THE THERMAL BEHAVIOUR OF THE QUADRUPOLE HYPERFINE INTERACTION IN $(NH_4)_2HfF_6$

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A TDPAC investigation has been accomplished on $(NH_4)_2 HfF_6$ between 14 and 620 K. A phase transition was observed below 390 K. The low temperature phase is characterized by two non-equivalent sites for hafnium atoms in a 1:1 ratio. The high temperature phase, on the other hand, is depicted by a unique quadrupole interaction. Above 400 K, the compound decomposes successively to $NH_4 HfF_5$, $NH_4 Hf_2 F_9$ and HfF_4. An enthalpy of 76 ± 4 kJ/mol could be determined for the $(NH_4)_2 HfF_6 \rightarrow NH_4 HfF_5 + NH_4 F$ chemical reaction. The hyperfine interaction and thermal evolution of $(NH_4)_2 HfF_6$ was found to be quite similar to that of $(NH_4)_2 ZrF_6$.

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1.   Introduction

The ammonium hafnium hexafluoride has been studied at room temperature by Mayer et al. [1] and at 77 K by Gerdau et al. [2] using the time-differential perturbed angular correlation technique (TDPAC). A unique electric field gradient (EFG) was found by both authors. Their results can not be clearly connected except by assuming a strong thermal dependence of the hyperfine quadrupole interaction.

Two modifications of $(NH_4)_2HfF_6$, characterized by intense asymmetric EFGs, were observed by Gerdau et al. at 4.2 K using Mössbauer spectroscopy [3].

It is also known that the compound under investigation becomes unstable at moderate temperatures. Heats of decomposition for the different steps of the thermal dissociation $(NH_4)_3HfF_7 \rightarrow (NH_4)_2HfF_6 \rightarrow NH_4HfF_5 \rightarrow Hf_4F$ have already been determined [4].

Here, applying the TDPAC technique on ^{181}Hf probes, we investigate the thermal behaviour of $(NH_4)_2HfF_6$ between 14 and 620 K and establish, when possible, a comparison with already reported results for the isomorphous compound $(NH_4)_2ZrF_6$ [5,6].

Up to now, X-ray diffraction data as well as the crystalline structures of the $(NH_4)_2HfF_6$ compound and most of its thermolysis products are unknown. Because of this, X-ray spectra obtained in the present work have been compared with those reported for zirconium analogous compounds [7].

2.   Experimental

The compound was prepared by adding solid NH_4F to a hot solution of HfO_2 in concentrated HF. The molar ratio NH_4F to HfO_2 was 2:1. Crystals were obtained after a slow evaporation at room temperature. Table 1 shows the diffraction data corresponding to an X-ray powder diagram taken on the as-prepared sample. These data are very similar to those reported by Gaudreau [7] for the disordered phase of $(NH_4)_2ZrF_6$.

The sample was capsulated in 0.5 cm³ sealed quartz tubes at atmospheric pressure and neutron irradiated in the RA-3 reactor of the Comisión Nacional de Energía Atómica.

The high resolution TDPAC set-up $(2\tau = 0.75$ ns$)$ and data handling which allowed us to obtain the spin rotation curves, as well as the heating and cooling systems, have been described elsewhere [6].

For the fitting procedure, we used a linear combination $\Sigma_n f_n G_2^n(t)$ of perturbing factors:

$$G_2(t) = s_{20} + \sum_{i=1}^{3} s_{2i} \exp(-\delta \omega_i t) \cos(\omega_i t), \qquad (1)$$

Table 1

X-ray diffraction data for $(NH_4)_2HfF_6$

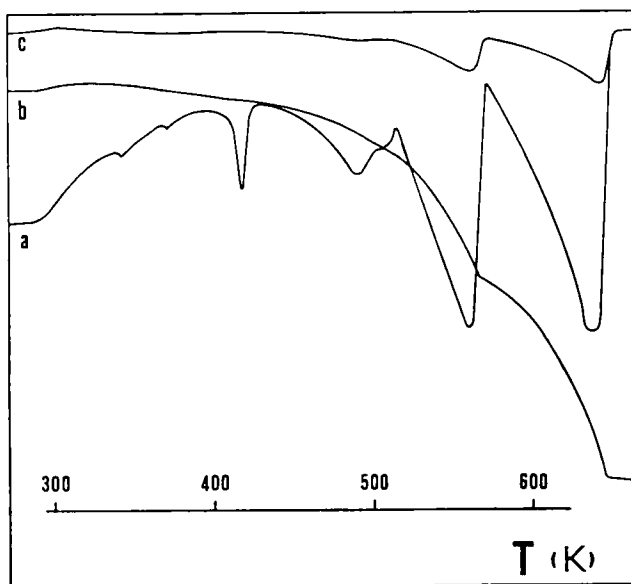| d (Å)	I/I_0	d (Å)	I/I_0
7.31	7	2.31	14
6.56	2	2.21	2
6.28	4	2.19	12
6.07	4	2.13	2
5.75	100	2.10	4
5.40	12	2.07	2
5.01	4	2.00	4
4.57	2	1.94	4
3.82	46	1.91	10
3.34	30	1.90	14
3.21	68	1.84	2
3.14	6	1.82	14
3.11	2	1.76	2
2.94	4	1.72	4
2.90	8	1.71	2
2.62	2	1.68	4
2.51	12	1.66	6
2.34	2	1.61	4

Fig. 1. Thermograms for $(NH_4)_2HfF_6$: (a) thermal differential curve, (b) thermogravimetric curve, and (c) differential weight curve. No changes were observed at temperatures above 700 K.

where s_{2i} are functions of the asymmetry parameter η, ω_i depend on both η and the quadrupole interaction frequency ω_Q, and δ stands for a possible frequency distribution. The coefficients f_n of the linear combination are the relative fractions of probes acted upon by each particular EFG.

Temperatures where changes could be expected were estimated via thermal differential and thermogravimetric analysis (TDA-TGA), performed between 293 and 800 K in air at atmospheric pressure and at a speed of 6 K/min (fig. 1).

Whenever a modification was observed in a TDPAC spectrum at a given temperature, a non-active sample was heated at this temperature and then cooled to room temperature. An X-ray powder diagram on the treated sample was then taken in order to obtain more insight about the change.

3.   Results and discussion

Selected spin rotation curves obtained at different temperatures are shown in fig. 2. In the range 14 − 293 K [see fig. 2(a), (b), (c)], no relevant changes were observed. Two different quadrupole interactions were needed to describe the spin rotation curves, their relative fractions keeping the ratio 1:1 and the frequency distributions being less than 3% over all the thermal range. Figure 3 shows the thermal behaviour of the fitted quadrupole frequencies and asymmetry parameters. When the asymmetry parameter that grows with temperature (▲ in fig. 3) approaches its maximum value ($\eta \rightarrow 1$), the two-site picture describing the interaction begins to be replaced by a simpler one corresponding to a single, symmetric and non-distributed interaction with $\omega_Q = 199 \pm 2$ Mrad/s. Figure 2(d) exhibits the spin rotation curve obtained at 390 K, which was fitted with 70% of the interaction just mentioned and 30% of the one depicting the lower temperature range 14 − 293 K. TDA and TGA results showed a sharp endothermic peak centered at 415 K and no relevant loss of weight, respectively. The change evidenced in the spin rotation curve was assumed to be due to the phase transition α-$(NH_4)_2HfF_6 \rightarrow \beta$-$(NH_4)_2HfF_6$, in analogy with that of $(NH_4)_2ZrF_6$ [6,8].

The 430 K spectrum [fig. 2(e)] was fitted with two interactions: the one corresponding to β-$(NH_4)_2HfF_6$ and another characterized by $\omega_Q = 66 \pm 1$ Mrad/s, $\eta = 0.02 \pm 0.02$ and $\delta = (13 \pm 2)\%$. Complementary information from TDA, TGA and X-ray spectra indicated that the reaction β-$(NH_4)_2HfF_6 \rightarrow NH_4HfF_5 + NH_4F$ had taken place. Thus, the quadrupole interaction parameters just reported belong to NH_4HfF_5.

Regarding the mentioned decomposition, we have calculated the equilibrium constant K_X for this reaction as indicated in ref. [6] : $K_X = f^2 /(1 - f^2)$, f being the relative fraction of NH_4HfF_5. Results versus the reciprocal temperature are plotted in fig. 4, together with those reported for the $(NH_4)_2ZrF_6$ decomposition. An enthalpy of (76 ± 4) kJ/mol was determined. The agreement with that deduced for the isomorphous zirconium compound, (82 ± 6) kJ/mol, is remarkable.
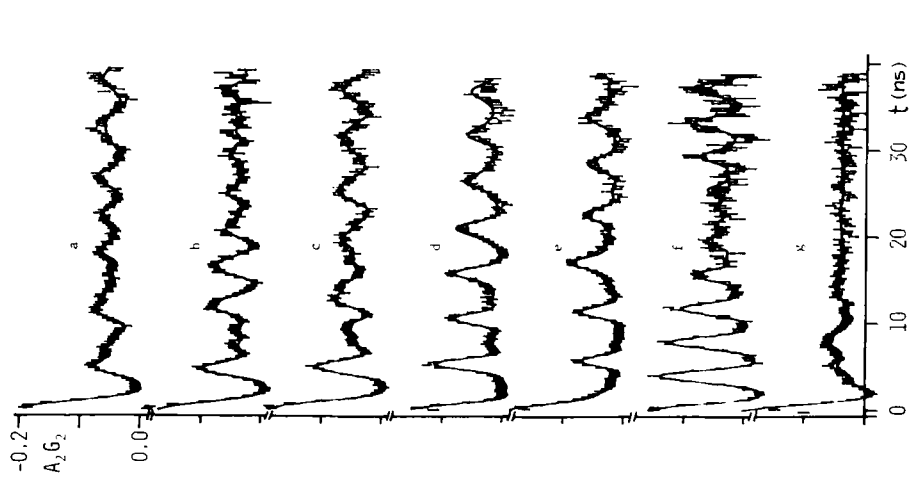
Fig. 3. Thermal evolution of the fitted hyperfine parameters corresponding to the low temperature phase of $(NH_4)_2HfF_6$. Different symbols are used to show the evolution of each site interaction.

Fig. 2. Spin rotation curves for $(NH_4)_2HfF_6$ at different temperatures: (a) 14 K, (b) 200 K, (c) 293 K, (d) 390 K, (e) 430 K, (f) 540 K, and (g) 620 K. Full lines are the fitted curves to the data.
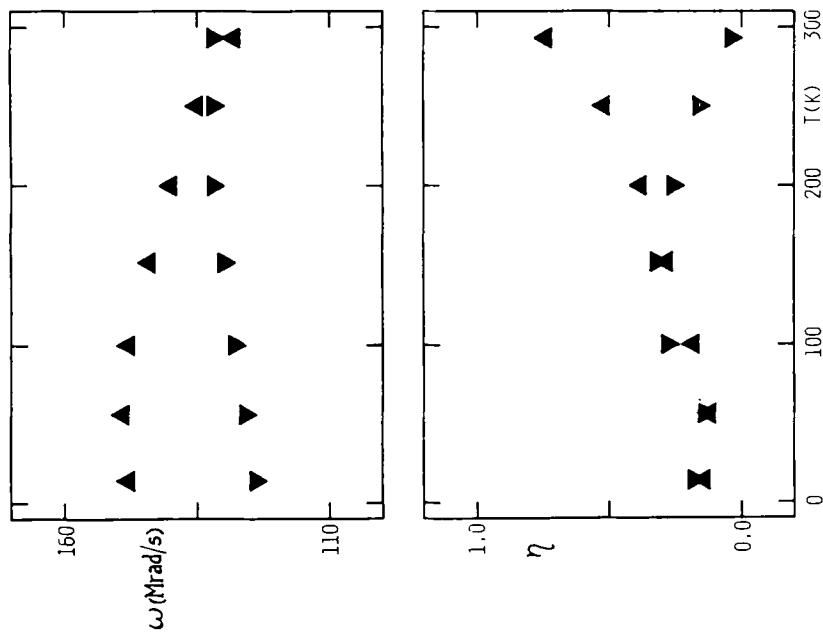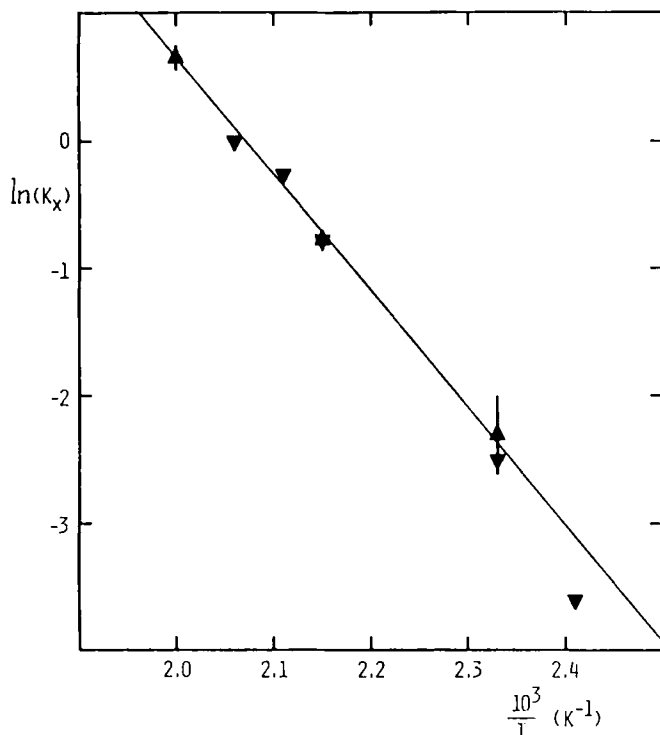
Fig. 4. Experimental equilibrium constant versus reciprocal temperature. ▲: $(NH_4)_2HfF_6$ to NH_4HfF_5 reaction, ▼: $(NH_4)_2ZrF_6$ to NH_4ZrF_5 reaction. The value at 500 K was calculated on the hypothesis that the reaction giving rise to $NH_4Hf_2F_9$ had not yet begun.

That fact that at 500 K the typical interaction of $NH_4Hf_2F_9$ [9] appeared in the spin rotation curves, reaching 100% of the relative fraction at 540 K [fig. 2(f)], allowed us to state that a new reaction had taken place in the sample.

The $NH_4Hf_2F_9$ quadrupole interaction remained up to 620 K, where it changed into that of HfF_4 [fig. 2(g)] [10].

Sets of quadrupole hyperfine parameters associated to all compounds involved in this work are shown in table 2.

Thermal analysis above 415 K (see fig. 1) can now be clearly interpreted. The peaks appearing in TDA are related to the successive steps of the β-$(NH_4)_2HfF_6$ → NH_4HfF_5 → $NH_4Hf_2F_9$ → HfF_4 decomposition.

Finally, it is interesting to mention that some of the active samples did not exhibit at room temperature the characteristic spin rotation curve shown in fig. 2(c). The thermal behaviour of the corresponding quadrupole interaction is not yet clearly understood. Investigations to elucidate this duality are in progress.

Table 2

Compound	T (K)		$V_{zz} (10^{17}$ V/cm^2)	η	δ (%)
		site 1	13.52 ± 1.62	0.87 ± 0.01	1 ± 1
α-$(NH_4)_2HfF_6$	293				
		site 2	13.94 ± 1.67	0.52 ± 0.01	1 ± 1
β-$(NH_4)_2HfF_6$	390		20.85 ± 2.50	0.05 ± 0.02	2 ± 1
NH_4HfF_5	430		6.92 ± 0.83	0.02 ± 0.02	13 ± 2
		site 1	15.93 ± 1.91	0.89 ± 0.01	1 ± 1
$NH_4Hf_2F_9$	540				
		site 2	28.19 ± 3.38	0*	11 ± 3
HfF_4	620		13.31 ± 1.60	0.34 ± 0.04	15 ± 3

Fitted values of the quadrupole hyperfine parameters associated to the different compounds investigated. The reported data correspond to temperatures where the abundance of each compound was maximum. A quadrupole moment $Q = 2.53$ b has been used for the derivation of V_{zz}. * indicates fixed parameter.

4.   Conclusions

The TDPAC technique applied to the study of the $(NH_4)_2HfF_6$ allowed us to draw the following conclusions:

(a) At room temperature, the $(NH_4)_2HfF_6$ presents a crystalline phase having two non-equivalent sites for hafnium positions in a ratio 1:1. A phase transition to a single-site lattice occurs at moderate temperatures.

(b) Above 400 K, the compound decomposes to NH_4HfF_5, $NH_4Hf_2F_9$ and HfF_4 at approximately 415 K, 465 K, and 600 K, respectively.

(c) The enthalpy of decomposition for the reaction β-$(NH_4)_2HfF_6$ $\rightarrow NH_4HfF_5 + NH_4F$ was determined to be very close to that reported for the equivalent reaction in the zirconium compound.

(d) The hyperfine interaction evolutions of hafnium and zirconium compounds exhibit a perfect analogy.

Acknowledgements

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