

# Study of the modifications of the electric field gradient in hexafluorohafnates of transition metals above room temperature

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The temperature dependence above room temperature of the hyperfine quadrupole interactions measured by the time differential perturbed angular correlations technique at hafnium sites in  $AHfF_6 \cdot nH_2O$ , with  $A = Co$  and  $Zn$  and  $n = 6, 4$  and  $0$ , is presented. The different steps of the dehydration process are reflected by modifications on the hyperfine quadrupole parameters at increasing temperature. The changes in the electric field gradient as water molecules are lost are interpreted in terms of distortions induced in the  $[HfF_6]^{2-}$  octahedrons.

## 1. Introduction

Many works have been published about the low temperature behavior of the family of compounds of general formula  $A^{II}B^{IV}F_6 \cdot 6H_2O$ , with  $A^{II} = Ni, Co$  and  $Zn$ , and  $B^{IV} = Si, Ti, Zr$ , and  $Hf$  (ref. [1] and references therein). On the other hand, only a few papers paid attention to the processes that take place above room temperature [2–4]. At room temperature, most of the compounds crystallize in the space group  $R\bar{3}$  ( $Z = 1$ ). The structure is composed of trigonally distorted  $[A^{II}(H_2O)_6]^{2+}$  and  $[B^{IV}F_6]^{2-}$  octahedrons linked by weak hydrogen bonds and packed in a CsCl structure [1].

The results reported by Davidovitch et al. [2] indicated that most of these compounds dehydrated in three steps, losing two water molecules in each one.

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The anhydrous compounds ( $A^{II}B^{IV}F_6$ ) exhibit two crystalline phases: the  $R\bar{3}$  one (low temperature) and the  $Fm\bar{3}m$  one (high temperature) [4].

During the last years, hyperfine techniques were extensively used in the microscopic study of the mechanisms involved in chemical reactions. Examples of the use of the time differential perturbed angular correlations (TDPAC) technique to study these processes are mentioned in the review paper of Butz and Lerf [5].

The thermal behavior (below the dehydration temperature) of the hyperfine quadrupole interaction for these kinds of compounds having hafnium as the central atom has been studied in detail in ref. [6].

In this paper, we report results obtained using the TDPAC technique for  $CoHfF_6 \cdot 6H_2O$  between 300 and 625 K, and  $ZnHfF_6 \cdot 6H_2O$  between 300 and 400 K. Measurements at higher temperatures indicated that both compounds decompose to hafnium oxide via a not yet elucidated set of reactions that seems to be dependent on the thermal history of the sample. This will be the subject of a forthcoming paper.

## 2. Experimental

The  $A^{II}HfF_6 \cdot 6H_2O$  samples were prepared following the method outlined by Davidovitch et al. [7]. The compounds were identified using X-ray powder diffraction analysis.

The TDPAC technique allows us to determine the hyperfine interaction between a radioactive nucleus, decaying through a two-step cascade, and its surroundings by measuring the time dependence of the angular distribution of the second nuclear emission (within the order of the mean lifetime of the intermediate state of the cascade) relative to the direction of the first one.

In the case of quadrupole interactions, the perturbation arises from the electric field gradient (EFG) acting on the quadrupole moment ( $Q$ ) of the intermediate nuclear level of the cascade.

This interaction is described by the so-called perturbation factor ( $A_{22}G_{22}(t)$ ) [8] that, in the case of a  $\gamma$ - $\gamma$  cascade with intermediate nuclear spin  $I = 5/2$  and static quadrupole interactions in polycrystalline samples, can be written as

$$G_{22}(t) = \sigma_{20} + \sum_{n=1}^3 \sigma_{2n} \cos(\omega_n t) e^{-\delta \omega_n t}. \quad (1)$$

In eq. (1),  $\omega_n$  are already-known functions [9] of the quadrupole frequency  $\omega_Q = e^2 Q V_{zz} / 4I(2I - 1)\hbar$  and of the asymmetry parameter  $\eta = V_{xx} - V_{yy} / V_{zz}$ , of the EFG, the  $\sigma_{2n}$  coefficients depend on  $\eta$ , and  $\delta$  measures the dispersion of the  $\omega_Q$  values arising from defects and/or impurities of the lattice.

Fluctuating EFGs can be described using the Abragam-Pound perturbation factor [10] deduced for fast relaxation processes, which can be written as

$$G_{22}(t) = e^{-\lambda t}, \quad (2)$$

where  $\lambda$  is a function of the correlation time associated to the relaxation process.

Whenever the probes of a certain sample are occupying non-equivalent sites, the situation is described considering a linear superposition of perturbation factors  $G_{2i}(t)$  as defined in eqs. (1) and/or (2),

$$G_{22}(t) = \sum_{i=1} f_i G_{2i}(t). \quad (3)$$

The  $f_i$  coefficients are the relative abundances of each interaction.

A nonlinear least-squares fitting program was used to draw the hyperfine quadrupole parameters  $\omega_Q$ ,  $\eta$  and  $\delta$  ( $\lambda$  if the case) and the relative fractions  $f$  from the experimental data.

The 133–482 keV  $\gamma$ – $\gamma$  cascade of the  $^{181}\text{Ta}$  used in this work as the TDPAC probe was obtained by thermal neutron irradiation of  $^{180}\text{Hf}$ . A two-CsF detector high time-resolution setup ( $2\tau = 0.75$  ns at Ta energies) supplied with an electric furnace, which permitted heating the samples in situ within  $\pm 1$  K, was used to obtain the experimental results. Details on the technique and other characteristics of the  $^{181}\text{Ta}$  cascade can be found elsewhere (ref. [8], and references therein).

### 3. Results

The room temperature spectra obtained for the cobalt and zinc compounds were identical to those reported in ref. [6].

Figure 1 shows the spectra obtained at selected temperatures where changes are clearly shown. Table 1 exhibits the hyperfine quadrupole parameters.

Figures 2(a) and 2(b) display the temperature behavior of the quadrupole interaction frequencies determined for each compound.

$\text{CoHfF}_6 \cdot 6\text{H}_2\text{O}$ : The room temperature TDPAC spectrum obtained for this sample showed a single quadrupole interaction arising from a weak ( $\omega_Q = 23.1_6$  Mrad/s), non-asymmetric and well-defined ( $\delta = 3_2\%$ ) EFG. At higher temperatures, the interaction is replaced by a slightly asymmetric new interaction which exhibits a higher quadrupole frequency. This latter interaction is again substituted at around 423 K by a dynamical interaction that remains up to 625 K, the highest temperature achieved for this sample.

$\text{ZnHfF}_6 \cdot 6\text{H}_2\text{O}$ : As in the preceding case, the room temperature spectrum of this sample presents a single interaction up to 350 K. The TDPAC spectrum obtained at 369 K was also fitted with a single quadrupole interaction of very similar shape to that of the room temperature one with a higher asymmetry parameter. The 395 K spectrum exhibited a coexistence of two interactions: a dynamical one (populated 70%) and a static interaction ( $\omega_Q = 112_1$  Mrad/s,  $\eta = 0.14_4$  and  $\delta = 2_1\%$ ) 30% populated.

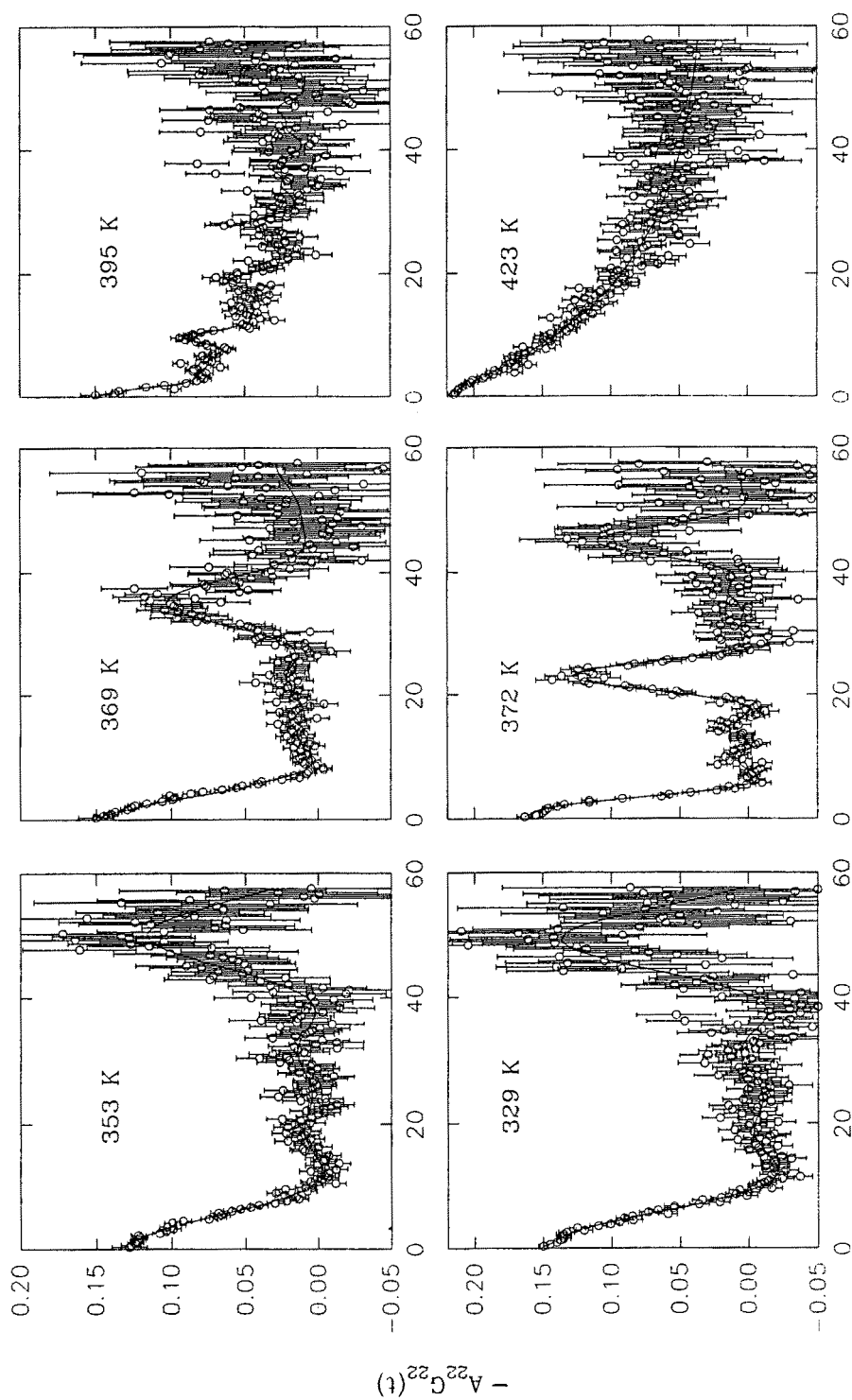


Fig. 1. For the Zn compound (upper), the corresponding  $\text{ZnHfF}_6 \cdot \text{H}_2\text{O}$ ,  $\text{ZnHfF}_6 \cdot 4\text{H}_2\text{O}$  and a coexistence of the cubic-hexagonal phase of the anhydrous compound  $\text{ZnHfF}_6$  are shown. In the case of the Co compound (lower), the hyperfine interaction pattern corresponding to the as-prepared compound, the  $\text{CoHfF}_6 \cdot 4\text{H}_2\text{O}$  and the cubic phase interaction of  $\text{CoHfF}_6$  are shown.

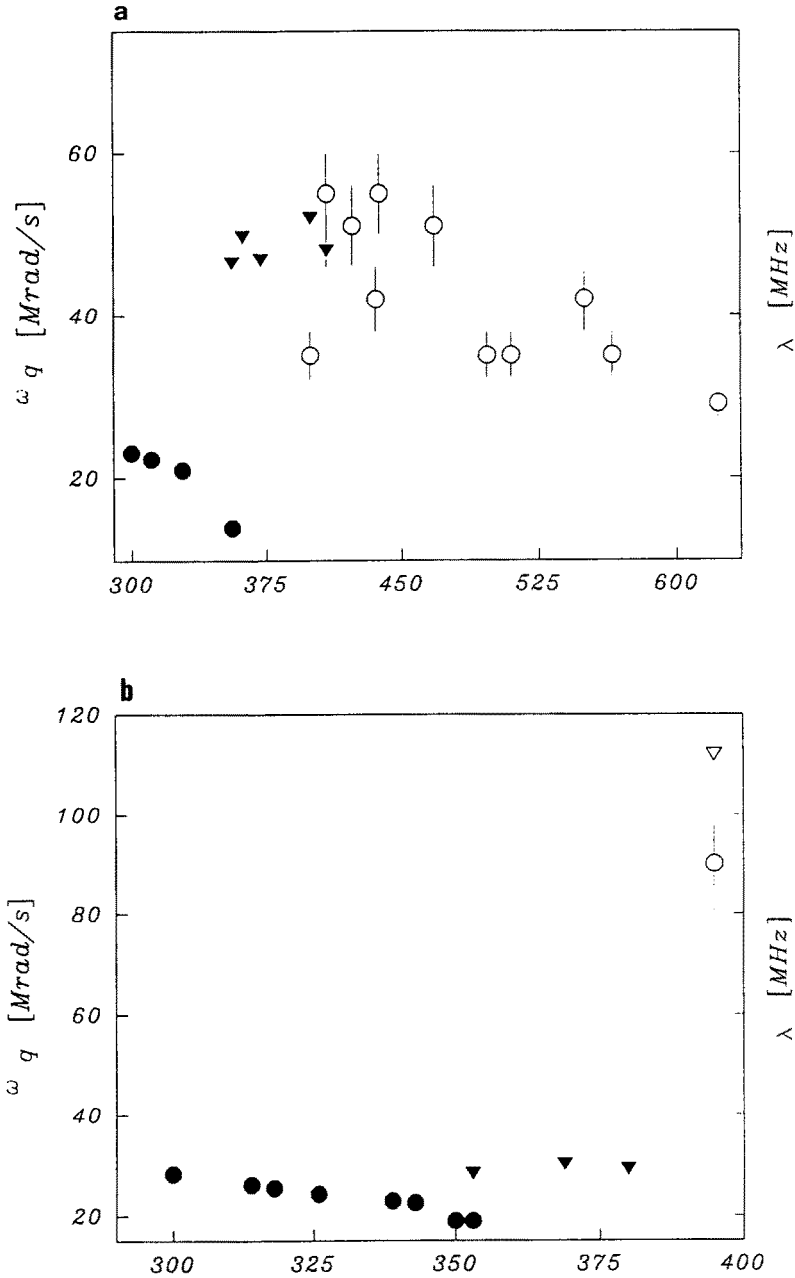


Fig. 2. Thermal behavior of the hyperfine quadrupole frequency ( $\omega_Q$ ) and relaxation parameter ( $\lambda$ ) in cobalt (a) and Zn (b) compounds. Full circles correspond to the hexaaquo compounds, full triangles represent the interactions in the tetraaquo compounds, an open triangle is used for the hexagonal phase of ZnHfF<sub>6</sub>, and open circles correspond to values of  $\lambda$  in MHz and must be read in the right axis of the figures.

Table 1

Hyperfine quadrupole parameters drawn from the TDPAC spectra for all the compounds investigated in this paper. Subscripts are the error bands determined for each parameter, (\*) means fixed parameter during the fit.

Compound	$T$ (K)	$\omega_Q$ (Mrad/s)	$\eta$	$\delta$ (%)
CoHfF <sub>6</sub> ·6H <sub>2</sub> O	329	19.6 <sub>6</sub>	0.00*	3 <sub>2</sub>
CoHfF <sub>6</sub> ·4H <sub>2</sub> O	372	49.7 <sub>2</sub>	0.08 <sub>3</sub>	1.5 <sub>4</sub>
CoHfF <sub>6</sub> (c)	423		$\lambda = 51_5$ MHz	
ZnHfF <sub>6</sub> ·6H <sub>2</sub> O	353	21.0 <sub>2</sub>	0.11 <sub>4</sub>	2 <sub>1</sub>
ZnHfF <sub>6</sub> ·4H <sub>2</sub> O	369	30.0 <sub>3</sub>	0.15 <sub>3</sub>	4 <sub>1</sub>
ZnHfF <sub>6</sub> (h)	395	112 <sub>1</sub>	0.14 <sub>4</sub>	2 <sub>1</sub>
ZnHfF <sub>6</sub> (c)			$\lambda = 90_{10}$ MHz	

#### 4. Discussion

The hyperfine quadrupole frequencies between room temperature and 350 K (Zn) and 353 K (Co) show a strong temperature dependence which has already been interpreted in ref. [6] as being due to modifications in the amplitude of the vibrational spectra. The sharp changes observed above those temperatures indicate that either phase transitions or chemical reactions occur.

In order to understand what the modifications observed in the hyperfine parameters mean, derivative thermogravimetric analysis (DTG) at a rate of 10 K/min was performed. The results of the thermogram indicated that the loss of mass corresponds to a two-step dehydration, first losing two water molecules and then losing the other four (the temperatures determined for these reactions can be seen in table 2). This two-step process has already been observed for the analogous compound NiHfF<sub>6</sub>·6H<sub>2</sub>O [3]. The temperatures at which the quadrupole interaction

Table 2

Start and end temperatures for the dehydration reactions reported in this paper.  $T_s$  means the temperature at which the derivative mass curve in the thermogram begins to change its slope.  $T_e$  means the temperature at which the derivative mass curve in the thermogram reaches its minimum, indicating the end of the mass loss.

A <sup>II</sup>	First dehydration		Second dehydration	
	$T_s$ (K)	$T_e$ (K)	$T_s$ (K)	$T_e$ (K)
cobalt	348	374	393	421
zinc	331	365	378	404

changes are in good agreement with those determined by DTG for the dehydration temperatures, indicating clearly that between 372 and 409 K (Co) and 369 and 380 K (Zn) the quadrupole parameters drawn from the TDPAC spectra can be associated with the respective tetrahydrates  $\text{CoHfF}_6 \cdot 4\text{H}_2\text{O}$  and  $\text{ZnHfF}_6 \cdot 4\text{H}_2\text{O}$ , and that the loss of two water molecules introduces a noticeable modification in the neighborhood of hafnium sites.

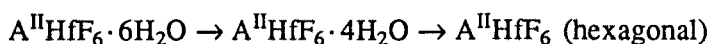
Consequently, at higher temperatures the quadrupole interactions observed correspond to those of the anhydrous compounds.

With regard to the anhydrous compounds, it is clear that they undergo a transition from the hexagonal phase to the cubic phase near 338 K for  $\text{CoHfF}_6$ ; no information was available for  $\text{ZnHfF}_6$ .

The analysis of TDPAC data together with the DTG results indicated that in the case of the cobalt compound, the anhydrous phase is obtained at temperatures where the stable one is the cubic phase. Thus, it is possible to relate the dynamic hyperfine quadrupole interaction (determined above 423 K) with the cubic phase of this compound. Dynamical EFGs associated with the cubic phase of these compounds have already been reported [3].

Dynamical interactions were also observed to be present in Zn (coexisting with static interactions). As in the latter case, it is interpreted as arising from the cubic phase of this compound. Related to the static quadrupole interaction, a similar quadrupole interaction was observed for the hexagonal phase of  $\text{NiHfF}_6$  [3]. By analogy, the static interaction determined at 395 K for Zn can then be related to its hexagonal phase.

Let us now discuss some common features of the hyperfine quadrupole interactions, disregarding the transition metal of the studied substances: the EFG, at hafnium sites, is stronger and more asymmetric as the transformations

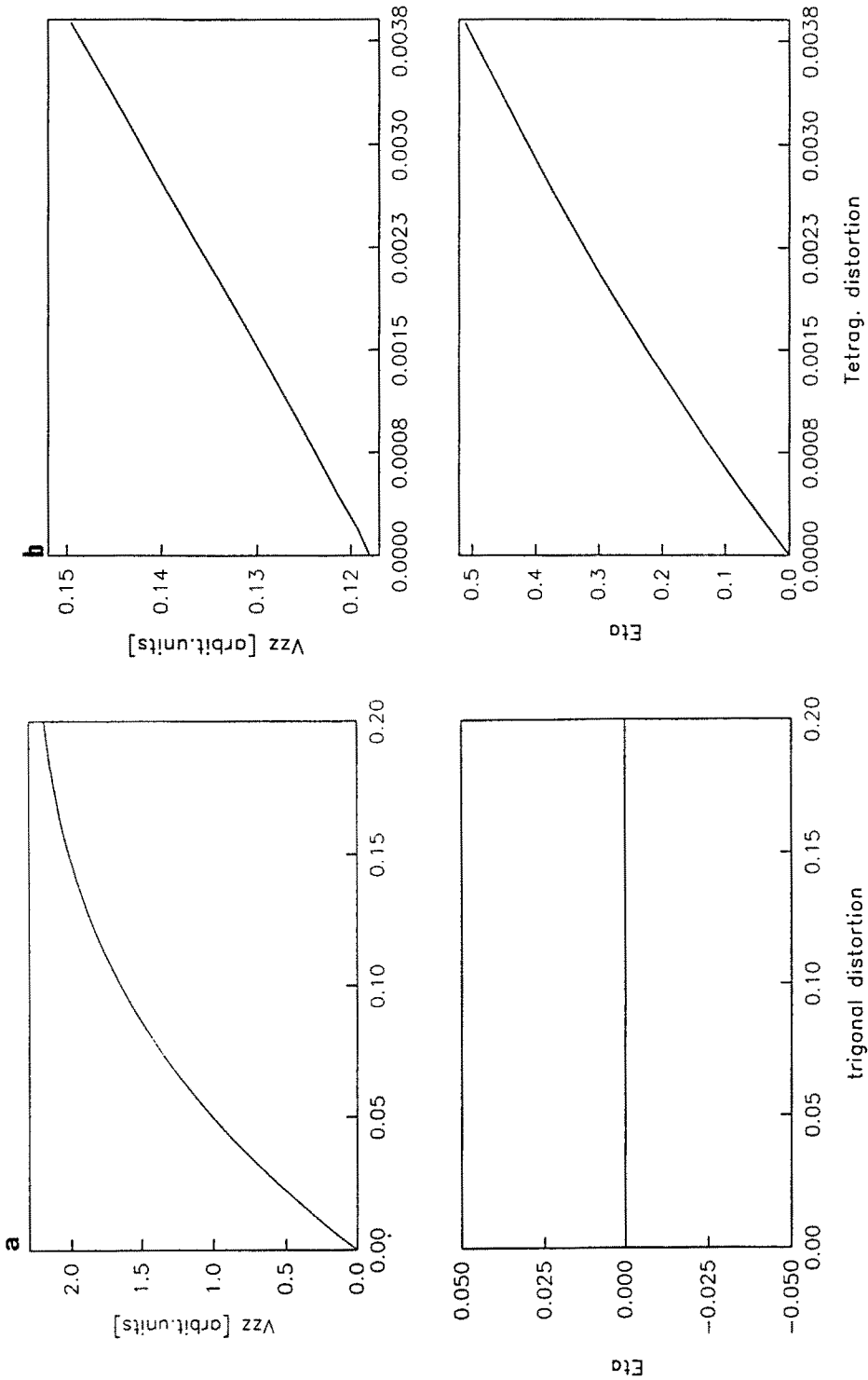


occur and certainly this is due to induced distortions in the  $[\text{HfF}_6]^{2-}$  octahedra [3].

Assuming that the consequences of the loss of water can be either an increase in the initial trigonal distortion or the addition of another distortion, point charge calculations, taking into account that the EFG is mainly due to the first coordination shell around the hafnium sites, were done involving both situations.

In the first case (fig. 3(a)), it is determined that only the  $V_{zz}$  component of the EFG varies as the trigonal distortion increases (the asymmetry parameter remaining unchanged,  $\eta = 0$ ). In the second case (fig. 3(b)) and assuming that the additional distortion is a tetragonal one, it is obtained that both the  $V_{zz}$  as well as  $\eta$  become greater with an increasing distortion.

These simple calculations could suggest that the loss of water molecules induces tetragonal distortions around the hafnium sites, giving rise to a more intense and asymmetric EFG.



**Fig. 3.** Calculated electric field gradient strength (upper) and asymmetry parameter (lower) for (a) trigonal distortion only; (b) tetragonal distortion plus 0.005 of trigonal distortion. The amount of each distortion is a dimensionless number that represents the fractional shift in the position of each atom arising from each distortion.



## 5. Conclusions

Using the TDPAC technique, we have described the hyperfine quadrupole parameters of  $\text{CoHfF}_6 \cdot 4\text{H}_2\text{O}$ ,  $\text{ZnHfF}_6 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoHfF}_6$  (cubic),  $\text{ZnHfF}_6$  (cubic), and  $\text{ZnHfF}_6$  (hexagonal), which all have analogous characteristics to those already determined for nickel compounds.

The changes in the EFG arise from the modifications induced in the hafnium surrounding as a consequence of a two-step dehydration process. This two-step process is observed for the first time in the case of the zinc compound, in disagreement with the results reported by Davidovitch et al. [2].

Point charge calculations taking the first coordination shell of the hafnium atom into account suggest that the trigonal distorted  $[\text{HfF}_6]^{2-}$  octahedra of the tetrahydrates and the anhydrous compound (hexagonal phase) could have additional distortions rather than an increase of the original one.

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