# TDPAC STUDY ON THE THERMAL STABILITY OF ZIRCONIUM TETRAFLUORIDE

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The thermal evolution of the hyperfine interaction in $\alpha$-$ZrF_4$ is investigated between 293 K and 788 K. The first change, observed at 534 K, is attributed to the appearance of the non-stoichiometric compound $ZrO_{1.3}F_{1.4}$. During the transformation, the relative fraction of the latter shows an Arrhenius behaviour with an activation energy $E_a$ = (22.6 ± 5.5) kJ/mol. At approximately 700 K, $ZrO_{1.3}F_{1.4}$ gives rise to the monoclinic phase of $ZrO_2$ and to $\beta$-$ZrF_4$ .

## 1. Introduction

This work was undertaken in order to obtain information about the thermal stability of $ZrF_4$ , since it constitutes one of the substances found in our systematic study of hexafluorzirconates of the type $A_2ZrF_6$ (see refs. [1 – 2] on $K_2ZrF_6$ and $(NH_4)_2ZrF_6$). The available literature about the thermal stability of $ZrF_4$ is confusing [3 – 6]. Although the final reaction product is generally $ZrO_2$ , a wide variety of zirconium oxifluorides are observed as intermediate products.

Waters [3], studying the thermal behaviour of the zirconium fluoride-water system, found a strong dependence of the resulting compounds on temperature and experimental conditions, giving a complex picture for the reactions observed.

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Four modifications have been reported by Gaudreau [4] for zirconium tetra-fluoride: the tetragonal $\alpha$ form, the monoclinic $\beta$ one, the so-called $\gamma$ phase, and an amorphous variety. Among these, the $\beta$ form proved to be the most stable and the one which the other forms turned into when heated.

A monoclinic crystalline structure and the atomic positions have been published in ref. [7], but the powder X-ray diagram from it does not agree with X-ray data published for $\beta$-ZrF$_4$ by Gaudreau.

In this work, we present an investigation of the hyperfine quadrupole interaction of $^{181}$Ta in ZrF$_4$ and its thermal evolution between 293 and 788 K. The results have been mainly obtained via the time-differential perturbed angular correlation technique (TDPAC).

## 2.    Experimental

The powder ZrF$_4$ samples used in this work were prepared by heating ZrF$_4$.3H$_2$O to moderate temperatures. They were then capsulated in quartz tubes, sealed in air at atmospheric pressure and neutron irradiated at the Comisión Nacional de Energía Atómica, Argentina.

The ordinary hafnium impurities in zirconium (about 3%) allowed us to employ the TDPAC technique on the well-known $133-482$ keV $\gamma-\gamma$ cascade of $^{181}$Ta.

Spin rotation curves $A_2 G_2(t)$ were obtained by applying the usual methodology already described in previous works (see, for example, ref. [8]). The hyperfine quadrupole parameters $\omega_Q$ (quadrupole interaction frequency), $\eta$ (asymmetry parameter), and $\delta$ (distribution width of frequencies) associated with the different interactions were determined through a least squares fit procedure which took into account the finite time resolution of our equipment ($2\tau = 0.75$ ns at hafnium energies).

Regarding the possibilities of simultaneous interactions, the function

$$G_2(t) = \sum_i f_i G_2^i(t) \tag{1}$$

was used for fitting the experimental data. Here, the coefficients $f_i$ stand for the relative populations of each interaction and $G_2^i(t)$ are the corresponding perturbation factors of static quadrupole interactions in polycrystalline samples:

$$G_2^i(t) = \sigma_{20}^i(\eta_i) + \sum_{n=1}^{3} \sigma_{2n}^i(\eta_i) \exp(-\delta_i \omega_n^i t) \cos(\omega_n^i t) . \tag{2}$$

The sample holder was supplied with a heating system that could stabilize the temperature within $\pm$ 1 K.

Although TDPAC has been the technique mainly used in this investigation, the results have been complemented with those from thermal differential and thermogravimetric analysis (DTA and TGA) and with X-ray diffraction patterns. The latter were obtained at room temperature after heating to different temperatures a single inactive sample of $ZrF_4 \cdot 3H_2O$.

## 3.  Results and discussion

Figure 1 shows some of the TDPAC spectra where the most noticeable changes can be seen. The similarity between the hyperfine interaction determined for $ZrF_4$ [see fig. 1(a)] of fitted quadrupole parameters $\omega_{Q_1} = (123 \pm 2)$ Mrad/s, $\eta_1 = 0.32 \pm 0.02$, $\delta_1 = (14 \pm 1)\%$ and that reported for $HfF_4$ (see ref. [8]) confirms the isomorphism of both compounds. No changes in the spin rotation curves were observed up to 530 K.

The diffraction data obtained after heating the inactive sample at 500 K for 30 hours indicated that it was composed of $\alpha$-$ZrF_4$ [4] and $ZrF_4 \cdot H_2O$ [9]. The difference between TDPAC and X-ray results may be explained by the fact that $ZrF_4$ is hygroscopic and that the X-ray analysis was performed on a sample exposed to atmospheric moisture. We can conclude then that the spin rotation curve of fig. 1(a) corresponds to the hyperfine interaction of the $\alpha$ modification of $ZrF_4$.

From 534 K on, TDPAC spectra had to be fitted with two contributions, that of $\alpha$-$ZrF_4$ plus another more intense and asymmetric one ($\omega_{Q_2} = (208 \pm 8)$ Mrad/s, $\eta_2 \sim 0.40 \pm 0.10$) which was highly distributed ($\delta_2 > 20\%$) and whose population gradually increased with temperature, approaching 100% at 588 K.

The X-ray diagram taken after heating at 600 K for 24 hours revealed the presence of $\alpha$-$ZrF_4$ and $ZrO_{1.3}F_{1.4}$ [4]. We associate the intense and highly distributed interaction frequency $\omega_{Q_2}$, fitted from 534 K on, to $ZrO_{1.3}F_{1.4}$. This compound would be the intermediate one in the reaction by which $\alpha$-$ZrF_4$ turns into $ZrO_2$. In fact, at 679 K the quadrupole hyperfine interaction typical of $ZrO_2$ ($\omega_{Q_3} = (121 \pm 1)$ Mrad/s, $\eta_3 = 0.36 \pm 0.02$, $\delta_3 = (2 \pm 1)\%$) [10] grew at the expense of that just mentioned and characterized by a ($\omega_{Q_2}, \eta_2, \delta_2$) interaction. At 700, 763 and 788 K, the change was enhanced and an additional contribution with hyperfine parameters $\omega_{Q_4} = (120 \pm 2)$ Mrad/s, $\eta_4 = 0.54 \pm 0.03$, and $\delta \sim 5\%$ also appeared.

Spin rotation curves obtained at room temperature immediately after 679, 700, 763, and 788 K measurements showed that the process just described was partially reversible.

X-ray information obtained after heating the inactive sample at 700 and 800 K for 24 hours showed the presence of monoclinic $ZrO_2$ and $ZrO_{1.3}F_{1.4}$. These two compounds had been found by Gaudreau [4] after heating a mixture of $\beta$-$ZrF_4$ and $ZrO_2$, when the mole fraction of the former was kept less than 0.36. The relative populations fitted within the range $700 - 788$ K allowed us to determine a mole fraction for the interaction characterized by the set ($\omega_{Q_4}, \eta_4$) lying between 0.1 and
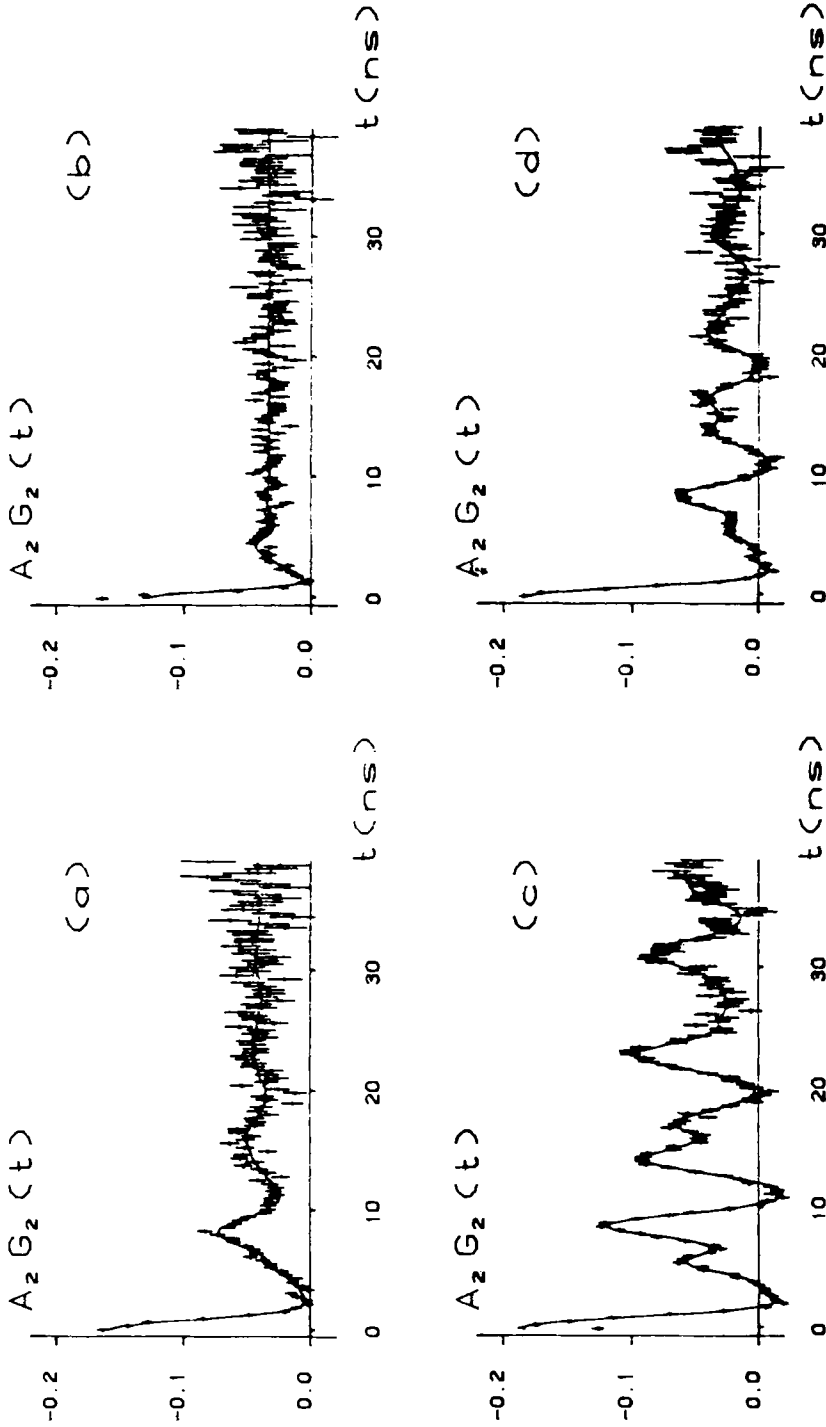
Fig. 1. Spin rotation curves at different temperatures. (a) $\alpha$-ZrF$_4$ at 293 K, (b) ZrO$_{1.3}$F$_{1.4}$ at 600 K, (c) ZrO$_2$ + $\beta$-ZrF$_4$ at 788 K, (d) ZrO$_2$ + ZrO$_{1.3}$F$_{1.4}$ at 293 K, after heating to 788 K. Full lines are the fitted curves.

0.2. Then, we inferred that the monochromatic interaction accompanying the one of $ZrO_2$ corresponded to $\beta$-$ZrF_4$.

At this point, a sample of $ZrO_2$ P.A. acquired from Alfa Products [11], the purity of which had been confirmed by X-ray analysis, was neutron irradiated for comparison with the $ZrO_2$ produced by thermolysis in this work. The fitting procedure yielded nearly 6% of the interaction just assigned to $\beta$-$ZrF_4$. Figure 2 shows the spin rotation curve and the corresponding set of fitted quadrupole parameters.
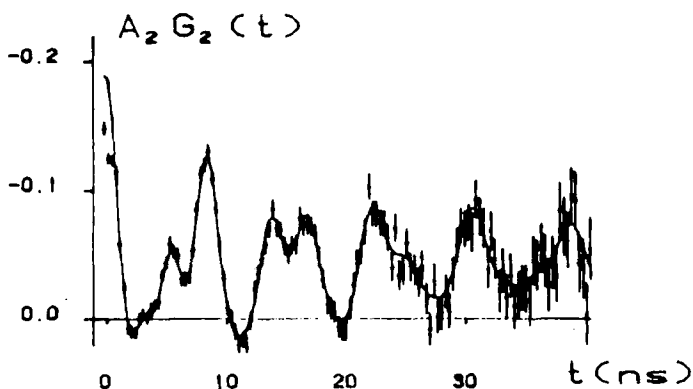


Fig. 2. Spin rotation curves corresponding to $ZrO_2$ acquired from Alfa Products [11]. The full line corresponds to the fitted curve assuming two interactions: $f_1 = (91 \pm 3)\%$, $\omega_{Q_1} = (123 \pm 1)$ Mrad/s, $\eta_1 = 0.33 \pm 0.01$; $f_2 = (6 \pm 3)\%$, $\omega_{Q_2} = (120 \pm 4)$ Mrad/s, $\eta_2 = 0.72 \pm 0.06$, both having negligible distribution widths.

TG and DT analysis performed on $ZrF_4 \cdot 3H_2O$ between 293 K and 1273 K in air at atmospheric pressure and at a speed of 6 K/min revealed the dehydration process through an endothermic peak at 338 K. A wide asymmetric peak around 578 K was attributed to the subsequent occurrence of $ZrO_{1.3}F_{1.4}$ and $ZrO_2$.

The processes observed all along the range can be summed up in the scheme:

$$\alpha\text{-}ZrF_4 \xrightarrow{534\text{ K}} ZrO_{1.3}F_{1.4} \xrightarrow{679\text{ K}} ZrO_2 + \beta\text{-}ZrF_4 ,$$
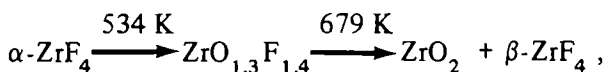
and can be thought of as follows: from 534 K on, the starting compound $\alpha$-$ZrF_4$ incorporates oxygen into the lattice to form the non-stoichiometric compound $ZrO_{1.3}F_{1.4}$. The latter has been described by Gaudreau [4] as a statistical distribution of oxygen and fluorine ions around zirconium, both playing the same role in the structure. At approximately 700 K, a new reaction begins, giving rise to $ZrO_2$. As a consequence, the remaining ions reorganize as $\beta$-$ZrF_4$.

It is interesting to inspect the thermal behaviour of the relative population of the non-stoichiometric oxifluoride when arising from $\alpha$-$ZrF_4$. Figure 3 shows that it obeys an Arrhenius law. Through a least squares fit, an activation energy $E_a$ = $(22.6 \pm 5.5)$ kJ/mol for the appearance of $ZrO_{1.3}F_{1.4}$ was determined.
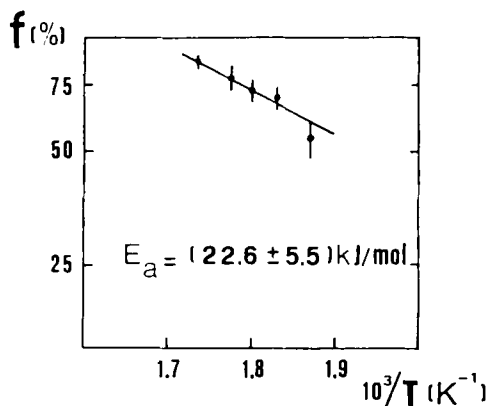


Fig. 3. Logarithmic plot of $ZrO_{1.3}F_{1.4}$ relative fraction as a function of reciprocal temperature. An Arrhenius behaviour was assumed for fitting the experimental points (full line).

## 4.    Conclusions

The thermal evolution of the hyperfine interaction in zirconium tetrafluoride in air could be associated to the occurrence of chemical transformations yielding $ZrO_{1.3}F_{1.4}$, $ZrO_2$ and $\beta$-$ZrF_4$.

The quadrupole interaction parameters of each compound found in this work are listed in table 1.

Table 1

Electric field gradient for the different compounds investigated, derived from the fitted quadrupole hyperfine parameters. A quadrupole moment $Q = 2.53$ b has been used for the derivation of $V_{zz}$

| Compound | $T$ (K) | $V_{zz}$ ($10^{17}$ V/cm$^2$) | $\eta$ | $\delta$ (%) |
|---|---|---|---|---|
| $\alpha$-$ZrF_4$ | 293 | $12.9 \pm 1.6$ | $0.32 \pm 0.02$ | $14 \pm 1$ |
| $ZrO_{1.3}F_{1.4}$ | 600 | $24.0 \pm 2.9$ | $0.30 \pm 0.10$ | $29 \pm 2$ |
| $ZrO_2$ | 788 | $12.6 \pm 1.5$ | $0.37 \pm 0.01$ | $3 \pm 1$ |
| $\beta$-$ZrF_4$ | 788 | $13.3 \pm 1.6$ | $0.56 \pm 0.06$ | $7 \pm 1$ |

From the thermal evolution of the relative fraction of the $ZrO_{1.3}F_{1.4}$, an activation energy $E_a = (22.6 \pm 5.5)$ kJ/mol was determined for the growing of this compound. The fact that this process obeys an Arrhenius law supports the idea of a statistical distribution of oxygen and fluorine ions in the lattice, already reported by Gaudreau in ref. [4].

## Acknowledgements

## References

[1]   J.A. Martinez, A.M. Rodriguez, M.C. Caracoche, R.C. Mercader, A.R. Lopez Garcia and P.C. Rivas, Hyp. Int. 13(1983)307.

[2]   A.M. Rodriguez, J.A. Martinez, M.C. Caracoche, P.C. Rivas, A.R. Lopez Garcia and S. Spinelli, J. Chem. Phys. 82(1985)1271.

[3]   T.N. Waters, J. Inorg. Nucl. Chem. 15(1960)320.

[4]   B. Gaudreau, Rev. Chim. Minerale 2(1965)1.

[5]   N.S. Nikolaev, Yu.A. Buslaev and M.P. Gustyakova, Russ. J. Inorg. Chem. 7(1962)869.

[6]   L. Kolditz and A. Feltz, Z. Anorg. Allg. Chem. 310(1961)217.

[7]   R.W.G. Wyckoff, *Crystal Structures*, Vol. 2 (Wiley, New York, 1965) p. 129.

[8]   J.A. Martinez, M.C. Caracoche, A.M. Rodriguez, P.C. Rivas and A.R. Lopez Garcia, Chem. Phys. Lett. 102(1983)277.

[9]   B. Kojic-Prodic, F. Gabela, Z. Ruzic-Toros and Sljukic, Acta Cryst. B37(1981)1963.

[10]   J. Yeshurum and B. Arad, J. Phys. C7(1974)430.

[11]   Alfa Products, 152 Andover Street, Danvers, Massachusetts 01923, USA.