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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 second year of the project. Unfortunately, as in the last period, no experiments in all five research subjects of the project (27P6) were executed owing to the suspension of the reactor operation. Here, we report some results which were obtained in previous periods and have already been published in journals or submitted for publication.

The reports presented here are as follows:

Report 1. Thermal Stability of Impurities Ba and La at the Substitutional Sites in Fe

Report 2. Thermal Stability of Cd and In Impurities in Fe₃O₄

Report 3. Formation Process of Oxygen Vacancy in Zinc Oxide

Main Points Described in the Reports in the Following Three Pages

The experimental techniques used to measure hyperfine fields are in common: γ - γ -rays time-differential perturbed-angular-correlation (TDPAC) technique. The nuclear probes and matters in which the probes are incorporated are (Report 1) ¹⁴⁰Ce arising from ¹⁴⁰Cs through ¹⁴⁰Ba and then ¹⁴⁰La (for short, ¹⁴⁰Ce(\leftarrow ¹⁴⁰La \leftarrow ¹⁴⁰Ba \leftarrow ¹⁴⁰Cs)) and Fe, (Report 2) ¹¹¹Cd(\leftarrow ¹¹¹In) and ¹¹¹Cd(\leftarrow ^{111m}Cd) and Fe₃O₄, and (Report 3) ¹¹¹Cd(\leftarrow ¹¹¹In) and 100 ppm Al-doped ZnO.

Report 1 describes thermal stability of Ba and La at the substitutional sites in Fe. Although neither Ba nor La atoms (also Ce atoms do not) form a solid solution with Fe (therefore, the only possible method for the incorporation of these atoms in Fe is ion implantation), which implies that these atoms bond with Fe atoms very weakly, these atoms at the substitutional sites do not move at temperatures at least as high as 673 K. This result was obtained in the condition that atomic vacancies produced in the ion implantation are hindered to move and bond with Ba or La. The pre-implanted He atoms play a role in keeping the atomic vacancies to stay.

The aims of implanting ¹⁴⁰Cs in Fe using the KUR-ISOL (Isotope Separator On-Line) were the following two things: the first thing is to measure the nuclear magnetic moment of the first 4⁺ excited state of ¹⁴⁰Ce having a neutron magic number and to compare it with the nuclear theory. The second thing is to study the state of impurities He and Ce in Fe experimentally. This knowledge is

important in materials science related to nuclear fusion reactor materials. The results are already reported in journals.

Report 2 describes the locations of Cd and In impurities in magnetite, Fe₃O₄, and their thermal stability, the details of which will be published in a journal.

About three decades ago, magnetic hyperfine field at ¹¹¹Cd(\leftarrow ¹¹¹In) chemically doped in Fe₃O₄ was measured to study the supertransferred magnetic field from the magnetic (Fe) ions via the oxygen ions to the nonmagnetic (Cd) ions. The location of In was assigned to the tetrahedral (A) site. However, quite recently, a paper was published stating that the location of In was the octahedral (B) site. W. Sato *et al.* succeeded in obtaining TDPAC spectra with damping free for the first time, concluded that the location of In is the A site, and moreover obtained a signal indicating that at high temperatures some In ions in the A sites move to the B sites, which is consistent with a density functional theory calculation.

Report 3 describes an experimental method to obtain the formation energy of oxygen vacancy in ZnO, which is an important physical quantity because oxygen vacancies can bring about, for example, ferromagnetism in ZnO. S. Komatsuda *et al.* obtained the temperature dependence of the rate constant for ¹¹¹In migration in high-temperature vacuum from Al aggregations in 100 ppm Al-doped ZnO to the substitutional defect-free Zn sites. Considering the migration of ¹¹¹In as being induced by the formation of oxygen vacancies, they obtained 0.72(6) eV as the formation energy of oxygen vacancy, which is consistent with theoretical calculations.

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INTRODUCTION: Previously, we projected 100-keV ¹⁴⁰Cs ions into Fe foils at KUR-ISOL and observed, using the time-differential perturbed angular correlation (TDPAC) technique on the 2083-keV state of ¹⁴⁰Ce, that about 35% of ¹⁴⁰Ce arising from the β^- decay of ¹⁴⁰Cs through ¹⁴⁰Ba and then ¹⁴⁰La occupy the substitutional sites with no lattice defects nearby [1, 2]. The half-lives of ¹⁴⁰Cs, ¹⁴⁰Ba and ¹⁴⁰La are 63.7 s, 12.8 d and 40.3 h, respectively. About a week after the end of the ¹⁴⁰Cs bombardments, when the TDPAC measurements were started, all ¹⁴⁰Cs had decayed out and the number ratio of ¹⁴⁰Ba to ¹⁴⁰La was constant, 0.85, calculated from the values of their half-lives. We think that those ¹⁴⁰Ba and ¹⁴⁰La leading to ¹⁴⁰Ce located at the substitutional sites also occupy the same substitutional sites. Since neither Ba nor La atoms (also Ce atoms do not) form a solid solution with Fe, it might be expected that they easily move into different places with increasing temperature and are finally segregated. This time, we report on the thermal stability of impurities Ba and La at the substitutional sites.

EXPERIMENTS: Two Fe samples were prepared: one is Fe irradiated with 100-keV ¹⁴⁰Cs⁺ at KUR-ISOL and the other is Fe irradiated with 4-keV He⁺ using an ion beam gun and subsequently with 100-keV ¹⁴⁰Cs⁺. We name the first sample ¹⁴⁰CeFe and the second ¹⁴⁰CeHe-doped Fe. For these two samples, 0.5-h annealing in vacuum was performed at a same time in a same furnace at 473, 673, 773, 873, 973 and 1073 K in this order. Before and after each annealing, room-temperature TDPAC spectra of ¹⁴⁰Ce were obtained with two measurement systems, each consisting of standard fast-slow electronic modules and four BaF₂ scintillation detectors. The relevant cascade γ rays are the 329–487-keV ones and the angles between the cascade γ rays are 90° and 180°.

RESULTS: Fig. 1(a) and 1(b) show the TDPAC spectra for ¹⁴⁰CeFe and ¹⁴⁰CeHe-doped Fe, respectively. The oscillation pattern seen in some of the spectra is due to a unique static magnetic hyperfine interaction at ¹⁴⁰Ce occupying the Fe substitutional site with no lattice defects nearby [1]. Hereafter, we call these ¹⁴⁰Ce "good" ¹⁴⁰Ce. From the oscillation amplitude, "good" ¹⁴⁰Ce are about 30% and 40% of the implanted ¹⁴⁰Ce, respectively, for unannealed ¹⁴⁰CeFe and ¹⁴⁰CeHe-doped Fe ("35%" in INTRODUCTION is the average of these two values). We now look at Fig. 1(a) downwards. The oscillation amplitude gets reduced by about 20% at the annealing temperature of 473 K and about 50% at 673 K. At the annealing temperature of 773 K, there is no noticeable oscillation component, i.e., there is no "good" ¹⁴⁰Ce in

¹⁴⁰CeFe. We may consider that with increasing annealing temperature, parent atoms (Ba and La) at the substitutional sites move into different places producing various hyperfine fields at the ¹⁴⁰Ce, and/or that with increasing temperature, atomic vacancies migrate and bond to still parent atoms of "good" ¹⁴⁰Ce, producing various hyperfine fields at the ¹⁴⁰Ce. As explained below, the latter explanation is adequate at least below a certain temperature (we call it T_b) between 673 and 773 K.

Fig. 1(b) shows that all "good" ¹⁴⁰Ce remain "good" in ¹⁴⁰CeHe-doped Fe until at 673 K and about 60% of them do not at 773 K. This observation means that parent atoms (Ba and La) at the substitutional sites do not move at least below T_b . We think that the pre-deposited He atoms form He–vacancy clusters with vacancies mainly produced in the He and ¹⁴⁰Cs bombardments and that at annealing temperatures higher than T_b , He and vacancies are released from those clusters, migrate and bond to parent atoms of "good" ¹⁴⁰Ce. This interpretation is consistent with relevant results of a thermal helium desorption spectroscopy experiment (ref. 6 in [2]).

A closer look at Fig. 1(b) shows that the oscillation amplitude increases with annealing temperature up to 673 K: at 673 K it is larger than by about 18% that before annealing. We need to examine this point by carrying out additional experiments with various doses of He, which may also elucidate the reason for the difference in the abundance of "good" ¹⁴⁰Ce between the two samples before annealing.

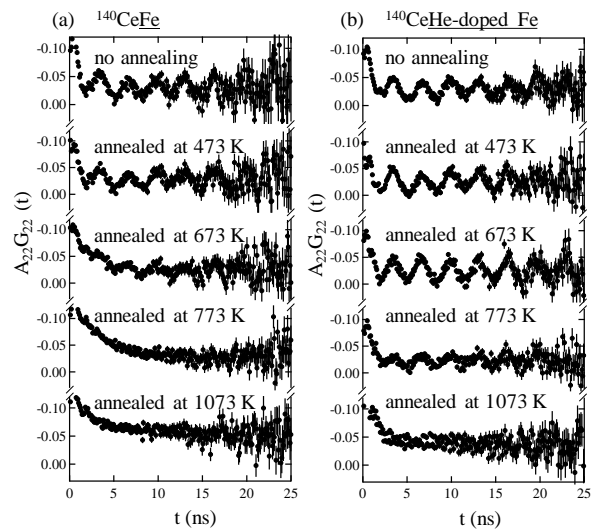


Fig. 1. Room-temperature TDPAC spectra for (a) ¹⁴⁰CeFe and (b) ¹⁴⁰CeHe-doped Fe, subjected to no annealing, 0.5-h annealing in vacuum at 473, 673, 773 and 1073 K (after annealed at 873 and 973 K).

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INTRODUCTION: Magnetite (Fe₃O₄) is one of the most promising magnetic compounds applicable to spintronic devices due to its excellent electric conductivity and magnetic property. In addition to the intriguing nature of pure Fe₃O₄, it has been demonstrated that the physical properties of the oxide vary with the introduction of impurity ions, which allows us to expect wider application of the doped oxide.

In this respect, our interest was directed to functions of nonmagnetic indium ions (In³⁺) in Fe₃O₄. The hyperfine fields at the impurity site have been reported in many papers in the past three decades; however, there is still a controversy even over their residential sites [1-3]. It is thus of importance for a basic study of solid-state physics of the compound to clarify the site(s) occupied by the impurity In ions.

In the present work, we succeeded in the preparation of ¹¹¹In-doped Fe₃O₄ exhibiting perturbed angular correlation (PAC) spectra with distribution-free Larmor frequencies composed of a unique component, and the impurity In site was unequivocally determined by a comparative study with the assistance of a different PAC probe ¹¹¹Cd (\leftarrow ^{111m}Cd). In addition to the site information, we successfully detected thermal behavior of In ions at high temperature. The element-dependent thermal stabilities observed for Cd and In are discussed.

EXPERIMENTS: About 3 mg of cadmium oxide (CdO) enriched with ¹¹⁰Cd was irradiated with thermal neutrons at Kyoto University Reactor to produce ^{111m}Cd. The neutron-irradiated CdO powder was then added into Fe₃O₄ powder and the homogenized mixture in the form of a disk was sintered at 1173 K for 45 min.

Commercially available ¹¹¹In HCl solution was added in droplets onto a disk of 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 (\leftarrow ^{111m}Cd) and ¹¹¹Cd (\leftarrow ¹¹¹In) probes were performed for the synthesized samples at various temperatures.

RESULTS: The TDPAC spectra of ^{111m}Cd (\rightarrow ¹¹¹Cd) and ¹¹¹Cd (\leftarrow ¹¹¹In) embedded in Fe₃O₄ are shown in Fig. 1. The Larmor frequencies ω_L observed for both probes at room temperature show good agreement with each other,

signifying that both probes reside in the same site. At high temperature above T_C , however, contrastive patterns appear in their spectra. For the ^{111m}Cd probe, the directional anisotropy is unperturbed during the time of the present observation. This observation clearly shows that the probe nucleus is surrounded by a charge distribution of cubic symmetry; that is, ^{111m}Cd ions initially occupy the tetrahedral *A* site. This is also true of the ¹¹¹In ions because of the same ω_L values at R. T. However, the different observation for the different probes at high temperature implies that the ¹¹¹In ions migrate into another site. The spectrum in Fig. 1(c) was well fitted assuming two different components: the major component is unperturbed and the minority has an axially symmetric electric field gradient. Detailed investigation of the temperature dependence of PAC spectra revealed that the minor component corresponds to the probes at the substitutional *B* site [4]. In addition, DFT calculations suggest that the thermal stability of In ions are lower at the *A* site than that of Cd [4]. From these observations, we conclude that Cd ions are stabilized in the *A* site at least in the present temperature range, while In ions at the *A* site jump out of the potential at high temperature to move into the *B* site. We believe that the thermally activated displacement of In ions could be an important clue to materials design for impurity-doped magnetite.

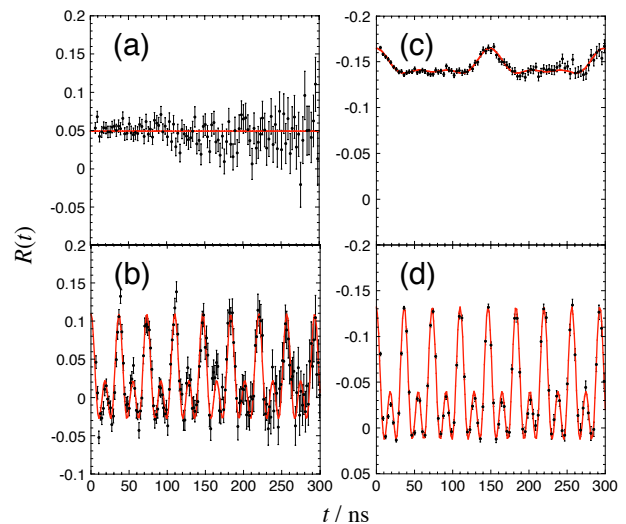


Fig. 1. PAC spectra (a) of ¹¹¹Cd (\leftarrow ^{111m}Cd) at 873 K, (b) of ¹¹¹Cd (\leftarrow ^{111m}Cd) at R. T., (c) of ¹¹¹Cd (\leftarrow ¹¹¹In) at 900 K, and (d) of ¹¹¹Cd (\leftarrow ¹¹¹In) at R. T.

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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. Extrinsic-semiconductor devices such as of Al-doped ZnO are expected to be in use under various ambient conditions; the states of being of impurity ions in the matrix are susceptible to change depending on the condition. 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. In the present work, in order to extend quantitative discussion on the kinetics of the formation process of oxygen vacancy, we evaluated the formation energy of oxygen vacancy from the temperature variation of the detrapping process during heat treatment in vacuum [3].

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 doped 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 vacuum, 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 come to detrapp from the Al aggregations in high-temperature vacuum 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. Their temperature variation is plotted in Fig. 1. 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 0.72 (6) eV. Because the dissociation process of the ¹¹¹In probe and Al would be induced by the formation of oxygen vacancies as discussed above, we suggest that the observed E_a is closely related to the formation energy of oxygen vacancies in Al-doped ZnO sample. This interpretation is supported by the fact that the present E_a value shows good agreement with the theoretical ones calculated for the formation energy of oxygen vacancies in ZnO (0.8 and 1.0 eV)[4,5].

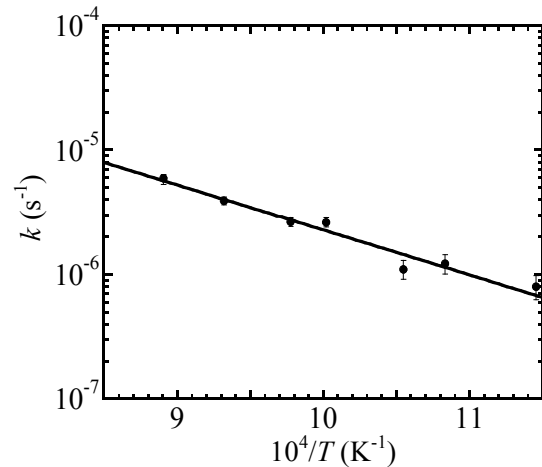


Fig. 1. Temperature dependence of the rate constant, k . An Arrhenius equation was used for the fit.

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