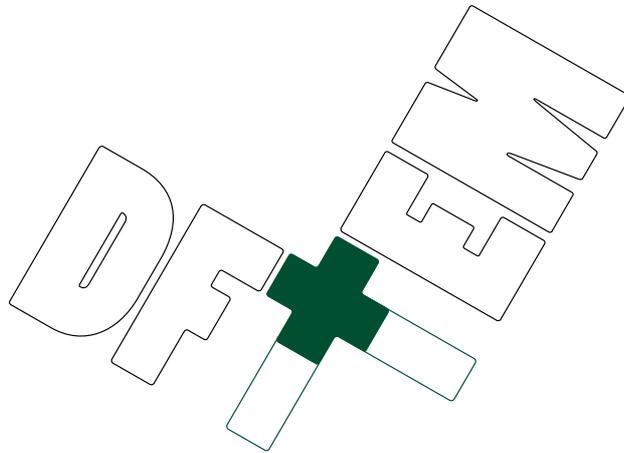


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Ab initio calculations of ^{27}Al quadrupolar parameters in fluoroaluminates

Monique Body,¹ Christophe Legein,¹ Jean-Yves Buzaré,¹
 Florent Calvayrac,¹ Gilles Silly,² and Peter Blaha³

¹*Institut de Recherche en Ingénierie Moléculaire et Matériaux fonctionnels,
 CNRS FR 2575, Université du Maine, Le Mans, FR 72085, France*

²*Laboratoire de Physicochimie de la Matière Condensée, CNRS UMR 5617,
 Institut Charles Gerhardt, Montpellier, FR 34095, France*

³*Institute of Materials Chemistry, Vienna University of Technology, A-1060 Vienna, Austria*

The development of reliable methods for electric field gradient calculations is a challenging task with considerable practical interest in solid state NMR : when intensity or chemical shielding is not informative, a problem arises in the assignment of the resonances. A strategy may be to compare the experimental values of the quadrupolar parameters to those obtained by theoretical calculations and to make assignments on this basis.

Previous studies [1-11] have shown the ability of the WIEN2k DFT code [12] to calculate the quadrupolar parameters from given structural data. The quadrupolar frequency ν_Q and the asymmetry parameter η_Q can be related to the EFG components through the following equations :

$$\nu_Q = \frac{3eV_{zz}Q}{2I(2I-1)h} \quad \text{and} \quad \eta_Q = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

The present study relies on ^{27}Al SATRAS and MQ-MAS spectra recorded for eleven compounds from the $\text{CaF}_2\text{-AlF}_3$ and $\text{BaF}_2\text{-AlF}_3$ binary systems and $\text{CaF}_2\text{-BaF}_2\text{-AlF}_3$ ternary system. The reconstruction of the SATRAS spectra, using the information issued from the MQ-MAS spectra when needed, leads to the precise determination of the NMR quadrupolar parameter values for fifteen aluminium sites, even for compounds with several crystallographic sites [13].

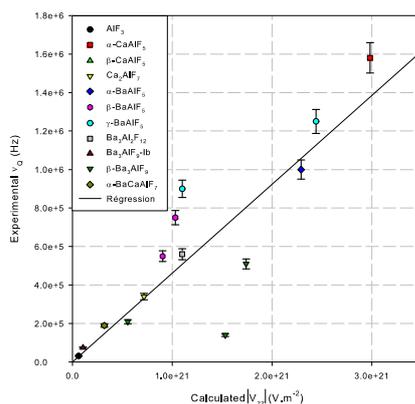


Fig. 1 Experimental quadrupolar frequency versus calculated $|V_{zz}|$. The solid line corresponds to the linear regression $\nu_Q = 4.619 \cdot 10^{-16}|V_{zz}|$ with $R^2 = 0.799$.

Preliminary calculations were performed using the crystallographic structures issued from XRD, taking $R_{MT}.K_{MAX} = 5$ and 100 k-points. For the multi-site compounds, the attributions were performed with respect to the proportionality between V_{zz} and ν_Q . The agreement between calculated and experimental values for both quadrupolar frequencies ν_Q and asymmetry parameters η_Q is not satisfactory as evidenced in figures 1 and 2. Moreover, this discrepancy is larger for the structures determined by X-Ray powder diffraction.

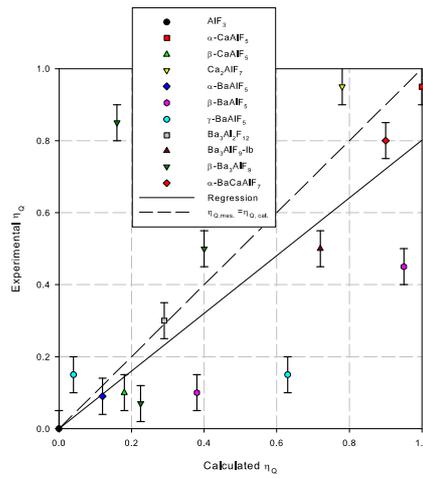


Fig. 2 Experimental asymmetry parameters versus calculated ones. The solid line corresponds to the linear regression $\eta_{Q,exp.} = 0.801\eta_{Q,cal.}$ ($R^2 = 0.406$) and the dashed one to $\eta_{Q,exp.} = \eta_{Q,cal.}$.

In a second step, the eleven structures have been optimized with WIEN2k code, by adjusting the atomic positions, keeping the experimental cell parameters unchanged, until the forces acting on all atoms are reduced to values lower than 3 mRy/u.a.. Final EFG computations were performed taking $R_{MT}.K_{MAX} = 8$ (7 for β - Ba_3AlF_9 owing to its complex structure). A comparison with the initial structures shows that the AlF_6^{3-} octahedron distortions are reduced in the optimized structures and the atomic position variations are globally in agreement with the uncertainties inferred from the XRD refinements. β - Ba_3AlF_9 is one exception: the shifts of the atomic positions reached 1.0 Å for two of the fluorine atoms. However, the resulting structure is more satisfactory as some crystallographic anomalies such as F-F distances ranging between 2.0 and 2.3 Å have now disappeared [13].

A really improved agreement is obtained after the structure optimizations for the quadrupolar parameters of ^{27}Al . This agreement concerns not only the quadrupolar frequency (figure 3), but also the asymmetry parameter (figure 4) which is much more difficult to reproduce, due to its high sensitivity to variations of the atomic positions around the studied nucleus. Moreover, from the slope of the linear regression, it is possible to infer the ^{27}Al quadrupolar moment. We obtain $Q(^{27}Al) = 1,6 (\pm 0,1) \times 10^{-29} \text{ m}^2$, which is slightly higher than the values calculated by Pyykkö [14]: $Q(^{27}Al) = 1,466 \times 10^{-29} \text{ m}^2$ or by Silly *et al.* [8]: $Q(^{27}Al) = 1,506 \times 10^{-29} \text{ m}^2$. In agreement with Iglesias *et al.* who performed the same kind of calculation on polymorphics of Al_2SiO_5 [1], all our results suggest that either the quadrupolar moment value given by Pyykkö [14] is underestimated, or the GGA approach in WIEN2k code introduces a systematic error in the description of the Al-X bonds.

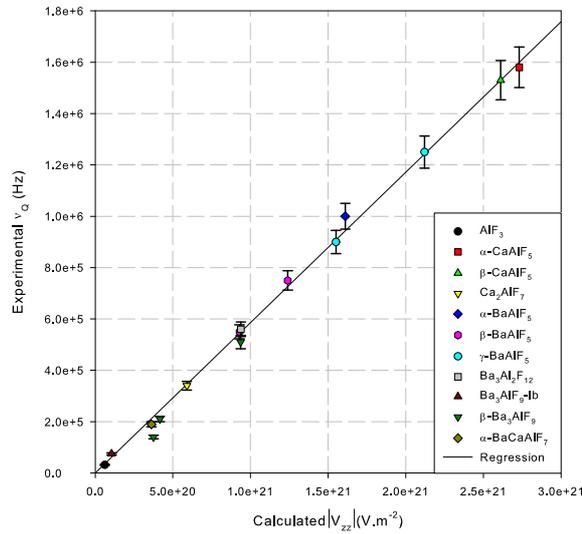


Fig. 3 Experimental quadrupolar frequency versus calculated $|V_{zz}|$ after structural optimization. The solid line corresponds to the linear regression $\nu_Q = 5.858 \cdot 10^{-16}|V_{zz}|$ with $R^2 = 0.996$.

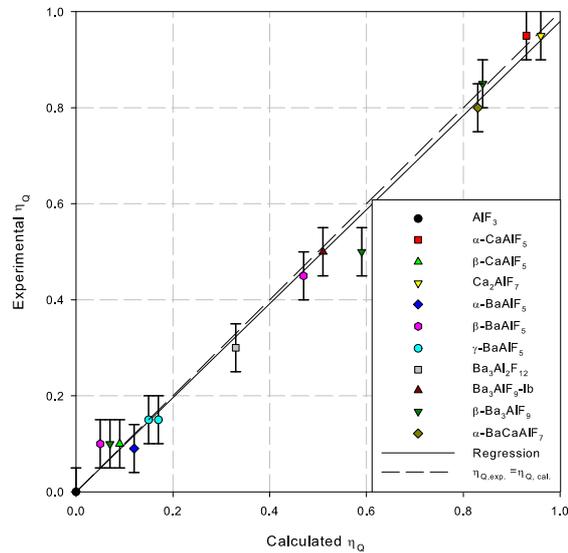


Fig. 4 Experimental asymmetry parameters versus calculated ones after structural optimization. The solid line corresponds to the linear regression $\eta_{Q,exp.} = 0.979\eta_{Q,cal.}$ ($R^2 = 0.992$) and the dashed one to $\eta_{Q,exp.} = \eta_{Q,cal.}$.

This study confirms that WIEN2k is a highly reliable ab initio method for calculation of the quadrupolar parameters. Structure optimization is an essential step to reach a fine agreement between calculated and experimental values, especially for structures determined from powder XRD. This approach, coupling NMR experiments and ab initio calculations, is extendable to other quadrupolar nuclei, and allows to refine crystallographic structures especially when they lack accuracy.

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