

Cluster Models and *ab Initio* Calculations of ^{19}F NMR Isotropic Chemical Shifts for Inorganic Fluorides

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^{19}F NMR isotropic chemical shift (δ_{iso}) calculations are performed in crystallized compounds using the GIAO method with the B3LYP hybrid functional at DFT level. Clusters centered on the studied fluorine atoms mimic the crystalline structures. The 6-311+G(d) basis set is chosen for the central fluorine atom, and the LanL2DZ basis set for the others. The metal atoms are described by the 3-21G(2d) basis set or, when not available, by the CRENBL basis set with the corresponding ECP, and augmented with 2d polarization functions when existing. First, for high-symmetry systems (MF , MF_2 , and MF_3 compounds), a systematization of the cluster building up from coordination spheres is proposed, generalized to fluoroperovskites and fluoroaluminates KAlF_4 and RbAlF_4 . When applied to rather low symmetry systems such as barium fluorometalates BaMgF_4 , BaZnF_4 , and Ba_2ZnF_6 , the definition of the coordination spheres is far from easy. Then, for structures built up from a MF_6 octahedron network, we may define different “starting clusters”: $[\text{FM}_2\text{F}_8]$ for the shared fluorine atoms, $[\text{FMF}_4]$ for the unshared ones, and $[\text{FBa}_4]^{7+}$ for the “free” ones. Analogous “starting clusters” are then tested on compounds from the $\text{NaF}-\text{AlF}_3$, $\text{BaF}_2-\text{AlF}_3$, and $\text{CaF}_2-\text{AlF}_3$ binary systems and for $\alpha\text{-BaCaAlF}_7$ that are also built up from a MF_6 octahedron network. For each of these corresponding fluorine sites, δ_{iso} values are calculated with the “starting clusters” and several larger clusters and compared to the experimental δ_{iso} values. For the barium-containing clusters, the RMS deviation is equal to 51 ppm. It is suggested that this result may be related to the poor quality of the barium basis sets for which no polarization functions are available for the moment. In total, chemical shifts were calculated for 122 fluorine sites, in a various range of compounds. For the clusters without barium, the *ab initio* method leads to a RMS equal to 22 ppm, which is a quite nice result keeping in mind that the ^{19}F chemical shift range is larger than 200 ppm.

1. Introduction

^{19}F MAS NMR spectra can provide important structural information on the environment of fluorine atoms in crystalline and disordered compounds through isotropic chemical shift (δ_{iso}) measurements. Due to increasing MAS speed, it is now possible to discriminate close isotropic peaks on the experimental spectra. So now the challenge is to perform a reliable attribution of the ^{19}F NMR lines to fluorine atoms. New tools are needed.

In numerous studies,^{1–7} the attribution was based on the intuitive idea that similar chemical shift values indicate similar environments. B. Bureau et al.⁸ recently proposed an improvement hereafter called the “superposition model”, which assigns isotropic chemical shifts to fluorine surroundings through the use of phenomenological parameters. This model was successfully applied to compounds from the $\text{BaF}_2-\text{AlF}_3$ and $\text{CaF}_2-\text{AlF}_3$ binary systems:⁹ a refinement of the phenomenological parameters leads to the attribution of NMR lines to fluorine atoms with a root mean square (RMS) value equal to 6 ppm.

Ab initio calculations of nuclear parameters have also been carried out using gauge-independent atomic orbitals (GIAO) at the Hartree–Fock (HF) or at the density functional theory (DFT) level. Using GAUSSIAN 94 and 98¹⁰ packages, satisfactory

results were obtained for fluorine-containing molecules,^{11–13} for fluoride crystalline compounds,^{14–20} and even for glassy phases.²⁰

In these latter studies, non-embedded cluster models were used to mimic the crystal structure. While questionable, this approach is the basic approach in the field and is supported by experimental measurements, which evidence that the main contribution to the isotropic chemical shift is due to the nearest neighbors. Unfortunately, no clear rule could be easily drawn to build up these clusters. The aim of the present paper is to apply *ab initio* calculations to a large number of inorganic fluorides, using a simple and systematic method in the choice of the basis sets and in the generation of the clusters. The ultimate purpose of this method is to be easily tractable to estimate chemical shifts in disordered materials, taking into account a minimum number of atoms.

The samples under study are the fluoroaluminates of the $\text{NaF}-\text{AlF}_3$, $\text{BaF}_2-\text{AlF}_3$, and $\text{CaF}_2-\text{AlF}_3$ binary systems, which have been chosen because they include numerous crystalline compounds whose structures are known. Moreover, the experimental chemical shifts are already known.^{4,9,21,22} The crystalline structures can be described from AlF_6^{3-} or NaF_6^{5-} octahedron networks. Only three kinds of fluorine atoms are encountered: shared fluorine atoms that bridge two MF_6 octahedra, unshared fluorine atoms that belong to only one MF_6 octahedron, and “free” fluorine atoms that are not embedded into any MF_6 octahedron.

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The paper is organized as follows. The first part is devoted to the computational procedures. The choice of the basis sets is done in the light of previous studies. Then a systematization of the cluster building-up is proposed for MF, MF_2 , and MF_3 compounds and applied to fluoroperovskites, fluoroaluminates KAlF_4 and RbAlF_4 , and barium fluorometalates BaMgF_4 , BaZnF_4 , and Ba_2ZnF_6 . From these first results, “starting clusters” are then deduced for shared, unshared, and “free” fluorine atoms.

The second part deals with the results of the calculations for compounds from the three binary systems mentioned above and for $\alpha\text{-BaCaAlF}_7$. For each fluorine site, δ_{iso} values are calculated with the “starting cluster” and several larger clusters, and compared to the experimental value. In the end, the “starting cluster” and the cluster that leads to the best agreement between calculated and experimental δ_{iso} values are retained. The results of the computations are presented for the compounds of each binary system. The influence of the barium atoms and the reliability of the “starting clusters” for the shared, unshared and “free” fluorine atoms are discussed.

2. Computational Method

2.1. Attribution of NMR Lines to Fluorine Sites. For MF, MF_2 , and MF_3 compounds, whose structures contain only one fluorine site, there is no problem of line attribution. The experimental values we used are those published in ref 8. For barium fluorometalates (BaMgF_4 , BaZnF_4 , Ba_2ZnF_6), $\alpha\text{-PbF}_2$, KAlF_4 , and RbAlF_4 , the attributions done by B. Bureau et al. are retained.⁸ For compounds from $\text{BaF}_2\text{-AlF}_3$ and $\text{CaF}_2\text{-AlF}_3$ binary systems, and for $\alpha\text{-BaCaAlF}_7$, experimental ^{19}F isotropic chemical shifts were measured and related to the fluorine sites, using the superposition model with refined parameters.⁹ These attributions will not be modified in this paper.

The external reference chosen for the isotropic chemical shifts is C_6F_6 . All experimental and calculated chemical shieldings are converted to chemical shifts using the following formula:

$$\delta_{\text{iso}} = \sigma_{\text{ref}} - \sigma_{\text{iso}}$$

with σ_{ref} (C_6F_6) = 353 ppm.^{8,15–18} To be consistent with our previous experimental results, $\alpha\text{-Na}_3\text{AlF}_6$ and $\text{Na}_5\text{Al}_3\text{F}_{14}$ compounds were specially synthesized by us²³ and the ^{19}F NMR spectra were recorded using high-speed MAS NMR technique at various spinning rates and numerically reconstructed. For $\alpha\text{-Na}_3\text{AlF}_6$, a single NMR line is measured at -22 ppm, which is consistent with previous studies.^{4,21} So the three fluorine sites²⁴ have the same experimental δ_{iso} value. From crystallographic data,²⁵ $\text{Na}_5\text{Al}_3\text{F}_{14}$ has three fluorine sites with different multiplicities: 4e for F1, 8h for F2, and 16i for F3. So three isotropic peaks are expected with relative intensities equal to 14.3, 28.6, and 57.1%, respectively. Q. Zeng and J. F. Stebbins⁴ obtained three peaks measured at -2 , -18 , and -27 ppm (-166 , -182 , and -191 ppm relative to CFCl_3 , $\delta_{\text{C}_6\text{F}_6}$ vs CFCl_3 -164.2 ppm),⁸ respectively, with relative intensity ratio of 2:1:4, using a Varian VXR-400 S spectrometer. To the contrary, L.-S. Du and co-workers,²² using a Chemagnetics CMX-360, obtained a spectrum showing only two peaks measured respectively at 0.4 and -25.7 ppm (-163.8 and -189.9 ppm relative to CFCl_3).⁸ Then, using a Bruker AMX-833 spectrometer, they showed that the most intense peak, previously measured at -25.7 ppm, split into two new peaks measured at -25.3 and -27.2 ppm, respectively.²² We recorded the $\text{Na}_5\text{Al}_3\text{F}_{14}$ spectrum with a Bruker Avance 300 spectrometer. The resultant spectrum had only two peaks and was similar to the spectrum previously recorded with the Chemagnetics CMX-360 spectrometer. Moreover, the X-ray

diffraction powder method confirms the purity of our sample. So we may infer that the peak measured at -18 ppm by Q. Zeng et al. is due to an impurity, which seems in agreement with the very low intensity of the corresponding line (Figure 1 in ref 4). The reconstruction of the spectrum collected at 35 kHz using two contributions for the most intense peak provides us with values for δ_{iso} similar to those obtained by L.-S. Du et al.: -2 , -23 , and -25 ppm with the same relative intensity ratio of 2:4:1. These latter chemical shift values are used in the following of the study.

2.2. Choice of the Basis Sets. The ab initio calculations of ^{19}F chemical shieldings σ_{iso} were carried out using the GAUSS-98W package¹⁰ on a Pentium 4 2.8 GHz personal computer with 512 MB of RAM.

S.-H. Cai et al. published ab initio computations¹⁴ on alkaline fluorides MF ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{and Rb}$). The $[\text{MF}_6]^{5+}$ cluster was built-up with M–F distances issued from crystallographic data and used with the 3-21G basis set for M and 6-311+G(d) basis set for F atoms. HF, BLYP, and B3LYP methods were employed. Then the calculated σ_{iso} values were compared to the experimental ones. The best correlation was reached using the B3LYP hybrid functional at DFT level.¹⁴

In a second paper,¹⁵ S.-H. Cai et al. tested five different basis sets with the B3LYP method. The following clusters were used: $[\text{FBe}_2\text{F}_6]^{3-}$ for BeF_2 , $[\text{FMg}_3\text{F}_9]^{4-}$ for MgF_2 , and $[\text{FM}_4\text{F}_6]^{+}$ for CaF_2 , SrF_2 , and BaF_2 . From comparison with experimental data, the best correlation was obtained when (1) the central fluorine atom was described with the 6-311+G(d) basis set, (2) the LanL2DZ basis set was chosen for the other fluorine atoms, and (3) the metal atoms were described with the CRENBL basis set used with the corresponding effective core potential (ECP) and augmented with 2d polarization functions (when they exist, which is not the case for the Ba atom).¹⁵ Then they applied this choice of basis sets to the MF compounds previously studied. The difference between calculated and experimental δ_{iso} values is less than 30 ppm.¹⁵ However, the CRENBL basis set was employed without the corresponding ECP for Li and Be atoms, which from our point of view disagrees with the basis set conception.

In a third study by S.-H. Cai et al.,¹⁶ calculations were applied to MF_2 ($\text{M} = \text{Cd}, \text{Zn}, \text{and Pb}$) and to MF_3 ($\text{M} = \text{Al}, \text{Ga}, \text{and In}$) compounds. For these MF_2 compounds, various clusters are employed while the $[\text{FM}_2\text{F}_8]^{3-}$ one is used for the MF_3 compounds.¹⁶ The selected basis sets are: (1) the Aug-cc-pVTZ basis set for the central fluorine atom, (2) the LanL2DZ basis set for the other fluorine atoms, and (3) the CRENBL basis set used with the corresponding ECP (except for Mg atom), and augmented with 2d polarization functions while existing, for all the metal atoms except for Al atom. In this case, the 3-21G-(2d) basis set is used.¹⁶ Moreover, to reduce the difference between calculated and experimental σ_{iso} values, several clusters were tested for MgF_2 and ZnF_2 , and the DZVP basis set was used for the Zn and Cd atoms in ZnF_2 and CdF_2 . Both MgF_2 and ZnF_2 adopt the rutile structure; however, two different clusters were selected: $[\text{FMg}_3\text{F}_9]^{4-}$ and $[\text{FZn}_3\text{F}_{11}]^{6-}$.¹⁶ The choice of the most suitable clusters and basis sets led to a satisfactory result: the largest difference between calculated and experimental δ_{iso} values was 31 ppm for a ^{19}F chemical shielding range of 200 ppm.¹⁶

In a fourth paper¹⁸ submitted at the same time as ref 17, S.-H. Cai et al. kept the same basis set choice as in their third study,¹⁶ with two adjustments. The ECP was added to the CRENBL basis set for the Mg atom and the 3-21G(2d) basis set was selected for the Li atom.

TABLE 1: Fluoride Compounds, Space Group, Clusters Used for Calculation, $\delta_{\text{iso,exp}}$, $\delta_{\text{iso,cal}}$ with Basis I and Basis II and $\Delta\delta_{\text{iso}} = \delta_{\text{iso,exp}} - \delta_{\text{iso,cal}}$ Values (ppm) for Basis II

compound	space group	cluster	$\delta_{\text{iso,exp}}$	basis I $\delta_{\text{iso,cal}}$	basis II $\delta_{\text{iso,cal}}$	$\Delta\delta_{\text{iso}}$
LiF	$Fm\bar{3}m$	[FLi ₆] ⁵⁺	-42	-115.8	-82.4	40.4
NaF	$Fm\bar{3}m$	[FNa ₆] ⁵⁺	-59	-83.3	-89.0	30.0
KF	$Fm\bar{3}m$	[FK ₆] ⁵⁺	32	25.5	23.0	9.0
RbF	$Fm\bar{3}m$	[FRb ₆] ⁵⁺	74	69.1	79.3	-5.3
CsF	$Fm\bar{3}m$	[FCs ₆] ⁵⁺	158	156.6	182.8	-24.8
AlF ₃	$R\bar{3}c$	[FAl ₂ F ₈] ³⁻	-5	-20.9	-8.5	3.5
GaF ₃	$R\bar{3}c$	[FGa ₂ F ₈] ³⁻	-3	15.2	10.6	-13.6
InF ₃	$R\bar{3}c$	[FIn ₂ F ₈] ³⁻	-42	-33.2	-46.0	4.0
CaF ₂	$Fm\bar{3}m$	[FCa ₄ F ₆] ⁺	58	52.0	55.2	2.8
SrF ₂	$Fm\bar{3}m$	[FSr ₄ F ₆] ⁺	81	62.9	70.4	10.6
BaF ₂	$Fm\bar{3}m$	[FBa ₄ F ₆] ⁺	153	142.4	/	10.6
CdF ₂	$Fm\bar{3}m$	[FCd ₄ F ₆] ⁺	-26	33.7	3.2	-29.2
β -PbF ₂	$Fm\bar{3}m$	[FPb ₄ F ₆] ⁺	129	148.2	/	-19.2
MgF ₂	$P4_2/mmm$	[FMg ₃ F ₁₁] ⁶⁻	-29	-117.1	-61.1	32.1
ZnF ₂	$P4_2/mmm$	[FZn ₃ F ₁₁] ⁶⁻	-36	-40.1	-27.7	-8.3
α -PbF ₂	$Pnma$	[FPb ₄ F ₈] ⁻	147	182.3	/	-35.3
		[FPb ₃ F ₂ Pb ₂ F ₆] ⁺	110	154.7	/	-44.7

These calculations are promising; however, a computational method must be easily tractable. So, the basis set choice must be as systematic as possible. In a recent study,¹⁷ we have compared the different basis sets already used in the three previous papers.^{14–16} For the central fluorine atom, the 6-311+G(d)¹⁵ and Aug-cc-pVTZ¹⁶ basis sets were both employed. The comparison of our results with those of ref 16 showed that the Aug-cc-pVTZ basis set increased notably the computational time without improving significantly the correlation between calculated and experimental σ_{iso} values. Consequently, we retained the 6-311+G(d) basis set to describe the central fluorine atom. For the other fluorine atoms, the LanL2DZ basis set was kept, as it was demonstrated in reference.¹⁵ In complement, for the metal atoms, the CRENBL basis set (basis I) and the 3-21G-(2d) basis set (basis II) were shown to be promising. To choose between them, we computed the σ_{iso} values for MF, MF₂, and MF₃ compounds and compared them to the experimental values. The RMS deviations were found equal to 36 and 21 ppm when metal atoms were described with bases I and II, respectively. Consequently, the 3-21G(2d) basis set was selected to describe the metal atoms in the following calculations. When this basis set was not available, as is the case for Ba and Pb atoms, the CRENBL basis set was retained. A comparison between the calculated and experimental δ_{iso} values is shown in Table 1 and Figure 1. A linear regression is performed over all these results and provides $\delta_{\text{iso,cal}} = 1.17 \delta_{\text{iso,exp}} - 4.6$ with a correlation coefficient R^2 equal to 0.95 and a RMS deviation of 23 ppm.

2.3. Cluster Build-up. S.-H. Cai et al.^{14–16} and Y. Liu et al.^{19,20} clearly showed that the calculated σ_{iso} values depend not only on the basis sets employed but also on the number of atoms included in the calculation. Consequently, still with the goal of working out a tractable method, some accurate rules for the cluster build-up have to be defined. A systematization of the cluster build-up is performed on highly symmetrical MF, MF₂, and MF₃ compounds already studied. Then it is applied on fluoroperovskites, fluoroaluminates KAlF₄ and RbAlF₄, and barium fluorometalates BaMgF₄, BaZnF₄, and Ba₂ZnF₆.

We chose a non-embedded cluster to keep the method as simple as possible. The cluster is spherical, centered on the observed fluorine atom. It contains at least the nearest neighboring atoms and, except for MF compounds, the influence of the next-nearest neighboring (NNN) atoms was systematically checked on the calculated results. It is important to note that all atoms included in the sphere are taken into account for the calculations.

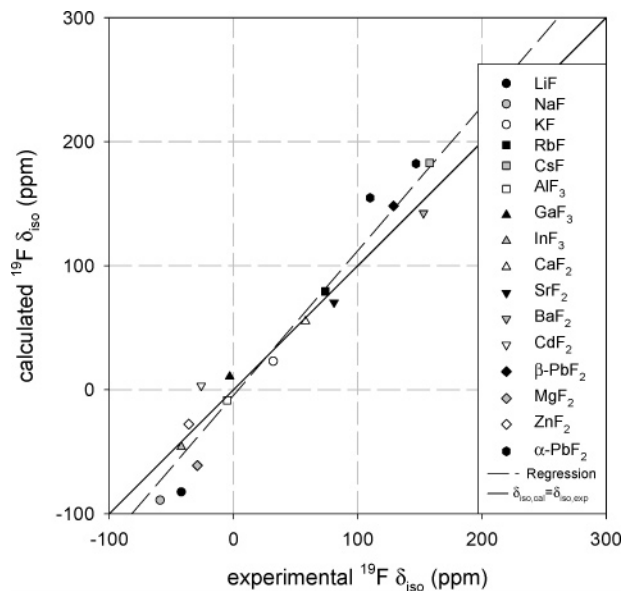


Figure 1. Calculated isotropic chemical shift values versus experimental values for MF, MF₂, and MF₃ compounds. The solid line corresponds to $\delta_{\text{iso,cal}} = \delta_{\text{iso,exp}}$. The dashed line corresponds to the linear regression.

2.3.1. MF, MF₂, and MF₃ Compounds. Alkali-metal fluorides MF (M = Li, Na, K, Rb, and Cs) are NaCl-like structures.^{26–30} Each fluorine atom sits at the center of a regular octahedron of alkali-metal atoms. Consequently, the simplest cluster for δ_{iso} calculation is [FM₆]⁵⁺. Computations were performed using this cluster with different basis sets^{14–17} and led to satisfactory agreements between experimental and calculated values (Table 1 and Figure 1).

The MF₃ (M = Al, In, and Ga) compounds are built up from MF₆³⁻ octahedra-sharing corners.^{31–33} So each fluorine atom is shared between two octahedra. As the cluster including the two metal atoms is not sufficient to mirror the atomic arrangement around the central F atom, it is extended to the NNN fluorines. The resultant [FM₂F₈]³⁻ cluster incorporates the first cationic and anionic spheres and is shown in Figure 2a. The corresponding calculated δ_{iso} values were found in good agreement with the experimental values (Table 1 and Figure 1).^{16,17}

Some alkaline earth metal fluorides MF₂ (M = Ca, Sr, and Ba), CdF₂, and β -PbF₂ adopt the fluorite structure.^{34–38} Each fluorine atom is a “free” atom surrounded by a regular tetrahedron of alkaline earth metal atoms, then by six next-nearest fluorine atoms. The associated [FM₄F₆]⁺ cluster, which includes the first cationic and anionic spheres, led to satisfactory agreement between calculated and experimental δ_{iso} values (Table 1 and Figure 1).^{15–17} The [FM₄]⁷⁺ cluster led to a slightly better agreement only for the BaF₂ compound with a calculated value equal to 155.5 ppm instead of 145.9 ppm for an experimental value measured at 153 ppm.

MgF₂ and ZnF₂ both adopt the rutile structure,^{39,40} so each fluorine atom is shared between three octahedra. By comparison with the [FM₂F₈]³⁻ cluster used for MF₃ compounds, the [FM₃F₁₁]⁶⁻ cluster used includes the central atom and the three metal atoms surrounded by four fluorine atoms (Figure 2b). These clusters led to acceptable results (Table 1 and Figure 1). S.-H. Cai et al. have tested larger clusters for both compounds, and in each case the best agreement between calculated and experimental δ_{iso} values was reached with a smaller cluster for MgF₂. They tentatively related this result to the fact that Zn has a stronger covalent character than Mg.^{16,18}

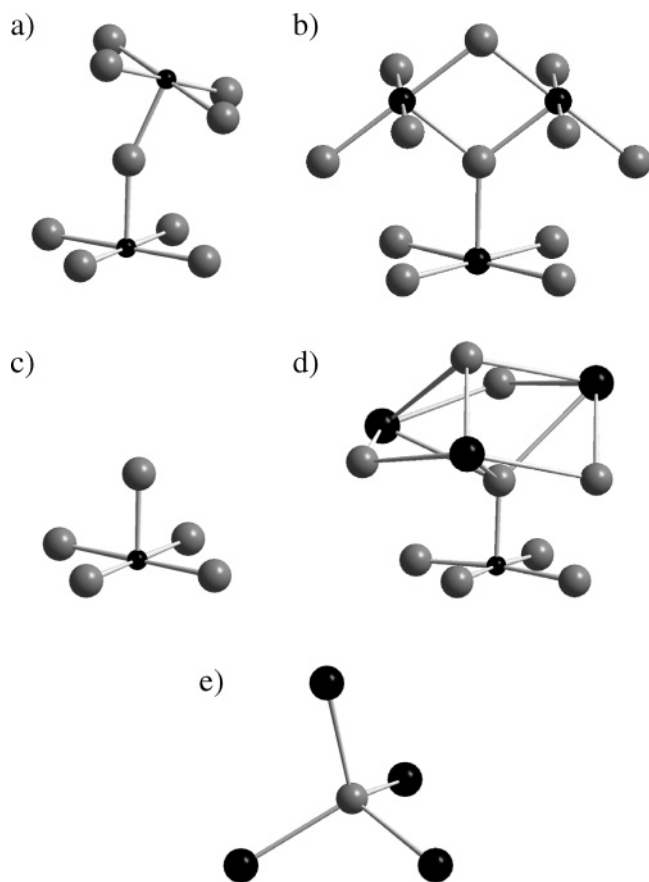


Figure 2. Examples of clusters used in calculation. (a) $[\text{AlF}_4\text{F}_8]^{3-}$ cluster for AlF_3 , (b) $[\text{FMg}_3\text{F}_{11}]^{3-}$ cluster for MgF_2 , (c) $[\text{FAlF}_4]^{2-}$ cluster for the unshared fluorine atom of KAlF_4 , (d) $[\text{FAlF}_4\text{FBaFBa}_2\text{F}_2]$ retained cluster for the unshared fluorine atom F7 in $\text{Ba}_3\text{Al}_2\text{F}_{12}$, and (e) $[\text{FBa}_4]^{7+}$ cluster for BaF_2 . Gray and black spheres represent fluorine and metal atoms, respectively.

α - PbF_2 adopts the $Pnma$ space group with two fluorine sites.⁴¹ The crystalline structure is less symmetric than the previous ones, and the coordination spheres are not so clearly defined. For F1, no atoms are present within the 3.2 to 3.8 Å distance range, so we considered that the first anionic sphere ended at 3.2 Å and we built up the $[\text{FPb}_4\text{F}_8]^-$ cluster. Similarly, for F2 no atoms are present within the 3.2 to 3.5 Å distance range. Consequently, we built up the $[\text{FPb}_3\text{F}_2\text{Pb}_2\text{F}_6]^+$ cluster. Both clusters, which are larger than those used by S.-H. Cai et al.,¹⁷ led to acceptable results (Table 1 and Figure 1).

2.3.2. Fluoroperovskites. The fluoroperovskites AMF_3 ($A = \text{K, Rb, Cs}$, and $M = \text{Ca, Cd, Mg, Zn}$) are built up from MF_6^{4-} octahedra-sharing corners,^{42–47} so all of the fluorine atoms belong to two octahedra as in MF_3 compounds and are shared. Then a similar cluster including the first cationic and anionic spheres is built up. Because four A metal and eight F atoms, which belong to the second cationic sphere and to the first anionic sphere respectively, are at the same distance from the central fluorine atom, the resulting cluster is $[\text{FM}_2\text{A}_4\text{F}_8]^-$. The corresponding calculated δ_{iso} values were found in good agreement with the experimental values (Table 2 and Figure 3).¹⁷ BaLiF_3 is an inverted fluoroperovskite,⁴³ but the suitable cluster follows the same rule and is found to be $[\text{FA}_2\text{M}_4\text{F}_8]^+$.¹⁷ KCaF_3 is an orthorhombically distorted fluoroperovskite at room temperature, and the crystalline structure exhibits four fluorine sites, with slightly different surroundings.⁴⁸ The fluorine atoms are all surrounded by two A atoms as nearest cations, then by four M metal atoms and six fluorine atoms. The cluster including all these atoms was tested for the four fluorine sites and led to

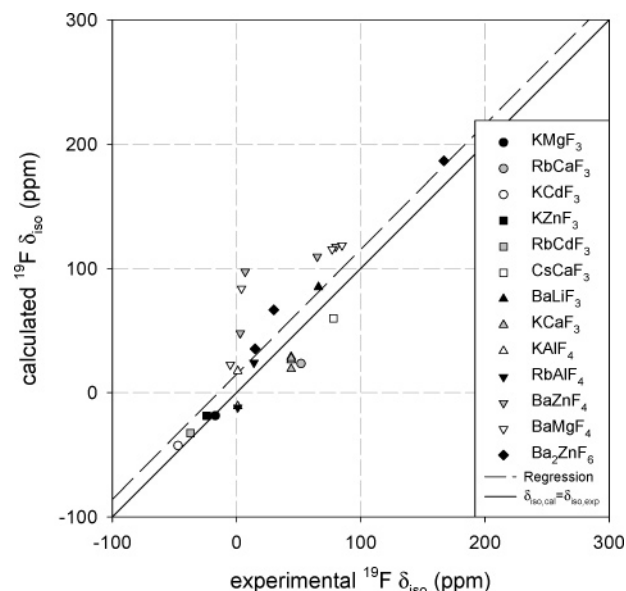


Figure 3. Calculated isotropic chemical shift values versus experimental values for some fluorides compounds. The solid line corresponds to $\delta_{\text{iso,cal}} = \delta_{\text{iso,exp}}$. The dashed line corresponds to the linear regression.

TABLE 2: Fluoride Compounds, Space Group, $\delta_{\text{iso,exp}}$, Clusters Used for Calculation, $\delta_{\text{iso,cal}}$, and $\Delta\delta_{\text{iso}} = \delta_{\text{iso,exp}} - \delta_{\text{iso,cal}}$ Values (ppm)

compound	space group	$\delta_{\text{iso,exp}}$	cluster	$\delta_{\text{iso,cal}}$	$\Delta\delta_{\text{iso}}$
KMgF_3	$Pm\bar{3}m$	-17	$[\text{FMg}_2\text{K}_4\text{F}_8]^-$	-18.5	1.5
KCdF_3	$Pm\bar{3}m$	-47	$[\text{FCd}_2\text{K}_4\text{F}_8]^-$	-42.7	-4.3
BaLiF_3	$Pm\bar{3}m$	66	$[\text{FLi}_2\text{Ba}_4\text{F}_8]^+$	84.9	-18.9
RbCaF_3	$Pm\bar{3}m$	52	$[\text{FCa}_2\text{Rb}_4\text{F}_8]^-$	23.4	28.6
KZnF_3	$Pm\bar{3}m$	-24	$[\text{FZn}_2\text{K}_4\text{F}_8]^-$	-18.7	-5.3
RbCdF_3	$Pm\bar{3}m$	-37	$[\text{FCd}_2\text{Rb}_4\text{F}_8]^-$	-32.7	-4.3
CsCaF_3	$Pm\bar{3}m$	78	$[\text{FCa}_2\text{Cs}_4\text{F}_8]^-$	59.8	18.2
KCaF_3	$B2_1/m$	44	$[\text{FCa}_2\text{K}_2\text{F}_6\text{KF}_2\text{K}]^-$	28.8	15.2
		44	$[\text{FCa}_2\text{KF}_2\text{KF}_4\text{KF}_2\text{K}]^-$	19.1	24.9
		44	$[\text{FCa}_2\text{F}_2\text{K}_2\text{F}_3\text{K}_2\text{F}_3]^-$	26.1	17.9
		44	$[\text{FCa}_2\text{KF}_2\text{KF}_4\text{KF}_2\text{K}]^-$	27.8	16.2
KAlF_4	$P4/mbm$	1	$[\text{FAl}_2\text{F}_8]^{3-}$	-10.9	11.9
		1	$[\text{FAlF}_4]^{2-}$	17.4	-16.4
RbAlF_4	$P4/mmm$	1	$[\text{FAl}_2\text{F}_8]^{3-}$	-11.9	12.9
		14	$[\text{FAlF}_4]^{2-}$	24.1	-10.1
BaZnF_4	$Cmc2_1$	80	$[\text{FZnFBa}_3\text{F}_6]$	117.4	-37.4
		65	$[\text{FZnBa}_2\text{F}_6\text{BaF}_2]^+$	109.5	-44.5
		7	$[\text{FZn}_2\text{F}_3\text{Ba}_2\text{F}_6]^-$	97.3	-90.3
		3	$[\text{FZn}_2\text{F}_2\text{BaF}_6\text{Ba}_2]^+$	47.8	-44.8
BaMgF_4	$Cmc2_1$	4	$[\text{FMg}_2\text{F}_6\text{Ba}_2\text{F}_3]^{2-}$	83.8	-79.8
		77	$[\text{FMgBa}_2\text{F}_6\text{Ba}_2\text{F}_2]^{2+}$	115.4	-38.4
		85	$[\text{FMgFBa}_3\text{F}_6]$	118.5	-33.5
		-5	$[\text{FMg}_2\text{F}_4\text{BaF}_4\text{Ba}_2]^+$	22.6	-27.6
Ba_2ZnF_6	$I4/mmm$	167	$[\text{FBa}_4\text{F}_8]^-$	186.5	-19.5
		15	$[\text{FZn}_2\text{F}_8\text{Ba}_4]^{3-}$	35.3	-20.3
		30	$[\text{FZnF}_8\text{Ba}_4]^+$	66.6	-36.6

a reasonable agreement between δ_{iso} calculated values and the experimental values (Table 2 and Figure 3). For all the fluoroperovskites, the suitable clusters include the second cationic sphere. For those fluoroperovskite compounds, S.-H. Cai et al. strangely chose to remove all the fluorine atoms present in the cluster sphere.¹⁸ A comparison between their results and ours shows that the maximum difference between measured and calculated δ_{iso} values is less than 30 ppm for both. These two methods lead to similar RMS deviations equal to 16 ppm, so there is no reason to remove the fluorine atoms.

2.3.3. Fluoroaluminates KAlF_4 and RbAlF_4 . The fluoroaluminates KAlF_4 and RbAlF_4 are built up from AlF_6^{3-} octahedra sharing four corners that form $[\text{AlF}_4]^-$ layers. In both com-

pounds, the crystalline structure exhibits two kinds of fluorine atoms, one shared and one unshared.^{49,50} The environment of the shared fluorine atoms is similar to the environment of the fluorine atoms in the AlF_3 compound. Consequently, the $[\text{FAl}_2\text{F}_8]^{3-}$ cluster is used for the calculation of δ_{iso} values, which led to satisfactory results: -7.4 ppm for KAlF_4 and -8.4 ppm for RbAlF_4 for experimental δ_{iso} values of 1 ppm (Table 2 and Figure 3). Increasing the cluster size in order to include the second cationic sphere improved the results only slightly for KAlF_4 . For the unshared fluorine atom, the cluster including the first cationic and anionic spheres becomes $[\text{FAlF}_4]^{2-}$. This cluster is shown in Figure 2c and led to suitable δ_{iso} values (Table 2 and Figure 3). The cluster extended to the second cationic sphere was also tested for both compounds, however, the result is disappointing (29.7 and 38.9 ppm compared to 1 and 14 ppm respectively).

2.3.4. Barium Fluorometalates BaMgF_4 , BaZnF_4 , and Ba_2ZnF_6 . Next, barium fluorometalates BaMgF_4 , BaZnF_4 , and Ba_2ZnF_6 are studied. As for the fluoroaluminates KAlF_4 and RbAlF_4 , the crystalline structures are built up from MF_6^{4-} octahedra forming $[\text{MF}_4]^{2-}$ layers,^{51–53} but for BaMgF_4 and BaZnF_4 compounds these layers are puckered. Four Ba atoms as in BaF_2 , and eight NNN fluorine atoms surround the “free” fluorine atom in Ba_2ZnF_6 . Both $[\text{FBa}_4]^{7+}$ and $[\text{FBa}_4\text{F}_8]^-$ clusters led to acceptable results: 199.8 and 191.0 ppm, respectively, for an experimental δ_{iso} value measured at 167 ppm. The shared atoms bridge two MF_6^{4-} octahedra, so the $[\text{FM}_2\text{F}_8]^{5-}$ cluster was tested again. When some barium atoms are present in the cluster sphere, they are taken into account. The resulting clusters led to strongly disappointing results. The disagreement between experimental and calculated δ_{iso} values may be larger than 200 ppm. A better agreement was reached when the $[\text{FM}_2\text{F}_8]^{5-}$ clusters were enlarged to the NNN atoms (Table 2 and Figure 3). The unshared fluorine atoms have environment similar to the unshared atoms in KAlF_4 and RbAlF_4 , so the $[\text{FMF}_4]^{3-}$ cluster was tested. Similarly, barium atoms may be present in this cluster and have to be included. Once more, the resulting clusters led to disappointing results. Then clusters of increasing sizes were tested. Finally it was deduced that the most suitable cluster includes three barium atoms and seven fluorine atoms (Table 2 and Figure 3). For these barium fluorometalates, S.-H. Cai et al. selected all the cations included in a 3.0 Å radius sphere, and surprisingly removed all the fluorine atoms from the clusters, except for the clusters of the “free” and shared fluorine atoms in the Ba_2ZnF_6 compound.¹⁸ As for the choice of the basis sets, we prefer to avoid exceptions and keep the same rule to build the clusters. Moreover, as they said, the advantage of the ab initio model compared to the superposition model is to take into account the contributions of the nearest anions to the central atom shielding.¹⁶ Consequently, we chose to retain all the anions included in the clusters for computations.

A comparison between our calculated and experimental δ_{iso} values is shown in Figure 3. A linear regression is performed on all these results and provides $\delta_{\text{iso,cal}} = 1.0 \delta_{\text{iso,exp}} + 14.6$ with $R^2 = 0.70$. The RMS deviation calculated at 33 ppm is becoming significant and is mainly due to the barium-containing compounds.

2.4. Definition of the “Starting Clusters”. From all these results, the building up of spherical clusters including the nearest and next-nearest neighboring atoms is easy only for compounds that crystallize in highly symmetrical structures such as MF , MF_2 , MF_3 , AMF_3 , and the fluoroaluminates KAlF_4 and RbAlF_4 . The calculations for barium fluorometalates BaMgF_4 , BaZnF_4 ,

TABLE 3: Fluorine Sites, $\delta_{\text{iso,exp}}$, Clusters Used for Calculation, $\delta_{\text{iso,cal}}$, and $\Delta\delta_{\text{iso}} = \delta_{\text{iso,exp}} - \delta_{\text{iso,cal}}$ Values (ppm) for Compounds of the $\text{NaF}-\text{AlF}_3$ Binary System

compound	site ^a	$\delta_{\text{iso,exp}}$	cluster ^b	$\delta_{\text{iso,cal}}^{b,c}$	$\delta_{\text{iso,cal}}$	$\Delta\delta_{\text{iso}}$
$\alpha\text{-Na}_3\text{AlF}_6$	F1 (s)	-22	$[\text{FAlNa}_3\text{F}_6\text{NaF}_4\text{Na}]^{3-}$	<i>No conv.</i>	-14.3	-7.7
	F2 (s)	-22	$[\text{FAlNa}_2\text{F}_4\text{Na}_2\text{F}_6]^{4-}$	-18.6	-18.6	-3.4
	F3 (s)	-22	$[\text{FAlNa}_2\text{F}_4\text{Na}_2\text{F}_6]^{4-}$	-22.2	-22.2	0.2
$\text{Na}_5\text{Al}_3\text{F}_{14}$	F1 (u)	-25	$[\text{FAlF}_4\text{Na}_4\text{F}_4\text{Na}]^-$	-47.1	-15.5	-9.5
	F2 (s)	2	$[\text{FAl}_2\text{F}_8\text{Na}_2\text{F}_2]^{3-}$	-9.2	4.4	-2.4
	F3 (u)	-23	$[\text{FAlNa}_2\text{F}_3\text{NaFF}_5]^{4-}$	-9.5	-22.3	-0.7

^a s and u indicate shared and unshared fluorine atoms, respectively.

^b The “starting clusters” and the corresponding calculated values are in italic. ^c No conv. indicates that the calculation does not converge.

and Ba_2ZnF_6 show that for low symmetry structures the definition of such spherical clusters becomes more difficult.

Nevertheless, it appears that for structures built up from MF_6 octahedra, similar fluorine environments may be related to similar “starting clusters”. The environments of shared fluorine atoms are similar to the fluorine atom one in AlF_3 , so the “starting cluster” is $[\text{FM}_2\text{F}_8]$ and an example is shown in Figure 2a. Unshared fluorine atoms belong to only one octahedron. By analogy to the fluoroaluminates KAlF_4 and RbAlF_4 , the “starting cluster” is $[\text{FAlF}_4]^{2-}$ and an example is shown in Figure 2c. This cluster seems to be too small. However, metal and fluorine atoms belonging to the sphere will be added according to our cluster build-up rules. This may be a problem with nearest heavy metal atoms, which are outside of this sphere. At last, the “free” fluorine atom has four barium atoms as nearest neighbors in Ba_2ZnF_6 . So the “starting cluster” is $[\text{FBa}_4]^{7+}$ as shown in Figure 2e.

As the compounds from $\text{NaF}-\text{AlF}_3$, $\text{BaF}_2-\text{AlF}_3$, and $\text{CaF}_2-\text{AlF}_3$ binary systems and $\alpha\text{-BaCaAlF}_7$ are built up from a MF_6 octahedron network, the “starting clusters” will give us a base for δ_{iso} computations and limit the number of clusters to be tested.

3. Results and Discussion

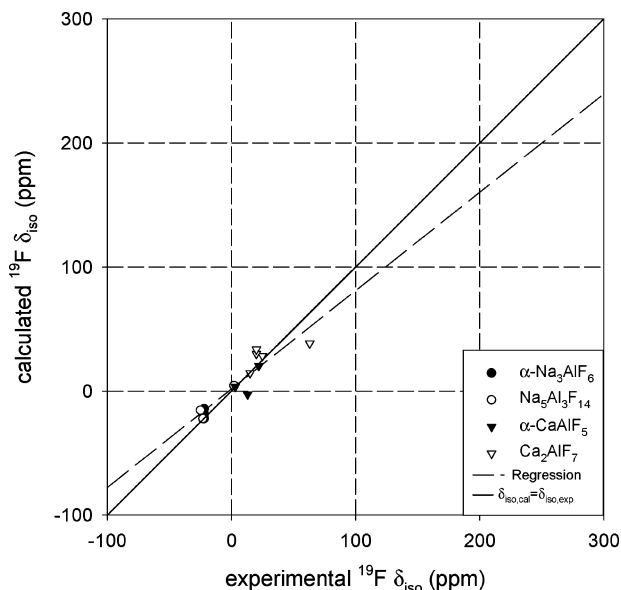
For the 79 fluorine sites of the compounds of the three studied binary systems and $\alpha\text{-BaCaAlF}_7$, several clusters of increasing radius are tested beginning with the “starting cluster”. The cluster that leads to the best agreement between calculated and experimental δ_{iso} values is retained. However, the computational time increases with the number of atoms, and the convergence failure is more often encountered (i.e., no solutions to the SCF equations met the convergence criteria after 128 cycles). Consequently, we limit the cluster size to 18 atoms. The cluster maximum radius is roughly equal to 3.8–4.0 Å, depending on the investigated structure, and corresponds to the commonly accepted range of the NMR effects.

3.1. Binary Systems. 3.1.1. $\text{NaF}-\text{AlF}_3$ Binary System. The three fluorine atoms of $\alpha\text{-Na}_3\text{AlF}_6$ are shared as they bridge an AlF_6^{3-} octahedron to a NaF_6^{5-} octahedron.²⁴ $\text{Na}_5\text{Al}_3\text{F}_{14}$ includes one shared and two unshared fluorine atoms.²⁵ For all these fluorine sites, the “starting clusters” lead to acceptable calculated δ_{iso} values, except for F1 of $\alpha\text{-Na}_3\text{AlF}_6$, which does not converge. The “starting clusters” and the corresponding $\delta_{\text{iso,cal}}$ values are indicated in italic in Table 3. For four fluorine sites, enlarging the cluster size improves the agreement between experimental and calculated δ_{iso} values. For F2 and F3 of $\alpha\text{-Na}_3\text{AlF}_6$, the “starting cluster” is the best one. When improving the agreement between experimental and calculated δ_{iso} values, the enlarged clusters and the corresponding calculated δ_{iso} values are also collected in Table 3. For the retained clusters, the RMS

TABLE 4: Fluorine Sites, $\delta_{\text{iso,exp}}$, Clusters Used for Calculation, $\delta_{\text{iso,cal}}$ and $\Delta\delta_{\text{iso}} = \delta_{\text{iso,exp}} - \delta_{\text{iso,cal}}$ Values (ppm) for Compounds of the $\text{CaF}_2\text{--AlF}_3$ Binary System

compound	site ^a	$\delta_{\text{iso,exp}}$	cluster ^b	$\delta_{\text{iso,cal}}^{\text{b,c}}$	$\delta_{\text{iso,cal}}$	$\Delta\delta_{\text{iso}}$
$\alpha\text{-CaAlF}_5$	F1 (s)	3	$[\text{FAl}_2\text{F}_2\text{CaF}_6\text{F}_2]^{3-}$	40.3	3.5	-0.5
	F2 (u)	22	$[\text{FAlCa}_2\text{F}_4\text{F}_7]^{5-}$	148.6	20.3	1.7
	F3 (u)	13	$[\text{FAlCa}_2\text{F}_4\text{F}_4]^{4-}$	70.7	-2.7	15.7
Ca_2AlF_7	F1 (f)	63	$[\text{FCa}_3\text{F}]^{4+}$	38.4	/	24.6
	F2 (u)	25	$[\text{FAlCa}_2\text{F}_4\text{F}_5]^{3-}$	No conv.	28.3	-3.3
	F3 (u)	15	$[\text{FAlCa}_2\text{F}_4\text{F}_3]^{3-}$	No conv.	14.5	0.5
	F4 (u)	20	$[\text{FAlCa}_2\text{F}_4\text{F}_6\text{Ca}]^{2-}$	141.9	30.0	-10.0
	F5 (u)	20	$[\text{FAlCa}_2\text{F}_4\text{F}_4]^{2-}$	103.8	33.5	-13.5

^a s, u, and f indicate shared, unshared and “free” fluorine atoms, respectively. ^b The “starting clusters” and the corresponding calculated values are in italic. ^c No conv. indicates that the calculation does not converge.

**Figure 4.** Calculated isotropic chemical shift values versus experimental values for compounds from NaF--AlF_3 and $\text{CaF}_2\text{--AlF}_3$ binary systems. The solid line corresponds to $\delta_{\text{iso,cal}} = \delta_{\text{iso,exp}}$. The dashed line corresponds to the linear regression.

deviation between experimental and calculated δ_{iso} values is equal to 5 ppm, which is a quite nice result.

3.1.2. $\text{CaF}_2\text{--AlF}_3$ Binary System. The $\alpha\text{-CaAlF}_5$ phase contains one shared fluorine atom and two unshared atoms. $\text{Ca}_2\text{-AlF}_7$ includes four unshared and one “free” fluorine atoms.⁹ The δ_{iso} values calculated using the “starting clusters” are less satisfactory than for the previous binary system. The “starting cluster” $[\text{FCa}_3\text{F}]^{4+}$ is retained only for the “free” fluorine atom. For the other atoms, a better agreement between experimental and calculated δ_{iso} values is reached with larger clusters. The fluorine sites, the $\delta_{\text{iso,exp}}$ values, the “starting clusters” and the retained clusters, and the corresponding $\delta_{\text{iso,cal}}$ values are collected in Table 4. Using the retained clusters and the corresponding $\delta_{\text{iso,cal}}$ values, the RMS deviation between experimental and calculated δ_{iso} values is equal to 12 ppm.

For the two binary systems NaF--AlF_3 and $\text{CaF}_2\text{--AlF}_3$, a comparison between calculated and experimental δ_{iso} values is shown in Figure 4. A linear regression performed on these results provides $\delta_{\text{iso,cal}} = 0.79 \delta_{\text{iso,exp}} + 1.6$ with $R^2 = 0.85$. The largest difference between measured and calculated values is equal to 24.6 ppm (Tables 3 and 4).

3.1.3. $\text{BaF}_2\text{--AlF}_3$ Binary System. $\alpha\text{-BaAlF}_5$, $\beta\text{-BaAlF}_5$, and $\gamma\text{-BaAlF}_5$ include shared and unshared fluorine sites.⁹ For all the shared fluorine atoms, the “starting clusters” led to the best

TABLE 5: Fluorine Sites, $\delta_{\text{iso,exp}}$, Clusters Used for Calculation, $\delta_{\text{iso,cal}}$ and $\Delta\delta_{\text{iso}} = \delta_{\text{iso,exp}} - \delta_{\text{iso,cal}}$ Values (ppm) for BaAlF_5 Phases

compound	site ^a	$\delta_{\text{iso,exp}}$	cluster ^b	$\delta_{\text{iso,cal}}^{\text{b}}$	$\delta_{\text{iso,cal}}$	$\Delta\delta_{\text{iso}}$
$\alpha\text{-BaAlF}_5$	F1 (u)	51	$[\text{FAlF}_4\text{Ba}_2\text{F}_4]^{2-}$	-43.3	98.5	-47.5
	F2 (u)	56	$[\text{FAlF}_4\text{BaF}_2\text{BaF}_4\text{Ba}]$	363.5	86.1	-30.1
	F3 (u)	41	$[\text{FAlF}_4\text{BaF}_2\text{BaF}_2\text{Ba}]^+$	-44.7	72.9	-31.9
	F4 (u)	32	$[\text{FAlF}_4\text{BaF}_2\text{BaF}_2\text{F}]^{2+}$	-47.2	97.8	-65.8
	F5 (s)	10	$[\text{FAl}_2\text{F}_8]^{3-}$	-11.6	/	21.6
$\beta\text{-BaAlF}_5$	F1 (s)	12	$[\text{FAl}_2\text{F}_8]^{3-}$	-9.6	/	21.6
	F2 (u)	22	$[\text{FAlF}_4\text{FBa}_2\text{F}_3\text{BaF}]^-$	-46.0	62.8	-40.8
	F3 (u)	58	$[\text{FAlF}_4\text{Ba}_2\text{F}_4\text{BaF}_2]^{2-}$	-47.5	72.3	-14.3
	F4 (u)	46	$[\text{FAlF}_4\text{BaF}_2\text{BaF}]^-$	-47.3	107.1	-61.1
	F5 (s)	18	$[\text{FAl}_2\text{F}_8]^{3-}$	-7.0	/	25.0
	F6 (u)	42	$[\text{FAlF}_4\text{FBa}_3\text{F}_4]^-$	-43.6	83.3	-41.3
	F7 (u)	39	$[\text{FAlF}_4\text{FBaF}_2\text{BaF}_2\text{F}_2]$	-44.0	61.6	-22.6
	F8 (u)	68	$[\text{FAlF}_4\text{Ba}_2\text{F}_8]^{6-}$	-47.0	103.6	-35.6
	F9 (u)	28	$[\text{FAlF}_4\text{BaF}_2\text{Ba}]^+$	-49.3	112.9	-84.9
	F10 (u)	26	$[\text{FAlF}_4\text{BaF}_2\text{BaF}_2\text{BaF}_2]^-$	-49.4	57.3	-31.3
$\gamma\text{-BaAlF}_5$	F1 (u)	43	$[\text{FAlF}_4\text{BaF}_2\text{BaF}_2\text{BaF}]^-$	-48.7	86.9	-43.9
	F2 (u)	46	$[\text{FAlF}_4\text{BaF}_2\text{BaF}_2\text{BaF}]^+$	-48.8	94.7	-48.7
	F3 (u)	51	$[\text{FAlF}_4\text{BaF}_2\text{BaF}_3\text{Ba}]$	-46.0	90.9	-39.9
	F4 (u)	34	$[\text{FAlF}_4\text{FBa}_2\text{FBaF}_2]$	-49.7	66.7	-32.7
	F5 (u)	43	$[\text{FAlF}_4\text{BaF}_3\text{BaF}_2\text{AlBa}]^{2+}$	-46.7	124.4	-81.4
	F6 (u)	21	$[\text{FAlF}_3]^{3-}$	-34.8	/	55.8
	F7 (u)	43	$[\text{FAlF}_4\text{FBa}_2\text{F}_4\text{Ba}]^-$	-44.9	102.6	-59.6
	F8 (u)	37	$[\text{FAlF}_3]^{3-}$	-32.9	/	69.9
	F9 (s)	30	$[\text{FAl}_2\text{F}_8]^{3-}$	-5.6	/	35.6
	F10 (s)	17	$[\text{FAl}_2\text{F}_8]^{3-}$	-5.3	/	22.3

^a s and u indicate shared and unshared fluorine atoms, respectively.

^b The “starting clusters” and the corresponding calculated values are in italic.

agreement between calculated and experimental δ_{iso} values. On the other hand, for all the unshared fluorine sites, a varying number of atoms has to be added to the “starting cluster” in order to minimize the difference between experimental and calculated δ_{iso} values. For F6 and F8 of $\gamma\text{-BaAlF}_5$, no suitable clusters were found. The fluorine sites, the $\delta_{\text{iso,exp}}$ values, the “starting clusters” and the retained clusters, and the corresponding $\delta_{\text{iso,cal}}$ values are collected in Table 5.

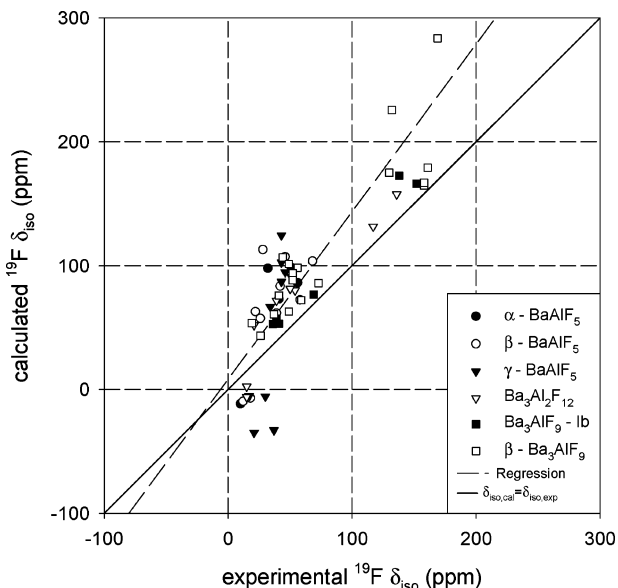
In $\text{Ba}_3\text{Al}_2\text{F}_{12}$, shared, unshared and “free” fluorine atoms are encountered.⁹ $\text{Ba}_3\text{AlF}_9\text{--Ib}$ and $\beta\text{-Ba}_3\text{AlF}_9$ phases contain only unshared and “free” fluorine sites.⁹ For all the shared fluorine atoms, the $[\text{FAl}_2\text{F}_8]^{3-}$ “starting clusters” led to a suitable agreement between calculated and experimental δ_{iso} values. This agreement was slightly improved by the addition of one fluorine atom to the cluster of F1 in $\text{Ba}_3\text{Al}_2\text{F}_{12}$ (Table 6). For the “free” fluorine sites, the $[\text{FBa}_4]^{7+}$ “starting clusters” are the most often encountered and led to a reasonable agreement between calculated and experimental δ_{iso} values. However, for F16 to F18 of $\beta\text{-Ba}_3\text{AlF}_9$, the environments of the central F atoms are atypical as the nearest neighbor is another fluorine atom. For these fluorine atoms, disappointing results are obtained using the “starting clusters”: the deviation between calculated and experimental δ_{iso} values is larger than 200 ppm. Increasing the cluster sizes for these three fluorine atoms does not allow us to reduce significantly the difference between experimental and calculated δ_{iso} values (Table 6). For the unshared F atoms, the δ_{iso} values calculated with the $[\text{FAlF}_4]^{2-}$ “starting clusters” are found between -50 ppm and -30 ppm when the experimental values are measured between 20 and 75 ppm. An addition of a varying number of NNN atoms to the “starting clusters” reduces the difference between calculated and experimental δ_{iso} values. The fluorine sites, the $\delta_{\text{iso,exp}}$ values, the “starting clusters” and the retained clusters, and the corresponding $\delta_{\text{iso,cal}}$ values are collected in Table 6.

For the $\text{BaF}_2\text{--AlF}_3$ binary system, using the retained clusters and the corresponding $\delta_{\text{iso,cal}}$ values, the RMS deviation between

TABLE 6: Fluorine Sites, $\delta_{\text{iso,exp}}$, Clusters Used for Calculation, $\delta_{\text{iso,cal}}$, and $\Delta\delta_{\text{iso}} = \delta_{\text{iso,exp}} - \delta_{\text{iso,cal}}$ Values (ppm) for $\text{Ba}_3\text{Al}_2\text{F}_{12}$, $\text{Ba}_3\text{AlF}_9\text{-Ib}$, and $\beta\text{-Ba}_3\text{AlF}_9$

compound	site ^a	$\delta_{\text{iso,exp}}$	cluster ^b	$\delta_{\text{iso,cal}}$	$\delta_{\text{iso,cal}}$	$\Delta\delta_{\text{iso}}$
$\text{Ba}_3\text{Al}_2\text{F}_{12}$	F1 (s)	15	$[\text{FAl}_2\text{F}_3\text{F}]^{4-}$	-5.9	2.3	12.7
	F2 (s)	15	$[\text{FAl}_2\text{F}_3]^{3-}$	-6.0	/	21.0
	F3 (f)	136	$[\text{FBa}_4]^{7+}$	157.5	/	-21.5
	F4 (f)	117	$[\text{FBa}_4]^{7+}$	131.5	/	-14.5
	F5 (u)	54	$[\text{FAlF}_4\text{FBa}_3\text{F}_3]^{2-}$	-47.6	80.0	-26.0
	F6 (u)	50	$[\text{FAlF}_4\text{Ba}_2\text{FBaF}_3]$	-46.9	81.3	-31.3
	F7 (u)	39	$[\text{FAlF}_4\text{FBaFBa}_2\text{F}_2]$	-48.2	71.7	-32.7
	F8 (u)	21	$[\text{FAlF}_4\text{BaF}_2\text{BaF}_3\text{Ba}]^{-}$	-48.9	52.0	-31.0
$\text{Ba}_3\text{AlF}_9\text{-Ib}$	F1 (u)	39	$[\text{FAlF}_4\text{Ba}_3\text{F}_3]^{-}$	-47.6	57.2	-18.2
	F2 (u)	41	$[\text{FAlF}_4\text{Ba}_3\text{F}_3]^{-}$	-49.0	52.9	-11.9
	F3 (f)	138	$[\text{FBa}_4]^{7+}$	172.7	/	-34.7
	F4 (f)	152	$[\text{FBa}_4\text{F}_7]$	169.7	166.2	-14.2
	F5 (u)	69	$[\text{FAlF}_4\text{Ba}_3\text{F}_4]$	-48.1	76.7	-7.7
$\beta\text{-Ba}_3\text{AlF}_9$	F6 (u)	36	$[\text{FAlF}_4\text{BaFBaF}_3\text{BaF}]^{-}$	-48.3	52.7	-16.7
	F1 (u)	26	$[\text{FAlF}_4\text{BaF}_3\text{FBaFBaF}]^{-}$	51.7	43.3	-17.3
	F2 (u)	56	$[\text{FAlF}_4\text{Ba}_2\text{FBaF}_3]$	-51.1	98.2	-42.2
	F3 (u)	73	$[\text{FAlF}_4\text{Ba}_2\text{F}_3\text{BaF}]$	-44.1	85.9	-12.9
	F4 (u)	37	$[\text{FAlF}_4\text{BaFBaFBaF}_2]$	-37.1	60.7	-23.7
	F5 (u)	59	$[\text{FAlF}_4\text{BaFBaFBaF}_2]$	-47.6	72.1	-13.1
	F6 (u)	49	$[\text{FAlF}_3\text{Ba}_2\text{F}_3\text{FBaF}]$	152.9	62.9	-13.9
	F7 (u)	19	$[\text{FAlF}_4\text{F}_2\text{Ba}_2\text{F}_2]^{2+}$	-44.8	53.5	-34.5
	F8 (u)	44	$[\text{FAlF}_2\text{Ba}_2\text{F}_2\text{F}_4\text{BaF}]^{-}$	167.5	106.5	-62.5
	F9 (u)	52	$[\text{FAlF}_3\text{BaF}]^{2-}$	-25.4	93.8	-41.8
	F10 (u)	41	$[\text{FAlF}_2\text{Ba}_2\text{F}_4\text{BaF}]^{+}$	126.9	75.9	-34.9
	F11 (u)	49	$[\text{FAlF}_2\text{BaF}_2\text{FBa}_2\text{F}_3]$	189.4	101.3	-52.3
	F12 (u)	52	$[\text{FAlF}_4\text{FBaFBa}_2\text{F}_2]$	-35.0	88.2	-36.2
	F13 (f)	158	$[\text{FBa}_4]^{7+}$	164.8	/	-6.8
	F14 (f)	158	$[\text{FBa}_4]^{7+}$	166.9	/	-8.9
	F15 (f)	161	$[\text{FBa}_4]^{7+}$	179.1	/	-18.1
	F16 (f)	169	$[\text{FBa}_3\text{F}_2\text{BaF}_2]^{2+}$	366.4	283.5	-114.5
	F17 (f)	149	$[\text{FBa}_2\text{F}]^{+}$	381.2	/	-232.2
	F18 (f)	132	$[\text{FF}_2\text{Ba}_2\text{AlBa}_2]^{8+}$	360.0	225.5	-93.5
	F19 (f)	130	$[\text{FBa}_2\text{F}_2\text{F}_4\text{BaF}_2\text{Ba}_2]^{+}$	244.0	174.9	-44.9

^a s, u and f indicate shared, unshared and “free” fluorine atoms, respectively. ^b The “starting clusters” and the corresponding calculated values are in *italic*.

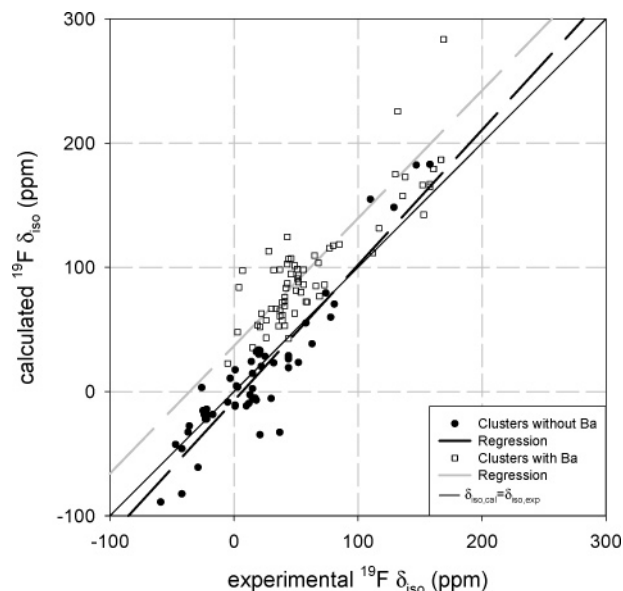
**Figure 5.** Calculated isotropic chemical shift values versus experimental values for compounds from $\text{BaF}_2\text{-AlF}_3$ binary systems. The solid line corresponds to $\delta_{\text{iso,cal}} = \delta_{\text{iso,exp}}$. The dashed line corresponds to the linear regression.

experimental and calculated δ_{iso} values is equal to 52 ppm. This last RMS deviation is larger than the previous ones. The largest difference between measured and calculated values is equal to 240 ppm (Tables 5 and 6). Figure 5, which shows a comparison between calculated and experimental δ_{iso} values, illustrates this. A linear regression leads to $\delta_{\text{iso,cal}} = 1.35 \delta_{\text{iso,exp}} + 8.0$ with $R^2 = 0.70$.

TABLE 7: Fluorine Sites, $\delta_{\text{iso,exp}}$, Clusters Used for Calculation, $\delta_{\text{iso,cal}}$, and $\Delta\delta_{\text{iso}} = \delta_{\text{iso,exp}} - \delta_{\text{iso,cal}}$ Values (ppm) for $\alpha\text{-BaCaAlF}_7$

site ^a	$\delta_{\text{iso,exp}}$	cluster ^b	$\delta_{\text{iso,cal}}$	$\delta_{\text{iso,cal}}$	$\Delta\delta_{\text{iso}}$
F1 (u)	37	$[\text{FAlF}_4\text{Ba}_2\text{F}_6]^{4-}$	-48.5	98.2	-61.2
F2 (u)	18	$[\text{FAlCa}_2\text{F}_4\text{F}_3]^{-}$	141.1	32.0	-14.0
F3 (u)	21	$[\text{FAlCa}_2\text{F}_4\text{F}_3]^{-}$	153.6	32.9	-11.9
F4 (f)	112	$[\text{FCa}_2\text{BaF}]^{4+}$	111.6	/	0.4
F5 (u)	41	$[\text{FAlF}_4\text{Ba}_2\text{FBaF}_2]^{+}$	-47.1	69.0	-28.0
F6 (u)	44	$[\text{FAlCa}_2\text{F}_4\text{BaF}_5]^{-}$	87.1	42.8	1.2
F7 (u)	37	$[\text{FAlF}_4\text{Ba}_2\text{FBaF}_4]^{-}$	-47.0	65.2	-28.2

^a u and f indicate unshared and “free” fluorine atoms, respectively. ^b The “starting clusters” and the corresponding calculated values are in *italic*.

**Figure 6.** Calculated isotropic chemical shift values versus experimental values for all the clusters with (white square) and without (black dot) barium atoms. The solid line corresponds to $\delta_{\text{iso,cal}} = \delta_{\text{iso,exp}}$. The gray and black dashed lines correspond to the linear regressions for clusters with and without barium atoms, respectively.

3.1.4. $\alpha\text{-BaCaAlF}_7$. $\alpha\text{-BaCaAlF}_7$ contains one “free” and six unshared fluorine sites.⁹ For the “free” fluorine atoms, the $[\text{FCa}_2\text{BaF}]^{4+}$ “starting cluster” leads to the best agreement between calculated and experimental δ_{iso} values. For the unshared fluorine atoms, a varying number of atoms has to be added to the $[\text{FAlF}_4]^{2-}$ “starting clusters” and all the retained clusters are different. The fluorine sites, the $\delta_{\text{iso,exp}}$ values, the “starting clusters” and the retained clusters, and the corresponding $\delta_{\text{iso,cal}}$ values are collected in Table 7. Using the retained clusters and the corresponding $\delta_{\text{iso,cal}}$ values, the RMS deviation between experimental and calculated δ_{iso} values is equal to 28 ppm, the largest difference being equal to 61 ppm.

To summarize, all the results (Tables 1 to 7) are gathered on the curve representing $\delta_{\text{iso,cal}}$ versus $\delta_{\text{iso,exp}}$ in Figure 6. The agreement between calculated and experimental values is quite fine for the clusters without barium with a RMS deviation equal to 22 ppm. On the contrary, for the clusters that contain barium atoms, the RMS deviation is equal to 51 ppm and some of the calculated values are really out of range. Linear regressions provide $\delta_{\text{iso,cal}} = 1.09 \delta_{\text{iso,exp}} - 7.3$ ($R^2 = 0.85$) and $\delta_{\text{iso,cal}} = 1.03 \delta_{\text{iso,exp}} + 36.7$ ($R^2 = 0.66$) for the clusters without and with barium, respectively.

3.2. Discussion. 3.2.1. Influence of Barium Atoms. Figure 6 confirms that the correlation between calculated and experimental δ_{iso} values obtained for the fluorine atoms of barium-

containing clusters is not really satisfactory. These results seem to point out that one key point is the description of the barium atom. A similar difficulty was already encountered applying the superposition model,⁹ in which two phenomenological parameter sets were needed to describe the barium atom, depending on the kind of fluorine atom it is linked to. It was tentatively related to the high number of electrons from the barium atom and its high polarizability. The present ab initio calculations seem to indicate that the CRENBL basis set used to describe the barium atoms is questionable. An improvement of the description of the barium atom may be to add d and f polarization functions. Such an improvement was already used by Tossell⁵⁴ for Ca and Sr in order to obtain accurate chemical shifts for ^{17}O in CaO and SrO. Unfortunately, these polarization functions do not exist yet for the barium atom.

3.2.2. Reliability of the "Starting Clusters". For the shared fluorine atoms of the compounds of the $\text{NaF}-\text{AlF}_3$, $\text{CaF}_2-\text{AlF}_3$, and $\text{BaF}_2-\text{AlF}_3$ binary systems, the $[\text{FM}_2\text{F}_8]$ "starting cluster" including other atoms that may be present in the cluster sphere is a satisfactory one, as the corresponding calculated δ_{iso} values are in good agreement with the experimental values.

For the "free" fluorine atoms, the "starting cluster" that includes the four nearest atoms led to satisfactory calculated δ_{iso} values in most of the cases. When the central fluorine atom is surrounded by four barium atoms as nearest neighbors, the suitable cluster is $[\text{FBA}_4]^{7+}$. In contrast, when the central fluorine atoms have another fluorine atom as nearest neighbor, no suitable cluster can be defined a priori.

For the unshared fluorine atoms of the compounds of the $\text{NaF}-\text{AlF}_3$ binary system, the $[\text{FAIF}_4]^{2-}$ "starting cluster" including all other atoms that may be present in the cluster sphere is a satisfactory one. The corresponding calculated δ_{iso} values are in quite good agreement with the experimental values. For the unshared fluorine atoms of the compounds of the $\text{CaF}_2-\text{AlF}_3$ and $\text{BaF}_2-\text{AlF}_3$ binary systems, and of $\alpha\text{-BaCaAlF}_7$, the prediction of a cluster is not so easy. The $[\text{FAIF}_4]^{2-}$ "starting cluster" must be enlarged. However, no rule for the enlargement of the "starting clusters" can be deduced from the comparison of the retained clusters. Nevertheless, $[\text{FAIF}_4\text{Ba}_3\text{F}_4]$ or $[\text{FAIF}_4\text{Ba}_3\text{F}_5]^-$ clusters are suitable for a majority (2/3) of the unshared fluorine atoms of the compounds of $\text{BaF}_2-\text{AlF}_3$ binary systems and of $\alpha\text{-BaCaAlF}_7$. As an example, the retained cluster for the unshared fluorine atom F7 in $\text{Ba}_3\text{Al}_2\text{F}_{12}$ is shown in Figure 2d.

4. Conclusion

To get a tractable ab initio method for calculation of ^{19}F isotropic chemical shifts, a systematization of the basis set choice and of the cluster building up was undertaken. In light of the previous studies, the basis sets were chosen to avoid exceptions. The central fluorine atom was described by the 6-311+G(d) basis set. For the other F atoms, the LanL2DZ basis set was used. For the metal atoms, the 3-21G(2d) basis set was chosen. When not available, the CRENBL basis set with the corresponding ECP, and augmented with 2d polarization functions when existing, is used.

The systematization of the cluster building-up was performed on highly symmetrical MF, MF_2 and MF_3 compounds, fluoroperovskites, fluoroaluminates KAlF_4 and RbAlF_4 , and barium fluorometalates BaMgF_4 , BaZnF_4 , and Ba_2ZnF_6 . From similarity between fluorine environments, "starting clusters" were defined for shared, unshared and "free" fluorine atoms. In any case, all the atoms included in the sphere containing the "starting clusters" were taken into account in the calculations.

These "starting clusters" were tested on compounds from the $\text{NaF}-\text{AlF}_3$, $\text{BaF}_2-\text{AlF}_3$, and $\text{CaF}_2-\text{AlF}_3$ binary systems that are built up from a MF_6 octahedron network. For each fluorine atom, several clusters were tested beginning with the "starting" one up to the cluster containing the NNN atoms at least. The cluster that led to the best agreement between calculated and experimental δ_{iso} values was retained. For the shared fluorine atoms, the $[\text{FM}_2\text{F}_8]$ "starting cluster" leads to satisfactory results. For the "free" fluorine atoms with four NN Ba atoms, the "starting cluster" $[\text{FBA}_4]^{7+}$ is also suitable. On the contrary, for the unshared atoms, the $[\text{FAIF}_4]^{2-}$ "starting cluster" leads to bad result in compounds of the $\text{BaF}_2-\text{AlF}_3$ and $\text{CaF}_2-\text{AlF}_3$ binary systems and has to be enlarged in most of the cases as it was foreseeable to take into account the metal and also the NN fluorine atom effects (Figure 2d). For some of the free and all the unshared fluorine atoms, the build up of the clusters remains empirical. This is the main limitation of the method.

Actually a more thorough study should be performed for each individual compound using a better computational method and cluster description. This is out of the scope of the present paper, which nevertheless shows that a fairly simple methodology yields adequate results over a wide range of fluoride compounds. The poor results for Ba-containing systems are probably due to the poor basis sets used for the Ba atom and should not detract from the overall reasonable results.

One way to overcome the limitation of the cluster method may be to take into account the crystal periodicity in the chemical shift computation through the use of software including periodic boundary conditions, as it was done for oxides in refs 55–57. Such work is now in progress for fluorides.

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