PHYSICAL REVIEW B VOLUME 34, NUMBER 3 1 AUGUST 1986

Time-differential perturbed-angular-correlation study of K_2HfF_6 polymorphism

M. C. Caracoche, P. C. Rivas, J. A. Martínez, A. M. Rodríguez,
M. T. Dova, and A. R. López-García
Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC 67,
1900 La Plata, Argentina

(Received 2 January 1986)

The thermal behavior of the hyperfine interaction in K_2HfF_6 was investigated by means of the time-differential perturbed-angular-correlation technique between 293 and 750 K. The quadrupole parameters associated with the monoclinic, orthorhombic, cubic, and trigonal phases have been determined. An activation energy $E_a = 86 \pm 16$ kJ/mol could be calculated for the monoclinic-to-orthorhombic phase transition taking place between 384 and 466 K. An analogy with the hyperfine interaction of the isomorphous compound K_2ZrF_6 could be established.

I. INTRODUCTION

It is known that hafnium and zirconium compounds present macroscopic isomorphism. The time-differential perturbed-angular-correlation (TDPAC) technique has proved that such isomorphism extends to microscopic scales, since similar quadrupole hyperfine interactions have been determined for both members of the following couples of substances: $(NH_4)_2ZrF_6$ (Ref. 1) and $(NH_4)_2HfF_6$ (Ref. 2), Rb_2HfF_6 (Ref. 3) and Rb_2ZrF_6, HfF_4 (Ref. 4) and ZrF_4 (Ref. 5), $NH_4Hf_2F_9$ (Ref. 6) and $NH_4Zr_2F_9$ (Ref. 7), and HfO_2 and ZrO_2 (Ref. 8). However, according to the TDPAC results obtained for K_2HfF_6 and K_2ZrF_6 in Refs. 9 and 10, respectively, this pair seems to be an exception.

A Mössbauer experiment carried out by Gerdau *et al.* on K_2HfF_6 (Ref. 11) at 4.2 K yielded $V_{zz} = (23.7 \pm 0.75)$ $10^{17}\,V/cm^2$ and $\eta = 0.89 \pm 0.02$. In addition, a TDPAC measurement performed at room temperature[12] exhibited a spin-rotation curve corresponding also to a very intense asymmetric electric field gradient (EFG). This spin-rotation curve proved to be quite different to the one previously reported by us for the same compound[9] but very similar to that determined for the isomorphous K_2ZrF_6.[10]

A thorough x-ray investigation on the K_2HfF_6 was carried out by Saalfeld *et al.*[13] between 293 and 783 K. The compound reveals a spectacular polymorphism presenting six phases all along the thermal range.

Regarding K_2ZrF_6, Novoselova *et al.*[14] have reported a transformation scheme but the crude line diagrams of the x-ray patterns they show do not allow a comparison with the corresponding K_2HfF_6 modifications.

Taking advantage of improved time resolution, we have reinvestigated the thermal evolution of the quadrupole hyperfine interaction in K_2HfF_6 between 293 and 750 K, in order to supply additional information about the missing isomorphism suggested by the literature. EFG's at hafnium sites have been derived via the TDPAC technique.

II. EXPERIMENTAL

The K_2HfF_6 was prepared by dissolving HfO_2 in 40% HF and then an aqueous solution of KF was added in stoichiometric proportions. Crystals were obtained by letting the solution evaporate at room temperature. An x-ray powder diagram of the as-prepared polycrystalline sample yielded the sequence of reflections corresponding to the monoclinic phase of the K_2HfF_6 reported in Ref. 13.

After identification, the substance was capsulated in a quartz tube, sealed in air at atmospheric pressure and neutron irradiated at the RA-3 reactor of the Comisión Nacional de Energía Atómica (Argentina) to produce hafnium activity. β^- decay of ^{181}Hf gave rise to the well known 133-482 keV γ-γ cascade of ^{181}Ta with an intermediate level of spin $I = \frac{5}{2}^+$ and a quadrupole moment $Q = 2.53$ barn, which acted as a TDPAC probe. A two-detectors CsF fast-slow coincidence system with a time resolution of 0.8 ns at Ta energies was used for data acquisition.

Let us denote, by $C(\theta, t)$, the coincidence counting rate of γ_1-γ_2 radiations measured for detectors forming an angle θ, t being the elapsed time between γ emissions. Following the theory of the perturbed angular correlations,[15] the perturbation factor $G_2(t)$, which contains all the physical information about the interaction between the EFG and the nuclear quadrupole moment, comes out determined by the ratio (assuming $A_4 \ll A_2$)

$$A_2 G_2(t) = 2\frac{C(\pi,t) - C(\pi/2,t)}{C(\pi,t) + 2C(\pi/2,t)} . \tag{1}$$

The EFG is described by two parameters: the quadrupole interaction frequency $\omega_Q = (eQV_{zz})/\{4I(2I-1)\hbar\}$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ being the reference axes chosen in such a way that the diagonal components of the EFG satisfy the condition $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$.

Using a nonlinear least-squares fit program that took into account the finite-time resolution of the equipment, the function

$$A_2 G_2(t) = A_2 \left[\sigma_{20}(\eta) + \sum_{i=1}^{3} \sigma_{2i}(\eta) e^{-\delta\omega_i t} \cos(\omega_i t) \right] \tag{2}$$

derived from Ref. 15 for a static quadrupole interaction in polycrystalline samples, was fitted to the experimental data. Here, σ_{2i} and ω_i are related to the quadrupole parameters and δ stands for a possible Lorentzian distribution of EFG's due to lattice imperfections. When the above function did not match the experimental data, a linear combination of the form $A_2\sum_i f_i G^i(t)$ was assumed. The underlying idea was to admit the existence of different EFG's acting on the TDPAC probes. Consequently, the f_i coefficients represent the relative fractions of each interaction. Time-dependent interactions were fitted using the Abragam and Pound's expression

$$A_2G_2(t)=A_2e^{-\lambda t}\,, \qquad (3)$$

where λ is linked to the correlation time of the dynamical process.[16]

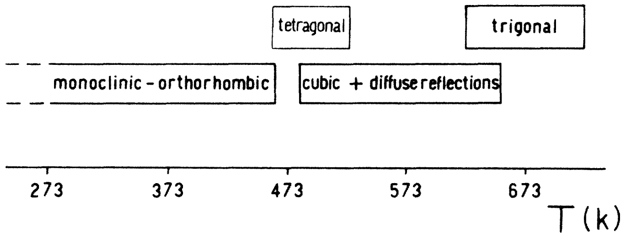
Data acquisition was performed at different temperatures of the sample within the range 293—750 K. The thermal stability of the heating system was of the order of ±1 K.

III. RESULTS

Figure 1 shows a selection of the spin rotation curves obtained at different temperatures. Six quadrupole hyperfine interactions were necessary to describe the whole thermal evolution of the spin-rotation curves between 293 and 750 K. The thermal dependence of the relative fractions associated to each interaction is plotted in Fig. 2. Table I lists the quadrupole parameters sets corresponding to the observed interactions at those temperatures where their relative fractions were maxima. It is also indicated as the symbols in Fig. 2 for each f_i.

IV. DISCUSSION

We shall discuss our results at the light of the information shown in Fig. 2, Table I, and the scheme of crystalline structures of K_2HfF_6



drawn from Saalfeld *et al.*[13]

The starting situation indicates that the compound has crystallized in the proper way and no radiation damage is present. Indeed, a one-site interaction associated to a very intense, asymmetric, and nondistributed EFG was enough to fit the experimental data. The spin-rotation curve at 293 K is in agreement with that reported by Gerdau for the same compound[12] and is also similar to the one found for the isomorphous K_2ZrF_6.[10] Besides, the EFG can be directly connected with that determined by Gerdau *et al.* at 4.2 K using Mossbauer spectroscopy,[11] suggesting that the monoclinic phase extends below room temperature to at least 4.2 K. There was no possibility of agreement between the present results and those reported in (Ref. 9), where an EFG of quadrupole parameters $|V_{zz}| = (7.60\pm0.91)\ 10^{17}\ \text{V/cm}^2$, $\eta=0.59\pm0.02$, and $\delta=(16\pm1)\%$ was found.

The one-site interaction mentioned above did not fit the experimental data from 384 K on, and a competing interaction had to be added. The interchange process be-

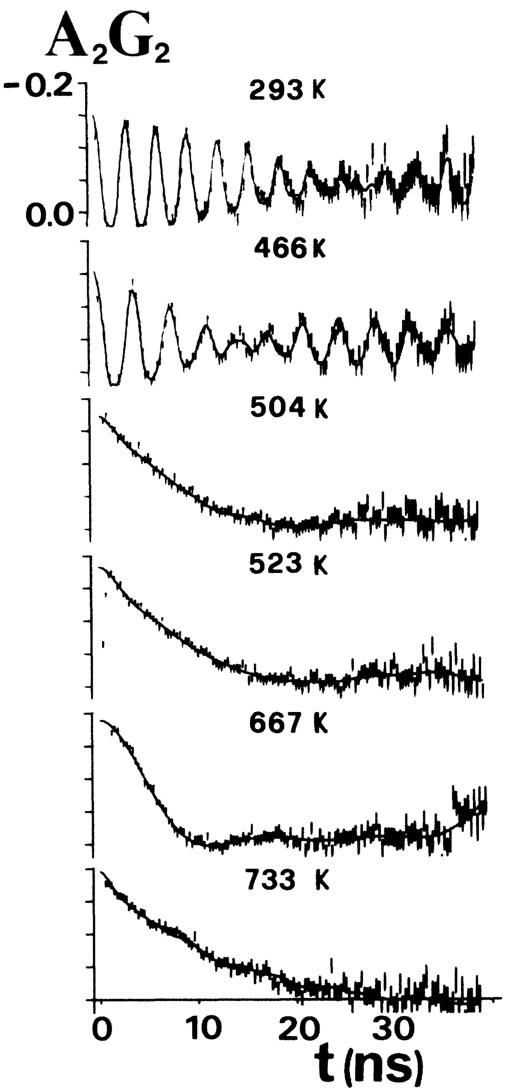


FIG. 1. Spin-rotation curves of K_2HfF_6 at different temperatures. Solid lines are the fitted curves to the data.

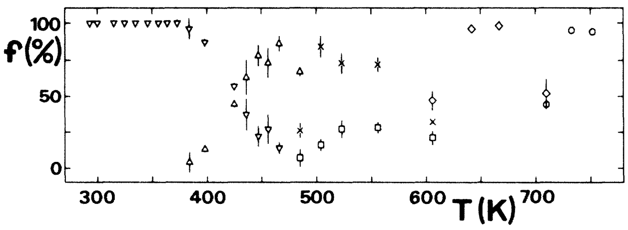


FIG. 2. Relative fractions thermal evolution for the different interactions observed in K_2HfF_6. ▽ denotes the monoclinic phase, △ the orthorhombic phase, × the cubic phase, □ the diffuse reflections, ◇ the trigonal phase, and ○ the decomposition process.

TABLE I. Typical values of the quadrupole hyperfine parameters corresponding to different crystalline structures in K_2HfF_6. The reported data correspond to temperatures where the relative fraction of each interaction was maximum.

Symbol	Crystalline structure	Temperature (K)	ω_Q (Mrad s^{-1})	V_{zz} (10^{17} V/cm^2)	η	δ (%)
▽	Monoclinic	293	193±1	20.2±2.4	0.93±0.01	1±1
△	Orthorhombic	466	161±1	16.9±2.0	0.86±0.01	2±1
×	Cubic	504	15±1	1.6±0.2	0 (fixed)	13±6
□	Diffuse reflections	523	53±3	5.6±0.7	0.41±0.10	19±7
◇	Trigonal	667	23±1	2.4±0.3	0 (fixed)	6±1
		733	$\lambda=(0.08\pm0.01)$ ns^{-1}			

tween both interactions can be clearly seen in Fig. 3, which also shows the thermal evolution of the quadrupole parameters involved. It is important to point out first of all that the quadrupole hyperfine interaction arising with increasing temperature (△) is very similar to one which it replaces (▽). Secondly, according to Saalfeld *et al.*,[13] the monoclinic structure found for the K_2HfF_6 at room temperature is a slight deviation of the orthorhombic phase of higher temperature which lasts up to 463 K. Now it is clear that the change observed in the range 384–466 K corresponds to the monoclinic to orthorhombic phase transition. It is interesting to notice that the relative fractions ratio of both interactions obeys a Boltzman distribution (see Fig. 4) from which an activation energy $E_a=(86\pm16)$ kJ/mol was calculated. The phase transition was reported to be displacive and reversible[13] and an interpretation of the activation energy obtained for such process is desirable.

Between 500 and 600 K, a complete change in the hyperfine pattern is observed (see Fig. 1). Two new interactions replace the former ones. One of them, related to a weak and symmetric EFG (×) and the other one describing a more intense, asymmetric, and distributed EFG (□). The first interaction was associated to the cubic phase. The second one presented a peculiar thermal evolution; while the quadrupole interaction frequency decreased as temperature increased, the asymmetry parameter exhibited a noticeable change near 523 K. The broadly distributed frequency determined for this interaction along with the thermal range over which it was present, suggested that it could be related to the diffuse reflections always appearing together with those of the cubic phase. We were not able to assign a quadrupole hyperfine interaction to the tetragonal phase.

At 642 and 667 K all the probe nuclei are acted by a new EFG (◇) which was linked to the trigonal phase. The last interaction, observed at temperatures above 700 K, exhibits dynamical characteristics, having been fitted according to Abragam and Pound's model. This situation had been already found at high temperatures in K_2ZrF_6 being attributed to the decomposition process.[10] In this work, at 733 and 750 K, the full anisotropy is achieved assuming about 5% of the typical interaction of the HfO_2,

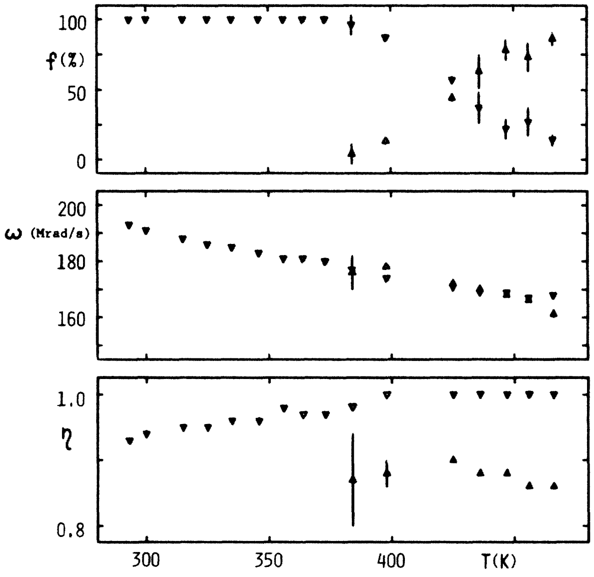


FIG. 3. Thermal evolution of the hyperfine quadrupole parameters corresponding to the monoclinic phase (▽) and the orthorhombic phase (△). The distribution width δ of both interactions remains negligible.

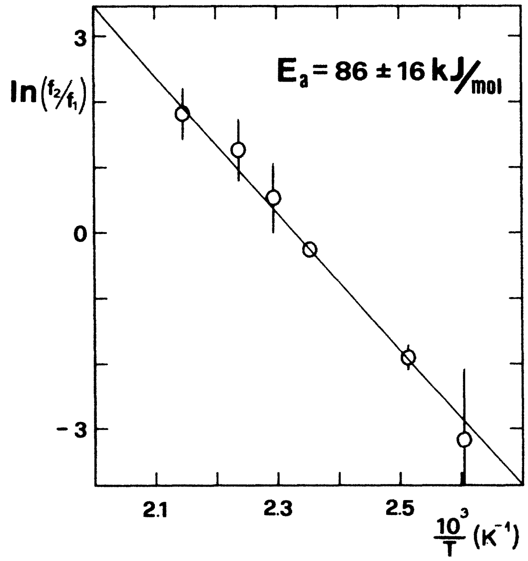


FIG. 4. Logarithmic plot of the relative fractions ratio f_2/f_1 as a function of reciprocal temperature. f_1 and f_2 stand for the relative fractions of ^{181}Ta probes in the monoclinic and the orthorhombic phases of K_2HfF_6, respectively.

clearly indicating that the K_2HfF_6 decomposition has begun. The mismatch between the present results and those reported in Ref. 9 may be due to the heating treatment performed in the first investigation in order to heal radiation damage. This could have led the K_2HfF_6 irreversibly to high-temperature phases.

Regarding the thermal behaviors of the isomorphous compounds K_2ZrF_6 and K_2HfF_6 the following remarks can be pointed out.

(1) At room temperature both present a very strong and highly asymmetric EFG. With increasing temperature, in K_2HfF_6 we could observe the monoclinic to orthorhombic phase transition.

(2) Above 473 K, a complete rearrangement of the structure, accompanied with an important increase of the volume, is reported for both compounds.[13,17] The effect is revealed by a new pattern of the hyperfine interaction [see Fig. 1 and Fig. 1(c) of Ref. 10]. The low frequency $\omega_Q \simeq 10$ Mrad s^{-1} and the asymmetry parameter $\eta = 0$ fitted in K_2ZrF_6 between 485 and 608 K, which was attributed to lattice defects, may instead correspond to the interaction appearing here over the same range and assigned to the cubic phase.

(3) The interaction connected here to the diffuse lines in the range 500–600 K is observed in K_2ZrF_6 to appear between 543 and 608 K.

(4) A complete agreement of the hyperfine interaction in the range 600–700 K can be established, suggesting that the trigonal structure is the typical phase for both compounds in this range.

A detailed x-ray investigation on the polymorphism of K_2ZrF_6 is expected to establish a closer association between structures and quadrupole hyperfine interactions of K_2ZrF_6 and K_2HfF_6.

V. CONCLUSIONS

The thermal evolution of the hyperfine interaction in K_2HfF_6 agrees fairly well with the x-ray investigation on its polymorphism performed by Saalfeld *et al.* We have been able to assign quadrupole parameters to the monoclinic, orthorhombic, cubic, and trigonal crystalline structures. It has also been possible to establish the quadrupole hyperfine interaction of the phase giving rise to the diffuse reflections.

We have determined that the monoclinic to orthorhombic transition begins at 384 K and that both phases coexist up to 466 K. An activation energy $E_a = (86 \pm 16)$ kJ/mol was calculated for this transition. The slight changes in the cell parameters of both structures yield very similar quadrupole hyperfine interactions. Dynamical effects described by the Abragam and Pound's model were associated to the K_2HfF_6 decomposition. The TDPAC technique has allowed to establish a close analogy between the hyperfine interactions of the isomorphous compounds K_2HfF_6 and K_2ZrF_6.

ACKNOWLEDGMENTS

The authors are indebted to S. Spinelli for obtaining the identificatory x-ray powder diagram. Financial support by Consejo Nacional de Investigaciones Científicas y Téchnicas and Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (Argentina) and Kernforschungszentrum Karlsruhe GmbH (West Germany) is also gratefully acknowledged.

---

[1] A. M. Rodríguez, J. A. Martínez, M. C. Caracoche, P. C. Rivas, and A. R. López García, Hyperfine Interact. **14**, 227 (1983).

[2] J. A. Martínez, P. C. Rivas, M. C. Caracoche, A. M. Rodríguez, A. R. López García, and S. Spinelli, Hyperfine Interact. **30**, 9 (1986).

[3] A. Vasquez, J. D. Rogers, and A. Maciel, Phys. Lett. **45A**, 253 (1973).

[4] J. A. Martínez, M. C. Caracoche, A. M. Rodríguez, P. C. Rivas, and A. R. López García, Chem. Phys. Lett. **102**, 277 (1983).

[5] P. C. Rivas, M. C. Caracoche, J. A. Martínez, M. T. Dova, and A. R. López García, Hyperfine Interact. **30**, 49 (1986).

[6] J. A. Martínez, M. C. Caracoche, A. M. Rodríguez, P. C. Rivas, and A. R. López García, Hyperfine Interact. **14**, 135 (1983).

[7] A. M. Rodríguez, J. A. Martínez, M. C. Caracoche, P. C. Rivas, A. R. López García, and S. Spinelli, J. Chem. Phys. **82**, 1271 (1985).

[8] J. Yeshurum and B. Arad, J. Phys. C **7**, 430 (1974).

[9] M. C. Caracoche, A. R. López García, J. A. Martínez, L. A. Mendoza Zelis, and R. C. Mercader, Phys. Rev. B **25**, 5972 (1982).

[10] J. A. Martínez, A. M. Rodríguez, M. C. Caracoche, R. C. Mercader, A. R. López García, and P. C. Rivas, Hyperfine Interact. **13**, 307 (1983).

[11] E. Gerdau, B. Scharnberg, and H. Winkler, *Hyperfine Interactions in Excited Nuclei* (Gordon Breach, New York, 1971), p. 861.

[12] E. Gerdau, Institut für Experimentalphysik der Universitat Hamburg Annual Report II, 1981 (unpublished).

[13] H. Saalfeld and W. Guse, Neues Jahrbuch Miner. Abh. **146**, 29 (1983).

[14] A. V. Novoselova, I. M. Korenev, and I. P. Simanov, Dokl. Akad. Nauk. SSSR **139**, 892 (1961).

[15] H. Frauenfelder and R. M. Steffen, in *Alpha-, Beta- and Gamma-ray Spectroscopy,* edited by K. Siegbahn (North-Holland, Amsterdam, 1968), Vol. 2, p. 997.

[16] A. Abragam and R. V. Pound, Phys. Rev. **92**, 943 (1953).

[17] G. A. Yagodin and V. I. Tarasov, Zh. Neorg. Khim. **5**, 1987 (1960) [Russ. J. Inorg. Chem. **5**, 967 (1960)].