Ab initio model-potential embedded-cluster study of Jahn-Teller parameters and electronic transition energies of Cr^{2+} in oxide and fluoride octahedral coordination

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In this paper we present the results of an *ab initio* model potential [J. Chem. Phys. **89**, 5739 (1988)] embedded-cluster calculation of the potential-energy surface parameters of the two lowest electronic states (^5E_g and $^5T_{2g}$) of Cr^{2+}-doped MgO, CaO, SrO, and $KMgF_3$ using the complete-active-space self-consistent-field [Chem. Phys. **48**, 157 (1980)] and the averaged coupled-fair functional (ACPF) [J. Chem. Phys. **82**, 890 (1985)] methods. Impurity-ligand equilibrium distances, vibrational frequencies, Jahn-Teller energies, and energy barriers between compressed and elongated D_{4h} structures of the $(CrO_6)^{10-}$ and $(CrF_6)^{4-}$ clusters are calculated using an embedding method that has been shown to be able to describe the differential effects brought about on a given cluster by the different host lattices. Vertical transition energies (both absorption and emission) between the two states at the optimized cluster geometries are also calculated, correlating two different sets of electrons through ACPF calculations. As in an earlier calculation of $3d^9$ and $4d^9$ transition-metal ions, the Jahn-Teller coupling is shown to be stronger in going from MgO to SrO, within the oxide family of lattices, being dynamic in all the lattices.

I. INTRODUCTION

In the last years, many efforts have been dedicated to the study of localized electronic states around point defects in solids, and in particular, in transition-metal–doped ionic crystals, since these materials are good candidates to be tunable lasers.[1] The knowledge of the local geometry around the impurities is of key importance to the study of the local energy spectrum of these materials, which is necessary information in determining their laser potentiality. Direct experimental measurements on the ground-state local geometry, such as those of extended x-ray absorption fine structure or x-ray absorption near-edge structure techniques, are very difficult and not exempt of uncertainties.[2] As a consequence, more conventional techniques, such as electron paramagnetic resonance, acoustic paramagnetic resonance (APR), and UV-visible spectroscopy, are used to indirectly obtain local structural information.[3–5] On the other hand, from the theoretical point of view, the cluster approximation[6] became an important tool, which led in the last years to the formulation of embedded-cluster techniques able to give direct qualitative and quantitative information about the distortion around the impurity in the ground state as well as in excited states of the embedded cluster. These circumstances make clear the claimed importance of a close collaboration between theoretical and experimental studies,[1] which could provide complementary information on a common problem.

It is along this line that the *ab initio* model-potential embedding method (AIMP) has been proposed[7] as a first-principles method able to take into account in an accurate manner not only the Madelung potential of an ionic lattice, but also other interactions between the cluster and the surrounding lattice: electrostatic deviation from a point-charge description of the ions and quantum exchange and orthogonality (or linear independency) interactions. Recently, the AIMP embedding method has been successfully applied to

the study of local geometry and Jahn-Teller parameters on the ground state of Cu^{2+}, Ag^{2+}:MO (M=Mg, Ca, Sr),[8] high-pressure effects on the photoluminescence of Cr^{3+}:K_2NaGaF_6,[9] the bonding between CO and the (100) surface of the MgO crystal,[10] local geometries and electronic spectra of V^{2+}-doped fluoroperovskites ($KMgF_3$, $KZnF_3$, $KCdF_3$, $CsCaF_3$) (Refs. 11 and 12), and local geometries and electronic absorption spectrum of Mn^{2+}:CaF_2.[13,14] These studies have shown the ability of the AIMP embedding method to describe the influence of environmental changes on the cluster geometry and electronic structure.

In this work we present an AIMP study of the potential-energy surface parameters of two electronic states (^5E_g ground state and $^5T_{2g}$ excited state) of Cr^{2+}-doped MgO, CaO, SrO, and $KMgF_3$ lattices, both in the O_h symmetry and in the D_{4h} symmetry originated from the $^5E_g \otimes e_g$ and $^5T_{2g} \otimes e_g$ Jahn-Teller coupling.[15] We used the complete-active-space self-consistent-field[16] (CASSCF) and averaged coupled-pair functional[17] (ACPF) methods in order to handle the electronic structure of the $(CrO_6)^{10-}$ and $(CrF_6)^{4-}$ clusters embedded, respectively, in AIMP representations of the MgO, CaO, and SrO lattices, on one hand, and of the $KMgF_3$ lattice, on the other hand. We have also calculated the vertical transition energies (both absorption and emission) between the ^5E_g ground state and the $^5T_{2g}$ state, which can be identified with the 10-Dq parameter used in the crystal field theory in O_h symmetry,[18] and between their respective D_{4h} distorted electronic states: $^5A_{1g}$, $^5B_{1g}$ and $^5B_{2g}$, ^5E_g.

The experimental knowledge of the ^5E_g and $^5T_{2g}$ potential-energy surfaces in these materials is very limited. To our knowledge, APR experiments have been performed in Cr^{2+}:MgO (Ref. 4) and Cr^{2+}:$KMgF_3$ (Ref. 5) and far-infrared spectrum,[19] phonon scattering,[20] and thermal conductivity[21] studies have been conducted in Cr^{2+}:MgO; the results have been interpreted by means of a dynamic Jahn-Teller distortion of the octahedral (CrX_6) cluster unit

(X=O, F), due to a strong vibronic coupling with the lattice vibrations.[22–24] These experimental efforts concentrate on the determination of parameters of the lowest vibronic states, such as the tunneling parameter (3Γ), the random strain splitting ($\bar{\delta}$), and spin-orbit coupling parameter (D).[15] Structural parameters related to the Jahn-Teller coupling, such as the Jahn-Teller energy (E_{JT}) or the barrier between elongated and compressed D_{4h} structures (2β) are obtained only in an indirect way from the experimental measurements, after making *a priori* hypothesis about the nature of the coupling. That very often makes the resulting structural parameters strongly dependent on the initial hypothesis and they usually span over very wide ranges, thus becoming estimates rather than definite measurements.[23] The aim of this work is to obtain the structural parameters of the materials from *ab initio* computer simulations, which are expected to be reliable on the basis of the previous studies on similar systems.[8–14]

In Sec. II, we present a summary of the method used in this work, together with the details of the calculations. Finally, in Sec. III we present the result of these calculations and a comparison with the experimental results presently available.

II. METHOD

The AIMP method used to perform the embedded-cluster calculations on the geometries and transition energies of the defect crystals Cr^{2+}:MO (M=Mg, Ca, Sr) and Cr^{2+}:$KMgF_3$ has been presented in Ref. 7; here we will only summarize its main features.

Based on the group function theory (GFT) developed by McWeeney[25] and Huzinaga and co-workers,[26] the AIMP embedding method assumes that a good approximation to the local electronic states associated to the impurity is the following antisymmetric product wave function:

$$\Psi^{crys} = M\hat{A}[\Phi^{clus}\Phi^A\Phi^B \cdots], \tag{1}$$

where Φ^{clus} stands for the arbitrary cluster group wave functions ($\Phi^{(CrO_6)^{10-}}$ and $\Phi^{(CrF_6)^{4-}}$ in this work) and $\Phi^A, \Phi^B, \ldots$, are the environmental group wave functions (M^{2+} and O^{2-} in the oxide calculations and K^+, Mg^{2+}, and F^- in the fluoride calculations in this work). If these functions are chosen to be strong orthogonal,[25] then the energy of the whole crystal takes the simple form

$$E^{crys} = E^{clus} + E^{clus-env} + E^{env}. \tag{2}$$

The basic approximation in the GFT is the neglect of the electron correlation effects between the cluster and the environment, while intracluster electron correlation is properly accounted for in the GFT, as well as electrostatic and quantum-mechanical interactions with the lattice (exchange and orthogonality). It is expected that these cluster-environment correlation effects do not play a significant role in the determination of the local properties that are the objective of our interest; if they did, the selection of a larger cluster able to include these interactions would become compulsory.

The plain application of the GFT requires the calculation of Coulomb and exchange two-electron integrals between the cluster and the environment group wave functions that can,

however, be treated in an approximate way:[7] following the ideas of the *ab initio* core model potential method,[27] complete-ion model potentials representing the true environment Coulomb and exchange potentials can be obtained from the group wave functions ($\Phi^A, \Phi^B, \ldots$) without the use of any parametrization procedure. This total-ion model potentials are built up from: (i) a local representation of the long- and short-range Coulomb potential, (ii) a non-local representation of the exchange and relativistic potentials (Darwin and mass-velocity potentials, if they are chosen to be present) (Ref. 28), and (iii) a total-ion projection operator, representing the cluster-lattice orthogonality terms. Then, the electronic structure of the cluster unit is obtained when it is embedded in a set of such total-ion model potentials, which are added to the one-electron isolated cluster Hamiltonian. The embedded-cluster Hamiltonian used in the calculation of the $E^{clus} + E^{clus-env}$ terms in Eq. (2), which are the relevant ones for the local structure of the cluster, reads

$$\hat{H}_{emb\ clus} = \hat{H}_{isol\ clus}$$
$$+ \sum_i^{clus} \sum_\mu^{env} \left[\frac{-Q_\mu}{r_{\mu i}} + \sum_k \frac{A_k^\mu \exp(-\alpha_k^\mu r_{\mu,i}^2)}{r_{\mu,i}} \right.$$
$$+ \sum_l \sum_{m=-l}^{+l} \sum_{a,b} |alm;\mu\rangle A_{l;ab}^\mu$$
$$\left. \times \langle blm;\mu| + \sum_c B_c^\mu |\phi_c^\mu\rangle\langle\phi_c^\mu| \right]. \tag{3}$$

In Eq. (3), the first term in the right-hand side is the isolated cluster Hamiltonian and the following terms represent the embedding potential. The second term in the right-hand side of Eq. (3) is the long-range embedding potential originated by ion μ on electron i, where Q_μ is the ionic charge. The third term is the short-range Coulomb model potential originated by the environmental ion μ; its parameters A_k^μ and α_k^μ, in an arbitrary number, are calculated by a least-square fitting to the true short-range Coulomb potential, $(Q_\mu - Z_\mu)/r_{\mu i} + \hat{J}_\mu(r_{\mu i})$, $\hat{J}_\mu$ being the one-electron Coulomb operator associated to the many-electron wave function of ion μ, Φ_μ. The fourth term is the exchange model potential of ion μ; it is the spectral representation of the negative of its true exchange operator, $\hat{K}_\mu$, on the subspace defined by the set of primitive Gaussian functions $|alm;\mu\rangle$ used in the expansion of its occupied orbitals ϕ_c^μ. As a consequence, the A_l^{ab} coefficients are the elements of the matrix

$$\underline{A}^\mu = -(\underline{S}^\mu)^{-1}\underline{K}^\mu(\underline{S}^\mu)^{-1}, \tag{4}$$

where $\underline{S}^\mu$ is the overlap matrix in the quoted subspace and $\underline{K}^\mu$ is the matrix of $\hat{K}_\mu$ in the same subspace. Finally, the last term is the projection operator of ion μ, originated by the restricted variational treatment,[26] which is responsible for preventing the collapse of the cluster wave function onto the environmental ion μ. B_c^μ is $-2\varepsilon_c^\mu$, where ε_c^μ is the orbital energy of the embedded ϕ_c^μ, and the index c runs over the occupied orbitals. As corresponding to the AIMP main idea,[27] the last three terms in Eq. (3) are calculated directly from the ϕ_c^μ orbitals, without resorting to any kind of parametrization procedure in terms of a reference, such as those followed in pseudopotential theory.

The model allows us to represent any degree of lattice polarization by performing an iterative procedure in which each group wave function is variationally optimized in the presence of the rest of the lattice, repeating this step until self-consistency is achieved.[29] Alternatively, more approximate wave functions can be obtained in only one step: the cluster group wave function is calculated as embedded in a set of frozen environment group wave functions located at their crystallographic sites, so excluding any degree of polarization.[7] This latter approach (frozen environment approach) is the one we have used in this work.

Next we present the details of the frozen environment calculations performed: environment wave functions and potentials, and defect cluster wave function.

A. Embedding model potentials

The embedding model potentials used in this work for the oxide lattices (MgO, CaO, and SrO) have been taken from Ref. 8. Nonrelativistic total-ion model potentials have been used for the MgO and CaO lattices, while the Cowan-Griffin model potential produced for the SrO lattice, which include mass-velocity and Darwin relativistic effects from the Sr^{2+} ions, have been used in the Cr^{2+}:SrO calculations. For the Cr^{2+}:$KMgF_3$ defect system, we have followed a completely parallel approach: the external group wave functions Φ^I ($I = K^+, Mg^{2+}, F^-$) have been obtained from a self-consistent embedded-ion calculation (SCEI) performed at the perfect host crystal geometry (O_h^1-P_{m3m} $a_0 = 3.973$ Å).[30] The SCEI procedure consists of a set of embedded-ion calculations, one per crystal component, which are iteratively repeated up to convergence in the orbitals of two successive iterations. In the case of the $KMgF_3$ SCEI calculation, first, a Hartree-Fock (HF) calculation on K^+, another one on Mg^{2+}, and a third one on F^- are performed, all of them embedded in a lattice of K^+, Mg^{2+}, and F^- ions represented by AIMP's corresponding to free ions, located at perfect lattice experimental sites. Then, with the resulting orbitals of these calculations, new AIMP's are calculated for the complete ions and they are used as embedding potentials in new HF calculations of K^+, Mg^{2+}, and F^-. This step is iterated up to convergence. This procedure was suggested by Adams[31] within a different method. The generated potentials are stored in data libraries and used in the $KMgF_3$ embedded $(CrF_6)^{4-}$ ab initio calculations using the Hamiltonian of Eq. (3). In these calculations we have used the K(4333/43), Mg(433/4), and F(53/5) basis sets from the compilation of Huzinaga,[32] split as (433111/4111), (43111/1111), and (5111/3111), respectively (an extra p-type function for anion, taken from Ref. 33, has been added to the fluorine basis set). All the detailed data referred to in this section are available from the authors upon request.

The embedding model potential used along these calculations includes the contributions from all the ions located within a cube whose edge is $4a_0$ for the oxide calculations ($2a_0$ for the fluoride calculations) and is centered in the Cr^{2+} impurity, which substitutes the alkaline-earth cation, in a similar way to that described in Ref. 8. Among them, the 172 (92 for $KMgF_3$) nearest neighbors of the $(CrO_6)^{10-}$ and $(CrF_6)^{4-}$ cluster are total-ion model potentials and the rest (up to 716 for MO and 482 for $KMgF_3$) are point ions bear-

ing the net charge of the ion they represent, except those located in the edge, which bear fractional charges according to Evjen's method.[34]

B. Defect cluster wave function

To perform the ab initio calculations on the embedded $(CrO_6)^{10-}$ and $(CrF_6)^{4-}$ clusters, we have used a basis set where the linear combination of atomic orbitals expansion is not confined to the first neighbors of the Cr^{2+} impurity (the standard in cluster calculations), but augmented with additional components located at the (100) cation second-neighbor sites. This approach has been referred to as first-neighbor-cluster/second-neighbor-basis-set (FN/SN) in Ref. 8, and its use has been shown to minimize the errors with respect to all-electron second- (100) neighbor cluster calculations.[8] To construct the basis set for the embedded cluster, we have used two different atomic basis sets for the chromium ion: the all-electron ($14s11p5d$) basis set of Wachters,[35] augmented with an extra d function[36] and an f polarization function,[37] without and with the f function, and contracted as (62111111/4211111/3111) and (62111111/4211111/3111/3), respectively. We will refer to these basis sets as basis set 1 and basis set 2. For the oxygen and the fluorine atoms, we have used the [He]-core ab initio model potential of Ref. 27(a). The corresponding ($5s/5p$) valence basis sets were augmented by one diffuse p function for anion (exponent 0.059 for the O atom and 0.074 for F) from Ref. 33 and contracted as (41/411).

Following the FN/SN approach, Gaussian basis set functions were included for the second (100) cation neighbors. The basis sets used in these centers are the same as in the corresponding calculations for Cu^{2+}, Ag^{2+}:MO, totally contracted as (10/4) for Mg^{2+}, (13/7) for Ca^{2+}, and (9/8) for the Cowan-Griffin relativistic Sr^{2+} ion. For Cr^{2+}:$KMgF_3$ we have used the Cr^{2+} second-neighbor (Mg^{2+}) $2s$ and $2p$ atomic orbitals resulting from the $KMgF_3$ embedded-Mg^{2+} calculation described above.

The embedded 70-electron $(CrO_6)^{10-}$ and $(CrF_6)^{4-}$ cluster wave functions and energies corresponding to the ^5E_g electronic ground state and $^5T_{2g}$ excited state were optimized along the octahedral totally symmetric stretch coordinate at the CASSCF level[16] [including the mainly $Cr(3d)$ t_{2g} and e_g orbitals in the active space; these calculations are referred to as CAS(4)] in order to obtain the impurity-ligand bond length and a_{1g} mode vibrational frequencies. For the Cr^{2+}:MgO system, this optimization was also performed correlating these four electrons by means of an ACPF (Ref. 17) calculation [referred to as ACPF(4)]. Taking the O_h equilibrium geometry and energy as the origin for tetragonal distortions, we have calculated the Jahn-Teller coupling of the ^5E_g and $^5T_{2g}$ states with the degenerate e_g vibrational mode, which splits the degeneracy of the ^5E_g electronic state into $^5A_{1g}$ and $^5B_{1g}$ states and the $^5T_{2g}$ state into $^5B_{2g}$ and ^5E_g states,[15] by searching for minima in the $e_{g,\theta}$ vibrational coordinate of the cluster (distortion that leads to D_{4h} structures). Finally, at the energy minima found in CAS(4) O_h and D_{4h} geometries, vertical transition energies have been calculated at three different levels of accuracy: (1) CAS(4) level; (2) ACPF(4) level, and (3) correlating at the ACPF level the four mainly $Cr(3d)$ electrons [already correlated at the ACPF(4) level] and twelve mainly ligand ($2p$) electrons,

TABLE I. Energy surface parameters for Cr^{2+}:MgO.

	CAS (4)		ACPF (4)	
	Basis set 1	Basis set 2	Basis set 1	Basis set 2
O_h structure, ^5E_g state				
r_e (Cr-O) (Å)	2.170	2.169	2.170	2.169
$\bar{\nu}_{a_{1g}}$ (cm^{-1})	650	650	650	650
$2\beta^{\text{a}}$ (cm^{-1})	-5	-5	-10	-10
Elongated D_{4h} structure, $^5B_{1g}$ state				
r_{ax} (Cr-O) (Å)	2.220	2.220	2.222	2.222
r_{eq} (Cr-O) (Å)	2.144	2.143	2.144	2.143
E_{JT} (cm^{-1})	480	485	495	510
$\bar{\nu}_{e_{g,\theta}}$ (cm^{-1})	520	515	520	515
Compressed D_{4h} structure, $^5A_{1g}$ state				
r_{ax} (Cr-O) (Å)	2.119	2.117	2.119	2.116
r_{eq} (Cr-O) (Å)	2.195	2.195	2.196	2.193
E_{JT} (cm^{-1})	475	480	485	500
$\bar{\nu}_{e_{g,\theta}}$ (cm^{-1})	510	505	510	510

$^{\text{a}}2\beta = E(\text{compressed}) - E(\text{elongated})$.

belonging to the a_{1g}, e_g, and t_{2g} irreducible representations [ACPF(16) level calculations]. This latter calculation, which is the one with the highest quality in this paper, corresponds to the application of the proposal of Pierloot and Vanquickenborne.[38]

III. RESULTS AND DISCUSSION

A. Local geometries and Jahn-Teller parameters

In order to assess the effects of the basis set and the different levels of calculation in the geometry parameters, we present in Table I the results of the calculations on the ground and excited states of Cr^{2+}:MgO performed with the basis sets 1 and 2 and at the CAS(4) and ACPF(4) levels.

First of all, we can see in Table I a comparison between the results using basis set 1 and basis set 2 for the calculation of the O_h equilibrium Cr-O distance (r_e) and a_{1g} vibrational frequencies ($\bar{\nu}_{a_{1g}}$) and the calculation of the Jahn-Teller parameters:[15] Jahn-Teller energies (E_{JT}), defined as the difference between the energies of the D_{4h} and O_h equilibrium configurations for each tetragonal distortion, $e_{g,\theta}$ vibrational frequencies ($\bar{\nu}_{e_{g,\theta}}$), calculated using the second derivative of the potential-energy surface in the D_{4h} minimum with respect to the $e_{g,\theta}$ vibrational coordinate, and axial (r_{ax}) and equatorial (r_{eq}) Cr-O distances, together with the barrier height between the Jahn-Teller minima (2β), calculated as the difference between the energies of the compressed and elongated structures $2\beta = E(\text{compressed}) - E(\text{elongated})$. We see that the results are very similar for both basis sets, with deviations always smaller than 0.002 Å in the distances and 10 cm^{-1} in the energies, for the elongated ($^5B_{1g}$ ground state) and compressed ($^5A_{1g}$ ground state) D_{4h} structures.

Also in Table I we present the result of the ACPF(4) calculation of the same properties, again with basis sets 1 and 2. We see that the distances and vibrational frequencies are the same as in the CAS(4) calculations. The difference is larger for the Jahn-Teller energies, which increase at the ACPF(4) level by an amount of up to 7%. For the linear coupling

TABLE II. Energy surface parameters for the ^5E_g ground state of Cr^{2+}, using basis set 1 at CAS(4) level. r_0 is the distance between the alkaline-earth and the anion in the undistorted lattice.

	MgO	CaO	SrO	KMgF$_3$
r_0 (Å)	2.106	2.405	2.580	1.987
O_h structure, ^5E_g state				
r_e (Cr-X) (Å)	2.170	2.350	2.513	2.062
$\bar{\nu}_{a_{1g}}$ (cm^{-1})	650	500	440	600
$2\beta^{\text{a}}$ (cm^{-1})	-5	20	75	5
Elongated D_{4h} structure, $^5B_{1g}$ state				
r_{ax} (Cr-X) (Å)	2.220	2.437	2.619	2.101
r_{eq} (Cr-X) (Å)	2.144	2.306	2.460	2.043
E_{JT} (cm^{-1})	480	605	565	365
$\bar{\nu}_{e_{g,\theta}}$ (cm^{-1})	520	345	280	540
$E_{\text{JT}}/\bar{\nu}_{e_{g,\theta}}$	0.92			
$\bar{\nu}_{e_{g,\theta}}/|2\beta|$	104			
Compressed D_{4h} structure, $^5A_{1g}$ state				
r_{ax} (Cr-X) (Å)	2.119	2.255	2.386	2.023
r_{eq} (Cr-X) (Å)	2.195	2.397	2.577	2.082
E_{JT} (cm^{-1})	475	625	640	370
$\bar{\nu}_{e_{g,\theta}}$ (cm^{-1})	510	320	235	530
$E_{\text{JT}}/\bar{\nu}_{e_{g,\theta}}$		1.95	2.72	0.70
$\bar{\nu}_{e_{g,\theta}}/|2\beta|$		16	3.13	106

$^{\text{a}}2\beta = E(\text{compressed}) - E(\text{elongated})$.

strength and the dynamic behavior within the e_g vibrational modes (see below), this change does not bring significant variations. Therefore, we can conclude that, in this case, the CAS(4) level, without the inclusion of f functions on the impurity ion basis set, is accurate enough for the calculation of geometries and Jahn-Teller parameters.

In Table II we present the results of a calculation of the ground-state Jahn-Teller parameters of Cr^{2+}:MgO, Cr^{2+}:CaO, Cr^{2+}:SrO, and Cr^{2+}:KMgF$_3$, at the CAS(4) level and using basis set 1. Together with the parameters already described, we present the ratios $E_{\text{JT}}/\bar{\nu}_{e_{g,\theta}}$ and $\bar{\nu}_{e_{g,\theta}}/|2\beta|$ for the most stable D_{4h} structure. These parameters are useful to understand the dynamics of the system.[15] The ratio $E_{\text{JT}}/\bar{\nu}_{e_{g,\theta}}$ is a quantitative measure of the linear Jahn-Teller coupling strength. If $E_{\text{JT}}/\bar{\nu}_{e_{g,\theta}} < 1$, the coupling is weak and, if $E_{\text{JT}}/\bar{\nu}_{e_{g,\theta}} \gg 1$, the coupling is strong. Between those limits, one should talk about intermediate coupling. On the other hand, the ratio $\bar{\nu}_{e_{g,\theta}}/|2\beta|$ is useful, within the strong linear coupling scheme, to identify dynamical and statistical behavior. According to Bersuker,[15] when the e_g vibrational energy is much higher than the barrier between equivalent minima ($\bar{\nu}_{e_{g,\theta}}/|2\beta| \gg 1$) the dynamics of the system is a *free internal rotation* between the three equivalent tetragonal minima, for intermediate values the system performs *hindered rotations* between the minima and, if $\bar{\nu}_{e_{g,\theta}}/|2\beta| \lesssim 1$, there are *pulsating or tunneling deformations*. For very low values of $\bar{\nu}_{e_{g,\theta}}/|2\beta|$, we reach the limit of the static Jahn-Teller effect. In Table III, we present the reported structural parameters derived from experimental measurements, together with the values calculated in this work. A direct comparison between them is not simple, since the experimental measurements are

TABLE III. Experimentally estimated and calculated Jahn–Teller parameters.

Reference	System	$\bar{\nu}_{e_{g,\theta}}$ (cm^{-1})	E_{JT} (cm^{-1})	$|2\beta|$ (cm^{-1})	$E_{JT}/\bar{\nu}_{e_{g,\theta}}$	$\bar{\nu}_{e_{g,\theta}}/|2\beta|$
22	Cr^{2+}:MgO	490[a]	1400[b]	775	2.85	0.63
23	Cr^{2+}:MgO	300–400[c]	1180–665		3.93–1.66	
5	Cr^{2+}:MgO	300–400[c]		76–587		3.95–0.68
This work	Cr^{2+}:MgO	520	480	5	0.92	104
5	Cr^{2+}:KMgF$_3$	300–400[c]	1500–850	120–750	5.00–2.13	2.5–0.53
This work	Cr^{2+}:KMgF$_3$	530	365	5	0.69	106

[a]Optical longitudinal mode frequency in MgO.[45]
[b]Accepted as approximate value, without further comments.
[c]Hypothetical values.

directly related to properties of the lowest vibronic states that depend mainly on parameters such as the random strain splitting ($\bar{\delta}$), the tunneling parameter (3Γ), and spin-orbit coupling parameter (D) or their ratios,[15] whereas they are more loosely related to the values of the Jahn-Teller energy, E_{JT}, and the e_g local mode vibrational frequency, $\bar{\nu}_{e_{g,\theta}}$, which are, on the other hand, direct results of our calculations. As a matter of fact, stable results of the structural parameters are very difficult to obtain from available experiments, since they are very sensitive to the approximations leading to the equations used for the analysis. As an example, parameters for Cr^{2+}:KMgF$_3$ have been derived from APR measurements (see Table III), under the assumption of strong Jahn-Teller coupling, as a function of the e_g mode vibrational frequency. But this frequency is experimentally unknown and a value of 300–400 cm^{-1} is assumed for it. Based on this supposition, values of $\bar{\nu}_{e_{g,\theta}}/|2\beta|$ ranging from 2.5 to 0.53 are obtained (i.e., from hindered rotation to a rather static dynamics), while the behavior is experimentally known to be dynamic.[5] Our results for E_{JT} and 2β are, anyway, very different from the experimental estimates, especially the barrier heights, which are very low. The lack of lattice distortion beyond the Cr^{2+} first neighbors and the inclusion of higher degrees of electron correlation in our calculations may affect these results,[8] but unless these effects were unexpectedly large, the resulting Jahn-Teller dynamics will be very similar. The inclusion of dipole polarization of the lattice on similar systems[11,13] showed that the results of these effects are very small on the distances and vibrational frequencies. The explanation of the differences between our results and the experimental estimates may reside in the inadequacy of the strong linear coupling approximation to explain the experiments, since according to our results it would rather be an intermediate coupling, which is more difficult to handle.

From Table II we can see that the most stable D_{4h} configuration resulting from our calculations is a compressed octahedron for all the systems except for Cr^{2+}:MgO. However, the absolute values of the barrier 2β are very small, so that the nature of the most stable D_{4h} structure is not as relevant as what kind of dynamics is induced by the $E \otimes e$ Jahn-Teller coupling in these systems.[15] Experimentally, this distortion has been proposed to be a compression for both Cr^{2+}:MgO (Refs. 20 and 22) and Cr^{2+}:KMgF$_3$ (Ref. 5) after fitting the lowest vibronic levels, but other experimental analyses leading to different distortions have been shown to be possible.[19,23] Our results suggest that both the compressed

and the elongated distortions are essentially equally stable, although the values of 2β could be affected (hopefully not largely) by the inclusion of lattice polarization and a higher degree of correlation.[39]

Experimentally, both Cr^{2+}:MgO (Refs. 22 and 23) and Cr^{2+}:KMgF$_3$ (Ref. 5) have been described as strongly coupled to their respective lattice vibrations, showing a dynamic behavior. The coupling has been reported to be stronger in Cr^{2+}:KMgF$_3$ than in Cr^{2+}:MgO (Ref. 5) based on the assumption of strong linear coupling. The calculated values for $E_{JT}/\bar{\nu}_{e_{g,\theta}}$ (Table II) do not support this assumption and suggest considering an intermediate Jahn-Teller coupling of similar size in both materials. This situation is very similar to that found in Cu^{2+}:MgO, where *ab initio* calculations[8] suggested the use of an intermediate coupling scheme to interpret the experimental results, rather than the strong-coupling scheme previously used. The calculated values for $\bar{\nu}_{e_{g,\theta}}/|2\beta|$ point towards a very dynamic Jahn-Teller behavior (actually, a completely free rotation) in both Cr^{2+}:MgO and Cr^{2+}:KMgF$_3$. On the other hand, the random strain effects, not considered in these calculations, are known to result in a slight enhancement of the static behavior of the Jahn-Teller dynamics, facilitating the localization on one of the three equivalent minima of the potential surface.[15] As a consequence, we should regard our results as tending to provide an image a little too dynamic for the Jahn-Teller coupling.[8]

Our results also suggest a dynamic behavior for Cr^{2+}:CaO and Cr^{2+}:SrO, although it is less dynamic in going from MgO to SrO (the behavior can be said to be a free rotation for MgO and CaO and a hindered rotation for SrO), following the trends of the host effects found in the study of Jahn-Teller parameters of $3d^9$ and $4d^9$ ions (Cu^{2+} and Ag^{2+}) in the same host crystals.[8] Comparing to those results, we see that the coupling strength is similar for Cr^{2+} and Cu^{2+} in these oxide lattices, while the behavior is much more dynamic for Cr^{2+} than for Cu^{2+}. The lack of experimental work on Cr^{2+}:CaO and Cr^{2+}:SrO does not allow a comparison with the theoretical trends found in this work.

In summary, our results suggest that the use of the strong linear coupling approximation for the interpretation of the experiments in Cr^{2+}:MgO and Cr^{2+}:KMgF$_3$ is unjustified. We believe that more experimental work is needed, interpreted on the basis of an intermediate coupling.

In Table IV, we present the Jahn-Teller parameters calculated for the coupling of the $^5T_{2g}$ excited state with the e_g

TABLE IV. Energy surface parameters for the $^5T_{2g}$ excited state of Cr^{2+}, using basis set 1 at CAS(4) level.

	MgO	CaO	SrO	$KMgF_3$
	O_h structure, $^5T_{2g}$ state			
r_e (Cr-X) (Å)	2.184	2.364	2.525	2.081
$\bar{\nu}_{a_{1g}}$ (cm^{-1})	660	510	445	620
	Elongated D_{4h} structure, $^5B_{2g}$ state			
r_{ax} (Cr-X) (Å)	2.208	2.408	2.583	2.094
r_{eq} (Cr-X) (Å)	2.173	2.342	2.496	2.075
E_{JT} (cm^{-1})	100	155	170	40
$\bar{\nu}_{e_{g,\theta}}$ (cm^{-1})	520	340	270	550
$E_{JT}/\bar{\nu}_{e_{g,\theta}}$	0.19	0.46	0.63	0.07

vibrational mode ($T \otimes e$ Jahn-Teller coupling). As deduced from the $E_{JT}/\bar{\nu}_{e_{g,\theta}}$ values, the Jahn-Teller coupling can be described as weak in all cases, in contrast with the results in the ^5E_g ground state. The most stable D_{4h} distortion is an elongated octahedron for all the systems. The host effect within the oxide family is again the same as in the ground states of the Cr^{2+}, Cu^{2+}, and Ag^{2+} impurities: more staticity is induced from MgO to CaO and SrO. No experimental measurements have been reported, to our knowledge, about the nature of the Jahn-Teller effect in this excited state.

B. Transition energies

In Table V we present the vertical absorption and emission energies, calculated from the equilibrium geometry of the clusters in the O_h symmetry, for the ^5E_g ground state and $^5T_{2g}$ first excited state. We have performed the calculation on Cr^{2+}:MgO with the two basis sets commented above, in order to estimate the effect of the addition of f functions to the transition-metal ion basis set on the transition energies. As can be seen in Table V, the variation due to the inclusion of f functions is always lower than 100 cm^{-1}, both in absorption and in emission. This effect is similar to that found by Pierloot and Vanquickenborne for transitions within a CrF_6^{3-} cluster.[38] Accordingly, we used basis set 1 for the

TABLE V. Vertical transition energies (cm^{-1}) in O_h symmetry.

		CAS(4)	ACPF(4)	ACPF(16)
	Absorption $^5E_g \rightarrow {}^5T_{2g}$			
MgO				
	Basis set 1	10365	10690	11430
	Basis set 2	10275	10630	11515
CaO		7035	7310	7545
SrO		4975	5195	4945
$KMgF_3$		8875	9125	9475
	Emission $^5E_g \leftarrow {}^5T_{2g}$			
MgO				
	Basis set 1	10100	10420	11150
	Basis set 2	10010	10365	11235
CaO		6890	7155	7345
SrO		4895	5110	4825
$KMgF_3$		8415	8660	8985

calculation of the vertical transitions presented in Tables V and VI for Cr^{2+} in the CaO, SrO, and $KMgF_3$ lattices. It is worth noticing that other theoretical calculations of the absorption spectrum of the $(CrF_6)^{4-}$ cluster exist in the literature, performed with a simpler representation of the lattice than that used in this work.[40,41]

Looking at the transitions for the different systems, we can see that the variation of the transition energy $^5E_g \rightarrow {}^5T_{2g}$, which can be identified as the 10Dq parameter, with the different systems, is the one that we should expect: the shorter the distance, the larger 10Dq. The value of the transitions is smaller for Cr^{2+}:SrO [$r(Cr-O)=2.513$ Å] than for Cr^{2+}:MgO [$r(Cr-O)=2.170$ Å], with an intermediate value for Cr^{2+}:CaO. The quantitative dependence of 10Dq ($^5E_g \rightarrow {}^5T_{2g}$) with the Cr-O distance, $r(Cr-O)$, in the MgO, CaO, SrO series is such that, if represented by the usual crystal field theory (CFT) (Ref. 18) formula $10Dq = cR_{M-L}^{-n}$, a value of n very close to 5 is found when the calculated results for $r(Cr-O)$ are used [5.0 in CAS(4), 4.9 in ACPF(4), and 5.7 in ACPF(16)]. However, if the host M-O distances are used instead, a value close to 5 is obtained from the pair CaO-SrO, but for the pair MgO-CaO the result is $n=3.0$. It is only when the local distortion induced by the impurity is taken into account (outwards in MgO and inwards in CaO) that the R_{M-L}^{-n} dependence of 10Dq becomes close to the simple CFT prediction. This result has been observed as well in the V^{2+} impurity in the fluoroperovskite series $KMgF_3$, $KZnF_3$, $KCdF_3$, and $CsCaF_3$,[11] where the experimental and computed 10Dq is well correlated to the calculated V-F distance rather than to the host distance. Finally, the value of 10Dq is greater for Cr^{2+}:MgO than for Cr^{2+}:$KMgF_3$, although the distance is similar (see Table II), due to the larger charge of the O^{2-} ions with respect to the F^- ions.

In Table VI we can see the absorption energies from the most stable Jahn-Teller distorted D_{4h} structure to both states coming from the tetragonal distortion of the $^5T_{2g}$ (O_h symmetry) state, ^5E_g and $^5B_{2g}$,[15] for the four systems under study. Since the distortion is a compression along the tetragonal axis, the ground state becomes $^5A_{1g}$, and the first excited state is of symmetry ^5E_g, except for the Cr^{2+}:MgO system, which undergoes an elongation. The ground state in that case is of symmetry $^5B_{1g}$ and the corresponding first excited state is $^5B_{2g}$. Since the nature of the most stable distortion is uncertain, due to the small value of the 2β parameter, we have included absorption from both (elongated and compressed) structures for Cr^{2+}:MgO. We can see that the transition energies are similar for both situations (some 250 cm^{-1} higher in the compressed distortion), so that the spectrum does not change significantly if the distortion resulted to be a compression also for Cr^{2+}:MgO. In Table VI we can also see that the inclusion of f functions on the chromium ion basis set does not bring any substantial change on these transitions either. On the other hand, the transition energies calculated at the ACPF (16) level in the D_{4h} symmetry are 350–1400 cm^{-1} larger than in the O_h symmetry. In the oxide lattices, the effect of the D_{4h} distortion is larger from MgO to SrO, in agreement with the calculated strength of the Jahn-Teller coupling. We report, also in Table VI, the vertical emission energies from the minimum of the $^5B_{2g}$ state, corresponding to an elongated octahedron, to the $^5A_{1g}$ and $^5B_{1g}$ states for all the systems. Again, we find differences

TABLE VI. Vertical transition energies (cm^{-1}) in D_{4h} symmetry.

		CAS(4)	ACPF(4)	ACPF(16)
		Absorption $^5B_{1g} \rightarrow {}^5B_{2g}$, ^5E_g, elongated octahedron		
MgO				
	Basis set 1	10880, 11545	11205, 11885	11895, 12920
	Basis set 2	10790, 11455	11155, 11840	12040, 13050
		Absorption $^5A_{1g} \rightarrow {}^5E_g$, $^5B_{2g}$, compressed octahedron		
MgO[a]				
	Basis set 1	11075, 11765	11400, 12110	12170, 13265
	Basis set 2	10985, 11680	11350, 12065	12310, 13390
CaO		7930, 8945	8205, 9240	8665, 10755
SrO		5875, 6995	6095, 7235	6515, 8445
KMgF$_3$		9495, 9885	9750, 10150	10090, 10685
		Emission $^5A_{1g}$, $^5B_{1g} \leftarrow {}^5B_{2g}$, elongated octahedron		
MgO				
	Basis set 1	9475, 10325	9780, 10645	10445, 11375
	Basis set 2	9385, 10235	9720, 10595	10570, 11510
CaO		6010, 7170	6255, 7440	6565, 7850
SrO		3990, 5160	4185, 5375	4790, 6110
KMgF$_3$		8110, 8565	8350, 8810	8640, 9130

[a]Included only for comparison (see text).

with the emission in O_h symmetry increasing from MgO to SrO, within the oxides series, ranging from 100 to 1100 cm^{-1}.

To our knowledge, there are no experimental reports about the d-d spectrum of Cr^{2+} in any of the host lattices studied here. There are some experiments of optical spectra, which present bands that have been assigned to Cr^{2+} in fluoride compounds, such as CrF_2,[42,43] $KCrF_3$,[43,44] Na_2CrF_4,[43,44] $NaCrF_3$,[43] and NH_4CrF_3.[44] All of them reported wide bands at about 11 000 and 14 000 cm^{-1}, assigned to transitions from the ground state of the Cr^{2+} ion, which is supposed to be the $^5B_{1g}$ state in these lattices, to the states coming from the octahedral $^5T_{2g}$ state ($^5B_{2g}$ and ^5E_g states). The splitting of these transitions (about 3000 cm^{-1}) is larger than that found in our calculations of Cr^{2+}:$KMgF_3$ (about 600 cm^{-1}), due to the fact that the Jahn-Teller distortion of the chromium site in these crystals is much larger than the one calculated in this work.[43]

IV. CONCLUSIONS

In this paper, we present the results of an *ab initio* model-potential embedded-cluster calculation on the Jahn-Teller energy surfaces of the ^5E_g ground state and $^5T_{2g}$ excited state of Cr^{2+}:MgO, Cr^{2+}:CaO, Cr^{2+}:SrO, and Cr^{2+}:$KMgF_3$, coupled to the e_g cluster vibrations. The ^5E_g state is split and the ground state results to be an elongated octahedron for Cr^{2+}:MgO (ground state $^5B_{1g}$) and a compressed octahedron for Cr^{2+}:CaO, Cr^{2+}:SrO, and Cr^{2+}:$KMgF_3$ (ground state $^5A_{1g}$), although the results show essentially the same stability for both distorted structures in Cr^{2+}:MgO and Cr^{2+}:$KMgF_3$. The Jahn-Teller parameters are consistent with a very dynamic picture for all the systems, as reported in several experimental studies, the linear coupling being strong for Cr^{2+}:CaO and Cr^{2+}:SrO, while it should be considered as intermediate between strong and weak in Cr^{2+}:MgO and

Cr^{2+}:$KMgF_3$. This fact could be responsible for the wide range of Jahn-Teller parameters proposed in the literature assuming strong linear Jahn-Teller coupling in order to interpret the experimental measurements. The different host effects found in the ground and excited states of the Cr^{2+} impurity in oxide family MgO, CaO, SrO is the same found for the ground states of the Cu^{2+} and Ag^{2+} impurities: the Jahn-Teller coupling is greater in going from MgO to SrO. On the other hand, in a given host, the Jahn-Teller coupling is similar for both Cr^{2+} and Cu^{2+}, but the behavior is more dynamic for Cr^{2+} than for Cu^{2+}.

We have also calculated the vertical absorption and emission energies between the ^5E_g ground state and the 10Dq $^5T_{2g}$ excited state in the O_h and D_{4h} geometries for all four systems. These energies show the expected trend with respect to the Cr-O distance. The correction brought about by the D_{4h} distortion in the spectra is of about 350–1400 cm^{-1}, the size of it growing towards SrO in the oxide series, consistent with the stronger Jahn-Teller coupling found. The splitting of the absorption transitions to the ^5E_g and $^5B_{2g}$ excited states for Cr^{2+}:$KMgF_3$ is smaller than that experimentally found in some fluoride crystals, as a consequence of the small Jahn-Teller distortion found in this work.

Finally, the CAS(4) level, without the inclusion of f functions on the impurity ion basis set, is accurate enough for the calculation of geometries and Jahn-Teller structural parameters.

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