Anomalous superhyperfine tensor observed in BaFCl doped with the 5d1 ion La2+: Role of 5d-4f hybridization


Abstract

The fluorine superhyperfine (shf) tensor measured in BaFCl:La2+ has been found to be practically isotropic, a result which is certainly anomalous when compared to that for d9 centers with one unpaired electron in a x2−y2 orbital. This puzzling fact has been explored by means of density functional calculations. Obtained results confirm that in the C4v equilibrium geometry the unpaired electron lies in a b1(~x2−y2) orbital which overlaps with the 2s orbitals of four F− ligands. For explaining the origin of the near isotropy, which is well reproduced by the present calculations, the simple D4h and C4v LaF42−, YF42−, and AgF42− centers have also been investigated. Although the obtained results stress the high dependence of the isotropic shf constant A5 on the metal-ligand distance R, a near isotropy of the shf tensor is only reached for LaF42− (but not for YF42−) under C4v symmetry which corresponds to the actual symmetry of the La2+ center in the BaFCl lattice. The origin of this peculiar situation is shown to come from the mixing between 5d and 4f orbitals of La2+ allowed in C4v symmetry thus stressing the [...]
Anomalous superhyperfine tensor observed in BaFCl doped with the 5d\(^{1}\) ion La\(^{2+}\): Role of 5d-4f hybridization

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The fluorine superhyperfine (shf) tensor measured in BaFCl:La\(^{2+}\) has been found to be practically isotropic, a result which is certainly anomalous when compared to that for 4f centers with one unpaired electron in a \(\alpha\) orbital. This puzzling fact has been explored by means of density functional calculations. Obtained results confirm that in the \(\text{C}_{4v}\) equilibrium geometry the unpaired electron lies in a \(b_1(\sim x^2-y^2)\) orbital which overlaps with the 2s orbitals of four F\(^{-}\) ligands. For explaining the origin of the near isotropy, which is well reproduced by the present calculations, the simple \(D_{4h}\) and \(C_{4v}\) LaF\(_4\)\(^{2-}\), YF\(_4\)\(^{2-}\), and AgF\(_4\)\(^{2-}\) centers have also been investigated. Although the obtained results stress the high dependence of the isotropic shf constant \(A_{i}\) on the metal-ligand distance \(R\) a near isotropy of the shf tensor is only reached for LaF\(_4\)\(^{2-}\) (but not for YF\(_4\)\(^{2-}\)) under \(\text{C}_{4v}\) symmetry which corresponds to the actual symmetry of the La\(^{2+}\) center in the BaFCl lattice. The origin of this peculiar situation is shown to come from the mixing between 5d and 4f orbitals of La\(^{2+}\) allowed in \(\text{C}_{4v}\) symmetry thus stressing the role played by 4f orbitals in bonding properties. Writing \(A_{i}=C R^{-n_{i}}\) it is shown that for the \(D_{4h}\) LaF\(_4\)\(^{2-}\) and YF\(_4\)\(^{2-}\) complexes the exponent \(n_{i}\) is around 20, while it is only equal to 4 for AgF\(_4\)\(^{2-}\). This huge difference is shown to stem from the quite distinct slope of the radial \(d\) wave function at the equilibrium distance for the two \(d^{1}\) centers and the \(d^{0}\) AgF\(_4\)\(^{2-}\) unit. Finally, the present calculations strongly support that the intense band peaked at 17 890 cm\(^{-1}\) recorded in the optical absorption spectrum of BaFCl:La\(^{2+}\) is indeed a \(5d\rightarrow4f\) transition.

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I. INTRODUCTION

A great deal of attention has been focused on insulating lattices with the PbFCl (matlockite) structure (Fig. 1) doped with divalent rare earth cations, in particular Eu\(^{2+}\) or Sm\(^{2+}\). This fact partially comes from the interest of such systems for information storage through a hole burning process, e.g., Refs. 1–3. Also systems such as BaFBr:Eu\(^{2+}\) are among those explored as storage phosphors\(^{4–9}\) for applications in medical x-ray radiography. Experimental data on La\(^{2+}\) impurities in BaFCl and SrFCl lattices displaying the matlockite structure have recently been reported.\(^{10}\) Although the La\(^{2+}\) cation is rather unusual\(^{10–13}\) it is, however, attractive from a fundamental standpoint. In this sense, its unpaired electron lies in a 5d orbital but the empty 4f orbital is only about 8000 cm\(^{-1}\) higher in energy in the free ion.\(^{14,15}\)

Electron paramagnetic resonance (EPR) spectra measured on \(\text{MFCI:La}^{2+}\) (\(M=\text{Ba}, \text{Sr}\)) samples show a resolved superhyperfine (shf) structure due to the interaction of the unpaired electron with four equivalent F nuclei, but that from neighboring Cl nuclei is not resolved.\(^{10}\) Another relevant experimental information comes from the measured gyromagnetic tensor \((\mathbf{g})\) which is found to exhibit axial symmetry \((\mathbf{g}_{x}=1.753, \mathbf{g}_{y} = 1.889\) for BaFCl:La\(^{2+}\)) the principal axis being the \(c\) axis of the host lattice\(^{10}\) (Figs. 1 and 2). These facts support that the La\(^{2+}\) impurity in BaFCl replaces the host lattice cation Ba\(^{2+}\) giving rise to a local \(\text{C}_{4v}\) symmetry. It is worth noting that in the perfect BaFCl lattice the Ba\(^{2+}\) cation is surrounded by nine halide ions:\(^{16}\) four F\(^{-}\) ions at 2.65 Å, four Cl\(^{-}\) ions at 3.28 Å, and finally another Cl\(^{-}\) ion at 3.196 Å lying on the principal axis. These data imply that the \(\beta\) angle defined in Fig. 1 is equal to 56°. As regards the location of unpaired electron in BaFCl:La\(^{2+}\) it is expected to lie just in a \(b_1(\sim x^2-y^2)\) orbital\(^{17}\) because \(|\mathbf{g}_{x}-\mathbf{g}_{y}| > |\mathbf{g}_{z}|\) (\(\mathbf{g}_{0}\) being the gyromagnetic factor of the free electron). It is worth noting that according to Figs. 1 and 2 a \(x^2-y^2\) orbital has zero overlap with the 3s wave functions of nearest Cl\(^{-}\) ions but not with the 2s wave functions of nearest F\(^{-}\) ions.

FIG. 1. (Color online) Unit cell of the BaFCl lattice exhibiting the matlockite structure with \(a=b=4.394\) Å and \(c=7.225\) Å. Axes and several distances used in the paper are drawn in the Figure. The substitutionsal position of La\(^{2+}\) impurity in the undistorted BaFCl lattice is shown. The form of the 2p(F\(^{-}\)) orbital involved in the \(b_1(\sim-x^2-y^2)\) level is also shown.
This implies a nonzero isotropic shf constant\(^\text{18}\) \(A_x\) for four F\(^{-}\)ligands which is well detected experimentally.

Despite these conclusions seem reasonable a puzzling issue comes when looking in detail at the measured shf tensor of the four fluoride ligand nuclei\(^\text{10}\) which conveys key information on bonding between La\(^{2+}\) impurity and F\(^{-}\)ligands. Let us denote by \(T_{x',z'}\), \(T_{x',y'}\), and \(T_{z',y'}\) the components of the diagonalized shf tensor corresponding to a ligand. The associated principal axes are shown in Fig. 2 and the measured values of \(|T_{x',z'}|\), \(|T_{x',y'}|\), and \(|T_{z',y'}|\) are displayed in Table I. As is usually observed for \(d^2\) impurities in \(D_{4h}\) or \(C_{4v}\) symmetry\(^\text{13,17,19}\) the values of \(|T_{x',z'}|\) and \(|T_{y',y'}|\) are very close despite the shf tensor is orthorhombic, according to the local symmetry around a ligand ion. Let us now call for simplicity \(T_{\|}=T_{x',z'}\) and \(T_{\perp}=(T_{x',y'}+T_{z',y'})/2\). It can be noticed that the fluorine shf tensor measured for MFCI:La\(^{2+}\) (\(M=\text{Ba, Sr}\)) is nearly isotropic as the ratio \(T_{\|}/T_{\perp}\) is 1.17 for BaFCl:La\(^{2+}\). This situation is, however, far from what is observed for the shf tensor of \(d^2\) impurities in elongated octahedral and \(C_{4v}\) symmetries with halides as ligands, where the unpaired electron is also lying in an \(-x^2-y^2\) orbital.\(^\text{19-22}\)

In these cases (as well as for divalent \(s^1\) impurities in \(O_h\) symmetry\(^\text{23}\)) the shf tensor is found to exhibit a clear anisotropic character. Representative values of \(T_{\|}\) and \(T_{\perp}\) for this kind of systems are collected in Table II. Microscopically, this anisotropy reflects that an \(x^2-y^2\) electron in a \(D_{4h}\) square-planar situation (with four ligands along \(X\) and \(Y\) axes) gives rise to bonding with valence \(p\) and also \(s\) ligand orbitals.\(^\text{17,24}\) For this reason there are two main contributions to \(T_{\|}\) and \(T_{\perp}\): one is the referred isotropic contribution \(A_x\) while the other one \(A_p\) reflects the admixture between \(x^2-y^2\) and a \(p\) valence ligand orbital. \(A_x\) and \(A_p\) quantities are related to \(T_{\|}\) and \(T_{\perp}\) ones by

\[
T_{\|}=A_x + 2A_p; \quad T_{\perp}=A_x - A_p
\]

Usually\(^\text{17-24}\) \(A_x > A_p\), though both quantities are of the same order of magnitude, thus giving rise to \(T_{\|}\) and \(T_{\perp}\) values which are rather different.

Additional problems appear in MFCI:La\(^{2+}\) (\(M=\text{Ba, Sr}\)) when looking at experimental absorption bands of La\(^{2+}\) impurity.\(^\text{10}\) In fact, in addition to a crystal field band peaked at 10 900 cm\(^{-1}\) another more intense band peaked at 17 890 cm\(^{-1}\) has clearly been observed for BaFCl:La\(^{2+}\) (see Fig. 3). Although the latter band was tentatively assigned\(^\text{10}\) to arise from a charge transfer transition this assignment is dubious when considering the optical electronegativity scale by Jørgensen.\(^\text{25,26}\) In this sense at constant oxidation state the optical electronegativity \(\chi\) increases upon increasing the
number of electrons in the d shell, being thus higher for a d⁹ ion than for d⁴. More precisely, the optical electronegativity expected for a 5d⁴ ion is equal to ~1.2 thus implying that the onset of the Cl⁻−La²⁺ charge transfer transitions would be placed above 40 000 cm⁻¹. It is also worth noting here that the first charge transfer transition observed in KCl:Ag⁺ appears₂⁷,₂⁸ at 21 000 cm⁻¹ despite the huge value of χ(Ag⁺) equal to 2.8.³⁹

The present work is aimed at clarifying these puzzling issues associated with the La²⁺ impurity embedded in the BaFCl lattice by means of electronic structure calculations on clusters in the framework of the density functional theory (DFT). Apart from reproducing the near isotropy of the fluorine shf tensor, a first objective of this work is to explore the main reason responsible for this unusual situation. For achieving this goal the calculation of the shf tensor for model systems can shed light on this relevant issue. So, in a first step, the variation of both T₀ and T₁ quantities as a function of the metal-ligand distance R has been calculated for octahedral LaF₆⁴⁻ and square-planar LaF₂⁻ and YF₄⁻ centers. In these cases the unpaired electron has always been located on the antibonding χ²−ψ² orbital for allowing a comparison with the results for BaFCl:La²⁺. In order to seek for differences between d⁴ and d⁹ ions calculations on the D₄h AgF₄⁻ species have also been carried out. In the later case the ground state has the unpaired electron in the x²−y² orbital.

In a second step T₀ and T₁ have been computed for C₄v LaF₄⁻ and YF₄⁻ complexes as a function of the distance ZC between the cation and the center of the ligand plane. In this process the distance between the impurity and the ligand has been fixed. The interest of comparing LaF₄⁻ and YF₄⁻ complexes lies in the fact that 4f orbitals are close to the valence d levels for La²⁺ ions⁴,¹⁵ but not in the case of the 4d¹ ion Y²⁺.

Another relevant goal of this work is to explore the sensitivity of the isotropic shf constant A₀ to variations of the metal-ligand distance R for O₈ and D₄h complexes involving 5d or 4d cations. It is worth noting that the R dependence of A₀ has been widely studied for 3d complexes with σ unpaired electrons in the ground state.¹⁸,²⁰,³¹–³₃ In these cases the law relating A₀ with R can be represented by

\[ A₀ = C R^{−n} \]

The exponent n₁ is known to lie in the 5–8 range for octahedral MnF₆⁴⁻, NiF₆⁴⁻, or FeF₆⁻ complexes or the tetragonally elongated NiF₆⁵⁻ unit. By virtue of this fact the experimental A₀ value has been used to monitor the variations of R induced by hydrostatic or chemical pressures in cubic fluoroperovskites containing Mn²⁺, Ni²⁺, Fe²⁺, or Ni⁺ impurities.¹⁸,²⁰,³¹–³₃ However, few works have investigated the R dependence of A₀ for 4d or 5d ions. In this field it is of particular interest to clarify whether the exponent n₁ is or not similar for divalent d⁴ and d⁹ ions. It should be recalled here that on passing from the 4d¹ Y²⁺ to the 4d⁹ Ag⁺ ion there is a progressive decrease of the ionic radius and at the same time the corresponding increase of both the ionization potential²⁴ and the optical electronegativity.²⁵

The last problem investigated in the present work concerns the origin of the intense band peaked at 17 890 cm⁻¹ observed¹⁰ for BaFCl:La²⁺. As shown in Sec. III D the results of present calculations shed light on this issue as well.

II. COMPUTATIONAL DETAILS

Calculations have been carried out in the framework of the DFT by means of the ADF code.³⁵ The generalized gradient approximation (GGA) exchange-correlation energy was computed using the functionals of Becke³⁶ and Lee-Yang-Parr³⁷ (BLYP) for exchange and correlation terms, respectively. It was verified that the obtained results are basically independent of the used functional. All atoms were described through basis sets of TZP [triple-ζ Slater-type orbitals (STOs) plus one polarization function] quality given in the program database, and using the frozen-core approximation for 1s–5p orbitals of La²⁺ and Ba²⁺, 1s orbital of F⁻, and 1s–2p orbitals of Cl⁻. Relativistic effects have been taken account through zeroth order regular approximation (ZORA), which includes the Darwin and mass-velocity terms, but not the spin-orbit interaction.³⁸ It is worth noting that both 5d and 4f orbitals are included in the employed basis set, such as it is done in a recent study on lanthanide complexes.³⁹ Calculations carried out for free La²⁺ ion give a 4f level lying above 6950 cm⁻¹ above the 5d level.

EPR spectra of BaFCl:La²⁺ support⁴₀ that the unpaired electron coming from La²⁺ is essentially localized in the...
LaF$_4$ClCl$_4$ complex formed by the impurity with the nine ligands. This situation, usually found for transition-metal impurities in insulating lattices, allows the use of small clusters for reproducing the electronic properties associated with the impurity cation. In all calculations the effects on the employed clusters due to the electric field from the rest of the lattice have been included by means of point charges.

Because of the low symmetry of the system and the fact that the impurity is lying neither in the plane formed by four F$^-$ ligands nor in that formed by four Cl$^-$ ligands (Fig. 1), the convergence of calculations has not always been easy to achieve. In a first step, the position of La$^{2+}$ impurity along the Z axis (Fig. 4) was optimized using the LaF$_4$ClCl$_4$Ba$_4$ cluster with 27 ions. Subsequently a LaF$_4$ClCl$_4$ClBa$_4$ cluster (Fig. 4) has been employed to study the fluorine ligand shf tensor and the optical absorption spectrum as well. It is worth noting that in this case the equilibrium positions of all ions involved in the LaF$_4$ClCl$_4$ complex have been taken from the calculation carried out on the 27 ion cluster. The g tensor can, in principle, be derived through the ADF package in a calculation where the spin-orbit coupling is included but no symmetry restrictions are taken into account. Unfortunately, no good SCF convergence has been achieved for the present problem.

III. RESULTS AND DISCUSSION

A. Electronic ground state and computed superhyperfine tensor for BaFCl:La$^{2+}$

Experimental results support that when a La$^{2+}$ impurity enters the BaFCl lattice it replaces a Ba$^{2+}$ ion and remains along the Z axis. Bearing in mind this fact, it has first been explored whether the equilibrium coordinate $Z_{eq}$ coincides or not with that for the host cation ($Z_{Ba}=1.48$ Å). DFT calculations indicate that the Ba$^{2+}$→La$^{2+}$ substitution induces a positive shift of 0.1 Å implying a slight motion of La$^{2+}$ towards the center of the nearest chlorine plane (Fig. 1).

At the equilibrium geometry bonding among La$^{2+}$ impurity and Cl$^-$ and F$^-$ ligands is found to be moderately ionic. For instance, the total Mulliken charge derived for one of the four F$^-$ ligands is equal to $-0.88e$ ($e=$proton charge). This charge is found to be equal to $-0.81e$ for each Cl$^-$ ion lying in the plane and to $-0.90e$ for the Cl$^-$ ligand lying along the c axis. This result confirms that chemical bonding between La$^{2+}$ and Cl$^-$ ligands is stronger than that between La$^{2+}$ and the four F$^-$ ligands. This idea is also consistent with the composition of the $b_1(\sim x^2-y^2)$ level: the unpaired electron is found to spend $\approx 1.9\%$ of the time on a $3p$ orbital of a Cl$^-$ ion of the upper plane while only $\approx 1.1\%$ on a $2p$ orbital of a F$^-$ ion of the lower plane (Fig. 1).

It is worthwhile to note that at the equilibrium geometry the lowest orbital (where the unpaired electron is placed) is found to be $b_1(\sim x^2-y^2)$. This fact thus supports the conclusion reached from the experimental g tensor. That result is reasonable if we take into account that in the antibonding $b_1(\sim x^2-y^2)$ orbital there is not $\sigma$ bonding with the four Cl$^-$ ligands lying above (Fig. 1) but $\pi$ bonding. By contrast, $\sigma$ bonding with such Cl$^-$ ligands is present in the antibonding $b_2(\sim xy)$ orbital which is found to be located at 9500 cm$^{-1}$ above the $b_1(\sim x^2-y^2)$ level.

Let us now focus on the calculated fluorine shf tensor. As it is usually obtained for $d^0$ impurities in $D_{4h}$ or $C_{4h}$ symmetry with an unpaired electron in the $x^2-y^2$ orbital the three components of the diagonalized shf tensor are found to be all positive. The calculated values at the obtained equilibrium geometry are $T_{x'y'}=46.7 \times 10^{-4}$ cm$^{-1}$, $T_{x'y}=47 \times 10^{-4}$ cm$^{-1}$, and $T_{x'z'}=53.4 \times 10^{-4}$ cm$^{-1}$ and thus not far from the absolute value of such quantities measured experimentally (Table I).

A significant information is also provided by the eigenvector associated with $T_{x'y'}$. From the present results the local Z’ axis (Fig. 2) is found to make an angle $(\pi/2-\alpha)=18.7^\circ$ with the crystal Z axis (Fig. 1). This value is again not far from the experimental measurement given in Table I. It is worth noting that the local Z’ axis essentially reflects the form of the $2p$ orbital on a fluorine ion involved in the $b_1(\sim x^2-y^2)$ level. Therefore the angle $(\pi/2-\alpha)=18.7^\circ$ just means that the $2p$ orbital on a fluorine ligand is not directed towards La$^{2+}$ but lies nearly perpendicular to the plane formed by four F$^-$ anions. In other words, the angle $(\pi/2-\alpha)$ is quite different from the geometrical angle $\beta$ also shown in Fig. 1. This fact is reasonable considering that chemical bonding is favored by an increase of the overlap between $2p(F^\prime)$ and $x^2-y^2$ wave functions. As the electronic density in a $x^2-y^2$ orbital is zero at the La$^{2+}$ position, this explains albeit qualitatively why $\beta>(\pi/2-\alpha)$. A similar situation to this one is found for $3d^3$ impurities in cubical geometry as well as for SrCl$_2$:B$^{2+}$ ($B=$Cu or Ag) or for CaF$_2$:Ni$^+$ involving a $C_{4h}$ symmetry.

Despite the problems for deriving the g tensor by means of the ADF package the calculated values of $d-d$ transitions appear to be not incompatible with the experimental $g_1$ and $g_\perp$ values. For instance, in a pure crystal field description where any covalency is neglected $g_1$ is just given by

FIG. 4. (Color online) Description of the clusters centered at La$^{2+}$ involving a total of 15 and 27 ions used in the present study. The 10 ions LaF$_4$ClCl$_4$ complex where the unpaired electron resides is also shown for comparison.
TABLE III. Dependence of $T_s$ and $T_d$ as a function of the metal-ligand distance $R$ (in Å) calculated for the octahedral LaF$_6^{2−}$ unit with the unpaired electron placed in the antibonding $x^2−y^2$ orbital. For the sake of clarity the corresponding values of $A_s$ and $A_p$ are also collected. All shf parameters are given in $10^{-4}$ cm$^{-1}$ units.

<table>
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<th>$R$</th>
<th>$T_s$</th>
<th>$T_d$</th>
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Here $\Delta_{xy}$ means the energy of the $b_1(−x^2−y^2)→b_2(−xy)$ electronic transition while $\xi=641$ cm$^{-1}$ is the spin-orbit coefficient for free La$^{2+}$. When a weak or moderate covalency is taken into account it reduces the value of $|g||g_0|$ with respect to that given by Eq. (3). This just means that the experimental $|g||g_0|=0.25$ value should be smaller than $8\xi/\Delta_{xy}=0.54$ derived using $\Delta_{xy}=9500$ cm$^{-1}$.

B. $O_h$ and $D_{4h}$ centers of $d^1$ and $d^9$ ions: $R$ dependence of $A_s$

Seeking to understand the results obtained in the preceding section, the dependence of $A_s$ on $R$ has first been investigated for simple centers involving La$^{2+}$, Y$^{2+}$, and Ag$^{2+}$ ions in $O_h$ or $D_{4h}$ symmetries. The $R$ dependences of calculated $T_s$ and $T_d$ quantities for octahedral LaF$_6^{2−}$ and square-planar LaF$_4^{2−}$ complexes are collected in Tables III and IV. The corresponding results for the $D_{4h}$ YF$_4^{2−}$ and AgF$_4^{2−}$ complexes are gathered in Tables V and VI.

Looking at Tables III–VI it can first be noticed that $A_s$ is found to be much bigger for the Ag$^{2+}$ center than for other cases. This result is consistent with an increase of covalence on going from $d^1$ species to the $d^9$ ion Ag$^{2+}$ in parallel to the well known increase of optical electronegativity. It should be recalled here than in the case of a free F$^−$ ligand the energy separation between 2$p$ and 2$s$ orbitals amounts to about 23 eV. By this remarkable fact bonding in complexes such as LaF$_6^{4−}$, LaF$_4^{2−}$, YF$_4^{2−}$, or AgF$_4^{2−}$ is thus mainly established through the valence 2$p$ orbitals of fluorine while the admixture with 2$s$ orbitals plays a secondary role. Along this line it was early noted that, in a series of complexes with the same ligand, an increase of covalence produces more changes on $A_p$ than on $A_s$.

A quite different situation happens, however, when considering the changes on both $A_s$ and $A_p$ quantities by modifying the metal-ligand distance $R$. Tables III–VI stress that in all cases $A_s$ is found to be much more sensitive than $A_p$ to $R$ variations. This situation is thus comparable to that encountered in the case of 3$d$ units with some unpaired electrons with $\sigma$ bonding such as it happens for $O_h$ MnF$_6^{4−}$, NiF$_6^{4−}$, or FeF$_6^{3−}$ complexes, A similar situation is found for the tetragonally elongated NiF$_6^{5−}$ center with an unpaired electron in the $x^2−y^2$ orbital. The quite different $R$ dependence of $A_s$ and $A_p$ in all these systems essentially reflects the more internal character of 2$p$(F$^−$) orbitals when compared to that of 2$p$(F$^−$) ones. Additional insight on this issue is given elsewhere.

Looking at Tables III–VI it can be noted that $A_s$ is much more sensitive to $R$ variations in the case of LaF$_4^{2−}$ and YF$_4^{2−}$ complexes than for the AgF$_4^{2−}$ unit. More precisely, the exponent $n_A$ in Eq. (2) is found to be equal to 18 for YF$_4^{2−}$ and 23 for LaF$_4^{2−}$ while only equal to 4.1 for AgF$_4^{2−}$. The obtained exponent for AgF$_4^{2−}$ is consistent with previous results obtained by means of MS-Xα and extended Hückel calculations. The origin of the different sensitivity of $d^1$ and $d^9$ ions to $R$ changes will be discussed in Sec. III E. Looking at the results for LaF$_6^{4−}$ and LaF$_4^{2−}$ complexes in Tables III and IV, it can be observed that, although $A_s$ changes significantly with $R$ (and thus the $T_s/T_d$ ratio), the calculated values of $T_s$ and $T_d$ do not reproduce an essentially isotropic shf tensor such as it has been measured for BaFCl:La$^{2+}$. As a similar situation is encountered for YF$_4^{2−}$ (Table V), this suggests that the near isotropy of the fluorine shf tensor in BaFCl:La$^{2+}$ might be connected to the actual $C_{4v}$ symmetry of La$^{2+}$ in that host lattice.

TABLE IV. The same as Table III but for the square-planar LaF$_4^{2−}$ center.

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TABLE V. The same as Table III but for the square-planar AgF$_4^{2−}$ center.

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<th>$T_d$</th>
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<td>260</td>
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TABLE VII. Dependence of \(T_1\) and \(T_\perp\) as a function of the off-center displacement \(Z_t\) (in Å) calculated for the octahedral LaF\(_4\)\(^{2-}\) unit with the unpaired electron placed in the antibonding \(x^2−y^2\) orbital. For the sake of clarity, the corresponding values of \(A_t\) and \(A_p\) are also collected. All shf parameters are given in 10\(^{-4}\) cm\(^{-1}\) units. It has to be remarked that although \(Z_t\) varies, the metal-ligand distance is kept frozen.

<table>
<thead>
<tr>
<th>(Z_t)</th>
<th>(T_\perp)</th>
<th>(T_1)</th>
<th>(A_t)</th>
<th>(A_p)</th>
<th>(T_1/T_\perp)</th>
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<td>84</td>
<td>31</td>
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<tr>
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<tr>
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<td>13</td>
<td>1.19</td>
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<tr>
<td>1</td>
<td>224</td>
<td>247</td>
<td>231</td>
<td>8</td>
<td>1.11</td>
</tr>
</tbody>
</table>

C. Influence of a \(C_{4v}\) distortion on the superhyperfine tensor of LaF\(_4\)\(^{2-}\) and YF\(_4\)\(^{2-}\)

Bearing in mind the preceding analysis and the position of the La\(^{2+}\) impurity in the BaFCl lattice (Fig. 1) it becomes necessary to explore how the \(T_1/T_\perp\) ratio is modified when the \(\tilde{F}^-\) (\(I=La, Y\)) impurity in the \(\tilde{F}_4\)\(^{2-}\) center is shifted from the center of the fluorine square along the \(OZ\) axis. Therefore, \(T_1\) and \(T_\perp\) have been calculated as a function of the out of plane distance \(Z_I\) between \(I\) and the ligand fluorine plane thereby keeping the \(I-F\) distance constant. This distance has been taken equal to 2.50 and 2.45 Å for LaF\(_4\)\(^{2-}\) and YF\(_4\)\(^{2-}\) complexes, respectively. Results of these calculations are collected in Tables VII and VIII.

The reported results for YF\(_4\)\(^{2-}\) show that both \(A_t\) and \(A_p\) quantities decrease when \(Z_I\) increases. The corresponding ratio \(T_1/T_\perp\) has a value equal to 2 when \(Z_I=1\) Å. However, a quite different situation is reached when looking at the results for the \(C_{4v}\) LaF\(_4\)\(^{2-}\) unit. In this case (Table VII) an increase of \(Z_{La}\) induces a decrement of \(A_p\) but at the same time an increase of \(A_t\) leading to a \(T_1/T_\perp\) ratio around 1.1 when \(Z_{La}=1\) Å. The origin of this distinct behavior found when comparing the two \(C_{4v}\) LaF\(_4\)\(^{2-}\) and YF\(_4\)\(^{2-}\) complexes has been verified to come from the existence of a symmetry allowed \(d-f\) hybridization in the former case which cannot take place for the \(4d^1\) \(Y^{2+}\) cation. Indeed, while the hybridization between a \(x^2−y^2\) \(d\) orbital and a \((x^2−y^2)\) \(f\) orbital is strictly forbidden when \(Z_{La}=0\) Å, this admixture becomes symmetry allowed when the La\(^{2+}\) cation is shifted to an out of plane position. We have verified in our calculations that when \(Z_{La}=1\) Å the amount of \(4f\) wave function into the \(b_1\) orbital is 26%. The existence of this significant \(5d-4f\) mixing found for the \(C_{4v}\) LaF\(_4\)\(^{2-}\) complex is not surprising if we take into account that the \(5d-4f\) separation for free La\(^{2+}\) ion is equal\(^{14,15}\) only to \(\approx8000\) cm\(^{-1}\).

The results collected in Tables II–VI thus shed light on the origin of the quasi-isotropy displayed by the fluorine shf tensor measured\(^{10}\) for MFCI:La\(^{3+}\) (\(M=Ba, Sr\)) lattices. Bearing in mind that this amazing feature is reasonably reproduced by calculations carried out on a simple LaF\(_2\)Cl\(_4\)\(^7\)-complex the present analysis supports that the quasi-isotropy of the shf tensor can actually be related to the fact that La\(^{2+}\) in the BaFCl host lattice is not lying at the center of the fluorine plane but well above (Fig. 1). This out of plane situation allows the \(5d-4f\) hybridization which strongly modifies the wave function and the dependence of \(A_t\) upon \(Z_{La}\).

Some hints about the different behavior of \(A_t\) and \(A_p\) quantities when \(Z_{La}\) increases can be obtained from the analysis in Sec. III A. If there is not any \(5d-4f\) hybridization the overlap between a pure \(x^2−y^2\) \(5d\) wave function and a \(2s\) wave function of a \(F^-\) ligand (and thus\(^{18}\) the \(A_t\) value) tends to decrease when \(Z_{La}\) increases even if the La\(^{2+}\)-F\(^-\) distance is kept. Nevertheless, the admixture of the \(4f\) \((x^2−y^2)\) wave function can compensate this decrement. It should be remarked now that the \(4f\) \((x^2−y^2)\) wave function is zero in the plane containing the La\(^{2+}\) impurity perpendicular to the \(Z\) axis in Fig. 1. By contrast, its importance increases following the value of the \(z\) coordinate, measured with respect to the La\(^{2+}\) position.

Let us now consider the overlap of the \((x^2−y^2)\) wave function when \(z=−Z_{La}\) and the \(2p\) wave function depicted in Fig. 1. According to this figure the \(2p\) wave function can be written as

\[\psi(p_x) = \sin|p_x| + \cos|p_x| \sin|p_y|.\]

In this case the overlap between the \((x^2−y^2)\) wave function around \(z=−Z_{La}\) and \(|p_x|\) is basically zero and thus this fact can give rise to a reduction of the \(A_p\) value.

D. \(5d\rightarrow4f\) transition observed in the optical absorption spectrum of BaFCl:La\(^{2+}\)

Let us now focus on the optical absorption spectrum of BaFCl:La\(^{2+}\). If the \(5d-4f\) separation for free La\(^{2+}\) ion is equal to \(\approx8000\) cm\(^{-1}\) it is thus not unreasonable that allowed \(5d\rightarrow4f\) transitions can be detected in the optical region. If the unpaired electron lies in the \(b_1(−x^2−y^2)\) orbital, jumps to \(4f\) levels transforming as the irreducible representations \(b_1\) and \(e\) are allowed under \(C_{4v}\) symmetry. Similarly the \(b_1(−x^2−y^2)\rightarrow e(xz, yz)\) crystal field transition becomes allowed in the \(C_{4v}\) group. By means of a LaF\(_2\)Cl\(_4\)\(^7\)-cluster the energy of this \(b_1(−x^2−y^2)\rightarrow e(xz, yz)\) transition has been calculated to be equal to 10 562 cm\(^{-1}\) which is not far from the value 10 940 cm\(^{-1}\) measured for BaFCl:La\(^{2+}\).
As regards the allowed $b_1(\sim x^2-y^2) \rightarrow 4f$ transitions the energy associated with the $b_1(\sim x^2-y^2) \rightarrow b_1[\sim z(x^2-y^2)]$ jump has also been calculated. The energy value calculated for this transition using a LaF$_4^{2-}$ center ($I$=La$_2^+$, Y$^{2+}$, Ag$^{2+}$) can be noticed that at this point the slope of the $d$ wave function is bigger for the two $d^1$ ions than for $Ag^{2+}$.

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E. Different $R$ dependence of $A_s$ for $d^1$ and $d^9$ centers: Microscopic origin

As shown in Sec. III B the present results indicate that $A_s$ is found to be much more sensitive to $R$ changes for the $d^1$ centers LaF$_4^{2-}$ and YF$_4^{2-}$ than in the case of AgF$_4^{2-}$ involving the $4d^9$ ion Ag$^{2+}$. It should be recalled here that the comparison is made placing the unpaired electron in the same $x^2-y^2$ orbital for the three centers. More precisely, the exponent $n_s$ involved in Eq. (2) is found to be equal to 18 and 23 for YF$_4^{2-}$ and LaF$_4^{2-}$, respectively. These values can be compared with those derived for MnF$_6$$^{2-}$ ($n_s=7.3$),$^{18}$ NiF$_6$$^{2-}$ ($n_s=7.6$),$^{32}$ FeF$_6$$^{3-}$ (lying in the 6–7.5 range)$^{33}$ or AgF$_4^{2-}$ ($n_s=4.1$) and thus support that $A_s$ is extraordinarily sensitive to $R$ variations of the metal-ligand distance in the case of $d^1$ centers. Although experimental data on LaF$_4^{2-}$ or YF$_4^{2-}$ impurities are certainly scarce$^{11-13}$ there is an observation which can be connected with this predicted strong sensitivity of $A_s$ to $R$ changes. In this sense relevant changes in the shf lines corresponding to the EPR spectra of CaF$_2$:La$^{2+}$ have been observed$^{12,43}$ by applying an uniaxial stress of only 0.04 GPa at a temperature $T=1.3$ K.

Let us now explore the surprisingly different $n_s$ exponent found for the square-planar LaF$_4^{2-}$ or YF$_4^{2-}$ and AgF$_4^{2-}$ centers. When $\sigma$ bonding is taking place the overlap integral $S_{ds}$ between the corresponding $d$-wave function and the valence $s$ orbital of the ligand.$^{18,24}$ Therefore, the $R$ dependence of $A_s$ is strongly related to that of the $dS_{ds}/dR$ quantity around the equilibrium position. As in AgF$_4^{2-}$, LaF$_4^{2-}$, and YF$_4^{2-}$ centers the ligand is the same it can reasonably be expected that the differences in both $dS_{ds}/dR$ and $n_s$ arise from a different slope of the radial $d$ wave function $R_d(r)$ around the equilibrium distance. The form of $P_d(r)=\pi R_d(r)$ corresponding to the valence $d$ orbital for free La$^{2+}$, Y$^{2+}$, or Ag$^{2+}$ ions is displayed in Fig. 5. It can be noticed that, according to the atomic radii values,$^{34}$ the tail of the $P_d(r)$ function is longer for La$^{2+}$ and Y$^{2+}$ ions than for Ag$^{2+}$. At the same time this tail is certainly more flat for Ag$^{2+}$ than for the two $d^1$ ions in the equilibrium region of AgF$_4^{2-}$, LaF$_4^{2-}$, and YF$_4^{2-}$ complexes. This subtle difference in the tail of the $d$ wave function is thus the main responsible for the huge difference between the $n_s$ exponents found for the two $d^1$ centers and AgF$_4^{2-}$.

IV. FINAL REMARKS

A theoretical study of the substitutional La$^{2+}$ impurity in BaFCl (where Ba$^{2+}$ is surrounded by nine F$^{-}$ or Cl$^{-}$ ions) has been carried out. Despite the problems raised by systems with $4f$ orbitals$^{39,44}$ the present results support that the closeness,$^{14,15}$ of $4f$ levels to the $5d$ level of La$^{2+}$ and also the $C_{4v}$ local symmetry are behind the anomalous near isotropic shf tensor measured$^{10}$ in BaFCl:La$^{2+}$. The analysis carried out in this work thus demonstrates the importance of $4f$ orbitals in the bonding between nearest anions and the La$^{2+}$ impurity. A similar conclusion has been reached in a recent study on lanthanide complexes.$^{39}$ As regards the origin of the optical absorption band peaked at 17 890 cm$^{-1}$ the present study strongly supports that it is an allowed $5d \rightarrow 4f$ transition and not a charge transfer excitation.

As a salient feature, the present results stress that the isotropic shf constant $A_s$ associated with $d^1$ ions can be extremely sensitive to variations of the metal-ligand distance. Therefore, these systems appear as good candidates for observing important changes of the shf tensor detected in EPR and electron nuclear double resonance spectra under relatively small pressures. Unfortunately little experimental work has been performed on this issue.

In the case of octahedral units involving $3d$ ions, the sensitivity of the cubic field parameter $10Dq$ has been pointed out to be related to that of $A_s$ associated with antibonding $e_g(x^2-y^2;3z^2-r^2)$ electrons.$^{24,33}$ By this reason, it is thus interesting to investigate the $R$ dependence of $10Dq$ in centers involving ions such as $Zr^{2+}$ ($4d^2$). Work along this line is now under development.

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