

Hyperfine characterization of ^{181}Ta in In_2O_3

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We present a perturbed-angular-correlation measurement of the hyperfine interaction at ^{181}Ta in indium sesquioxide, giving the hyperfine characterization of $^{181}\text{Hf} \rightarrow ^{181}\text{Ta}$ in substitutional cation sites of the lattice. Our results indicate that the probes produce a distortion of the oxygen next-neighbors arrangement.

In previous investigations, we have extensively studied indium sesquioxide with the perturbed angular correlation (PAC) technique using $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ probes.¹⁻³ Our experiments, and similar ones performed by other authors⁴⁻⁷ show two static quadrupole interactions associated with ^{111}Cd probes in substitutional cation sites. The characteristics of these two static interactions revealed that no distortion of the crystalline lattice is produced in the close vicinity of $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ probes.

When measurements are performed on powder samples a fluctuating hyperfine field is present at room temperature (RT), besides the two quadrupole interactions. This time-dependent interaction arises from electron holes bound to the acceptor ion Cd. The existence of holes has been attributed to the delayed rearrangement of the electron shells after the radioactive electron-capture decay of ^{111}In (usually called aftereffects).³ In order to confirm the relation of the fluctuating interaction with the probe's properties, it seems important to investigate this compound with other PAC probes.

We present in this Brief Report a PAC study of In_2O_3 using ^{181}Hf , which decays through β emission to excited states of ^{181}Ta .

In_2O_3 crystallizes in the bixbyite structure (space group $Ia\bar{3}$, $a = 10.177 \text{ \AA}$), with the cations forming a nearly face-centered cubic lattice in which six out of the eight tetrahedral sites are occupied by oxygen.⁸ The elementary cell of the oxide lattice consists of eight such cubes, containing 32 In^{3+} , and 48 O^{2-} ions. Due to their different O_6 coordinations, the corner sites (25% of total sites) and the face-centered sites (75%) are not equivalent.

Our experiment was performed on film samples prepared by thermal evaporation of high-purity $\text{In}(5 \text{ N})$ in a vacuum chamber where after air evacuation a flux of pure oxygen was introduced and kept at a pressure of about 2×10^{-3} Torr. The estimated thickness of the films was 200 nm and the temperature of the substrate (alumina) during evaporation was around 30°C.

^{181}Hf ions with energies of 150 keV were implanted

using the ion accelerator of the Institut für Strahlen und Kernphysik ISKP (Bonn). The total calculated dose was 10^{13} ion/cm².

The samples were submitted to one-hour-annealing treatments in air with temperatures between 200°C < T_A < 1200°C in 100°C steps.

PAC measurements were performed at RT after each annealing treatment. The complete crystallization was reached after the 800°C annealing. No change in the PAC spectra was found after further annealings at 800°C < T_A < 1200°C.

A conventional 4-detector apparatus with BaF_2 scintillators was used on the well-known 133-482-keV γ - γ cascade of ^{181}Ta . The time resolution of the experimental set-up was 0.9 ns (full width half maximum of the prompt peak). Theoretical functions of the form $A_2G_2(t)$ folded with the time resolution curve were fitted to the experimental $R(t)$ asymmetry ratio:

$$R(t) = 2 \frac{N(180^\circ, t) - N(90^\circ, t)}{N(180^\circ, t) + 2N(90^\circ, t)}. \quad (1)$$

For polycrystalline samples and a nuclear spin $I = \frac{5}{2}$ of the intermediate level, the perturbation factor for static electrical quadrupole interactions has the form

$$G_2(t) = \sum_i f_i \sum_{n=0}^3 S_{2n,i} \cos(\omega_n t) \exp(-\delta_i \omega_n t), \quad (2)$$

where f_i are the relative fractions of nuclei that experience a given perturbation. The ω_n frequencies are related by $\omega_n = g_n(\eta) \nu_q$ to the quadrupole coupling constant $\nu_q = eQV_{zz}/h$. The g_n and S_n coefficients are known functions of the axial-asymmetry parameter $\eta = (V_{xx} - V_{yy}) / V_{zz}$, where V_{ii} are the principal components of the electric field gradient (EFG) tensor. The exponential functions account for a Lorentzian frequency distribution of relative width δ around ω_n .

We show in Fig. 1(a) a typical spectrum characteristic of all the PAC measurements performed after annealing

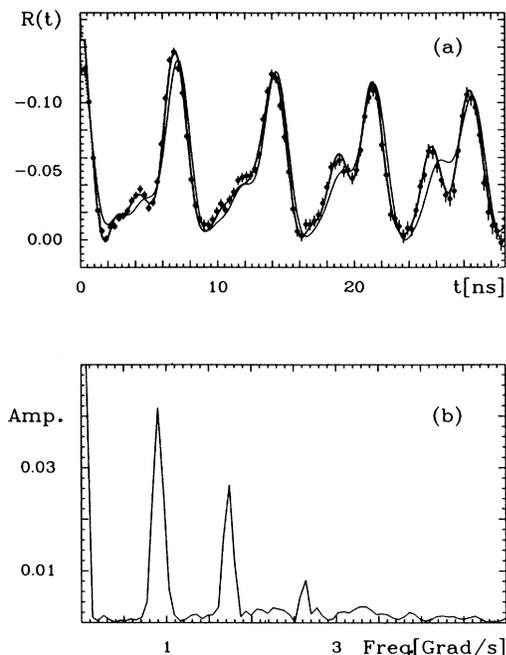


FIG. 1. (a) Typical PAC spectrum of $^{181}\text{Hf}/^{181}\text{Ta}$ in In_2O_3 measured at RT. Narrow line indicates the least-squares fit of Eq. (2) to the data assuming a unique static electric quadrupole interaction. The thicker curve represents the best fit to the data with hyperfine parameters quoted in the text. (b) Fourier spectrum of the PAC spectrum shown in (a).

in the range $800^\circ\text{C} < T_A < 1200^\circ\text{C}$. Figure 1(b) shows the corresponding Fourier transform of the $R(t)$ data which indicates the ω_n frequency spectrum. Although the Fourier spectrum shows one main frequency which could correspond to one hyperfine interaction, a least-squares fit of the PAC spectrum with only one interaction does not reproduce the data pattern [narrow line in Fig. 1(a)]. The best fit is obtained with two interactions characterized by the following parameters:

$$f_1 = 74_1\%, \quad \omega_{Q1} = 146.6_2 \text{ Mrad/s},$$

$$\eta_1 = 0.11_1, \quad \delta_1 = 0.00_1\%,$$

$$f_2 = 26_4\%, \quad \omega_{Q2} = 145.6_7 \text{ Mrad/s},$$

$$\eta_2 = 0.35_1, \quad \delta_2 = 0.01_1\%.$$

The relative fractions of both interactions (3:1) are consistent with a homogeneous population of both cation sites in the lattice.

From crystalline considerations one could expect that

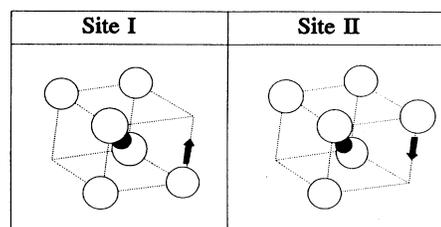


FIG. 2. Schematic representation of both cation sites in the bixbyite structure of In_2O_3 . Arrows show a possible oxygen displacement compatible with the measured hyperfine parameters (see text).

the EFG associated with these two sites should be quite different. Indeed, as we mentioned at the beginning, the results of PAC measurements in In_2O_3 with ^{111}In probes were in good agreement with the expected results from crystalline considerations. In that case, the experimental results were well reproduced by a point charge model (PCM) calculation which shows a $\omega_a/\omega_s = 0.54$ with $\eta_a = 0.93$ and $\eta_s = 0$ for the asymmetric and symmetric sites, respectively. The frequency ratio and asymmetry parameters found with ^{181}Hf probes suggest a distortion of the charge distribution around the probe.

The fact that the hyperfine parameters of both measured interactions are very close, indicates that the probe tends to arrange the first neighbor's oxygen distribution in a similar configuration in both sites.

In Fig. 2 we show a schematic representation of one possible oxygen rearrangement which can lead to the measured hyperfine interactions. Indeed a PCM calculation indicates that a 25% displacement of the oxygen in site I, as shown with arrows in Fig. 2, and a 22% displacement of the corresponding in site II, reproduce the EFG ratio found in this experiment.

This measurement does not allow us to determine whether the distortion is produced by the ^{181}Hf or ^{181}Ta ions. Nevertheless, the fact that no time-dependent interaction is present in our spectra indicates that the atomic rearrangement must take place before the emission of the first γ ray of the cascade. Given the very long lifetime ($18.1 \mu\text{s}$) of the γ cascade departure state, if it were only Hf, but not Ta, which produces the observed distortion, there is enough time after the β decay of Hf for the distortion to relax before the γ cascade begins. Hence, whether or not there is distortion around the Hf ion, there certainly is around the Ta daughter.

Further experiments in bixbyite oxides of Y, Dy, and Yb using ^{181}Hf probes have been undertaken in order to extend the comparison of PAC measurements with ^{111}In and ^{181}Hf probes. A complete analysis of these data is currently in progress.

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