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Objective and Participating Research Subjects

The main objectives of this project research are the investigation of the nuclear structure of unstable neutron-rich nuclei and also the local properties of matters using short-lived nuclei.

This period is the last year of the project. Unfortunately, as in the previous two periods, no experiments in all five-research subjects of the project (28P4) were executed owing to the suspension of the reactor operation. Here, we present two reports showing results which were obtained in previous periods:

- Report 1. Site-to-Site Migration of In Impurity in Fe_3O_4
Report 2. Atmospheric Dependence of Formation Process of Oxygen Vacancy in Zinc Oxide

Main Points Described in the Reports in the Following Two Pages

The two reports are concerned with the behavior of indium impurities (about 100 ppt) in metal oxides, Fe_3O_4 and 100-ppm Al doped ZnO. Impurities (not limited to indium) in these oxides may modify their intrinsic properties to be functional materials. They obtained information on the behavior of indium impurities by measuring hyperfine fields (specifically, electric field gradients) at ^{111}Cd arising from ^{111}In via electron capture. The experimental technique used to measure the hyperfine fields are in common: γ - γ -rays time-differential perturbed-angular-correlation (TDPAC) technique.

The main point of Report 1 is that indium ions occupying the *A* sites (tetrahedral sites) of Fe_3O_4 at room temperature migrate to the *B* sites (octahedral sites) at a high temperature with a certain probability.

The main point of Report 2 is that indium ions forming aggregates with Al in ZnO at room temperature migrate to the defect-free Zn sites at a high temperature in argon gas atmosphere with an activation energy, which is related to the formation of oxygen vacancy.

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INTRODUCTION: Magnetite (Fe₃O₄) is one of the most promising iron compounds applicable to spintronic devices due to its excellent electric conductivity and magnetic property. In addition to the intriguing nature of pure Fe₃O₄, it is well known that impurity-doped Fe₃O₄ exhibits different physical properties, which allows us to control and optimize the properties for wider application of the doped oxide.

In this respect, our interest was directed to thermal stability and behavior of nonmagnetic indium ions (In³⁺) in Fe₃O₄. Although the residential site of In ions have still been controversial [1, 2], our recent experiment by means of the time-differential perturbed angular correlation (TDPAC) technique revealed that radioactive ¹¹¹In ions exclusively occupy the substitutional *A* sites at room temperature [3]. In addition to the information, in this report, we show an evidence for thermal behavior of impurity In ions, which migrate into the *B* site at around the Curie temperature ($T_C = 858$ K).

EXPERIMENTS: Commercially available ¹¹¹In HCl solution was added in droplets onto a disk of polycrystalline Fe₃O₄. It then underwent heat treatment in a vacuum quartz tube at 1373 K for 3 h for the diffusion of the radioisotope. TDPAC measurements of the ¹¹¹Cd(¹¹¹In) probe were performed for the synthesized samples at various temperatures.

RESULTS: The TDPAC spectra of ¹¹¹Cd(¹¹¹In) embedded in Fe₃O₄ are shown in Fig. 1. The spectral pattern obtained above T_C drastically changes due to magnetic transition from ferrimagnetism to paramagnetism. For the measurement above T_C , the spectrum in Fig. 1(a) can be analyzed assuming only electric quadrupole interaction between the probe nucleus and the extranuclear charge distribution. The spectral analysis provided the value of the nuclear quadrupole frequency $\nu_Q = 7.04(4)$ Mrad s⁻¹ at 900 K. Here, one should note the fact that the oscillatory structure in Fig. 1(a) is on a plateau-like high base line, which is ascribable to majority ¹¹¹In ions residing in the *A* site in cubic symmetry. For the spectra obtained below T_C shown in Figs. 1(b) and 1(c), on the other hand, typical magnetic perturbation was observed. However, we notice a gradually damped structure in Fig. 1(b), and the

spectrum was reproduced with two components having slightly different Larmor frequencies ν_L . Because the probe site of the minor second component experiences an electric field gradient above T_C as stated above, the damped spectrum in Fig. 1(b) was fitted on the presumption that the second component is perturbed by a magnetic interaction combined with an electric quadrupole interaction, whereas the first component at the *A* site is perturbed only by a magnetic interaction. The values of the Larmor frequencies optimized by the fit are $\nu_{LA} = 74.99(1)$ and $\nu_{LB} = 70.30(1)$ Mrad s⁻¹ for the first and second components, respectively. Because their ratio $\nu_{LA}/\nu_{LB} = 1.067$ is in excellent agreement with that of the hyperfine fields at Fe nuclei occupying the *A* and *B* sites $H_A/H_B = 1.068$, revealed by Mössbauer spectroscopy [4], this observation undoubtedly suggests that the second component having appeared at the high temperature is assignable to ¹¹¹In at the *B* site. The present observation demonstrates that the site-to-site migration of In takes place at around the magnetic transition; this phenomenon implies that doped Fe₃O₄ is a promising material that realizes charge transportation triggered by magnetic transition.

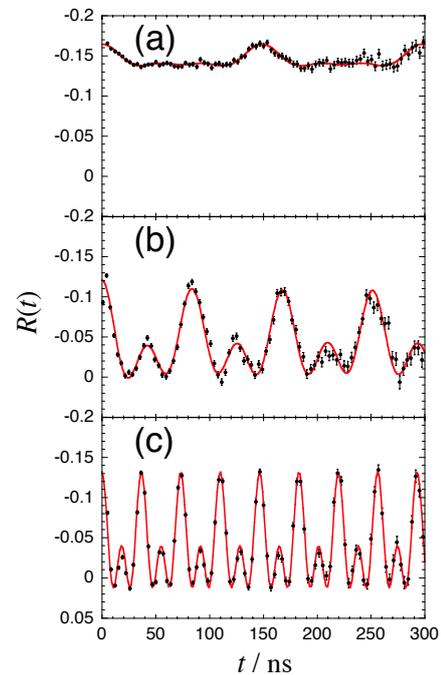


Fig. 1. TDPAC spectra of ¹¹¹Cd(¹¹¹In) in Fe₃O₄ (a) at 900 K, (b) at 773 K, and (c) at R. T.

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PR4-2 Atmosphere Dependence of Formation Process of Oxygen Vacancy in Zinc Oxide

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INTRODUCTION: Defect-induced properties of zinc oxide (ZnO) have been attracting much attention toward their application to functional materials in a wide field of industry. Especially, physical properties brought about by Al ions and/or oxygen vacancies in ZnO are one of the most intriguing topics for the development of future electronic devices. For a practical use of Al-doped ZnO device, therefore, we have investigated the local structures in Al-doped ZnO under various ambient conditions by means of the time-differential perturbed angular correlation (TDPAC) method. In one of our previous TDPAC studies, we observed contrasting atmosphere dependence of the stability of aggregations of ¹¹¹In and Al impurities doped in 100 ppm Al-doped ZnO: (i) Al and In impurities associate with each other by their thermal diffusion in air, and (ii) the ¹¹¹In probe is detrapped from the Al aggregations in high-temperature vacuum, resulting in substitution at defect-free Zn sites [1,2]. Detailed investigation of the thermal behavior of the impurities has revealed that the dissociation reaction is triggered by the formation of oxygen vacancies. Furthermore, the formation energy of oxygen vacancy in vacuum was evaluated from the temperature variation of the rate constants estimated from the annealing time dependence of the TDPAC spectra [3]. In the present work, based on the further investigation of TDPAC spectra for Al-doped ZnO obtained by isochronal annealings in Ar gas atmosphere, we examine the atmosphere dependence of the formation process of oxygen vacancy.

EXPERIMENTS: For the synthesis of 100 ppm Al-doped ZnO, stoichiometric amounts of Al(NO₃)₃ · 9H₂O and ZnO powder were mixed in ethanol. The suspension was heated to evaporate the ethanol until dryness. The powders were pressed into disks and sintered in air at 1273 K for 3 h. Commercially available ¹¹¹In HCl solution was added in droplets onto the sintered disks. The initial concentration of ¹¹¹In ions in the sample was typically ~100 ppt. After the disks were dried up by heat, they again underwent heat treatment in air at 1373 K for 2 h. Following the doping of ¹¹¹In, each disk was separately sealed in different quartz tubes in Ar gas atmosphere, and 24-h isochronal annealing was performed one by one at different temperatures (873~1148 K). The TDPAC measurements were carried out for the 171-245 keV cascade γ rays of the ¹¹¹Cd(\leftarrow ¹¹¹In) probe with the intermediate state of $I = 5/2$ having a half-life of 85.0 ns.

RESULTS: It was found from the TDPAC spectra of the ¹¹¹In(\rightarrow ¹¹¹Cd) in 100 ppm Al-doped ZnO heat-treated at various temperatures that ¹¹¹In probes are detrapped from the Al aggregations during the annealing in Ar gas by degrees. It was revealed that this detrapping process is controlled by the first-order rate law. For the first-order reaction of the dissociation process, we obtained the rate constant k at different temperatures. Figure 1 shows the temperature variation of k values. A least-squares fit to the k values was then carried out with the following Arrhenius equation:

$$k = \nu_0 \exp(-E_a / k_B T)$$

and the activation energy, E_a , was evaluated to be 2.05 (15) eV. Because the dissociation process of the ¹¹¹In probe and Al would be induced by the formation of oxygen vacancies, we suggest that the observed E_a is closely related to the formation energy of oxygen vacancies in Al-doped ZnO sample[3]. This E_a value is larger than that obtained in vacuum (0.72(6) eV[3]). This atmosphere dependence of the formation energy of oxygen vacancies is now under consideration.

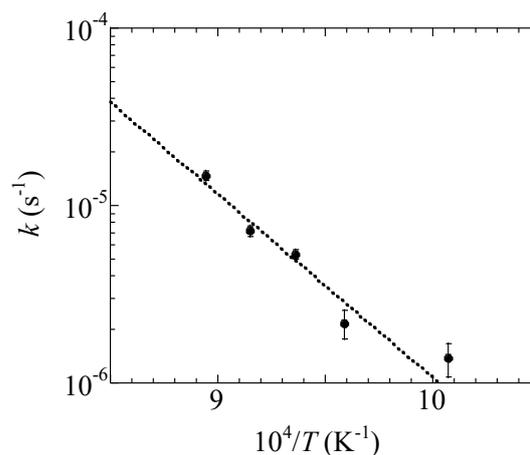


Fig. 1. Temperature dependence of the rate constant, k . An Arrhenius equation was used for the fit.

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