

HYPERFINE INTERACTION OF ZrO_2 – TETRAGONAL PHASEM.C. CARACOCHÉ*, M.T. DOVA[☆], A.R. LÓPEZ GARCÍA[†], J.A. MARTÍNEZ*

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The quadrupole hyperfine interaction of the tetragonal phase of the zirconium oxide has been measured at 1523 K using the time-differential perturbed angular correlation technique. The electric field gradient at zirconium sites was determined to be $V_{zz} = (17.5 \pm 0.4) \cdot 10^{17} \text{ Vcm}^{-2}$ and axially symmetric.

Due to its high melting point and chemical stability, ZrO_2 constitutes a refractory oxide of great interest and a prospective material for the investigation of high-temperature processes. Zirconia can exist in several modifications. It is monoclinic at room temperature and transforms reversibly to the tetragonal structure above 1273 K and to the cubic structure at higher temperatures [1]. The monoclinic to tetragonal transition has been employed in the transformation toughening of ceramics [2]. The crystalline structure of the monoclinic modification has already been determined [3]. In addition, the hyperfine quadrupole interaction characterizing this phase has been reported by Yeshurum et al. [4] and by the present authors [5].

Concerning the tetragonal form, its lattice parameters and atomic positions are known [6]. As the reversible polymorphic transformation involved causes cracking and sometimes complete disintegration of the specimen, the stabilization of this high-temperature phase has been the goal of many investigations, and additional information about it is desirable in order to extend the practical use of ZrO_2 .

In this paper, we report the electric field gradient (EFG) corresponding to the tetragonal form of ZrO_2 at Zr sites, which we determined at 1523 K by means of the time-differential perturbed angular correlation (TDPAC) technique.

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A sample of ZrO_2 , acquired from Fluka, was capsulated in a quartz tube for neutron irradiation. Making profit of hafnium impurities in zirconium, we have applied the TDPAC technique to the well-known 133–482 keV γ – γ cascade of ^{181}Ta following the β^- decay of ^{111}Hf . The experimental investigation of the perturbed angular correlation allows us to determine the EFG acting on the probe nuclei, and to characterize it by the quadrupole interaction frequency $\omega_Q = eQV_{zz}/4I(2I-1)\hbar$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where $I = 5/2$ and $Q = 2.53$ b are the spin and the quadrupole moment of the intermediate level, respectively. The principal axes of the EFG tensor are chosen in such a way that the diagonalized components of the EFG satisfy the condition:

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|.$$

Experimental data handling has already been described in previous papers (see, for example, ref. [7]). The time resolution at hafnium energies was determined to be $2\tau = 0.75$ ns. Data acquisition was performed at different temperatures of the sample within the range 293–1600 K. The thermal stability of the heating system was of the order of ± 5 K.

Figure 1 shows the spin rotation curves of ZrO_2 obtained at 293 K and 1323 K. Both of them exhibit the typical pattern of the monoclinic phase ($V_{zz} = (13.2 \pm 0.5) \cdot 10^{17}$ Vcm^{-2} , $\eta = 0.32 \pm 0.01$ at 293 K), although the first one also shows the presence of a second contribution.

In fig. 2, the spectrum obtained at 1523 K can be seen. Here, all zirconium sites are subject to a unique, symmetric and well-defined EFG, with $V_{zz} = (17.5 \pm 0.4) \cdot 10^{17}$ Vcm^{-2} . We have associated this interaction with the tetragonal phase of zirconia, the corresponding phase transition having occurred between 1323 K and 1523 K.

From the analysis of the quadrupole parameters fitted in the spectra taken at different temperatures, we could infer that:

- The typical interaction of the monoclinic form of ZrO_2 is accompanied at room temperature by 5% of another interaction, which we think is due to an impurity produced during the zirconium oxide synthesis. This interaction disappeared in the following measurement performed at 773 K, in agreement with Koički's observation in HfO_2 [8] that post-irradiation annealings at increasing temperatures improved the detailed structure of the TDPAC pattern.
- The slow decrease of ω_Q as temperature increases from 293 K to 1323 K suggests a weak lattice expansion (see table 1). At the same time, the η behaviour indicates a gradual and slight loss of symmetry at Zr sites.
- The quadrupole parameters fitted at 1523 K are those which characterize the high temperature tetragonal phase of ZrO_2 . They reveal a strong and axially symmetric EFG. Certainly, the variation in the observed V_{zz} -value

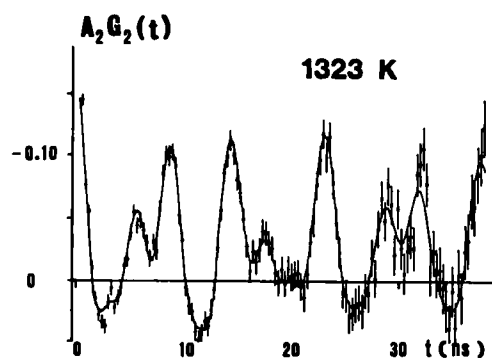
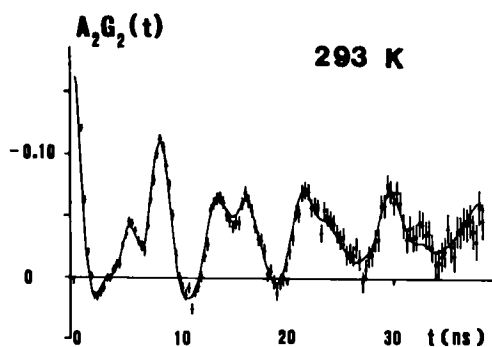


Fig. 1. Spin rotation curves of the monoclinic form of ZrO_2 at 293 K and 1323 K. The solid lines are the fitted curves to the experimental data.

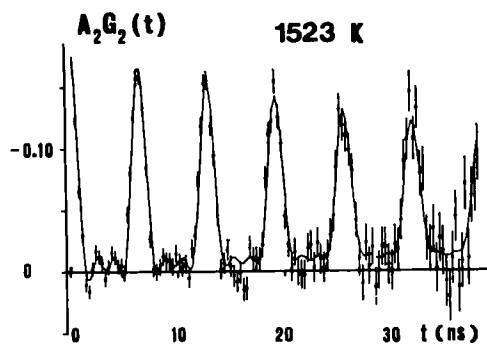


Fig. 2. TDPAC pattern of tetragonal ZrO_2 . The solid line is the fitted curve to the data.

Table 1
 Quadrupole hyperfine parameters of ZrO₂ monoclinic form

| T (K) | ω_Q (Mrad s ⁻¹) | η |
|---------|------------------------------------|-------------|
| 293 | 126 ± 1 | 0.33 ± 0.01 |
| 773 | 119 ± 1 | 0.38 ± 0.01 |
| 973 | 118 ± 1 | 0.40 ± 0.01 |
| 1323 | 117 ± 1 | 0.43 ± 0.01 |

when going from the monoclinic to the tetragonal form is related to the volume contraction reported for this transition [9].

An additional aspect is worth mentioning. While on heating, at 1323 K, 100% of the monoclinic phase was present, on cooling the TDPAC pattern at the same temperature revealed the presence of 7% of the tetragonal form. This observation is undoubtedly related to the existence of hysteresis. Heating again the sample to 1523 K, the monoclinic to tetragonal phase transition did not occur. The experimental arrangement did not allow us to achieve the temperature at which the transition accomplished for a second time. We think this situation reflects the martensitic nature of the transformation as it was already reported [10].

EFGs theoretical calculations for both modifications, monoclinic and tetragonal, using the ionic point charge model, yielded values quite different from the experimental ones determined in this work. Other models have not been attempted because of the lack of information about the bonds between the zirconium and oxygen atoms.

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