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Time-Differential Perturbed Angular Correlation of ^{140}Ce Implanted in Highly Oriented Pyrolytic Graphite

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Using an ion implantation method, we introduced cerium nuclei in highly oriented pyrolytic graphite (HOPG), and have studied their behavior by means of the time-differential perturbed angular correlation technique. The time-variant directional anisotropy for the present pseudo-single crystalline sample is little different from that for polycrystalline graphite. Temperature dependence has been observed on the electric quadrupole interaction between the probe nuclei and the extranuclear charge distribution: the anisotropy shows gradual attenuation at room temperature, whereas the effect of an electrostatic perturbation is implied in the spectrum at 10 K. For the chemical state of the probe atom in HOPG, the trivalent state is suggested from the large magnitude of the electric field gradient at the probe nucleus.

1. Introduction

The physical properties of graphite compounds, represented by Li_xC_6, have attracted much interest, and the investigations on their electric conductivity have realized industrial application of the material as an electrode of a rechargeable battery.[1] In relation to this study, further investigation on doped graphite compounds have been made, and some intriguing properties on the mobility and occupying sites of the doped atoms have been reported. Zabel et al.[2] succeeded in observing dynamic motion of intercalate alkali-metal atoms (Li, K, Rb, and Cs) in graphite, estimating the diffusion constants and activation energies for each of the atoms. For highly oriented pyrolytic graphite (HOPG) doped with boron atoms, there is a report that the dopant is substituted for the carbon atom rather than is intercalated in the layers like the alkali-metal atoms.[3] It is suggested from these observations that behavior of atoms in graphite indeed depends on the introduced elements having intrinsic chemical properties. Because doped graphite is expected to exhibit unique properties on account of the two-dimensional (2D) structure, it should be interesting to study the case for dopants of other types of elements.

In our previous work, we studied the behavior of Ce atoms implanted in *polycrystalline* graphite by means of the time-differential perturbed angular correlation (TDPAC) method, and obtained an implication that the Ce nuclei are dynamically perturbed from the extranuclear field.[4] As the principal axis of the electric quadrupole interaction is randomly oriented due to the sample form, however, the experimental results do not allow discussing whether the motion is two dimensional. In expectation of directional information of the dynamic motion, therefore, Ce atoms were implanted in *pseudo-single crystal* HOPG in the present work.

For the observation of the behavior of dopant atoms, the TDPAC method was employed again. In this spectroscopy is applied a nuclear technique in which one observes the time variation of the directional anisotropy of a γ–γ cascade from excited nuclei. By observing the time-variant anisotropy, one can obtain direct information concerning the fluctuation of the principal axis of the electric field gradient (EFG) produced at the site of the probe nucleus. In other words, this method allows evaluating the magnitude of the EFG and/or the reorientational correlation time of the probe nucleus. Taking advantage of this spectroscopy, we discuss the interacting nature between the probe and the matrix carbon atoms.

2. Experiment

HOPG with a size of approximately 6 mm $\phi \times 1$ mm was stuck on a Teflon-sheet backing of $1 \times 10 \times 10$ mm^3, and then attached to the ion beam collector equipped at the isotope separator on-line installed at the target chamber (T-1) in Kyoto University Reactor (KUR-ISOL). The fission products derived from the enriched ^{235}U target in the chamber were rapidly transported into the ion source equipped outside the reactor. After surface ionization, they were accelerated by the acceleration voltage up to 30 kV and were separated according to their charge-to-mass ratios by the analyzer magnet. The ion beam of interest, ^{140}Cs, was reaccelerated by the acceleration voltage of 80 kV and was kept implanted in the target HOPG for approximately 30 h. The number of implanted ^{140}Cs atoms was estimated to be approximately 1×10^{11} in total. Detailed description and schematic diagrams of the system of KUR-ISOL appear in References 5–7. The probe nucleus ^{140}Ce is provided through the disintegration process shown in Figure 1. Figure 2 shows a typical γ-ray spectrum from a sample after

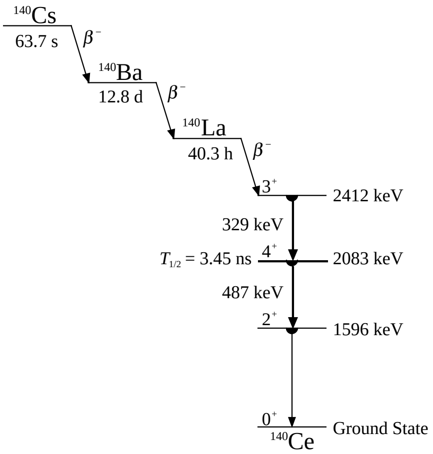

Figure 1. Simplified decay scheme of ^{140}Ce disintegrated from ^{140}Cs.

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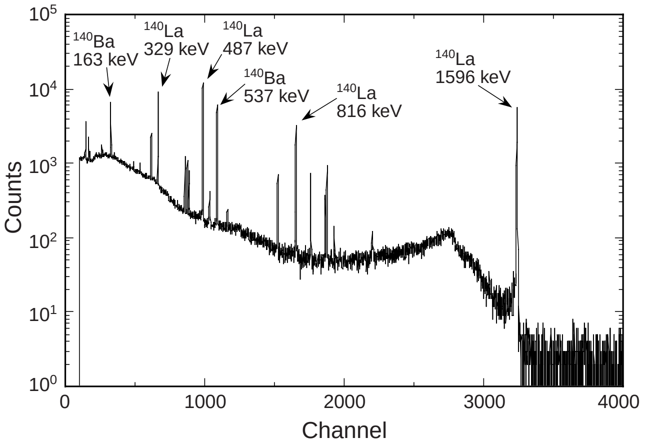

Figure 2. γ-ray spectrum measured for a sample 4 days after the implantation of ^{140}Cs.

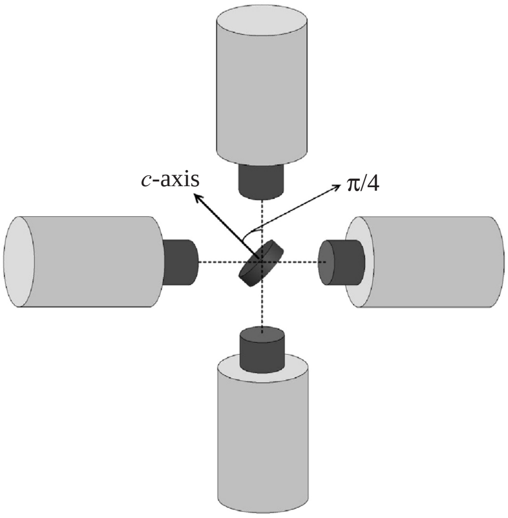

Figure 3. Schematic geometry of the HOPG and BaF_2 scintillation counters.

the implantation. It was confirmed by the spectrum that the projectile was well isolated in the mass separation process.

After radioactive equilibrium between ^{140}Ba and ^{140}La was achieved, TDPAC measurements were performed at 298 and 10 K for the probe ^{140}Ce on the 329-487 keV cascade γ rays with the intermediate state of 4^+ having a half-life of 3.5 ns. In the present work, the directional anisotropy of the angular correlations of the cascade γ rays was observed at $\pi/2$- and π-radian directions with a conventional four-detector system. The pseudo-single crystalline sample was placed so that the *c*-axis would be parallel to the detector plane and each detector would be directed to the 2D plane at $\pi/4$ radian as illustrated in Figure 3. For the coincidence detection, BaF_2 scintillation counters with 1.5 in. $\phi \times 1$ in. pure crystal were adopted; the time resolution of the present system was estimated to be 500 to 600 ps based on the full width at half maximum of peaks for prompt coincidence. As regards solid angle correction for the γ-ray detection, this work followed a method developed by Lawson and Frauenfelder.[8]

3. Results and Discussion

TDPAC spectra of ^{140}Ce implanted in HOPG are shown in Figure 4. In the present work, we defined the directional anisotropy, $R(t)$, which is a function of the time-differential perturbation factor, $G_{22}'(t)$, by a simple arithmetic operation as

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

where t is the time interval between the cascade γ rays and

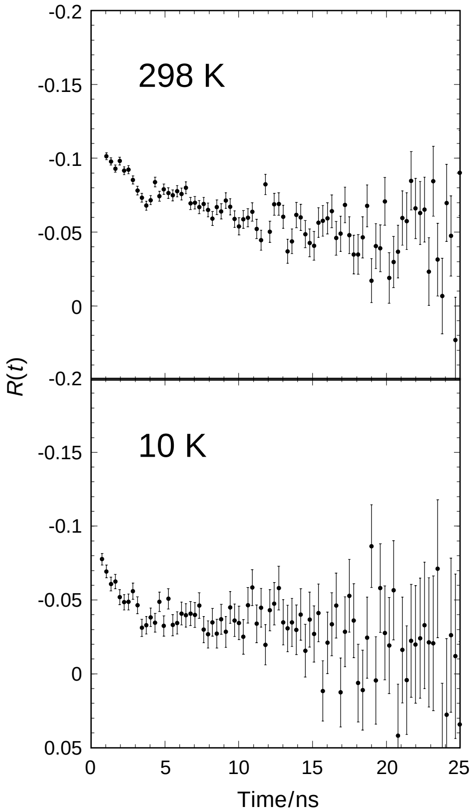

Figure 4. TDPAC spectra of ^{140}Ce implanted in HOPG at 298 and 10 K.

$N(\theta, t)$ denotes the number of the coincident events observed at an angle, θ. As the present sample is a pseudo-single crystal, the observed data are to be dealt with accordingly. It is difficult, however, to see clear difference in the spectra from those observed for polycrystalline graphite investigated in the previous work.[4] More specifically, the time spectra do not reflect the difference of the sample form, that is, the orientation of the *c*-axis. For simplicity, therefore, we hereafter treat the data in the same way as the case for a polycrystalline sample.

One can see for the time spectrum observed at room temperature that the directional anisotropy shows gradual relaxation with a slight oscillatory structure at about 3 ns. This relaxation appears to be an exponential-type attenuation following

$$G_{22}'(t) = \exp(-\lambda t), \tag{2}$$

which was deduced by Abragam and Pound[9, 10] using the diffusion approximation for the typical case that the fluctuation of the extranuclear field is so fast that the static interaction with the probe nucleus is hardly kept during the time window of the intermediate state of the cascade. As for the dip at around 3 ns, coexistence of another small component experiencing a static perturbation may be suggested.

The TDPAC spectrum at 10 K shows rather fast attenuation of the directional anisotropy. After the rapid attenuation, however, the anisotropy maintains an almost constant value even until 25 ns. Taking into account the magnitude of the hard core,[11] there is a possibility at this low temperature that the probe has a static electric quadrupole interaction with the extranuclear charge distribution. In the limited case for an axially symmetric EFG produced at the probe nucleus by the outer surrounding charge distribution, the perturbation factor for the present cascade can be expressed by

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

in the case of a polycrystalline source. Here, ω_Q stands for the electric quadrupole frequency defined by

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

with the EFG at the site of the probe nucleus, V_{zz}. In eq 4, Q represents the nuclear quadrupole moment of the intermediate state of the cascade (= 0.35 ± 0.07 barn) and I is the nuclear spin (= 4 for the present case).[12] For the interpretation of the 10-K spectrum, simulated perturbation patterns are drawn based on eq 3 in Figure 5. Distributions are assumed for the electric quadrupole frequency as

$$G_{22}^{\text{static}}(t)_{\delta\omega_Q} = a_0 + \sum_{i=1}^{7} a_i \exp\left(-\frac{1}{2}\delta^2\omega^2_{Qi}t^2\right)\cos\omega_{Qi}t, \tag{5}$$

where eq 3 is expressed in a general form as

$$G_{22}^{\text{static}}(t) = a_0 + \sum_{i=1}^{7} a_i \cos\omega_{Qi}t. \tag{6}$$

The relative width, δ, is defined by $\delta = \sigma/\omega_Q^0$, where σ is the width of the distribution and ω_Q^0 is the centroid of ω_Q for each term. The simulated line with $\delta = 0.5$ appears to reproduce fairly well the low temperature spectrum by assuming another component.

The observations above are reasonably explained. It is considered that the probe atoms at low temperature should occupy certain stable site(s) after the implantation, having a static interaction with the outer surrounding carbon atoms. The wide distribution of the electric quadrupole frequency could be attributed to thermal vibration at the optimum potential well and/or to slight differences in the EFGs due to different occupied sites. At room temperature, on the other hand, the exponentially attenuating component predominates in the time spectrum; this may imply nuclear spin relaxation caused by a dynamic perturbation from the extranuclear fluctuation. Considering the thermal motion of alkali-metal atoms in graphite-intercalated compounds,[2] the present phenomenon could be interpreted as a thermally activated relative motion of the probe against ambient carbon atoms. For investigating whether the motion is two dimensional, sample annealing following the implantation would be needed.

Based on the assumption that the solid line in Figure 5 reproduces the spectrum at 10 K with an additional component, the EFG at the site of the probe nucleus is as large as $\left|V_{zz}\right| = 1 \times 10^{19}$ V/cm^2. After β^- disintegration of a trivalent La^{3+}, the daughter nuclide should take tetravalent state, Ce^{4+}, in most cases as reported in References 13–18, and the estimated EFG value for ^{140}Ce^{4+} is $\left|V_{zz}\right| \sim 10^{17}$ V/cm^2.[19] From the circumstantial evidence that the difference of the outer surrounding lattice distribution makes little distinction among the EFGs at ^{140}Ce^{4+}, we propose that the present large EFG be assigned to the distortion of the extranuclear charge distribution caused by a 4*f* electron in trivalent Ce^{3+}. At the TDPAC measurement, the valence state of the probe is considered to have become trivalent through a prompt rearrangement of the electronic configuration.

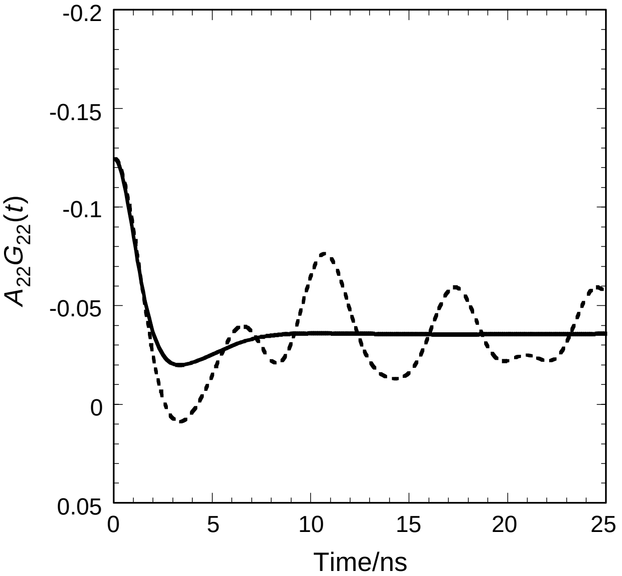

Figure 5. Simulated perturbation patterns for the case of an axially symmetric electric field gradient for a polycrystalline source. The electric quadrupole frequency is assumed as $\omega_Q = 5 \times 10^7$ rad/s. The dotted and solid lines correspond to the frequencies with distributions of $\delta = 0$ and $\delta = 0.5$, respectively. The angular correlation coefficient is assumed to be $A_{22} = -0.125$.

4. Summary

The TDPAC method has been applied to the study of Ce-implanted HOPG. The time spectra for the pseudo-single crystal are little different from those for polycrystalline graphite, which implies that the principal axis of the EFG at each probe nucleus is not oriented to the same direction in the sample. At room temperature, the directional anisotropy of the cascade shows exponential-type relaxation in the present time window, whereas the low-temperature spectrum reflects an electrostatic interaction with a wide distribution of the EFG. These observations may suggest the temperature dependence of the mobility of the implanted Ce atoms. For more detailed discussion on the direction of the field in HOPG, it is essential to observe the angular correlation for the sample with the *c*-axis perpendicular to the detector plane as well.

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(11) The angular correlation in a polycrystalline sample is never wiped out completely because a certain fraction of nuclei experience the static field in such a direction that their correlation is unperturbed or only slightly attenuated.

It is to be noted that the present spectra are regarded as ones for a polycrystalline sample as described in the text.
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