

TEMPERATURE DEPENDENCE OF THE HYPERFINE INTERACTION IN $(\text{NH}_4)_2\text{ZrF}_6$ A.M. RODRÍGUEZ*, J.A. MARTÍNEZ**, M.C. CARACOCHE**, P.C. RIVAS
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The thermal evolution of the hyperfine quadrupole interaction in $(\text{NH}_4)_2\text{ZrF}_6$ has been investigated via TDPAC from 14 to 400 K. A phase transition is detected near 370 K. The low-temperature phase exhibits two sites equally populated for ^{181}Ta probes. The associated electric field gradients are described by both high asymmetry parameters and high interaction frequencies. On the other hand, the high-temperature phase corresponds to an unique axially symmetric and more intense electric field gradient.

1. Introduction

Continuing our high-resolution TDPAC measurements on hafnium and zirconium complexes [1-3], we report in this paper results on the thermal evolution of the quadrupole hyperfine interaction in $(\text{NH}_4)_2\text{ZrF}_6$ from 14 to 400 K.

The easy substitution of Zr atoms by Hf atoms and the well-known properties of the 482 keV ($\frac{5}{2}^+$) level of ^{181}Ta produced by β^- decay of ^{181}Hf make the application of the TDPAC technique suitable for an investigation of hyperfine interactions in zirconium compounds.

No previous literature on hyperfine data has been found on the complex under investigation. Bulk information reported by Gaudreau [4] indicates that $(\text{NH}_4)_2\text{ZrF}_6$, when produced via thermolysis of $(\text{NH}_4)_3\text{ZrF}_7$, decomposes into $(\text{NH}_4)_2\text{ZrF}_6$ around 393-398 K. Two phases are reported by this author for $(\text{NH}_4)_2\text{ZrF}_6$, depending on thermal treatments: the disordered phase when $(\text{NH}_4)_3\text{ZrF}_7$ is heated to 473 K and quenched, and the ordered phase when a slower cooling is performed. Their X-ray spectra are quite similar, differing only in weak lines.

2. Experimental

The compound was prepared by dissolving zirconium (10% Hf) in concentrated hydrofluoric acid and adding an aqueous solution of ammonium fluoride in stoichiometric proportions. Crystals were finally obtained after slow evaporation at room temperature. X-ray analysis on a powder sample showed that, with the exception of one weak line, the diffraction pattern was consistent with the ordered phase of $(\text{NH}_4)_2\text{ZrF}_6$. It was also possible to sort out lines belonging to $(\text{NH}_4)_3\text{ZrF}_7$.

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The ^{181}Hf activity was obtained by irradiating the compound in the RA-3 reactor of Comisión Nacional de Energía Atómica, Argentina.

The high-resolution TDPAC setup ($2\tau = 0.75$ ns) and further data handling, as well as the fitting procedure, have already been described in ref.[1].

A linear combination of static electric quadrupole interaction perturbation factors of the form

$$G_z(t) = \sigma_{z0}(\eta) + \sum_{n=1}^3 c_{-n}(\eta) e^{-\delta_n t} \cos(\omega_n t)$$

led to satisfactory fits for all temperatures. The coefficients of the linear combination were interpreted as the relative populations of the sites occupied by ^{181}Ta probes at different environments.

As it is known, TDPAC technique allows the determination of, from ω_n values, the quadrupole interaction frequency ω_Q (proportional to the maximum component V_{zz} of the electric field gradient (EFG)) and the asymmetry parameter η defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$. A lorentzian distribution of width δ was introduced to account for a possible spread of the interaction frequencies.

The uncertainty in the temperature determination was about ± 1 K.

3. Results and discussion

In an attempt to estimate the influence of $(\text{NH}_4)_2\text{ZrF}_6$ present in the sample, and bearing in mind that its decomposition temperature into $(\text{NH}_4)\text{ZrF}_5$ was reported to be approximately 395 K, results at room temperature were compared before and after a thermal treatment at 400 K. No significant changes of the interaction were observed, unless near $t = 0$. So, the influence of $(\text{NH}_4)_2\text{ZrF}_6$ was disregarded and the fits were performed neglecting the first three channels ($t < 1$ ns).

Fig.1 shows the spin-rotation curves obtained at different temperatures. In fig.2 the fitted quadrupole hyperfine parameters, tabulated in table 1, are plotted versus temperature. All interactions were found to have negligible frequency distribution widths ($\delta < 2\%$) which, thus, have not been included in the figure.

At low temperature, two interactions were needed to explain the observed perturbation. Both interactions exhibit the same population, but the thermal behaviours of the corresponding EFGs are rather different. Indeed, one of them seems to be not very dependent on temperature: while the interaction frequency weakly decreases, the associated η value shows a slight variation presenting a maximum at around 170 K. The other one shows a stronger thermal dependence. As can be observed in fig.2, the quadrupole frequency of this site decreases and the η value monotonically increases, reaching the full asymmetry ($\eta \approx 1$) near 343 K.

Hereinafter, a new intense and symmetric EFG must be included to explain part of the observed interaction. Its population grows with temperature at the expense of the former ones. This undoubtedly indicates that a phase transition is taking place.

At 400 K, where the relative population of the new phase attains 80%, an additional contribution to the EFG is needed to give account of the experimental data. This situation was interpreted in terms of thermolysis of the compound, reported by Gaudreau [4] at the same temperature. A more detailed investigation of this decomposition, as well as the TDPAC study of the products involved, is in progress.

Unfortunately, crystalline structure data at any temperature are lacking and no theoretical predictions of EFG at ^{181}Ta sites could be performed. Nevertheless, the mere inspection of the thermal behavi-

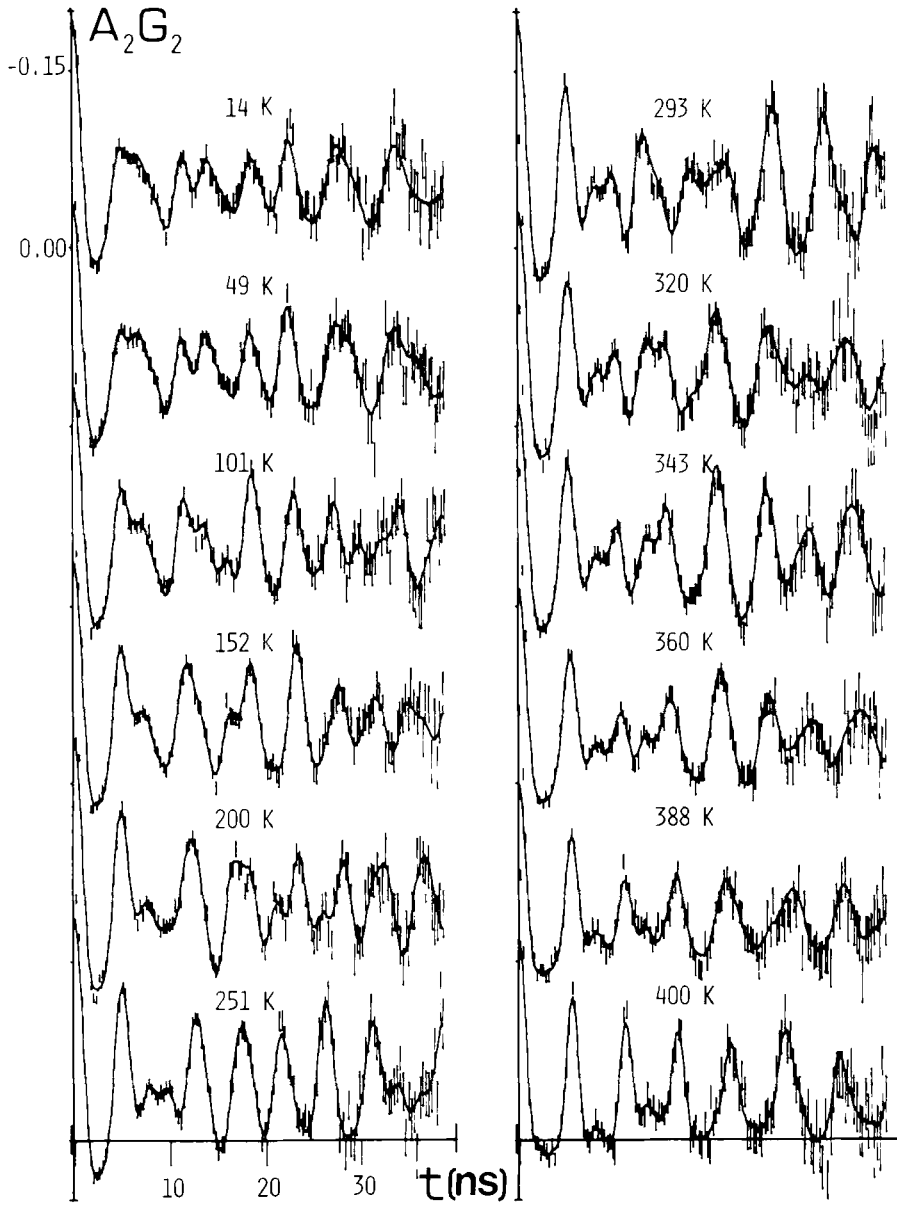


Fig.1. Spin-rotation curves for $(\text{NH}_4)_2\text{ZrF}_6$, obtained at different temperatures.

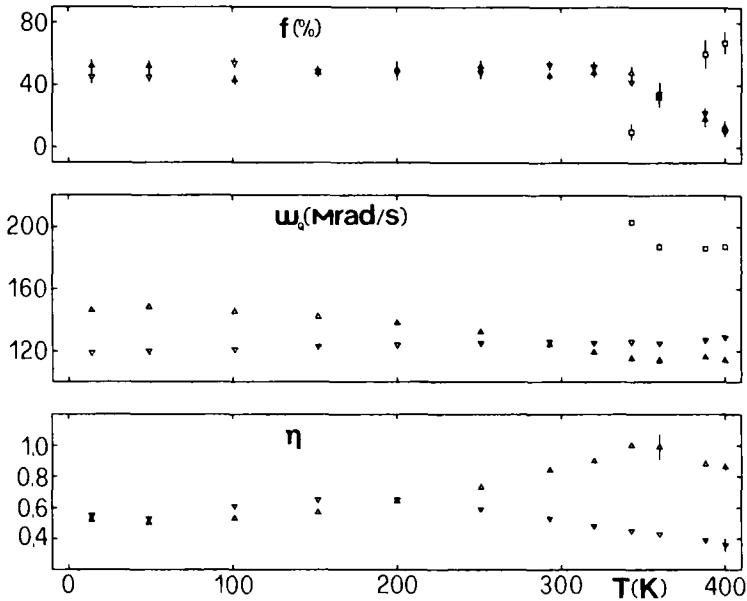


Fig.2. Thermal evolution of the fitted hyperfine parameters. Different symbols are used to show the evolution of each interaction. At 400 K, parameters corresponding to a 10% fraction of a fourth contribution to the EFG have not been plotted.

Table 1

Quadrupole interaction parameters deduced from the fits at different temperatures

T(K)	f_1 (%)	ω_{Q1} (Mrad/s ⁻¹)	η_1	f_2 (%)	ω_{Q2} (Mrad/s ⁻¹)	η_2	f_3 (%)	ω_{Q3} (Mrad/s ⁻¹)
14	52 ₄	146 ₁	0.52 ₁	45 ₄	119 ₁	0.55 ₁		
49	52 ₃	148 ₁	0.50 ₁	45 ₃	120 ₁	0.53 ₁		
101	43 ₃	145 ₁	0.53 ₁	54 ₃	121 ₁	0.61 ₁		
152	48 ₃	142 ₁	0.57 ₁	49 ₃	123 ₁	0.65 ₁		
200	50 ₅	138 ₁	0.64 ₁	48 ₅	124 ₁	0.65 ₁		
251	52 ₄	132 ₁	0.73 ₁	48 ₄	125 ₁	0.59 ₁		
293	46 ₂	124 ₁	0.84 ₁	53 ₃	126 ₁	0.53 ₁		
320	48 ₂	119 ₁	0.90 ₁	52 ₃	125 ₁	0.48 ₁		
343	48 ₄	115 ₁	1.00*	42 ₁	126 ₁	0.45 ₁	10 ₅	203 ₁
360	32 ₄	114 ₂	0.99 ₃	34 ₂	125 ₁	0.43 ₁	34 ₆	187 ₂
388	18 ₅	116 ₁	0.88 ₁	22 ₃	127 ₁	0.39 ₁	60 ₉	186 ₁
400	13 ₄	114 ₁	0.86 ₂	10 ₃	129 ₁	0.36 ₄	67 ₇	187 ₁

The third component of the EFG from 343 to 400 K was observed to be axially symmetric.

*This parameter was kept fixed.

our of the hyperfine interaction from 14 to 400 K allows us to point out some interesting features.

First of all, a phase transition is detected around 370 K. Due to the wide temperature range within which the transition takes place, the above temperature was stated as that where both phases are present in approximately the same amount. The fact already mentioned that no significant changes were observed in spectra taken at room temperature before and after a thermal treatment at a temperature higher than the transition one, indicates that this process is reversible.

The hyperfine interaction of the low temperature phase suggests the existence of two inequivalent structural sites for Zr in $(\text{NH}_4)_2\text{ZrF}_6$.

The temperature dependence of the asymmetry parameters and quadrupole frequencies of this phase can not be understood in terms of a simple isotropic lattice expansion. Probably, simultaneous effects of expansion and reorientation might explain the different behaviours of both sites.

The temperature range at which the high temperature phase is observed does not allow us to establish the thermal tendency of its hyperfine parameters.

Finally, we would like to mention the fact that the beginning of the phase transition observed near 343 K, being simultaneous with the arrival to full asymmetry of one of the sites in the low-temperature phase, has attracted our attention. This situation has already been observed in other works performed on K_2ZrF_6 (2), K_3HfF_6 (5) and $(\text{NH}_4)_2\text{HfF}_6$ (6) Whether a common physical phenomenon is connected to these processes is open to question.

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