Ab initio model potential study of the optical absorption spectrum of Mn^{2+}-doped CaF$_2$

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An *ab initio* calculation of the optical absorption spectrum of Mn^{2+}-doped CaF$_2$ is performed in which electrostatic and quantum embedding effects originated by a relaxed and polarized CaF$_2$ lattice on the ligand field ground and excited states of a MnF$_8^{6-}$ cluster have been considered. The theoretical spectrum is calculated by means of the complete active space self-consistent-field (CASSCF) and average coupled pair funtional (ACPF) methods, correlating up to 23 electrons. An excellent overall agreement with the experiments is found and a detailed analysis of the results is presented. The initial assignment of the $^4A_{1g}(^4G)$ and $^4E_g(^4G)$ states, lately reversed, is supported. The wrong assignment of the $^4T_{1g}(^4P)$ state is shown to be responsible for a recently proposed change of the value of the crystal field splitting parameter initially accepted, $10Dq=4250$ cm^{-1}, which is in turn supported here. Also, new assignments for the absorptions to the $^4T_{1g}(^4F)$ and $^4T_{2g}(^4F)$ excited states are suggested. © *1995 American Institute of Physics.*

I. INTRODUCTION

Transition metal ion-doped halide crystals constitute a kind of point defects in solids of enormous basic and technological interest associated to the rich electronic structure exhibited by the d^n manifold of the impurity in the crystal field.[1–6] It is well-known that d^n impurities can notably alter the properties of the host crystals in different ways. Noteworthy, and most related to the interests of this work, they can give origin to local absorption/emission bands within the spectral region where the host is transparent, this being of fundamental and practical interest.[1–6] They can also alter the efficiency for production of color centers in halide crystals after ionizing irradiation.[1,7,8] They can sensitize or be sensitized along energy transfer processes involving codoped rare earth impurities, this augmenting further their importance in the search for new phosphors and laser systems.[9–11] Numerous examples of these impurity induced changes and their technological applications can be found in the literature devoted to the research of potential solid state lasers, radiation damage, etc.[1–11] Notably, most of the effort has been concentrated on the study of $3d$ impurities in six- and fourfold coordination as well as on impurities showing local spin-allowed absorption/emission bands. Mn^{2+}-doped fluorite is an exception to this. In this material Mn^{2+} occupies Ca^{2+} sites, therefore being in eightfold fluorine coordination. Furthermore, its d^5 manifold leads, in the low field of fluorite, to a spin sextet ground state, $^6A_{1g}$, and a number of quartet excited states, which means that, in addition to the usual parity forbiddance of $d-d$ transitions, all ground state absorption bands are also spin forbidden, this resulting in very inconvenient oscillator strengths of some 10^{-6}–10^{-7} and very high excited state lifetimes.[12] Yet, CaF$_2$:Mn^{2+} has been extensively studied because of its various applications. It is used as a scintillation detector and it is an important material in thermoluminiscence dosimetry.[13,14] It has also been investigated along radiation damage studies aimed at increasing the efficiency for production of intrinsic point defects in fluorite.[7,8] Also, very recent studies in energy transfer in halide crystals point towards potential laser applications of Mn^{2+}-doped fluorite through Eu^{2+}-sensitized Mn^{2+} fluorescence.[10,11] All these applications have motivated a considerable amount of experimental work on the unirradiated, irradiated, and codoped samples.[1,2,5,7–20] Interestingly, more complex defects than the simple substitutional impurity formed in CaF$_2$:Mn^{2+} originate as the material is either irradiated or codoped whose nature is not fully understood. Parallely, the optical properties of these defects, being closely related to those of the simplest defect, change showing some new and very convenient features which, in particular, result in different ways to overcome the high forbiddance of the CaF$_2$:Mn^{2+} absorption bands. In fact, the defects which are formed after irradiation lead to bands with much higher oscillator strengths.[7,8] Also, systems like CaF$_2$:Mn^{2+},Eu^{2+} show typical Mn^{2+} emission (shifted by only some 6 out of 495 nm) after absorption in wavelengths corresponding to Eu^{2+} bands, this being achieved at Mn^{2+} concentrations which are not sufficient to produce Mn^{2+} direct excitation.[10] Consequently, the definite assignment of energy levels in the CaF$_2$:Mn^{2+} simplest material is necessary to help to understand the more complex defects which have just been mentioned.

In this line, although the general features of the Mn^{2+}-$3d^5$ manifold of CaF$_2$:Mn^{2+} have been long known, it is only recently that the detailed optical absorption spectrum of the unirradiated material has been reported.[12] As is usual for this kind of systems, the electronic transitions have been interpreted[12] by means of the crystal field theory,[21] which enjoys the property of being a simple, fast predictive tool for the $3d^n$ spectrum of transition metal ions in ionic crystals. Within this context, the value of the cubic crystal field splitting parameter previously reported by Alonso and Alcalá,[16] $10Dq=4250$ cm^{-1}, was confirmed by McKeever *et al.*[12] and has been widely accepted in spite of the fact that

another value of 8100 cm^{-1} had been tentatively proposed by Bagai and Warrier from the analysis of the ultraviolet absorption spectrum.[22] The detailed optical absorption spectrum[12] was also used to clarify the energy level assignments corresponding to the luminescence emission of CaF$_2$:Mn^{2+} and to discuss on the nature of the complex defects (and absorption spectra) observed after irradiation.[12]

From the theoretical point of view, modeling the defects mentioned above is very difficult; this is particularly so for the ones produced after irradiation and for the extended defects associated with codoping. Yet, it is again useful and possible to study the simplest Mn^{2+} defect at an *ab initio* level. If the local ground state absorption bands are to be calculated in CaF$_2$:Mn^{2+}, it is well-known that the following methodological requirements must be met: First, the calculations can be confined to the obtention of the defect cluster (MnF$_8^{6-}$) wave functions and energies, as long as an accurate embedding potential is used which adequately represents the surrounding fluorite crystal. In particular, the interactions between the cluster electronic density and the surrounding calcium and fluorine ions have to be considered and must include not only point charge electrostatic effects (Madelung potential), but also quantum exchange and orthogonality repulsion.[23] This type of embedding is crucial if the local geometry of the defect is to be computed prior to the spectral calculation, following the standard *ab initio* procedure. Otherwise, if the cluster geometry is optimized along *in vacuo* calculations, the defect clusters dissociate, and, if a Madelung embedding potential (or any simpler representation of it) is used, cluster bond lengths exceedingly large (in the order of tenths of Å) and too small vibrational frequencies are found, all of which is directly associated to methodologically insufficient treatment of the host effects.[23] Also, the electronic transitions should be affected by such type of interactions with the surrounding fluorite components (indirectly, through the actual equilibrium structures obtained, and also directly, depending on the nature of the connected states). But, even though the use of accurate embedding potentials reduces the explicit cluster size to the impurity and its first neighbors, the use of another very demanding methodological requirement has to be met. Namely, the use of good basis sets and the inclusion of sufficient electron correlation within the cluster are necessary along *ab initio* calculations of electronic transitions. However, while it is simple, from the computational point of view, to include quantum-mechanical embedding along standard molecular cluster calculations,[23,24] responding to the latter requirement is actually very demanding, particularly in eightfold coordination, where even restricting the active space to the mainly Mn(3d) and F(2p) orbitals leads to 53 electrons to be correlated. All this contributes to the fact that *ab initio* embedded-cluster calculations are very scarce in eightfold coordinated impurities.[25]

However, it is possible to proceed along more approximate routes which, using no or classical embedding, incorporate instead empirical structural information (when available) into the *ab initio* treatment so as to atenuate the impact of the host effects in the calculated electronic transitions and, on the other hand, truncate the multiconfigurational expan-

sions. In this line, a very recent calculation of the optical absorption spectrum of CaF$_2$:Mn^{2+} has been reported by Lewandowski and Wilson[26] in which the *ab initio* multiconfigurational self-consistent-field (MCSCF) method has been used for a MnF$_8^{6-}$ cluster *in vacuo*, using the available x-ray absortion near-edge structure (XANES) experimental Mn–F distance.[27] [Note that in Ref. 27 the reported XANES distance is 2.20 Å, the direct extended x-ray-absortion fine-structure (EXAFS) distance is 2.243 Å, and the estimated EXAFS distance after including a shift taken from measurements in MnF$_2$ is 2.273 Å. Fortunately, the $3d^5$ ligand field spectrum in a cubic field is only slightly dependent on the ligand field and, so, on the metal-ligand distance.] As a consequence of those calculations, some questions on the previous detailed interpretation of the $3d^5$ manifold of CaF$_2$:Mn^{2+} have been raised:[26] First, an inversion of the relative location of the first $^4A_{1g}$ and ^4E_g excited states has been suggested, and, secondly, a significant increase (by about 20%) of the accepted crystal field splitting parameter of this material has been proposed, this conclusion being of particular concern since, as commented above, it can affect further interpretations of spectroscopic data of related, more complex Mn^{2+} defects and, in general, of similar systems.

In this work we present the results of an *ab initio* model potential (AIMP) embedded cluster study of the optical absorption spectrum of Mn^{2+}-doped fluorite following a different methodological strategy. In effect, the AIMP method is used to represent the surrounding fluorite.[23,28] Through the AIMP embedding potentials interactions of the MnF$_8^{6-}$ cluster with the host ions of both electrostatic (long- and short-range, up to lattice dipole polarization effects) and quantum nature (short-range exchange and lattice/cluster orthogonality effects) are considered.[23,28] This, not only allows for the calculation of the embedded-cluster ground and excited electronic states without the risks of getting artificial "variational distortions" associated to classical embedding,[29] but it also enables a local geometry optimization prior to the calculation of the absorption spectrum, EXAFS and/or results being only used (when available) to contrast the calculated distorted ionic sites, which, for this case, have actually been calculated elsewhere[28] for the Mn^{2+} first and second neighbors in CaF$_2$:Mn^{2+}, as well as for more distant ones. As a consequence of the size of the problem, we also have to assume a considerable truncation on the multiconfigurational expansion of the cluster wave function with respect to that necessary for correlating all of the valence cluster electrons, but the truncation used is much less severe for the calculation of the vertical absorption spectrum than that employed for the geometry optimization.[28] In particular, we have correlated up to 23 electrons by applying the size-consistent averaged coupled pair functional method (ACPF) (Ref. 30) onto the multireference space corresponding to $(3d^n)$-complete-active-space self-consistent-field wave functions (CASSCF).[31] In principle, reasonable results should be expected from these calculations, since, on the one hand, the size-consistent ACPF method is very well suited for handling the correlation effects in the electronic transitions under consideration, and, on the other hand, the AIMP embedding

TABLE I. Equilibrium distance and respiratory vibrational frequency of the S$=\frac{5}{2}$ and S$=\frac{3}{2}$ states of the Mn$^{2+}-3d^5$ manifold of CaF$_2$:(MnF$_8^{6-}$).

State	$^6A_{1g}$	$^4T_{1g}(^4G)$	$^4T_{2g}(^4G)$	$^4A_{1g}(^4G)$	$^4E_g(^4G)$	
r_e(Mn–F)/Å	2.249	2.238	2.246	2.248	2.248	
$\bar{\nu}(a_{1g})$/cm^{-1}	431	426	429	431	431	
State	$^4T_{1g}(^4P)$	$^4T_{2g}(^4D)$	$^4E_g(^4D)$	$^4A_{2g}(^4F)$	$^4T_{1g}(^4F)$	$^4T_{2g}(^4F)$
r_e(Mn–F)/Å	2.258	2.245	2.248	2.246	2.250	2.254
$\bar{\nu}(a_{1g})$/cm^{-1}	435	429	431	431	431	435

method has been shown to properly take into account the crystal environment effects on spectroscopic properties of similar systems, such as K$_2$NaGaF$_6$:Cr^{3+} (Ref. 32) and V^{2+}-doped fluoroperovskites.[33] It is found that, after including atomic correlation corrections, the general agreement with the experimental spectrum is excellent. The initial assignment of the first $^4A_{1g}$ and ^4E_g excited states by McKeever *et al.*[12] is supported by our calculations, and new assignments of some high energy transitions are proposed which support, as well, the initially accepted and lately questioned[26] value of the crystal field splitting parameter 10Dq of Alonso and Alcalá.[16]

In Sec. II we present an outline of the methods used and the details of the calculations, in Sec. III we show the results and we discuss them together with the experimental and previous theoretical data. The conclusions of the discussion are presented in Sec. IV.

II. METHOD AND DETAILS OF THE CALCULATIONS

As commented above, the optical absorption spectrum of unirradiated manganese-doped CaF$_2$ is due to Mn^{2+} impurities which substitute Ca^{2+} ions in the center of a cube of F$^-$ ions.[1,2] Consequently, we performed *ab initio* calculations in several electronic states of a CaF$_2$-embedded MnF$_8^{6-}$ cluster. Spin-orbit effects are known to play an insignificant role in this spectrum[12] and all the calculations presented here omit these interactions.

As an embedding technique, we used the *ab initio* model potential / shell model method (AIMP/SM), proposed in Ref. 28 as an extension of the AIMP embedding method[23] in order to include site relaxation and dipole polarization of lattice ions very distant from the local defect. Ref. 28 contains all the neccessary details of the AIMP/SM method as well as the results of its application to the study of the local distortions on the system under study. The embedding AIMP's representing complete-Ca^{2+} and complete-F$^-$ ions in CaF$_2$ are available from the authors upon request.[34] According to the AIMP/SM embedding method, the Hamiltonian of the embedded MnF$_8^{6-}$ cluster incorporates the effects of a CaF$_2$ lattice which has been relaxed and polarized in a manner consistent with the electronic structure of the cluster. The embedding operators bring, to the otherwise isolated cluster, lattice effects of long- and short-range electrostatic nature (up to lattice dipole polarization effects) and of short-range quantum nature (exchange interactions and cluster/lattice orthogonality effects).

For the MnF$_8^{6-}$ cluster we used effective core potentials, in particular, *ab initio* core model potentials (AIMP).[35] For Mn we used the relativisc AIMP corresponding to a [Mg]-core and the valence basis set from Ref. 36, which, upon addition of one p-polarization function,[37] one d-diffuse function,[38] and a three-primitive contracted f-polarization function,[39] resulted in a contraction pattern (711/321/3111/3). For F we used the nonrelativistic [He]-core AIMP and valence basis set from Ref. 35 extended with one p-diffuse function for anion,[40] the final basis set pattern being (41/411). This molecular basis set differs from the one in Ref. 28 by the presence of the f-functions on Mn, which are expected to be more important for spectroscopic calculations than for geometry optimizations.

In order to undertake the spectroscopic studies, we firstly performed a series of complete-active-space self-consistent-field (CASSCF) calculations[31] using D_{2h} symmetry restrictions, with five electrons on an active space defined by the e_g and t_{2g} molecular orbitals of main character Mn(3d); (i) on the $^6A_{1g}$ ground state; (ii) on the $^4A_{1g}(^4G)$, $^4E_g(^4G)$, $^4E_g(^4D)$, and $^4A_{2g}(^4F)$ states (the parent free-ion terms have been included in the notation); and (iii) on the $^4T_{1g}(^4G)$, $^4T_{2g}(^4G)$, $^4T_{2g}(^4D)$, $^4T_{1g}(^4P)$, $^4T_{1g}(^4F)$, and $^4T_{2g}(^4F)$ states, with molecular orbitals optimized in the average root in the two last cases. These kind of calculations involve a very small degeneracy breakdown of the ^4T states, which is irrelevant for the absorption spectrum. Using this level of calculation together with the distorted CaF$_2$ lattice obtained for the $^6A_{1g}$ ground state in Ref. 28, we optimized the Mn–F distance and calculated the respiratory vibrational frequency of all the states; the results are presented in Table I. In it we can see that the 2.249 Å found for the ground state distance is essentially identical to the 2.251 Å value obtained with a basis set lacking the f-polarization functions.[28] Also, the very small ligand field dependency of all the states under consideration is clearly reflected in the low values of the equilibrium distance shifts. All of the a_{1g} vibrational frequencies are remarkably similar.

Then, at the equilibrium distance of the ground state, and always with the embedded cluster hamiltonian, we performed a series of (approximately size-consistent) average coupled pair funtional (ACPF) calculations[30] oriented towards a reliable computation of the absorption spectrum. First, we calculated the ACPF energies of all the cited states, using the respective sets of molecular orbitals obtained in the CASSCF calculations already described and the respective active spaces, correlating only the five active electrons of

TABLE II. d–d spectrum of free-ion Mn^{2+}. Atomic correlation corrections appear in parentheses. All numbers in cm^{-1}.

	CASSCF	ACPF(5)	ACPF(11)	Experiment[a]
$^6S\rightarrow{}^4G$	32 255(−5 410)	30 540(−3 695)	29 480(−2 635)	26 845
$\rightarrow{}^4P$	37 220(−8 022)	32 785(−3 587)	31 920(−2 722)	29 198
$\rightarrow{}^4D$	39 990(−7 648)	36 690(−4 348)	35 590(−3 248)	32 342
$\rightarrow{}^4F$	53 820(−10 202)	49 190(−5 572)	48 020(−4 402)	43 618

[a]Reference 45. Weight-averaged results over the spin-orbit components.

main character Mn(3d). We call these calculations ACPF(5). Then, in order to handle extra atomic correlation effects, we included the single and double excitations from the occupied molecular orbitals of main character Mn(3p), so correlating 11 electrons, ACPF(11). Finally, to the ACPF(5) many-electron space we added the single and double excitations from the occupied molecular orbitals of main character F(2p) appearing in the a_{1g} block (one), e_g block (one), and t_{2g} block (two), in an attempt to study the effects of ligand correlation; this is the extension to cubic coordination 8 of the recipe by Pierloot and Vanquickenborne for octahedral coordination 6.[41] The resulting calculation, in which 23 electrons are correlated, is called ACPF(23).

In order to know the atomic correlation errors which are inherent to the basis set and wave functions used, we performed CASSCF, ACPF(5), and ACPF(11) electrons on the d–d spectrum of the isolated Mn^{2+} ion. The results are presented in Table II, where the atomic correlation corrections for each method have been included in parentheses. These corrections will be transferred to the embedded MnF$_8^{6-}$ cluster calculations later on.

The calculations have been done using the MOLCAS-2 package[42] for molecular electronic structure calculations, the ECPAIMP program[24] for evaluating AIMP core and embedding potential integrals, and the ENEBRO program[43] for performing the cycles of the AIMP/SM embedding method.

III. RESULTS AND DISCUSSION

We present in Table III the results of the absorption spectrum calculated at different correlation levels. All the calculations have been done with the lattice and cluster geometries

obtained in the AIMP/SM CASSCF calculation on the $^6A_{1g}$ ground state. In the notation of the excited states we include the parent free-ion terms.

The uncorrected results show the importance of the manganese 3d electron correlation effects [ACPF(5) vs CASSCF] and the very small effect of the 3p correlation [ACPF(11)] as well as the ligand correlation included by means of the ACPF(23) calculation. After including the respective free-ion parent term atomic electron correlation corrections[46] from Table II, all the results are much closer; we take this as an indication of stability of the results, and we do not expect very significant changes of our best calculation [corrected ACPF(23)] upon extension of the atomic correlation treatment, in this case.

In Table IV we compare our results with the experiments. One can see that the general agreement with the experimental values is excellent, the deviations being systematically positive. There is one exception to this behavior; the $^6A_{1g}\rightarrow{}^4T_{1g}(^4P)$ deviates −2018 cm^{-1}, which, in addition to being negative, is exceptionally large. Since there is nothing special to the $^4T_{1g}(^4P)$ state which justifies such an exceptional behavior, we think that our results indicate a wrong assigment of the 33 890 cm^{-1} peak in Ref. 12.

This conclusion is supported as well by the following facts. First, the MCSCF calculations from Lewandowski and Wilson[26] in Table IV [which include an arbitrary shift of −5220 cm^{-1} in all of the transitions in order to match the $^6A_{1g}\rightarrow{}^4E_g(^4G)$ absorption] lead to a value for this transition significantly shorter than 33 890 cm^{-1} as well, again the only one showing significant negative deviations from the experiments, in spite of the sensible methodological differ-

TABLE III. Calculated absorption spectrum of CaF$_2$:(MnF$_8^{6-}$). All numbers in cm^{-1}.

		Uncorrected				Corrected[a]			
				ACPF				ACPF	
		CASSCF	(5)	(11)	(23)	CASSCF	(5)	(11)	(23)
$^6A_{1g}$	$\rightarrow{}^4T_{1g}(^4G)$	29 960	27 155	26 120	26 540	24 550	23 460	23 485	22 845
	$\rightarrow{}^4T_{2g}(^4G)$	31 715	29 925	28 965	29 500	26 305	26 230	26 330	25 805
	$\rightarrow{}^4A_{1g}(^4G)$	31 805	30 115	29 120	29 770	26 395	26 420	26 485	26 075
	$\rightarrow{}^4E_g(^4G)$	31 935	30 200	29 220	29 875	26 525	26 505	26 585	26 180
	$\rightarrow{}^4T_{2g}(^4D)$	39 130	35 780	34 790	35 465	31 480	31 430	31 540	31 120
	$\rightarrow{}^4E_g(^4D)$	39 550	36 195	35 195	36 000	31 900	31 850	31 950	31 650
	$\rightarrow{}^4T_{1g}(^4P)$	38 735	35 385	34 750	35 465	31 710	31 800	32 030	31 880
	$\rightarrow{}^4A_{2g}(^4F)$	51 335	47 750	46 645	47 900	42 135	42 180	42 245	42 330
	$\rightarrow{}^4T_{1g}(^4F)$	53 990	49 425	48 460	49 465	43 790	43 850	44 060	43 895
	$\rightarrow{}^4T_{2g}(^4F)$	54 100	49 830	48 910	50 095	43 900	44 260	44 510	44 525

[a]Results corrected with the atomic correlation effects from Table II.

TABLE IV. Absorption spectrum of Mn^{2+}-doped CaF_2. All numbers in cm^{-1}. Numbers in braces are questioned in the text.

	This work	Experiment[a]	Ref. 26[b]	CFT[c]
$^6A_{1g}\rightarrow{}^4T_{1g}(^4G)$	22 845	22 675	23 310	23 062
$\rightarrow{}^4T_{2g}(^4G)$	25 805	24 950	25 000	24 806
$\rightarrow{}^4A_{1g}(^4G)$	26 075	25 316	25 490	25 300
$\rightarrow{}^4E_g(^4G)$	26 180	25 510	25 245	25 300
$\rightarrow{}^4T_{2g}(^4D)$	31 120	29 850	31 780	30 007
$\rightarrow{}^4E_g(^4D)$	31 650	31 250	32 180	30 767
$\rightarrow{}^4T_{1g}(^4P)$	31 880	[33 898]	32 825	31 962
$\rightarrow{}^4A_{2g}(^4F)$	42 330	41 660	45 165	41 668
$\rightarrow{}^4T_{1g}(^4F)$	43 895	[41 660]	46 295	41 897
$\rightarrow{}^4T_{2g}(^4F)$	44 525	[42 735]	47 100	42 926
		[43 500]		

[a]Values and assignments from Ref. 12. Numbers in braces are questioned in the text.
[b]After including an arbitrary shift of $-5\,220$ cm^{-1} in order to match the $^6A_{1g}\rightarrow{}^4E_g(^4G)$ absorption. Note that the assignment of the $^4E_g(^4G)$ and $^4A_{1g}(^4G)$ states in Ref. 26 is reversed here.
[c]Crystal field theory results using the parameters from Ref. 12.

ences with our calculations; it is performed using a different Mn–F distance, different level of correlation treatment, different basis set, and, in addition, it is a *cluster-in-vacuo* calculation. Second, the results of the simple crystal field theory (CFT) using the parameters from Ref. 12, $10Dq=4200$ cm^{-1}, $B=781$ cm^{-1}, and $C=3498$ cm^{-1}, also included in Table IV, lead to a specially large deviation in this electronic transition as well. One should note at this point that the CFT calculation reported in Ref. 12 using the same parameters is either mistaken or misprinted for the three $^6A_{1g}\rightarrow{}^4T_{1g}$ transitions, and, whereas the errors in the reported[12] $^4T_{1g}(^4G)$ (22 675 cm^{-1}) and $^4T_{1g}(^4F)$ (41 670 cm^{-1}) do not lead to significant consequences, that in the $^4T_{1g}(^4P)$ state (33 333 cm^{-1}) could be responsible for the assignment under consideration. Finally, McKeever *et al.*[12] comment that in their absorption spectrum after background substraction (Fig. 1 in Ref. 12) "only minor absorptions from other impurities are noticed, notably in the 250–300 nm region." In particular, the peak under consideration [a small shoulder at 295 nm close to other shoulders of equal size, at smaller wavelengths, which were considered to be due to other impurities, and clearly separeted from the $^4T_{2g}(^4D)$ and $^4E_g(^4D)$ peaks] lies within this region and the possibility of assigning it to the unwanted impurities rather than to the Mn^{2+} defect should be considered.

In summary, we therefore think that the 33 890 cm^{-1} peak should not be assigned to the Mn^{2+} impurity, since there is no theoretical support for it and the possibility of it being due to other impurities exists. This fact has a direct consequence in the values of the CFT parameters normally used as a fast interpretative and predictive tool. In effect, assigning the 33 890 cm^{-1} peak to the $^4T_{1g}(^4P)$ state leads to an abnormally large value of the crystal field splitting parameter, $10Dq$, in a fitting of the CFT levels to the experiments. As a matter of fact, Lewandowski and Wilson[26] recently proposed a value of 5070 cm^{-1} for the $t_{2g}-e_g$ crystal field splitting, much larger than the previously proposed (and usually accepted) by Alonso and Alcalá[16] of 4200 cm^{-1}. [They proposed $10Dq^\star=5700$ cm^{-1} within a scheme in which $Dq^\star$ corresponds to an octahedral coordination

6 O_h, so that the crystal field splitting in cubic coordination 8 O_h is, within the CFT language, $\varepsilon(t_{2g})-\varepsilon(e_g)=\frac{8}{9}10Dq^\star$. Within the more usual scheme in which Dq corresponds to coordination 8 O_h, and $\varepsilon(t_{2g})-\varepsilon(e_g)=10Dq$, their proposal corresponds to $10Dq=5070$ cm^{-1}.] We also obtain $10Dq=5072$ cm^{-1} in a least square fitting of the CFT levels to the experiments in Table IV in which fixed values of $B=781$ cm^{-1} and $C=3498$ cm^{-1} are used, the root mean square deviation being 541 cm^{-1}. However, if the assignment of the $^4T_{1g}(^4P)$ level is discarded, the least square fitting leads to $10Dq=4364$ cm^{-1}, very close to the accepted value of Alonso and Alcalá,[16] and the root mean square deviation is lowered to 244 cm^{-1}. Mention must be made that the spectrum under consideration has a very small overall dependence on the crystal field splitting and acceptable values of $10Dq$ span over a wide range (from 4200 cm^{-1} to 4600 cm^{-1} the root mean square deviation is lower than 250 cm^{-1}, for instance).

Other remarks on the assignments are pertinent as well from our calculations. The $^4A_{1g}(^4G)$ and $^4E_g(^4G)$ states are degenerate within the CFT framework, and their observed splitting is a consequence of covalency and interactions with higher electronic configurations, so that CFT cannot be used as a tool for the proper assignment of the peaks at 25 316 cm^{-1} and 25 510 cm^{-1}. They had, respectively, been assigned to the $^4A_{1g}(^4G)$ and $^4E_g(^4G)$ states,[12] in accordance with previous assignment in related hosts, in particular with absorption and magnetic circular dichroism spectra in $CdF_2:Mn^{2+}$,[47] but the reverse assignment has been proposed as a consequence of the *cluster-in-vacuo* MCSCF calculations from Ref. 26. We, however, obtain the $^4A_{1g}(^4G)$ slightly below the $^4E_g(^4G)$ state, in support of the former assignment. Also, the single narrow peak at 41 660 cm^{-1} (see Fig. 1 in Ref. 12) has been simultaneously associated with the $^4A_{2g}(^4)$ and $^4T_{1g}(^4F)$ states. In this case, even the simpler CFT predicts a non-negligible splitting, which is larger in the more sophisticated embedded cluster *ab initio* calculation of this work. This suggests that it is improbable that both states are responsible for the same peak. In addi-

tion, our results would be more consistent with the assignment of the 42 735 cm^{-1} peak to the $^4T_{1g}(^4F)$ rather than to the $^4T_{2g}(^4F)$ state. This would be consistent as well with the assignment of a shoulder at wave numbers larger than the 42 735 cm^{-1} peak,[12] approximately at 43 500 cm^{-1}, which has not been adscribed to any level, to the $^4T_{2g}(^4F)$ state.

IV. CONCLUSIONS

An *ab initio* calculation of the optical absorption spectrum of Mn^{2+}-doped CaF_2 has been presented in which electrostatic and quantum embedding effects of a distorted and dipole-polarized flourite lattice on the ground and excited states of a MnF_8^{6-} cluster have been considered. The theoretical spectrum calculated by means of the CASSCF and ACPF methods, correlating up to 23 electrons, shows an excellent overall agreement with the experimental observations. Based on this agreement, a detailed analysis of the results has been presented which (i) supports the initial assignments of the absorptions to the $^4A_{1g}(^4G)$ and $^4E_g(^4G)$ states, which had lately been questioned; (ii) suggests the existence of a wrong assignment of the absorption to the $^4T_{1g}(^4P)$, and shows that this is responsible for a recent reevaluation of the initially accepted value of the crystal field splitting parameter $10Dq = 4250 \ cm^{-1}$, which is in turn supported here; and (iii) suggests new assignments for the absorptions to the $^4T_{1g}(^4F)$ and $^4T_{2g}(^4F)$ excited states.

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