Ab initio model potential study of environmental effects on the Jahn–Teller parameters of Cu^{2+} and Ag^{2+} impurities in MgO, CaO, and SrO hosts

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In this paper, the differential effects brought about by the MgO, CaO, and SrO family of hosts on the topology of the energy surface corresponding to the ground state of the clusters $(CuO_6)^{10-}$ and $(AgO_6)^{10-}$ along the a_{1g} and $e_{g,\theta}$ vibrational modes, are studied by means of the *ab initio* embedding model potential method (AIEMP) at the restricted open-shell Hartree–Fock level. For all six defect crystals, the equilibrium geometries, Jahn–Teller energies, vibrational frequencies, and relative energies between D_{4h} elongated and compressed structures (energy barriers) have been calculated using (a) two different definitions of the defect cluster, namely $(MeO_6)^{10-}$ and $(MeO_6M_6)^{2+}$ (Me=Cu, Ag; M=Mg, Ca, Sr), (b) two different cluster LCAO expansions (including or not impurity second neighbor components), and (c) relativistic Cowan–Griffin *ab initio* (core and environment) model potentials. The results show the importance of using basis set functions located at lattice sites next to the $(CuO_6)^{10-}$ and $(AgO_6)^{10-}$ clusters in order to mimic the results of the larger clusters $(CuO_6M_6)^{2+}$ and $(AgO_6M_6)^{2+}$. The net relativistic effects calculated for SrO:Cu^{2+}, Ag^{2+} and the individual contributions due to the impurity and to the environmental Sr^{2+} ions have been analyzed, all of them being rather small. The use of a simple point-charge model for the MgO, CaO, and SrO crystalline environments (Madelung potential) is shown to be inadequate and to lead to meaningless results, in agreement to what has been found in previous studies of bulk and surface defects in other ionic crystals. Given that the Ag^{2+} impurity in SrO, CaO, and MgO hosts is accepted to be an exceptionally clear example of transition from static to dynamic Jahn–Teller effect at low temperature, the reproduction of this trend can be considered to be a demanding test for an embedding method like the AIEMP: A joint analysis of our calculations and the available EPR experimental results is presented which reveals an agreement in the conclusion that the environmental effects promote stronger Jahn–Teller coupling from MgO to SrO. Also, the inadequacy of the strong linear Jahn–Teller coupling approximation for MgO:Cu^{2+} is suggested to be responsible for the present incomplete understanding of the features of its EPR spectrum, in contrast with the other systems.

I. INTRODUCTION

The environmental effects on local properties of condensed matter are presently being the object of increasing theoretical interest.[1-3] A number of theoretical methods prepared to take into account such effects in quantum mechanical calculations exists (see Ref. 4 and references therein), and new ones are being proposed.[1]

In this sense, the *ab initio* embedding model potential method, AIEMP, has been proposed[5] and further generalized[3,4,6] as an embedding method able to take into account not only the environmental Madelung effects on the properties of a given *cluster*, but also, in an approximate manner, the environmental quantum effects of exchange and orthogonality, as well as relativistic effects. Its implementation in standard quantum chemistry program packages is a rather simple task, since it only involves the addition of new one electron operators to the isolated-cluster hamiltonian. The AIEMP method results from the application of the *ab initio* core model potential techniques[7] to the embedding problem.

Recently, the AIEMP method has been successfully ap-

plied to represent (i) environmental effects on the bonding between CO and the MgO (100) surface[8] and (ii) differential environmental effects on the local distortion and photoluminescence of K_2NaGaF_6:Cr^{3+} due to applied hydrostatic pressure.[9] These studies have shown that the AIEMP method is capable of modeling subtle changes on the interactions between a given cluster and its crystalline environment which may considerably affect local properties of defects. In this work we present an AIEMP study of the parameters of the ground state potential energy surfaces of the MO:Me^{2+} (M=Mg, Ca, Sr; Me=Cu, Ag) defect series whose aim is twofold: First, we have carried out a number of calculations in order to check the ability of the method to represent the different environmental effects originated by the family of hosts MgO, CaO, and SrO on the topology of the ground state energy surfaces of the Cu^{2+} and Ag^{2+} impurities. In fact, the EPR spectra observed for Ag^{2+} in the host crystal series SrO, CaO, and MgO have been reported to provide an exceptionally clear example of the unusual spectral features associated to the transition from static to dynamic Jahn–Teller effect at low

temperature.[10] If we consider that the three hosts are, in principle, very similar crystals, and that the transition on the type of Jahn–Teller effect shown depends on far from large changes of the parameters of the potential energy surfaces, such as the Jahn–Teller energy, the vibrational frequencies, and the energy differences between different distorted structures of the embedded MeO_6 cluster, we can conclude that this is a demanding test case for an embedding method. Second, we have performed an analysis of the following methodological aspects: (i) the treatment of the impurity second neighbors either as part of the variational quantum cluster or as part of the frozen environment; (ii) the use of cluster basis set components whose role is to provide a high degree of orthogonality beween the cluster wave function and the wave functions associated to the lattice components; (the conclusions of these analyses have already been used in the applications of the method cited above[9]); and (iii) the importance of relativistic effects due to lattice components located at or beyond second neighbor sites.

II. METHOD

The *ab initio* embedding model potential method (AI-EMP) used here to perform the embedded-cluster calculations on the defect crystals $MO:Me^{2+}$ (M=Mg, Ca, Sr; Me=Cu, Ag) has been presented in Refs. 4 and 5; here we only summarize its main features and describe the details of the embedding model potentials, the embedded-cluster basis sets and the geometry optimization procedures.

Following the group function theory developed by McWeeny[11] and by Huzinaga,[12] on which the AIEMP approach is based, the local electronic states of the defect crystals $MO:Me^{2+}$ associated to the impurity can be approximated by the following generalized antisymmetric product wave function:

$$\Psi^{crys} \simeq N \hat{A} [\Phi^{MeO_6^{10-}} \Phi^{M^{2+}} \cdots \Phi^{O^{2-}} \cdots] \qquad (1)$$

which leads to the total energy expression

$$E^{crys} \simeq E^{MeO_6^{10-}} + E^{MeO_6^{10-} - env} + E^{env} \qquad (2)$$

when the embedded group functions $\Phi^{MeO_6^{10-}}$, $\Phi^{M^{2+}}$, $\Phi^{O^{2-}}$, $\cdots$ are strong orthogonal.[11]

It has been shown elsewhere[4,5] that using the AIEMP procedure it is possible to obtain both an approximate embedded-cluster wave function, $\Phi^{MeO_6^{10-}}$, and energy, ($E^{MeO_6^{10-}} + E^{MeO_6^{10-} - env}$), corresponding to Eqs. (1) and (2), by using slightly modified versions of standard *ab initio* molecular quantum mechanical programs. In fact, along the AIEMP method, the electronic structure of the cluster unit can be variationally obtained as embedded in a set of total-ion model potentials which are added to the one-electron isolated-cluster Hamiltonian. These total-ion model potentials are built up from (1) a local representation of the total-ion Coulomb operator, (2) a nonlocal spectral representation of the total-ion exchange operator, and, eventually, of mass-velocity and Darwin operators, and (3) a total-ion projection operator; all of them are

obtained from the suposedly known environment frozen-group total-ion wave functions $\Phi^{M^{2+}}$ and $\Phi^{O^{2-}}$. The potentials, (i) represent quite accurately the long- and short-range effects on the $(MeO_6)^{10-}$ cluster due to the frozen-group wave functions $\Phi^{M^{2+}}$ and $\Phi^{O^{2-}}$ located at crystallographic sites and (ii) prevent the variational collapse of the embedded-cluster electronic density onto the surrounding lattice by projecting out the environment group wave functions $\Phi^{M^{2+}}$, and $\Phi^{O^{2-}}$.

Along this frozen-environment approach, the embedded group functions $\Phi^{M^{2+}}$, and $\Phi^{O^{2-}}$ and their corresponding total-ion model potentials are obtained once and for all at a preparatory step performed on the perfect host crystal prior to the calculations leading to the embedded-cluster wave function and potential energy surfaces, so excluding any degree of lattice polarization.

The obtention of the nonrelativistic and Cowan–Griffin relativistic embedding model potentials and the details of the cluster basis set expansions and geometry optimizations are described next.

A. Nonrelativistic embedding model potentials

Owing to the ionic character of the MgO, CaO, and SrO host crystals, acceptable descriptions of the external group functions $\Phi^{M^{2+}}$ (M=Mg, Ca, Sr) and $\Phi^{O^{2-}}$ suitable to generate the nonrelativistic *ab initio* (frozen) embedding model potentials, have been obtained from closed-shell monoconfigurational self-consistent embedded-ion calculations according to the suggestions by Adams:[13] Calculations on M^{2+} and O^{2-} embedded in an MO lattice, for which an initial model potential representation is assumed, provide $\Phi^{M^{2+}}$ and $\Phi^{O^{2-}}$; these total-ion wave functions are then used to generate a new AIEMP representation of the lattice ions. New calculations on M^{2+} and O^{2-} embedded in the new model potential representation of the MO lattice are performed, and the process is repeated up to self-consistency in the $\Phi^{M^{2+}}$ and $\Phi^{O^{2-}}$ wave functions. In these *self-consistent embedded-ion* calculations the perfect host crystal structures are used[14] [a_0(MgO)=4.2112 Å, a_0(CaO)=4.8105 Å, a_0(SrO)=5.1602 Å]. The basis sets used for the embedded-ion calculations are the Mg(433/4), Ca(4333/43), Sr(43333/433/4), and O(53/5) basis sets from the compilation by Huzinaga and co-workers[15] splitted as (43111/211), (433111/4111), (4333111/43111/211), and (5111/3111), respectively (a *p*-type Gaussian function for anion has been added to the oxygen basis set[16]) along the embedded-ion calculations. Once the embedded group functions $\Phi^{M^{2+}}$ and $\Phi^{O^{2-}}$ have been obtained for each crystal (MgO, CaO, and SrO) they automatically generate the corresponding total-ion *ab initio* embedding model potentials which include the usual long-range Coulomb, short-range Coulomb, exchange, and projector components[4,5]

$$V_{lr-Coul}^{I,MP}(i) + V_{sr-Coul}^{I,MP}(i) + V_{exch}^{I,MP}(i) + Proj^I(i), \qquad (3)$$

where $I = M^{2+}, O^{2-}$.

B. Cowan–Griffin relativistic embedding model potential for SrO

The major relativistic effects can be straightforwardly included in the *ab initio* (core or environment) model potential method[7,17] along the Cowan–Griffin approximation.[18] In this work we have obtained the Cowan–Griffin (CG) relativistic AIEMP for SrO in order to ascertain the relativistic effects originated by crystal components which are beyond the first neighbors of the impurity (usually the cluster limit), and which are essentially due to the strontium ions. The CG AIEMP for SrO is constructed as follows. First, the numerical CG solution is obtained for the isolated-Sr^{2+} cation. The atomic relativistic core orbitals ([Ar], $3d$ core) are expressed analytically and used to construct the usual core potentials:[7] Coulomb, exchange, and projection operators, which, thereby, bring indirect relativistic effects due to core orbital change. The mass-velocity (MV) and Darwin (DW) potentials corresponding to the $4s$ and $4p$ orbitals are also obtained along the CG isolated-Sr^{2+} calculation. Second, $4s$, $4p$-valence Cowan–Griffin embedded-Sr^{2+} calculations are performed completely analogous to the ones described in Sec. II A, where the [Ar], $3d$ core AIMP and the usual spectral representation of the $4s$, $4p$ MV and DW potentials obtained in the isolated-ion calculation described above are used. The CG total-ion model potential so obtained includes the following components: the long- and short-range Coulomb, exchange, and projection operators formally identical to the ones in Eq. (3), but constructed with the CG relativistic (isolated/embedded) orbitals, plus the spectral representation of the $4s$, $4p$ MV and DW potentials. The nonrelativistic embedded-O^{2-} wave function and AIEMP obtained as a result of this self-consistent procedure naturally differs from that corresponding to the nonrelativistic SrO described in Sec. II A.

C. First neighbor cluster calculations: $(CuO_6)^{10-}$, $(AgO_6)^{10-}$

The CG relativistic and nonrelativistic *ab initio* core model potentials and valence basis sets of Ref. 7 have been used all throughout the embedded-cluster calculations, the atomic cores used being [He] for oxygen, [Mg] for copper, and [Zn] for silver. In Table I we show the contraction patterns used for the valence basis set of the 63 valence electron $(CuO_6)^{10-}$ and $(AgO_6)^{10-}$ clusters. For the transition metals and the oxygen, we have considered an additional splitting of the s and d functions compared to the ones tested along molecular valence calculations elsewhere.[7] As usual, extra functions have been added to the valence bases: one p-type polarization function[15] and one d-diffuse function[19] for the transition metal elements Cu and Ag, and one p-diffuse for the oxygen.[16] Polarization functions of higher angular momentum have not been included: In fact, it has been shown [along isolated-$(CrF_6)^{3-}$ cluster calculations] that the inclusion of f functions on the transition metal basis set does not bring any changes at the CAS SCF level[20] (equivalent, for the electronic states studied in this work, to the restricted open-shell HF level

TABLE I. Basis sets used in the embedded-cluster calculations.

A. First neighbor embedded-clusters: $(MeO_6)^{10-}$

Element	Atomic core	Valence basis set
Cu	[Mg]	(7,1,1/3,2,1*/3,1,1,1)
Ag	[Zn]	(9,1,1/5,2,1*/3,2,1,1)
O	[He]	(4,1/4,1,1)
Mg		(10/3,1)
Ca		(13/6,1)
Sr (nonrelativistic)		(16/9,1)
Sr (quasirelativistic)		(9/7,1)

B. Second neighbor embedded-clusters: $(MeO_6M_6)^{2+}$

Element	Atomic core	Valence basis set
Mg	[He]	(10/3,1)
Ca	[Ne]	(13/6,1)
Sr (nonrelativistic)	[Ar],$3d$	(16/9,1)
Sr (quasirelativistic)	[Ar],$3d$	(9/7,1)

used here); they appear to be active only when more than the d electrons of the metal are correlated.[20] Also, we have performed exploratory calculations including one d-type polarization function in the oxygen basis set and we have found insignificant effects on the local geometries and Jahn–Teller energies of $(AgO_6)^{10-}$ in SrO.

Optionally, as commented below, additional basis set components, located at the (100) second neighbor sites, have been added to the (63 electron) $(CuO_6)^{10-}$ and $(AgO_6)^{10-}$ embedded-cluster basis sets. Also in Table I A the patterns used for these extra functions are indicated; they correspond, in all cases, to the outermost s and p occupied orbitals of the embedded-ion preparatory calculations. As an example, CaO:$(AgO_6)^{10-}$ calculations have been done using two different basis sets: One (the standard in cluster calculations), where the LCAO expansion is confined to the first neighbors and therefore includes only the Ag and O basis set components of Table I A. Another one, where the LCAO expansion is extended to include functions located at the (100) second neighbor Ca sites; these basis set functions are the Ca^{2+} $3s$ and $3p$ solutions of the self-consistent embedded-ion calculations on CaO contracted as (13)s and (6,1)p functions, respectively. We will refer to the two different types of calculations as FN/FN (first neighbor cluster/first neighbor LCAO expansion) and FN/SN (first neighbor cluster/second neighbor LCAO expansion). It should be noticed that in all cases the cluster wave function is a 63 valence electron wave function.

The embedding model potential used along the FN/FN and FN/SN calculations includes the contributions from all ions located within a cube, centered at the impurity site, whose edge is $4a_0$. Among these ions, the 118/172 next to the reference cluster are considered to be total-ion model potentials along the (FN/FN)/(FN/SN) calculations, while the remaining ions are considered to be point charges bearing the ionic charge corresponding to a completely ionic crystal in all cases except for the frontier ions, for which Evjen's fractional charges are used.[21]

As to the geometry optimizations leading to the calcu-

lated local distortion produced by the impurity, we have proceeded as follows. The octahedral $(MeO_6)^{10-}$ (Me $=Cu,Ag$) embedded-clusters have ^2E_g electronic ground states which have been studied here at the monoconfigurational level by solving the restricted open-shell Hartree–Fock–Roothaan (ROHF) equations of Ref. 22 on the $t_{2g}^6 e_g^3 - {}^2E_g$ in order to obtain the equilibrium geometry and vibrational frequency corresponding to the a_{1g} stretching mode of the $(MeO_6)^{10-}$ unit as embedded in the fixed AIEMP described above. Taking the O_h equilibrium geometry $r_e(Me-O; O_h)$ and embedded-cluster energy as the origin for tetragonal distortions, and always within the ROHF level for the 63-electron cluster wave function, we have calculated the Jahn–Teller coupling of the ^2E_g electronic state with the doubly degenerate e_g vibrational mode, which splits the ^2E_g states into $^2A_{1g}$ and $^2B_{1g}$ states, by searching for minima with respect to the $e_{g,\theta}$ coordinate leading to D_{4h} compressed/elongated structures. These structures have been allowed to relax, mantaining the D_{4h} symmetry, in many of the cases presented here, but the effect of this final relaxation has been found to be negligible. All the calculations (both for O_h and D_{4h} symmetries) have been done using real cartesian gaussian functions and imposing only D_{2h} symmetry restrictions to the integral evaluation and many-electron cluster wave functions.

D. Second neighbor cluster calculations: $(CuO_6M_6)^{2+}$, $(AgO_6M_6)^{2+}$

In this case, the six (100) second neighbors of the impurity (Mg^{2+}, Ca^{2+}, or Sr^{2+}) are explicitly included in the definition of the cluster, adding their 48 valence electrons to the 63 valence electrons of the $(MeO_6)^{10-}$. In Table I B we have collected the atomic cores and valence basis set patterns used for the second neighbors which have been taken from the self-consistent-embedded-ion solutions. This type of calculations will be referred to as SN/SN (second neighbor cluster/second neighbor LCAO expansion).

The embedding model potential used here coincides with the one described above and used along the FN/SN calculations, except for the six (100) second neighbor alkaline earth total-ion model potentials, which are not included in the embedding potential since they are explicitly treated as part of the cluster.

The $(MeO_6M_6)^{2+}$ embedded-cluster geometry optimization is performed following the same steps as described above where only the oxygen ligands are allowed to move along the a_{1g} or $e_{g,\theta}$ coordinates. Again, the ROHF level is adopted for the expansion of the 111-valence–electron $(MeO_6M_6)^{2+}$ embedded-cluster wave functions.

III. ANALYSIS OF AIEMP RESULTS ON MO:Cu^{2+}, Ag^{2+}

A. Importance of second neighbor components of the cluster basis sets

It is well known that along solid-state cluster calculations (both isolated-cluster and embedded-cluster), the cluster molecular orbitals used to construct the mono/ multiconfigurational cluster wave functions are expressed in terms of LCAO expansions confined to the cluster nuclei. This approximation is based on the physically sound assumption that the electronic states which are responsible for the local properties of condensed matter are well localized within the cluster volume. However, it is also known that delocalization affects not only the representation of periodic properties in the solid state; as a matter of fact, delocalization has been recognized as one of the sources of error in the cluster approximation, collectively referred to as finite-cluster-size artificial effects.[23] And, even when dealing with well-localized properties of point defects, where localization techniques like the ones developed in the context of cluster-based building block approaches (see Ref. 6 and references therein) are not expected to be necessary, it is still important to take into account a certain degree of delocalization which stems from the necessary orthogonality between orbitals belonging to the cluster group and to the neighboring electronic groups, or, equivalently, from their necessary mutual linear independency, in methods where strong orthogonality is not the choice. This may demand the use of LCAO expansions not so local, where the inclusion of basis set components on lattice sites facilitates the fulfillment of the necessary cluster-lattice strong orthogonality conditions. An obvious improvement on this line is the extension of the LCAO expansion so as to include components located next to the cluster boundaries. It should be noticed that the role of this type of extra functions is well known in the model potential method: In effect, along core model potential calculations in molecules it is a well-established practice the inclusion, in the valence basis set, of corelike basis functions as well as orthogonalization functions which are not associated to participation of the atomic cores in the bonding, but whose role is to allow the valence orbitals to show the correct nodal structure in the core regions.[7] Parallely, in embedding model potential calculations in clusters, the use of basis set components located at the nearest neighbor sites facilitates the fulfilment of the necessary cluster-environment orthogonality. Their use should be more necessary in cases where the cluster vibrations studied point directly towards nearest neighbor lattice sites (see below) as well as when the extent of boundary ions is large.

In this work we have examined the role of second neighbor basis functions on the $(CuO_6)^{10-}$ and $(AgO_6)^{10-}$ embedded-cluster results by including or not, on the molecular basis set, the Mg^{2+}, Ca^{2+}, or Sr^{2+} s and p contracted functions of Table I A. (FN/SN vs FN/FN calculations.) In order to have a reference to which the results of these calculations could be compared, we have also performed the second neighbor cluster calculations described in Sec. II D and labeled SN/SN. In Table II we have collected the results of all the three types of calculations for the MO:Ag^{2+} systems; equivalent calculations on MO:Cu^{2+} lead to the same conclusions and are not tabulated here.

Looking at Table II, several conclusions can be immediately drawn. First, it is apparent that the FN basis set provides shorter bondlengths and larger vibrational fre-

TABLE II. AIEMP ground state energy surface parameters calculated using different clusters and basis sets (see the text for details). For SrO, first and second entries show the nonrelativistic and quasirelativistic results, respectively. All results correspond to calculations where the [Zn] core of Ag²⁺ is represented through a quasirelativistic CG-AIMP.

		MgO		Ag²⁺ CaO			SrO		
Cluster	FN	FN	SN	FN	FN	SN	FN	FN	SN
basis set	FN	SN	SN	FN	SN	SN	FN	SN	SN
Octahedral structure, ^2E_g ground state									
r_e(Ag–O) (Å)	2.134	2.210	2.205	2.304	2.385	2.393	2.462	2.525	2.536
								2.548	2.548
$\bar{\nu}(a_{1g})$ (cm⁻¹)	810	705	710	610	525	520	500	445	440
								435	440
Compressed D_{4h} structure, $^2A_{1g}$ ground state									
E_{JT} (cm⁻¹)	630	740	740	770	950	980	870	1050	1150
								1090	1090
$\bar{\nu}(e_{g,\theta})$ (cm⁻¹)	680	545	600	450	370	350	325	270	260
								245	250
r_{axial}(Ag–O) (Å)	2.091	2.154	2.150	2.232	2.283	2.284	2.350	2.381	2.380
								2.394	2.395
r_{equat}(Ag–O) (Å)	2.156	2.238	2.233	2.340	2.436	2.447	2.513	2.597	2.614
								2.626	2.625
Elongated D_{4h} structure, $^2B_{1g}$ ground state									
E_{JT} (cm⁻¹)	595	700	695	730	855	880	775	895	955
								895	885
$\bar{\nu}(e_{g,\theta})$ (cm⁻¹)	680	560	605	460	370	375	345	320	310
								285	280
r_{axial}(Ag–O) (Å)	2.178	2.266	2.260	2.376	2.480	2.493	2.559	2.649	2.665
								2.674	2.672
r_{equat}(Ag–O) (Å)	2.113	2.182	2.178	2.268	2.338	2.343	2.407	2.463	2.471
								2.486	2.487

quencies than the reference SN/SN calculations, the deviations being larger than the error limits usually accepted in the AIMP method.[7] This result can be recognized, along AIMP calculations,[7] as the typical response of the molecular framework to a too rigid basis set: since the FN cluster basis set is not flexible enough to provide a high degree of orthogonality with the external ions, the movement of the oxygens away from the second neighbors artificially reduces the overlap. This typical truncation error effect has been shown to systematically disappear when the rigidity of the basis set is removed by the use of orthogonality functions, which bring the quality of the AIMP results back to its standard limits:[7] In MO:Ag²⁺, when the second neighbor basis set functions are included (FN/SN) the results of the calculations get very close to the reference SN/SN ones, as can be seen on Table II.

Let us mention now two conclusions that can be drawn from the observation of the similarity between the FN/SN and SN/SN results. First, it is an indication of the quality of the embedding model potentials used for the impurity second neighbors, since the Coulomb, exchange, and orthogonality interactions between the cluster and the second neighbors are *explicitly* evaluated in the SN/SN calculations, whereas they are approximated according to the AIMP method in the FN/SN calculations. Second, it suggests that the (100) second neighbor alkaline earths are indeed *frozen* M²⁺ ions since the degree of polarization allowed for at the ROHF level of the SN cluster does not bring about significant changes. However, we would like to

consider this observation an indication rather than a conclusion, since the basis set used for the valence of the alkaline earths (one contracted s and two contracted p functions), might be considered somewhat restrictive.[24] In fact, even though we have found that the use of an additional d contracted function on strontium in the basis set of the SN/SN calculation on SrO:Me²⁺ (corresponding to its $3d$ orbital) does not bring significant changes on the results of the octahedral structures [0.003 Å in the bondlength and 1 cm⁻¹ in the $\bar{\nu}(a_{1g})$], further splitting of the s and p functions, and inclusion of $4d$-like functions which could reveal a not so unperturbed Sr²⁺ have not been considered.

B. Cowan–Griffin relativistic effects in SrO:Cu²⁺, Ag²⁺ systems

As commented above, the relativistic effects are approximately taken into account along AIMP calculations at the Cowan–Griffin level of approximation (quasirelativistic), and they can be assessed by comparing quasi- and nonrelativistic results. In this work, we have used CG-AIMPs and nonrelativistic AIMPs for the atomic cores of the impurities Cu²⁺ and Ag²⁺ as well as for the complete-Sr²⁺ environmental ions of the SrO host, so that we can estimate the net relativistic effects on SrO:Cu²⁺ and SrO:Ag²⁺ as well as the individual contributions due to the impurity and to the strontium ions.

Prior to the estimation of the relativistic effects, we can observe in Table II that the FN/SN results show higher quality when the strontium ions are considered to be qua-

TABLE III. Relativistic effects on the parameters of the ground state energy surface of $SrO:Cu^{2+}, Ag^{2+}$ as calculated on the second neighbor embedded-clusters. See the text for details.

| | $SrO:Cu^{2+}$ | | | | $SrO:Ag^{2+}$ | | | |
	NR	QR	Cu	Sr	NR	QR	Ag	Sr
Octahedral structure, ^2E_g ground state								
r_e(Me–O) (Å)	2.498	2.511	0	0.013	2.541	2.548	−0.005	0.012
$\bar{\nu}(a_{1g})$ (cm^{-1})	410	405	−5	0	430	440	10	0
Compressed D_{4h} structure, $^2A_{1g}$ ground state								
E_{JT} (cm^{-1})	490	440	−40	−10	1120	1090	30	−60
$\bar{\nu}(e_{g,\theta})$ (cm^{-1})	185	185	−10	10	290	250	−30	−10
r_{axial}(Me–O) (Å)	2.359	2.371	−0.008	0.020	2.393	2.395	−0.013	0.015
r_{equat}(Me–O) (Å)	2.568	2.582	0.003	0.011	2.615	2.625	−0.001	0.011
Elongated D_{4h} structure, $^2B_{1g}$ ground state								
E_{JT} (cm^{-1})	290	240	−25	−25	915	885	40	−70
$\bar{\nu}(e_{g,\theta})$ (cm^{-1})	220	215	20	−25	310	280	0	−30
r_{axial}(Me–O) (Å)	2.597	2.605	−0.001	0.009	2.664	2.672	0.001	0.007
r_{equat}(Me–O) (Å)	2.449	2.465	−0.001	0.017	2.480	2.487	−0.009	0.016

sirelativistic (second entries of Table II) than when they are not (first entries of Table II) as a consequence of the relativistic contraction of the strontium ions, which makes the frozen-Sr^{2+} approximation (accepted at the FN/SN level), more accurate and, consequently, the complete-Sr^{2+} CG-AIEMP more reliable. This different quality, although not large, is sufficient to lead to uncertainties in the relativistic changes estimated from the FN/SN calculations, due to the rather small magnitude of these effects. As a consequence, we have estimated them from the SN/SN calculations and the results of the analyses are presented in Table III.

In Table III, the columns labeled NR correspond to calculations on the $(MeO_6Sr_6)^{2+}$ (Me = Cu, Ag) clusters, embedded in SrO lattice, for which the Me core, the cluster Sr cores, and the complete Sr^{2+} environmental ions are represented by nonrelativistic AIMPs. The columns labeled QR correspond to the same kind of calculations but all the AIMPs being quasirelativistic. Therefore, the difference between QR and NR results correspond to the net relativistic effects. In the columns labeled Cu and Ag we have tabulated the respective individual contributions to the relativistic effects due to the impurity alone, estimated as the difference between the calculations which differ from the NR ones only in that the impurity is considered to be quasirelativistic (tabulated, for $SrO:Ag^{2+}$, in the first entries of Table II), and the NR results themselves. Finally, the difference between the QR results and the previous ones show the individual relativistic effects ascribable to strontium ions and are tabulated in Table III under the heading Sr.

First of all, it can be seen that the net relativistic effects are very small, because there is, in general, either a total compensation of the individual effects or a partial compensation in favor of the changes imposed by the alkaline earth. In fact, a small elongation of the impurity-ligand bond lengths is observed which results from larger relativistic contractions of the O–Sr bonds than from the Cu, Ag–O bonds. The Jahn–Teller energies are reduced by 10%–17% in $SrO:Cu^{2+}$ while for $SrO:Ag^{2+}$ the opposite effects of Ag and Sr lead to Jahn–Teller energies only

slightly reduced (by less than 5%). The vibrational frequencies do not change in $SrO:Cu^{2+}$ as a result of the opposite effects of Cu and Sr in both the compressed and elongated structures, while in $SrO:Ag^{2+}$ the individual effects, being smaller, do not compensate each other leading to net reductions of the $\bar{\nu}(e_g)$ by about 10%–15%.

C. The point-charge embedding potential

Finally, in Table IV, we can compare the AIEMP results (FN/SN) with the ones produced by a point-charge representation of the environment (PC) where the short-range Coulomb, exchange, projector, and relativistic operators are excluded from the embedding potentials, and only the Madelung potential is retained. As can be seen, the failure of the point-charge embedding approach is patent for CaO and SrO, where it leads to unacceptable results for the Jahn–Teller energy and/or the vibrational frequencies of the elongated D_{4h} structures. This, apart from the discussion which could be made on the results of the MgO host, invalidates this kind of embedding potential to estimate the differential effects due to changes in the environment. The necessity of including the quantum interactions with the frozen environments is apparent. The same type of analysis and conclusions have been shown in other bulk and surface defect studies.[5,8,9]

IV. COMPARISON WITH EXPERIMENTS

In this section we present the comparison of our best results (SN/SN) with experimental measurements. Raman scattering[25] and EPR spectra[10,26] on $MgO:Cu^{2+}$, $CaO:Cu^{2+}$, $MgO:Ag^{2+}$, $CaO:Ag^{2+}$, and $SrO:Ag^{2+}$ have been measured and analyzed including random strain effects on the lowest vibronic states of each system, overriding previous analysis of EPR experiments on $MgO:Cu^{2+}$ and $CaO:Cu^{2+}$ which did not include them.[27–30] Also, disregarding random strain effects, the EPR spectrum of $SrO:Cu^{2+}$ has been interpreted as due to an off-center Cu^{2+} impurity,[31] in contrast to the other five on-center defects.

TABLE IV. Results of embedded-cluster calculations of the parameters of the ground state energy surface of MO:Ag^{2+} (M=Mg,Ca,Sr), as calculated using the *ab initio* embedding model potential (AIEMP) and point charge embedding potential (PC) to represent the MgO, CaO, and SrO hosts.

| | MgO:Ag^{2+} | | CaO:Ag^{2+} | | SrO:Ag^{2+} | |
	AIEMP	PC	AIEMP	PC	AIEMP	PC
Octahedral structure, ^2E_g ground state						
r_e(Ag–O) (Å)	2.210	2.406	2.385	2.537	2.548	2.603
$\bar{v}(a_{1g})$ (cm^{-1})	705	410	525	330	435	310
2β (cm^{-1})[a]	-40	860	-95	6675	-195	84710
Compressed D_{4h} structure, $^2A_{1g}$ ground state						
E_{JT} (cm^{-1})	740	1770	950	1685	1090	1470
$\bar{v}(e_{g,\theta})$ (cm^{-1})	545	300	370	245	245	225
r_{axial}(Ag–O) (Å)	2.154	2.217	2.283	2.306	2.394	2.366
r_{equat}(Ag–O) (Å)	2.238	2.501	2.436	2.652	2.626	2.722
$E_{JT}/\bar{v}(e_{g,\theta})$	1.4		2.6		4.4	
$\bar{v}(e_{g,\theta})/|2\beta|$	13.6		3.9		1.3	
Elongated D_{4h} structure, $^2B_{1g}$ ground state						
E_{JT} (cm^{-1})	700	2630	855	8360	895	86180
$\bar{v}(e_{g,\theta})$ (cm^{-1})	560	245	370	2500	285	9990
r_{axial}(Ag–O) (Å)	2.266	2.717	2.480	3.268	2.674	3.336
r_{equat}(Ag–O) (Å)	2.182	2.251	2.338	2.171	2.486	2.237
$E_{JT}/\bar{v}(e_{g,\theta})$		10.7		3.3		8.6
$\bar{v}(e_{g,\theta})/|2\beta|$		0.3		0.4		0.1

[a]$2\beta=E$(compressed) $-E$(elongated).

A direct comparison with these experiments is not simple, since they are related to properties of the lowest vibronic states that depend mainly on parameters such as the random strain splitting, $\bar{\delta}$, and the tunneling splitting, 3Γ, or their ratio, $\bar{\delta}/3\Gamma$, and are more loosely related to the values of the Jahn–Teller energy, E_{JT}, and the e_g local mode vibrational frequency, $\bar{v}(e_g)$, which are a direct result of our calculations. In this respect, it has been pointed out[25] that the E_{JT} is a property very difficult to obtain from these kind of experiments, since it is very sensitive to the approximations leading to the equations used for the analysis of the experiments. As an example, the Raman scattering experiments on CaO:Cu^{2+} have been succesfully interpreted adopting a cluster-model (coupling with only one effective vibrational mode) and a strong linear coupling approximation;[25] however, the test of internal consistency of the cluster-model parameters is not exempt of difficulties and, particularly, values of E_{JT} ranging from 900 to 6000 cm^{-1} have been estimated.[25] No other estimated value of E_{JT} has been reported, to our knowledge, for the rest of systems.

We may remark that it is the *complementarity* of the informations directly obtained for these systems from the experiments and from the *ab initio* calculations what creates the difficulties for a direct comparison of results; but this complementarity is also what makes more valuable the efforts for (experimental and *ab initio* theoretical) joint analyses.

In Table V we present the calculated values of E_{JT} and $\bar{v}(e_g)$ for the compressed and elongated tetragonal structures. The values of 2β defined as the energy difference between both structures, $2\beta=E$(compressed) $-E$(elongated), are also presented, as well as the ratios $E_{JT}/\bar{v}(e_{g,\theta})$, which are a measure of the strong/weak linear JT coupling, and the ratios $\bar{v}(e_{g,\theta})/|2\beta|$, useful to identify

statical/dynamical behavior within the strong linear JT coupling approximation.

We will concentrate on the differential effects of the MgO, CaO, and SrO lattices, whose reproduction is the main goal of this work. In this sense, the EPR spectra of Ag^{2+} in MgO, CaO, and SrO, as well as the one of Cu^{2+} in CaO, have been succesfully interpreted within the cluster-model and strong linear JT coupling approximations, including random strain effects.[10,26] The same analysis only produced an incomplete explanation of the spectrum of MgO:Cu^{2+}.[10,26] On the basis of the ratio $\bar{\delta}/3\Gamma$, the Jahn–Teller effect was described as static in SrO:Ag^{2+}, quasistatic in CaO:Ag^{2+}, and quasidynamic in MgO:Ag^{2+} and CaO:Cu^{2+}, always within the strong linear coupling approximation. Since the term *dynamic* for the Jahn–Teller effect may induce to some confusion[32] because it does not differentiate the cases of (i) weak linear JT coupling and (ii) strong linear JT coupling with very low barrier between equivalent minima, the dynamics of those systems may be more clearly described according to Bersuker:[32] in SrO:Ag^{2+} there is a static tetragonal distortion of the six oxygens surrounding the transition metal ion, in CaO:Ag^{2+} there is a pulsating deformation or tunneling between the three equivalent tetragonal distortions, and in MgO:Ag^{2+}, as well as in CaO:Cu^{2+}, the movement of the oxygens is better described as a hindered internal rotation between the three local minima.

Our calculated values of $\bar{v}(e_g)/|2\beta|$ are 1.2, 3.5, and 15.0 for Ag^{2+} in SrO, CaO, and MgO, respectively, and they correspond to a qualitative tendency in agreement with the experimental results: the pass between the three equivalent minima is facilitated going from SrO to MgO. As to the quantitative agreement, in SrO:Ag^{2+} our results correspond to an image of pulsating deformation rather than to the one of static distortion experimentally ob-

TABLE V. Calculated ground state energy surface parameters.

| | Cu^{2+} | | | Ag^{2+} | | |
	MgO	CaO	SrO	MgO	CaO	SrO
Octahedral structure, ^2E_g ground state						
r_e(Me–O) (Å)	2.143	2.339	2.511	2.205	2.393	2.548
$\bar{\nu}(a_{1g})$ (cm^{-1})	615	460	405	710	520	440
2β (cm^{-1})	−90	−130	−200	−40	−100	−205
Compressed D_{4h} structure						
Ground state	$^2A_{1g}$	$^2A_{1g}$	$^2A_{1g}$	$^2A_{1g}$	$^2A_{1g}$	$^2A_{1g}$
E_{JT} (cm^{-1})	335	450	440	735	980	1090
$\bar{\nu}(e_{g,\theta})$ (cm^{-1})	400	235	185	600	350	250
r_{axial}(Me–O) (Å)	2.100	2.244	2.371	2.150	2.284	2.395
r_{equat}(Me–O) (Å)	2.165	2.387	2.582	2.233	2.447	2.625
$E_{JT}/\bar{\nu}(e_{g,\theta})$	0.8	1.9	2.4	1.2	2.8	4.4
$\bar{\nu}(e_{g,\theta})/|2\beta|$	4.4	1.8	0.9	15.0	3.5	1.2
Elongated D_{4h} structure						
Ground state	$^2B_{1g}$	$^2B_{1g}$	$^2B_{1g}$	$^2B_{1g}$	$^2B_{1g}$	$^2B_{1g}$
E_{JT} (cm^{-1})	245	320	240	695	880	885
$\bar{\nu}(e_{g,\theta})$ (cm^{-1})	450	270	215	610	375	280
r_{axial}(Me–O) (Å)	2.183	2.423	2.605	2.260	2.493	2.672
r_{equat}(Me–O) (Å)	2.123	2.298	2.465	2.178	2.343	2.487

served; in CaO:Ag^{2+} we obtain a transition between pulsating deformations and hindered rotation rather than clear tunneling or pulsating deformations, and in MgO:Ag^{2+} our result is a quite free internal rotation, rather than a hindered rotation. This means that the image provided by our results is systematically less static than the one deduced from the experiments.[10,26] However, this lack of quantitative agreement must not be regarded as a failure of the AIMP embedding method, since it is uniformly consistent with the following facts: The first one is that we are considering the Jahn–Teller coupling of the ^2E_g electronic states with a pure local vibrational mode of e_g symmetry, rather than with an effective cluster mode, in which effects of lattice modes of the same symmetry are also considered, as is the case of the analysis of the experimental results. Also, our calculation of the internal energy of the embedded-clusters does not include the effects of random strains, which have been proven to be crucial to understand the dynamics of these systems,[10,26] and which are known to promote a transition to the static JT effect.[32] This means that we should, in fact, expect to obtain computed potential energy surfaces corresponding systematically to a less static dynamics than that experimentally observed. The second fact is that our present calculations do not include intracluster correlation effects nor lattice polarization/relaxation. We expect that inclusion of intracluster correlation would affect the energy barriers, as in the case of [Cu(H$_2$O)$_6$]$^{2+}$,[33] while its effect on vibrational frequencies would be essentially negligible, as proven in [Cu(H$_2$O)$_6$]$^{2+}$ (Ref. 33) and in K$_2$NaGaF$_6$:Cr^{3+} (Ref. 9) systems, thus changing the values of $\bar{\nu}(e_g)/2\beta$ and the image of the dynamics of a particular system. However, we can expect that the correlation and environmental effects are not coupled, as it has been shown in K$_2$NaGaF$_6$:Cr^{3+} at different pressures,[9] so that the differential effects of the MgO, CaO, and SrO lattices would be essentially unchanged by intracluster correlation. We can not estimate, at this point, the effects of lattice polarization/relaxation,

and studies to clarify this are being conducted, but, unless they are unexpectedly large and they act compensating the differences between MgO, CaO, and SrO, we can conclude from the present calculations that the differences in static environmental effects brought about by MgO, CaO, and SrO on Ag^{2+} can be largely responsible for differential features of the EPR spectra shown by Ag^{2+} in the three oxides.

The only experimental values reported for $\bar{\nu}(e_g)$ and $|2\beta|$ are, to our knowledge, those corresponding to CaO:Cu^{2+}.[25] $\bar{\nu}(e_g)$ has been estimated to be 300–350 cm^{-1} but a single unambiguous value has not been reported. Our value of 235 cm^{-1} lies considerably below this range. We cannot expect, however, that our result would change significantly upon inclusion of correlation.[9,33] In addition, along the AIEMP study of hydrostatic pressure effects on K$_2$NaGaF$_6$:Cr^{3+} (Ref. 9) the calculated value of the vibrational frequencies and of their shifts with the environmental changes brought about by pressure have been shown to be in close agreement with definite experimental measurements.[34] As to the value of $|2\beta|$, although the experimental barrier, 43 cm^{-1}, might be slightly affected by the assumption of strong linear JT coupling approximation, our result of 130 cm^{-1} appears to be poor. This is not strange since it should be affected by correlation, as commented above. The lack of experimental results for Cu^{2+} in MgO and SrO does not allow to check whether the differential effects due to the environment are reproduced or not.

Our calculated values of the ratio $E_{JT}/\bar{\nu}(e_g)$, which could be slightly increased by correlation,[33] support the assumption of strong linear JT coupling adopted for the interpretation of the experimental results in all the systems except in MgO:Cu^{2+}. It is only in this system that the features of the EPR spectrum have been only partially understood after including random strain effects: our results suggest that the use of an intermediate (between weak and strong) linear JT coupling could be more appropriate for its interpretation. For a given ion, it is clear that the envi-

ronmental effects promote stronger linear coupling from MgO to SrO; for a given host, Ag^{2+} shows stronger linear couplings than Cu^{2+}.

Let us now comment on the nature of the most stable tetragonal distortion. Our calculations lead to the compressed distortion as the most stable one for the six systems under consideration. This has been proposed for CaO:Cu^{2+} by Low and Suss,[28] although they classified the Jahn–Teller effect as static in this case, in order to interpret the EPR line width behavior using the theoretical analysis of O'Brien,[35] and also by Coffman et al.[29] No other reports on the most stable geometry of these systems exist, to our knowledge, though a large variety of empirical data on distortions originating from the vibronic properties of the (CuO$_6$)$^{10-}$ Jahn–Teller center and determined by the nature of the crystal environment (plasticity)[32] is available, the majority of them corresponding to a tetragonal elongation. An indirect test of the results on the most stable geometries can be made taking into account that the symmetry of the first excited vibronic singlet (which in some cases has been experimentally determined) is A_1 or A_2 depending on the nature of the most stable distortion and the symmetry of the electronic nondegenerate ground state at that particular nuclear configuration.[30] In effect, we obtain the $E_g(\theta)$ ($3z^2-r^2$ if the C_4 axis is z) as the ground electronic state at the most stable compressed tetragonal distortion. This corresponds to a first excited vibronic singlet of symmetry A_1.[30] Its experimental determination can be made from the shifts of peaks in the vibronic EPR spectrum, once the sign of the g_2 electronic factor of the parametric spin Hamiltonian is known.[32] This sign has been directly measured for CaO:Cu^{2+} (Ref. 26) and MgO:Ag^{2+},[10] leading to the conclusion that the first excited vibronic siglet is A_1 in CaO:Cu^{2+} and A_2 in MgO:Ag^{2+}. Our results agree with the experiments in CaO:Cu^{2+} and they do not in MgO:Ag^{2+}; we recall that, in the latter case, we obtain a stabilization energy respect to the elongated structure of only 40 cm^{-1} which is the smallest of the six systems under consideration, and which may be affected by cluster correlation and lattice relaxation/polarization. For CaO:Ag^{2+} and SrO:Ag^{2+} on the other hand, the sign and value of the g_2 parameter has been only estimated from the experimentally mesured $g_\parallel$ and $g_\perp$ spin Hamiltonian constants by using an expression which assumes a dynamical Jahn–Teller effect,[10] leading to an A_2 as the first excited vibronic singlet, with which our results disagree. It should be taken into account, at this point, that the absolute values of g_2 for SrO:Ag^{2+} and CaO:Ag^{2+} are rather small, together with the fact that these two are the systems in which the Jahn–Teller effect has been reported as "static" and "quasistatic," so that the experimental determination of the symmetry of the first excited vibronic singlet is not as definite in SrO:Ag^{2+} and CaO:Ag^{2+} as in MgO:Ag^{2+} and CaO:Cu^{2+}. This is consistent with the fact that the values of the vibronic reduction factor g[32,36] deduced from the estimated values of g_2 for CaO:Ag^{2+} and SrO:Ag^{2+} show an opposite behavior to the expected one:[10] they deviate from 0.5 as the Jahn–

Teller effect becomes more static, while the opposite trend must be true.[32,36]

V. CONCLUSIONS

In this paper we have applied the *ab initio* embedding model potential (AIEMP) method to the study of the ground state energy surface of Cu^{2+} and Ag^{2+} defects in MgO, CaO, and SrO hosts at the restricted open-shell Hartree–Fock level. We have calculated the equilibrium geometries, Jahn–Teller energies, and vibrational frequencies corresponding to the elongated and compressed tetragonal structures of the MeO$_6$ clusters (Me=Cu,Ag) and we have found that the local electronic ground state is, for all six defects, a $^2A_{1g}$ state corresponding to a compressed tetragonal structure, resulting, in all cases but MgO:Cu^{2+}, from a *strong* linear Jahn–Teller coupling.

The analysis of our results along the host series MgO, CaO, and SrO, clearly shows the following trend: the linear Jahn–Teller coupling becomes stronger from MgO to SrO. This environmental effect is in agreement with the interpretations of the available Raman scattering and EPR experiments in the MO:Ag^{2+} series although our results show a less static dynamics than the experimental ones.

We have also used the Madelung embedding potential to represent the MgO, CaO, and SrO environments along embedded-cluster calculations. The results are shown to be meaningless both for a given defect crystal and for the doped MgO, CaO, and SrO, series. Clearly, only when the external ions are represented by distinct electronic group functions whose effects (short-range Coulomb, exchange, orthogonality, relativistic) are transported to the cluster Hamiltonian by their corresponding *ab initio* embedding model potentials, the results become meaningful and show trends consistent with the available experimental data.

We have also analyzed the role of impurity second neighbor basis set functions in the (CuO$_6$)$^{10-}$ and (AgO$_6$)$^{10-}$ LCAO expansions which are found to be important in order to mimic the results of the larger embedded-clusters (CuO$_6$M$_6$)$^{2+}$ and (AgO$_6$M$_6$)$^{2+}$. Finally, mass-velocity and Darwin relativistic effects due to the impurity and to the environmental Sr^{2+} ions have been investigated, all of which are found to be rather small.

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