QUADRUPOLE HYPERFINE INTERACTION AND THERMAL STABILITY OF $ZrF_4 . 3H_2O$

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The quadrupole hyperfine interaction of $ZrF_4 . 3H_2O$ is reported. This compound is observed to dehydrate to ZrF_4 at 325 K. Spectra taken on cooling were observed to be time dependent, and the rehydration process involved was investigated at 293, 298 and 302 K. Contrary to what had previously been determined in $HfF_4 . 3H_2O$, no intermediate compound was observed to participate in the reaction investigated, thus confirming structural differences already reported to exist between these iso-formulae compounds.

1.   Introduction

In most cases, iso-formulae zirconium and hafnium compounds present such a close similitude in their physical and chemical properties that an analogous behaviour is expected. With regard to ZrF_4 and HfF_4, it is known [1] that both crystallize in the monoclinic system, the atomic positions having been determined to be very similar. However, it is also known that the corresponding trihydrated fluoride compounds have different structures. The $ZrF_4 . 3H_2O$ compound crystallizes in the triclinic system [2], forming dimers, and the water molecules are directly bound to the central atom. On the other hand, $HfF_4 . 3H_2O$ has been indexed in the monoclinic system [3], exhibiting a chain structure. One of the water molecules is not coordinated to the hafnium atom, but is held between chain-like complexes by hydrogen bonds.

In a previous article [4], we have reported the quadrupole hyperfine interaction in $HfF_4 . 3H_2O$ and its dehydration products, using the TDPAC technique. It was determined that the kinetics of the HfF_4 hydration at room temperature involved

the presence of $HfF_4 . H_2O$ as an intermediate compound and satisfied a first-order kinetics law.

In this work, using high resolution TDPAC equipment (2τ = 0.75 ns), we have investigated the hyperfine interation in $ZrF_4 . 3H_2O$ as a function of temperature until its dehydration. A comparison with the iso-formulae hafnium compound is also presented. The kinetics of the reverse process was measured, cooling the sample to different temperatures.

2.   Experimental

The TDPAC technique is based on the determination of the angular correlation of the radiation emitted by a nucleus. Under suitable conditions, a $\gamma-\gamma$ cascade may be used for this purpose, the angular correlation of the second radiation being determined relative to a selected emission direction of the first one. When the chemical surrounding of the nucleus (called probe) creates an electric field gradient (EFG), the hyperfine interaction between the latter and the quadrupole moment Q of the intermediate level of the cascade may be observed. It is usual to characterize the EFG through its major component V_{zz} and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. The hyperfine interaction perturbs the angular correlation of the radiation in such a way that is described by the perturbation factor $G_2(t)$. For a static quadrupole interaction in a polycrystalline sample, it has the form:

$$G_2(t) = \sigma_{20} + \sum_{n=1}^{3} \sigma_{2n} e^{-\delta\omega_n t} \cos(\omega_n t), \qquad (1)$$

where σ_{2n} are functions of η, the frequencies ω_n are also functions of η and of V_{zz}, and δ is the frequency distribution width. A linear combination

$$G_2^\star(t) = \sum_i f_i G_2^i(t)$$

of perturbation factors is used when unequivalent chemical environments for the probe nuclei exist. A nonlinear least-squares fit of $A_2 G_2^\star(t)$ to the experimental data allows the determination of the relative fractions f_i of the different chemical surroundings and the corresponding EFG's components and frequency distribution widths. The A_2 factor describes the unperturbed angular correlation of the radiations. Further details about the TDPAC technique can be found in ref. [5].

In order to measure the angular correlation of the radiation, we used the 482 keV, I = 5/2⁺, Q = 2.53 b level of ¹⁸¹Ta, which is the intermediate level of the 133−482 keV $\gamma-\gamma$ cascade following the β^- decay of ¹⁸¹Hf. Powder samples of $ZrF_4 . 3H_2O$ were prepared by dissolving natural Zr (which contains about 5% of Hf

impurities) in concentrated hydrofluoric acid and allowing the solution to evaporate at room temperature. As usual, it was assumed that hafnium atoms are distributed in a statistical way, replacing substitutional zirconium atoms in the sample. Hence, they are affected by the EFG present in the host lattice. The compounds were identified by means of X-ray powder analysis, and then capsulated in air in 0.5 cm^3 sealed quartz tubes at atmospheric pressure. [181]Hf activity was obtained by thermal neutron irradiation in the RA-3 reactor of the Comisión Nacional de Energía Atómica (Argentina). The TDPAC equipment was supplied with an electric furnace which permitted heating the sample in situ, stabilizing within ± 1 K.

Knowing that ZrF$_4$.3H$_2$O dehydrates at moderate temperatures [6], spectra were taken on heating at intervals of approximately 5 K until the typical pattern of ZrF$_4$ was achieved. With the aim of studying the reversibility of the process, once dehydrated, the sample was cooled and successive measurements at a given temperature were performed until no changes were observed. Three series of measurements at 293, 298 and 302 K were carried out in this way. Each measurement had a duration of one day.

3.   Results and discussion

The TDPAC spectrum of the unannealed neutron irradiated ZrF$_4$.3H$_2$O is shown in fig. 1(a). No radiation damage was noticeable. An interaction with quadrupole parameters V_{zz} = $(20.5 \pm 0.5)10^{17}$ V/cm^2 and η = 0.83 ± 0.01 characterizes this compound at 293 K. This interaction remains unique up to 321 K, showing only a slight increase of 5% in the asymmetry parameter. At 325 K (see fig. 1(b)), the hyperfine pattern suddenly changed into the one corresponding to ZrF$_4$, previously reported in ref. [6], evidencing undoubtedly a complete dehydration of the starting compound. Waters, studying the ZrF$_4$-H$_2$O system [7], as well as Gaudreau, investigating zirconium compounds [8], have instead reported the obtainment of ZrF$_4$.H$_2$O as the thermolysis product of ZrF$_4$.3H$_2$O above 350 K, and no mention has been made of the ZrF$_4$ compound. Taking into account that the identification of ZrF$_4$.H$_2$O by both authors was carried out by X-ray diffraction at room temperature, an inactive sample of ZrF$_4$.3H$_2$O was heated at 500 K for 30 h, under similar experimental conditions to those of the TDPAC measurements. The subsequent X-ray pattern obtained at room temperature showed the presence of ZrF$_4$.H$_2$O. The discrepancy between the information derived from TDPAC and that of refs. [7] and [8] can thus be understood in terms of the high hygroscopicity of ZrF$_4$. In effect, this compound, observed by us to exist at 325 K, probably hydrated to ZrF$_4$.H$_2$O when the temperature was lowered and the quartz tube opened in order to obtain the X-ray spectrum.

With regard to the spectra taken during the subsequent hydration process, these were fitted satisfactorily with a linear combination of the typical interactions of exclusively ZrF$_4$.3H$_2$O and ZrF$_4$. The time evolution of the relative fractions f_i (proportional to the amounts of ZrF$_4$.3H$_2$O and ZrF$_4$ present in the sample) reflected
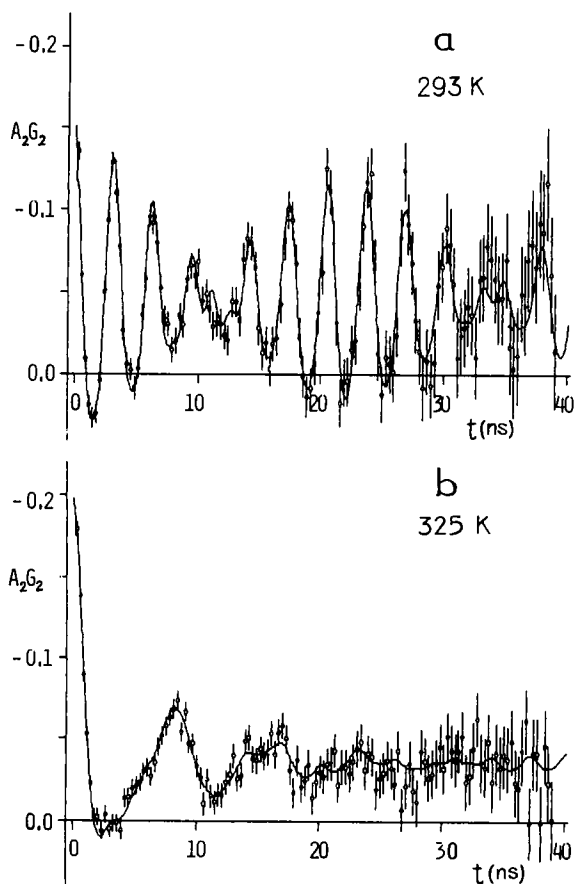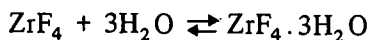
Fig. 1. TDPAC spectra of (a) $ZrF_4 \cdot 3H_2O$ at 293 K, (b) ZrF_4 at 325 K. Full lines are the fitted curves to the data.

the hydration kinetics. In fig. 2, the relative fractions of ZrF_4 are plotted versus time for the three different temperatures investigated. Considering the observed interactions, the reaction

$$ZrF_4 + 3H_2O \rightleftharpoons ZrF_4 \cdot 3H_2O$$

was supposed to occur.

The very simple first-order kinetics law $d[A]/dt = k[A]$, ($[A]$: ZrF_4 mole fraction), which had proved satisfactory when investigating the HfF_4 hydration [4], could be used here successfully only for fitting the room temperature data (dashed line in fig. 2). At 298 K and 302 K, to the contrary, the following second-order law had to be used:
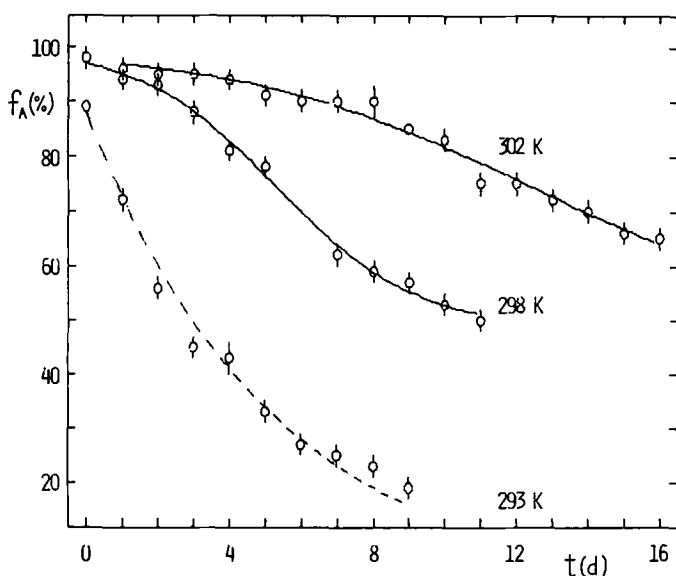
Fig. 2. Time evolution of ZrF₄ average relative fraction at different temperatures. The dashed line corresponds to a first-order kinetics rate law fit. The full lines are the fitted curves assuming a second-order kinetics rate law.

$$\frac{d[A]}{dt} = -k\,[A]\,[B] + k'\,[B]^2\,, \tag{2}$$

with $[B]$ the mole fraction of $ZrF_4.3H_2O$. The solution $[A]$ was then integrated over the time of measurement to be fitted (full lines in fig. 2) to the ZrF_4 experimental relative fraction f_A.

From the impossibility of assuming a unique kinetics law to fit all experimental curves, it can be inferred that, depending on temperature, the rate-determining step of the reaction has changed. In effect, as temperature rises towards the dehydration temperature (325 K), a feedback term standing for the dehydration of $ZrF_4.3H_2O$ has to be considered in the kinetics law.

Summing up, the quadrupole hyperfine interaction of $ZrF_4.3H_2O$ has been determined at room temperature. This interaction was different to the already reported one for the $HfF_4.3H_2O$ compound [4], as was expected because of their dissimilar crystalline structures. Its thermal evolution presents no relevant changes up to 321 K. At 325 K, the compound dehydrates to ZrF_4. A difference between the thermal behaviour of $HfF_4.3H_2O$ and $ZrF_4.3H_2O$ can thus be established. The HfF_4 compound is obtained at 393 K [9] and the ZrF_4 compound at 325 K. The $HfF_4.3H_2O$ dehydration is observed by TDPAC to take place via an intermediate compound, $HfF_4.H_2O$ [4], while no intermediate compound is observed in the $ZrF_4.3H_2O$

dehydration. It is probable that these facts may be connected to the different binding of the water molecules to the central atoms in both substances.

Finally, it is worth remarking that the application of the TDPAC technique has made it possible, once the products involved in the chemical reaction have been identified, to determine accurately the relative fractions of the individual constituents of the phases mixture, identical to their mole fractions, and to follow them in time in a nondestructive way.

Acknowledgements

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