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Time-differential perturbed-angular-correlation investigation of phase transitions and dynamical effects in K_2HfF_6

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Time-differential perturbed-angular-correlation measurements on K_2HfF_6 have been performed as a function of temperature in the range 20 – 500 °C. Three phase transitions are observed at temperatures around 165, 310, and 440 °C. The last two phases exhibit time-dependent interactions which are interpreted on the basis of a diffusion model. Activation energies of 0.68 ± 0.03 and 0.10 ± 0.01 eV are deduced for the diffusion processes involved.

INTRODUCTION

Time-dependent interactions in several hexa- and heptafluoride complexes of tetravalent metals were observed by time-differential perturbed angular correlations[1] (TDPAC) as well as by nuclear magnetic resonance[2,3] (NMR) experiments. Depending on the compound investigated, different interpretations have been given to account for the dynamical behaviors observed.

Vasquez *et al.*,[4,5] studying Rb_2HfF_6 and Cs_2HfF_6 compounds by TDPAC, have assumed that the relaxation processes were produced by the jump diffusion of a vacancy among the cation sites, but the behavior of the interaction with temperature was not clearly elucidated. In the case of the dynamical interactions also observed by TDPAC in $(NH_4)_3HfF_7$, K_3HfF_7, and Na_3HfF_7,[6–8] the interpretation was based on the F^- anionic motion around Hf sites.

Dynamical processes revealed by the NMR experiments performed on ^{19}F for potassium hexa- as well as heptafluoride complexes of Ti and Zr have been explained assuming the reorientation of the whole anionic group coordinated to the tetravalent metal. In effect, Tarasov and Buslaev,[3] studying the molecular motion of $ZrF_7{}^{3-}$ in K_3ZrF_7, concluded that their results could be understood in terms of two structural nonequivalent sites for the $ZrF_7{}^{3-}$ ions, one of which was associated with a reorientating group. The authors also noticed that as temperature decreased, the population ratio of rotating to static sites changed as a result of the freezing of the reorientating groups.

Moreover, in a recent paper, Moskvich *et al.*[2] have concluded that reorientation as well as diffusion of the $TiF_6{}^{-2}$ group are responsible for the time-dependent interactions experimentally observed by NMR on the K_2TiF_6 complex.

In this work we investigate the K_2HfF_6 compound via the TDPAC technique using the 133 – 482 keV γ-γ cascade of ^{181}Ta produced by β^- decay of ^{181}Hf. The temperature dependence of the quadrupole interaction between the $\frac{5}{2}^+$, 482-keV, 10.8-ns intermediate state[9] and its surroundings was measured within the range 20 – 500 °C.

Earlier investigations on K_2HfF_6 have shown that:

(i) At room temperature, the crystalline structure is orthorhombic with a tetramolecular unit cell.[10]

(ii) The electric field gradient at 4.2 K is $V_{zz} = (23.7 \pm 0.75) \times 10^{17}\ \mathrm{V\,cm^{-2}}$ and $\eta = 0.89 \pm 0.02$, as determined by Gerdau *et al.* via Mössbauer effect.[11]

(iii) It is also known that the isomorphous compound K_2ZrF_6 undergoes several phase transitions according to the following scheme[12]:

$$\begin{tikzcd}
\alpha \arrow[r, "240\,^{\circ}\mathrm{C}"] & \beta \arrow[r, "298\,^{\circ}\mathrm{C}"] & \gamma \arrow[r, leftrightarrow, "445\,^{\circ}\mathrm{C}"] \arrow[ll, bend left, "130\,^{\circ}\mathrm{C}"] & \delta \arrow[r, leftrightarrow, "585\,^{\circ}\mathrm{C}"] & K_3ZrF_7 + \text{liquid} .
\end{tikzcd}$$

EXPERIMENTAL

The TDPAC technique measures the radiation-angular distribution perturbations due to the interaction between a radioactive nucleus and its surroundings. For a given γ-γ cascade, the angular distribution of the second emission with respect to the first one is described by

$$W(\theta,t)=\sum_{k=0}^{k_{\max}} A_k G_k(t) P_k(\cos\theta)\ , \qquad (1)$$

where θ is the angle between the directions of the emission of the γ rays, t is the time elapsed between γ emissions, A_k depend on the spins involved in the cascade and the multipolarities of the radiations, $G_k(t)$ are the perturbation factors describing the hyperfine interactions nucleus-surroundings, and $P_k(\cos\theta)$ are the Legendre polynomials. The number of detected coincidences $C(\theta,t)$ is related to $W(\theta,t)$ by means of

$$C(\theta,t)=C_0\exp(-t/\tau_N)W(\theta,t) \qquad (2)$$

where τ_N is the lifetime of the intermediate state of the cascade and θ is now the angle between detectors' axes. In our case, being $A_4 << A_2$, the experimental $G_2(t)$ factor can be deduced by calculating the ratio

$$2\,\frac{C(180°,t)-C(90°,t)}{C(180°,t)+2C(90°,t)}=A_2G_2(t)\ . \qquad (3)$$

A conventional automated fast-slow coincidence setup of two 5-cm – 5-cm NaI(Tl) detectors was used, with a time resolution $2\tau=3.2$ ns. The sample temperature, with an uncertainty of ± 2 °C, was measured with an iron-constantan thermocouple.

Three powder samples were used for data acquisition. They were activated by thermal neutron irradiation in the RA-3 reactor of Comisión Nacional de Energía Atómica (Argentina). From the very beginning, it was found that the spin rotation curves at certain temperatures were dependent on the thermal history. This dependence disappeared after annealing for 72 h at 530 °C. The fact that all three samples showed the same behavior after this annealing, yielding the same results, indicated that radiation damage had been removed in this way.

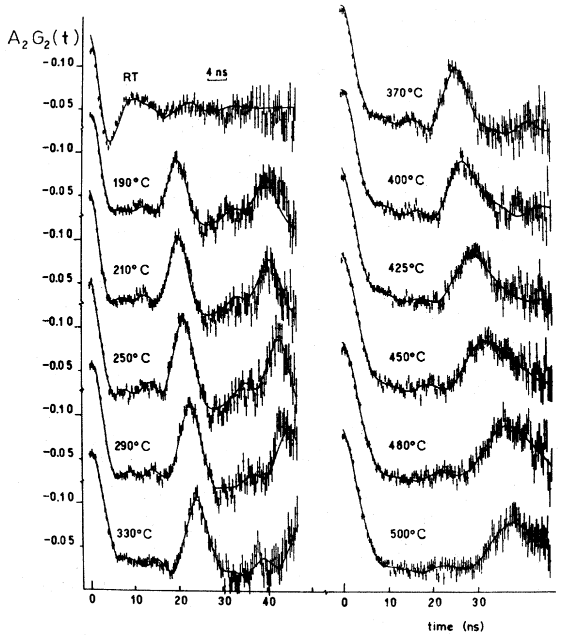

FIG. 1. Spin-rotation curves obtained for K_2HfF_6 at different temperatures.

$A_2G_2(t)$ curves obtained from coincidence spectra are shown in Fig. 1 for temperatures ranging from room temperature to 500 °C. Special care was taken to ensure equal geometry and high statistics for all measurements. For the fitting procedures, the following attenuation factor was used:

$$G_2(t)=\sum f_i G_2^i(t)\ , \qquad (4)$$

where $G_2^i(t)$ are the attenuation factors involving fractions f_i of probe nuclei. Finite time resolution was taken into account by the nonlinear least-squares-fitting program which was run on a PDP11/34 computer.

RESULTS

No significant changes were observed in spectra obtained from 20 to 150 °C. Very good fits were obtained in this range using the normal attenuation factor for a static quadrupole interaction:

$$G_2(t)=\sum_{n=0}^{3} s_{2n}e^{-\delta\omega_n t}\cos(\omega_n t) \qquad (5)$$

plus an additional f_0 base line. In formula (5), $s_{2n}=s_{2n}(\eta)$ are tabulated geometrical coefficients, $\omega_n=\omega_n(V_{zz},\eta)$ are the quadrupole interaction frequencies associated to the transitions among the $(2I+1)$ nuclear levels of the intermediate state, δ characterizes a Lorentzian distribution around ω_n, and V_{zz} and η are the components of the electric field gradient (EFG).[13]

It can be seen from Fig. 2 that spin rotation

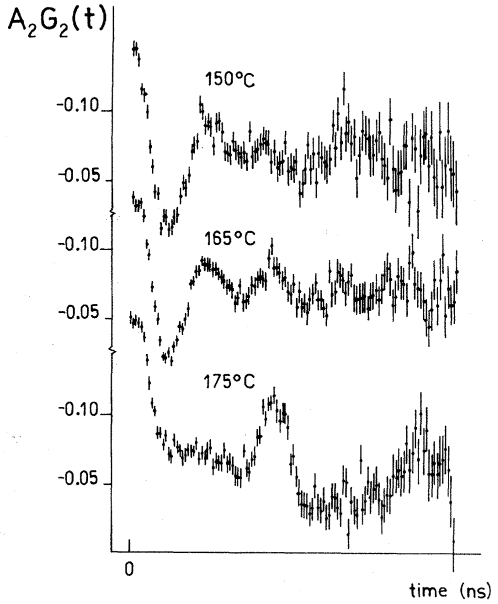

FIG. 2. TDPAC spectra showing the phase transition around 165 °C.

curves obtained from 150 to 175 °C show an evolution towards a new interaction pattern that remained up to 500 °C.

It was not possible to fit all the spectra from 190 to 500 °C, see Fig. 1, using the same analytical function. Nevertheless, when fitted they had 20–30 % of a common component, consisting of a Lorentzian distribution of frequencies around zero. This component, denoted hereafter by $f_0G_2^0(t)$ is expressed by

$$f_0G_2^0(t)=f_0\sum_{n=0}^{3}s_{2n}(\eta=0)e^{-n\delta_0 t}\,. \tag{6}$$

Between 190 and 290 °C, the fitting function $G_2(t)$ is comprised also of a fraction f_1 of nuclei experiencing a quadrupole perturbation described by Eq. (5).

From 330 to 500 °C an additional contribution $f_2G_2^2(t)$ involving a second interaction frequency had to be included in order to obtain satisfactory fits. In fact, by this means an improvement of better than 20% was achieved in the χ^2's values. At the same time, the interaction already existing in the previous range of 190–290 °C evidenced relaxation effects. Attempts to assign a similar dynamical characteristic to the f_2 populated interaction were unsuccessful. It is important at this point to remark the impossibility of fitting these spectra assigning a distributed character to either of the two frequencies.

According to the above description, the corresponding fitting function was written as

$$G_2(t)=f_0G_2^0(t)+f_1e^{-\lambda t}\left[\sum s_{2n}^1 e^{-\delta^1\omega_n t}\cos(\omega_n^1 t)\right] +f_2\left[\sum s_{2n}^2 e^{-\delta^2\omega_n^2 t}\cos(\omega_n^2 t)\right]. \tag{7}$$

The modulating factor $e^{-\lambda t}$ accounts for the dynamical behavior of the quadrupole interaction involving the fraction f_1 of probe nuclei. Ordinary behavior with thermal lattice expansion is observed for each contribution.

DISCUSSION

Our results show that four different phases can be identified over the range studied. The low-temperature phase, from room temperature to 150 °C, is described by a quadrupole parameters set which depends very weakly on temperature. For the room-temperature measurements, the following values were obtained: $|V_{zz}|=(7.60\pm0.91)\times10^{17}$ V cm^{-2}, $\eta=0.57\pm0.02$, $\delta=0.16\pm0.01$. Around 165 °C a first-order phase transition takes place (see Fig. 2).

A second phase is observed above 175 °C. This phase, in the temperature range from 190 to 290 °C, is mainly described by a static monochromatic quadrupole interaction acting on about 70% of probe nuclei. Typical values for this phase are $|V_{zz}|=(5.24\pm0.63)\times10^{17}$ V cm^{-2} and $\eta=0.19\pm0.01$ at 210 °C. The remaining 30% of nuclei experienced a distribution of EFG's around zero. The corresponding δ_0 values, Eq. (6), were found to be of the order of 30 MHz throughout this temperature range. The large fraction of probe nuclei feeling this interaction which does not exist in the previous phase rules out an explanation already argued by other authors based on the existence of habitual concentrations of impurities or lattice defects. Therefore, we had been led to suppose that this important percentage of probe nuclei is located in disordered surroundings as found by means of other techniques in similar compounds.

Between 330 and 425 °C a new phase characterized by three different components is observed. Approximately 50% of the probe nuclei experience a fluctuating EFG of about $|V_{zz}|=4.5\times10^{17}$ V cm^{-2} and $\eta=0.15$. The relaxation constant λ in Eq. (7), related to the fluctuating field, ranges from 0.0075 ± 0.0025 ns^{-1} at 330 °C to 0.0475 ± 0.0100 ns^{-1} at 425 °C. A fraction of 25% of probe nuclei are affected by an additional clear-cut but weaker static interaction of high asymmetric character [e.g., $|V_{zz}|=(2.36\pm 0.28)\times 10^{17}\ \mathrm{V\,cm^{-2}}$ and $\eta=0.64\pm 0.06$, for 370 °C]. This two-well-defined-sites picture has already been found to reproduce the experimental situation in other highly coordinated fluoride compounds.[3,7,8] The remaining nuclei feel a distribution around zero which gets narrower with increasing temperature. In fact, as temperature rises, the frequency distribution width decreases from 28±10 MHz at 300 °C to 8±3 MHz at 425 °C, showing a behavior quite different from that found over the previous phase.

Above 425 °C, the quadrupole interaction presents the same three EFG's components picture, but the relaxation constant exhibits a different temperature behavior and instead of a distribution of EFG's around zero, an unperturbed site is observed. Representative values of the two components of the EFG are $|V_{zz}|=(3.15\pm 0.38)\times 10^{17}\ \mathrm{V\,cm^{-2}}$, $\eta=0.28\pm 0.04$ (relaxing site) and $|V_{zz}|=(1.57\pm 0.19)\times 10^{17}\ \mathrm{V\,cm^{-2}}$, $\eta=0.81\pm 0.58$ (static site), at 480 °C.

Figure 3 shows the temperature dependence observed for the relaxation constants λ between 330 and 500 °C. Relaxation times calculated as λ^{-1} were found to lie between 20 and 133 ns. A comparison with the characteristic time of the interaction allows us to ensure the applicability of the slow rotational diffusion model proposed by Marshall and Meares.[14] This model relates the relaxation constant λ to the rotational diffusion coefficient D by means of $\lambda=6D$. Therefore, as temperature increases an Arrhenius behavior for λ is to be expected. According to this model, two clearly different activation energies can be deduced: $E_a=0.68\pm 0.03$ eV for the 330–425 °C range and $E_a=0.10\pm 0.01$ eV for the higher range 450–500 °C.

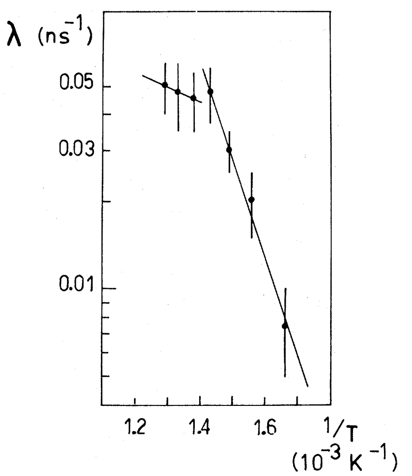

FIG. 3. Temperature dependence of the relaxation constant λ.

CONCLUSIONS

The four phases reported for K_2ZrF_6 by Novoselova *et al.*[12] are also observed in the isomorphous K_2HfF_6. Nevertheless, the critical temperatures are quite different from theirs and no irreversible processes have been found.

The dynamical interaction observed in this work can be described successfully by the model proposed by Marshall and Meares in terms of a slow rotational diffusion. At the same time, it has been demonstrated that TDPAC may be used as a useful technique to determine activation energies for diffusion processes.

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