

TDPAC study of the thermal evolution of the quadrupole parameters in $\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$ between 30 and 400 K

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The thermal evolution of the quadrupole parameters determined using the time differential perturbed angular correlation technique at titanium sites, in $\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$ is presented. The study of the thermal behavior of the hyperfine quadrupole interaction allows one to observe the occurrence of a structural phase transition around 140 K. The thermal evolution of the hyperfine quadrupole frequency of the high temperature phase was interpreted in terms of the flip motion of the water molecules through an ad hoc model. Parameters associated with the model are in good agreement with independent data obtained by Raman scattering. The agreement gives support to the model to be a valuable tool to study the dynamics of molecular groups in crystalline hydrates.

1. Introduction

$\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$ is one of the members of the family of compounds of general formula $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{F}_6 \cdot 6\text{H}_2\text{O}$, where A^{II} is a divalent first-row transition metal and B^{IV} is Hf, Zr, Ti, Sn, etc. It was reported [1] that most of these compounds undergo a phase transition between a trigonal high temperature phase ($R\bar{3}m$ or $R\bar{3}$, $Z = 1$) and a monoclinic low temperature one ($\text{P}2_1/c$, $Z = 2$). In the case of $\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$, the lattice parameters of the $R\bar{3}m$ phase were reported to be $a = 6.4 \text{ \AA}$ and $\alpha = 96^\circ$ [2]. The atomic positions of this phase are not known yet. However, it is

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known that the molecular structure can be described as alternating chains of $[\text{TiF}_6]^{2-}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ octahedral ions linked by hydrogen bonds. In this compound, the transformation between the $R\bar{3}m$ and the $P2_1/c$ phases has been reported to occur at around 130 K [1–7]. The transition can be described as a displacive one in the sense of Megaw [8]: structural relations between the high and the low temperature phases, no breaking bonds and small and reversible atomic displacements. The relevant features of the high temperature phase are the following: (1) the polyhedra that constitute the molecular structure undergo fast reorientational motions around their symmetry axis; (2) the water molecules perform a flip motion around their C_2 symmetry axis. On the other hand, the low temperature $P2_1/c$ phase does not display these motions and it was suggested in ref. [1] that the freezing of the motions can be considered as the onset of the phase transformation. Existing data describing the phase transition report only the behavior of magnetic and quadrupole properties determined at the fluor, hydrogen and/or transition metal site. In this paper the thermal evolution of the hyperfine quadrupole interaction in $\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$ is studied using the time differential perturbed angular correlation technique to give more information on the phase transition process and the dynamics of the molecular groups of the $\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$ lattice. For the first time, the thermal evolution of the hyperfine quadrupole interaction determined at the B^{IV} site during the phase transition is presented.

2. Experimental

The TDPAC technique allows one to determine the hyperfine interaction between a radioactive nucleus, decaying through a two-step cascade, and its surrounding, by measuring the time dependent angular distribution of the second nuclear emission of the cascade relative to the direction of the first one.

For the case of quadrupole interactions, the interaction arises from the electric field gradient (EFG) acting on the quadrupole moment Q of the intermediate nuclear level of the cascade. For polycrystalline samples and static EFG, the interaction is described by the so-called perturbation factor $G_{22}(t)$ that, in the case of a γ – γ cascade with intermediate nuclear spin $I = 5/2$, has the form [9]

$$G_{22}(t) = \sigma_{20} + \sum_{n=1}^3 \sigma_{2n} \cos(\omega_n t) e^{-\delta \omega_n t}. \quad (1)$$

In eq. (1) ω_n are already known functions [9] of the quadrupole interaction frequency $\omega_Q = e^2 Q V_{zz} / 4I(2I - 1)\hbar$ and of the asymmetry parameter $\eta = (V_{xx} - V_{yy}) / V_{zz}$ which fully describe the EFG (V_{ij} being the electric field gradient components). The σ_{2n} coefficients depend also on η and δ measures the FWHM of the ω_Q distribution produced by defects and/or impurities of the lattice.

Whenever the probes of a certain sample are occupying non-equivalent sites,

the situation is described considering a linear combination of perturbation factors as defined in eq. (1),

$$G_{22}(t) = \sum_i f_i G_{22i}(t), \quad (2)$$

where the f_i coefficients are the relative abundances of each interaction.

Fitting procedures allow to determine the hyperfine quadrupole parameters ω_Q , η and δ and the relative abundances f_i , from the experimental data.

Data were obtained using the very well known 133–482 keV γ – γ cascade of ^{181}Ta as TDPAC probe which is produced by thermal neutron irradiation of ^{180}Hf .

$\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$ samples (doped with 5% in weight of natural hafnium) were prepared following the method outlined by Davidovitch et al. [10]. The samples were checked using X-ray powder diffraction in order to ensure that the compound was properly prepared.

Measurements above room temperature were performed using a two CsF detectors high-resolution setup ($2\tau = 0.75$ ns at Ta energies) supplied with an electric furnace to heat the samples, in situ, up to 400 K within ± 1 K. Below 300 K TDPAC spectra were obtained using a four NaI(Tl) detectors setup ($2\tau = 2.5$ ns at Ta energies) with a sample holder in a He-flux cryogen to cool the samples down to 30 K.

3. Results and discussion

At room temperature a symmetric and non-distributed single interaction was used to fit the experimental result (fig. 1) the hyperfine parameters of which can be seen in table 1. The single interaction picture gave also sufficient fits to the results obtained between 140 and 400 K. In this thermal range, the only feature was the monotonous decreasing of the hyperfine quadrupole frequency from about 70 Mrad/s at 140 K to 20 Mrad/s at 400 K (see fig. 2). This fact must be examined carefully and we will do this in section 4.

Below 140 K two additional hyperfine interactions (named hereinafter A and B) were needed to fit the TDPAC spectra, clearly evidencing that a new phase appears in the system. The transition was determined to be reversible. The quadrupole parameters associated to this phase, at 188 K, can be seen in table 1. It must be mentioned that the relative fractions of the new interactions remained close to a 1 : 1 ratio from 30 to 140 K. This fact, which is consistent with the crystallographic description of the low temperature phase, gives better support to a two inequivalent molecules per unit cell picture.

Related to the low temperature interactions, the thermal behavior of interaction A seems to be the regular one as expected from a standard lattice expansion. On the other hand, the hyperfine quadrupole parameters of the interaction B clearly appears to be a branching of those of the high temperature interaction, indicating

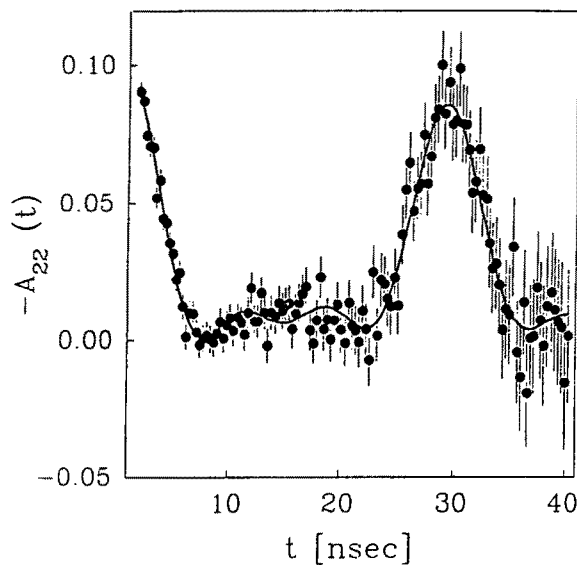


Fig. 1. TDPAC spectrum obtained at 293 K. The solid line is the fit curve assuming a single quadrupole interaction.

that the associated hafnium sites have a close connection with those of the $R\bar{3}m$ phase.

Summing up, the behavior of the hyperfine quadrupole interactions reveals the development of a reversible phase transition around 140 K that modifies the lattice of the $\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$ from its $R\bar{3}m$ phase to a two-titanium-sites low temperature phase. The suggestion of a $P2_1/c$ symmetry of the low temperature phase is supported by our results. Although it was not possible to go from an $R\bar{3}m$ to a $P2_1/c$ symmetry in a continuous way, our TDPAC experiment shows a sequence of small changes that connects the sites of the phases involved in the transition and, in this sense, it is possible to infer that the phase transformation is displacive like.

4. Thermal evolution of the quadrupole interaction frequency

There are many models devoted to the understanding of the thermal behavior of the hyperfine quadrupole interaction frequency [11–14]. One of the most used is

Table 1

Hyperfine parameters deduced from the TDPAC spectra obtained at selected temperatures.

T (K)	Interaction	ω_Q (Mrad/s)	η	δ (%)
293	—	36.9_3	0.09_5	3_1
118	A	34.7_5	0.50_2	0_2
118	B	70_3	0.43_5	15_6

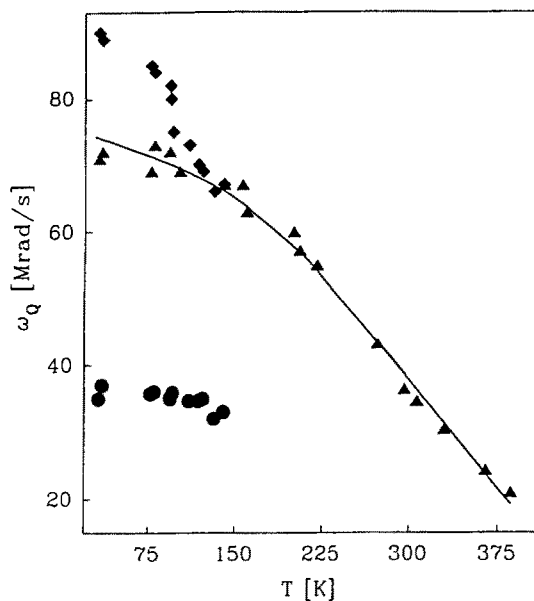


Fig. 2. Thermal evolution of the hyperfine quadrupole frequency between 30 and 400 K. The fit of the Bayer–Kushida and the flip model to the experimental data is indicated by the solid line.

that proposed by Bayer [11] and Kushida and coworkers [12]. In this model, the decrease of the quadrupole interaction frequency at increasing temperatures is attributed to the enlargement of the amplitude of the optical vibro-rotational modes of the lattice. The expression given by Kushida is the following:

$$\omega_Q(T) = \omega_0 \left(1 - \frac{3}{8\pi^2} \sum_i \frac{h}{\theta_i \nu_i} \left[\frac{1}{2} + (e^{h\nu_i/kT} - 1)^{-1} \right] \right), \quad (3)$$

where ω_0 is the quadrupole interaction frequency at $T = 0$ K, ν_i are the vibro-rotational frequencies of the lattice and θ_i are the corresponding inertia constants. However, as it was pointed out by Bayer in his pioneer work, analytical expressions are only obtained in perturbative approximation and, of course, it is not possible to use these expressions to give account of the TDPAC results where a 70% variation in the hyperfine quadrupole frequency is observed.

In order to explain such an important variation, in the following a suitable model will be developed that, along with the Bayer–Kushida one, reproduces the experimental behavior determined in the hyperfine interaction frequency.

As it was mentioned before, the water molecules undergo flip motions around their C_2 symmetry axis. This movement can be described assuming that hydrogen atoms are placed in a double-equivalent-minimum potential [1]. Despite the actual shape of the potential curve, it is well known [15] that the low energy spectrum of a double-minimum potential consists of nearly equal-spaced doublets of energy

levels. It will be assumed that the hydrogen sublattice will create, depending on its state, different electric field gradients at probe sites. Calculating the Boltzmann factor of each energy level it is easy to conclude that the only relevant levels at temperatures up to 400 K, are the first two levels (first pair)^{#1}. If this is so, the problem can be treated as a two-level problem and, within the frame of the classical statistics, the following expression for the mean value of the electric field gradient due to the hydrogen sublattice is obtained:

$$\bar{V}_{zz} = V_{zz}^g \frac{1 + R e^{-E_0/kT}}{1 + e^{-E_0/kT}}, \quad (4)$$

where E_0 is the energy gap between levels, V_{zz}^g is the major component of the EFG which arises from the atomic configuration related to the ground state and R is the ratio between the V_{zz} of the excited state and V_{zz}^g (see fig. 3). As the flip movement of the hydrogen atoms is the starting point to state the model, it will be termed, hereinafter, the flip model.

As it was mentioned before, the experimental results can be fitted using the Bayer–Kushida together with the flip model. The best fit was achieved using two terms of the sum of the Bayer–Kushida model. Results are shown in fig. 2. All the parameters involved in the fit are listed in table 2. The E_0 value (545_{50} cm^{-1}) can be compared to that obtained using Raman scattering in $\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$ [18]. Data reported from the study of the thermal dependence of the FWHM of the symmetric stretching mode ν_s of the water molecules yield an E_0 value of 598_{43} cm^{-1} . It must be noted that the agreement is really satisfactory. This agreement gives a solid support to include the movement of water molecules as an important source of the thermal variation of the EFG, which is well described through the flip model presented here.

^{#1} To estimate the occupation number of the energy levels, an $X^2 + X^4$ double-well potential (with typical barrier of 6 kcal/mol) was used.

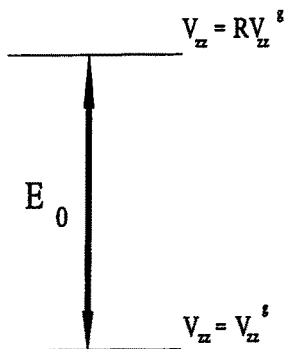


Fig. 3. Energy levels used to work out the flip model, see text.

Table 2

Parameters used and obtained during the fit of the thermal behavior of the quadrupole frequency of the $R\bar{3}m$ phase in $\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$. The calculated parameters were obtained using the interatomic distances reported for $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ [16]. BK means Bayer–Kushida model and FL means flip model. The assignment of the vibra-rotational frequencies to the calculated inertia constants was done following the criterion suggested in ref. [17]. The parameters ω_Q^g and V_{zz}^g (eq. (4)) are related through $\omega_Q^g = e^2 Q V_{zz}^g / 4I(2I - 1)\hbar$.

Parameter	Value	Obtained from
ω_0 (Mrad/s) (BK)	69 ₃	fitted
ν_1 (cm ⁻¹) (BK)	15	ref. [3]
θ_1 (uma Å ²) (BK)	213.7	calculated
ν_2 (cm ⁻¹) (BK)	35	ref. [3]
θ_2 (uma Å ²) (BK)	120.3	calculated
ω_Q^g (Mrad/s) (FL)	7.5 ₇	fitted
E_0 (cm ⁻¹) (FL)	545 ₅₀	fitted
R (FL)	-34 ₈	fitted

5. Conclusions

The analysis of our TDPAC results permits to draw some conclusions.

First of all, the $\text{NiTiF}_6 \cdot 6\text{H}_2\text{O}$ undergoes a reversible phase transition around 140 K, the low temperature phase exhibiting two nonequivalent titanium sites. This results supports the already suggested monoclinic $P2_1/c$ structure with two molecules per unit cell for the low temperature phase. According to the thermal behavior displayed by one of the interactions of the low temperature phase (an asymptotic evolution of the hyperfine parameters of the interaction B to those of the $R\bar{3}m$ phase) the phase transformation clearly exhibits a displasive character.

The thermal evolution of the quadrupole interaction frequency observed for the $R\bar{3}m$ phase can be understood combining the Bayer–Kushida and the flip models.

The value of the energy gap between the two levels of the flip model deduced from the TDPAC results agrees very well to that independently obtained from Raman scattering experiments. This fact indicates that the flip model can be considered a useful tool for both, the understanding of the thermal behavior of the quadrupole interaction frequency and the drawing of relevant information on the dynamics of the molecular groups in these salts.

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