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PAC study of dynamic hyperfine interactions at ^{111}In-doped Sc_2O_3 semiconductor and comparison with *ab initio* calculations

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Abstract Time-Differential γ-γ Perturbed-Angular-Correlation (PAC) measurements were performed in ^{111}In-difussed Sc_2O_3 polycrystals in order to characterize the electric-field-gradient tensor at ^{111}Cd nuclei located at the two non-equivalent cation sites of the host lattice. The experimental data were compared with *ab initio* calculations performed using the Full-Potential Augmented Plane Wave plus local orbital (FP-APW+lo) method in the framework of the Density Functional Theory. The PAC experiments were carried out in air in the temperature range 10–900 K. The spectra present a strong damping below 650 K. This damping is associated with dynamic hyperfine interactions that were analyzed with the perturbation factor proposed by Bäverstam et al.. A model based in the population of impurity levels that are introduced by the Cd probes (supported by FP-APW+lo results) is proposed in order to explain the origin of the observed dynamic interactions.

Keywords PAC · Dynamic interactions · Sc_2O_3 · ^{111}In/^{111}Cd · *Ab initio* calculations

1 Introduction

In the last three decades, the Time-Differential γ-γ Perturbed-Angular Correlation (PAC) spectroscopy was largely applied in condensed-matter physics. By means

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of this technique it is possible to measure a physical quantity of a solid in its ground state, i.e., the electric-field gradient (EFG) at the site of a suitable probe isotope (generally an impurity) adequately introduced in the system under study. Due to the EFG's r^{-3} dependence on the distance from the probe-nucleus to the charge sources, the EFG "felt" by the nucleus reflects sensitively the non-spherical electronic charge distribution around the probe-atom. Therefore, the EFG is one of the most powerful tools to unravel the modifications in the electronic band structure and the atomic relaxations introduced by the impurities in semiconducting oxides at a sub-nanoscopic scale.

In experiments performed at room-temperature (RT) with ^{111}In/^{111}Cd as probe in bixbyites [1, 2], the presence of dynamic hyperfine interactions originated in the electron-capture (EC) decay *after-effects* (AE) appeared selectively, depending on the fact that the indigenous cation presents closed electronic shells (Sc, Y, and In) or if it has not complete electronic shells (bixbyites with rare-earth as cation) [3, 4]. In effect, while nothing special is observed in the PAC spectra at RT in rare-earth sesquioxides, in the case of Y_2O_3, Sc_2O_3, and In_2O_3 the spectra taken at RT presents a strong damping compared to the spectra taken at higher temperatures. As this damping is reversible with temperature any form of radiation damage cannot cause it. Moreover, the damping at the two cationic sites can neither be described by a Lorentzian nor by a Gaussian static frequency distribution, and the experimental hard-core value is smaller than the expected value. These features reflect the presence of dynamic hyperfine interactions (DHI) in Y-, Sc-, and In-sesquioxides. In all previous reports these DHI were ascribed to both cation sites and the same dynamic parameters were proposed (fixed) for both sites. Moreover, it was proposed that a unique (i.e., constant) EFG for each site was present for all temperatures. Enlighten by recent *ab initio* electronic structure calculations of the EFG at impurity sites in oxides [5, 6] and particularly in some bixbyites [7–9] we considered necessary to revisit these experiments in order to analyze both cation sites separately.

In this work, PAC experiments using ^{111}In-difussed Sc_2O_3 polycrystals have been performed at the IPEN facility in order to measure the EFG at ^{111}Cd nuclei located at both cation sites of the semiconductor lattice. The experimental results are compared with recent *ab initio* calculations performed with the Full-Potential Augmented Plane Wave plus local orbital (FP-APW+lo) method in the framework of the Density Functional Theory (DFT).

2 Crystal structure, sample preparation and PAC technique

Sc_2O_3 is a semiconductor that crystallizes in the cubic bixbyite structure ($a = 9.845$ Å). The unit cell contains 32 Sc and 48 O atoms. This structure presents two non-equivalent cationic sites, called C and D, with relative abundance $f_C : f_D = 3{:}1$, both coordinated with 6 nearest oxygen neighbors (ONN). Site D is axially symmetric and site C is highly asymmetric. The atomic positions are determined by four internal parameters: u, which determines the positions of the Sc atoms at site C, and x, y, and z that determine the positions of the O atoms [10].

In order to obtain the ^{111}Cd-doped Sc_2O_3 samples, $^{111}InCl_3$ was dropped onto a Sc_2O_3 (99.999% purity) powder pellet and thermally diffused in N_2 atmosphere (3×10^8 Pa) in several steps from 423 K to 1073 K. The diffusion process was monitored by PAC measurements. After diffusion, the temperature dependence of the EFG was measured in the range 10–900 K using a conventional slow–fast coincidence PAC spectrometer with four conical BaF_2 detectors disposed in a 90° coplanar geometry. The experimental perturbation functions $R(t)$ were derived from 12 measured coincidence spectra, four taken between the detectors positioned at 180° and eight at 90°.

In PAC experiments, a “static” damping of the $R(t)$ spectra occurs if probes located in equivalent crystal sites observe slightly different static EFGs due to distortions in their neighborhood. In a dynamic situation, the environment of individual probes changes during the lifetime of the intermediate state of the γ-γ cascade, leading to a “dynamic” damping and phase shifts in the spectra. In the case of ^{111}In, after the K-electron EC decay to^{111}Cd and the subsequent Auger process, the probe-atom is in a highly charged state far out of the equilibrium. In semiconductors, depending on the electronic characteristics of the probe-host system, the probe can remain in an unstable charge state for a time long enough to reach the sensitive time-scale of the $I = 5/2+$ intermediate level in ^{111}Cd (in the order of ns) [11]. In the “time-window” of the PAC measurement, transitions among different unstable charge states of the ^{111}Cd atom can occur. These transitions produce a time-dependent local charge distribution around the probe, producing a dynamic change of the EFG (in sign, magnitude and/or symmetry), called AE in the pionners papers. If the probe decays to a final stable charge state before the end of the time-window of the measurement, the DHI changes to a static regime. A simple model used to describe dynamic interactions was proposed by Bäverstam and Othaz (BO) [12, 13], which has seen a renovated use nowadays [14]. Based in this model, our $R(t)\ \left(= A_{22}^{\exp} G_{22}^{\exp}(t)\right)$ spectra were fitted using a multiple-site perturbation factor for nuclear-electric quadrupole interactions modified conveniently at each site to consider the time-dependent EFGs:

$$G_{22}^{\exp}(t) = f_D G_{22}^{dyn.D}(t) \cdot G_{22}^{stat.D}(t) + f_c G_{22}^{dyn.C}(t) \cdot G_{22}^{stat.C}(t), \tag{1}$$

where $G_{22}^{stat.i}$ ($i = C$ or D) represents the standard static perturbation factor [6] and $G_{22}^{dyn.i}$ is the dynamic perturbation factor that, in the BO model, is given by:

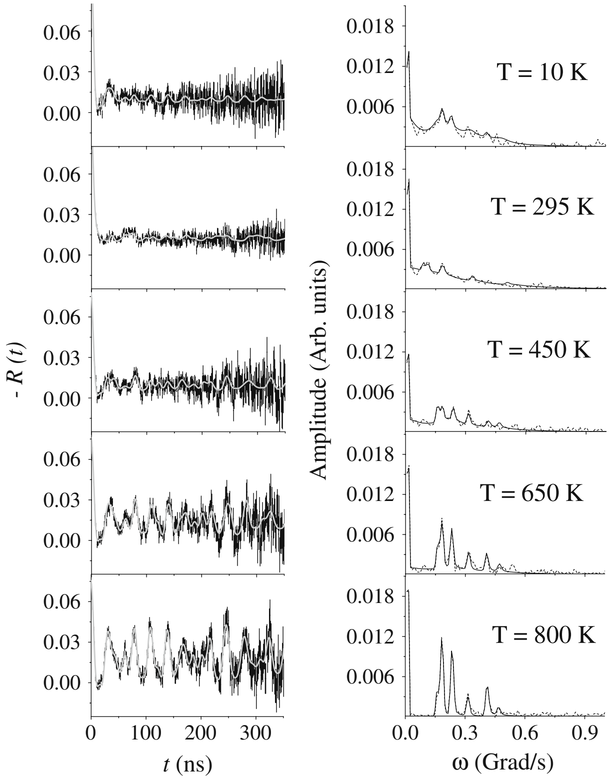
$$G_{22}^{dyn.i}(t) = \frac{\lambda_g^i}{\lambda_g^i + \lambda_r^i} + \frac{\lambda_r^i}{\lambda_g^i + \lambda_r^i} \exp\left[-\left(\lambda_g^i + \lambda_r^i\right)t\right], \text{ with } i = C \text{ or } D. \tag{2}$$

The λ_r parameter is called the Abragam and Pound’s relaxation constant and it is related with the strength of the dynamic interaction [13]. The λ_g is the recovery constant and it is related with the time that the time-dependent interaction “lives”. The inverse of the $\lambda_g\left(\tau_g = \lambda_g^{-1}\right)$ is the mean lifetime of the electron hole(s) trapped at the probe-atom.

3 PAC results and discussion

In Fig. 1 we present the $R(t)$ spectra and their Fourier transforms taken at the indicated measuring temperature after the diffusion process was completed. Below 650 K a strong dampening of the $R(t)$ signal begins to be appreciable. From 200 K to 450 K the dynamic interaction is remarkable and the signal is slightly recovered below 200 K. Above 700 K the dampening is negligible. Two well-defined hyperfine

Fig. 1 R(t) spectra (*right*) and their Fourier transform (*left*) taken at representative indicated measuring temperatures

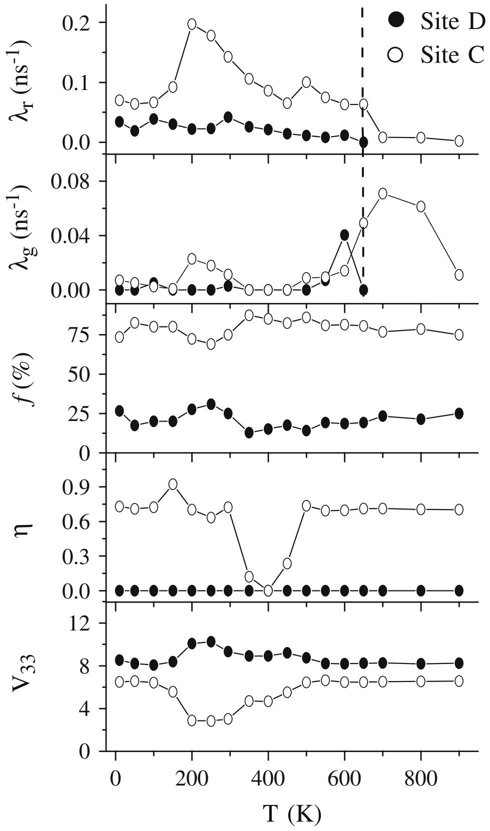


interactions were necessary to fit the experimental spectra in the whole temperature range. These interactions correspond to ^{111}Cd probes located at undisturbed (very low EFG distributions) cation sites *C* and *D* of the bixbyite structure. The quadrupole frequency distributions were fixed in the values adjusted at 900 K. At 900 K, the values for the largest principal component of the EFG tensor, V_{33}, and the asymmetry parameter η, are $V_{33} = 6.56\,(1) \times 10^{21}\ \mathrm{V/m^2}$ and $\eta = 0.70(1)$ for ^{111}Cd located at site *C* and $V_{33} = 8.22\,(1) \times 10^{21}\ \mathrm{V/m^2}$ and $\eta = 0.0$ for site *D* ($Q = 0.83(13)\ b$ [15] was used in order to obtain V_{33} from the nuclear quadrupole frequency). These experimental hyperfine parameters are in excellent agreement with the experimental results reported by Bartos et al. [3] and with the *ab initio* FP-APW+lo electronic structure calculations reported by some of us for Cd-doped Sc_2O_3 [8]: $V_{33} = 6.75\,(1) \times 10^{21}\ \mathrm{V/m^2}$ and $\eta = 0.74$, and $V_{33} = 8.05\,(1) \times 10^{21}\ \mathrm{V/m^2}$ and $\eta = 0.0$, for sites *C* and *D*, respectively.

Figure 2 shows the experimental hyperfine parameters as a function of the measuring temperature. The experimental population ratio is in agreement with the relative abundance of the cation sites in the bixbyite structure. V_{33} and η remain almost constant at high and low temperatures. But in the temperature range where the dynamic interactions and the spectra dampening are more intense, the hyperfine parameters corresponding to site *C* present a considerable variation.

Inspecting the trend of the dynamic parameters as a function of temperature, we can observe that below 650 K the relaxation constant for Cd probes located at site

Fig. 2 Temperature dependence of the hyperfine parameters. V_{33} is in units of 10^{21} V/m^2



C, $\lambda_r(C)$, is always larger than that related with probes at site D, having a maximum value at 200 K (consistent with the strongest dampening of the spectra). Above 650 K, $\lambda_r(D)$ goes to zero, indicating that dynamic interactions are not present at all in this range for the symmetric site (the dash line separates the temperature ranges where the EFG at site D is static or dynamic). The recovery constant λ_g behaves similar for T > 600 K, indicating a decrease of the lifetime of the electron holes at site C at higher temperatures (consistently with the recovery of the spectra due to the short harly for both sites (the electron hole's lifetime is rather long) but $\lambda_g(C)$ increases holes's lifetimes and also due with the decrease of $\lambda_r(C)$, i.e., decrease of the strength of the EFG fluctuation).

Preliminary *ab initio* APW+lo calculations of the EFG as a function of the charge state of the impurity, treated self-consistently, start to enlighten this situation [8]. These calculations show that, in the case of site D, the EFG is constant in sign, orientation, and symmetry and varies very slightly in magnitude (less than 2%) with the charge state of the probe. On the other hand, the EFG tensor at site C changes in magnitude, symmetry, sign, and orientation for different charge states of the Cd probe. Also the sudden variation in $\eta(C)$ and the slow decrease of $V_{33}(C)$ between 300 K and 500 K are qualitatively well described by the variation of the EFG predicted by these calculations when 1 or 2 electron holes are trapped at the

Cd probe. This behaviour, already observed in other impurity-host systems [5, 6], is directly correlated with the symmetry of the electronic charge density, that depends on the symmetry of the considered site and the electronic configuration of the probe-atom. In the case of Cd-doped Sc_2O_3, the impurity induce an acceptor impurity level at the Fermy energy. When all the orbital symmetries are present at the impurity level with the same weight, the change in its electronic occupation does not change the symmetry of the charge density, and in consequence the EFG remains constant (as occurs in site *D*). On the other hand the EFG strongly depends on the charge state of the impurity if some symmetries are not present (or not present with the same weight) in the impurity level (as in the case of the asymmetric site *C*). In this scenario, we attribute the large difference of the Abragam and Pound's relaxation constant λ_r at site *C* and *D* to the different EFG dependence on the charge state of the impurity at each site that have very different coordination symmetries. The variation in V_{33} and η observed at site *C* at intermediate temperatures (where the dynamic processes are stronger) are correlated with different final charge states of the impurity level, i.e., with different stable EFGs at site *C* reached as the final step of the relaxation process at each temperature. Finally, the recovery constant of the $R(t)$ signal is independent of the symmetry of each site. This can be easily understood if the electron availability and/or mobility are proposed to be characteristic of the bulk and not of a certain site.

4 Conclusions

From the experimental results and their comparison with first-principles calculations, we can conclude that the dynamic interaction observed at Cd impurities located at *C* sites is more intense than the dynamic interaction at the *D* site. The combination theory-experiment enabled us to propose a model for the origin of the dynamic hyperfine interactions in Cd-doped Sc_2O_3. The Cd impurities introduce impurity acceptor levels of a particular symmetry in the band-gap of the semiconductor. In the case of the asymmetric site *C*, different charge states of the impurity produce different electron densities, leading to very different EFG tensors. If transitions among the different charge states of the impurity towards a stable situation occur during the time-window of the PAC measurement, a dynamic interaction will be observed. In the case of site D, due to the symmetry of this site, the charge density in the close vicinity of the Cd probe is nearly independent of the occupation (charge state) of the impurity level. For this reason, the transition to the stable charge state involves similar EFG tensors. In consequence, the dynamic interaction has a smaller intensity.

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