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Dynamic hyperfine interactions in ^{111}In(^{111}Cd)-doped ZnO semiconductor: PAC results supported by *ab initio* calculations

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A B S T R A C T

In this work, we present results of Time-Differential γ–γ Perturbed-Angular-Correlations (PAC) experiments performed in ^{111}Cd-doped ZnO semiconductor. The PAC technique has been applied in order to characterize the electric-field-gradient (EFG) tensor at (^{111}In (EC)→) ^{111}Cd nuclei located, as was later demonstrated, at defect-free cation sites of the ZnO host structure. The PAC experiments were performed in the temperature range of 77–1075 K. At first glance, the unexpected presence of low-intensity dynamic hyperfine interactions was observed, which were analyzed with a perturbation factor based on the Bäverstam and Othaz model. The experimental EFG results were compared with *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), using the Wien2K code. The presence of the dynamic hyperfine interactions has been analyzed enlightened by the FP-APW+lo calculations of the EFG performed as a function of the charge state of the cell. We could correlate the large strength of the dynamic hyperfine interaction with the strong variation of the EFG due to changes in the electronic charge distribution in the Cd vicinity during the time-window of the PAC measurement. It was also revealed that the Cd impurity decays to a final stable neutral charge state (Cd^{2+}) fast enough (in few ns) to produce the nearly undamped observed PAC spectra.

1. Introduction

Zinc oxide (ZnO) is one of the most promising wide band gap oxides used in several fields of technology due to its semiconducting properties. Doped ZnO can present intriguing physical properties depending on the type and concentration of the dopant. For example, Coey et al. reported room temperature (RT) ferromagnetism with a large magnetization in ZnO doped with transition metal elements [1]. Other authors have reported lack of ferromagnetic order in ZnO doped with magnetic impurities such as Co [2,3]. Moreover, the origin of the observed ferromagnetism is not yet established, but there is strong evidence that defects have an important role in the ferromagnetic order in such materials and the ferromagnetism coupling is mediated by carriers [4]. In order to understand the modifications induced in the ZnO matrix by the inclusion of the impurities it is necessary to observe what happens in the surrounding of the dopants. Local measurements such as those capable to characterize atomic positions are therefore needed to help in this striking issue. However, recent Time-Differential γ–γ Perturbed-Angular Correlations (PAC) measurements [5] at the subnanoscopic scale have also shown divergent results. While Mercurio et al. have observed a weak local magnetism below RT in ZnO samples doped with Co and Cd [6], Dogra et al. have not [7]. Besides other structural characterizations, the magnetism was studied in these PAC experiments via the hyperfine magnetic field sensed at the ^{111}Cd impurity probe-atom. In addition, a very subtle damping of the experimental signal was observed at intermediate temperatures, attributing to the usual (*static*) structural distribution of faraway defects from the Cd impurity site. For these reasons, in order to correctly describe the electronic and magnetic properties of this double-doped system enlightened by future PAC experiments of this kind, it is imperative to know accurately if the dopants substitute the Zn atoms at cation sites, the local structure at these impurity sites, the charge state of the impurities, and if magnetic solutions can be predicted in this system from, e.g., a first-principles calculation. In addition, it is essential to know which is the perturbation factor (*static* or *dynamic*) that has to be used to correctly describe the PAC signals in this impurity–host system. To address these questions, we have to first considerthe simpler Cd-doped ZnO system.

In order to understand the structural and electronic properties induced in the ZnO semiconductor by the inclusion of the Cd

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impurity it is necessary to determine the structural and electronic local modifications in its close neighborhood. The electric-field-gradient (EFG) tensor is an observable strongly dependent on the distribution of the electronic charge density around the atomic site where the EFG is measured, due to the r^{-3} dependence from its charge sources. The EFG reflects the non-spherical behavior of the charge distribution in the sub-nanoscopic environment of certain radioactive probe isotopes adequately introduced in the host structure, PAC spectroscopy being the most suitable experimental technique to measure it with high precision. For nuclear–quadrupole interactions, the PAC method is based on the determination of the hyperfine interaction between the electric–quadrupole moment of the probe-nucleus and the EFG tensor acting at the nucleus.

In the last years, *ab initio* band structure calculations have been applied successfully to the study of structural and electronic modifications induced by the inclusion of the impurities in doped semiconductors (see, e.g. [5]). To validate the *ab initio* predictions obtained from electronic structure calculations of the impurity–host system it is desirable to reproduce some physical quantity extremely dependent on the electronic charge distribution in the close neighborhood of the impurity and that could be measured with high accuracy. Therefore, the EFG observed at the ^{111}Cd impurity site is specially adequate to perform such a combined experimental–*ab initio* study of the structural and electronic properties of the Cd-doped ZnO initial system.

On the other hand, in PAC experiments using ^{111}In as probe-atom in binary oxides, the presence of dynamic hyperfine interactions (DHI) originating from the electron-capture (EC) decay *after-effects* (AE) of the $^{111}\mathrm{In(EC)}\rightarrow{}^{111}\mathrm{Cd}$ tracers has been observed in some characteristic systems [8,9]. In the last decades it was believed that the $^{111}\mathrm{Cd}^{2+}$ probe located at isovalent cation sites in oxide semiconductors and insulators could not present this type of DHIs, since it could not trap a stable electron hole. However, we reported recently the presence of ECAE's DHI observed in ^{111}In(EC)^{111}Cd impurities located at Sn^{2+} sites of the SnO semiconductor, Sn being isovalent to Cd [10]. In order to understand the origin of the presence or absence of these DHI in ^{111}In-doped oxides, first-principles calculations of the impurity–host system are necessary. In this sense, from a fundamental point of view, it is also interesting to perform PAC experiments to search for ECAE in ^{111}In-doped oxides where Cd is isovalent with their cations, as in Cd-doped ZnO.

In this work we present PAC experiments performed at the IPEN facility using ^{111}In(EC)^{111}Cd-doped ZnO polycrystalline powder samples to characterize the EFG tensor and the local environment at ^{111}Cd impurities in the semiconductor host structure. The PAC measurements were confronted to *ab initio* calculation predictions performed with the Full-Potential Augmented Plane Wave plus local orbital (FP-APW+lo) method, in the framework of the Density Functional Theory (DFT). The presence of ECAE's dynamic hyperfine interactions was investigated in a wide temperature range and a model based on an *ab initio* study of the EFG at the impurity site as a function of the charge state of the supercell is proposed.

2. Sample preparation and PAC technique

The hexagonal crystalline structure of zinc monoxide is called zincite and has one non-equivalent cation site coordinated with 4 nearest oxygen neighbors (ONN). These ONN are located at the corners of a tetrahedron slightly distorted in the *c* direction. The ZnO unit cell presents two Zn and two O atoms (for more information see Ref. [11]).

To obtain ^{111}Cd-doped ZnO samples, some drops of $^{111}\mathrm{InCl_3}$ were deposited onto zinc monoxide powder pellets. The ^{111}In thermal diffusion was performed at vacuum atmosphere (10^{-3} Torr) in steps from 423 K to 1000 K. The diffusion was monitored with the PAC technique. After the diffusion process, the EFG temperature dependence was measured in the temperature range of 77–1075 K. The PAC measurements were performed in a conventional slow–fast coincidence PAC spectrometer with four conical $\mathrm{BaF_2}$ detectors sited in a 90° coplanar geometry. The experimental perturbation functions $R(t)$ were obtained from twelve coincidence spectra, four taken with the detectors located at 180° and eight at 90° [12].

In PAC measurements, a static EFG distribution is observed if probes located in equivalent crystallographic sites "sense" slightly different static EFGs due to small modifications in their neighborhood. In the case of a DHI, the vicinity of individual probes changes during the lifetime of the intermediate state of the γ–γ cascade of the ^{111}Cd nuclei, and then a dynamic damping is detected. After the EC decay of ^{111}In and the following Auger process, the ^{111}Cd atom is in a highly unstable charged state. In semiconductor oxides, depending on the electronic and structural properties of the impurity–host system, the ^{111}Cd probe can trap some electron holes for a time long enough (in the order of ns) to reach the sensitive $I=5/2+$ intermediate state of the ^{111}Cd nuclei. In the time interval of the PAC coincidence detection, transitions between different charge states out of the equilibrium can occur producing a time-dependent EFG at the ^{111}Cd site. This effect was called *after-effects* in the pioneering papers [8,9]. In the case that the probe reaches the final stable charge state before the end of the PAC time window, the DHI transforms to a static regime. In this work, we used the Bäverstam and Othaz (BO) model [13] to treat the DHI. From this model, the experimental $R(t)$ $(=A_{22}^{exp}G_{22}^{exp}(t))$ spectra were fitted using the following perturbation factor that takes into account the time-dependent EFGs of the nuclear–electric quadrupole interactions:

$$G_{22}^{exp}(t)=G_{22}^{dyn}(t)G_{22}^{stat}(t), \tag{1}$$

where G_{22}^{stat} is the standard static perturbation factor for $I=5/2$ and polycrystalline samples [5] and G_{22}^{dyn} is the dynamic factor that, in the BO model, is given by

$$G_{22}^{dyn}(t)=\frac{\lambda_g}{\lambda_g+\lambda_r}+\frac{\lambda_r}{\lambda_g+\lambda_r}\exp\left[-(\lambda_g+\lambda_r)t\right], \tag{2}$$

where λ_r is called the Abragam and Pound's relaxation constant that is related with the strength of the DHI [14]. λ_g is the recovery constant and is related with the time that the DHI "lives" ($\tau_g=\lambda_g^{-1}$ is the mean lifetime of the electron holes trapped at the probe-atom [9]).

3. PAC results and *ab initio* calculations

In order to fit the experimental $R(t)$ spectra we used one well-defined hyperfine interaction in the whole temperature range. The quadrupole frequency distribution was fixed in the value fitted at high temperature (1075 K). This interaction was attributed to ^{111}Cd located at defect-free cation sites of the zincite structure. In Fig. 1 we show the PAC spectra and their Fourier transforms taken at the indicated temperature after the diffusion process. The character of the interaction is dynamic in the temperature range 400–1000 K and was analyzed with the BO model. The intensity of the DHI is very appreciable around 400–600 K. Below 400 K and over 1000 K the DHI disappears and the interaction is in a static regime. The experimental EFG tensor is characterized by $V_{33}=1.59(1)\times10^{21}$ V/m^2 and $\eta=0.08(1)$ at *RT*.

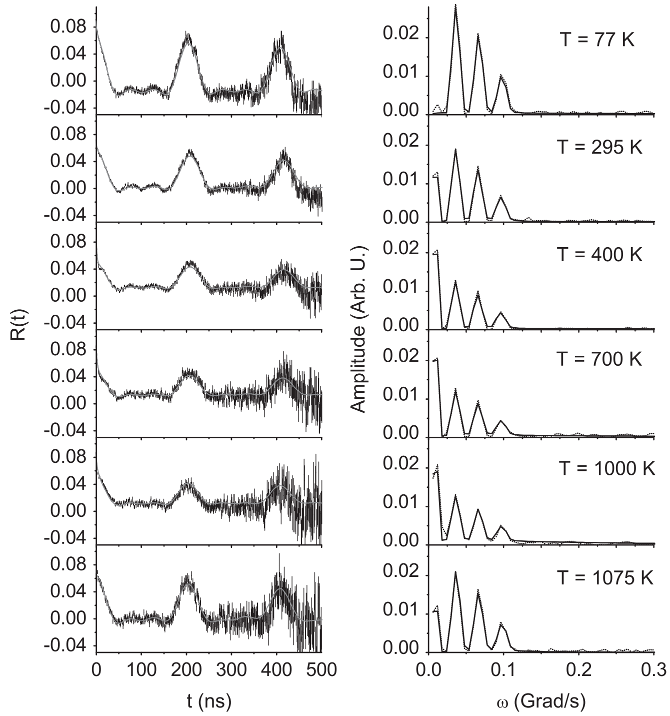

Fig. 1. $R(t)$ spectra (right) and their Fourier transforms (left) taken at representative indicated temperatures.

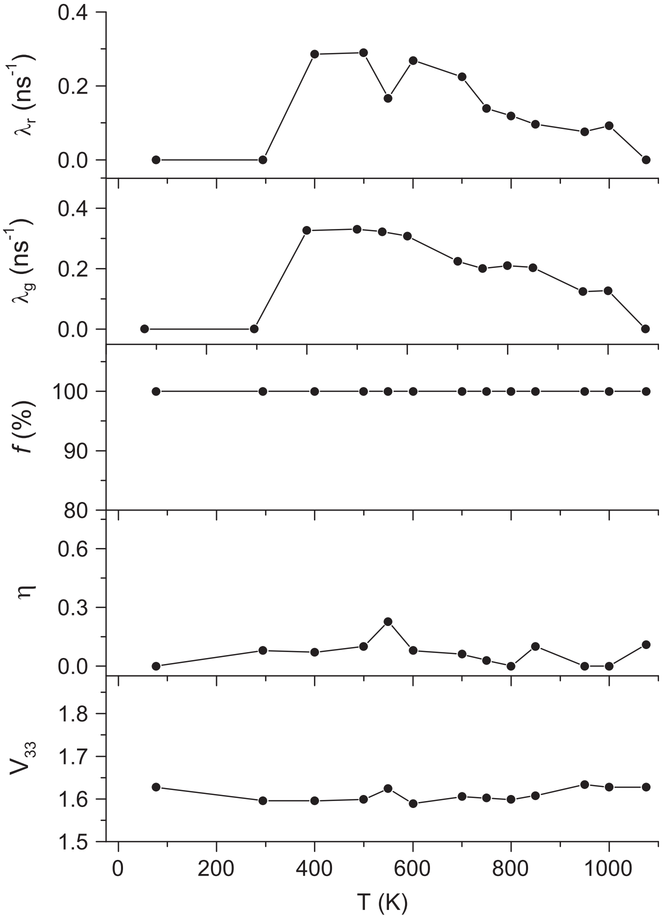

Fig. 2. Temperature dependence of the hyperfine parameters.

In Fig. 2 we plotted the fitted hyperfine parameters as a function of temperature. The parameters that characterize the EFG tensor, V_{33} (in units of 10^{21} V/m^2) and η, are constant in the whole temperature range. In the range 400–700 K, the relaxation constant λ_r is very large, larger than the λ_r value observed at ^{111}Cd located at site C of the bixbyite Sc_2O_3 [15]. On the other hand, in the same temperature range the recovery constant λ_g is also rather large (in this case, it is 3 times larger than the values seen in Sc_2O_3:^{111}In [15]), indicating that the mean lifetime of the electron holes in the ^{111}Cd neighborhood is short. Over 700 K, both dynamic parameters (λ_r and λ_g) decrease monotonously until it becomes zero. Below 400 K, the λ_r relaxation constant is null indicating that the hyperfine interaction is static.

Preliminary *ab initio* calculations in a supercell of Cd-doped ZnO were performed with the WIEN2k implementation [16] of the FP-APW+lo method in the Generalized Gradient Approximation (WC-GGA) [17]. To guarantee the dilution of the impurity, a supercell (SC) containing three ZnO unit cells in the *a* and *b* directions and two unit cells in the *c* direction was constructed and one Zn atom was replaced by a Cd atom (dilution 1:36). In order to get the equilibrium atomic positions, once self-consistency of the potential was achieved, quantum-mechanically-derived forces on the ions were calculated, they were displaced according to a Newton-damped scheme, and the new positions for the atoms in the SC were obtained. This procedure was repeated until the forces on the ions were below a tolerance value of 0.005 eV/Å. The EFG dependence with the charge state of the SC at the Cd site, treated self-consistently, was determined. The EFG calculations as a function of the charge state of the SC show that V_{33} changes 6% if an electron is added to the SC, while it changes 18% and 28% when 1 and 2 electrons are removed from the system, respectively. The V_{33} value calculated at the Cd impurity site for the case of the *neutral* cell (i.e., a Zn atom is replaced by a Cd atom in the SC) is 1.68×10^{21} V/m^2, in excellent agreement with the V_{33} experimental value. The *ab initio* asymmetry parameter is null, in agreement with the experimental value, since the first-principles calculations preserve the symmetry group of the ZnO unit cell.

From the comparison between the dynamic hyperfine parameters and the *ab initio* calculations we observe that if the Cd impurity in ZnO trapped one or two electrons holes after the EC decay AE, the EFG tensor should be around 20–30% smaller than the final stable EFG sensed by the ^{111}Cd atom when these holes are ionized some ns later. This behavior of the EFG can be correlated with the large value of the relaxation constant λ_r. But the fact that λ_g is also rather large means that in a very short time the ionization of all the probes leads to the *neutral* Cd^{2+} final state. In this sense, the λ_g dependence with temperature explains why the spectra seems to be only slightly damped.

4. Conclusions

From this combined experimental–*ab initio* approach we conclude that the PAC results are in excellent agreement with a scenario where the ^{111}Cd impurities are localized at defect-free cation sites of the ZnO structure. Also, it demonstrates that the Cd impurity decays to the final *neutral* charge state (Cd^{2+}) before or during the time-window of the PAC measurement depending on measuring temperature. The DFT calculations and a careful analysis of the spectra revealed the presence of the *a priori* unexpected ECAE's DHI and enabled us to correlate the high strength of the relaxation constant of the BO model with the strong dependence of the EFG on the charge state of the supercell. On the other hand, the apparent low intensity damping of the spectra can be understood from the fact that the electron hole mean lifetime is rather short (*fast recovery*) along the temperature range in which the DHI is present. A detailed *ab initio* study of electronic and magnetic properties in Cd- and Cd/Co-doped systems is in progress together with new PAC experiments in Co/^{111}Cd-doped ZnO.

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