

Perturbed Angular Correlation Measurements in BaHfO₃*

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Time Differential Perturbed Angular Correlations are reported for the 133 KeV - 482 KeV cascade of Ta181, resulting from the β -decay of ^{181}Ta in the compound BaHfO₃. The results are analyzed in terms of a quadrupolar interaction between the Ta nuclei and a simple approximated distribution of electric field gradients resulting from defects in the crystal. An analytical expression for the attenuation factor $G_2(t)$ is used, taking into account directly the interaction between the Ta nuclei and the near neighbors defects. A Lorentzian function, around zero, is used for the frequency distribution resulting from the interaction with other defects.

Foram medidas correlações Angulares Diferenciais Perturbadas para a cascata 133 KeV - 482 KeV, do Ta181, proveniente do decaimento β - do ^{181}Ta . Os resultados são analisados em termos da interação quadrupolar entre o núcleo de Ta e uma distribuição aproximada de gradientes de campo elétrico, resultante dos defeitos no cristal. Utiliza-se uma expressão analítica para o fator de atenuação $G_2(t)$ que leva em consideração, diretamente, a interação entre o núcleo de Ta e os defeitos em

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vizinhos mais próximos. Para a distribuição de frequências usa-se uma distribuição Lorentziana, em torno de zero, resultante da interação com os outros defeitos.

1. INTRODUCTION

Time Differential Perturbed Angular Correlations (TDPAC) is an important technique to study hyperfine interactions. Among the possible detected effects, the electric quadrupolar interaction can be of prime importance to study crystalline properties^{1,2}. Not only the values of nuclear quadrupole moments and electric field gradients (EFG) can be studied, but other important phenomena in solids, as relaxation processes, crystal impurities and imperfections, and so forth, have a marked influence on the results. Here, we report on TDPAC measurements in the BaHfO₃ compound. Since the Hf site has cubic symmetry, the EFG tensor, in a perfect crystal, is zero, and the attenuation factor $G_2(t)$ (Ref.3) should be time independent and equal to 1. This does not agree with our experimental results in BaHfO₃, which show a decrease of the $G_2(t)$ curve down to the hard core value. Our interpretation is that this behavior can be understood in terms of crystal imperfections.

2. THEORETICAL CONSIDERATIONS

When we study the TDPAC between gamma radiations, the $G_2(t)$ attenuation factor, for a pure quadrupole interaction, takes the following form:

$$G_2(t) = \sum_n \sigma_n \cos(\omega_n t)$$

where $\omega_0=0$, and the ω_n 's and σ_n 's are known functions of the asymmetry parameter η and of the quadrupole frequency³

$$v_Q = eQV_{zz} / [4I(2I-1)] .$$

In the case of BaHfO₃, the point symmetry of the Hf ions is cubic and we should expect, if the crystal is perfect, $V_{zz}=0$ at the Hf sites. Due

to the existence of defects randomly distributed in the crystal, we can have a finite frequency distribution around $\nu_0 = 0$. To take into account this possibility, we must modify Eq.1.

Following the same ideas expressed by Livi⁴ and Bertschart⁵, we have assumed an approximation to the true physical situation, in order to obtain an analytical form for $G_2(t)$. The resulting expression is composed of two parts: one part is given by the nuclei which have a defect as a nearest neighbor, in which case contributions due to more distant defects were ignored; and the second one is due to the remaining nuclei, for which a Lorentzian distribution of axially symmetric ($\eta = 0$) field gradients, around $V_{zz} = 0$, was assumed.

With these assumptions, we can calculate an expression for $G_2(t)$, performing the necessary time and frequency convolutions⁶. The result is

$$G_2(t) = \sum_n \sigma_n \frac{F \operatorname{Re}\{W(Z_n)\}}{\exp(Z_0^2) \operatorname{erfc}(Z_0)} + \frac{(1-F) \exp(Y_n^2) \operatorname{erfc}(Y_n)}{\exp(Z_0^2) \operatorname{erfc}(Z_0)}, \quad (2)$$

where

$$Z_0 = (\sqrt{2}/2) (\tau_R - t/\tau_R),$$

$$Z_n = (\sqrt{2}/2) \omega_n \tau_R + i(Z_0 + (\sqrt{2}/2) \omega_n \delta \tau_R),$$

$$Y_n = Z_0 + \left(\frac{\sqrt{2}}{2} n \Gamma \tau_R\right),$$

$W(Z_n)$ is a complex function related to the complementary error function $\operatorname{erfc}(Z_n)$ (Ref.7); F defines the percentage of the first term in relation to the other; A is the inverse of the lifetime of the intermediate level; Γ is the width of the frequency distribution of ν_{ij} around zero; $\delta \nu_n$ is the width of the frequency distribution around ν_n , and τ_R defines the time resolution of our equipment

For the time resolution and frequency distributions, we used functions of the forms⁶:

$$R(t-t') = \exp\left[-(t-t')^2/2 \tau_R^2\right] ,$$

and

$$P(\omega-\omega_0) = 1/[1+(\omega-\omega_0)^2/\Gamma^2] ,$$

($\Gamma = \delta\omega_0$ for the second term of Eq.2)

Equation 2 involves several approximations. Among the most important ones, we made the assumption of Lorentzian frequency distributions, for the terms arising from nearest neighbor impurities, and the approximation of a Lorentzian function, around zero, representing the remaining distribution of field gradients, arising from the random distribution of impurities in the crystal.

A nonlinear least squares program was written to fit the experimental data to Eq.2. It was found convenient to use the resultant fitted parameters, of the $n = 1$ terms of Eq.2, to represent approximately the distribution of the quadrupole interaction frequencies ν_Q as defined above. These fitted frequency distribution curves can be used to determine a rough value of the concentration of defects, since the area of the peak, corresponding to the discrete frequency component, divided by the total area of the distribution function, is the product NC , where N is the coordination number for nearest neighbor defect sites, and C is the concentration of defects.

3. RESULTS AND DISCUSSION

Using a conventional fast-slow coincidence circuit, with two NaI(Tl) detectors, we measured the 133 keV - 482 keV cascade in Ta¹⁸¹. Our time resolution was 2.3 ns (FWHM) for the involved gamma ray energies.

The BaHfO₃ compound was prepared as follows:

The Hafnium was weighed as metal and transformed into hydrated oxide by precipitation, with ammonium hydroxide, from a sulphuric acid solution. After being washed, the oxide was suspended in water, and a stoichiometric

tric amount of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was added. The resultant slurry was dried under constant agitation. The solid mass was heated at 1200°C , for 12 hours, and then moistened, ground and heated again up to the same temperature. An X-ray analysis of the compound showed the typical pattern of the BaHfO_3 cubic structure, with a lattice parameter of 4.171 \AA (Ref. 8). The Hf activity was produced by irradiating the compound with neutrons. After activation, the sample was annealed, at 1200°C , for 24 hours.

Several TDPAC measurements were done with two samples which were prepared separately. The measurements were performed at various temperatures - from liquid Nitrogen temperature up to 800°C .

In Fig. 1, we show the results of $A_2G_2(t)$, for the two different samples at 20°C . The solid lines are least squares fittings using functions of form (2). The values obtained for the different parameters are indicated in the figures.

The curves obtained for other temperatures (-195°C , 500°C , 700°C) did not show any change, and can be fitted with values for the parameters which are the same as those for 20°C , within the experimental errors.

In Fig. 2, we show a frequency distribution curve, which we obtained using the parameters from the fitting to $G_2(t)$ of sample 1 (see Fig. 1). The plot was made in such a way that the areas, resulting from the two terms of Eq. 2, are in the same ratio as given by the least squares parameters. The dotted lines were used to emphasize the areas S_0 (frequencies around zero) and S_1 (frequencies around ν_1 in the fit). Through a simple calculation, using these areas, one can estimate the product of concentration by coordination number, for defect sites around the Hf nuclei (NC). Our values for NC , in the two samples, are always less than .005.

To test the idea that the ν_1 's, in our curves, come from near neighbors defects, we assumed vacancies created in the Oxygen positions in BaHfO_3 . A computer program was made to calculate the frequency distribution resulting from the referred vacancies.

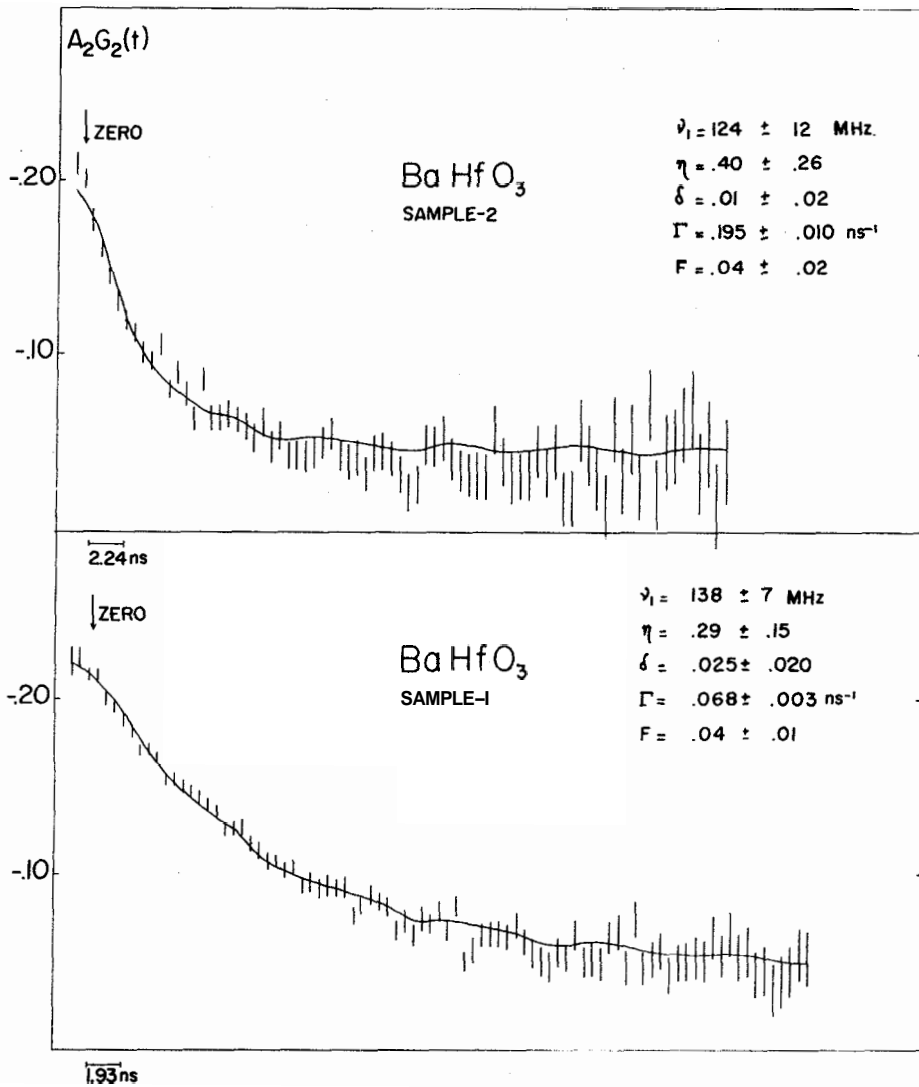


Fig.1 - $A_2G_2(t)$ coefficient for the perturbed angular correlation in two different samples of BaHfO_3 , at 20°C .

We simulated the physical situation by distributing, at random, a given number of defects (defined by the concentration, and by a fixed radius around a Hf nucleus) in the crystal. The resulting frequency distributions have the same general form as those published by Kajfosz⁹. Due to the r^{-3} -dependence of the electric field gradient components, the contribution of defects, other than the first near neighbors, tend to be very close to zero.

Using the results for NC, the simulation in no way reproduces the patterns obtained from the least squares fittings (see Fig.2 for sample number 1). The widths, around zero, and around the first nearest neighbor frequencies, are one order of magnitude lower than the experimental ones. Other suppositions concerning the strength of the interaction do not change the non-coincidence. Furthermore, if ν_1 comes from nearest neighbor interactions, it is very difficult to accept that it is located under the tail of the other neighbors.

We believe that the ν_1 values in our measurements can be attributed to a small mixture (less than .5%) of impurities in the samples; maybe some portion of HfO_2 (the ν_1 values are comparable¹⁰) that did not react to form BaHfO_3 . These small amounts cannot be detected in a X-ray analysis but appear in our TDPAC measurements.

In this case, all the interactions in BaHfO_3 can be represented by a frequency distribution around zero. This corresponds to assuming that $F = 0$ in Eq.2.

The ratio of the resulting widths, in sample 1 and sample 2 (68 MHz and 195 MHz respectively), gives then a rough approximation to the concentration ratio for the defects in these two samples. Determination of the concentration of defects, in each sample, could be obtained from the simulations if the nature of the defects or defect, and their interactions with the Hf nuclei, could be determined.

We believe that our interpretation, based on Eq.2, is useful for the understanding of the quadrupolar interaction in BaHfO_3 and in other cases.

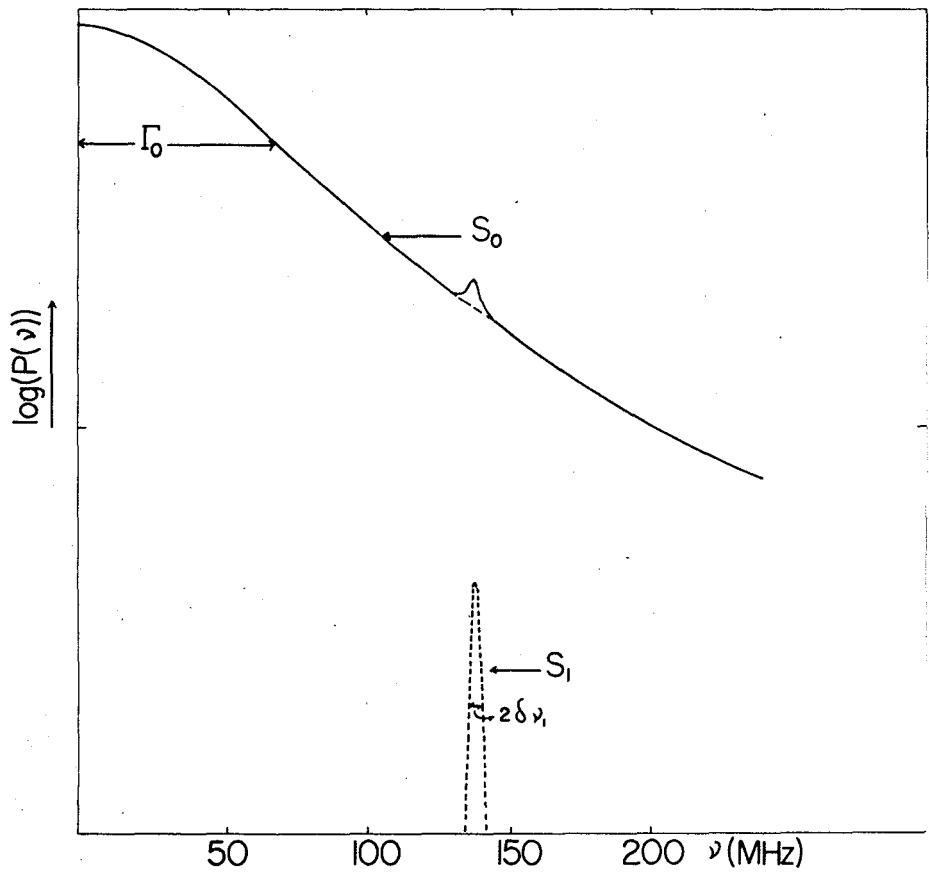


Fig. 2 - Frequency distribution resulting from a least squares fitting (based on Eq.2) to $A_2G_2(t)$, for sample 1 at 20°C.

In other experiments (Refs. 4,5,11,12,13), where similar results were reported, we think that the present interpretation of the hyperfine interaction in an insulating cubic crystal leads to a better understanding of the experimental results. For metallic systems, calculations have been done ^{9,11} based on arguments similar to those used here.

Our experiment with Hf in the BaHfO₃ compound shows that impurities have a marked influence upon the expected curves for $G_2(t)$. Thus, we think it is of interest to further investigate this, and other similar systems, in order to learn more about the exact nature of the imperfections and the resulting frequency distributions. It would be important to measure compounds where we could control the concentration of defects and their nature.

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