Local Magnetic Field of a Perovskite Manganite La$_{0.7}$Ca$_{0.3}$MnO$_3$

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The time-differential perturbed angular correlation method with the ^{140}Ce probe was applied to a microscopic investigation on a perovskite manganite, La$_{0.7}$Ca$_{0.3}$MnO$_3$. A drastic change was observed in the time evolution of the directional anisotropies around the Curie temperature ($T_c \sim$ 245 K), reflecting the paramagnetic-ferromagnetic phase transition. The internal magnetic field at the probe nucleus stabilized at the *A* site was estimated to be $B_{int} =$ 6.9 ± 0.3 T at 240 K, whereas no appreciable magnetic field was observed at 260 K. From a comparative study using two different probe-introduction methods, in addition, we found that ascendant ions of the probe, ^{140}Ba and ^{140}La, can be located at the *A* site by heat treatment.

1. Introduction

Perovskite manganese oxides (*A*MnO$_3$) are known to exhibit the effect of colossal magnetoresistance (CMR), a phenomenon that electrical resistivity undergoes a drastic change as large as five to six orders of magnitude by an applied magnetic field.[1] Because of this unique physical property expected for wide application, much attention has been given to these oxides since the first discovery of this phenomenon.[2] In general, the CMR mechanism is associated with the notion of double exchange interaction arising from the Mn-Mn electronic hopping.[3] However, discussion on the mechanism is, in most cases, based on macroscopic quantities such as resistivity and magnetization, and there still remain discrepancies between those experimental results and theory.[4] For better understanding of the mechanism, it is necessary to provide insight into the intriguing property by different approaches as well.

From this point of view, our interest was directed to the atomic-level observation of what is happening at lattice sites of manganite compounds by means of the time-differential perturbed angular correlation (TDPAC) technique. The TDPAC method is a nuclear spectroscopy that provides microscopic information on local fields in matter through hyperfine interactions between probe nuclei and the surrounding spins and charge distribution.[5] By observing the time-evolving directional anisotropy of cascade γ rays, we can obtain direct information on the extranuclear field. With recent development of the radiation detection technique, this method has been widely applied to researches of condensed matter physics as well as nuclear physics.[6] Because of high sensitivity of this spectroscopy, we can expect to obtain unique information that is not available from the bulk measurements.

In the present work, we chose a perovskite La$_{0.7}$Ca$_{0.3}$MnO$_3$ as the sample, which exhibits the CMR effect by the paramagnetic-ferromagnetic phase transition ($T_c \sim$ 245 K). It is reported that the CMR effect is strongly related with the ordering of the *A*-site ions in some type of perovskite manganites;[7,8] in that sense, it is important to examine the hyperfine field acting at the *A*-site ions. We thus employed the ^{140}Ce as the probe for the present TDPAC measurements because their ascendants ^{140}La and ^{140}Ba, which are initially introduced in the sample,

are expected to substitute for the intrinsic *A*-site ions, La^{3+} and Ca^{2+}. In the present work, two different probe introduction methods were tested for the evaluation of the influences of those methods on the lattice structure. Preliminary results are presented here on the emergence of a hyperfine magnetic field at their residence sites by showing the drastic change of the time evolutions of the directional anisotropies at temperatures above and below T_c.

2. Experiments

2.1. Sample preparation and characterization. Powder La$_{0.7}$Ca$_{0.3}$MnO$_3$ was synthesized by a conventional solid-state reaction in air.[9,10] Stoichiometric amounts of starting powder materials (MnO$_2$, La$_2$O$_3$, and CaCO$_3$) were thoroughly mixed in a mortar. The powder mixture was calcined on a platinum plate at 1273 K for 12 h. After cooling down to room temperature, the sample was again ground to uniformity, and it was then pressed into a disc. Finally, the disc was sintered on the platinum plate at 1473 K for 96 h. A powder X-ray diffraction and magnetization measurements showed that the sample was of a single phase, reproducing reports in literature on analogous perovskites.[9,11]

2.2. Probe introduction and TDPAC measurements. We adopted neutron irradiation as a method of the production of the ^{140}Ce probe. Powder La$_{0.7}$Ca$_{0.3}$MnO$_3$ of 20 mg was sealed in a quartz tube evacuated. Neutron irradiation was performed for the sealed sample in a pneumatic tube at Kyoto University Reactor (KUR) with a thermal neutron flux of 2.75×10^{13} cm^{-2} s^{-1} for 1 min. The parent of the probe was produced by the ^{139}La(n,γ)^{140}La reaction.

An ion-implantation method was tried as another way for the production and introduction of the ^{140}Ce probe, a descendant of a fission product ^{140}Cs. A disk of polycrystalline La$_{0.7}$Ca$_{0.3}$MnO$_3$ with a size of approximately 6 mm$\phi \times$ 1 mm was attached to the ion beam collector equipped at the isotope separator on-line installed at KUR (KUR-ISOL). The ion beam of ^{140}Cs was kept implanted in the La$_{0.7}$Ca$_{0.3}$MnO$_3$ sample at the total acceleration voltage of 100 kV. The number of the implanted ^{140}Cs atoms was estimated to be approximately 1.6×10^{11} in total. Schematic diagrams of the system of KUR-ISOL appear elsewhere,[12,13] and the irradiation condition is described in detail in our previous paper.[14] It was confirmed by a γ-ray spectrum of the implanted sample that the projectile was well isolated in the

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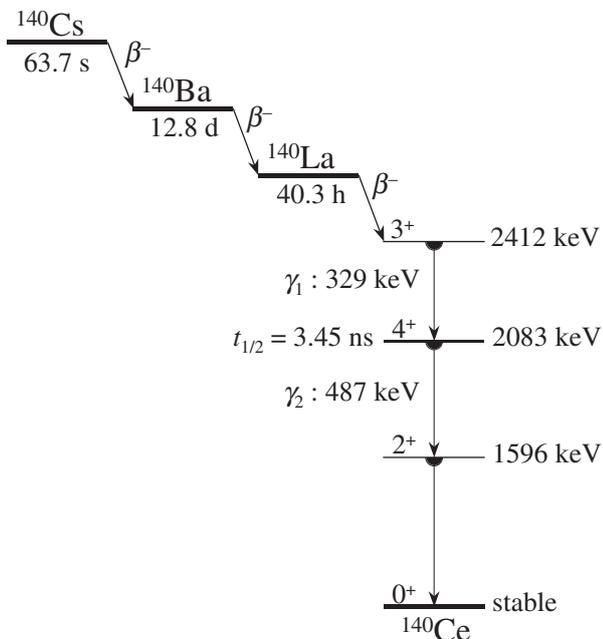
Figure 1. Simplified decay scheme of ^{140}Ce formed in the disintegration from ^{140}Cs.

Figure 2. TDPAC spectra of ^{140}Ce formed in a perovskite manganite La$_{0.7}$Ca$_{0.3}$MnO$_3$ by neutron irradiation. The measurements were performed at temperatures indicated. In (a) and (b) are shown those for the as-irradiated sample, and in (c) and (d) for the annealed one.

mass-separation process.[15]

   After the probe introduction by each method, TDPAC measurements were performed for the "as-irradiated" and "as-implanted" samples prepared by the neutron irradiation and the ^{140}Cs implantation, respectively, at temperatures around T_c for the probe ^{140}Ce on the 329–487 keV cascade γ rays with the intermediate state of $I^\pi = 4^+$ having a half-life of 3.45 ns. A simplified decay scheme of ^{140}Ce formed in the disintegration from ^{140}Cs is shown in Figure 1.[16] (Note that the disintegration starts from the parent nucleus ^{140}La for the probe production by the neutron irradiation.) In the present work, the directional anisotropy of the cascade γ rays was observed at $\pi/2$- and π-radian directions with a conventional four-detector system. BaF$_2$ scintillation detectors were adopted due to their excellent time resolution. The as-irradiated and as-implanted samples underwent heat treatment at 1473 K in air, and TDPAC measurements were again carried out on the same condition for the investigation of the annealing effect.

3. Results and Discussion

   3.1. Electromagnetic field at the La sites. Figure 2 shows the TDPAC spectra obtained at around T_c for the sample prepared by the neutron irradiation: on the left are those for the as-irradiated sample and on the right for the annealed one. The directional anisotropy on the ordinate, $A_{22}G_{22}(t)$, was deduced with the following simple operation:

$$A_{22}G_{22}(t) = \frac{2[N(\pi,t) - N(\pi/2,t)]}{N(\pi,t) + 2N(\pi/2,t)}. \tag{1}$$

Here, A_{22} denotes the angular correlation coefficient, $G_{22}(t)$ the time-differential perturbation factor as a function of the time interval, t, between the relevant cascade γ-ray emissions, and $N(\theta,t)$ the number of the coincident events observed at an angle, θ.

   One can see the effect of the heat treatment for the spectra observed at 240 K. The neutron irradiation in a reactor is considered to cause damages to the crystal structure by the so-called radiation effect and/or hot atom effect. The slightly damped structure of the 240 K spectra for the as-irradiated sample suggests that the surroundings of the probe nuclei were
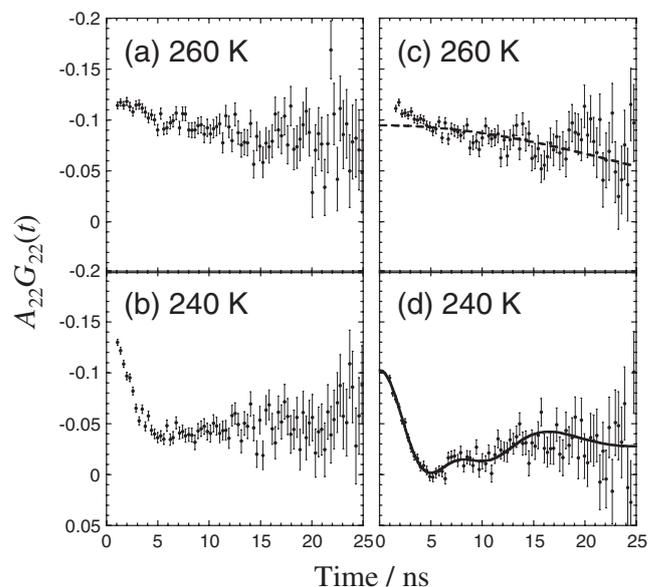
damaged by radiation. The spectral change evidently shows that the lattice structure was, to some extent, recovered by the annealing. Because the spectra for the annealed sample should reflect the original structure of La$_{0.7}$Ca$_{0.3}$MnO$_3$ better, we discuss them below rather than those for the as-irradiated sample.

   There are obvious distinctions in the time evolution between the spectra at temperatures above and below T_c, which reflects the paramagnetic-ferromagnetic phase transition. Reproducibility of the spectra was confirmed by repeated measurements changing temperature up and down. In the paramagnetic state, it is generally considered that an electric field gradient (EFG) arising from the ambient charge distribution is the only factor perturbing the probe nucleus. Accordingly, the slow attenuation of the directional anisotropy observed in the spectra at 260 K should be ascribed to a weak electric quadrupole interaction with the outer lattice. In the case of an axially symmetric EFG, the perturbation factor is expressed for the present case as

$$G_{22}^{\mathrm{EFG}}(t) = \frac{1}{1155}[331 + 10\cos(3\omega_Q t) + 81\cos(9\omega_Q t)$$
$$+ 180\cos(12\omega_Q t) + 175\cos(15\omega_Q t) + 196\cos(21\omega_Q t)$$
$$+ 126\cos(24\omega_Q t) + 56\cos(36\omega_Q t)], \tag{2}$$

where ω_Q represents the electric quadrupole frequency described by

$$\omega_Q = \frac{eQ|V_{zz}|}{4I(2I-1)\hbar}. \tag{3}$$

Here, Q (= 0.35 (7) b for the relevant case[16]) denotes the nuclear quadrupole moment of the intermediate state, V_{zz} the principal axis of the EFG, and I (= 4) the nuclear spin at the intermediate state of the cascade. However, a least-squares fit with the above perturbation function for an assumed single component does not reproduce well the 260 K spectrum as indicated by a broken line in Figure 2(c). Initial transition to the ferromagnetic phase may have been observed at this temperature, or the spectra may consist of ensemble of multiple components with
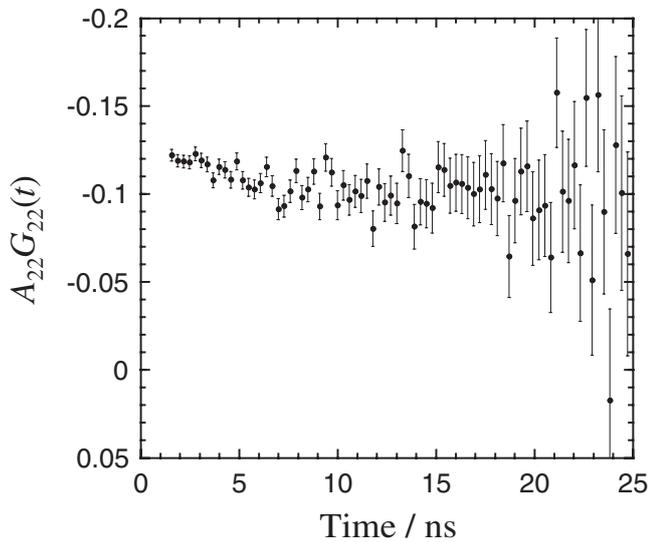
Figure 3. TDPAC spectra of ^{140}Ce formed in the disintegration from ^{140}Cs implanted in a perovskite manganite La$_{0.7}$Ca$_{0.3}$MnO$_3$. The measurement was performed for the as-implanted sample at 240 K.

widely ranged EFGs due to insufficient heat treatment. As for the 240 K spectrum, on the other hand, an oscillatory structure appears in the time evolution of the directional anisotropy, which can be assigned to the Larmor precession of the probe nucleus caused by a hyperfine magnetic interaction with the internal field in the ferromagnetic phase. When the probe nucleus is perturbed by an internal magnetic field, the time-differential perturbation factor is described as

$$G_{22}^{\mathrm{IMF}}(t) = \frac{1}{5}[1 + 2\cos(\omega_L t) + 2\cos(2\omega_L t)], \tag{4}$$

where ω_L is the Larmor frequency caused by the relevant hyperfine interaction. Regarding the oscillatory structure in Figure 2(d) as a perturbation by the magnetic interaction, a least-squares fitting was carried out with eq 4 for the principal component. Here, Gaussian distributions were assumed for the Larmor frequency in eq 4 as

$$G_{22}^{\mathrm{IMF}}(t) = \sum_i a_i \exp(-\frac{1}{2}\delta^2 \omega_{L_i}^2 t^2)\cos(\omega_{L_i} t). \tag{5}$$

The relative width δ in eq 5 is defined by $\delta = \sigma/\omega_{L_i}$, where σ is the width of the distribution of the Larmor frequency in each term. From the fit, the internal magnetic field acting at the site of the ^{140}Ce nucleus was estimated to be $B_{\mathrm{int}} = 6.9 \pm 0.3$ T at 240 K. It is to be noted that this is a preliminary result because perturbation by the EFG, which would be negligibly small compared with that by the magnetic field, was not taken into consideration for the present fitting. The evaluation of the magnitude is now underway in comparison with reports for other manganite in the ferromagnetic region.[8,17]

3.2. Residence sites of ^{140}Cs. In Figure 3 is shown the TDPAC spectrum measured at 240 K for the sample prepared by the ^{140}Cs implantation (as-implanted). For the samples without the heat treatment, one can see contrasting time evolutions between Figures 2(b) and 3 in spite of the identical sample probed by the same nuclei. It is obvious from these figures that the implanted Ce nucleus does not feel a distinct magnetic field below T_c as opposed to the one produced by the neutron irradiation. A conceivable cause for the little, if any, magnetic field at the probe site is the formation of lattice defects. Since the ^{140}Cs ions were kinetically introduced into the host La$_{0.7}$Ca$_{0.3}$MnO$_3$,
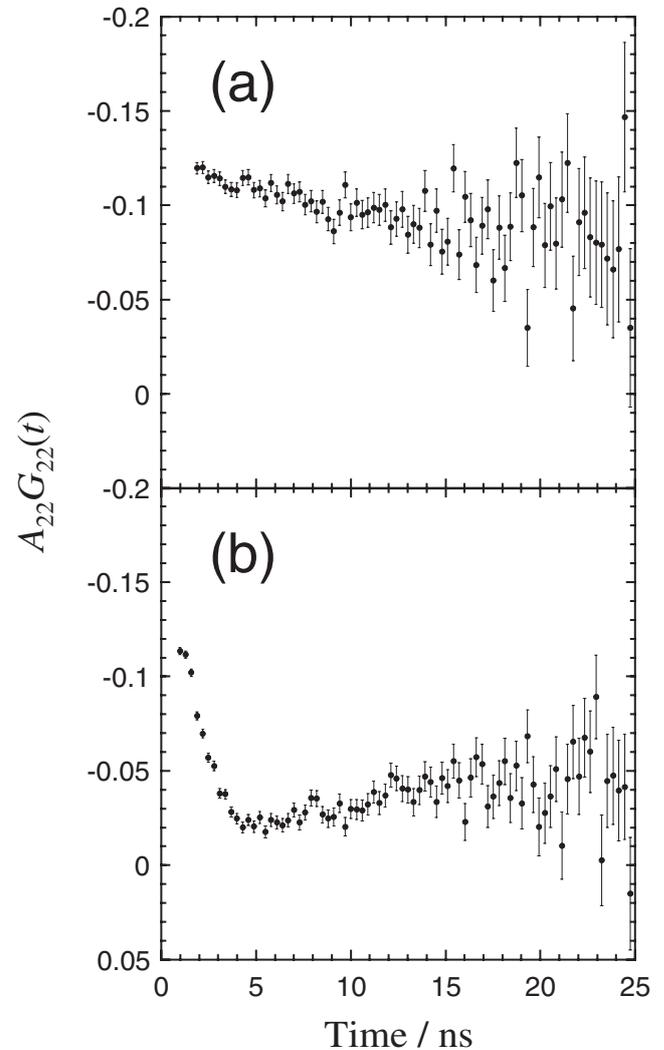
Figure 4. TDPAC spectra of ^{140}Ce formed in the disintegration from ^{140}Cs implanted in a perovskite manganite La$_{0.7}$Ca$_{0.3}$MnO$_3$. The measurements were performed for the annealed sample (a) at 260 K and (b) at 240 K.

the implantation process may have caused defects in the crystal. There are two possible types of defects in the present case: one is the irradiation damage in the crystal structure and the other the occupation of some interstitial sites by the incident ^{140}Cs ions. Because the Cs ions are introduced as univalent impurities in the system, they possibly occupy some interstitial sites rather than substitutional lattice. As a result, for the as-implanted sample, the descendant ^{140}Ce probes would remain at the initial sites, where total magnetic field transferred from Mn ions is not operative. The same is true of the case for the formation of the irradiation damage; the Cs ions could not be stabilized at the *A* sites in the as-implanted sample, meaning that the ^{140}Ce probe does not feel magnetic perturbation.

TDPAC spectra for the ^{140}Cs-implanted sample with the heat treatment are shown in Figure 4. We can see a drastic change in the directional anisotropy at 240 K, and the oscillating patterns seen in Figures 2(d) and 4 are similar to each other. Because the half-life of ^{140}Cs is as short as 63.7 s, almost all the implanted ions should have been disintegrated to ^{140}Ba ($T_{1/2} = 12.8$ d) or ^{140}La ($T_{1/2} = 40.3$ h) during the heat treatment. From the similarity of the spectra for the annealed samples, it would be natural to consider that the implants thermally migrates to the *A* sites, where they are well stabilized. This observation clearly suggests that ^{140}Ba substitutes for the *A*-site atoms, likely Ca, as the same alkaline-earth homologue exhibiting a similar chemical behavior.

4. Summary

We have applied the TDPAC technique with the ^{140}Ce probe for the investigation of a transferred magnetic field at the *A* sites of a perovskite manganite $La_{0.7}Ca_{0.3}MnO_3$. Two different methods were employed for the probe introduction to the sample: one is neutron irradiation in a nuclear reactor for the ^{139}La(n,γ)^{140}La reaction and the other is the ion-implantation of ^{140}Cs, an ascendant of the probe ^{140}Ce.

A drastic change was observed in the time evolution of the directional anisotropies between temperatures above and below T_c. The change can plausibly be attributed to the paramagnetic-ferromagnetic phase transition. A least-squares fit was performed, accordingly, for the 240 K spectrum by assuming that the oscillatory structure reflects a hyperfine interaction between the probe nucleus and the magnetic field transferred from ambient Mn ions, resulting in $B_{int} = 6.9 \pm 0.3$ T. For further information on the *A* site, temperature dependence of the internal magnetic field needs to be investigated.

No distinct magnetic field was observed for the as-implanted sample even at temperature below T_c. Because the incident ion is Cs^+, it is considered that their residence sites are not necessarily the substitutional lattice sites. It was ascertained by a TDPAC measurement after annealing the sample that β^--disintegrated implants, ^{140}Ba and ^{140}La, migrates to the *A* site during the heat treatment. In order to examine the effect of the implantation, it would be interesting to employ ^{140}Ba and/or ^{140}La ions as an incident beam.

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