

**ANOMALOUS THERMAL BEHAVIOUR OF  $\beta$ -(NH<sub>4</sub>)<sub>2</sub>HfF<sub>6</sub>**A.M. RODRÍGUEZ<sup>\*</sup>, M.C. CARACOCHE<sup>‡</sup>, J.A. MARTÍNEZ<sup>‡</sup>

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It has been determined that the thermally activated  $\alpha \rightarrow \beta$  transition occurring in (NH<sub>4</sub>)<sub>2</sub>HfF<sub>6</sub> at about 370 K is not always reversible. The  $\beta$ -phase hysteresis was investigated between 14 and 400 K. It was possible to explain previously published results without considering the Goldanskii–Karyagin effect.

**1. Introduction**

The hyperfine interaction in (NH<sub>4</sub>)<sub>2</sub>HfF<sub>6</sub> has been investigated by several authors. Mayer et al. [1], at room temperature and Gerdau et al. [2], at 77 K, determined the hyperfine interaction at hafnium sites in this compound using the time-differential perturbed angular correlations technique (TDPAC). The interaction they observed was unique and corresponded to an asymmetric and strong electric field gradient (EFG). Gerdau et al. [3], using Mössbauer spectroscopy, reported two modifications for the compound at 4.2 K. The corresponding spectra were fitted by the authors using a unique anisotropic  $f$ -factor interaction (Goldanskii–Karyagin effect [4]) for each modification.

Recently, using high resolution TDPAC equipment with which the time resolution was improved by a factor of 3, we have studied the thermal evolution of the hyperfine interaction in (NH<sub>4</sub>)<sub>2</sub>HfF<sub>6</sub> [5] from 14 to 400 K. The compound presents two thermally related phases: the low temperature  $\alpha$ -phase (two equally populated

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sites for the <sup>181</sup>Ta probes) and the high temperature  $\beta$ -phase (a unique site for the probes) starting around 340 K. In that paper it was mentioned that some non-published spectra exhibited, at room temperature, a hyperfine interaction which could not be assigned to the  $\alpha$ -phase, even though the corresponding X-ray powder diagrams did not reveal any significant difference from those taken on samples showing neatly the  $\alpha$ -phase TDPAC pattern.

In the present paper, we study the thermal evolution of these spectra and give a re-interpretation of the results obtained by other authors.

## 2. Experiment and results

The compound was prepared and identified as indicated in ref. [5].

The experimental set-up and the data handling have been described in ref. [6].

In all cases, the data were fitted with linear combinations of perturbation factors

$$G_2(t) = S_{20} + \sum_i S_{2i} \exp(-\delta \omega_i t) \cos(\omega_i t),$$

where the frequencies  $\omega_i$  are functions of the EFG acting on the probe nuclei, described by its major component  $V_{zz}$  and its asymmetry parameter  $\eta$ , the coefficients  $S_{2i}$  are functions of  $\eta$ , and  $\delta$  stands for a possible distribution of the frequencies due to statistical irregularities in the lattice.

Figure 1 shows the TDPAC spectra of (NH<sub>4</sub>)<sub>2</sub>HfF<sub>6</sub> which could not be assigned to the  $\alpha$ -phase published in [5]. In order to satisfactorily fit these spectra, it was necessary to consider a linear combination of three perturbation factors. Two of them corresponded to the  $\alpha$ -phase and the third one to a very strong, asymmetric and highly distributed EFG.

Figure 2 shows the thermal evolution of the hyperfine parameters belonging to the latter interaction. From 250 K on, as the population begins to grow, the interaction gradually becomes more symmetric and monochromatic. At 400 K it corresponds fairly well with the  $\beta$ -phase interaction, and this correspondence led us to call this state "undercooled  $\beta$ -phase".

The observation of this phase may probably be related to the reversibility of the transition  $\alpha \rightarrow \beta$ . On this subject, the following could be established: whenever the sample is cooled from a temperature where  $\alpha$  and  $\beta$  phases coexist, the interaction at room temperature is that of the  $\alpha$ -phase, clearly indicating that the ordinary  $\beta \rightarrow \alpha$  process has taken place. On the contrary, when cooling down from a temperature where only  $\beta$ -phase is present (the  $\alpha \rightarrow \beta$  transition has been accomplished), the room temperature pattern shows the interactions corresponding both to the  $\alpha$ -phase and to the undercooled  $\beta$ -phase. These results suggest that the existence of "seeds" of  $\alpha$ -phase immersed in  $\beta$ -phase favours the reverse transformation  $\beta \rightarrow \alpha$ .

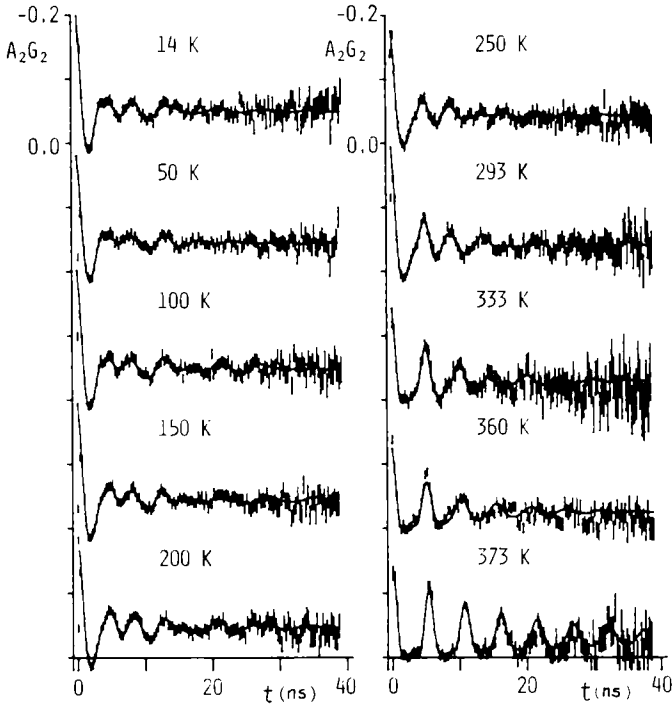


Fig. 1. TDPAC spectra of (NH<sub>4</sub>)<sub>2</sub>HfF<sub>6</sub> obtained at different temperatures. Full lines correspond to the best fits which were achieved using a three-sites model.

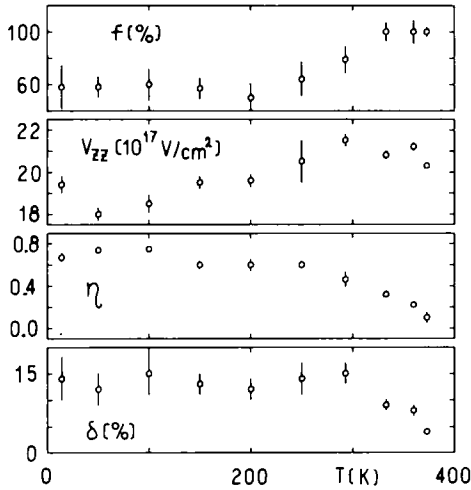


Fig. 2. Thermal evolution of the hyperfine parameters of the undercooled  $\beta$ -phase. In the upper figure, the symbol  $f$  represents the relative fraction of the interaction.

The reason why the  $\beta \rightarrow \alpha$  transition appears as a hard process might be related to the fact that the  $\alpha$ -phase exhibits two inequivalent sites for the hafnium probes, while the  $\beta$ -phase has only one. Hence, on cooling, the system must build up a phase with two distinct probe surroundings. This process seems to be more difficult in the absence of  $\alpha$ -phase seeds which would act as templates. This difficulty could be the origin of the distortion and the disorder of the undercooled  $\beta$ -phase.

Let us now compare our results with those of Gerdaud and co-workers [3]. These authors reported two different Mössbauer spectra for the  $(\text{NH}_4)_2\text{HfF}_6$ , denoted as modification I and II, which could not be explained in terms of simple interactions. In fact, to give an account of the shape of the spectra, an anisotropic Debye–Waller factor (Goldanskii–Karyagin effect) had to be assumed.

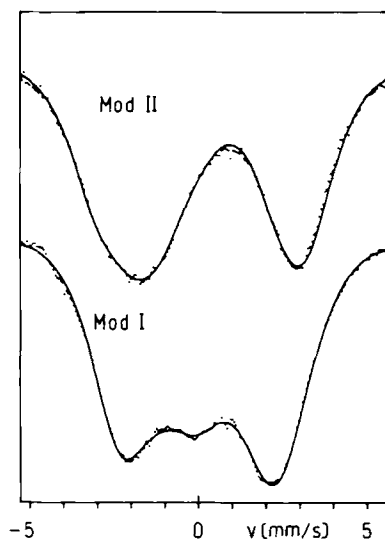


Fig. 3. Mössbauer spectra taken from ref. [3]. The full lines correspond to the fit we performed in this work.

Figure 3 shows Gerdaud's experimental data. The full lines correspond to the fit we performed in the light of our TDPAC results. Table 1 lists the corresponding Mössbauer parameters obtained via a nonlinear least-squares fit. These results allowed us to state that the spectra can be interpreted as being due to the coexistence of different interactions: the presence of the two sites of the  $(\text{NH}_4)_2\text{HfF}_6$   $\alpha$ -phase in one case (Mod. I), and a mixture of  $\alpha$  and undercooled  $\beta$ -phase in the other case (Mod. II). Modification I also contains about 20% of an interaction of hyperfine characteristics similar to those reported in [3] for  $(\text{NH}_4)_3\text{HfF}_7$ , which was not observed in our TDPAC experiments.

Table 1

Hyperfine parameters fitted for the experimental data obtained from ref. [3]. The first two lines in both Modifications correspond to the interactions of the  $\alpha$ -phase (in Mod. II, slightly distorted). The remaining interaction in Mod. I could be assigned to (NH<sub>4</sub>)<sub>3</sub>HfF<sub>7</sub>, and in Mod. II it clearly corresponds to the undercooled  $\beta$ -phase

	$f(\%)$	$V_{zz} (10^{17} \text{ V/cm}^2)$	$\eta$	IS (mm/s)	$2\Gamma$ (mm/s)
Mod I	43(1)	14.8(1)	0.74(1)	0.23(1)	2.70(3)
	35(1)	– 12.9(1)	0.87(1)	0.02(1)	2.02(3)
	22(1)	– 8.3(1)	0.63(0)	0.25(1)	2.15(3)
Mod II	20(1)	14.8(1)	0.88(2)	0.01(2)	2.30(6)
	29(1)	– 11.8(1)	0.33(2)	0.27(2)	2.30(4)
	51(1)	– 18.5(1)	0.25(1)	0.05(2)	2.30(4)

### 3. Conclusions

The application of the high resolution TDPAC technique allows us to conclude that:

(a) The  $\alpha \rightarrow \beta$  transition in (NH<sub>4</sub>)<sub>2</sub>HfF<sub>6</sub> is not always completely reversible. Under given conditions, the high temperature  $\beta$ -phase shows a strong hysteresis effect, remaining even when cooling to 14 K, although with hyperfine parameters rather distorted.

(b) The Mössbauer spectra of (NH<sub>4</sub>)<sub>2</sub>HfF<sub>6</sub> obtained by Gerdau et al. [3] can be explained without considering the existence of the Goldanskii–Karyagin effect but instead in terms of the interactions determined in this investigation.

(c) The TDPAC technique, provided a high resolution set-up is used ( $\tau \cong 0.75$  ns in our case), allows a more detailed analysis of the hyperfine interactions than the Mössbauer spectroscopy on <sup>178</sup>Hf, on account of the broad line width involved ( $2\Gamma = 1.96$  mm/s  $\cong 3.14 \cdot 10^{17}$  V/cm<sup>2</sup>).

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