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Theory of bound polarons in oxide compounds

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We present a multilateral theoretical study of bound polarons in oxide compounds MgO and α-Al_2O_3 (corundum). A continuum theory at arbitrary electron-phonon coupling is used for the calculation of the energies of thermal dissociation and photoionization [optically induced release of an electron (hole) from the ground self-consistent state], as well as optical absorption to nonrelaxed excited states. Unlike the case of free strong-coupling polarons, where the ratio κ of the photoionization energy to the thermal dissociation energy was shown to be always equal to 3, here this ratio depends on the Fröhlich coupling constant α and the screened Coulomb interaction strength β. Reasonable variation of these two parameters has demonstrated that the magnitude of κ remains usually in the narrow interval from 1 to 2.5. This is in agreement with atomistic calculations and experimental data for hole O^- polarons bound to the cation vacancy in MgO. The thermal dissociation energy for the ground self-consistent state and the energy of the optically induced charge transfer process (hops of a hole between O^{2-} ions) have been calculated using the quantum-chemical method INDO (intermediate neglect of the differental overlap). Results obtained within the two approaches for hole O^- polarons bound by the cation vacancies (V^-) in MgO and by the Mg^{2+} impurity (V_{Mg}) in corundum are compared to experimental data and to each other. We discuss a surprising closeness of the results obtained on the basis of independent models and their agreement with experiment.

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The properties of polarons and bipolarons in oxide materials continue to attract considerable attention in solid-state and materials physics due to their possible relevance to the high-T_c superconductivity.[1] Theory for large-radius[2] and small-radius[3] polarons is well developed. At moderate temperatures polarons are usually bound to defects (vacancies or impurities) unavoidably present in any material. Examples are a hole trapped by the cation vacancy in MgO (called the V^- center) and a hole trapped by the Mg^{2+} impurity substituting for a regular Al^{3+} atom in Al_2O_3 (called the V_{Mg} center).[4]

Fundamental characteristics of free polarons are energies of their photoionization ($E^f_{\rm opt}$) and thermal dissociation ($E^f_{\rm th}$). From the well-known theorem 1:2:3:4 derived by Pekar[5] for relations between the average kinetic energy of the electron, the polarization energy of the crystal, $E^f_{\rm polariz}$, the modulus of the electron eigenenergy E^f_e, and the average potential energy of the interaction between the electron and the polarized crystal in the strong-coupling polarons, it follows, in particular, that the ratio between the photoionization energy $E^f_{\rm opt}=|E^f_e|$ and the thermal dissociation energy $E^f_{\rm th}=|E^f_e|-E^f_{\rm polariz}$ for a free polaron $\kappa^f\equiv E^f_{\rm opt}/E^f_{\rm th}=|E^f_e|/(|E^f_e|-E^f_{\rm polariz})$ equals exactly 3. A generalization of this ground-state theorem, which relates the interaction energy to the kinetic energy for free polarons, was derived by Lemmens, De Sitter, and Devreese for all values of the electron-phonon coupling constant.[6] Optical transitions of large polarons with taking relaxed excited states into account were examined in Ref. 7.

Calculation of the ratio $\kappa=E_{\rm opt}/E_{\rm th}$ of the photoionization and thermal dissociation energies allows one to examine the adequacy of different theoretical approaches to bound polarons. In the present paper we analyze this problem in two ways: using an extended *continuum* theory of large-radius *bound* polarons and performing *atomistic* calculations for the particular hole polarons in the above-mentioned ionic solids—MgO and corundum (α-Al_2O_3). These two types of calculations allow us to draw conclusions as to how the continuum approach can describe models, where the lattice polarization is of Fröhlich type, while the state of charge carriers is of small radius (such a model has been suggested, e.g., in Ref. 8 for a small Fröhlich polaron). In the framework of this approach, unknown values of the macroscopic parameters should be obtained from comparison with experimental data. At the same time, we examine the efficiency of the microscopic quantum-mechanical approaches for solving the aforementioned problems of bound states.

A variational theory of bound polaron states which embraces the overall interval of values of the Fröhlich coupling constant α and of the strength β of the Coulomb interaction

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between a band charge carrier and a charged impurity was developed in Ref. 9. The Hamiltonian of an electron (hole) in the field of an impurity interacting with the polar longitudinal optical (LO) phonons is

$$H=\frac{\mathbf{p}^2}{2m_b}-\frac{e^2}{\varepsilon_0 r}+\sum_{\mathbf{k}}\hbar\omega_{\mathrm{LO}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}+\sum_{\mathbf{k}}(V_k a_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}+\mathrm{H.c.}),\tag{1}$$

where $\mathbf{r}$ is the position coordinate operator of the electron (hole) with band mass m_b, $\mathbf{p}$ is its canonically conjugate momentum operator, and $a_{\mathbf{k}}^{\dagger}$ and $a_{\mathbf{k}}$ are the creation (and annihilation) operators for LO phonons of wave vector $\mathbf{k}$ and frequency ω_{LO}. The V_k are Fourier components of the electron- (hole-) phonon interaction

$$V_k=-i\frac{\hbar\omega_{\mathrm{LO}}}{k}\left(\frac{4\pi\alpha}{V}\right)^{1/2}\left(\frac{\hbar}{2m_b\omega_{\mathrm{LO}}}\right)^{1/4},\tag{2}$$

with the Fröhlich coupling constant

$$\alpha=\frac{1}{\hbar\omega_{\mathrm{LO}}}\frac{e^2}{\sqrt{2}}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right)\sqrt{\frac{m_b\omega_{\mathrm{LO}}}{\hbar}},\tag{3}$$

where ε_0 and ε_∞ are the static and high-frequency dielectric constants of the crystal, respectively. Choosing Feynman units, when the polaron radius $\sqrt{\hbar/(2m_b\omega_{\mathrm{LO}})}$ and the phonon energy $\hbar\omega_{\mathrm{LO}}$ serve as units of length and energy, respectively, we represent the second term on the right-hand side of Eq. (1) in the form $-\beta/r$, where the dimensionless Coulomb interaction strength relates to the Fröhlich coupling constant (3) as follows:

$$\beta=2\alpha/(\varepsilon_0/\varepsilon_\infty-1).\tag{4}$$

The approach, developed by Devreese *et al.*,[9] consists of two stages. First, the unitary transformation is performed:

$$U=\exp\left[\sum_{\mathbf{k}}(V_k a_{\mathbf{k}}\rho_{\mathbf{k}}-\mathrm{H.c.})\right],\quad \rho_{\mathbf{k}}=\langle\phi_n|e^{i\mathbf{k}\cdot\mathbf{r}}|\phi_n\rangle,\tag{5}$$

where $|\phi_n\rangle$ is the electron (hole) wave function, which will be found variationally. This transformation of the Hamiltonian (1) results in

$$H'\equiv U^{-1}HU=H_0+\sum_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}+H_{int},\tag{6}$$

$$H_0=\mathbf{p}^2-\frac{\beta}{r}+\sum_{\mathbf{k}}|V_k|^2|\rho_{\mathbf{k}}|^2-\sum_{\mathbf{k}}|V_k|^2(\rho_{\mathbf{k}}^{*}e^{i\mathbf{k}\cdot\mathbf{r}}+\mathrm{c.c.}),\tag{7}$$

$$H_{int}=\sum_{\mathbf{k}}[V_k a_{\mathbf{k}}(e^{i\mathbf{k}\cdot\mathbf{r}}-\rho_{\mathbf{k}})+\mathrm{H.c.}].\tag{8}$$

Second, the following trial function is proposed in Ref. 9, which is proved to be a fair approximation for all values of α and β:

$$|\psi\rangle=c|0\rangle|\phi_n\rangle+\sum_{\mathbf{k}}V_k^{*}g_{\mathbf{k}}^{*}(e^{-i\mathbf{k}\cdot\mathbf{r}}-\rho_k^{*})|0\rangle|\phi_n\rangle,\tag{9}$$

where c is a normalization constant and $|0\rangle$ is the phonon ground state. The variational principle with the trial function (9) results in

$$\frac{g_{\mathbf{k}}}{c}=-\frac{1-|\rho_{\mathbf{k}}|^2}{D_1(\mathbf{k})+D_2(\mathbf{k})+(1-|\rho_{\mathbf{k}}|^2)\chi/2},\tag{10}$$

where

$$\chi=\frac{1}{c}\sum_{\mathbf{k}}|V_k|^2(1-|\rho_{\mathbf{k}}|^2)(g_{\mathbf{k}}+g_{\mathbf{k}}^{*}),\tag{11}$$

$$D_1(\mathbf{k})=\langle\phi_n|(e^{i\mathbf{k}\cdot\mathbf{r}}-\rho_{\mathbf{k}})H_0(e^{-i\mathbf{k}\cdot\mathbf{r}}-\rho_{\mathbf{k}}^{*})|\phi_n\rangle,\tag{12}$$

$$D_2(\mathbf{k})=(1-|\rho_{\mathbf{k}}|^2)(1-\langle\phi_n|H_0|\phi_n\rangle).\tag{13}$$

The variational energy for the bound polaron is found to be

$$E=\langle\phi_n|H_0|\phi_n\rangle+\frac{\chi}{2}.\tag{14}$$

This energy is to be minimized with respect to the parameters entering the trial function $|\phi_n\rangle$. It is this minimal energy which relates to the thermal dissociation of a polaron bound to an impurity: $E_{\mathrm{th}}\equiv|E_{\mathrm{min}}|$. The electron (hole) eigenenergy is $E_c=E_{\mathrm{min}}-E_{\mathrm{polariz}}$, where E_{polariz} is the elastic energy of the polarization (i.e., the energy of the ionic polarization due to a lattice energy gain after self-consistent relaxation). The minimal energy, which is absorbed during the photoionization of a bound polaron [the optically induced release of an electron (hole) from the ground state], equals the modulus of the electron (hole) eigenenergy $|E_c|$:

$$E_{\mathrm{opt}}\equiv|E_c|=E_{\mathrm{th}}+E_{\mathrm{polariz}}.\tag{15}$$

Hence, the ratio of the photoionization energy and the thermal dissociation energy is

$$\kappa\equiv\frac{E_{\mathrm{opt}}}{E_{\mathrm{th}}}=\frac{E_{\mathrm{th}}+E_{\mathrm{polariz}}}{E_{\mathrm{th}}}.\tag{16}$$

In order to find the ratio κ, it is necessary to calculate the eigenenergy and the energy of the polarization field. Under the unitary transformation of Eq. (5), the Hamiltonian of the phonon subsystem turns to

$$H'_{ph}\equiv U^{-1}\sum_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}U=\sum_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}+\sum_{\mathbf{k}}|V_k|^2|\rho_{\mathbf{k}}|^2-\sum_{\mathbf{k}}(V_k\rho_{\mathbf{k}}a_{\mathbf{k}}+\mathrm{H.c.}).\tag{17}$$

Averaging the transformed Hamiltonian of the phonon subsystem on the trial function (9) gives the energy of the polarization field in a polaron bound to an impurity:

$$E_{\mathrm{polariz}}\equiv\langle\psi|H'_{ph}|\psi\rangle=\frac{\lambda}{1+\lambda}+\sum_{\mathbf{k}}|V_k|^2|\rho_{\mathbf{k}}|^2,\tag{18}$$

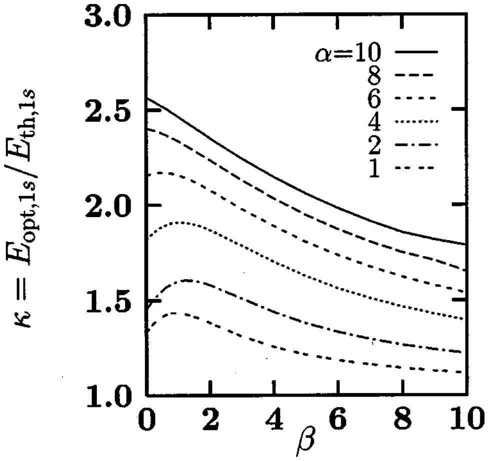

FIG. 1. Ratio $\kappa(\alpha,\beta)$ of the photoionization and thermal dissociation energies as a function of the strength of the Coulomb interaction β for a large polaron bound to an impurity with different values of the Fröhlich coupling constant α. Note that for large constants α, the calculated values $\kappa(\alpha,0)$ tend to 3, in conformity with the limiting result of the adiabatic theory (Ref. 5).

with

$$\lambda=\sum_{\mathbf{k}} \frac{|V_k|^2(1-|\rho_{\mathbf{k}}|^2)^3}{[D_1(\mathbf{k})+D_2(\mathbf{k})-(1-|\rho_{\mathbf{k}}|^2)\chi/2]^2}. \tag{19}$$

The variational parameters which deliver a minimum to the polaron energy, should be substituted into Eq. (18). In particular, for a spherically symmetrical variational function $|\phi_n\rangle$ the expressions on the right-hand side of Eq. (18) can be simplified to

$$\lambda=\frac{2\alpha}{\pi}\int_0^\infty dk\frac{(1-|\rho_k|^2)^3}{[D_1(k)+D_2(k)-(1-|\rho_k|^2)\chi/2]^2}, \tag{20}$$

$$\sum_{\mathbf{k}} |V_k|^2|\rho_{\mathbf{k}}|^2=\frac{2\alpha}{\pi}\int_0^\infty dk|\rho_k|^2. \tag{21}$$

Using for the ground state the hydrogenlike function, which was suggested in Ref. 9,

$$|\phi_{1s}\rangle=\frac{a^{3/2}}{2^{3/2}\sqrt{\pi}}e^{-ar/2}, \tag{22}$$

with a variational parameter a, we obtain the ratio $\kappa(\alpha,\beta)=E_{\mathrm{opt},1s}/E_{\mathrm{th},1s}$ as a function of the parameters α and β for a bound large polaron.

Results of the numerical calculation of the ratio $\kappa(\alpha,\beta)$ for a polaron bound to an impurity at $0\leqslant\alpha\leqslant 10$ and $0\leqslant\beta\leqslant 10$ are plotted in Fig. 1. As follows from this figure, for all $\alpha\neq 0$ the ratio $\kappa(\alpha,\beta)>1$. This inequality arises due to the following fact. During the photoionization process, the electron (hole) is released from the polarization potential well which is frozen, being adjusted to the electron (hole) wave function in the polaron ground state, while in the case of a thermal dissociation of the bound polaron there occurs a disintegration of the polarization state and, consequently, the coupling of the electron (hole) to the polarization well weakens continuously during this process.

As seen from Fig. 1, a decrease of the Coulomb attraction parameter β at a fixed value of α leads to a rise in the ratio $\kappa(\alpha,\beta)$, except for the region of β less than or of the order of unity at $\alpha<8$. In particular, at $\alpha=10$ and $\beta=0$, $\kappa(\alpha,\beta)$ is as large as 2.6, already close to but still smaller than 3, obtained in the polaron theory in the limit $\alpha\to\infty$. When increasing α, at a fixed value of β, the role of the interaction of an electron (hole) with polarization enhances, and thus, the value of the ratio $\kappa(\alpha,\beta)$ rises. A weak maximum in the region of small values of $\beta\sim 1$ at $\alpha<8$ apparently reflects a transition from the two-center state of a polaron moving around the impurity center to a one-center state, where an electron (hole) is in a unique potential well due to the common action of the polarization field and of the impurity center.

Further, we consider the excited state of the bound polaron in the nonrelaxed polarization well of the $1s$ ground state of Eq. (14), which will be referred to as a nonrelaxed excited state. The factors $V_k^*\rho_{\mathbf{k}}^*$ at $a_{\mathbf{k}}^\dagger$ and $V_k\rho_{\mathbf{k}}$ at $a_{\mathbf{k}}$ in the unitary transformation of Eq. (5) have the meaning of shifts of the polarization vibrations due to the interaction of the polarization field with the electron in the state φ_n:

$$U^{-1}a_{\mathbf{k}}U=a_{\mathbf{k}}-V_k^*\rho_{\mathbf{k}}^*, \quad U^{-1}a_{\mathbf{k}}^\dagger U=a_{\mathbf{k}}^\dagger-V_k\rho_{\mathbf{k}}. \tag{23}$$

Hence, the wave function of the nonrelaxed excited state $2p$ in the frozen polarization well correlated to the electron state $1s$ has the form

$$|\psi_{2p}\rangle=c|0\rangle|\phi_{2p}\rangle+\sum_{\mathbf{k}} V_k^*g_{\mathbf{k}}^*A_{\mathbf{k}}|0\rangle|\phi_{2p}\rangle,$$

$$A_{\mathbf{k}}=e^{-i\mathbf{k}\cdot\mathbf{r}}-\rho_{\mathbf{k}}^{*1s},$$

where $\rho_{\mathbf{k}}^{1s}=\langle\phi_{1s}|e^{i\mathbf{k}\cdot\mathbf{r}}|\phi_{1s}\rangle$. Like in the case of self-consistent polaron states, $g_{\mathbf{k}}$ is a variational function. After transformations similar to the above-described ones we obtain the following variational energy of the nonrelaxed excited $2p$ state:

$$E_{2p}^{1s}=\langle\phi_{2p}|H_0|\phi_{2p}\rangle+\frac{\chi_{2p}^{1s}}{2}, \tag{24}$$

wherein

$$|\phi_{2p}(\mathbf{r})\rangle=\frac{b^{5/2}}{2^{5/2}\sqrt{\pi}}e^{-br/2}r\cos\theta,$$

b is a variational parameter, and θ is the angle between $\mathbf{r}$ and the z axis. In Eq. (24),

$$\chi_{2p}^{1s}=-\frac{\alpha}{\pi}\int_0^\infty dk\int_0^\pi \sin\theta d\theta$$

$$\times\frac{\langle A_{\mathbf{k}}^*A_{\mathbf{k}}\rangle^2}{D_1^{1s}(\mathbf{k})+D_2^{1s}(\mathbf{k})-\langle A_{\mathbf{k}}^*A_{\mathbf{k}}\rangle\chi_{2p}^{1s}/2}, \tag{25}$$

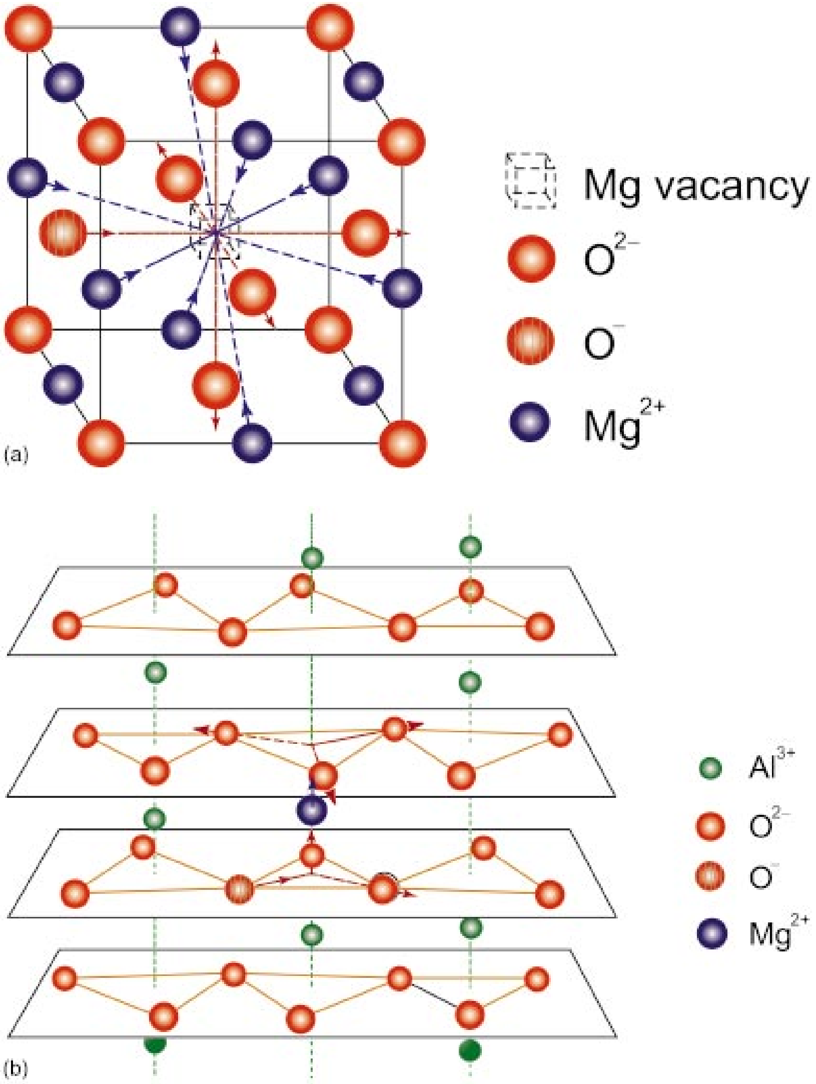

FIG. 2. (Color) Visualization of the atomic structure of the V^- center in MgO (a) and the V_{Mg} center in corundum (b) as calculated by means of the INDO method. In the V^- center five nearest-neighbor O atoms move outwards from the Mg vacancy by about 1% a_0 (the lattice parameter), whereas the O atom with a hole (shaded) is attracted to the Mg vacancy by 3% a_0, which makes the dominant contribution to the energy gain due to the lattice relaxation.

$$D_1(\mathbf{k})=\langle \phi_{2p}|A_{\mathbf{k}}H_0A^*_{\mathbf{k}}|\phi_{2p}\rangle, \tag{26}$$

$$D_2(\mathbf{k})=\langle A^*_{\mathbf{k}}A_{\mathbf{k}}\rangle(1-\langle \phi_{2p}|H_0|\phi_{2p}\rangle). \tag{27}$$

The thermal dissociation of the excited state $(2p)$ in the polarization well adjusted to the ground state $(1s)$ is $(E_{\mathrm{th}})^{1s}_{2p}=|E^{1s}_{2p,\min}|$.

The elastic energy of the polarization field is

$$(E_{\mathrm{polariz}})^{1s}_{2p}=\frac{\lambda_{2p}}{1+\lambda_{2p}}+\sum_{\mathbf{k}}|V_k|^2|\rho^{1s}_{\mathbf{k}}|^2, \tag{28}$$

which is similar to that for the $1s$ state. The first term on the right-hand side of this equation is by two orders of magnitude smaller than the second one; therefore, in both cases,

$$E_{\mathrm{polariz}}\approx\sum_{\mathbf{k}}|V_k|^2|\rho^{1s}_{\mathbf{k}}|^2. \tag{29}$$

The electron (hole) eigenenergy, corresponding to the nonrelaxed excited state $2p$ of a bound polaron, is

$$(E_c)^{1s}_{2p}=E^{1s}_{2p,\min}-E_{\mathrm{polariz}}, \tag{30}$$

and the minimal energy, which would be absorbed during the photoionization of a bound polaron from its nonrelaxed excited state $2p$, $(E_{\mathrm{opt}})^{1s}_{2p}=|(E_c)^{1s}_{2p}|$, takes the form

$$(E_{\mathrm{opt}})^{1s}_{2p}=(E_{\mathrm{th}})^{1s}_{2p}+E_{\mathrm{polariz}}. \tag{31}$$

Calculations for large polarons were performed with the following parameters. (i) For MgO, $\hbar\omega_{\mathrm{LO}}=0.09$ eV, $\varepsilon_\infty=2.96$ and $\varepsilon_0=9.86$,[10] and $m_b=2.77m_0$,[11] where m_0 is the bare electron mass; according to the definition (8), $\alpha=4.83$, whereas the calculation by Eq. (4) gives $\beta=4.14$. (ii) For α-Al_2O_3, $\hbar\omega_{\mathrm{LO}}=0.07$ eV (this value is suggested in Ref. 12 as an average of the phonon energies corresponding to three modes which provide the strongest contributions to the dielectric dispersion; this average value is in good agreement with more recent data,[13] where the measured optical phonon energy range is from 0.052 to 0.108 eV), $\varepsilon_\infty = 3.1$, and $\varepsilon_0 = 9.0$ (Ref. 12). An estimate of the hole effective mass in corundum from the experimental value $E_{\rm opt} = 2.58$ eV gives $m_h = 4.0 m_0$ and, consequently, $\alpha = 5.41$, $\beta = 5.66$.

Atomistic calculations for bound hole polarons were performed using the quantum-chemical method INDO (intermediate neglect of the differential overlap) (Ref. 14) modified for ionic solids.[15] This is based on the Hartee-Fock formalism and allows self-consistent calculations of the atomic and electronic structure of pure and defective crystals; that is, we are able to simulate polarons making no *a priori* assumptions about their geometrical structure. The INDO method was successfully applied for the study of many defects in oxide crystals (see the review article in Ref. 16 and references therein). Quantum cluster is embedded into the electrostatic field of the infinite nonpoint crystalline lattice. To model a hole polaron, we remove one electron from the cluster and allow all atoms to relax to the minimum of the total energy which gives us the atomic structure of a polaron. The analysis of a relevant final charge density distribution characterizes the polaron's electronic structure. Calculations of the difference of total energies for the ground and excited states with a fixed lattice geometry permit, in principle, to find the activation energy E_{opt} of a charge transfer process, when a hole after optical stimulation hops between O^{2-} ions. In its turn, the thermal dissociation energy $E_{\rm th}$ is calculated as the energy gain due to atomic displacements induced by a hole. Results of the INDO method are illustrated in Fig. 2.

In MgO, calculations were done for 125-atom clusters, modeling 9 spheres of atoms surrounding a cation vacancy in the coordinate origin. The basis set is the same as in our previous MgO studies.[17] In corundum, 65-atom stoichiometric clusters containing 13 formula units were used. The INDO parameters and basis set remain also the same as in previous α-Al_2O_3 calculations.[18] Both our microscopic calculations and electron spin resonance (ESR) data[2] demonstrate that a hole is well localized by a single oxygen atom, forming O^- ion considerably displaced from its regular lattice site. Practically, it is difficult to achieve a convergence in the self-consistent-field calculations for the delocalized (band) states necessary for calculations of the photoionization energy. This is also the case in our calculations for MgO and corundum. Neither are we aware of the relevant experimental data on optical ionization energies of these polarons.

Results of calculations for the V^- centers in MgO by the theories CTAC (continuum arbitrary-coupling theory), CTSC (continuum strong-coupling theory), and INDO and the available experimental data are collected in Table I.

The thermal dissociation energy $E_{\rm th}$ obtained in the continuum theory is close to the experimental value; the difference of about 10% between them seems to be within the limits of the error of measurement. The INDO method gives the value of $E_{\rm th}$ which is also close to the experimental data. The energy $E_{\rm opt}$ calculated in the continuum theory and within the INDO approach are both in good agreement with experiment. It is worth noting that CTAC better compares with experiment than CTSC.

TABLE I. Theoretical and experimental values of the $E_{\rm th}$ and $E_{\rm opt}$ for a polaron bound to the Mg vacancy (the V^- center) in MgO. CTAC, CTSC, and INDO stand for continuum arbitrary-coupling theory, continuum strong-coupling theory, and microscopic quantum-chemical approach, correspondingly; experimental values are given in the last column. $\hbar\omega_{ex}$ is a transition energy between the ground and excited states. The sign ''−'' indicates that the respective quantities were not calculated; the indexes g and e label, correspondingly, the ground and excited states (those states are $1s$ and $2p$ in CTAC).

Energies (eV)	CTAC	INDO	CTSC	Experiment
$E_{\rm th}$	1.24	1.6	1.15	1.4[a]
$E_{\rm opt}$	2.2	2.2	2.13	2.3[b]
$(E_{\rm opt})_e^g$	1.13	−	0.96	
$\hbar\omega_{ex} = E_{\rm opt} - (E_{\rm opt})_e^g$	1.07	−	1.16	
$E_{\rm polariz}$	0.9	−	0.97	
κ	1.77	1.38	1.85	1.64

[a] Reference 4.
[b] Reference 19.

A detailed discussion of the optical properties of the V^- centers in MgO has been presented in terms of small-radius polarons by Schirmer.[19] Theory predicts the ratio of the optical to thermal *reorientation* energy to be 4, and the ratio to polarization energy to be 2. The latter relation is also supported by our CTSC calculations (Table I). A very qualitative discussion of the large-radius vs small-radius hole polarons in corundum has been done in Ref. 24.

As distinct from the case of MgO, calculation of the polaron energy spectra in corundum is lacking for some material parameters. The band mass m_b has not been measured; the value $\hbar\omega_{\rm LO} = 0.07$ eV (Ref. 12) is not fully reliable; the thermal dissociation energy for the ground state of the V_{Mg} center is not known. The value of 0.7 eV from Table II is, in fact, the activation energy of a free small polaron,[23] which can be only conventionally considered as $E_{\rm th}$. It is worth noting, that the shell-model calculation underestimates the energy $E_{\rm th}$, resulting with 0.56 eV.[22] The energy $E_{\rm th}$ calculated by using the continuum theory is close to the respective result of the INDO approach; both of them differ from the experimental value.

TABLE II. Same as Table I for the V_{Mg} center in α-Al_2O_3.

Energies (eV)	CTAC	INDO	Experiment
$E_{\rm th}$	1.22	1.26	0.68[a], 0.7[b]
$E_{\rm opt}$	(2.58)[c]	−	2.58[a]
$(E_{\rm opt})_e^g$	1.15	−	
$\hbar\omega_{ex} = E_{\rm opt} - (E_{\rm opt})_e^g$	1.43	−	
$E_{\rm polariz}$	1.36	−	
κ	2.11	−	3.68

[a] Reference 20.
[b] Reference 21.
[c] The value of the energy $E_{\rm opt} = 2.58$ eV was used to estimate the effective mass of a hole: $m_b = 4 m_0$.

In conclusion, we have shown that the continuum arbitrary-coupling theory (CTAC) of large bound polarons qualitatively and quantitatively describes the energy spectrum and transition energies for the impurity centers in oxide compounds MgO and α-Al_2O_3. The thermal dissociation energies obtained in the framework of CTAC are rather close to the results of INDO. The CTAC has the advantage that it allows one to describe the impurity energy spectrum in detail. The surprising fact that two essentially different approaches have led to close results seems to be indicative of a dualistic nature of the bound polarons, which combine a *macroscopic* scale of polarization changes with *microscopic* (atomlike) charge carrier states. The efficiency of the proposed macroscopic approach to the bound polarons in the aforementioned oxides is probably due to the fact that the specific features of the small-radius (atomlike) states of charge carriers do not appreciably influence the distribution of the polarization field that is induced by themselves.

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