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TEMPERATURE DEPENDENCE OF THE ELECTRIC FIELD GRADIENT AT Ta NUCLEI IN HAFNIUM PYROVANADATE

L.A. MENDOZA-ZÉLIS, * A.G. BIBILONI, ** M.C. CARACOCHE, A.R. LOPÉZ-GARCÍA, ** J.A. MARTÍNEZ, R.C. MERCADER and A.F. PASQUEVICH ***

Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

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The electric field gradient EFG in hafnium pyrovanadate has been measured at Hf sites at different temperatures with the time-differential perturbed angular correlation method. The results obtained show the existence of a phase transition around 110°C.

1. Introduction

The synthesis of the new compound HfV_2O_7 among several vanadium oxoanions reported by Baran [1], suggested the possibility of helping to its structural knowledge by means of the time-differential perturbed angular correlation method using the well-known γ_{133}–γ_{482} keV cascade of ^{181}Ta.

Previous experimental data obtained by X-rays in HfV_2O_7 showed that its structure was cubic or pseudocubic with a lattice parameter $a = 26.388 \pm 0.007$ Å [1]. This result arises from the study of a series of weak lines in the powder diagram which could not be indexed on the basis of a smaller cell ($a = 8.787 \pm 0.003$ Å) corresponding to the more intense lines of the same diagram.

The behaviour of similar compounds suggests the existence of a phase transition in HfV_2O_7 at a temperature of a few hundred degrees centigrades. In fact, the ZrP_2O_7 exists in three crystalline varieties, two of which are related by a reversible phase transition at about 300°C [2–3]. In the high temperature variety the P-O-P bridge of the P_2O_7 anion is linear and the compound is cubic with a lattice parameter of about 8 Å. At low temperatures, however, the bridge is bent and it is necessary to assign a lattice parameter three times greater than the former in order to span the crystal.

* Fellow of CONICET, Argentina.
** Member of Carrera del Investigador Científico, CONICET, Argentina.
*** Fellow of Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Buenos Aires, Argentina.

In this work, the EFG at the Hf position in HfV_2O_7 has been measured as a function of temperature with the purpose of confirming the existence of the predicted phase transition.

2. Experimental procedures and results

The sample was prepared by means of a solid reaction between V_2O_5 and HfO_2 at 600°C. X-ray analysis of the resultant powder showed no presence of HfO_2 within 5%. The compound was irradiated in the RA-3 reactor of the Comisión Nacional de Energía Atómica, Argentina. Afterwards, it was annealed 24 h at 500°C in order to remove possible radiation damage.

Time coincidence spectra were recorded in three different positions on a conventional two-detector setup having INa(Tl) 5 X 5 cm crystals and XP-1021 photomultipliers. Time resolution was 3.7 ns.

In the present case the cascade of interest was the γ_{133}–γ_{482} keV of ^{181}Ta populated by the decay of the 45 d isotope ^{181}Hf. The intermediate level is characterized by spin $I = \frac{5}{2}$, half-life $T_{1/2}$ = 10.6 ns and quadrupole moment Q = 2.53 b [4].

Measurements were performed at 494, 411, 300, 196, 101 and 23°C. As a phase transition was found to occur between 196°C and 101°C, new measurements were carried out at 85, 115 and 135°C. The temperature uncertainty was ± 3°C.

Time spectra were corrected by accidental coincidences and normalized. Then, the $A_2G_2(t)$ were calculated. Fourier analysis of these curves showed a typical pattern of quadrupole interaction frequencies corresponding to an asymmetric EFG.

The function:

$$A_2G_2(t) = A_2\,[s_{20} + \sum_{n=1}^{3} s_{2n}\,e^{-\delta\omega_n t}\cos\omega_n t] \tag{1}$$

was fitted to the experimental data taking into account the finite resolution of the system. In this expression $s_{2n}(\eta)$ are functions of the asymmetry parameter η (see appendix), δ is a Lorentzian distribution width around ω_n,

$$\begin{aligned} \omega_1 &= eQV_{zz}\sqrt{7(3+\eta^2)}\,\sin(\tfrac{1}{3}\,\text{arc cos}\,\beta)/10\hbar\,, \\ \omega_2 &= \omega_1\,[\tfrac{1}{2}\sqrt{3}\,\text{cotg}\,(\tfrac{1}{3}\,\text{arc cos}\,\beta) - \tfrac{1}{2}]\,, \\ \omega_3 &= \omega_1 + \omega_2 \end{aligned} \tag{2}$$

with

$$\beta = 80(1-\eta^2)/[\tfrac{28}{3}(3+\eta^2)]^{3/2}\,.$$

The experimental data and the fitted curves at four different temperatures are shown in fig. 1. The results for the interaction frequency, asymmetry parameter, distribution width and V_{zz} are listed in table 1.

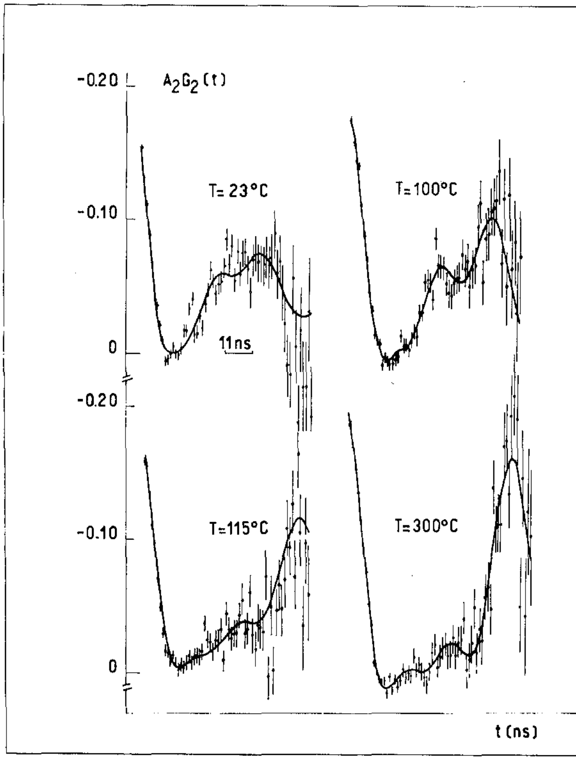

Fig. 1. Experimental data for $A_2G_2(t)$ at different temperatures. The fitted curves are drawn.

Fig. 2 shows V_{zz}, η and δ as a function of temperature. All of them display a discontinuity at 110°C. These curves suggest the following remarks:

(a) From 135 to 500°C, the EFG seems to be not affected by crystalline thermal

Table 1.
Quadrupole interaction parameters deduced from the fits at different temperatures..

T(°C)	ω_1(MHz)	η	δ	$V_{zz}(10^{17}V/cm^2)$
23	134(3)	0.44(3)	0.14(3)	1.96(13)
85	134(3)	0.48(2)	0.10(2)	1.91(12)
101	119(3)	0.42(2)	0.06(2)	1.76(11)
115	96(3)	0.26(3)	0.07(3)	1.56(11)
135	88(2)	0.19(3)	0.03(2)	1.47(9)
196	94(1)	0.23(1)	0.01(1)	1.55(9)
300	94(2)	0.20(2)	0.03(1)	1.56(10)
411	95(2)	0.12(5)	0.02(1)	1.63(10)
494	100(2)	0.16(2)	0.01(1)	1.69(11)

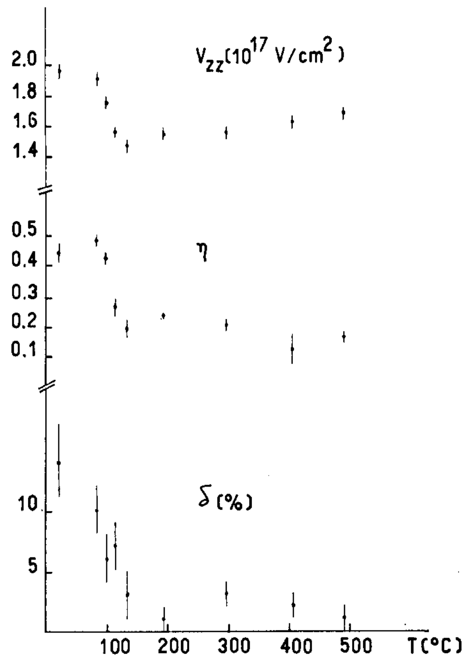

Fig. 2. Temperature dependence of the electric field gradient V_{zz}, the asymmetry parameter η and the frequency distribution width δ.

expansion, since V_{zz}, η and δ remain constant within the experimental errors.

(b) At low temperatures the EFG is more asymmetric and more distributed than that obtained at high temperatures. In fact, a change of more than 70% in η and δ occurs when temperature increases, but the change in V_{zz} is only of 20%.

By analogy with ZrP_2O_7, the last remark would support the hypothesis for a non-linear V-O-V bridge in HfV_2O_7 at low temperatures because in this case, at Hf sites, the EFG loses its symmetry and becomes more distributed, while no significant change in magnitude occurs.

3. Conclusions

The behaviour of EFG with temperature shows the existence of a phase transition in the neighbourhood of 110°C.

Although the experimental method does not permit to conclude about the characteristics of the phases involved, a comparison with the properties of ZrP_2O_7 suggests that those are the low and high temperature phases, with non-linear and linear V-O-V bridge, respectively, mentioned by Chaunac [2].

Point charge calculation of the EFG at Hf sites were performed for the structure of the isomorphous compound ZrP_2O_7 [5–6]. The resulting EFG was 20 times greater than the experimental values. This implies that a better knowledge of the HfV_2O_7 structure is needed to explain the observed EFG.

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Appendix

The perturbation factor for a non-axially symmetric interaction in a powder source is [7]:

$$G_{kk}(t) = \sum_{\substack{m,m' \\ m_a, m_b}} \sum_N (-1)^{2I+m_a+m_b} \begin{pmatrix} I & I & k \\ m_a' & -m_a & N \end{pmatrix} \begin{pmatrix} I & I & k \\ m_b' & -m_b & N \end{pmatrix}$$

$$\times \, e^{-i(E_m - E_{m'})t/\hbar} \langle m | m_b \rangle^* \langle m | m_a \rangle \langle m' | m_b' \rangle \langle m' | m_a' \rangle^* .$$

For a static quadrupole interaction, this expression becomes for $I = \frac{5}{2}$ and $k = 2$:

$$G_{22}(t) = s_{20} + \sum_{n=1}^{3} s_{2n} \cos \omega_n t ,$$

where ω_n are given in eq. (2) and s_{2n} are:

$$s_{20} = \frac{1}{2} \sum_{m=1/2}^{5/2} S(m, m) ,$$

$$s_{21} = S(\tfrac{1}{2}, \tfrac{3}{2}) ,$$

$$s_{22} = S(\tfrac{3}{2}, \tfrac{5}{2}) ,$$

$$s_{23} = S(\tfrac{1}{2}, \tfrac{5}{2}) .$$

with

$$S(m, m') = \tfrac{1}{35} a_m^2 a_{m'}^2 \{\tfrac{1}{3} [5 b_m b_{m'} - c_m c_{m'} - 4]^2 + 10 [b_m c_{m'} - b_{m'} c_m]^2$$

$$+ 4 [c_m - c_{m'}]^2 + [\sqrt{5} b_m + 3 c_{m'}]^2 + [\sqrt{5} b_{m'} + 3 c_m]^2\} ,$$

$$a_m = (1 + b_m^2 + c_m^2)^{-1/2} ,$$

$$b_m = \sqrt{10}\, \eta / \left(\frac{Em}{\hbar \omega_Q} - 10 \right) ,$$

$$c_m = \sqrt{18}\,\eta / \left(\frac{Em}{\hbar\,\omega_Q} + 2\right) ,$$

and where E_m are the eigenvalues of the interaction hamiltonian.

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