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Nuclear Quadrupole Interaction in Hafnon*

A. VASQUEZ, J. D. ROGERS, A. MACIEL and E. R. FRAGA

Instituto de Física , .Universidade Federal do Rio Grande do Sul, Porto Alegre RS

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The electric quadrupole interaction of ^{181}Ta nuclei at Hafnium sites in $HfSiO_4$ has been measured using perturbed angular correlation techniques. The measured interaction frequency was $\omega_0 = 690 \pm 20$ Mrad/sec and the asymmetry parameter, η, was found to be zero. The dependence of these parameters on temperature between – 170°C and 840°C was found to be negligible.

No presente trabalho relatamos medidas da interação quadrupolar em núcleos de Ta^{181} nas posições do Hafnio em $HfSiO_4$, utilizando a técnica da correlação angular perturbada Foram determinadas a frequência de interação $\omega_0 = 690 \pm 20$ Mrad/seg e o fator de assimetria $\eta = 0$. No intervalo de temperaturas de – 170°C a 840°C não houve variação apreciável destes parâmetros.

1. Introduction

Electric quadrupole interactions have recently been determined for a number of compounds of Hafnium using both perturbed angular correlation techniques and the Mossbauer effect[1]. We report here on a study of quadrupole interactions in $HfSiO_4$ by perturbed angular correlation ás a function of temperature between – 170°C and 840°C. We feel that the results of these measurements are especially interesting since the compound $HfSiO_4$ is isomorphic to $ZrSiO_4$ for which the structure of the unit cell has been determined.

2. Experimental Details

We have studied the time dependence of the angular correlation between the 133 keV and 482 keV gamma rays in ^{181}Ta following the decay of

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Postal address: Av. Luiz Englert s/n, 90000 - Porto Alegre RS.

^{181}Hf in a polycrystailine sample of $HfSiO_4$. In the presence of quadrupole interactions, the angular correlation function can be expressed in the form[2]

$$W(\theta, t) \cong 1 + A_2 G_2(t) P_2(\cos\theta) + A_4 G_4(t) P_4(\cos\theta), \quad (1)$$

where A_2 and A_4 are the usual coefficients for the unperturbed decay and $G_k(t)$ are the perturbation factors. In the case of interest, the term with $k = 4$ is negligible and the perturbation factor $G_2(t)$ can be written[3]

$$G_2(t) = o, + \sum_{i=1}^{3} \sigma_i \cos(\omega_i t),$$

where the a factors depend on the asymmetry parameter, ν, of the electric field gradient and the o's depend both on ν and on the value of the electric field gradient V_{zz} at the nuclear site.

The polycrystalline sample of $HfSiO_4$ was prepared in the usual way[4] by firing HfO_2 and SiO_2 at 1100°C for 24 hours. X-ray analysis was then performed and the lines measured in Ref. 4 were obtained with the correct intensity. In addition, a Raman scattering of the sample was done. The internal normal vibrational modes (Al, E, 2F) of the silicate (point group T_d) at sites of symmetry D_{2d} were observed with the same spectral splitting as for Zircon ($ZrSiO_4$).

The inactive sample was irradiated with neutrons in the reactor of the IEA in São Paulo to obtain radioactive Hafnium. Following the irradiation, a further annealing at 1100°C for 180 hours was carried out

The measurements were performed with a typical fast-slow coincidence spectrometer using three photomultipliers with NaI(Tl) crystals. A time resolution of 2.0 nsec was obtained.

The observed correlations were analyzed initially by Fourier techniques, followed by a non-linear least squares fit using the frequencies determined from the Fourier analysis as starting parameters. The fitting function used was a convolution of Eq. (1) with a Gaussian as approximation to the time resolution curve. The convolution was carried out numerically in the region near $t = 0$ where an analytic expression can not be obtained. A Gaussian distribution of frequencies was assumed. Details of the analysis program have been published elsewhere[5].

The measured $A_2 G_3(t)$ for a temperature of 20°C is shown in Fig. 1. The solid line is the theoretical fit obtained from the least squares program.

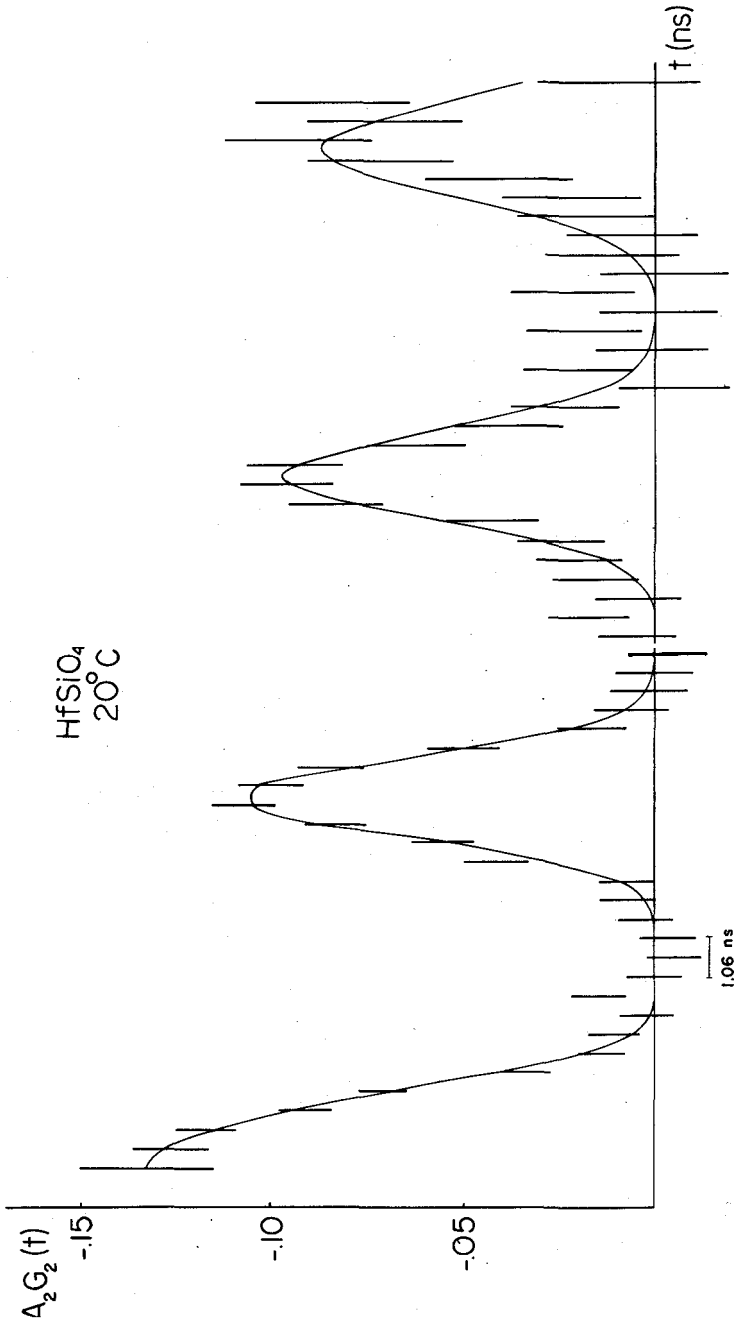

Fig. 1 $A_2G_2(t)$ coefficient for the perturbed angular correlation in Hafnon at 20°C.

This curve is typical of that obtained for all temperatures. Table 1 summarizes the values of ω_0, η, and the distribution parameter δ defined as in Ref. 3 obtained from the least squares fits to the data for each temperature. As can be seen, within the errors, there is no significant variation of the parameters as a function of temperature.

Temperature	– 170°C	20°C	400°C	490°C	650°C	750°C	840°C
V_0(MHz)	109. ± 3.	110. ± 3.	106. ± 3.	105. ± 3.	105. ± 3.	106. ± 5.	106. ± 5.
η	0. ± .05	0. ± .05	0. ± .05	0. ± .05	0. ± .05	0. ± .06	0. ± .06
δ	.03 ± .01	.03 ± .01	.04 ± .01	.03 ± .01	.03 ± .01	.02 ± .02	.04 ± .02
V_{zz}(10^{17} V/cm^2)	11.9 ± .3	12.0 ± .3	11.6 ± .3	11.4 ± .3	11.5 ± .3	11.5 ± .5	11.5 ± .5

3. Discussion

As a result of comparison between recent Mossbauer and Perturbed Angular Correlation experiments on various Hafnium compounds[1], it is known that in strongly bound ionic compounds the impurity Tantalum feels the same field gradient as the original Hafnium ion. It can thus be implied that the ionic structure of the Ta impurity is that of Ta^{5+} in those compounds such as $HfSiO_4$ where the original Hafnium ion has 4+ valency. This being the case, the principal contribution to the field gradient should be from the lattice since Ta^{5+} has a configuration $5d^0$.

To test the consistency of this assumption, we have calculated the electric field gradient based on a point charge approximation. The oxygen positions were taken as those from $ZrSiO_4$ which is isomorphous to $HfSiO_4$, and the parameters u and v specifying the oxygen positions (see, e.g., Ref. 6 for details) were allowed to vary from 0.17 to 0.20 and from 0.34 to 0.36 respectively, corresponding to typical values found in other MRO, type compounds for which the detailed structure is known[6]. The field gradients found using a Sternheimer factor of 62.2[7] vary between 4.5 x 10^{17} Volt/cm^2 and 49 x 10^{17} Volt/cm^2, which may be compared to our value of 11.5 x 10^{17} Volt/cm^2 determined experimentally, supposing $Q(5/2^+) = 2.53$ b.

We conclude that although the calculation qualitatively reproduces the experimental results, supporting the idea that the major contribution to the field gradient is due to the lattice, more detailed comparisons to determine possible contributions from dipolar, or covalency effects, e.g., would require a direct measurement of the oxygen positions in the compound

$HfSiO_4$, and in particuiar an accurate determination of the oxygen position parameter u, which is the most sensitive parameter in the model.

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