

VIII-II-1. Project Research

Project 5

PR5 Project Research on Material Science Using Short-Lived Nuclei and Radiations

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Objective and Participating Research Subjects

The main objectives of this project research are the investigation of the local properties of materials using short-lived radioactive nuclei and its related subjects, and the synthesis of new functional materials employing radiation from ^{60}Co .

This period is the second year of the project. Unfortunately, since the reactor had remained stopped owing to the delay of the shipment of LEU (Low-Enriched Uranium) fuel, most of the experiments in the project which depended on the reactor could not be carried out and will be postponed.

The research subjects (PRS) executed in this period are as follows:

PRS-3 Property Measurements of a LaBr_3 Scintillator as a Fast γ -ray Detector (Y. Kojima *et al.*).

PRS-4 (a) Magnetic Moment of the $3/2^+$ State in ^{165}Ho ;
(b) Observation of Local Field in Silver-Doped ZnO (Y. Ohkubo *et al.*).

PRS-5 Mössbauer Spectroscopic Study of Fe-Oxypnictide Superconductors (M. Seto *et al.*).

PRS-6 Measurement of the Hyperfine Field in Mavicyanin by the PAC Method Using ^{111}Cd Probes (A. Yokoyama *et al.*).

PRS-7 Synthesis and Physical Properties of Four-Legged MX-Ladder Complex, $[\text{Pt}(\text{en})(\text{bpy})\text{I}]_4(\text{NO}_3)_8 \cdot 16\text{H}_2\text{O}$ (en: ethylenediamine, bpy: 4,4'-bipyridine) (H. Kitagawa *et al.*).

PRS-8 Gamma-Irradiation Effect on the Thermal Properties of Biodegradable Polymers: Poly(Lactic Acid) and Poly(Caprolactone) (M. Minagawa *et al.*).

Main Results and Contents of This Report

The half-life of the nucleus is one of clues to understanding the nuclear structure. Using γ -ray standard sources ^{152}Eu , ^{137}Cs , and ^{60}Co , Y. Kojima and K. Shizuma (PRS-3) did a feasibility test, giving a positive result, of a new scintillation material LaBr_3 for near future half-life measurements on short-lived fission products at KUR-ISOL which demand good energy resolution as well as good time resolution.

The electromagnetic moment of the nucleus is a valuable physical quantity to study the nuclear structure and also the local electronic structure in materials. M. Tanigaki *et al.* (PRS-4a) successfully observed the Larmor frequency for the 362-keV state of ^{165}Ho in Dy_2O_3 powder using the time-differential perturbed angular correlation (TDPAC) technique with an external magnetic field. (^{165}Dy , a parent of ^{165}Ho , was produced via neutron activation of ^{164}Dy at KURRI-LINAC.) The

derived magnetic moment is $+2\sim 3 \mu_N$, tentatively assuming the paramagnetic correction factor for a free Ho^{3+} ion.

Zinc oxide, a semiconductor with a relatively large band gap, has several favorable properties in materials science. W. Sato *et al.* (PRS-4b) measured at room temperature, using the TDPAC technique with radioactive ^{111}In on the market, the local electric field gradient (EFG) at ^{111}Cd ($\leftarrow^{111}\text{In}$) introduced in 0.5 at.% Ag-doped ZnO. The observed spectra indicate that there is more than one local structure around the probe nucleus.

Iron-based oxypnictides LaFePO were recently found to exhibit superconductivity, although these compounds include a magnetic element Fe. The most concern is the superconducting mechanism. In order to examine whether ferromagnetism coexists with superconductivity on the microscopic scale, S. Kitao *et al.* (PRS-5) measured the ^{57}Fe -Mössbauer spectra for a non-superconductor LaFeAsO and a 26-K superconductor $\text{LaFeAsO}_{0.89}\text{F}_{0.11}$ in the temperature range between 298 and 4.2 K under no external magnetic field. From the results that $\text{LaFeAsO}_{0.89}\text{F}_{0.11}$ does not exhibit any magnetic order, whereas LaFeAsO does, they concluded that F doping causes superconductivity while suppressing magnetic order.

Using the TDPAC technique, T. Kubota *et al.* (PRS-6) measured at a temperature a little below room temperature the EFG at ^{111}Cd ($\leftarrow^{111}\text{In}$) incorporated in mavicyanin, a protein having a single metal site. The present aim of the experiment is to examine whether ^{111}Cd occupies the metal site. The preliminary result is that there are two perturbations on the ^{111}Cd γ -ray angular correlation, one of them being a time-dependent electric quadrupole interaction.

Electronic systems having a ladder lattice show a variety of physical properties depending on the number of legs within the ladder. Kitagawa *et al.* (PRS-7) successfully synthesized four-legged ladder complex containing iodine, $[\text{Pt}(\text{en})(\text{bpy})\text{I}]_4(\text{NO}_3)_8 \cdot 16\text{H}_2\text{O}$ (en: ethylenediamine, bpy: 4,4'-bipyridine), and studied its electronic state by taking the reflectance and Raman spectra. ^{129}I -Mössbauer spectra will be taken to examine the electronic structure on the Pt-I chain.

Minagawa *et al.* (PRS-8) studied oxidative thermal degradation of two biodegradable polymers and also ^{60}Co - γ -ray-irradiation effects on their degradation temperature. The conclusion is that γ -ray-irradiation has little effect on the degradation temperature for the biodegradable polymers, while, as previously observed by them, γ -ray-irradiation recovers oxidation resistance of a non-biodegradable polymer, poly(carbonate).

PR5-1 Property Measurements on a LaBr₃ Scintillator as a Fast γ -ray Detector

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INTRODUCTION: Lifetimes of excited levels in nuclei are one of the most important nuclear data. This is because lifetimes are related to nuclear matrices which are essential input parameters to understand the nuclear structure. The delayed coincidence method is generally used to measure lifetimes approximately from 0.1ns to 1 μ s. As γ -ray detectors, BaF₂ scintillators show best performance because of its very short decay time of 0.8ns [1]. However, the energy resolution of BaF₂ is \sim 13% at 662keV. This poor resolution causes difficulties in peak identification.

Recently, a new scintillation material LaBr₃ has been developed and becomes available commercially [2]. The LaBr₃ has attractive features for lifetime measurements: good energy resolution ($<$ 3% at 662keV) and good time resolution (a few hundreds picoseconds). It suggests that LaBr₃ scintillators can be used as a fast γ -ray detector instead of BaF₂.

In this work, we studied properties of a LaBr₃ detector, aiming to apply it to lifetime measurements on short-lived fission products at KUR-ISOL.

EXPERIMENTS: The detection system used in this study consists of a LaBr₃ and a plastic scintillation detector. The LaBr₃ detector was produced by Canberra; the crystal of 1.5 inch in diameter and 1.5 inch in thickness was coupled with a Hamamatsu 14-pin photomultiplier (PMT). For β -ray detection, a 1mm-thick plastic scintillator (pilot-U) was used with a Hamamatsu H2431-51 assembly. The pilot-U has a short decay time of 1.4 ns, and the H2431-51 consists of a fast time response PMT. Energy resolutions of the LaBr₃ detector were measured using ¹⁵²Eu, ¹³⁷Cs and ⁶⁰Co standard sources. To evaluate timing properties, prompt β - γ time spectra were obtained using ¹³⁴Cs and ⁶⁰Co sources.

RESULTS: Figure 1 shows energy resolutions of the LaBr₃ detector observed at an applied voltage of 800V. The resolution of 2.4% obtained for a 662-keV γ -ray was about 5 times better than that of typical BaF₂ scintillation detectors. Energy resolutions were also measured at 600 and 700V because the recommended voltage provided by the manufacturer was 600-800V. No difference was observed for γ -ray peak shapes in this range. However, pulse heights of the PMT anode output are low at 600-700V and anode signals of X-rays will not exceed a minimal discrimination level of measuring modules. Thus, 800V was applied in following experiments.

The LaBr₃ contains naturally abundant ¹³⁹La and α -decaying isotopes, so that a self-background was observed at a counting rate of about 62cps. A Ba X-ray peak, in particular, is possible interference in measuring

rare-earth elements of low fission yields.

Fig. 2 shows a typical prompt time spectrum. The time resolution (FWHM) was 410ps for the 796-keV and 380ps for 1332-keV γ -rays. In energies less than 100keV, resolutions of around 1ns were observed while detailed experiments are now in progress. Therefore, the LaBr₃ detector can be applied for lifetime measurements in \sim 1ns range. On-line lifetime measurements on neutron-rich short-lived isotopes will be performed in FY2010.

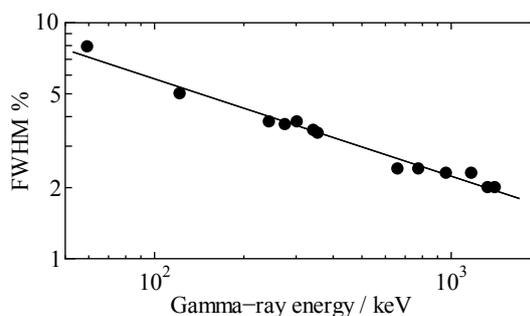


Fig. 1. Energy resolution of the LaBr₃ detector at an applied voltage of 800V.

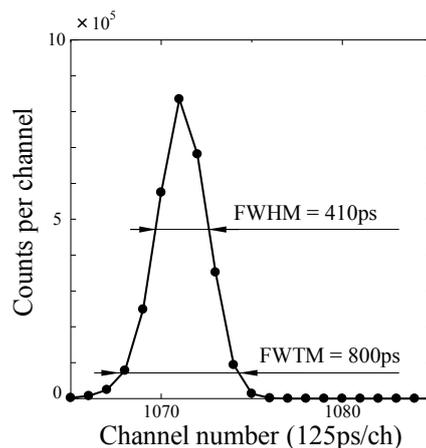


Fig. 2. Prompt time spectrum observed for the 796-keV γ -ray from ¹³⁴Cs.

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INTRODUCTION: Electromagnetic moments of nuclei are important physical quantities not only for nuclear structure studies, but also for the investigation of the electromagnetic structures in materials. Reliable values of electromagnetic moments of radioactive nuclei are essential especially for probe nuclei of rare-earth elements in ferromagnetic materials through hyperfine interactions since it is difficult to apply the conventional NMR technique due to their very high resonance frequencies and shallow skin depths. One such example is Ho in Fe, which, as Torumba *et al.* have pointed out, is important for evaluating first principle calculations [1]. This time, we succeeded in observing the Larmor precession for the 362 keV state in ^{165}Ho ($I^\pi = 3/2^+$, $T_{1/2} = 1.512$ μs) in Dy_2O_3 by use of the perturbed angular correlation technique, intending to determine the magnetic moment and apply it to the measurement of the hyperfine field at Ho in Fe.

EXPERIMENTS: TDPAC measurements were performed on the 633-362 keV γ - γ cascade of ^{165}Ho populated by the β -decay of ^{165}Dy ($T_{1/2} = 2.3$ h). ^{165}Dy were produced by activating ^{164}Dy in natural Dy_2O_3 powder by the thermal neutron flux obtained from the 30 MeV electron linac at KURRI. Then the powder was compacted into a tablet of 5 mm ϕ and placed under a static external magnetic field of 0.3 T at room temperature. A conventional three-counter technique was performed with BaF_2 detectors and a newly developed multi-dimensional data acquisition system based on WE-7562 MCA modules of WE-7000 series available from Yokogawa Electric Corporation. All the gamma-ray cascades detected by any two detectors within the time width of 2 μs were once recorded in a set of list files, then the offline analysis was performed to select the events of the 633-362 keV γ - γ cascade and to obtain the PAC spectrum. As shown in Fig. 1, a clear perturbation pattern was observed, and the Larmor frequency was determined to be -32.3 ± 0.6 MHz from this spectrum.

RESULTS: The magnetic moment for this state was tentatively deduced to be $+2\sim 3$ μ_N under the assumption that the paramagnetic correction factor for free Ho^{3+} ions [2] is applicable to the present case. Taking the uncer-

tainty of the paramagnetic correction factor in Dy_2O_3 into account, the deduced magnetic moment would be consistent with a simple model calculation of the magnetic moment for rotational state nuclei. An accurate evaluation of the paramagnetic correction factor for Ho in Dy_2O_3 is now in progress to finalize the magnetic moment value.

ACKNOWLEDGMENTS: The authors are grateful to the staff at the electron linac facility at KURRI for the operation of linac and beam handling. This work was supported by Grant-in-Aid for Scientific Research (C) (19540291) from the Japan Society for the Promotion of Science (JSPS).

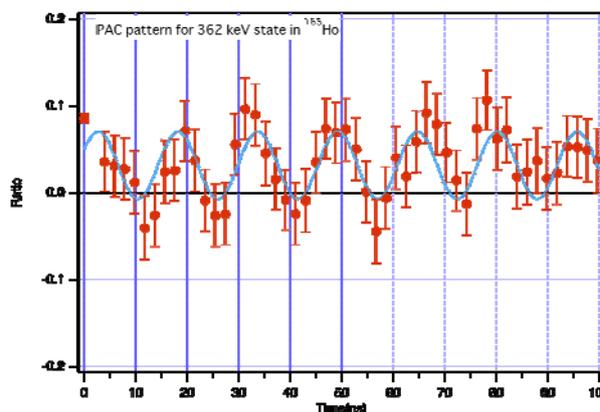


Fig. 1. PAC pattern of $3/2^+$ state in ^{165}Ho in Dy_2O_3 at $B_{ext} = 0.3$ T.

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INTRODUCTION: Zinc oxide (ZnO) is an intrinsic *n*-type semiconductor having optoelectronic properties, and it is known that its conductivity is controllable by changing the element and concentration of impurities doped. For its wider industrial application as a conduction-controlling device, *p*-type ZnO needs to be synthesized, and it is therefore essential to study physical and chemical state of the impurities as well as their residence sites. In the present work, we have synthesized silver-doped ZnO and measured local fields at the impurity sites by means of the time-differential perturbed angular correlation (TDPAC) method with the probe ¹¹¹Cd formed in the disintegration of ¹¹¹In. We here report a preliminary result implying that the probe nuclei occupy more than one unique site.

EXPERIMENTS: For the synthesis of 0.5 at.% Ag-doped ZnO, stoichiometric amounts of Ag(NO₃)₃ and ZnO powder were thoroughly mixed in a mortar. The mixture was pressed into a couple of disks, and they were sintered in air at 1173 K. Commercially available ¹¹¹In HCl solution was then added in droplets onto the disks. They again underwent heat treatment in air separately at different temperatures of 1173 and 1373 K. After pounding each disk again, the powder samples were sealed in quartz tubes in vacuum. TDPAC measurements were then performed for each sample at room temperature for the probe ¹¹¹Cd (←¹¹¹In) on the 171-245 keV cascade γ rays with the intermediate state of *I* = 5/2 having a half-life of 85 ns.

RESULTS: Fig. 1 shows the TDPAC spectra of ¹¹¹Cd embedded in the 0.5 at.% Ag-doped ZnO samples. The directional anisotropy on the ordinate, $A_{22}G_{22}(t)$, was deduced with the following simple operation:

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

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 coincidence events observed at an angle, θ . Because the present samples are nonmagnetic, the oscillating patterns can be assigned as those arising from electrostatic interactions between the probe nucleus (*I* = 5/2) and the

surrounding charge distribution. The spectra were thus fitted following our previous works[1, 2]. In the spectrum in Fig. 1(a), one can see a damped oscillatory structure together with a small peak, at around 200 ns, characteristic of the component for the substitutional Zn site (Component I hereafter) [1]. The immediate damping of the oscillation shown by a dip structure at around 15 ns is analogous to the one observed for Al-doped ZnO[2]. The dip can be reproduced by a fit assuming a wide distribution for the relevant quadrupole frequency, which implies that charge distribution surrounding the probe is not unique except for a small fraction (12(2)%) of Component I. Expecting a uniform charge distribution in the vicinity of the probe, we prepared another sample by heat treatment at a higher temperature (1373 K). The spectrum in Fig. 1(b) exhibits an oscillatory pattern having a better-defined structure; suggesting that the fraction of the ¹¹¹Cd probe nuclei interacting with Ag impurities became small, whereas Component I was considerably enhanced. For the understanding of this fractional change, conditions for the introduction of Ag ions should be further investigated.

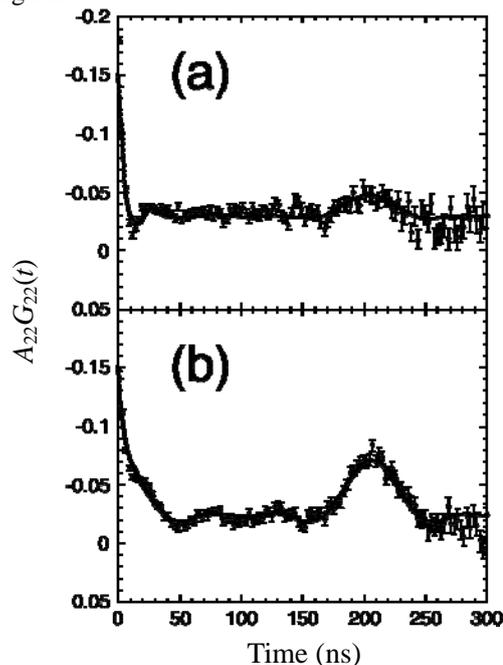


Fig. 1. TDPAC spectra of ¹¹¹Cd(←¹¹¹In) in 0.5 at.% Ag-doped ZnO at room temperature. Heat treatments for thermal diffusion of ¹¹¹In were performed (a) at 1173 K and (b) at 1373 K.

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INTRODUCTION: Recently, Kamihara *et al.* discovered a new series of superconductors in Fe-oxipnictides LaFePO[1] and, successively, F-doped LaFeAsO_{1-x}F_x with the transition temperature (T_C) of 26 K[2]. Since magnetic elements, such as Fe, had been thought to be incompatible with the emergence of superconductivity, these reports surprised many researchers and have brought extensive following researches[3]. Moreover, first-principles calculations for the Fe-oxipnictides showed that the 3d-bands of Fe are primary components of the Fermi level. This fact implies that the Fe is the key element of the superconductivity in the Fe-oxipnictides. The observed relatively high T_C implies that the mechanism of this superconductivity may not be explained by the conventional Bardeen-Cooper-Schrieffer theory. There is the possibility to have some relationship between the magnetism and the mechanism of their superconductivity. Therefore, Fe-Mössbauer spectroscopy is one of the most essential methods to investigate the electronic states and magnetic properties to clarify the nature of their superconductivity.

EXPERIMENTS: The experiment was performed by conventional Mössbauer equipment using a ⁵⁷Co source in a Rh matrix with a nominal activity of 1.85 GBq. Each spectrum was calibrated using an α -Fe foil and referenced to it. The measurements at lower temperatures down to 4.2 K were performed using a liquid-He-flow cryostat. The LaFeAsO_{1-x}F_x and LaFeAsO samples were synthesized by a method described elsewhere[2] and verified by X-ray diffraction to be a single phase with slight amounts of impurities. The electric resistivity measurement of the F-doped sample showed a midpoint T_C of 26 K and an onset T_C of 32 K for $x = 0.11$. The LaFeAsO did not undergo a superconducting transition, but had an anomaly at around 150 K. For the Mössbauer measurements, we used samples with mass ~25 mg mixed with BN and polyethylene powder and pressed to form a pelletized disk with a diameter of 10 mm.

RESULTS AND DISCUSSION: The Mössbauer studies of the undoped LaFeAsO, which does not show superconductivity, revealed the existence of a magnetic order at the Néel temperature (T_N) of about 140 K[4]. Typical spectra are shown in Fig. 1(a). The internal magnetic

field reaches 5.3 T at 4.2 K. This finding of the magnetic order is consistent with neutron scattering experiment[5]. On the other hand, F-doped LaFeAsO_{1-x}F_x which shows superconductivity exhibits no magnetic order down to 4.2 K as shown in Fig. 1(b). Therefore, it was concluded that the F-doping suppresses the magnetic order of the LaFeAsO and causes the emergence of the superconductivity. Further researches have been performed with external magnetic fields and using the nuclear resonant scattering technique and revealed new facts in these compounds[6,7].

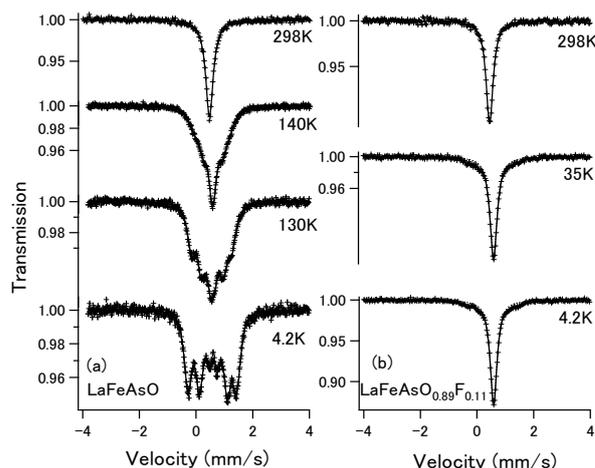


Fig. 1. Typical Mössbauer spectra of (a) LaFeAsO and (b) LaFeAsO_{0.89}F_{0.11} from 298 to 4.2 K.

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INTRODUCTION: The structure around the metal site of mavicyanin, a protein molecule with a single copper site, and those for four-coordinate chelate complexes having similar structures around their metal sites to that of the protein were investigated by using time-differential perturbed angular correlation (TDPAC) of γ -rays from parent nuclei ^{117}Cd , $^{111\text{m}}\text{Cd}$ etc. [1-6]. In a previous study for the protein by using the ^{111}Ag nuclei, we assumed there might be several possible sites for the probe nuclei so that we have difficulties in obtaining reliable results from TDPAC spectra. In the present study, ^{111}In parent nuclei ($T_{1/2} = 2.81\text{d}$) were introduced into mavicyanin in order to ascertain which site(s) of protein the probe nuclei are settled in.

EXPERIMENTS: An aqueous solution containing ^{111}In was purchased from Nihon Medi-Physics Co. Ltd. A tracer solution of ^{111}In was mixed with a $200\mu\text{l}$ solution of ca. 0.1mM copper-free recombinant mavicyanin adjusted to $\text{pH}=5.0$ with an acetate buffer solution, and with indium-ion carriers so as to be 0.1mM indium solution. Then, the solution was let stand for 10 hours at 4°C and subject to dialysis treatment to eliminate unbound indium ions. Besides, an additional treatment with EDTA was done to aim to remove indium ions at possible unfavorable sites of protein. Finally, sucrose was added at a concentration of 50 weight % in the solution to slow down rotational motion, which would otherwise damp an oscillation pattern of the typical TDPAC spectrum. The

sample solution obtained in the above-described procedure was analyzed by the PAC technique at a temperature of some degrees below room temperature while being cooled on a Peltier device.

RESULTS: Results of TDPAC spectra on the sample solutions with and without the EDTA treatment made no significant difference. Therefore, we have still no evidence that suggests the interference from sites other than the expected metal site of the protein.

In case of the present study, the adopted expression of $A_{22}G_{22}(t)$ is given as follows.

$$A_{22}G_{22}(t) = A_{22}(1 - P) + A_{22} \left[P \exp(-t/\tau_c) \frac{1}{5} \left\{ 1 + \frac{13}{7} \cos(6\omega_Q t) + \frac{10}{7} \cos(12\omega_Q t) + \frac{5}{7} \cos(18\omega_Q t) \right\} \right],$$

where the perturbation factor $G_{22}(t)$ for an ensemble of randomly oriented molecule in liquid is assumed to be a function of the electric quadrupole frequency ω_Q and the correlation time, τ_c , but the asymmetry parameter of the electric field gradient is fixed to be 0. P stands for the occupation probability in sites of the protein.

Table 1 lists the parameter values obtained by a least square fit for the measured spectrum. It demonstrates that two components, presumably one from probes bound to the protein and the other from those in soluble species, contribute to the data. We found it necessary to discuss the site occupation of the PAC probes in the protein based on further substantive experiments.

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Table 1. Parameter values obtained by a least-squares fit.

sample	Parent probe (\rightarrow Probe)	ω_Q (Mrad/s)	P (%)	τ_c (ns)
mavicyanin (pH 5.0)	^{111}In (\rightarrow ^{111}Cd)	15.5 (11)	58.1 (18)	20.9 (70)

採択課題番号 21P5-6 ガンマ線摂動角相関法による銅タンパク活性位の動的挙動の研究 プロジェクト
(金沢大・理工研究域) 横山明彦、佐藤 渉 (金沢大・院自然) 貝谷英樹、荒木幹生、浅野敦史
(京大・原子炉) 大久保嘉高、高宮幸一

PR5-6 Synthesis and Electronic State of Four-Legged MX-Ladder Complex, $[\text{Pt}(\text{en})(\text{bpy})\text{I}]_4(\text{NO}_3)_8 \cdot 16\text{H}_2\text{O}$ (en: ethylenediamine, bpy: 4,4'-bipyridine)

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INTRODUCTION: Recent years, the electronic system of the ladder lattice has attracted much attention due to a variety of physical properties strongly depending on the number of legs within a ladder [1]. In this work, we focused on the control of the three-dimensional shape of one-dimensional (1-D) halogen-bridged transition-metal complex (MX-chain) which has structural flexibility by substitution of their structural components, such as metal ions, organic ligands, and counterions resulting in various electronic states of the 1-D chain [2]. We successfully synthesized four-legged ladder complex, $[\text{Pt}(\text{en})(\text{bpy})\text{I}]_4(\text{NO}_3)_8 \cdot 16\text{H}_2\text{O}$ (**1**) (en: ethylenediamine, bpy: 4,4'-bipyridine). Moreover, we clarified its electronic state.

EXPERIMENTS: I_2 was slowly diffused into a water/methanol (1:1) solution containing $[\text{Pt}(\text{en})(\text{bpy})]_4(\text{NO}_3)_8$ in the presence of excess amount of NO_3^- . Needle shaped single crystals of **1** were obtained after several weeks. Raman spectrum was recorded on a single crystal of **1** with a JASCO NRS-1000 using a microscope. A Showa Optronics GLG5601 He-Ne laser provided the exiting line (632.8 nm), and the incident-laser was polarized parallel to the c^* axis (chain direction).

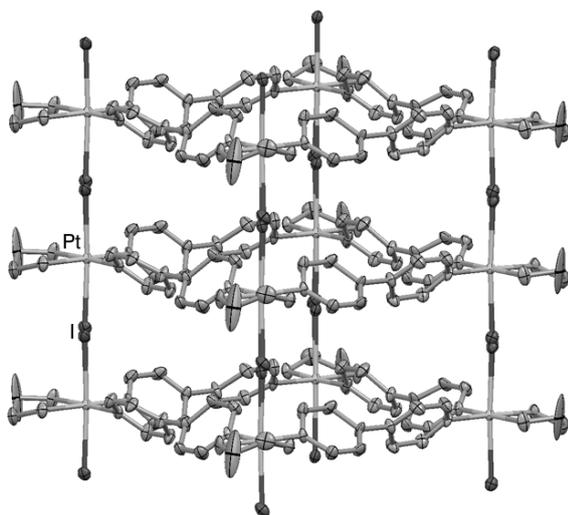


Fig. 1. Crystal structure of **1** at 100K.

RESULTS: The single crystals of **1** were obtained from the reaction of tetranuclear platinum macrocyclic com-

plex, $[\text{Pt}(\text{en})(\text{bpy})]_4(\text{NO}_3)_8$ and I_2 in a mixture of water and methanol. The crystal structure of **1** was determined using single crystal X-ray crystallography, as shown in Fig. 1. Every platinum ion is bridged by iodide ion resulting in MX-chain. These MX-chains are connected by bpy ligand to form the four-legged ladder structure along the c -axis. It is worth noting that 1-D channel with is formed inside the tube, and disordered crystallization water molecules are located inside the channel.

To obtain the information electronic state of **1**, diffuse reflectance spectrum and Raman spectrum measurements were performed at room temperature. In the diffuse reflectance spectrum, broad band could be assigned inter-valence charge transfer transition (IVCT) from Pt^{II} to Pt^{IV} within one chain was observed at 1.2 eV. In addition, very strong $\nu(\text{Pt}-\text{I})$ stretching mode with several of its overtone was observed at 122 cm^{-1} in the Raman spectrum (Fig. 2). This strongly activated overtone progression is attributable to the resonance with the IVCT ($\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{IV}}$) transition. These results were consistent with X-ray crystal structure analysis indicating that the electronic states within one MX-chain of **1** is a $\text{Pt}^{\text{II}}/\text{Pt}^{\text{IV}}$ mixed valence CDW state.

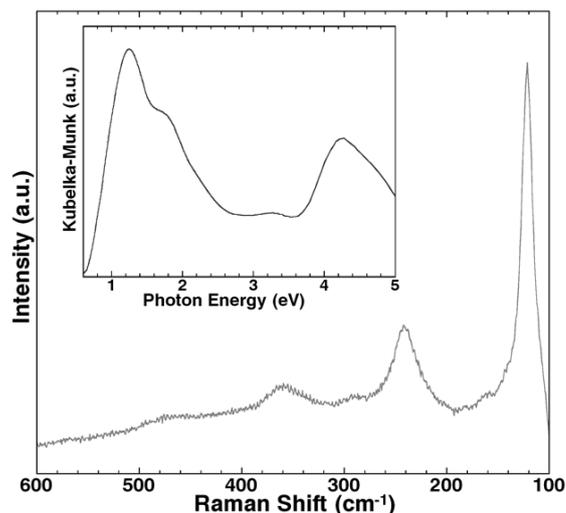


Fig. 2. Raman spectrum of **1** (inset: Diffuse reflectance spectrum of **1**).

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PR5-7 Gamma-Irradiation Effect on the Thermal Properties of Biodegradable Polymers: Poly(Lactic Acid) and Poly(Caprolactone)

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INTRODUCTION: The γ -irradiation effect on the thermal properties of two biodegradable polymers was studied. High energy irradiation effect has not yet been investigated.

EXPERIMENTAL: The samples were poly (lactic acid) (PLA) and poly(caprolactone) (PCL). Thermogravimetric / differential thermal analysis (TG-DTA) was carried out on the Rigaku thermoflex TG-DTA under the following conditions: sample weight, 5mg; heating rate, 5–40°C/min; atmosphere, under N₂, in air, and O₂ stream (20ml/min).

RESULTS AND DISCUSSION: We have established a novel evaluation method for the oxidative thermal degradation of polymers based on the heating rate dependence of the degradation temperature (T_d) from TG-DTA data. Fig. 1 shows typical examples of PLA. This polymer shows sharp degradation behavior as evidenced by quite a narrow temperature range. Here, T_{d1} and T_{d2} are defined as the degradation initiation and termination temperature derived from the slope of TG curve. Even though O₂ exists in the atmosphere, zone-width was small and almost constant. In the case of PCL, however, the zone-width shifted to lower temperature and the width increased remarkably (Fig. 2). It is apparent that the degradation was strongly affected by O₂ and it occurred gradually over a wide temperature region.

When γ -irradiation was carried out for a week (100 hr), however, little effect was observed in the TG-DTA data (Figs. 1 and 2, right). This makes a clear contrast with the results that we reported before for poly(carbonate) (PC) [1]. As shown in Fig. 3, the T_d value rather increased after γ -irradiation.

Generally, γ -irradiation brought about a remarkable decrease in T_d , but under very weak γ -irradiation conditions like in the present experiment, the value of T_d rather increased. This is probably due to chemical cross-linking in the PC sample. In the case of PLA, in contrast, the two opposite effects compensate each other, and the total balance between the deterioration and

improvement equilibrates moderately.

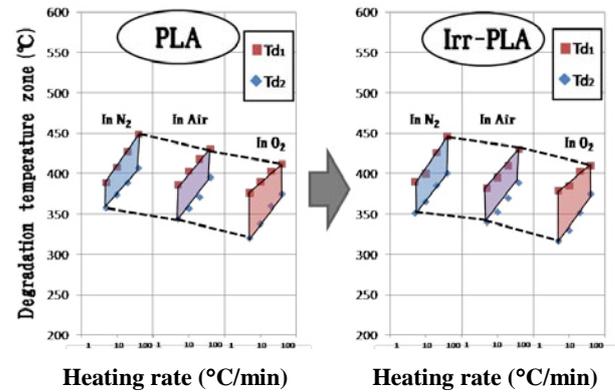


Fig. 1. Comparison of T_d between PLA and Irr-PLA.

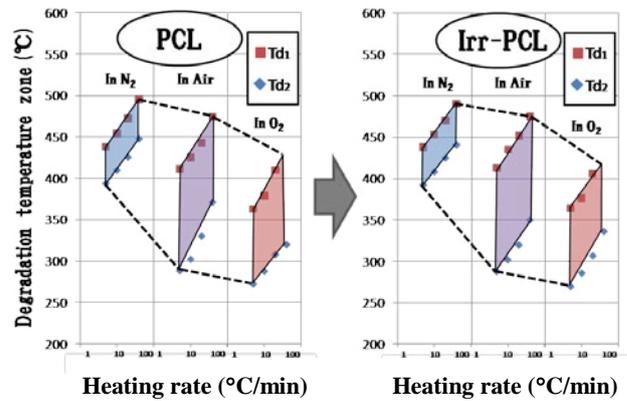


Fig. 2. Comparison of T_d between PCL and Irr-PCL.

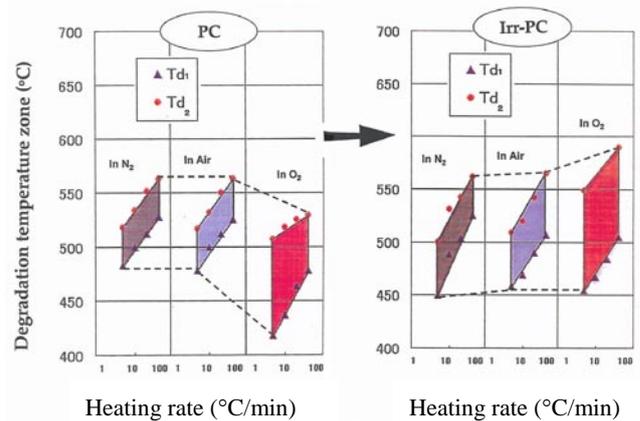


Fig. 3. Comparison of T_d between PC and Irr-PC.

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