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TDPAC study of hexafluorohafnates of transition metals

M A Taylor†§, M Ceolin†§, J A Martínez†||, P C Rivas†¶,
M C Caracoche†||, H Saitovitch‡ and P R J Silva‡

† Departamento de Física, Universidad Nacional de La Plata, CC67, (1900) La Plata, Argentina

‡ Centro Brasileiro de Pesquisas Físicas, CNPq, Rua Dr Xavier Sigaud 150, 22290, Rio de Janeiro, Brasil

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Abstract. The hyperfine quadrupole interaction of $\text{CoHfF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnHfF}_6 \cdot 6\text{H}_2\text{O}$ was determined at room temperature for the first time. The thermal behaviour of the electric field gradient at hafnium sites in the compounds $\text{AHfF}_6 \cdot 6\text{H}_2\text{O}$ (where A is Co, Ni or Zn), determined using the time differential perturbed angular correlations (TDPAC) technique, is presented in the range from 16 K up to the dehydration temperature. The Bayer-Kushida model has proved to give a good account of the thermal evolution of the quadrupole interaction observed. Frequencies of 371.3 cm^{-1} , 409.5 cm^{-1} and 325.4 cm^{-1} have been drawn, which could be associated to the asymmetric stretching mode of the $[\text{HfF}_6]^{2-}$ ions of $\text{CoHfF}_6 \cdot 6\text{H}_2\text{O}$, $\text{NiHfF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnHfF}_6 \cdot 6\text{H}_2\text{O}$.

1. Introduction

The $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{F}_6 \cdot 6\text{H}_2\text{O}$ family of compounds with A = 3d transition metals and B = Si, Ti or Zr has been studied extensively over the last few years (see [1] and references therein). The reason for such research is that the important number of phase transitions that these compounds exhibit, offer the possibility of shedding some light on the mechanisms involved.

The $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{F}_6 \cdot 6\text{H}_2\text{O}$ compounds (A = Ni, Co, Zn) crystallize at room temperature in the $R\bar{3}$ group with $Z = 1$. Basically, the structure is composed of $[\text{BF}_6]^{2-}$ and $[\text{A}(\text{H}_2\text{O})_6]^{2+}$ octahedral ions linked by hydrogen bonds and packed in a trigonal distorted CsCl structure. Below room temperature, a phase transition was reported to occur for some of these compounds [1, 2]. It was suggested from x-ray studies that the structure of the low-temperature phase is isomorphous with that of $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ ($P2_1/c$, $Z = 2$).

The available literature is mainly devoted to the members of the family where B is Si or Ti. A few studies have been reported for zirconium compounds and no information exists for the case of hafnium compounds. In this paper we present the temperature dependence of the hyperfine quadrupole interaction determined at hafnium sites in

§ Fellow of CONICET, Argentina.

|| Member of Carrera del Investigador Científico of CICPBA, Argentina.

¶ Member of Carrera de Apoyo a la Investigación of CONICET, Argentina.

NiHfF₆·6H₂O, CoHfF₆·6H₂O and ZnHfF₆·6H₂O between 16 K and the dehydration temperature.

2. Experimental

In a time differential perturbed angular correlation (TDPAC) experiment, the angular distribution of the radiation coming from an excited nuclear level is measured relative to the direction of emission of a previous radiation, in a two-step decay of a probe nucleus. Perturbations due to extranuclear fields acting on the intermediate level of the cascade are reflected in the time dependence (within the order of the mean life τ of the intermediate level) of the angular distribution. The hyperfine interaction takes place between the quadrupole moment Q of the intermediate nuclear level of the probe and the electric field gradient V_{ij} (EFG) created by the nearby charge distribution, and is described by the perturbation factor $G_2(t)$ which, for a γ - γ cascade and in the case of static quadrupole interactions in polycrystalline samples, takes the form:

$$G_2(t) = \sigma_{20} + \sum_{i=1}^3 \sigma_{2i} \exp(-\delta\omega_i t) \cos(\omega_i t) \quad (1)$$

where σ_{2i} and ω_i are known functions of the quadrupole frequency $\omega_Q = eQV_{zz}/4I(2I-1)\hbar$, (I being the nuclear spin of the intermediate level) and of the asymmetry parameter of the electric field gradient $\eta = (V_{xx} - V_{yy})/V_{zz}$. The frequency distribution width δ describes a Lorentzian frequency distribution around ω_i due to lattice imperfections and/or impurities. Details about the technique and physical background are given elsewhere [3].

To consider inequivalent chemical environments, a linear combination

$$G_2(t) = \sum f_i G_{2i}(t) \quad (2)$$

is used. In this case the coefficients f_i are interpreted as the relative fractions of probes experiencing each environment.

The A^{II}HfF₆·6H₂O (A = Co, Ni, Zn) compounds were prepared following Davidovich *et al* [4]. X-ray powder diffraction patterns were used to identify the samples. The compounds were capsulated in air at atmospheric pressure in 0.5 cm³ sealed quartz tubes. The activity of ¹⁸¹Hf, giving rise to the 133–482 keV γ - γ cascade of ¹⁸¹Ta used in this work as a TDPAC probe, was obtained by thermal neutron irradiation of the samples in a flux of 10¹³ cm⁻² s⁻¹.

Measurements above room temperature were performed using a conventional two CsF detectors experimental set-up with a time resolution of $2\tau = 0.75$ ns at Ta energies, supplied with an electric furnace that allowed heating of the sample *in situ* within ± 1 K. Below room temperature the experimental data were obtained in the Centro Brasileiro de Pesquisas Físicas at Rio de Janeiro (Brasil) with a four NaI(Tl) detector equipment ($2\tau = 2.5$ ns at Ta energies). The samples were mounted in this case in a He gas flux cryostat.

A non-linear least-square fitting program was used to fit the experimental data to the theoretical model of equation (2).

3. Results

Before any thermal treatment was performed on the samples, room temperature TDPAC spectra were taken to characterize the compounds at a microscopic level through the determination of their hyperfine quadrupole interaction. For the three compounds a unique interaction describing a weak, symmetric and non-distributed EFG was obtained. This indicated that the probes were placed at very well defined crystallographic positions. The quadrupole parameters deduced for the interactions determined at room temperature were: $\omega_Q = 30.9_2 \text{ Mrad s}^{-1}$, $\eta = 0.0_*$ and $\delta = 3.0_2\%$, $\omega_Q = 23.1_1 \text{ Mrad s}^{-1}$, $\eta = 0.0_*$ and $\delta = 3.0_1\%$, $\omega_Q = 28.2_2 \text{ Mrad s}^{-1}$, $\eta = 0.0_*$ and $\delta = 3.0_3\%$ in $\text{NiHfF}_6 \cdot 6\text{H}_2\text{O}$, $\text{CoHfF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnHfF}_6 \cdot 6\text{H}_2\text{O}$ respectively (* means fixed parameter during the fit).

The dehydration temperatures of each compound were determined by thermal gravimetric analysis. They were 403 K for $\text{NiHfF}_6 \cdot 6\text{H}_2\text{O}$, 374 K for $\text{CoHfF}_6 \cdot 6\text{H}_2\text{O}$ and 365 K for $\text{ZnHfF}_6 \cdot 6\text{H}_2\text{O}$.

The behaviour of the quadrupole interaction in each of the samples over the whole thermal range investigated could be described assuming that three different EFGs acted on the probes, their coexistence dependent on temperature. One of them, that already reported as characterizing each compound at room temperature, behaved ordinarily, its quadrupole parameters showing always reproducible values. The other two interactions were observed to exhibit relative fractions which seemed to be related to the cooling rate of the sample in the sense that the slower the rate, the less the relative fractions. They also exhibited a poor reproducibility of the quadrupole parameters set at a given temperature. This experimental evidence led us to assume that these two interactions were depicting metastable states of the compounds, their varying relative fractions indicating that part of the samples had not achieved the equilibrium thermodynamic state and thus we did not investigate them. The well behaved interaction was then assumed to represent the hyperfine quadrupole interaction produced by the lattice at hafnium sites for each compound and the discussion will be focused on this.

4. Discussion

Figure 1 shows the evolution of the quadrupole interaction frequency in each compound. As can be seen, the interaction observed at room temperature evolved down to the lowest temperatures showing a strong temperature dependence. The asymmetry parameter η and the frequency distribution width δ remained constant within the studied temperature range, close to zero and lower than 3% respectively. No discontinuity was observed in the temperature behaviour of the quadrupole interaction frequency. This fact, together with the behaviour described for η and δ , strongly suggests that none of the samples undergoes a phase transition from 16 K to the dehydration temperature.

As was mentioned before, the quadrupole interaction frequency determined in $\text{CoHfF}_6 \cdot 6\text{H}_2\text{O}$, $\text{NiHfF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnHfF}_6 \cdot 6\text{H}_2\text{O}$ was strongly dependent on temperature. In order to estimate the contribution of the thermal expansion of the lattice to the temperature behaviour of the quadrupole frequency, point charge calculations of the variation of the EFG at the probe sites as lattice expands were performed. This was done assuming both that the structure of the compounds is isomorphous to those with Si as the central atom ($\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$, $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ of reference [5]) and that the lattice expansion is very similar to that of the $\text{NiZrF}_6 \cdot 6\text{H}_2\text{O}$ reported

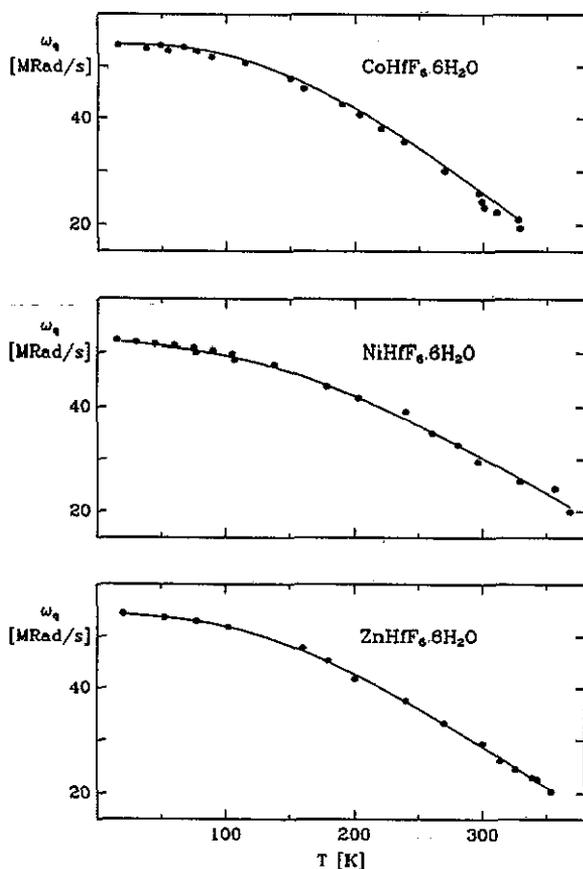


Figure 1. Thermal behaviour of the quadrupolar frequency observed in $A\text{HfF}_6 \cdot 6\text{H}_2\text{O}$ ($A = \text{Co}, \text{Ni}, \text{Zn}$). The solid line represents the fitted curve assuming two terms of equations [2].

in reference [6]. A change of 5% in the quadrupole interaction frequency between 10 K and room temperature was calculated, which is in disagreement with the value of approximately 50% drawn from the measurements in the same temperature range.

On the other hand, it is possible to give an account of the temperature dependence of the quadrupole interaction frequency if the model developed by Bayer [7] and Kushida *et al* [8] is assumed. In this model, the quadrupole interaction energy depends on the time average of the EFG (the time dependence of the EFG being due to local lattice fluctuations). Kushida *et al*, considering that the main contributions to the fluctuations of the EFG are due to the internal and external vibrations of the molecular groups of the lattice, give an analytical expression of the temperature dependence of the quadrupole interaction frequency as follows:

$$\omega_q(T) = \omega_{q0} \left\{ 1 - \frac{3}{8\pi^2} \sum_i \frac{h}{\theta_i \nu_i} \left[\frac{1}{2} + \left(\exp\left(\frac{h\nu_i}{kT}\right) - 1 \right)^{-1} \right] \right\} \quad (3)$$

where ω_{q0} is the quadrupole frequency for the case of rigid crystal lattice, θ_i are constants with units of inertia momentum and ν_i are the frequencies of the normal vibrations. Because of the negligible contribution of the high-frequency terms, most cases in the literature are well described taking into account up to two terms in equation (3). Under

Table 1. Parameters obtained using the Bayer–Kushida model to fit the experimental values of the quadrupolar frequency.

Compound	ω_{Q0} (Mrad s ⁻¹)	θ_1 (10 ⁻⁴⁸ K gm ²)	ν_1 (cm ⁻¹)	θ_2 (10 ⁻⁴⁸ K gm ²)	ν_2 (cm ⁻¹)
CoHfF ₆ ·6H ₂ O	102.4	2.69	371.3	60.9	137.8
NiHfF ₆ ·6H ₂ O	92.7	2.40	409.5	695.0	48.3
ZnHfF ₆ ·6H ₂ O	91.3	3.26	325.4	1103.6	44.7

the same condition, results from the fitting procedure are shown in table 1 and are plotted as solid lines in figure 1. Comparing the frequencies that we have determined with those obtained by Choudhury *et al* [9] for ZnTiF₆·6H₂O and MnTiF₆·6H₂O using Raman spectroscopy, it seems reasonable that the mode with the high frequency could be associated to the asymmetric stretching mode of the [HfF₆]²⁻ octahedron. On the other hand, the low-frequency mode is not easy to compare to any vibrational mode observed in similar compounds and it will remain unidentified. The inertia constants θ_i obtained are within an order of magnitude of ordinary inertia momenta of inorganic molecules.

5. Conclusion

The hyperfine quadrupole interaction in CoHfF₆·6H₂O, NiHfF₆·6H₂O and ZnHfF₆·6H₂O between 16 K and their dehydration temperatures have been measured using the time differential perturbed angular correlations technique. Unlike most of the compounds of the A^{II}B^{IV}F₆·6H₂O family, our experiments reveal that the three compounds investigated do not exhibit phase transitions within the investigated thermal range. The hyperfine quadrupole frequency determined for each compound displays a strong temperature dependence which could not be explained as due to the thermal expansion of the lattice. Instead, considering a two vibrational mode approximation of the Bayer–Kushida model, it is possible to fit the experimental data. The mode of the higher frequency was associated with the asymmetric stretching mode of the [HfF₆]²⁻ octahedron.

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