Ab initio model potential embedded-cluster study of the ground and lowest excited states of Cr^{3+} defects in the elpasolites Cs_2NaYCl_6 and Cs_2NaYBr_6

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In this paper we present the results of an *ab initio* model potential (AIMP) embedded-cluster study of the ground and lowest excited states of Cr^{3+} defects in the elpasolites Cs_2NaYCl_6 and Cs_2NaYBr_6; complete active space SCF (CASSCF) and averaged coupled-pair functional (ACPF) calculations are performed on $CrCl_6^{3-}$ and $CrBr_6^{3-}$ clusters embedded in *ab initio* model potential representations of the surrounding lattices Cs_2NaYCl_6 and Cs_2NaYBr_6. The experimental structural data are revisited and some new results are found which differ significantly from those available in the literature. The calculated local structure parameters and electronic transition energies which can be compared to experiments are found to be very good; new structural and spectroscopic results are produced which have been neither measured nor calculated, which are complementary to the available ones, and whose quality is expected to be high as well. In particular, the question of the competition of the excited-state absorptions with the potential vibronic laser emission has been adressed: A considerable overlap between the broad $^2E_g \rightarrow {}^2A_{1g}$ excited-state absorption and $^4A_{2g} \leftarrow {}^4T_{2g}$ emission bands is predicted in both materials, which must result in a reduction in the emission efficiency. Finally, it is shown that the quantum mechanical embedding effects due to the fact that the external Cs^+, Na^+, Y^{3+}, Cl^-, and Br^- ions are not point charges, are non-negligible; lacking of these effects must be one of the reasons which make previous Density Functional Theory calculations show significantly larger discrepancies with the available experiments. © *1998 American Institute of Physics.* [S0021-9606(98)00905-2]

I. INTRODUCTION

The properties of the ground and low-lying excited states of local defects made of transition metal impurities in ionic crystals are of great interest due to their relevant role in the laser activity of these materials.[1–3] Of particular interest is the knowledge of the energy differences between the electronic states involved in laser-related mechanisms (pumping, emission, excited-state absorption and emission, cross-relaxation, etc.) but also the knowledge of the characteristics of their potential energy surfaces, such as equilibrium geometries, vibrational frequencies, Jahn–Teller distortions, Jahn–Teller stabilization energies, etc. This makes the field specially well disposed for a fruitful combination of the information gathered by experimental and theoretical techniques.[4] In effect, many of the properties of interest are directly accesible to the experimental methods and are measured with high precision, particularly those related to energy differences between states. However, some other properties are either difficult to measure, like the equilibrium structures of the local defects on their ground states,[5] or not directly measurable, like the equilibrium structures of the local defects on their excited states, the Jahn–Teller distortions, and Jahn–Teller stabilization energies, which, instead, are some-times *estimated* from experimental data to which they are related according to approximate interpretative models.[6–9] The latter properties are, however, a direct product of first principles theoretical calculations. In consequence, once they have been contrasted, the nonemprical theoretical methods should aim to be included in the row of techniques which are routinely used to gather information about these materials and their properties.

In these circumstances, the growing interest of the application of *molecular* nonempirical theoretical methods (well established in quantum chemistry) to the field of local defects in ionic crystals is natural, since they are specially designed to handle *local* problems. In this task they face the *embedding problem*, that is, the necessity of including in a balanced and accurate way the effects of the surrounding solid on the electronic structure of that piece of material which is considered to be responsible for the local properties under study. Several methods have been proposed to implement correct embedding effects in molecular calculations and some of them have been in use for years.[10,11] The *ab initio* model potential embedded-cluster method (AIMP) formulated in our laboratory[12–15] has been succesfully applied to the calculation of structural and spectroscopic properties of a number of transition metal doped ionic crystals[4] and, in particular, to d^3 impurities doped in low field hosts.[16–19]

The isoelectronic Cr^{3+} (Refs. 9,20–26) and V^{2+} (Refs. 24,27–29) impurities doped into low-field materials have

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been widely investigated using a variety of experimental techniques, as a consequence of the well-known quality of some Cr^{3+}-based laser materials,[1,2,30] and in an attempt to find new vibronic solid state lasers of comparable pumping efficiency, low excited-state absorption or nonradiative losses, tunable in the infrared spectral range, and operative at room temperature. This effort still continues, involving more complex d^3 charged defects resulting from local charge compensation.[31–36] The investigations aim at measuring in detail the electronic spectra originating in the ground states (ground state absorption) and also in the excited states (excited-state absorption and emission difference spectra), as well as their host variations, temperature dependences, pressure induced changes, etc. As a result of such a simultaneous effort of different experimental groups, a considerable amount of definite information has been accumulated, at a time that new questions have been raised and gaps of information have become apparent. From the point of view of quantum chemistry, the former may serve to establish good references to test the abilities of *ab initio* methods to model the systems and their properties; the latter may become the goals of complementary theoretical studies. These two lines form the strategy of the work that we have been conducting in our laboratory, which involves, among others, d^3 impurities in low-field crystals.[16–19]

In fact, the *ab initio* model potential method for embedding was proposed[12] based on the *Group Function Theory* of McWeeny and Huzinaga,[37,38] well-rooted in the field of molecular quantum chemistry. The method was conceived as a response to the experimental evidences of host effects beyond the first neighbors of the impurity and was intended to be capable of accurately predicting local structure parameters, electronic transitions, and their variations with the crystalline environment. Consequently, it was tested against available accurate experiments: The predictions of the local structure were shown to be very close to the results of extended x-ray absorption fine structure (EXAFS) measurements in Mn^{2+}-doped CaF$_2$.[15] The pressure induced shifts of ligand-field electronic transitions and vibrational frequencies observed experimentally in K$_2$NaGaF$_6$:Cr^{3+}[23] were used to test the ability of the AIMP embedded-cluster method to model the environmental changes caused by hydrostatic pressure in Ref. 17. The quality of the calculated electronic transitions from the ground state and from excited states, and their host variations was tested in a series of low-field V^{2+}-doped fluoroperovskites[18,19] versus available experiments.[28,29]

In addition, the method was used to contribute complementary information in a series of d^3-doped low-field hosts: It was first used to calculate the multimode $T_1 \otimes (\epsilon + \tau_2 + \tau_2')$ Jahn–Teller coupling in order to clarify whether the local structure of Cr^{3+} defects in fluorite was nearly octahedral or D_{3d} distorted.[16] Calculations were also done in order to help to interpret observed irregular dependences of the 10Dq electronic transition[24,27] with structural data of the hosts in V^{2+}-doped fluoroperovskites.[18] It was also used to study the competition between laser emission, reabsorption, and excited-state absorption in the same materials.[19] In this case,

the convenience of applying simultaneously experimental and theoretical techniques became particularly clear since it was possible to calculate the infrared excited-state absorption, lying in the spectral region where spontaneous fluorescence makes the experimental difference spectra uncertain,[24,28,29] with the same methodological treatment and, therefore, accuracy as that attained in the calculated visible excited-state absorption, where the experiments actually served as an accurate reference test, and so, some new information about the emission/excited-state absorption competition could be obtained.

Also parallel to the experimental work described above, studies are in progress in our laboratory including other d^3-doped low-field hosts. Their interest stems from the fact that either the experimental work is relatively scarce or low-symmetry charged-defects are created whose local structure and bonding can be studied through *ab initio* calculations. In this paper we present the results of the calculations of the structure and spectroscopy of the ground and low-lying local excited states of Cr^{3+}-doped elpasolites Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$ where the available experimental work is not as extensive and, therefore, the possibility of producing new information from our theoretical calculations is wider. In effect, high-resolution absorption, magnetic circular dichroism (MCD), and luminiscence spectra have been published for Cs$_2$NaYCl$_6$:Cr^{3+}.[9,20] The emission spectrum has been reported for Cs$_2$NaYBr$_6$:Cr^{3+},[9] but it is not so well-resolved; the absorption spectrum has not been published for the bromide, to our knowledge. The excited-state absorption spectra have not been measured in these materials, and we are not aware of any reports on the measurements of the local distortions produced by Cr^{3+} defects in the two elpasolites. Yet, the observed ^{4}T$_{2g} \rightarrow$ ^{4}A$_{2g}$ luminescence spectrum of Cs$_2$NaYCl$_6$:Cr^{3+} is so detailed that the application of approximate models to estimate excited-state structural information from intensity distributions in the vibronic progressions may be expected to lead to accurate values of the distortions of the ^{4}T$_{2g}$ excited state with respect to the ^{4}A$_{2g}$ ground state of the CrCl$_6^{3-}$ cluster.[9] Furthermore, recently, Density Functional Theory (DFT) calculations on the ground and low-lying states of the Cr^{3+}-doped elpasolites Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$ have been presented where the effects of the host crystals are either neglected[39] or modeled by Madelung embedding potentials.[40] This should allow for a somehow limited comparison of the results obtained through DFT and *ab initio* embedded-cluster methods, due to the fact that the embedding used in the DFT calculations is not quantum mechanical.

In this paper we have performed complete-active-space self-consistent-field (CASSCF)[41] and averaged coupled-pair functional (ACPF)[42] calculations on the units CrCl$_6^{3-}$ and CrBr$_6^{3-}$, respectively, embedded in *ab initio* model potential representations of the Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$ lattices, including a large number of AIMP's which embody the quantum mechanical potentials created by the Cs$^+$, Na$^+$, Y^{3+}, Cl$^-$, and Br$^-$ ions located at the experimental lattice sites, according to the prescriptions of Refs. 12 and 13. The CASSCF method has been used for the structural calcula-

tions and the ACPF method, which includes size-consistent correlation effects in an approximate way, has been applied to the calculations of electronic transitions. These are the levels of methodology which were previously found to be adequate for the same properties of similar systems, as mentioned above. In order to be able to make a direct comparison with the DFT results, we have also done calculations with simpler, Madelung embedding potentials (corresponding to point-charge descriptions of the lattice ions,) which have been shown before to lead to artificially distorted ground and excited state structures.[12,17,43–46]

In Sec. II we present a summary of the method as well as all the neccessary details of the calculations. We start Sec. III with a revision of the structural data that have been estimated from experimental measurements, and continue it with the presentation and discussion of the results, which are compared with the DFT calculations and with the experiments when available. Finally, we write the conclusions in Sec. IV.

II. METHOD AND DETAILS OF THE CALCULATIONS

The optical spectra of Cs^{3+}-doped elpasolites Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$, where some of the Y^{3+} ions are substituted by Cr^{3+}, correspond to electronic transitions between electronic states localized in the Cr^{3+} impurities and in their first coordination shell of Cl$^-$ and Br$^-$. They are mainly affected by the Cr^{3+}–Cl$^-$ and Cr^{3+}–Br$^-$ bonding interactions, and, in order to handle them, we performed CASSCF[41] and ACPF[42] *ab initio* calculations on the (CrCl$_6$)$^{3-}$ and (CrBr$_6$)$^{3-}$ defect clusters; the details are reported in Sec. II B. But the wave functions of those local electronic states are also influenced by the embedding effects brought about by the rest of the Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$ crystal lattices. We handled them by embedding the (CrCl$_6$)$^{3-}$ and (CrBr$_6$)$^{3-}$ clusters in appropriate representations of the Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$ crystals according to the *ab initio* model potential embedding technique;[12,13,15] the details are reported in Sec. II A. The CASSCF and ACPF calculations have been performed with the MOLCAS-3 package[47] which receives the AIMP one-electron integrals calculated with the ECPAIMP program.[48]

A. The AIMP embedding technique

The *ab initio* model potential embedding technique used here, which has been successfully applied to a number of cases similar to the present ones,[4] is a practical implementation of the group function theory developed by McWeeny[37] (in the context of intermolecular interactions) and Huzinaga[38] (in the context of frozen-core molecular calculations) to the study of local properties of imperfect ionic crystals. It has been presented in Refs. 12 and 13 for *ab initio* calculations on clusters embedded in unpolarized, unrelaxed, frozen ionic lattices, and extended in Ref. 15 in order to embed clusters, when neccessary, in relaxed, dipole polarized ionic lattices, making use of the empirical shell-model description of the lattice.[49] It is an efficient way of including embedding effects of electrostatic nature (long-range Coulomb or Madelung effects, and short-range Cou-

lomb effects) as well as of quantum nature (exchange effects, cluster/lattice orthogonality or linear-independency effects, and spin-free relativistic effects) in the calculations of properties dominated by intracluster interactions (including dynamical correlation effects) and nondynamical interactions between the cluster and its environment. The embedding technique finally involves the correction of the one-electron terms in the Hamiltonian of the cluster by adding one-electron potentials of the form

$$\sum_{\mu} [V_{\mu}^{lr-Coul}(i) + V_{\mu}^{sr-Coul}(i) + V_{\mu}^{Exch}(i) + P_{\mu}(i)], \quad (1)$$

where μ runs over the ions of the crystal, $V_{\mu}^{lr-Coul}(i)$ stands for the long-range Coulomb potential created by the lattice ion μ on the cluster electron i [note that $\sum_{\mu} V_{\mu}^{lr-Coul}(i)$ is the Madelung potential], $V_{\mu}^{sr-Coul}(i)$ is the short-range Coulomb potential, $V_{\mu}^{Exch}(i)$ is the exchange potential, and $P_{\mu}(i)$ is a projection operator which prevents the collapse of the cluster wave function onto the lattice ion μ. The detailed form of all these operators, which is identical to the one of the AIMP *core* potentials[50] used in valence-only molecular calculations, can be found in Refs. 12 and 13, together with the procedure which leads to the values of their parameters starting from the wave functions of the ions, $\Phi(\mu)$.

In this work, we obtained embedding potentials [Eq. (1)] for Cs$^+$, Na$^+$, Y^{3+}, and Cl$^-$, on the one hand (Cs$_2$NaYCl$_6$), and for Cs$^+$, Na$^+$, Y^{3+}, and Br$^-$, on the other (Cs$_2$NaYBr$_6$), starting from closed-shell monoconfigurational self-consisted field wave functions $\Phi(Cs^+)$, $\Phi(Na^+)$, etc., which resulted from *self-consistent embedded-ions* calculations, SCEI, on Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$. The SCEI process on Cs$_2$NaYCl$_6$, i.e., consists of an iterative series of SCF calculations on the ions Cs$^+$, Na$^+$, Y^{3+}, and Cl$^-$, respectively, embedded in an AIMP representation of the Cs$_2$NaYCl$_6$ lattice, that produce SCF wave functions and, from them, new AIMP embedding potentials which can be used in a new iteration; this process is stopped when the ionic wave functions are converged. The embedding potentials were located at experimental sites [Cs$_2$NaYCl$_6$(O$_h^5$-F$_{m3m}$): a_0 = 10.739 67 Å, x_{Cl}=0.243 93; Cs$_2$NaYBr$_6$(O$_h^5$-F$_{m3m}$): a_0=11.304 76 Å, x_{Br}=0.244 62].[51] All-electron SCF calculations were performed on Na$^+$, Y^{3+}, and Cl$^-$ with basis sets (43/4), (4333/433/43), and (333/33) of Ref. 52 splitted as (4111/1111), (433 111/43 111/ 211 111), and (33 111/3111), respectively. Effective core potential SCF calculations with the spin-free relativistic CG-AIMP method[53,54] were performed on Cs$^+$ and Br$^-$, using a [Cr,4d]-core and a (11/10) basis set splitted as (322 211/ 322 111) in Cs$^+$ and a [Ar,3d]-core and a (9/8) basis set splitted as (32 211/32 111) in Br$^-$, all data taken from Ref. 54. The embedding model potentials so produced for the ionic components of the elpasolites Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$ were stored in libraries for the present and future calculations; they are available from the authors.[55]

For the study of Cr^{3+}-doped Cs$_2$NaYCl$_6$ a (CrCl$_6$)$^{3-}$ cluster was embedded in 482 model potentials representing Cs$^+$, Na$^+$, Y^{3+}, and Cl$^-$ ions plus 2696 extra

point-charges which allowed for a correct description of the long-range Madelung potential, all of them located at experimental sites.[51] The same number of embedding potentials and point-charges was used for the study of Cr^{3+}-doped Cs$_2$NaYBr$_6$.

B. The $(CrCl_6)^{3-}$ and $(CrBr_6)^{3-}$ defect clusters

All the calculations on the embedded clusters $(CrCl_6)^{3-}$ and $(CrBr_6)^{3-}$ used an all-electron description of the chromium atom with the $(14s11p5d)$ basis set of Wachters[56] augmented with one d-type diffuse function[57] and one $(3f)$ polarization function,[58] contracted as $(62\,111\,111/4\,211\,111/3111/3)$. The chlorines in $(CrCl_6)^{3-}$ were described using the [Ne]-core *ab initio* model potential and the $(7s6p)$ valence basis set of Ref. 50, augmented with one diffuse p function for the anion[59] and one d-type polarization function,[52] contracted as $(61/511/1)$. The bromines in $(CrBr_6)^{3-}$ were described with the [Ar.3d]-core spin-free relativistic Cowan–Griffin *ab initio* model potential from Ref. 54 and the $(9s8p4d)$ spin-orbit-corrected valence basis set from Ref. 60 contracted as $(81/611/31)$; here the outermost p-primitive Gaussian type function is diffuse enough to represent anionic electron densities (exponent 0.09). The basis sets of both $(CrCl_6)^{3-}$ and $(CrBr_6)^{3-}$ clusters were augmented with extra functions located at the Na$^+$ sites which are next-neighbor to the halogen ions in the direction of the cluster axes. These functions were the 2s and 2p orbitals of the Na$^+$ ions which resulted from the respective SCEI calculation, contracted as $(7/4)$. So, the basis set of the embedded $(CrCl_6)^{3-}$ cluster was made of 176 contracted Gaussian functions and the one of the embedded $(CrBr_6)^{3-}$ cluster was made of 206 contracted Gaussian functions.

The $^4A_{2g}$ ground state and the low-lying excited states $^4T_{2g}$, $^4T_{1g}a$, $^4T_{1g}b$, ^2E_g, $^2T_{1g}$, $^2T_{2g}$, and $^2A_{1g}$ of the embedded 69-electron $(CrCl_6)^{3-}$ and $(CrBr_6)^{3-}$ clusters have been studied. The wave functions and energies of the $^4A_{2g}$, $^4T_{2g}$, $^4T_{1g}a$, and ^2E_g states were optimized along the octahedral totally symmetric stretch coordinate in order to obtain impurity-ligand equilibrium distances and a_{1g} vibrational frequencies, and those of the $^4T_{2g}$ state were also optimized along the $e_g(\theta)$ vibrational coordinate, which leads to D$_{4h}$ symmetry, in order to study the Jahn–Teller distortions of this excited state. All the geometry optimizations were performed in complete active space SCF calculations (CASSCF)[41] including three active electrons in the mainly-Cr($3d$) t_{2g} and e_g molecular orbitals. The calculations of the spectra included dynamical correlation by means of the averaged coupled-pair functional method (ACPF),[42] which is approximately size-consistent, using the previous CASSCF configuration space as the reference. In these ACPF calculations, 15 electrons were correlated which correspond to the molecular orbitals with a dominant character Cr($3d$) and Cl($3p$) or Br($4p$) belonging to the a_{1g}, e_g, and t_{2g} irreducible representations of the O$_h$ group (or their corresponding ones in D$_{4h}$ symmetry). These calculations will be referred to as ACPF-15. In the spectroscopic transitions between states

originated from different terms of the Cr^{3+} ion, we include an empirical correlation energy correction originated from the fact that the correlation level used in the $(CrCl_6)^{3-}$ and $(CrBr_6)^{3-}$ clusters already produces (known) errors in the transitions of the free Cr^{3+} ion.[61] In effect, ACPF calculations on isolated Cr^{3+} correlating only the $3d$ electrons and using the same basis set lead to 16 400 and 17 003 cm^{-1} for the ^{4}F$\rightarrow^4$P and ^{4}F$\rightarrow^2$G transitions, which must be compared with the J-averaged experimental values 13 758 and 14 699 cm^{-1}, respectively;[62] the errors, -2642 cm^{-1} and -2304 cm^{-1} are expected to be transferred to the corresponding states of the $(CrCl_6)^{3-}$ and $(CrBr_6)^{3-}$ clusters. We correct with -2642 cm^{-1} the transitions from the $^4A_{2g}$ ground state or the $^4T_{2g}$ excited state to the $^4T_{1g}b$ excited state and with -2304 cm^{-1} those from the $^4A_{2g}$ ground state to the ^2E_g, $^2T_{1g}$, $^2T_{2g}$, and $^2A_{1g}$ states.

Some geometry optimizations were repeated at the ACPF-15 level in order to check the importance of dynamical correlation, the results being of a very minor effect, in the line of previous observations.[17,15,63,18] Also, effects of the relaxation and polarization of the crystalline lattice surrounding the clusters were explored with the AIMP/SM method of Ref. 15, which combines the AIMP embedding technique with the empirical shell-model,[49] and they were found to be insignificant on the calculated geometries and vibrational frequencies of the $^4A_{2g}$, $^4T_{2g}$, $^4T_{1g}a$, and ^2E_g states of the embedded $(CrCl_6)^{3-}$ and $(CrBr_6)^{3-}$ clusters.

III. RESULTS AND DISCUSSION

A. Experimental structural data revisited

There is no experimental information on the local distortion produced in Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$ by Cr^{3+} defects in their ground states. However, the distortions of the CrCl$_6^{3-}$ clusters in the $^4T_{2g}$ excited state with respect to the $^4A_{2g}$ ground state have been estimated by Knochenmuss *et al.*[9] from the analysis of the following experimental data: (i) intensity distributions in the vibronic progressions within the $^4T_{2g} \rightarrow {}^4A_{2g}$ luminescence, (ii) Jahn–Teller plus spin-orbit splittings of the electronic origins of this emission band, and (iii) the Stokes shifts, defined as the energy difference between absorption and emission maxima; the latter being the only experimental data used to estimate the mentioned relative distortions of the CrBr$_6^{3-}$ clusters. We have repeated the analysis, using identical assumptions and formulas, but our results differ to some extent with those published in Ref. 9. In consequence, we present here a brief discussion on the geometry distortions estimated from the available experimental data.

If reasonable assumptions are accepted, such as harmonic behavior and equal ground and excited state vibrational force constants,[9,64] the excited state distortions with respect to the ground state are related to the Huang–Rhys parameters, S_i, the vibrational frequencies, ν_i, and force constants, f_i, by

$$(\Delta Q_i)^2 = \frac{2S_i h\nu_i}{f_i}, \qquad (2)$$

TABLE I. Experimental estimates of the distortions of the CrX$_6^{3-}$ units in the $^4T_{2g}$ excited state with respect to the $^4A_{2g}$ ground state. The vibrational frequencies, $\bar{\nu}_i$, and Huang–Rhys factors, S_i, are taken from Ref. 9; the estimates obtained in Ref. 9 appear in braces.

Cs$_2$NaYCl$_6$:Cr^{3+}				Cs$_2$NaYBr$_6$:Cr^{3+}			
$\bar{\nu}_{a_{1g}}$/cm^{-1}	$S_{a_{1g}}$	$\Delta Q_{a_{1g}}$/Å	$\Delta R_{\text{Cr–X}}(a_{1g})$/Å	$\bar{\nu}_{a_{1g}}$/cm^{-1}	$S_{a_{1g}}$	$\Delta Q_{a_{1g}}$/Å	$\Delta R_{\text{Cr–X}}(a_{1g})$/Å
291[a]	1.6[b]	+0.102 [+0.13]	+0.042 [+0.053]	183[c]	3.7[d]	+0.13 [+0.22]	+0.053 [+0.090]
$\bar{\nu}_{e_g}$/cm^{-1}	S_{e_g}	ΔQ_{e_g}/Å	$\Delta R_{\text{Cr–X}_{X,Y}}(e_g)$/Å	$\bar{\nu}_{e_g}$/cm^{-1}	S_{e_g}	ΔQ_{e_g}/Å	$\Delta R_{\text{Cr–X}_{X,Y}}(e_g)$/Å
227[a]	1.6[e]	−0.116 [−0.15]	+0.033 [+0.043]	144[c]	3.0[d]	−0.13 [−0.22]	+0.037 [+0.063]
Total distortion				Total distortion			
$\Delta R_{\text{Cr–X}_Z}$/Å		$\Delta R_{\text{Cr–X}_{X,Y}}$/Å		$\Delta R_{\text{Cr–X}_Z}$/Å		$\Delta R_{\text{Cr–X}_{X,Y}}$/Å	
−0.02 [−0.03]		+0.08 [+0.10]		−0.02 [−0.04][f]		+0.09 [+0.15]	

[a]Ground state vibrational frequency.
[b]From intensity distributions of the $^4T_{2g} \rightarrow {}^4A_{2g}$ luminiscence.
[c]Correspond to the YBr$_6^{3-}$ unit rather than to CrBr$_6^{3-}$.
[d]From the Stokes shift after several assumptions (see text).
[e]Average of 1.7, from the intensity distribution, and 1.5, from Ham quenching.
[f]−0.05 is in fact reported in Ref. 9.

where i denotes the ith normal mode and $S_i h \nu_i$ is the excited state energy stabilization corresponding to the distortion. Since the force constant is related to the vibrational frequency and the vibrations reduced mass, μ_i, by $f_i = \mu_i 4\pi^2 \nu_i^2$, and the wave number is $\bar{\nu}_i = \nu_i/c$, we can use

$$(\Delta Q_i)^2 = \frac{S_i \hbar}{\pi \mu_i c \bar{\nu}_i}. \tag{3}$$

Using $\hbar = 1.054\,572\,67 \times 10^{-34}$ J s, $c = 299\,792\,458$ m s^{-1}, and $\mu_i = (M_X / \text{amu}) \cdot 1.660\,540\,20 \times 10^{-27}$ kg, $(i = a_{1g}, e_g)$ where M_X is the mass of the ligand X (we used 35.453 amu for Cl and 79.904 amu for Br), we get

$$(\Delta Q_i)^2 = \left[67.4305 \cdot \frac{S_i}{(M_X/\text{amu})(\bar{\nu}_i/\text{cm}^{-1})} \right] \text{Å}^2, \tag{4}$$

which is valid if i is the a_{1g} or e_g normal mode. The mass-independent normal coordinates fulfilling Eqs. (2) and (4) are defined in Ref. 64; from them, one can calculate the respiratory contribution to the distortion of the CrX$_6^{3-}$ unit,

$$\Delta R_{\text{Cr–X}}(a_{1g}) = (6)^{-1/2} \Delta Q_{a_{1g}}, \tag{5}$$

as well as the equatorial and axial D$_{4h}$ contributions to the total distortion,

$$\Delta R_{\text{Cr–X}_{X,Y}}(e_g) = -(12)^{-1/2} \Delta Q_{e_g}, \tag{6}$$

$$\Delta R_{\text{Cr–X}_Z}(e_g) = -2\Delta R_{\text{Cr–X}_{X,Y}}(e_g). \tag{7}$$

We summarize the results of the application of Eqs. (4)–(6) in Table I.

The estimate of $\Delta Q_{a_{1g}}$ from experimental data in Cs$_2$NaYCl$_6$:Cr^{3+} relies on a value of $\bar{\nu}_{a_{1g}}$ which has been obtained from the fine structure of the $^4T_{2g} \rightarrow {}^4A_{2g}$ emission and a value of the Huang–Rhys factor $S_{a_{1g}}$ resulting from fitting the intensity distribution of such a fine structure to

$I_n = S_i^n \exp(-S_i)/n!$. Since both of them are very reliable, the same should be expected for the estimate of the respiratory contribution to the distortion. The estimate of ΔQ_{e_g} in the same material uses a highly reliable value of $\bar{\nu}_{e_g}$ as well, which has been obtained in the same way as the value of $\bar{\nu}_{a_{1g}}$. The value of S_{e_g} results from the average of 1.7, from the intensity distribution, and 1.5, which has been calculated by fitting the splittings of the $^4T_{2g}$ magnetic dipole origins produced by the simultaneous action of the spin-orbit coupling and the Jahn–Teller effect (Ham quenching) to a reasonable model.[9,65] As we comment below, a higher value of S_{e_g} is as well possible within the same model if it is combined with a larger Jahn–Teller energy; this would slightly increase the estimated D$_{4h}$ distortion. (We should note that Wilson and Solomon[64] claim a maximum precision of 10% for the estimates obtained by this procedure.)

The estimates of $\Delta Q_{a_{1g}}$ and ΔQ_{e_g} from experimental data on Cs$_2$NaYBr$_6$:Cr^{3+} are indeed of a lower reliability. On the one hand, the vibrational frequencies of the doped material are unknown and those of the YBr$_6^{3-}$ unit have been used instead in Ref. 9. On the other hand, the fine structure of the emission band has not been observed and the Huang–Rhys factors have been obtained only from the Stokes shift ($S_{\text{tot}} = (\text{Stokes shift} - 2h\nu_{enabling})/[h(\nu_{a_{1g}} + \nu_{e_g})]$) after a row of assumptions. The $^4T_{2g} \leftrightarrow {}^4A_{2g}$ Stokes shift of this material, defined as the energy difference between the broad absorption band and the broad emission band maxima, is reported to be 2200 cm^{-1} in Ref. 9; however, the corresponding broad absorption band of this material has never been reported, to our knowledge. The emission band is indeed recorded in Ref. 9 (Fig. 1) with full width at half maximum of 1200 cm^{-1}. In these circumstances, the precision of the reported value of 2200 cm^{-1} must be considered to be

TABLE II. Structural properties of the ground and excited states of Cr^{3+}-doped Cs_2NaYCl_6 and Cs_2NaYBr_6. Units are Å and cm^{-1}.

		$Cs_2NaYCl_6:Cr^{3+}$ $R_{Y-Cl}=2.619$ Å[a] This work[b]				$Cs_2NaYBr_6:Cr^{3+}$ $R_{Y-Br}=2.765$ Å[a] This work[b]			
		DFT[c]	Madelung	AIMP	Experiment	DFT[c]	Madelung	AIMP	Experiment
$^4A_{2g}$	R_{Cr-X}	2.436	2.479	2.428		2.591	2.608	2.543	
	$\bar{\nu}(a_{1g})$	230	259	297	291[d]	149	167	196	
	$\bar{\nu}(e_g)$	245	166	228	227[d]	158	112	155	149[e]
^2E_g	R_{Cr-X}		2.477	2.427				2.541	
	$\bar{\nu}(a_{1g})$		258	297	310[f]			195	
$^4T_{2g}$	$R_{Cr-X}(O_h)$		2.521	2.464			2.649	2.577	
	$\Delta R_{Cr-X}(a_{1g})$[g]		+0.042	+0.036	+0.042[h]		+0.041	+0.034	+0.053[h]
	$\bar{\nu}(a_{1g})$		255	298	310[f]		164	195	
	$T_2 \otimes e$ Jahn–Teller distortion. $^4B_{2g}(D_{4h})$ state: distortions with respect to the $^4T_{2g}(O_h)$ equilibrium geometry								
	$\Delta R_{Cr-X_Z}(e_g)$[i]	−0.120	−0.076	−0.066[h]		−0.113	−0.071	−0.074[h]	
	$\Delta R_{Cr-X_{X,Y}}(e_g)$[h]	+0.059	+0.038	+0.033[h]		+0.057	+0.035	+0.037[h]	
	$\bar{\nu}(e_g)$		191	232	237[f]		130	158	
	E_{JT}	285	730	470	330[j]	440	690	430	
	distortions with respect to the $^4A_{2g}(O_h)$ ground state equilibrium geometry								
	ΔR_{Cr-X_Z}[g]	−0.05	−0.078	−0.040	−0.02[h]	−0.07	−0.072	−0.037	−0.02[h]
	$\Delta R_{Cr-X_{X,Y}}$[g]	+0.09	+0.101	+0.074	+0.08[h]	+0.12	+0.098	+0.069	+0.09[h]
$^4T_{1g}a$	$R_{Cr-X}(O_h)$		2.540	2.477			2.665	2.587	
	$\bar{\nu}(a_{1g})$		247	290			159	191	

[a]Host data from Ref. 51.
[b]CASSCF calculations with a classical Madelung embedding and with quantum AIMP embedding.
[c]Reference 40, Density Functional Theory calculations with a gradient correction and Madelung embedding potential. See Ref. 39 for dependences of the results on the DFT methodological details.
[d]Reference 9.
[e]Reference 9; tentative assignment from the Raman spectrum of 8% Cr doped sample.
[f]Reference 20.
[g]Displacements with respect to the $^4A_{2g}(O_h)$ ground state Cr−X distance.
[h]See Table I and text.
[i]Displacements with respect to the $^4T_{2g}(O_h)$ Cr−X distance.
[j]Estimated in Ref. 9 after several assumptions. See text for a discussion on the validity of other, larger estimated values.

very low. Furthermore, the enabling frequency used, 93 cm^{-1}, is a rough estimate starting from that of the chloride material, 154 cm^{-1}, which is in turn an estimate. Finally, it was assumed that $S_{tot}=S_{a_{1g}}+S_{e_g}$ and $|\Delta Q_{a_{1g}}|=|\Delta Q_{e_g}|$ [or, equivalently, $S_{a_{1g}}/S_{e_g}=(\nu_{e_g}f_{a_{1g}})/(f_{e_g}\nu_{a_{1g}})=\bar{\nu}_{a_{1g}}/\bar{\nu}_{e_g}$] which for the YBr_6^{3-} unit in Cs_2NaYBr_6 ($\bar{\nu}_{a_{1g}}=183$ cm^{-1}, $\bar{\nu}_{e_g}=144$ cm^{-1})[9] leads to $S_{a_{1g}}=3.7$ and $S_{e_g}=3.0$ which have been used in Table I. Now, if we take into account (i) that the application of this procedure to the chloride material gives $S_{tot}=3.6$[9] (we obtain 2.8 by using a Stokes shift of 1740 cm^{-1} together with the enabling frequency of 154 cm^{-1}, $\bar{\nu}_{a_{1g}}=291$ cm^{-1}, and $\bar{\nu}_{e_g}=227$ cm^{-1}, all of them reported in Ref. 9) which must be compared with the sum $S_{a_{1g}}+S_{e_g}$, 3.2 cm^{-1}, (ii) that $S_{tot}=6.9$ was reported for the chloride material in another study,[22] and (iii) that the estimated $|\Delta Q_{a_{1g}}|$ and $|\Delta Q_{e_g}|$ in the chloride differ by more than 10%, one should conclude that the distortions estimated for the bromide material are only rough estimates.

B. Structural results

In Table II we present the structures of the Cr^{3+}-defect in the Cs_2NaYCl_6 and Cs_2NaYBr_6 elpasolites, in its ground and low lying states, that result from our *ab initio* calculations, as well as the a_{1g} and e_g vibrational frequencies. They correspond to the CASSCF calculations with three active electrons in the space of the t_{2g} and e_g molecular orbitals of main character $3d(Cr^{3+})$. Together with our best results, which include a quantum AIMP embedding, we present those of a calculation in which only the Madelung contributions to the embedding effects are included (under the label ''Madelung''), so that we could ascertain the size of the quantum embedding effects on these structural properties. The table also shows the available experimental data and estimates, and the results of Density Functional Theory calculations by Gilardoni *et al.*[40] which include only Madelung embedding effects.

The quality of the AIMP structural results as compared with the experimental ones is excellent, close to the limits of what can reasonably be expected from the precision attainable with the *ab initio* methods and with the methods of analysis of the experimental data involved here. The vibrational frequencies of $Cs_2NaYCl_6:Cr^{3+}$, which are the structural properties of these materials which have been measured with a higher precision, are very well reproduced, both in the ground and in the excited states. This fact suggests the possibility of a slight underestimation of the $\bar{\nu}(e_g)$ in the $^4A_{2g}$

ground state of the bromide compound which resulted from a tentative assignment of the Raman spectrum of a 8% Cr doped sample of Cs$_2$NaYBr$_6$.[9] The absolute distances in the CrCl$_6^{3-}$ and CrBr$_6^{3-}$ units in these materials have not been measured, but the estimates of the relative distortions in the excited $^4T_{2g}$ state with respect to the ground $^4A_{2g}$ states obtained from experimental data are very close to the ones calculated in this work; in particular, they are more or less the same in Cs$_2$NaYCl$_6$:Cr^{3+} and in Cs$_2$NaYBr$_6$:Cr^{3+} according to our calculations and they are only slightly larger in Cs$_2$NaYBr$_6$:Cr^{3+} according to the experimental estimates. The size of the $^4T_{2g} \otimes e_g$ Jahn–Teller distortions show as well a remarkable agreement. Since the e_g vibrational frequency in the $^4T_{2g}$ state of Cs$_2$NaYCl$_6$:Cr^{3+} is also of high quality, it is to some extent striking the difference between the Jahn–Teller stabilization energy calculated and that estimated from the experiments in this material, and it deserves further comments.

Here, we would like to comment on the comparison between the Jahn–Teller stabilization energy, E_{JT}, of the $^4T_{2g}$ state calculated here, 470 cm^{-1}, and the value reported by Knochenmuss *et al.*[9] estimated from experimental measurements, 330 cm^{-1}. Knochenmuss *et al.*[9] use as a source of information the experimental splittings of the $^4T_{2g}$ magnetic dipole origins of Cs$_2$NaYCl$_6$:Cr^{3+}, which are labeled E'', $U'_{3/2}$, $U'_{5/2}$, and E' in the limit of zero Jahn–Teller coupling and valued 0, 6, 18, and 33 cm^{-1}, respectively.[9] These are used to fit the parameters of an effective Hamiltonian which includes spin-orbit and Jahn–Teller effects up to second order;[65] first, reasonable values are chosen for the Crystal Field Theory (CFT) parameters 10Dq, B, C/B, and ζ (13000, 570, 6.0, and 170 cm^{-1}, respectively,) then, the above mentioned splittings are drawn versus $3E_{JT}/h\bar{\nu}(e_g)$, and finally, the best value of $3E_{JT}/h\bar{\nu}(e_g)$ is picked up, so leading to E_{JT} since the vibrational frequency $\bar{\nu}(e_g)$ is known from an independent source.[20] However, in Cs$_2$NaYCl$_6$:Cr^{3+}, the splittings calculated in this way only fit to the experimental ones in the range of $3E_{JT}/h\bar{\nu}(e_g)$ of very small slopes (see Fig. 6 in Ref. 9 and Fig. 4 in Ref. 65), so leading to a significant imprecision in E_{JT}. Furthermore, the absolute values of the splittings depend on the CFT parameters 10Dq, B, C/B, and, specially, on the orbital spin–orbit coupling constant ζ, chosen to be 170 cm^{-1} by the authors.[9,65] Other values are possible, as is often the case when parametric models are used. In effect, Schwartz[20] reports term-dependent values of $\zeta(^4A_{2g}) = 74$ cm^{-1}, $\zeta(^2T_{1g}) = 230$ cm^{-1}, and $\zeta(^4T_{2g}) = 150$ cm^{-1}, the latter ones estimated from the term splittings using different values of the CFT parameters (10Dq = 12 800 cm^{-1}, B = 600 cm^{-1}, and C/B = 5.25, plus the Racah–Trees correction parameter $\alpha = 78.2$ cm^{-1}) and including the Jahn–Teller effect implicitly, through the reduction of ζ (Ham spin–orbit reduction.[66]) Since Knochenmuss *et al.* consider the Ham reduction of the spin–orbit splittings of the $^4T_{2g}$ term explicitly, their parameter ζ should include only the spin-orbit reduction with respect to the free-Cr^{3+} value (270 cm^{-1}) which is due to the crystal field and bonding effects and, in consequence, is

significantly larger than 150 cm^{-1}. (225 cm^{-1} is accepted for K$_2$NaGaF$_6$:Cr^{3+};[67] 210 and 270 cm^{-1} have been published for MgO:Cr^{3+}.[68,69]) Values of ζ significantly larger than 170 cm^{-1} are still consistent with the experimental splittings of the $^4T_{2g}$ term, but only if a larger E_{JT} is accepted as well. This would be in a higher agreement with our *ab initio* results.

The difference between the ''AIMP'' and the ''Madelung'' columns in Table II gives the size of the embedding effects that are not included in the point-charge approximation for the environmental crystal lattice, as calculated by the present method. These effects include both the electrostatic ones resulting from the fact that the lattice ions have a charge distribution rather than a point charge, and the ones of quantum nature, exchange, and orthogonality or linear -independency.[12] One can observe that these embedding effects are by no means negligible and they shorten the metal-ligand distance, as was the case in many other transition metal doped ionic hosts,[12,17,44] leading, in these materials, to a further shortening with respect to the perfect-host distance. The relative respiratory distortions between different states are less sensitive to the embedding effects, probably due to the fact that all of the states studied here show relatively small density changes with respect to one another. The vibrational frequencies, the Jahn–Teller distortions, and the Jahn–Teller stabilization energies suffer very significant changes as a consequence of the quantum embedding effects, as previously shown in similar cases.[44]

The DFT calculations in Ref. 40 include only Madelung embedding effects and, in consequence, they should be compared with our Madelung-embedding *ab initio* calculations rather than with our AIMP-embedding ones. As seen in Table II, no clear systematics can be detected in such a comparison. In the DFT calculation the bond distance in the ground state is 0.04 Å shorter for the chloride and 0.02 Å shorter for the bromide. The vibrational frequency $\bar{\nu}(a_{1g})$ is smaller and the $\bar{\nu}(e_g)$ is larger than the *ab initio* ones in both compounds. The total distortions in the $^4T_{2g}$ excited state with respect to the $^4A_{2g}$ ground state are slightly smaller than the *ab initio* ones in the chloride and slightly larger in the bromide, drawing an overall image in which the distortions in the bromide are significantly larger than the distortions in the chloride, in contrast with the *ab initio* results. The Jahn–Teller stabilization energy of the $^4T_{2g}$ state resulting from the Madelung-embedded DFT calculation, 285 cm^{-1}, is closer to the uncorrected experimental estimate, 330 cm^{-1}, than the corresponding Madelung-embedded *ab initio* result, 730 cm^{-1}. However, one should have in mind that a higher experimental estimate of the E_{JT} energy is reasonable, as commented above, that the quantum embedding effects will lower the present DFT result if these effects are transferable from the *ab initio* calculations to the DFT ones, at least qualitatively, since they lower E_{JT} down to 470 cm^{-1} in the *ab initio* calculation, and that the E_{JT} value is itself very sensitive to the conditions of the DFT calculation (Bellafrouh *et al.*[39] report for CrCl$_6^{3-}$ *in vacuo* E_{JT} ($^4T_{2g}$) values ranging from 662 cm^{-1} to 1400 cm^{-1} in three rea-

TABLE III. Spectroscopic results: Absorption and emission spectra. All numbers in cm^{-1}.

	$Cs_2NaYCl_6:Cr^{3+}$			$Cs_2NaYBr_6:Cr^{3+}$		
	DFT[a]	This work[b]	Experiment	DFT[a]	This work[b]	Experiment
Vertical absorption						
$^4A_{2g}\rightarrow {}^4T_{2g}$	9808	12 065	12 800[c]	9769	12 490	
$\rightarrow {}^4T_{1g}a$	17 202	18 610	~18 200[c]	15 389	18 415	
$\rightarrow {}^4T_{1g}b$		28 410	~28 400[c]		28 835	
$\rightarrow {}^2E_g$	11 525	15 360	14 435[d]	11 160	15 070	
$\rightarrow {}^2T_{1g}$		15 945	15 050[d]		15 495	
$\rightarrow {}^2T_{2g}$		21 670	~20 050–20 300[d]		21 200	
$\rightarrow {}^2A_{1g}$		25 520	~24 800[d]		25 670	
Vertical emission from $^4T_{2g}$						
$^4A_{2g}\leftarrow {}^4T_{2g}$ O_h	8010	11 380		7990	11 920	
$^4B_{1g}(^4A_{2g})\leftarrow {}^4B_{2g}(^4T_{2g})$ D_{4h}		10 425	~10 900–11 200[e]		11 090	~10 100–10 300[e]
$^4A_{2g}\leftrightarrow {}^4T_{2g}$ Stokes shift	1798	1640	1600–1900[f]	1779	1400	2200[g]
$^4A_{2g}\leftrightarrow {}^4T_{2g}$ MD origin		11 670[h]	11 800[d]			

[a]Reference 40, Density Functional Theory calculations with a gradient correction and Madelung embedding potential. See Ref. 39 for dependences of the results on the DFT methodological details.
[b]ACPF-15 calculations with quantum AIMP embedding (see text).
[c]Peak maximum from Ref. 20.
[d]Reference 20.
[e]Peak maximum from Ref. 9.
[f]From Fig. 1 of Ref. 9; 1740 cm^{-1} is reported in Ref. 9 without further comments.
[g]Reported in Ref. 9; however, no report exists of the Franck–Condon absorption to our knowledge.
[h]Vibrationally uncorrected. The excited state minimum is that of the D_{4h} component $^4B_{2g}$.

sonable DFT calculations, depending on their details.)

Since the size of the quantum embedding effects in the structural properties of the Cr^{3+} defects in the materials $Cs_2NaYCl_6:Cr^{3+}$ and $Cs_2NaYBr_6:Cr^{3+}$ is very significant, as we have shown, and the available DFT results do not include them,[40,39] it is not possible to draw a definite conclusion on the relative ability of *ab initio* and DFT methods to produce reliable structures in the ground and excited states of this kind of materials. However, if the size of these effects were transferable from the *ab initio* to the DFT calculations, which seems reasonable, the previous comparison would be indicating a higher reliability of the structural data produced by the *ab initio* methods used here with respect to those produced by the DFT methods used in Refs. 40 and 39.

C. Spectroscopic results

We present in Table III the results of our calculations on the vertical absorption ligand field spectrum from the ground state, $^4A_{2g}$, of the Cr^{3+} defect in $Cs_2NaYCl_6:Cr^{3+}$ and $Cs_2NaYBr_6:Cr^{3+}$, as well as the vertical emission from the $^4T_{2g}$ excited state and its corresponding Stokes shift and magnetic dipole origin. In the table we include the best DFT results from Ref. 40, with a gradient correction and Madelung embedding effects only. The results are compared with the available experimental data. High-resolution absorption, MCD, and luminiscence spectra have been published for $Cs_2NaYCl_6:Cr^{3+}$,[20,9] but only a not so well resolved emission spectrum has been reported for $Cs_2NaYBr_6:Cr^{3+}$;[9] although the absorption spectrum has not been published for the bromide, a Stokes shift (defined as the energy difference

between absorption and emission maxima) of 2200 cm^{-1} has been reported by the authors of the emission spectrum.[9]

We observe in Table III a very good overall agreement between our calculations and the available experimental measurements, in the line of what was found in the ligand field spectra of other transition metal impurities in ionic crystals such as $K_2NaGaF_6:Cr^{3+}$,[17] $CaF_2:Mn^{2+}$,[70] V^{2+}-doped fluoroperovskites,[18,19] and $MgO:Ni^{2+}$.[71] The deviations from the experiments in the vertical absorption and emission spectra of $Cs_2NaYCl_6:Cr^{3+}$ are within 1000 cm^{-1}, except the $^4A_{2g}\rightarrow {}^2T_{2g}$ which is within 1500 cm^{-1}, the overall quality being higher than that of the DFT calculation. The Stokes shift in this material is also good, as a consequence of the quality of the vertical absorption and emission. Finally, the magnetic dipole origin is as well excellent; our result is a vibrationally uncorrected one, but the vibrational corrections are expected to be low, so that the deviation after vibrational corrections would no doubt be lower than 1000 cm^{-1}. This comparison of the theoretical and experimental MD origin is important, since it is not biased by assumptions on the intensity profile, which are implicit on the comparison between the calculated vertical absorption spectra and the observed band maxima. In $Cs_2NaYBr_6:Cr^{3+}$, the experimental data are more scarce and the only clear comparison can be made on the vertical emission $^4T_{2g}\rightarrow {}^4A_{2g}$. Our result is reasonable and still lies within the 1000 cm^{-1} margin of deviation. However, the deviation is positive here whereas it is negative in the chloride. This might be a consequence of the ligand correlation effects, which are expected to be larger in the bromide compound, so leading to larger positive deviations in the calculated spectra. The size of them, in any case, does

TABLE IV. Spectroscopic results: Excited state absorption spectra. All numbers in cm^{-1}.

			Cs$_2$NaYCl$_6$:Cr^{3+}	Cs$_2$NaYBr$_6$:Cr^{3+}
$^4T_{2g}\rightarrow$	$^4T_{1g}$a	O_h	6420	5830
		D_{4h}	6735,8920	5995,8330
	$^4T_{1g}$b	O_h	15 750	15 910
		D_{4h}	16 420,17 043	16 460,16 865
$^2E_g\rightarrow$	$^2T_{1g}$	O_h	585	425
	$^2T_{2g}$	O_h	6310	6130
	$^2A_{1g}$	O_h	10 160	10 600

not seem to be so large as to make the present calculation unreasonable, and one could expect that the calculated vertical absorption spectrum of Cs$_2$NaYBr$_6$:Cr^{3+} would show larger positive deviations with respect to the experimental one, if available, of an order of 2000 cm^{-1}. The Stokes shift calculated for the bromide seems to be underestimated when compared with the reported value; we should, however, consider that the precision of this experimental result might be significantly lower than the one for the chloride, as discussed in Sec. III A.

Finally, in Table IV we present the results of the calculation of the vertical excited-state absorption spectra (ESA) originating in the $^4T_{2g}$ and ^2E_g states. The electronic transition energies from the $^4T_{2g}$ have been evaluated at the $^4T_{2g}$ octahedral equilibrium distance and at the tetragonally distorted structure, which reveals the Jahn–Teller effect on the excited-state absorptions. The Jahn–Teller effect on the electronic transitions from the ^2E_g have been found to be negligible and, therefore, only the octahedral results are tabulated. The ESA spectra have not been measured in the Cs$_2$NaYCl$_6$:Cr^{3+} and Cs$_2$NaYBr$_6$:Cr^{3+} materials nor have they been calculated, to our knowledge. However, since the same kind of calculation led to very close results with respect to available experimental ESA data in very similar materials like V^{2+}-doped fluoroperovskites,[19] the results of Table IV can be used to discuss the role that ESA may have as a loss mechanism of a potential laser emission in the Cs$_2$NaYCl$_6$:Cr^{3+} and Cs$_2$NaYBr$_6$:Cr^{3+} materials. In this sense, it is important to investigate two circumstances: the overlap between the ESA bands and the fluorescence of the materials, which could result in a reduction of the emission efficiency, and the overlap between ESA bands and ground-state absorption bands used for pumping, which could result in a reduction in pumping efficiency. If the ESA electronic transitions included in Table IV are compared with the vertical emission and ground-state absorptions listed in Table III under the label ''This work,'' it can be seen that the excited-state absorptions from the quartet are well separated from the emission and ground state absorptions. However, the $^2E_g\rightarrow$ $^2A_{1g}$ electronic transition should show a considerable overlap with the emission $^4A_{2g}\leftarrow$ $^4T_{2g}$ band in both crystals. In effect, the band maxima are calculated to be very close: 265 cm^{-1} for the chloride and 490 cm^{-1} for the bromide. Furthermore, similarly to the emission, the $^2E_g\rightarrow$$^2A_{1g}$ band is expected to be broad given the difference in octahedral equilibrium positions found between both states ($^2A_{1g}$ is found

to be shifted off the ^2E_g by 0.03 x Å in the chloride and 0.03y Å in the bromide crystal). The overlap between these bands should reduce the emission efficiency notably, in particular if the higher quartets $^4T_{1g}a$ and/or $^4T_{1g}b$ are used for pumping the sample.

IV. CONCLUSIONS

In this paper, we presented the results of an *ab initio* model potential embedded-cluster study of the ground and lowest excited states of Cr^{3+} defects in the elpasolites Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$, where the Cr^{3+} ions substitute on-site Y^{3+} cations. We performed CASSCF and ACPF calculations on CrCl$_6^{3-}$ and CrBr$_6^{3-}$ clusters embedded in their respective crystal lattices represented by a large number of Cs$^+$, Na$^+$, Y^{3+}, Cl$^-$, and Br$^-$ complete-ion *ab initio* model potentials. We showed that the size of the lattice embedding effects beyond the Madelung ones are very significant in the structural properties of these materials and cannot be neglected. We calculated the structures of the substitutional defects in their ground and excited states, vibrational frequencies, Jahn–Teller stabilization energies and ligand field absorption, emission, and excited-state-absorption electronic spectra.

The experimental structural data on these materials has been revisited and some new results were found which significantly differ from those in the literature. Some of the structural and spectroscopic information produced in the present calculations could be succesfully compared with available experimental data. New structural and spectroscopic information was produced, complementary to the already available, which had never before been measured nor calculated; in particular, the calculated excited-state absorption spectrum suggests the existence of a competition between the broad $^2E_g\rightarrow$$^2A_{1g}$ excited-state absorption and the $^4A_{2g}\leftarrow$$^4T_{2g}$ emission bands in both materials, which must result in a reduction in the emission efficiency and be detrimental for a potential vibronic laser.

Finally, we made a comparison with existing DFT calculations in which only Madelung embedding effects were included, which showed a higher quality of the *ab initio* embedded-cluster results. The present study is in the line of showing that present days standard quantum chemistry *ab initio* methods, updated with proper embedding techniques, are capable of providing structural and spectroscopic information of doped ionic solids which is *complementary* to that attainable from experimental techniques.

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