

TDPAC INVESTIGATION ON  $\text{NH}_4\text{Hf}_2\text{F}_9$ 

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Time-differential perturbed angular correlation (TDPAC) measurements in  $\text{NH}_4\text{Hf}_2\text{F}_9$  were performed between 15 and 580 K. The compound was found to be stable in the whole temperature range and no phase transitions were observed. Experimental results could be explained assuming two equally populated quadrupole interactions which suggest a neat inequivalence between the two sites occupied by the hafnium atoms in the molecule.

## 1. Introduction

Hyperfine interactions in fluoride complexes of hafnium have been extensively investigated [1]. The recent development of  $\text{CsF}$  detectors with a very fast time response allows extension of the investigation to other compounds of the same type which exhibit very intense electric field gradients (EFG) [2].

Via the determination of the EFG components at the radioactive probe site, the TDPAC technique yields information about the probe neighbourhood.

In this work, the temperature dependence of the hyperfine interaction at hafnium sites in  $\text{NH}_4\text{Hf}_2\text{F}_9$  was studied between 15 and 580 K. The 482 keV,  $\frac{5}{2}^+$  state of  $^{181}\text{Ta}$  populated through  $^{181}\text{Hf}$   $\beta^-$ -decay was used as TDPAC probe. The existence of two of these probes per molecule in the compound offers the possibility of getting interesting information about the corresponding environments.

## 2. Experimental

Following the procedure described by Gaudreau [3] for the fluoride complexes of zirconium and ammonium,  $\text{NH}_4\text{Hf}_2\text{F}_9$  was obtained by thermolysis of a powder sample of  $(\text{NH}_4)_2\text{HfF}_6$  which had been previously activated in the RA3 reactor of the Comisión Nacional de Energía Atómica, Argentina. In fact, the X-ray powder diffraction pattern taken at room temperature on a sample heated during 24 hours at 540 K showed excellent agreement with that reported by Gaudreau for  $\text{NH}_4\text{Zr}_2\text{F}_9$  [3].

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A conventional two  $\text{CsF}$  detector coincidence setup with a time resolution of  $2\tau = 750$  ps was used for TDPAC data acquisition. Data handling, as well as the fitting procedure, were performed according to the methodology described earlier [4]. The uncertainty in the temperature was estimated as  $\pm 1$  K.

### 3. Results and discussion

Typical spectra of  $\text{NH}_4\text{Hf}_2\text{F}_9$  taken at 15, 293 and 580 K are shown in fig.1. The absence of any apparent change all along the temperature range indicates not only that this compound is stable up to 580 K, once obtained from the thermolysis of  $(\text{NH}_4)_2\text{HfF}_6$ , but also that no phase transition has occurred.

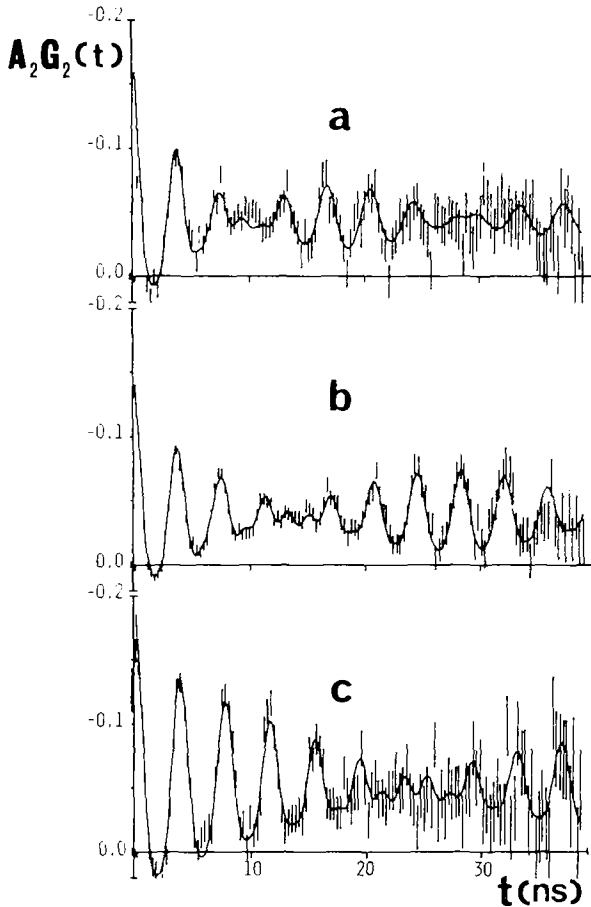


Fig.1. Spin-rotation curves for  $\text{NH}_4\text{Hf}_2\text{F}_9$  obtained at (a) 15 K, (b) 293 K, (c) 580 K.

Attempts to fit the spin-rotation curves on the basis of a unique quadrupole interaction were not successful. However, significant improvements were achieved when assuming two different EFGs. The appropriate fitting function for the attenuation factor was:

$$G_2(t) = f_0 + f_1 G_2^{(1)}(t) + f_2 G_2^{(2)}(t) \quad , \quad (1)$$

where the  $G_2^{(i)}(t)$  are known functions of the quadrupole hyperfine parameters, i.e. the quadrupole interaction frequency  $\omega_Q$ , the asymmetry parameter  $\eta$  and the frequency distribution width  $\delta(5)$ , associated to the different fractions  $f_i$  of probe nuclei.

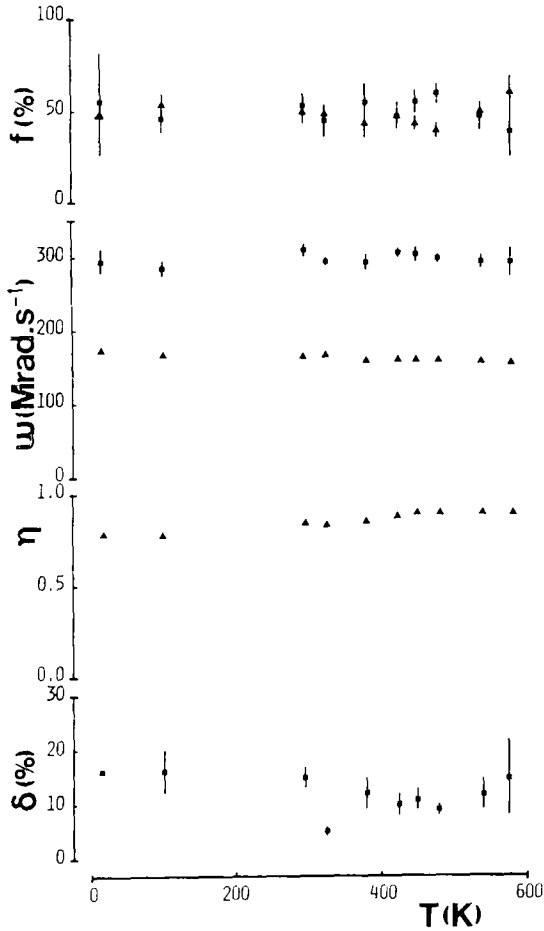


Fig.2. Thermal evolution of the hyperfine parameters deduced from the fits. Two different symbols are used in order to show the evolution of each interaction.

Fig.2 shows the thermal evolution of the hyperfine parameters deduced from the fits. All over the temperature range the fraction  $f_0$  of unperturbed nuclei was found to be lower than 4%. Each of the remaining fractions kept around 50%, indicating unambiguously the inequivalent character of the sites occupied by the two hafnium atoms in the  $\text{NH}_4\text{Hf}_2\text{F}_9$  molecule.

In fact, the fractions  $f_1$  and  $f_2$  are related to two quite different EFGs. One of them, highly asymmetric and monochromatic, is characterized by a quadrupole frequency of about  $160 \text{ Mrad}\cdot\text{s}^{-1}$  which exhibits an ordinary evolution with temperature. The other one, depicted by an extremely high and distributed frequency ( $\omega_Q \approx 300 \text{ Mrad}\cdot\text{s}^{-1}$ ,  $\delta \approx 12\%$ ) is axially symmetric. The thermal behaviour of this latter EFG is not clearly elucidated and could be probably masked due to the great errors determined through the fitting procedure.

Near 600 K, a sudden change in the hyperfine spectrum took place. The typical pattern of fig.1 was replaced by another corresponding to a broadly distributed interaction. This process was observed to be irreversible. In order to explain this change, an X-ray powder diffraction spectrum at room temperature was taken on a sample heated around 600 K. Results showed a good agreement with the  $\alpha\text{-F}_4\text{Zr}$  X-ray pattern reported by Gaudreau [3], leading us to conclude that the  $\text{NH}_4\text{Hf}_2\text{F}_9$  has decomposed into some crystalline variety of  $\text{F}_4\text{Hf}$ .

The crystalline structure of the  $\text{NH}_4\text{Hf}_2\text{F}_9$  has not been reported. Hence, no attempts were intended on calculating the EFG. However, the TDPAC technique made it possible to distinguish two non-equivalent sites for hafnium atoms in the  $\text{NH}_4\text{Hf}_2\text{F}_9$  molecule.

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