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Time-differential perturbed-angular-correlation study of phase transitions and molecular motions in $K_3(Hf,Zr)F_7$

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Using time-differential perturbed-angular correlation, two thermal reversible phase transitions have been observed in both isostructural compounds K_3HfF_7 and K_3ZrF_7: the orthorhombic-to-tetragonal transition, occurring in K_3HfF_7 around 275 K, and the tetragonal-to-disordered cubic transition, which developed from room temperature (RT) over a wide thermal range. It has been inferred that ionic complexes $MF_7{}^{3-}$ in the tetragonal and cubic phases have the same structure, and that the cubic phase appears due to the onset of their reorientational motion. The detailed investigation performed on K_3HfF_7 has allowed the determination of a two-stage mechanism for this movement: a slow diffusional reorientation near RT and an isotropic fast relaxation at higher temperatures. Activation energies for different thermal ranges have been calculated.

I. INTRODUCTION

The crystalline structure of K_3ZrF_7 is known to be face-centered cubic ($a = 9.36$ Å) with some randomness of distribution among the positions provided by the space-group $Fm3m$.[1] Though the crystalline structure of K_3HfF_7 has not been reported, it is assumed, as usual, that this substance is isostructural with K_3ZrF_7. Tananaev and Guzeeva[2] have investigated both compounds via differential thermal analysis (DTA). In heating from room temperature (RT), they have found only one endothermic peak around 1200 K, which was associated with melting.

Two phases have been reported to exist for K_3ZrF_7: the orthorhombic one[3] at low temperatures and the disordered cubic form at room temperature. However, a tetragonal phase, coexisting with the cubic one over a long thermal range, was observed in K_3HfF_7.[4] Also, depending on the heating treatments, a tetragonal or disordered cubic phase was obtained at RT by Zachariasen *et al.*[5] for K_3UF_7, reported to be isostructural with K_3ZrF_7. These authors determined that the x-ray diffraction patterns of both phases were strikingly similar, the tetragonal phase pattern containing a number of additional lines, and they suggested that the cubic phase was a disordered form of the tetragonal modification.

Even when all the authors agreed that the cubic phase has four equivalent molecules per unit cell with some randomness in the orientation of the MF_7^{3-} ($M =$Hf, Zr) ions, the geometry of the ion and the nature of the disorder have not been established yet. The most recent literature available states that the structure is described by a regular[5] (D_{5h} symmetry) or nearly regular[6] pentagonal bipyramid. Zachariasen[5] also proposed that the ion complexes had the same shape as those of the tetragonal phase and, in agreement with Hurst and Taylor,[6] that the disorder could be due to the reorientation of the fivefold axis among the 24 equivalent orientations of the ion.

K_3HfF_7 has already been investigated using the time-differential perturbed-angular-correlation (TDPAC) technique. The first work was performed by Settè-Camara[4] with a TDPAC setup with 3.5 ns time resolution. A superposition of a static and a time-dependent interaction was observed at RT, while the x-ray diffraction data exhibited a mixture of tetragonal and disordered cubic phases, the tetragonal vanishing when heated at 420 K. Results at 77 K were fitted assuming a very distributed unique static interaction. At 403 K, the static interaction present at RT had nearly disappeared, and at 573 K the interaction involved was fully dynamic. The author associated the static interactions to the tegragonal phase, and the dynamic one to the cubic phase. The experimental determination of the relaxation constants between 408 and 568 K allowed the author to calculate the activation energy for the movements observed in the cubic phase. A second investigation was performed by Prestwich *et al.*[7] who studied the compound between 77 and 318 K. A sudden change observed at 250 K was associated with a structural orthorhombic-to-cubic phase transition and no mention was made of a tetragonal phase. The authors also found that from 77 K on, the orthorhombic phase presents two nonequivalent sites with relative fractions of 70 and 30% and that from 170 K on, the less populated one undergoes a gradual "conformational change," its quadrupole frequency converging to that of the other site, and its asymmetry parameter increasing significantly. Above 250 K a purely dynamic interaction was satisfactorily fitted to the experimental data, but the thermal behavior of the relaxation constant could not be elucidated.

The most recent and complete NMR investigation on K_3ZrF_7 was performed by Reynhardt *et al.*[8] between 67 and 301 K. The results led the authors to assume that the orthorhombic unit cell also contains four molecules, which are not equivalent. Above 263 K, the isotropic reorientation of all $ZrF_7{}^{3-}$ complexes turns them equivalent and gives rise to the cubic phase, for which an activation energy of (0.095 ± 0.004) eV was determined.

In this paper we present a new, thorough investigation of the quadrupole hyperfine interaction in K_3HfF_7 between 47 and 1260 K and complementary results on the isomorphous compound K_3ZrF_7. Using high-resolution TDPAC equipment, we have undertaken this work in order to clarify the polymorphism of the substances under study and to draw additional information about the reorientation mechanisms involved in the high-temperature disordered cubic phase.

II. EXPERIMENT

Samples of K_3HfF_7 (K_3ZrF_7) were prepared dissolving 200 mg of HfF_4 (125 mg of ZrF_4 + 10 mg of HfF_4) in 4 ml of hot 1-N hydrofluoric acid and adding 12 ml of a saturated solution of KF. The solutions were cleared by addition of 1 ml of 4-N hydrofluoric acid and left to cool slowly and to crystallize. In the case of the zirconium compound, due to the already established experimental evidence of the substitutional incorporation of hafnium impurities in zirconium compounds, hafnium nuclei also acted as TDPAC probes.

X-ray powder-diffraction patterns exhibited all the lines of the fcc lattice and also others which could be associated to a tetragonal one which, for the case of the zirconium compound, presented cell parameters $a=8.95$ Å and $c=18.08$ Å ($c/a=2.02$). The tetragonal phase was predominant. DTA obtained by heating the samples at 5 K/min in air from RT to 1073 K for K_3HfF_7 and to 773 K for K_3ZrF_7 showed no noticeable peaks.

In order to obtain ^{181}Ta probes for the TDPAC experiments, powder samples of the compounds were irradiated with thermal neutrons in the RA-3 reactor of the Comisión Nacional de Energía Atómica, Argentina. The experimental setup was a two-CsF detector system coupled to a standard fast-slow coincidence circuit. The time resolution at ^{181}Ta energies was 0.75 ns. A helium closed-cycle cryogenic system and a heating system attached to the sample holder, which could stabilize the temperature within ±1 K, were used to obtain the spectra below and above RT.

By means of a nonlinear least-squares fitting program, a linear combination of perturbation factors like

$$G_{22}(t)=\sum_i f_i G_{22}^{(i)}(t)$$

was fitted to the experimental data, where the f's represent the relative fractions in which the interactions described by the different perturbation factors are present.

Four different perturbation factors were used in this work, i.e.

$$G_{22}(t)=\sigma_{20}+\sum_{k=1}^{3}\sigma_{2k}\cos(\omega_k t)e^{-\delta\omega_k t} \tag{1}$$

for static quadrupole interactions in a polycrystalline sample, where the σ's are functions of the asymmetry parameter η, the ω's are functions of the quadrupole frequency ω_q and η, and δ stands for a frequency distribution width,

$$G_{22}(t)=\left[\sigma_{20}+\sum_{k=1}^{3}\sigma_{2k}\cos(\omega_k t)\right]e^{-\lambda t}\ , \tag{2}$$

the attenuation factor deduced by Marshall and Meares,[9] on the basis of a slow rotational diffusion model where λ^{-1} is the reorientational correlation time, Abragam and Pound's perturbation factor in the limit of fast relaxation $\langle\omega_q^2\rangle^{1/2}\tau c \ll 1$:[10]

$$G_{22}(t)=e^{-\lambda t} \tag{3}$$

with a decay constant[11]

$$\lambda=100.8\langle\omega_q^2\rangle\tau_c(1+\eta^2/3)\ , \tag{4}$$

$\langle\omega_q^2\rangle$ denoting the average square quadrupole interaction frequency, and finally, the attenuation factor deduced from the Dattagupta-Blume theory in the isotropic random-phase approximation[12] often used to interpolate between the region of slow and fast relaxation

$$G_{22}(t)=\left[\sigma_{20}+\sum_{k=1}^{3}\sigma_{2k}\cos(\omega_k t)\right]e^{-\lambda t} + \left[\sigma_{20}^2+\frac{1}{2}\sum_{k=1}^{3}\sigma_{2k}^2\cos(\omega_k t)\right]\lambda t\ , \tag{5}$$

λ being a measure of the probability per unit time of a jump from a given stochastic state to another. Details of the experimental and data handling can be found elsewhere.[13]

III. RESULTS AND DISCUSSION

For the hafnium compound, spectra were taken at small temperature intervals in order to study, in detail, the thermal evolution of the electric field gradient (EFG) at hafnium sites. For the isomorphous zirconium compound, a smaller number of measurements was taken instead. Selected spectra are shown in Figs. 1 and 2.

Starting spectra at RT for both compounds, K_3HfF_7 and K_3ZrF_7, revealed the presence of two interactions. One of them, the dynamic interaction, was fitted using Eq. (2) for K_3HfF_7 and Eq. (5) for K_3ZrF_7; the involved quadrupole frequencies were coincident with those associated with the static interaction. Table I lists the fitted quadrupole parameters. This result, along with x-ray diffraction data, allowed us to identify the static interaction with hafnium and zirconium environments in the tetragonal phase, and the dynamic interaction to environments in the disordered cubic phase. The coincidence in the interaction frequencies was interpreted on the idea that the ion complexes of the tetragonal and cubic phases have the same structure. As a consequence, the time-

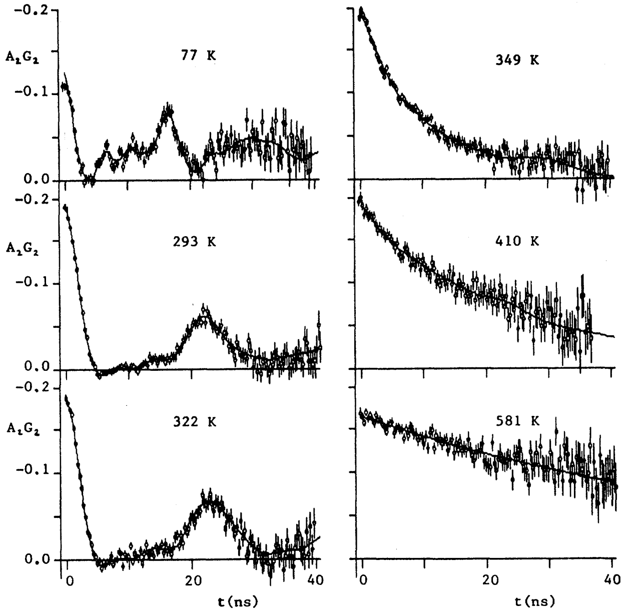

FIG. 1. Spin-rotation curves of K_3HfF_7 at different temperatures. Solid lines are the fitted curves to the data.

dependent interaction can be realized in terms of the existence of reorientational motions of some of the MF_7^{3-} complexes.

In Fig. 3 the thermal evolution of the fitted quadrupole parameters for K_3HfF_7 between 47 and 410 K is plotted. In the range 47–240 K the hyperfine interaction presented two static components in a nearly 2:1 ratio, characterized at 47 K by quadrupole parameters $\omega q_1=(59\pm1)$ Mrad/s, $\eta_1=0.34\pm0.02$ and $\omega_{q_2}=(96.7\pm0.7)$ Mrad/s, $\eta_2=0.59\pm0.01$. The first of them, and the more abundant, exhibited a considerable frequency distribution width ($\delta\simeq10\%$). These results are similar to those obtained by Prestwich *et al.*,[7] but do not agree with those of Settè-Camara,[4] perhaps because of the high-frequency distribution which only affected EFG he observed. We have interpreted this two-interaction picture as describing the low-temperature orthorhombic phase reported by Buslaev for K_3ZrF_7,[3] in disagreement with Reynhardt's hypothesis, which states that the orthorhombic unit cell contains four nonequivalent molecules. On heating, the thermal evolution of the first hyperfine component was not relevant and the second one showed a slight decrease in the quadrupole frequency and an increasing asymmetry parameter. These effects increased from 180 on, and above 240 K, the corresponding population diminished favoring that of the other interaction. Finally, at 275 K, the whole lattice became described by a unique and very distributed static interaction ($\delta\simeq20\%$) of quadrupole parameters $\omega q_3=(54.8\pm1.0)$ Mrad/s and $\eta_3=0.27\pm0.03$.

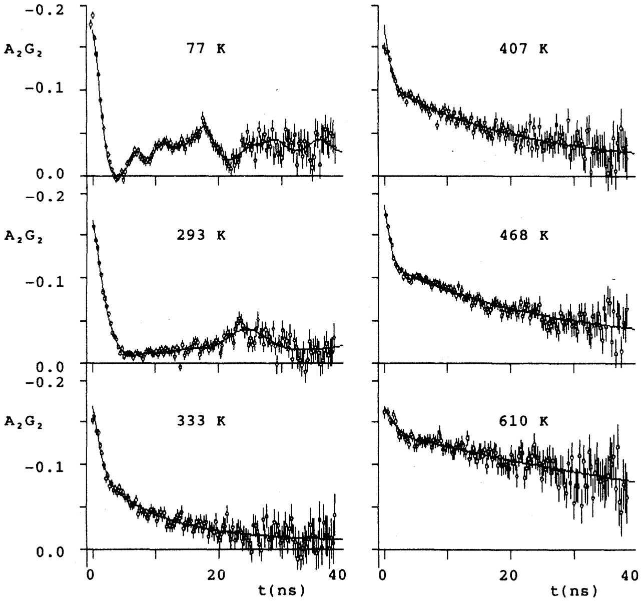

FIG. 2. TDPAC spectra of K_3ZrF_7 at selected temperatures. Solid lines are the fitted curves to the data.

The room-temperature spectrum taken during the increasing temperature series of measurements was fitted satisfactorily with the same parameters as the initial one, indicating that the differences observed between room temperature and 47 K adhered to completely reversible changes. Realizing that the static EFG determined in the

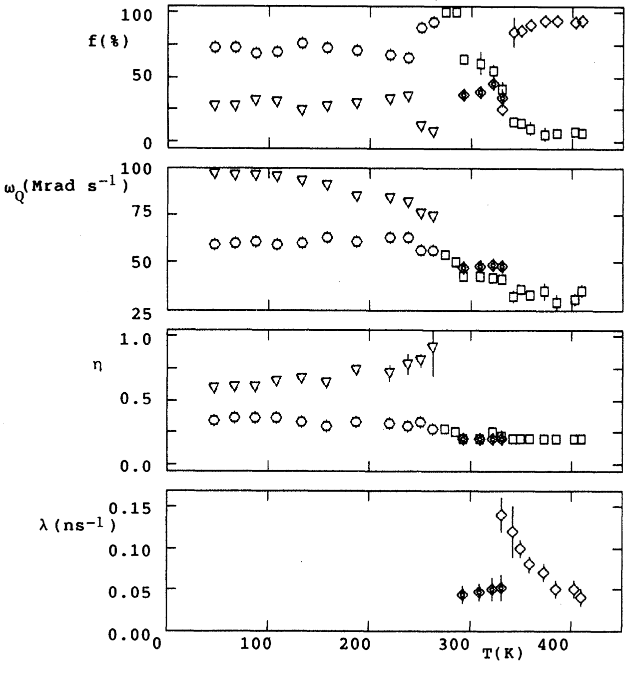

FIG. 3. Thermal evolution of the relative fractions and quadrupole parameters of the hyperfine interactions determined in K_3HfF_7 between 47 and 410 K. (○) and (▽) symbols denote orthorhombic sites, (□) denotes tetragonal sites, and (◇) and (◈) denote disordered cubic sites.

TABLE I. Abundances and quadrupole parameters corresponding to the different structural phases of K_3HfF_7 and K_3ZrF_7. (a): orthorhombic phase, (b): tetragonal phase, (c): disordered cubic phase, (*): fixed parameter.

		K_3HfF_7			K_3ZrF_7		
T (K)		f (%)	ω_q (Mrad/s)	η	f (%)	ω_q (Mrad/s)	η
77	(a)	68(4)	61.1(1.0)	0.35(0.02)	64(5)	64.0(2.0)	0.24(0.04)
		32(3)	96.0(1.0)	0.66(0.03)	34(4)	90.1(1.0)	0.56(0.03)
293	(b)	64(4)	42.9(0.8)	0.21(0.06)	60(6)	43.4(1.3)	0.21(0.05)
293	(c)	36(2)	47.4(0.4)	0.20(*)	40(2)	43.3(9.6)	0.20(*)

room-temperature spin-rotation curve described the same site as the unique one fitted at 275 K and also at 285 K, we have concluded that at these temperatures the compound was in the tetragonal phase. So, the change from the two-interaction picture (47–270 K) to that of one interaction at 275 K has been interpreted as the result of the orthorhombic↔tetragonal phase transition. It is known that displacive transitions of low-energy barrier, where neither interatomic bonds are broken nor new ones are formed, give rise to a new structure which is capable of being derived from the old one by a continuous and reversible process of atomic small displacements, thus leading to a close approximation between the symmetries of the phases connected by the transition.[14] The experimental evidence that the most populated site of the orthorhombic phase presents an EFG increasingly similar to that characterizing the tetragonal form and the reversible character of the orthorhombic-tetragonal transition, might be associated to the existence of a close orientational relation between the ion complexes in both sites, due to which, the transition would not change the topology and could be classified microscopically as a displacive one. Unfortunately the scarce available crystallographic data about the involved phases does not allow us to confirm this hypothesis. Regarding the above-mentioned modifications observed from 180 K, they indicate some instability of one of the sites of the orthorhombic phase, then confirmed it by the decrease of its relative fraction above 240 K. These effects can be seen as preparatory of the forthcoming structural change in the sense that, for the displacive transition to occur, it seems necessary that, first, the orthorhombic lattice was described by a unique site, just the one of the quadrupole parameters very similar to those identifying the tetragonal lattice.

Between 293 and 330 K the dynamic hyperfine component gradually increased and satisfied Marshall and Meares's model in the frame of slow rotational diffusion of molecular complexes [Eq. (2)]. From 340 K on, a better fit was obtained using Abragam and Pound's fast relaxation model [Eqs. (3) and (4)]. Simultaneously, the tetragonal phase diminished abruptly until it vanished completely above 400 K. Bearing in mind that the D_{5h} symmetry proposed for the $MF_7{}^{3-}$ complexes presents 24 equivalent positions for the fivefold axis, it seemed reasonable to associate the movement observed in the initial stage (293–330 K) to the reorientation of the molecular axes along these positions. At higher temperatures, instead, the observed fluctuating interaction matched a model where molecules reorientate isotropically in the limit of fast relaxation. The dynamic characteristics described would allow us to classify the tetragonal-cubic transition as a orientation-switching one, since the disorder begins with a change in the orientation of the molecular axes and the onset of complete rotation occurs at higher temperatures. This type of transition, frequently extended over a wide thermal range, has been observed in many compounds involving small molecular ions.[14]

Hyperfine results indicated that the disordered cubic modification was stable up to around 900 K. The reversibility of the tegragonal-to-cubic transition was repeatedly confirmed taking spectra at RT which were always fitted in agreement with the starting one.

Figure 4 shows the thermal behavior of the relaxation constant experimentally determined from 330 K. For the region 293–330 K, where the tetragonal phase is still predominant, the fitted λ values were subjected to great uncertainties. This situation prevented us from drawing any clear temperature dependence, and consequently no activation energy could be determined for the molecular

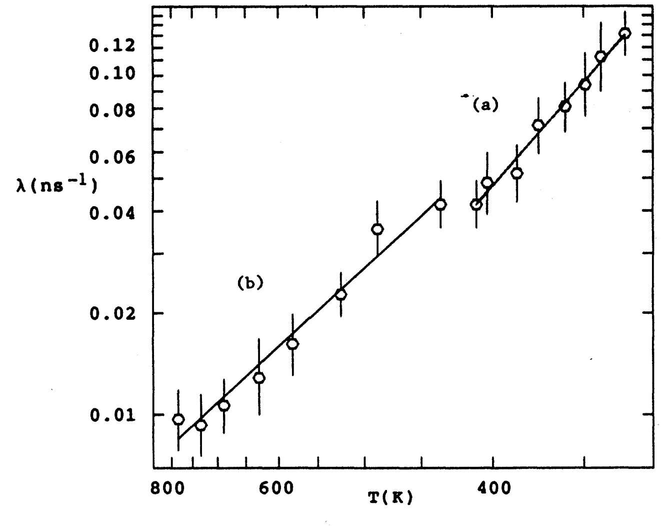

FIG. 4. Thermal behavior of the relaxation constants for isotropic fast relaxation movements in the cubic phase of K_3HfF_7. (a) in the presence of the tetragonal phase, (b) in the presence of the pure cubic phase.

axes reorienting along the 24 equivalent positions. Nevertheless, the involved correlation times were estimated to be approximately 20 ns, fulfilling the conditions of the model assumed.

Within the range 330–900 K the $\lambda(1/T)$ function suggests an exponential dependence of the form $\lambda = Ae^{E_a/kT}$ from which two activation energies of (0.17 ± 0.02) eV and (0.14 ± 0.02) eV could be calculated. In order to estimate the magnitude of the correlation times, the $\langle \omega_q^2 \rangle$ value involved in Eq. (4) was assumed as that associated to the quadrupole frequency determined for the static ion complexes of the tetragonal phase and also for the slowly reorienting complexes of the disordered cubic phase at lower temperatures. Also, any thermal dependence of the fluctuating EFG was neglected. Under these assumptions, the correlation times obtained ran between 0.85 and 0.06 ns. It is worth mentioning that the change in the slope of the $\lambda(1/T)$ function occurred just at the temperature where the compound completely achieved the cubic phase. A comparison between the activation energies determined for the ranges 330–410 K and 435–900 K indicates that the disappearance of the tetragonal phase causes a reduction in the energy barrier for the activation of the isotropic reorientational motion.

Regarding the compound K_3ZrF_7, the spectrum taken at 77 K was quite compatible with the two-site picture, identifying the low-temperature orthorhombic phase (see Table I). The time-dependent interaction fitted at RT did not satisfy either the slow rotational diffusion model or the fast relaxation one. Instead, the Dattagupta-Blume theory[12] had to be assumed. So, contrary to what had been determined in K_3HfF_7, reorientation of ZrF_7^{3-} ions involved isotropic movements and no selected orientations for the molecular axes were observed, at least at RT and above. From 330 K on, no static interactions, were necessary but two different time-dependent interactions, were necessary to satisfactorily fit the spin-rotation curves. The new dynamic component obeyed the fast relaxation model and increased up to 670 K, where it achieved the 100% population.

Figure 5 shows the thermal behavior of the relaxation constants determined from the fits. While for the upper points [Fig. 5(a)] an activation energy of (0.016 ± 0.010) eV was calculated, the fast relaxation reorientation mechanism [Fig. 5(b)] threw an activation energy of (0.11 ± 0.01) eV. The correlation times for both movements, with the same hypothesis about $\langle \omega_q^2 \rangle$ that was assumed for K_3HfF_7, showed that the time associated to the fast relaxation were shorter than the others and that all of them, independently of the model assumed, showed the ordinary tendency of diminishing as temperature increased.

Above 900 K the spin-rotation patterns of both compounds began to change, revealing typical static interactions. The corresponding fits threw axially symmetric EFG's of quadrupole frequency $\omega_q \simeq 75$ Mrad/s. In the case of K_3ZrF_7, an additional EFG was determined. In spite of Tananaev and Guzeeva's observation that K_3HfF_7 and K_3ZrF_7 melt without decomposition, Novoselova *et al.*,[15] while studying the KF-ZrF_4 system, have reported that, from 1121 K on, the $K_5Zr_2F_{13}$ modification could be formed starting from K_3ZrF_7. It seemed reasonable, then, to suppose that the static EFG common to both compounds would depict the compound $K_5M_2F_{13}$, but no hypothesis could be made about the second hyperfine component present in the case of the zirconium sample. The interactions just described remained when the temperature was lowered, indicating the irreversibility of the decomposition process.

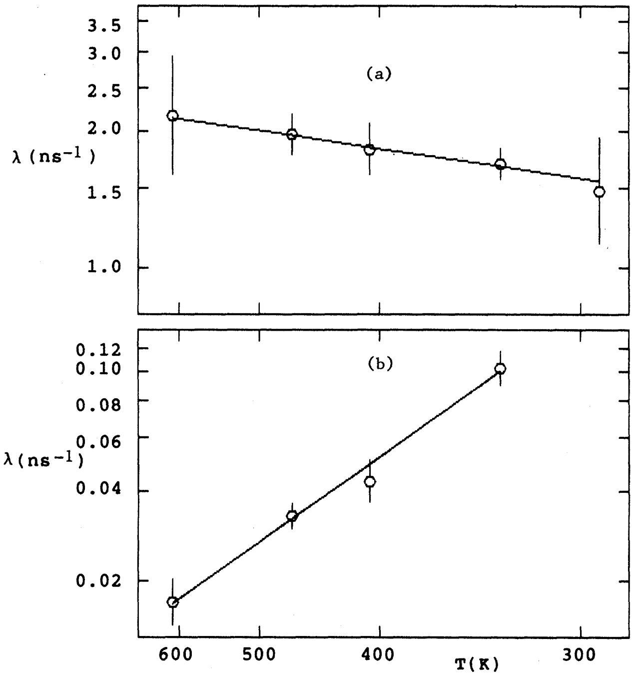

FIG. 5. Relaxation constant vs reciprocal temperature for isotropic reorientations in K_3ZrF_7. (a) $\lambda = 1/\tau_c$, (b) $\lambda \propto \langle \omega_q^2 \rangle \tau_c$.

CONCLUSIONS

The relevant information contained in this investigation, drawn mainly from the thermal evolution of the hyperfine interaction in K_3HfF_7, can be summed up in the following points.

(1) Contrary to what was reported by other authors about the existence of a unique phase transition in $K_3(Hf,Zr)F_7$ between an ordered phase—either the orthorhombic or the tetragonal—and the disordered cubic form occurring near RT, in this work the thermal behavior of the hyperfine interaction determined by TDPAC has been interpreted in terms of the existence of three crystalline modifications: the orthorhombic, the tetragonal, and the disordered cubic, appearing successively at increasing temperatures. While the transition between the first two presents premonitory effects and takes place in a narrow thermal interval, the second one involves the reorientational movement of the MF_7^{3-} ionic complexes and develops gradually over a long thermal range. Perhaps the short interval of temperature between the occurrence of the tetragonal phase and the appearance of

the cubic phase, added to the similtude of the quadrupole parameters associated to the tetragonal phase and to the moving ionic structures in the first stage of their reorientation, led previous investigators to interpret the changes observed near RT as a sole phase transformation.

(2) The coincidences found in the quadrupole parameters of the interactions describing the tetragonal and cubic phases, and the onset of the reorientational motion of the ionic groups as the unique evidence of the appearance of the cubic modification, seem to confirm Zachariasen's proposals that the ion complexes of both phases are the same and that the cubic phase is a disordered form of the tetragonal one.

(3) We have been able to infer some features of the phase transitions observed, i.e.: (a) both of them are reversible, (b) the orthorhombic-tetragonal transition takes place around 275 K and is indicated by the change from a two-static-interaction picture to a one-static-interaction picture. A premonitory effect, by which the less populated site of the orthorhombic phase converted into the other, rendered the orthorhombic lattice to promptly suffer the forthcoming transformation. This one, occurring between structures with very small hyperfine differences, can perhaps conform a displacive transition, (c) the detailed hyperfine study performed on K_3HfF_7 allowed us to establish a two-stage mechanism for the reorientation of the molecular axes of the ionic groups: in the beginning along selected directions and at higher temperatures as an isotropic fast relaxation. This experimental evidence prompted us to classify the changes observed as characterizing an "orientation-switching" phase transition. Activation energies for the isotropic motions were determined for both compounds.

(4) Some differences observed during the thermal evolution of the hyperfine interaction in K_3HfF_7 and K_3ZrF_7 deserve to be discussed: (a) While at RT a slow reorientation of the molecular axes along selected directions was inferred for K_3HfF_7, in the zirconium compound the molecular ions were already reorienting isotropically, though not yet in the fast relaxation limit. (b) Even when in K_3HfF_7, the reorientation takes place through a two-stage mechanism, one after the other as temperature increases, in K_3ZrF_7 two reorientation movements coexist over a wide thermal range. The question of whether this evidence is related to two, not exactly equivalent, probes surrounding the zirconium disordered cubic lattice is still open. (c) In spite of the similar magnitude of the activation energies for the fast isotropic reorientation in both compounds, that of zirconium indicated a lower-energy barrier. This fact, along with the situation that the cubic phase is completely achieved in K_3ZrF_7 at a lower temperature, seems to indicate that dynamic processes in the zirconium lattice take place more easily. (d) Both compounds behave differently upon thermal decomposition.

(5) The application of the TDPAC technique, through its possibility of detecting simultaneous interactions of very similar hyperfine parameters and of yielding information about dynamic processes taking place within its time window, has made it possible to determine, unambiguously, small changes occurring in the local structures surrounding hafnium sites which reveal the existence of thermal phase transitions, and also to point out some of their microscopic features. Bearing in mind the analogy between the x-ray diffraction patterns of the tetragonal and cubic phases, and the absence of any noticeable peak in the DTA, the amount of information drawn in this investigation about the appearance of the cubic phase, the range of coexistence of the linked phases and their relative abundances, and the dynamic processes involved in the high-temperature disordered modification seems satisfactory.

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