

***Ab initio* model potential embedded cluster calculations including lattice relaxation and polarization: Local distortions on Mn²⁺-doped CaF₂**

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The *ab initio* model potentials initially developed as effective core potentials, have been proposed as embedding potentials in the field of embedded cluster calculations on impurities in ionic crystals [J. Chem. Phys. **89**, 5739 (1988)] and, since then, efficiently used in the theoretical study of bulk and surface problems. These potentials bring into an *ab initio* cluster calculation, classical and quantum mechanical interactions with a frozen crystalline environment (Madelung, short-range Coulomb, exchange, and orthogonality) at a reasonable cost. In this paper, we extend the *ab initio* model potential embedding method in order to include the effects of dipole polarization and site relaxation of lattice ions external to the cluster, which are represented by an empirical shell model. We apply the method to the *ab initio* calculation of local distortions around a Mn²⁺ impurity in CaF₂ lattice in the ground state (⁶A_{1g}) and two excited states (⁴T_{1g}, ⁴A_{1g}) of the cubic MnF₈⁶⁻ embedded cluster. In this material, x-ray-absorption near-edge structure and extended x-ray-absorption fine-structure measurements exist which provide quantitative experimental values of first and second coordination shell distortions around Mn²⁺ in its ground state; the comparison with these experiments is very satisfactory. The calculated distortions in the excited states are indirectly validated by calculations of absorption/emission transitions. © 1995 American Institute of Physics.

I. INTRODUCTION

The local geometries around impurities in ionic crystals, in their ground and excited states, are primary properties that govern the spectroscopic behavior of these systems, which enjoy of fundamental and technological interest. Unfortunately, their direct experimental measurement, mainly through x-ray-absorption near-edge structure (XANES) and extended x-ray-absorption fine-structure (EXAFS) techniques, poses large difficulties, which are related to the fact that these experiments are expensive and far from routinary, as well as to the large uncertainties that sometimes accompany the result,¹ the measurements being restricted to the ground state geometries. Trying to overcome these difficulties, other more conventional experimental information, such as EPR spectra and zero-phonon absorption/emission lines, have been used in order to indirectly deduce the distance between the impurity and its first neighbors;² in this case, the gathered information is limited to a single distance corresponding to the impurity ground state on a highly symmetric site. On the other hand, the long developments in quantum chemistry led, in the field of isolated molecules, to very efficient theoretical methods able to provide accurate quantitative geometries for the ground and excited molecular states, no matter how complicated they are. In these circumstances, the accepted importance of a close collaboration between theory and experimentation in order to facilitate new achievements in the field of doped materials,³ becomes exceptionally clear.

From the theoretical point of view, the cluster approximation⁴ proved itself to be a very fruitful tool, and the last years witnessed a series of developments in embedded cluster approaches. In the case of ionic crystals, the

simple embedding of a chosen cluster in the Madelung potential created by a set of point charges has been and still is very often used; however, it has been shown to lead to incorrect results of geometry related properties, such as bond distances,⁵ Jahn–Teller distortions,⁶ high-pressure effects on absorption/emission spectroscopy,⁷ and bonding properties at surfaces.⁸ Recent systematic studies are pointing out the weakness of such an approximation.⁹ As a matter of fact, several embedding techniques exist which go well ahead of the point charge approximation.^{5,10–13} In particular, the *ab initio* model potential embedding method^{5,14} (AIMP), which is a practical implementation of the group function theory developed by McWeeny¹⁵ and Huzinaga,¹⁶ translates to the field of ionic crystals the experience gathered in effective core potential molecular calculations.¹⁷ According to the AIMP embedded cluster method, model potentials representing complete cations and complete anions from an ionic lattice are calculated and straightforwardly added to the one-electron contribution to the Hamiltonian of an otherwise isolated cluster in any standard *ab initio* molecular method. The AIMP calculation corresponds to a multiatomic cluster embedded in a frozen crystalline lattice. Its main achievements are the following. (i) The intracuster bonding properties can be calculated at a highly sophisticated level; in particular, the state-of-the-art standard correlation techniques of molecular quantum chemistry can be used with essentially the same effort as in the case of isolated molecules, since the AIMP embedding only requires the modification of the one-electron integrals. (ii) The major environmental effects on the cluster are included in an approximate manner, both the purely electrostatic (Madelung and short-range Coulomb) and the quantum mechanical ones (exchange and orthogonality). Its main shortcoming lies in the fact that the formulation in Refs. 5 and 14 does not allow for the effects of dipole polarization and relaxation of lattice sites external to the

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cluster, which, although not being the dominant environmental effects on the local properties, may become important in the cases of large local distortions and charge defects. This problem was addressed in Refs. 18 and 19, where the procedure for a completely *ab initio* approach to lattice polarization and relaxation was discussed; the practical difficulties are still large, unfortunately, in order to make in a systematic way such kind of calculations.

As a consequence, we propose in this paper a simpler method for handling the residual environmental effects: AIMP/SM. In it, the AIMP embedding approach is used for the embedded cluster, whereas an empirical shell model (SM) description is adopted for the rest of the ionic lattice, which is able to represent ionic polarizabilities and interionic short-range interactions dependent on the polarization of the ions.²⁰ An iterative procedure is followed in order to make both descriptions (embedded cluster and shell model lattice) consistent to each other. At consistency, the cluster is embedded in a relaxed and polarized lattice which, in addition to the electrostatic effects on the cluster, still exerts those of exchange and orthogonality. This method is inspired in that of Ref. 21, ICECAP, from where the main idea of joining a quantum mechanical description of the cluster with an empirical shell model description of the lattice has been adopted. The main differences with ICECAP lie in the embedded cluster methods involved and in the procedure of joining the quantum mechanical cluster calculation and the shell model lattice relaxation.

Recent XANES and EXAFS measurements exist in Mn^{2+} -doped fluorite, CaF_2 , (Ref. 22) (where the Mn^{2+} substitutional impurities occupy Ca^{2+} sites), which provide quantitative site positions not only for the first eight F^- neighbors of the Mn^{2+} impurity, but also for the Ca^{2+} and F^- ions located in a second coordination shell. In order to test the performance of the AIMP/SM method, we calculated the local distortions produced by the Mn^{2+} impurity in CaF_2 , in the ground state (${}^6A_{1g}$) and two excited states (${}^4T_{1g}$ and ${}^4A_{1g}$) of the embedded cluster MnF_8^{6-} , using complete active space self-consistent field²³ (CASSCF) and average coupled-pair functional²⁴ (ACPF) wave functions. The site coordinates obtained for the first F^- neighbors, which are part of the quantum mechanical cluster, and for the second coordination ions Ca^{2+} and F^- , which are part of the environmental lattice, are very satisfactory. Furthermore, even though it is not the goal of this paper to perform an analysis of the electronic spectra of $\text{CaF}_2:\text{Mn}^{2+}$, we performed preliminary calculations of some of the absorption and emission transitions in order to make an indirect test of the calculated geometries in the excited states; the results are as well satisfactory.

In Sec. II we present the AIMP/SM method. We describe in Sec. III the calculations performed on the CaF_2 -embedded MnF_8^{6-} and we discuss the results in Sec. IV. The conclusions are presented in Sec. V.

II. AIMP/SM METHOD

In this section, we describe a method for performing *ab initio* model potential embedded cluster calculations consistent with a shell model description of an ionic lattice, which we call AIMP/SM. The AIMP/SM method is aimed to be

applied to the calculation of local properties associated to defects in ionic crystals, such as, for instance, those appearing when impurities substitute perfect crystal components or when molecules are adsorbed at the crystal surface. In these cases, it is expected that the major changes originated by the presence of the defect occur in a localized region of space. Then, one defines as *cluster* an arbitrarily chosen set of nuclei and associated electrons (more rigorously, electron wave functions) which are expected to be most responsible for the local properties under study and which, in consequence, will be studied by means of *ab initio* methods able to accurately describe its bonding interactions. The rest of the crystal is defined as the *environment* and, even if it is not expected to be directly responsible for the local properties under study, its effect on them has to be accounted for, although without paying too much computational effort for it.

Within the AIMP/SM method, an iterative procedure is undertaken which consists of two main steps: a series of *ab initio* calculations on an embedded cluster leading to a potential energy surface, followed by a relaxation and polarization of the *environment*. In Secs. II A and II B we summarize, respectively, the shell model description of the ionic lattice used in the latter step and the AIMP embedded cluster method used in the former step. We take $\text{CaF}_2:\text{Mn}^{2+}$ as an example.

A. Shell model

In order to be able to efficiently polarize and relax the environmental crystal lattice, we use a shell model description of it. The shell model is a widely used pair potential model proposed by Dick and Overhauser²⁰ to avoid the polarization catastrophe,²⁵ inherent to ionic models that take into account the dipole polarization due, exclusively, to the electric field in the ionic sites; it is achieved by including the polarization due to the repulsive short-range interactions. This leads to a model in which the short-range interionic interactions change as a consequence of the polarization of the ions.

The shell model is implemented in several programs. We used in this work Norgett's HADES (Ref. 26), and complete descriptions of the shell model formulations can be found in Refs. 27 and 28. Briefly, each lattice ion, say μ , is described by a core and a shell, with respective charges $Q_{c\mu}$ and $Q_{s\mu}$ such that $Q_{c\mu} + Q_{s\mu} = Q_\mu$, the ionic charge. The core and shell of a single ion interact with a harmonic potential $\frac{1}{2}K_\mu r_{c\mu,s\mu}^2$, $r_{c\mu,s\mu}$ being the distance between them. Cores and shells of different ions interact electrostatically. Finally, short-range interactions exist between the shells of different ions. The explicit overall interaction energy is then

$$e_{\text{int}} = \sum_{\mu} \left(\frac{1}{2} K_{\mu} r_{c\mu,s\mu}^2 + \frac{1}{2} \sum_{\nu \neq \mu} (\phi_{\mu\nu}^{\text{lr}} + \phi_{\mu\nu}^{\text{sr}}) \right), \quad (1)$$

where $\phi_{\mu\nu}^{\text{lr}}$ and $\phi_{\mu\nu}^{\text{sr}}$ are the long-range and short-range interionic potentials:

$$\phi_{\mu\nu}^{\text{lr}} = \frac{Q_{c\mu}Q_{c\nu}}{r_{c\mu,c\nu}} + \frac{Q_{c\mu}Q_{s\nu}}{r_{c\mu,s\nu}} + \frac{Q_{s\mu}Q_{c\nu}}{r_{s\mu,c\nu}} + \frac{Q_{s\mu}Q_{s\nu}}{r_{s\mu,s\nu}}, \quad (2)$$

$$\phi_{\mu\nu}^{\text{sr}} = A_{\mu\nu} \exp(-r_{s\mu,s\nu}/\rho_{\mu\nu}) - \frac{C_{\mu\nu}}{r_{s\mu,s\nu}^6}, \quad (3)$$

the r 's being the distances between cores and shells of ions μ and ν , and $A_{\mu\nu}$, $\rho_{\mu\nu}$, and $C_{\mu\nu}$ being the short-range interaction parameters corresponding, in this case, to a Buckingham potential. Other short-range potentials are often used as well. The shell model parameters $Q_{s\mu}$, K_μ , $A_{\mu\nu}$, $\rho_{\mu\nu}$, and $C_{\mu\nu}$, are usually calculated by empirical procedures and tested by setting their predictions against a wide range of data.²⁹ With the interaction potentials completely specified, the positions of ion cores and shells are conveniently modified until the calculated forces on them are nule. In order to deal with defects that perturb the lattice at a very long distance, special treatments are used for distant polarizable regions,³⁰ whose effect on the region closer to the defect is included in a more approximate manner, rather than with the explicit contribution to Eq. (1).²⁸

B. AIMP embedded cluster

In this subsection, we summarize the main features of the *ab initio* model potential embedding method, which is a practical implementation of the group function theory developed by McWeeny¹⁵ (in the context of intermolecular interactions) and Huzinaga¹⁶ (in the context of frozen core molecular calculations) to the study of local properties of imperfect crystals. It has been presented in Refs. 5 and 14 for *ab initio* calculations on clusters embedded in unpolarized, unrelaxed frozen lattices. Here we extend it to embed clusters in shell model relaxed, polarized ionic lattices.

First, taking the $\text{CaF}_2:\text{Mn}^{2+}$ example for simplicity, we assume that some properties of the Mn^{2+} -doped CaF_2 (where the Mn^{2+} ions substitute Ca^{2+} ions with a first coordination shell of eight F^- ions in the corners of a cube) such as the local structure or the ligand-field absorption/emission electronic transitions, are affected by the interactions within a MnF_8^{6-} unit (cluster,) including correlation effects and by nondynamical quantum mechanical interactions between this unit and the rest of the ionic lattice (environment,) such as long- and short-range Coulomb, exchange, and orthogonality interactions, but they should not be affected by correlation effects between the MnF_8^{6-} cluster and the environment. Then, according to McWeeny,¹⁵ a good approximation for the wave function of the imperfect crystal local states is

$$\Psi_{\text{crys}} = M \hat{A} (\Phi_{\text{MnF}_8^{6-}} \Phi_{\text{env}}), \quad (4)$$

where M is a normalization constant, \hat{A} is an intergroup antisymmetrizer, $\Phi_{\text{MnF}_8^{6-}}$ is the antisymmetric embedded cluster wave function, describing N_{clus} electrons, which can be any suitable mono- or multiconfigurational expansion, and Φ_{env} is the environmental wave function which can, in turn, be chosen to be the antisymmetric product of group wave functions representing all the Ca^{2+} and F^- components of the environment, $\Phi_{\text{env}} = M' \hat{A}' [\Phi_{\text{Ca}^{2+}} \cdots \Phi_{\text{F}^-} \cdots]$. This approximation leads, when the embedded group functions are strong-orthogonal,¹⁵ to a partitioning of the crystal total energy in terms of the cluster energy, environmental energy, and interaction energy between cluster and environment,

$$E_{\text{crys}} = E_{\text{MnF}_8^{6-}} + E_{\text{MnF}_8^{6-}\text{-env}} + E_{\text{env}}. \quad (5)$$

Here, all the direct dependency on the cluster nuclei and wave function is included in $E_{\text{MnF}_8^{6-}} + E_{\text{MnF}_8^{6-}\text{-env}}$, which reads as

$$\begin{aligned} & E_{\text{MnF}_8^{6-}} + E_{\text{MnF}_8^{6-}\text{-env}} \\ &= \sum_{\alpha}^{\text{MnF}_8^{6-}} \sum_{\mu}^{\text{env}} \frac{Z_{\alpha} Z_{\mu}}{R_{\alpha\mu}} + \sum_{\alpha}^{\text{MnF}_8^{6-}} \langle \Phi_{\text{env}} | - \sum_i^{\text{N}_{\text{env}}} \frac{Z_{\alpha}}{r_{\alpha i}} | \Phi_{\text{env}} \rangle \\ &+ \langle \Phi_{\text{MnF}_8^{6-}} | \hat{H}_{\text{emb-MnF}_8^{6-}} | \Phi_{\text{MnF}_8^{6-}} \rangle, \end{aligned} \quad (6)$$

where α runs over the cluster nuclei, μ runs over the environmental nuclei, i runs over electrons, the first right hand side term is the repulsion between nuclei in the cluster and in the environment, the second is the attraction between the cluster nuclei and the environmental electrons, and the third one is the interaction between the cluster electrons and the entire crystal, $\hat{H}_{\text{emb-MnF}_8^{6-}}$ being the embedded cluster Hamiltonian.

The two first terms in the right hand side of Eq. (6) are simple to calculate once frozen wave functions for the environmental ions are known. Minimizing the third term leads to a variational embedded $\Phi_{\text{MnF}_8^{6-}}$. In order to do so, we use the restricted space variational method of Huzinaga¹⁶ and, in addition, we adopt the AIMP approximation for environmental Coulomb and exchange operators;^{5,14} in this case, the variational procedure is performed simply by using a standard *ab initio* method, such as SCF, CASSCF, MRCI, ACPF, or others, and the following embedded cluster Hamiltonian:

$$\hat{H}_{\text{emb-MnF}_8^{6-}} = \hat{H}_{\text{isolated-MnF}_8^{6-}} + \sum_i^{\text{MnF}_8^{6-}} \sum_{\mu}^{\text{env}} [V_{\mu}^{\text{lr}}(i) + V_{\mu}^{\text{sr}}(i)]. \quad (7)$$

Here, $V_{\mu}^{\text{lr}}(i)$ is the long-range embedding potential originated by ion μ on electron i , which is

$$V_{\mu}^{\text{lr}}(i) = - \frac{Q_{\mu}}{r_{\mu i}}, \quad (8)$$

Q_{μ} being the ionic charge ($Q_{\text{Ca}^{2+}} = +2$, $Q_{\text{F}^-} = -1$) located at the ionic site, if the ion is unpolarized, and

$$V_{\mu}^{\text{lr}}(i) = V_{c\mu}^{\text{lr}}(i) + V_{s\mu}^{\text{lr}}(i) = - \frac{Q_{c\mu}}{r_{c\mu,i}} - \frac{Q_{s\mu}}{r_{s\mu,i}}, \quad (9)$$

$Q_{c\mu}$ and $Q_{s\mu}$ being the core and shell charges of ion μ , located at their respective sites, if the ion is polarized. The corresponding short-range embedding potential, which is located at the shell site, is

$$\begin{aligned} V_{\mu}^{\text{sr}}(i) &= \sum_k \frac{A_k^{\mu} \exp(-\alpha_k^{\mu} r_{s\mu,i}^2)}{r_{s\mu,i}} + \sum_l \sum_{m=-l}^{+l} \sum_{a,b} |alm; \mu\rangle \\ &\times A_{l,ab}^{\mu} \langle blm; \mu | + \sum_c B_c^{\mu} | \phi_c^{\mu} \rangle \langle \phi_c^{\mu} |. \end{aligned} \quad (10)$$

The first term on the right-hand side of Eq. (10) 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}_μ being the one-electron Coulomb operator associated to the many-electron wave function of ion μ , Φ_μ . The second 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 . In consequence, the $A_{l;ab}^\mu$ coefficients are the elements of the matrix \underline{A}^μ resulting from the transformation

$$\underline{A}^\mu = -(\underline{S}^\mu)^{-1} \underline{K}^\mu (\underline{S}^\mu)^{-1}, \quad (11)$$

where \underline{S}^μ is the overlap matrix on the quoted subspace, and \underline{K}^μ is the matrix of \hat{K}_μ in the same subspace. The third term in the right-hand side of Eq. (10) is the projection operator of ion μ , originated by the restricted variational treatment,¹⁶ which is responsible for preventing the collapse of the cluster wave function onto the environmental ion μ . B_c^μ is $-2\epsilon_c^\mu$, 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,¹⁷ all three terms in Eq. (10) are calculated directly from the ϕ_c^μ orbitals, once they are known,^{5,14} without resorting to any kind of parametrization procedure in terms of a reference, such as those followed in pseudopotential theory.

In the earliest application of the AIMP embedding method,⁵ orbitals corresponding to the free ions were used in order to produce the short-range model potentials [Eq. (10)]; since then, however, a self-consistent embedded ions calculation (SCEI) is performed on the perfect crystal as a preliminary step in order to generate them.^{6-8,31} 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 sample case, the SCEI calculation on CaF_2 means, firstly, an SCF calculation on Ca^{2+} and another one on F^- , both of them embedded in a lattice of Ca^{2+} and F^- ions represented by AIMP's [Eqs. (8)–(10)] corresponding to free ions, located at perfect lattice experimental sites. Then, with the resulting orbitals of both calculations, new AIMP's are calculated for the complete ions and they are used as embedding potentials in new SCF calculations on embedded Ca^{2+} and F^- . This step is iterated up to convergence. This series of atomic calculations, suggested by Adams within a different method³² is, in fact, used by Luaña *et al.* as a tool for calculating distances and other properties in perfect and defective crystals;³³ here, however, they are only used as a preliminary step from which the converged atomic orbitals for both ions are taken and used to generate complete Ca^{2+} and complete F^- AIMP's. These are conveniently stored in data libraries and used, when required, in CaF_2 -embedded MnF_8^{6-} *ab initio* calculations using the Hamiltonian in Eq. (7). If the defect under consideration is other than substitutional Mn^{2+} , the Ca^{2+} and F^- AIMP's will still be the same.

C. Iterative AIMP and SM calculations

We describe in this subsection the way in which the AIMP and SM calculations are joined together and made mutually consistent. Our goal here is to minimize the defective crystal energy calculated by means of the approximate, mixed expression

$$E_{\text{crys}} = E_{\text{MnF}_8^{6-}}(\Phi_{\text{MnF}_8^{6-}}, \underline{R}) + E_{\text{MnF}_8^{6-}\text{-env}}(\Phi_{\text{MnF}_8^{6-}}, \underline{R}, \underline{r}_c, \underline{r}_s) + e_{\text{env}}(\underline{r}_c, \underline{r}_s), \quad (12)$$

with respect to the cluster wave function, $\Phi_{\text{MnF}_8^{6-}}$, the positions of the cluster nuclei, \underline{R} , and the positions of the cores and shells of the environmental ions, \underline{r}_c and \underline{r}_s . In Eq. (12), we use the convention of writing with uppercase E the energies calculated with the AIMP embedded cluster method [Eq. (6)], whatever the chosen *ab initio* method is (SCF, CASSCF, MRCI, ACPF, or others), and with lowercase e those calculated with the shell model [Eq. (1)]. In addition we make explicit the direct dependencies of the cluster energy, the interaction energy between cluster and environment, and the environmental energy, respectively. Obviously, Eq. (12) implies the selection of an *ab initio* quantum mechanical description of the cluster and its interactions with the surroundings, and an empirical description of the interactions within the surroundings.

In order to achieve the minimization, we undertake an iterative procedure consisting of the following steps.

(1) A shell model calculation on the perfect crystal is performed, starting with the ions at experimental sites, leading to core and shell positions, $\underline{r}_c, \underline{r}_s$. In the sample case, CaF_2 , forces on ions are zero and this step does not relax nor polarize the lattice.

(2) The positions of the environmental cores and shells, \underline{r}_c and \underline{r}_s , are taken from the previous step and fixed. $E_{\text{MnF}_8^{6-}} + E_{\text{MnF}_8^{6-}\text{-env}}$ [Eq. (6)] is minimized with respect to the cluster wave function and the cluster nuclei positions. Let us call $\underline{R}^{(e)}$ the resulting coordinates. This step involves the calculation of a series of points of the AIMP embedded MnF_8^{6-} energy surface in its ground state. The corresponding values of $E_{\text{MnF}_8^{6-}} + E_{\text{MnF}_8^{6-}\text{-env}}$ are stored.

(3) The cluster, MnF_8^{6-} , is now represented by means of shell model ions, with core and shell coordinates \underline{R}_c and \underline{R}_s , respectively, and the values of their shell model parameters are determined by a least-squares fitting of the analytical expression $e_{\text{MnF}_8^{6-}} + e_{\text{MnF}_8^{6-}\text{-env}}$ [see Eq. (1)] to the values of $E_{\text{MnF}_8^{6-}} + E_{\text{MnF}_8^{6-}\text{-env}}$ calculated in step (2). Details of the fitting procedure are presented in the Appendix. In practice we found here that, usually, a very good fitting is obtained by fixing all the interaction parameters to the values chosen in the literature for perfect crystals, except those representing the short-range interaction [Eq. (3)] between the impurity and its first coordination shell, in this case, between the Mn^{2+} and the F^- components of the MnF_8^{6-} cluster.

(4) The positions of the cluster cores, \underline{R}_c , are fixed to the $\underline{R}^{(e)}$ values resulting in step (2), and values of \underline{r}_c , \underline{r}_s , and \underline{R}_s

are calculated such that the forces on the environmental cores and shells, as well as in the cluster shells, calculated with the shell model interaction potential

$$e_{\text{MnF}_8^{6-}}(\underline{R}_c, \underline{R}_s) + e_{\text{MnF}_8^{6-}\text{-env}}(\underline{R}_c, \underline{R}_s, \underline{r}_c, \underline{r}_s) + e_{\text{env}}(\underline{r}_c, \underline{r}_s) \quad (13)$$

are zero.

(5) Convergence in the values of $\underline{R}^{(e)}$ obtained in step (2) and in the values of \underline{r}_c and \underline{r}_s obtained in step (4) in two iterations is checked. If not yet reached, \underline{r}_c and \underline{r}_s are transferred to step (2) and the four last steps are repeated.

This iterative procedure is expected to converge to a unique geometry of cluster and environment, so that the choice of shell model calculation for step (1) (perfect crystal vs already doped crystal with some initial shell model parameters for the interaction between crystal and environment) is irrelevant. The one proposed here seems to be reasonable and has been found to be useful. Moreover, although this iterative procedure achieves the minimization of Eq. (12), others might be designed that achieve the same goal, as well. We may comment, as an example, that, at consistency, the \underline{R}_s resulting from step (4) is the same as that resulting from step (3), so that if \underline{R}_s is fixed in step (4) the final result is the same.

Taking the relaxed, polarized shell model environmental lattice resulting from this procedure, embedded MnF_8^{6-} wave functions can be calculated for its ground and excited states, as well as sought properties; in particular, the calculation of $E_{\text{MnF}_8^{6-}} + E_{\text{MnF}_8^{6-}\text{-env}}$ [Eq. (6)] leads to embedded cluster energy surfaces, from which equilibrium geometries, vibrational frequencies, transition energies, crossing points, etc., can be obtained.

It is to be noted that the intracluster and cluster-environment shell parameters obtained by this procedure [step (3)] at consistency, are such that a single shell model calculation on the defective crystal, using them, and letting all the coordinates free (cores and shells of cluster and environment,) leads to exactly the same result as the whole AIMP/SM procedure.

III. DETAILS OF THE CALCULATIONS

Substitutional Mn^{2+} impurities in CaF_2 occupy Ca^{2+} sites, in the center of a cube of F^- ions.^{34,35} Consequently, the AIMP/SM calculations performed in this paper correspond to an embedded MnF_8^{6-} cluster, which is the simplest cluster in which the Mn–F interactions can be taken into account in a fully *ab initio* approach.

In the AIMP embedded cluster calculation, the environmental lattice is defined in the following manner. All the environmental Ca^{2+} and F^- ions included within a cube of edge length $2a_0$, centered on the impurity, are represented by complete ion AIMP's. The rest of ions in a cube of edge length $4a_0$ are represented by point charges, which are fractional for the frontier ions.³⁶ This lattice definition is larger than was found to be necessary in order to reach convergence in the energy difference between two points of the cluster energy surface.⁵ The Ca^{2+} and F^- AIMP's have been obtained in SCEI SCF calculations on CaF_2 , with the embed-

ding potentials located at experimental perfect lattice sites ($a_0=5.462\,94\text{ \AA}$).³⁴ In these, the (53/5) basis set from Ref. 37 has been used for F^- , extended with a p diffuse function for anion (Ref. 38), the final contraction pattern being (5111/3111). For Ca^{2+} , a Cowan–Griffin relativistic *ab initio* core model potential approximation, CG-AIMP, has been adopted,³⁹ with a [Ne] core and a (31111/3111) basis set.

In MnF_8^{6-} we applied the AIMP frozen core approximation. For Mn we used the relativistic CG-AIMP corresponding to a [Mg]-core and the valence basis set from Ref. 39; upon addition of one p polarization function (Ref. 37) and one d diffuse function (Ref. 40), the final basis set pattern is (711/321/3111). For F we used the [He]-core AIMP and valence basis set from Ref. 17, extended with one p diffuse function for anion (Ref. 38), the final basis set pattern being (41/411).

We performed calculations on the ground state of the cubic MnF_8^{6-} cluster, ${}^6A_{1g}$, of main character $e_g^2 t_{2g}^3$, and two excited states, ${}^4T_{1g}$ and ${}^4A_{1g}$, of main character $e_g^3 t_{2g}^2$ and $e_g^2 t_{2g}^3$, respectively. We used first the complete active space SCF method,²³ with five electrons in the active space defined by the mainly Mn(3*d*) molecular orbitals e_g and t_{2g} . Then, electron correlation effects have been partially estimated by means of the average coupled-pair functional method,²⁴ based on the CASSCF configuration space, correlating the outermost e_g and t_{2g} electrons.

The details of the shell model description of the lattice have been taken from Ref. 41, in particular, set I parameters. The region surrounding the defect in which Eq. (1) is explicitly evaluated (region I) includes 215 ions within an approximated radius of 3.2 lattice units from the defect. Region II a,²⁸ in which the ion equilibrium positions are calculated using Mott–Littleton's approximation,³⁰ extends up to 5.4 lattice units. These conditions have been found to lead to convergence in the defective crystal energy in similar systems.^{42,43} The shell model calculations have been performed using HADES.^{26–28} In the fitting procedure of step (3) in Sec. II C (see the Appendix) the only necessary parameters were those of the short-range Mn–F intracluster interaction. Upon convergence in the iterative AIMP/SM method, they are $A_{\text{Mn,F}}=2973.2622\text{ eV}$, $\rho_{\text{Mn,F}}=0.245\,18\text{ \AA}$, and $C_{\text{Mn,F}}=0$ (fixed), for the CASSCF calculation on the ${}^6A_{1g}$ ground state. Using these parameters in a single SM calculation leads to the same cluster and environment geometries than the whole AIMP/SM calculation, which requires five iterations to converge up to less than 0.0005 \AA in all coordinates. (Note that the SM calculation takes an insignificant part of each cycle computing time.) However, one should consider that these parameters are only valid for representing the embedded cluster energies within the range of Mn–F distances used, more or less 5% surrounding the equilibrium distance and, in particular, if this short-range potential were to be used in lattice dynamics calculations it should be complemented with a steeper contribution at very short Mn–F distances.

IV. RESULTS AND DISCUSSION

We present in Table I the equilibrium bond distance between Mn and F in the cubic MnF_8^{6-} , as well as the respira-

TABLE I. Mn–F equilibrium distance and a_{1g} vibrational frequency of CaF_2 -embedded MnF_8^{6-} .

	${}^6A_{1g}$		${}^4T_{1g}$		${}^4A_{1g}$	
	CASSCF	ACPF	CASSCF	ACPF	CASSCF	ACPF
	Mn–F distance, ^a in Å					
AIMP	2.277	2.278	2.266	2.266	2.276	2.277
AIMP/SM	2.251	2.252	2.240	2.240	2.250	2.251
	a_{1g} vibrational frequency, in cm^{-1}					
AIMP	416	416	412	413	416	416
AIMP/SM	432	433	427	428	432	432

^aPerfect lattice Ca–F distance is 2.366 Å (Ref. 34).

tory vibrational frequency, as calculated with a frozen environment embedded cluster approach, AIMP, and with a relaxed, polarized environment embedded cluster approach, AIMP/SM, in the states ${}^6A_{1g}$, ${}^4T_{1g}$, and ${}^4A_{1g}$. In the AIMP/SM calculations, the sites of the lattice cores and shells have been obtained for the ground state, ${}^6A_{1g}$, at the CASSCF level, and used in the remaining cases.

We first observe in Table I that correlating the Mn(3d) electrons (ACPF) does not affect significantly the local distortions nor the vibrational frequencies, in agreement with results in similar systems;⁷ this is so, independently of the state and of the lattice relaxation/polarization. All the calculated local geometries correspond to inwards distortions respect to the pure CaF_2 crystal. In the ground state, using a frozen lattice (AIMP), the bond length shortening is 3.8% of the perfect lattice, becoming 4.9% when the lattice is relaxed and polarized (AIMP/SM). This means that lattice relaxation/polarization enhances the distortion corresponding to the frozen lattice calculation; in this case, by more than 25%. Our best Mn–F distance, 2.252 Å, means a smaller distortion than the one expected from the straightforward use of the crystal radii mismatch, -0.16 Å.⁴⁴ Parallel to the additional bond length shortening, the AIMP/SM calculation produces slightly larger vibrational frequencies than the AIMP calculation.

In Table II we present the comparison of our results on the distortions in the first and second coordination shells with those determined from EXAFS experiments.²² We include in Table II the EXAFS results as measured, as well as those resulting after a shift estimated from EXAFS measurements on MnF_2 .²² It is perhaps appropriate to remind the reader at this point that large uncertainties in the local distortions obtained from EXAFS measurements are not rare.¹ Moreover, as an example of the difficulties faced by the experimental

techniques in order to derive quantitative local distortions in this kind of materials, let us comment on the analysis of the XANES measurements in $\text{CaF}_2:\text{Mn}^{2+}$ led to a Mn–F distance of 2.20 Å and a Mn–Ca distance of 3.66 Å.²² Finally, the ground state Mn–F distance in $\text{CaF}_2:\text{Mn}^{2+}$ was estimated to be 2.265 Å, from an analysis of the experimental isotropic superhyperfine constant A_S by means of an overlap model of the bonding.²

In the AIMP/SM column of Table II we observe that the relative distortion is calculated to be larger for the first coordination shell, as expected. The absolute and relative values of the AIMP/SM distances agree within acceptable margins with the experiments, both for the first and second coordination shell ions. The larger discrepancy seems to be in the case of the second shell F^- ions; this might be related to the fact that a very large structural disorder for the anion shell was found in EXAFS.²² In our opinion, the results in Table II tend to credit not only the qualitative but also the quantitative local distortions calculated for the ground state by means of the AIMP/SM method. This is so, of course, provided a reasonable cluster is chosen and a high quality *ab initio* method is used.

In order to get some sense of how much the lattice description has changed due to the impurity, we present in Table III the calculated ion displacements with respect to their perfect lattice sites as well as their dipole polarization. A significant lattice distortion is observed which, in this case, is accompanied by a very small lattice polarization.

As seen in Table I we calculated local distortions on excited states as well. It, in fact, requires no more computational effort than the corresponding calculation on the ground state. However, a direct quantitative comparison with experiments is not possible in this case, since no experimental technique has so far been developed which could directly give such an information. (We may stress at this point on the *complementarity* between the informations gathered by the use of experimental techniques and computational methods in the field of doped crystals.³) In order to have an indirect estimation of the quality of the AIMP/SM excited state local geometries, we performed preliminary calculations of the absorption electronic transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}$, as well as of the ${}^6A_{1g} \leftarrow {}^4T_{1g}$ emission (from the minimum of the ${}^4T_{1g}$ energy surface), which is, to our knowledge, the only measured emission;⁴⁵ these are presented in Table IV. Although it is well known that the ACPF wave functions used in this work, correlating only five electrons, will not be of sufficient quality to quantitatively describe these transi-

TABLE II. Distances between the Mn^{2+} impurity and the first and second coordination shell ions, in Å. Percentage distortion with respect to the perfect lattice are shown in parentheses.

	CaF_2^a	AIMP	AIMP/SM	EXAFS ^b	EXAFS ^c	
F	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	2.366	2.277 (–3.8)	2.251 (–4.9)	2.243 (–5.2)	2.273 ± 0.01 (–3.9)
Ca	$(\frac{1}{2}, \frac{1}{2}, 0)$	3.863		3.822 (–1.1)	3.827 (–0.9)	3.84 ± 0.02 (–0.5)
F	$(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$	4.530		4.508 (–0.5)	4.419 (–2.5)	4.43 ± 0.03 (–2.2)

^aReference 35, perfect lattice data.

^bReference 22, direct results.

^cReference 22, estimated values after corrections from measurements on MnF_2 .

TABLE III. Calculated ion displacements and polarizations. All distances in Å.

Ion	Lattice site ^a	Distance to origin		Cartesian displacements ^b			μ/D^c
F	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	2.3655	core	-0.0661	-0.0661	-0.0661	0.03
			shell	+0.0022	+0.0022	+0.0022	
Ca	$(\frac{1}{2}, \frac{1}{2}, 0)$	3.8629	core	-0.0290	-0.0290	0	0.01
			shell	-0.0005	-0.0005	0	
F	$(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$	4.5296	core	-0.0238	-0.0008	-0.0008	0.02
			shell	-0.0018	-0.0004	-0.0004	
Ca	(1,0,0)	5.4629	core	-0.0119	0	0	0.01
			shell	+0.0003	0	0	
F	$(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$	5.9531	core	-0.0081	-0.0081	-0.0013	0.02
			shell	+0.0009	+0.0009	+0.0016	
Ca	$(1, \frac{1}{2}, \frac{1}{2})$	6.6907	core	-0.0062	-0.0008	-0.0008	0.00
			shell	-0.0001	+0.0001	+0.0001	
F	$(\frac{5}{4}, \frac{1}{4}, \frac{1}{4})$	7.0966	core	-0.0103	-0.0017	-0.0017	0.00
			shell	-0.0004	+0.0000	+0.0000	
F	$(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$	7.0966	core	+0.0006	+0.0006	+0.0006	0.00
			shell	-0.0002	-0.0002	-0.0002	
Ca	(1,1,0)	7.7258	core	-0.0057	-0.0057	0	0.00
			shell	-0.0001	-0.0001	0	
F	$(\frac{5}{4}, \frac{3}{4}, \frac{1}{4})$	8.0798	core	-0.0022	-0.0018	+0.0003	0.00
			shell	-0.0000	-0.0001	-0.0003	
Ca	$(\frac{3}{2}, \frac{1}{2}, 0)$	8.6377	core	-0.0024	+0.0002	0	0.00
			shell	0.0000	+0.0002	0	

^aLattice units, $a_0=5.46294$ Å (Ref. 34) centered on Mn^{2+} .

^bCore displacements are referred to perfect lattice sites and shell displacements are referred to core sites. Core and shell charges are, respectively, +1.38 and -2.38 a.u. for F^- and -3.24 and +5.24 a.u. for Ca^{2+} (Ref. 41).

^cLocal dipole moment respect to the center of charge.

tions (detailed calculations of the absorption/emission spectra at a higher level of electron correlation are underway⁴⁷), they are appropriate for monitoring the excited state geometry, as described later.

First, we observe in Table IV that lattice relaxation/polarization has a minor influence on the electronic transitions under study, which, on the other hand, are very sensitive to intracuster electron correlation effects (ACPF vs CASSCF), as expected. We observe too that the transitions calculated with the ACPF method, correlating only five electrons, are larger than the experimental ones. The differences have to accommodate several effects. Of them, some 3400 cm^{-1} correspond to insufficient atomic correlation,⁴⁸ since the free Mn^{2+} parent transition ${}^6S \rightarrow {}^4G$ is calculated to be 30 190 cm^{-1} with the basis set and ACPF method used in the

TABLE IV. Vertical electronic transitions, in cm^{-1} .

	CASSCF	ACPF	Experiment
${}^6A_{1g} \rightarrow {}^4T_{1g}$ absorption			
AIMP	29 910	27 500	22 675 ^a
AIMP/SM	29 660	27 220	
${}^6A_{1g} \rightarrow {}^4A_{1g}$ absorption			
AIMP	31 675	29 790	25 316 ^a
AIMP/SM	31 650	29 770	
${}^6A_{1g} \leftarrow {}^4T_{1g}$ emission			
AIMP	29 820	27 400	20 202 ^{a,b}
AIMP/SM	29 560	27 110	

^aReference 46.

^bReference 45.

MnF_8^{6-} , whereas the experimental J -averaged value is 26 800 cm^{-1} .⁴⁹ The 1100 cm^{-1} remaining up to the 4500 cm^{-1} deviation in the absorption transitions are reasonable to accommodate molecular correlation and basis set effects.⁷ In the ${}^6A_{1g} \leftarrow {}^4T_{1g}$ emission, the deviation with experiment is larger than the corresponding absorption by 2400 cm^{-1} . This is consistent with the fact that a Jahn–Teller effect exists in the ${}^4T_{1g}$ excited state which lowers the energy respect to the a_{1g} minimum; if the vertical emission is produced from a lower local symmetry, the transition energy is reduced, both because of the Jahn–Teller stabilization of the ${}^4T_{1g}$ state and the instabilization of the ${}^6A_{1g}$ state at the lower symmetry. Since 2400 cm^{-1} can be an acceptable reduction of the emission by the Jahn–Teller effect on the excited state, we may conclude that the a_{1g} local geometry of the excited state is acceptable.

Finally, another indirect check of the quality of the ${}^6A_{1g}$ ground state geometry is deduced from the absorption spectrum. The ${}^6A_{1g} \rightarrow {}^4A_{1g}$ energy is essentially independent of the Mn–F distance, whereas the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ energy depends on it. Now, since both transitions are calculated with the same deviation respect to the experiment, the contribution to the deviation in ${}^6A_{1g} \rightarrow {}^4T_{1g}$ due to a wrong Mn–F distance must be very small.

V. CONCLUSIONS

In this paper we presented the AIMP/SM method, which is an extension of the AIMP embedded cluster method⁵ to consider environmental relaxation and dipole polarization effects through the use of an empirical shell model description of the lattice in ionic crystals.²⁰ In AIMP/SM the *ab initio* description of the embedded cluster and the shell model description of the lattice are made mutually consistent. The method was applied to the calculation of local distortions around a Mn^{2+} impurity in fluorite, CaF_2 , by means of an embedded MnF_8^{6-} cluster, in which CASSCF and ACPF wave functions were used. Local distortions were calculated for the ground state ${}^6A_{1g}$ and for the ${}^4T_{1g}$ and ${}^4A_{1g}$ excited states of MnF_8^{6-} . $CaF_2:Mn^{2+}$ was chosen because recent XANES and EXAFS measurements exist in this material leading to ground state first and second coordination shell distortions.²² The comparison with these experiments is very satisfactory. The quality of the calculated geometries was also indirectly monitored by calculations of absorption/emission transitions.

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APPENDIX

Given a set of N points of an AIMP energy surface of a cluster embedded in a given lattice of coordinates r_c and r_s , a shell model analytical expression is used to represent them by performing the fitting procedure described in this Appendix.

Let us define

$$E^{(k)} = E_{\text{clus}}(\underline{R}^{(k)}) + E_{\text{clus-env}}(\underline{R}^{(k)}, \underline{r}_c, \underline{r}_s) \quad (\text{A1})$$

and

$$e^{(k)} = e_{\text{clus}}(\underline{R}_c^{(k)}, \underline{R}_s) + e_{\text{clus-env}}(\underline{R}_c^{(k)}, \underline{R}_s, \underline{r}_c, \underline{r}_s), \quad (\text{A2})$$

with

$$e_{\text{clus}}(\underline{R}_c^{(k)}, \underline{R}_s) = \sum_{\mu}^{\text{clus}} \left(\frac{1}{2} K_{\mu} r_{c\mu,s\mu}^2 + \frac{1}{2} \sum_{\nu \neq \mu}^{\text{clus}} (\phi_{\mu\nu}^{\text{lr}} + \phi_{\mu\nu}^{\text{sr}}) \right), \quad (\text{A3})$$

$$e_{\text{clus-env}}(\underline{R}_c^{(k)}, \underline{R}_s, \underline{r}_c, \underline{r}_s) = \sum_{\mu}^{\text{clus}} \sum_{\nu}^{\text{env}} (\phi_{\mu\nu}^{\text{lr}} + \phi_{\mu\nu}^{\text{sr}}), \quad (\text{A4})$$

$\phi_{\mu\nu}^{\text{lr}}$ and $\phi_{\mu\nu}^{\text{sr}}$ corresponding to Eqs. (2) and (3). ($\underline{R}^{(k)}, E^{(k)}$) is one of the points ($k=1, N$) of the energy surface resulting from an AIMP embedded cluster calculation, whereas $e^{(k)}$, with $\underline{R}_c^{(k)} = \underline{R}^{(k)}$, is a function of the set of shell model parameters K_{μ} , $Q_{s\mu}$, $Q_{s\nu}$, $A_{\mu\nu}$, $\rho_{\mu\nu}$, and $C_{\mu\nu}$, which describe the intracluster interactions, ($\mu \in \text{clus}$, $\nu \in \text{clus}$) and the interactions between the cluster components and the environment components, ($\mu \in \text{clus}$, $\nu \in \text{env}$) as well as of the shell positions of the cluster ions, \underline{R}_s .

The following square deviation is defined as

$$\chi^2 = \sum_k^N (E^{(k)} - E_0 - e^{(k)})^2, \quad (\text{A5})$$

where E_0 stands for the energy of the separated cluster components. Then, the following fitting procedure is undertaken.

(1) The $Q_{s\mu}$ and K_{μ} parameters for all the defective crystal components, $\mu \in (\text{clus} \cup \text{env})$, are taken from the literature and they will never be changed.

(2) Short-range shell model interaction parameters are chosen as well for all the present interactions: $A_{\mu\nu}, \rho_{\mu\nu}, C_{\mu\nu}, \mu \in \text{clus}, \nu \in (\text{clus} \cup \text{env})$.

(3) The $e^{(k)}$ function corresponding to $\underline{R}_c^{(k)} = \underline{R}^{(e)}$, the minimum of the energy surface, is minimized respect to \underline{R}_s .

(4) χ^2 is minimized respect to the shell model short-range interaction parameters, $A_{\mu\nu}, \rho_{\mu\nu}, C_{\mu\nu}$. Usually, very good fittings are obtained if only the $\mu, \nu \in \text{clus}$ parameters are let free in this step. In the case of CaF_2 -embedded MnF_8^{6-} , fixing all parameters except those for $\mu = \text{Mn}^{2+}$ and $\nu = \text{F}^-$ was found to be good enough. At this step, two possibilities exist: either the value of E_0 is calculated and fixed, or it is taken as one more fitting parameter. In the numerical experiments performed, both approaches led to equally good results.

(5) Go to (3) unless convergence exist in all \underline{R}_s , $A_{\mu\nu}$, $\rho_{\mu\nu}$, and $C_{\mu\nu}$'s.

The results of this fitting procedure guarantee that, in single shell model calculation on the defective crystal in which the environmental components are fixed whereas the cluster components are allowed to relax and polarize, the resulting cluster core sites are the same as the nuclear equilibrium positions obtained in the AIMP embedded cluster calculation leading to $E^{(k)}$ and, at the same time, the resulting cluster shell sites are the same as the ones obtained in this fitting procedure.

We may mention here that other fitting procedures have been tried along this work. In particular, handling the cluster shell sites \underline{R}_s as fitting parameters which minimize χ^2 has been found to often lead to unreasonable results.

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