Electric field gradient at the $^{111}\text{Cd}(\leftarrow ^{111}\text{In})$ site in Ga-doped ZnO

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Summary. The time-differential perturbed angular correlation (TDPAC) method was applied to a study of the local environment at the $^{111}\text{Cd}(\leftarrow ^{111}\text{In})$ probe nucleus introduced in 0.5 at. % Ga-doped ZnO. The TDPAC spectrum obtained at room temperature suggests that the doped Ga ions reside at the substitutional Zn site and they are locally associated in immediate proximity to the probe, reflecting strong attractive force between the probe and the dopants. The relative width of the magnitude of the electric field gradient produced at the probe nucleus shows that the doped Ga ion(s) adjacent to the probe is/are diversely distributed compared with doped In ion(s).

1. Introduction

Zinc oxide (ZnO) is an intrinsic $n$-type semiconductor with a property of transparent conductivity, and its industrial applications are strongly expected because of its abundant natural resources. It is known that the electric conductivity of ZnO changes depending on how impurities are distributed in the matrix; however, this fact contrarily means that the electric properties can be governed by controlling the distribution nature of impurities [1]. It is therefore of great importance to investigate their physical states as in the matrix by obtaining atomic-level information on their residence sites as well as electronic states.

For the study of the electromagnetic field in the vicinity of dilute impurities incorporated in condensed matter, nuclear techniques with radioactive probes are very suited because of their high sensitivity. We thus applied, to our recent study on ZnO doped with In [2], the time-differential perturbed angular correlation (TDPAC) method with the $^{111}\text{Cd}$ probe formed in the disintegration of $^{111}\text{In}$. The TDPAC method is a nuclear spectroscopic technique, which provides local information in matter through hyperfine interactions between probe nuclei and the surrounding spins and charge distribution [3,4]. Applying this spectroscopy, we obtained the following unexpected results for 0.5 at. % In-doped ZnO [2]: (i) the probe ions occupy a single site (hereafter denominated Site A) with a distinct field from that in undoped ZnO (Site B) at almost the same high fraction ($\sim 87\%$), (ii) despite presumably enhanced carrier density brought about by the contribution from the 0.5 at. % In donors, Site A is less accessible to conduction electrons than Site B is, and (iii) these two different components at Sites A and B coexist in a more dilute 0.05 at. % In-doped sample at the total fraction of about 86%. The above observations (i) and (iii) signify the possibility of local associations of the impurity In ions, but the identification of Site A in the In-doped ZnO has not been attained yet.

For further investigation of the local sites at In ions, a comparative study of other group 13 elements functioning as donors in the group II-VI compound semiconductor should be a great help. From this point of view, we have examined local fields at the $^{111}\text{Cd}(\leftarrow ^{111}\text{In})$ probe introduced in Ga-doped ZnO. The present paper discusses the charge distribution in the vicinity of the probe in comparison with the results obtained for ZnO samples doped with In and Al [2,5].

2. Experiment

For the synthesis of 0.5 at. % Ga-doped ZnO, we followed the same procedure taken in the previous work for the 0.5 at. % In-doped ZnO [2]. Stoichiometric amount of Ga(NO$_3$)$_3$·xH$_2$O ($x \sim 9$) of a purity of 99.9% was dissolved in ethanol, and then ZnO powder (99.999%) was added in the solution. The suspension was heated to dryness while stirred on a magnetic stirrer. The uniformly mixed powder was then pressed into a disk, and it was sintered on a platinum plate in air at 1273 K for 3 h.

The powder X-ray diffraction pattern of the synthesized sample is shown in Fig. 1, together with those for undoped, 0.5 at. % Al- and In-doped ZnO samples for comparison. For all the samples, the lattice constants remained unchanged after the doping and new phases that possibly arise from the dopants were not at all detected within the present detection precision.

Commercially available $^{111}\text{In}$ HCl solution was added in droplets onto the sintered disk. After the disk was dried
up by heat, it again underwent heat treatment in air at 1373 K for 2 h. The disk sample was then ground into power, and sealed in a quartz tube in vacuum. TDPAC measurements were performed at room temperature for the probe $^{111}\text{Cd}(\leftarrow ^{111}\text{In})$ on the cascade $\gamma$ rays, $G_{22}(t)$ the time-differential perturbation factor as a function of the time interval, $t$, between the cascade $\gamma$-ray emissions, and $N(\theta, t)$ the number of the delayed coincidence events observed at an angle, $\theta$. For the $\gamma$-ray detection, BaF$_2$ scintillation detectors were adopted due to their excellent time resolution.

3. Results and data analysis

The TDPAC spectrum of $^{111}\text{Cd}(\leftarrow ^{111}\text{In})$ introduced in the 0.5 at. % Ga-doped ZnO is shown in Fig. 2(a), and that for the 0.5 at. % In-doped ZnO is cited in Fig. 2(b) as a comparative reference from our previous work [2]. One can obviously see an oscillatory structure with fast damping in the spectrum in Fig. 2(a). Because this oscillatory structure is analogous to those obtained for the In-doped ZnO sample, we attributed it to the so-called “aftereffect” typically accompanying the electron capture decay of $^{111}\text{In}$ [3, 7, 8]. As is the case for the In-doped sample, accordingly, the TDPAC spectrum for the present Ga-doped ZnO was fitted with the following equation for the time-differential perturbation factor, $G_{22}(t)$ [9]:

$$ G_{22}(t) = G_{22}^{\text{stat}}(t) G_{22}^{\text{damp}}(t). $$

Here, $G_{22}^{\text{damp}}(t)$ represents the dynamic perturbation part for the damping effect on the static perturbation $G_{22}^{\text{stat}}(t).$ The
Recognizing this proposition, the large difference in the magnitude of the EFG produced at the $^{111}$Cd($\rightarrow^{111}$In) nucleus between the undoped and In- or Ga-doped sample is explained by assuming local associations of In/Ga ion(s) around the $^{111}$Cd($\rightarrow^{111}$In) probe. Taking into consideration that $^{111}$In$^{3+}$ can substitute for lattice Zn$^{2+}$ as discussed above, one can reasonably expect Ga$^{3+}$ to reside at the identical lattice site as well on account of its ionic radius, which is close to that of Zn$^{2+}$, and of the same stable charge state (III) as In$^{3+}$. The 0.5 at. % doped In$^{3+}$/Ga$^{3+}$ as substituent ion(s) should hence be adjacent to the probe, producing the large EFG values.

Relating to the EFG produced at the probe, the fraction, $f$, and the relative width, $\delta$, could also be important clues to the determination of the local structure in the vicinity of the probe. The large values of $f$ for both of the In-/Ga-doped ZnO clearly suggest that the attractive force between the probe and the associating In/Ga ion(s) is considerably strong; namely, the probe and the doped ion(s) likely form some defined structure on local scale. In addition, the relative widths, $\delta$, of the EFGs listed in Table 1 have large difference between In- and Ga-doped samples. Specifically, the charge distribution surrounding the probe in the In-doped sample is more fixed compared with those for the Ga-doped. If the distribution of the EFG originates in the main from other co-doped impurity ions (In or Ga), it would be suggested that In ions are easily associated together leading

![Graph](image.png)

**Table 1.** Parameter values obtained by least-squares fits on the TDPAC spectra of $^{111}$Cd($\rightarrow^{111}$In) embedded in 0.5 at. % Ga-, In-, and Al-doped ZnO, and in undoped ZnO.

| Dopant | $|V_{zz}|$ (10$^3$ V/m$^2$) | $\delta$ (%) | $f$ (%) | $\eta$ |
|--------|-----------------|-------------|--------|-------|
| Ga     | 11(2)           | 8.6(6)      | 85(1)  | 0.20(3)|
| In     | 6.1(9)          | 0.9(8)      | 87(1)  | 0.10(3)|
| Al     | 8.6(14)         | 34(4)       | 97(3)  | 0.55(3)|
| undoped| 1.7(3)          | 0           | 86(1)  | 0     |
to the formation of a well-defined local structure compared with the case of Ga.

As for the Al-doped ZnO, the $\delta$ value is much greater than those for In- and Ga-doped samples as indicated in Table 1. This wide distribution is possibly due to high concentration of Al ions. Expecting a spectral difference such as that observed for a more dilute 0.05 at. % compared with 0.5 at. % In-doped ZnO [2], therefore, a TDPAC measurement was also performed for 0.05 at. % Al-doped ZnO sample synthesized in the same way as above described. Fig. 3 shows a TDPAC spectrum obtained for the sample at room temperature together with that for 0.5 at. % Al-doped [5]. Contrary to the expectation, there is little difference between the samples doped with Al of the different concentrations. We found from these observations that the doped Al$^{3+}$ ions diversely distribute around the probe at least under the present experimental condition [13].

5. Conclusions

The local field at the $^{111}$Cd($\rightarrow^{111}$In) probe nucleus introduced in 0.5 at. % Ga-doped ZnO was investigated by the TDPAC method. As observed for 0.5 at. % In-doped ZnO, the spectrum suggests that the doped Ga ions as well as the probe reside at the substitutional Zn site and they are locally associated in the vicinity of the probe, reflecting strong attractive force with the probe. However, the relative width of the magnitude of the EFG unequivocally shows that the doped Ga ion(s) adjacent to the probe is/are diversely distributed compared with the In ions. This trend is more pronounced for 0.5 and even 0.05 at. % Al-doped ZnO. For more specific information on the probe site in the doped ZnO, calculation by the density functional theory is now under progress.

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13. For the origin of the fast damping in the spectra of Al-doped ZnO, we should take into consideration the effect of a presumed local spin provided by the donor impurities. Assuming a local field produced by a spin, we have thus attempted to fit the data; however, every attempt has not been successful yet. This failure may be reasonable because paramagnetic spin fluctuation is too fast for the probe nucleus to feel the field produced by the spin(s).