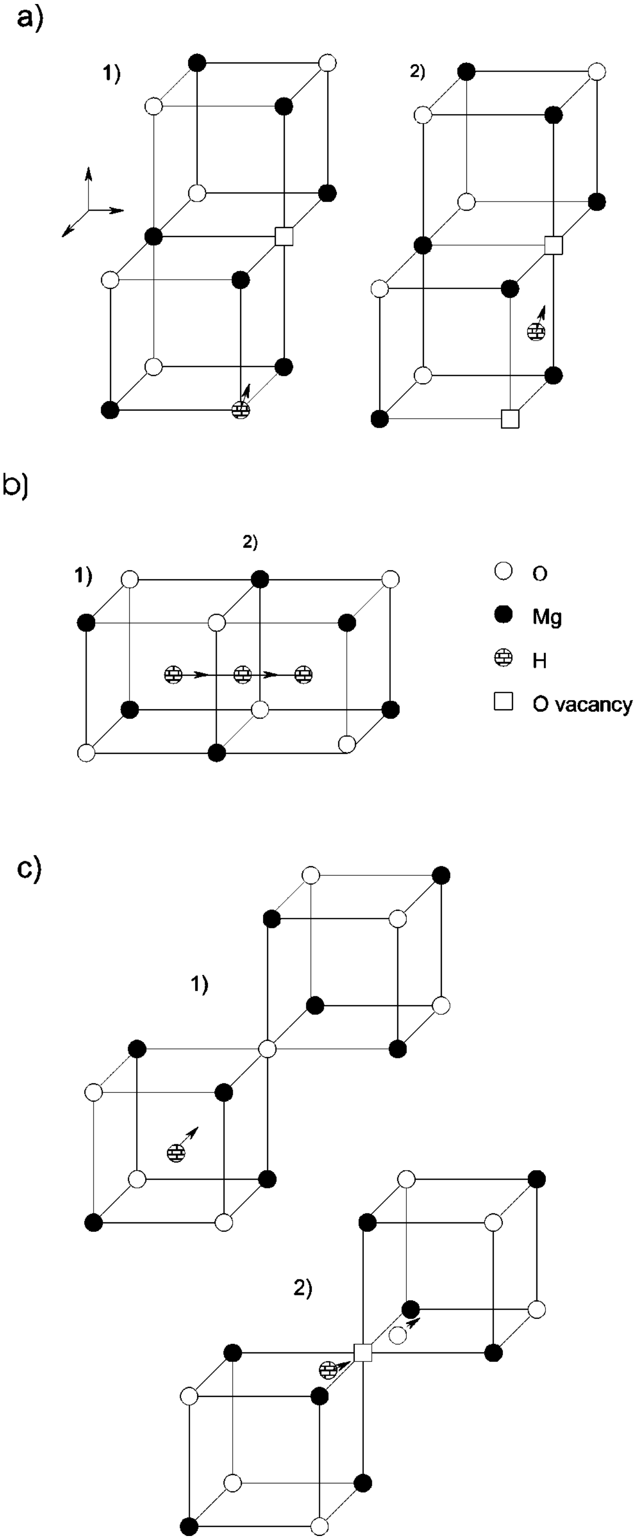

FIG. 3. (a)Vacancy mechanism of the substitutional H^- atom diffusion: (1) the initial (ground) state, (2) the saddle point. (b) Direct jump of the H^- interstitial through the cube face during its [100] hop. (c) Collinear interstitial mechanism of the H^- diffusion; (1) the initial state, (2) the saddle point.

B. Hydrogen diffusion

There are several possible mechanisms for the hydrogen diffusion in MgO. In principle, the substitutional ion can either jump by exchanging its position with an O vacancy

TABLE III. Atomic displacements (in units of $a_0 = 2.1$ Å) and charges on ions (in e) around H^- ions in MgO during its diffusion hop along the [100] axis obtained in the *ab initio* HF calculation [see Fig. 3(b)].

	Equilibrium point configuration					Saddle point configuration			
	Coordinates					Coordinates			
Aton	*x*	*y*	*z*	Charge on ion	Atom	*x*	*y*	*z*	Charge on ion
H	0.50	0.00	0.00	−0.352	H	0.00	0.00	0.00	−0.431
Mg	0.02	0.46	0.46	1.607	Mg	0.00	0.51	0.51	1.746
O	−0.07	0.54	−0.54	−1.745	O	0.00	0.61	−0.61	−1.714
Mg	0.95	−0.45	0.45	1.640	Mg	0.92	−0.47	0.47	1.701
O	1.04	0.54	0.54	−1.834	O	0.99	0.50	0.50	−1.859
Mg	−0.98	−0.48	0.48	1.843	Mg	−0.92	−0.47	0.47	1.701
O	−1.00	0.49	0.48	−1.834	O	−0.99	0.50	0.50	−1.859

(the vacancy mechanism), or become an interstitial. If it goes to the interstitial position, there are again two possibilities: to make direct hops along the [100] axis, or along the [111] axis via the so-called collinear interstitial mechanism. All three mechanisms are shown schematically in Fig. 3. Using the *ab initio* HF method, we first modeled a standard vacancy mechanism [Fig. 3(a)] and found that this is not energetically feasible since the exchange of positions between an H^- ion and an O vacancy requires a very large activation energy due to the mutual repulsion of these two positively charged defects. This is compatible with the activation energy value (4.85 eV) found for H^- diffusion by the vacancy mechanism using the shell model.[22] The likely alternative is to assume that a substitutional H^- defect leaves the O site to an interstitial position and then moves through the crystal as an interstitial [Fig. 3(b)]. We have simulated the H^- ion diffusion by such a direct interstitial mechanism using the the above described *ab initio* HF method. The $[Mg_{40}O_{40}H]^-$ cluster employed in these *ab initio* calculations contained two adjacent cubes. The basis set was placed on 13 central atoms, and the other atoms were represented by pseudopotentials. The quantum cluster was embedded in the crystal field modeled by 172 point charges. Twelve atoms nearest to the defect were allowed to relax. In the equilibrium configuration, the H^- ion is situated in an interstitial position in the cube center, then it hops along the [100] axis [Fig. 3(b)] with the saddle point at the cube face.

The effective ionic charges and displacements are summarized in Table. III. The largest displacements correspond to NN O atoms due to the Coulomb repulsion with the H^- ion. Our calculations show that such direct interstitial jumps require an activation energy of about 3 eV.

Of great interest is the simulation of the third diffusion mechanism, the collinear interstitial mechanism for the H^- ion diffusion [Fig. 3(c)] where an interstitial H^- ion moves from the center of the cube along the [111] body diagonal and in its saddle point forms a dumbbell with an O^{2-} ion in a regular site. Recent shell-model calculations for self-interstitials (Mg^{2+},O^{2-}) in MgO show that the activation energy for collinear interstitial diffusion could be about half of that for direct interstitial jumps.[42] However, in our case with an asymmetric H^--O^{2-} dumbbell, it is non-trivial to optimize the defect geometry in the saddle point.

III. CONCLUSIONS

The two different calculation methods used for quantum chemical simulations of the substitutional H^- ions in MgO gave very similar results for its equilibrium geometry and predict an optical absorption energy as high as 10 eV. This conclusion is confirmed by analysis of the experimental data for substitutional H^- ions in a number of alkali halides.

The calculated positions of the excited energy levels of H^- ions in MgO, close to the bottom of the conduction band, are similar to recent results on F^+ centers, which are other positively charged defects in the oxygen sublattice.[42,43] Another similarity is that for both defects the activation energies for diffusion were found to be close.[42–44]

We would like to stress that the calculation of optical properties of charged impurities with diffuse excited states remains a challenging problem requiring development of new accurate and consistent formalisms. As was recently demonstrated in the study of the O^- impurities in BaF_2,[45] the results of the calculations for optical excitation energy depend considerably on (1) the basis set optimization, (2) Pauli and other cluster-embedding effects, (3) inclusion of adequate basis functions for host crystal ions, corresponding to the unoccupied orbitals (conduction band) of the ground state, (4) treatment of the correlation corrections, and (5) the long-range polarization of the rest of the crystal.

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