Perturbed-Angular-Correlation Studies on ^{111}Cd and ^{117}In in Pyrochlore $\text{Cd}_2\text{Nb}_2\text{O}_7$

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The nuclear-electric-quadrupole interactions at ^{111}Cd and ^{117}In nuclei arising from ^{111m}Cd and ^{117}Cd , respectively, chemically introduced in pyrochlore ferroelectric $\text{Cd}_2\text{Nb}_2\text{O}_7$ ($T_C = 196\text{ K}$) were studied using the perturbed-angular-correlation technique. At temperatures above T_C , there is one type of Cd sites. However, at liquid nitrogen temperature, below T_C , there are two types of Cd sites. The ratio of the electric quadrupole frequency of ^{117}In to that of ^{111}Cd is anomalously deviated from a value expected from the purely ionic In and Cd ions in the same lattice environment.

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1. Introduction

Cadmium pyrochlore oxides with the formula Cd_2M_2O_7 show a variety of physical properties, depending on M . Several of them undergo a structural phase transition at $\sim 200\text{ K}$, which seems to be related to their interesting physical properties emerging. $\text{Cd}_2\text{Re}_2\text{O}_7$ may be such an example. Although this oxide exhibits superconductivity at as low as $1\sim 2\text{ K}$, a structural phase transition at $\sim 200\text{ K}$ is considered to change the electronic state of its high temperature phase, leading eventually to the appearance of the superconductivity.¹⁾ For the Re sites, nuclear magnetic resonance (NMR) and quadrupole resonance (NQR) are excellent microscopic probes for the structure and electronic states. On the other hand, in the case of the Cd sites, NQR technique is not applicable to the nuclear ground states of the stable Cd isotopes, because those spin (I) values are either 0 or $1/2$. However, another nuclear technique called perturbed angular correlation (PAC) could be effective because this technique can be used for radioactive ^{111}Cd (245-keV level) with $I = 5/2$.

In the present study, in order to examine the applicability of PAC technique to the structural study on cadmium pyrochlore oxides, we performed PAC measurements at 77, 290, and 1073 K on ^{111}Cd arising from ^{111m}Cd incorporated in polycrystalline $\text{Cd}_2\text{Nb}_2\text{O}_7$. This pyrochlore oxide is a ferroelectric with $T_C = 196\text{ K}$ and is subject to a structural phase transition at the same temperature.²⁾ We also performed PAC measurements at 77 and 299 K on ^{111}Cd in polycrystalline $\text{Cd}_2\text{Ta}_2\text{O}_7$. Although this pyrochlore oxide is subject to a phase transition near 200 K, it does not exhibit ferroelectricity below the transition temperature.²⁾ Moreover, we carried out PAC measurements on ^{117}In (660-keV level) with $I = 3/2$ arising from ^{117}Cd in these oxides. It is expected that a structural relaxation may take place when ^{117}Cd changes to ^{117}In , because the ionic radius of In^{3+} ion

(92 pm)³⁾ is smaller than that of Cd^{2+} (110 pm),³⁾ the Coulomb interaction between In and O ions is stronger than that between Cd and O ions, and the oxygen array is not close-packed. Two assumptions that Cd and In are in the same lattice environment and that those ions are in the purely ionic states lead to the ratio of the electric quadrupole frequency ω_Q of $^{117}\text{In}^{3+}$ to that of $^{111}\text{Cd}^{2+}$ being 2.3. A deviation of the measured ratio from 2.3 may indicate a structural relaxation or a participation of the $5s$ and $5p$ electrons in the bonding in addition to the purely ionic bonding.

The room-temperature $\text{Cd}_2\text{Nb}_2\text{O}_7$ structure belongs to the $Fd\bar{3}m$ space group, as general high-temperature-phase pyrochlores do. The Cd and Nb ions form identical pyrochlore lattices (networks of corner-sharing tetrahedra, see Fig. 1). However, there are two non-equivalent oxygen sites, and the Nb ions are located within oxygen octahedra, whereas the Cd ions within scalenohedra (distorted cubes).

Fig. 1 Unit cell displaying only cation arrays in the room-temperature pyrochlore $\text{Cd}_2\text{Nb}_2\text{O}_7$ structure (closed circles: Cd; open circles: Nb). These two types of cations are not in the equivalent lattice positions. Nb ions are located within oxygen octahedra, whereas the Cd ions within scalenohedra (distorted cubes).

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2. Experimental Procedures

2.1 Sample preparation

$\text{Cd}_2\text{Nb}_2\text{O}_7$ ($\text{Cd}_2\text{Ta}_2\text{O}_7$) polycrystalline samples containing ^{111m}Cd and those containing ^{117}Cd were prepared with an identical method,^{4,5)} for LiNbO_3 and LiTaO_3 containing those Cd isotopes. The parent nuclei ^{111m}Cd and ^{117}Cd were separately produced by irradiating enriched ^{110}CdO and ^{116}CdO , respectively, with thermal neutrons at the research reactor of Kyoto University. The irradiated oxides, mixed with high-purity powders of CdO and Nb_2O_5 (Ta_2O_5), and then pressed into pellets, were sintered in air at 1100°C for about 1 h, and thereby obtained were samples containing ^{111m}Cd and those containing ^{117}Cd . Owing to the short half-lives of ^{111m}Cd (49 min) and ^{117}Cd (2.5 h), samples were prepared for each PAC-measurement temperature. The room-temperature x-ray-diffraction pattern of a sample after a PAC measurement showed a single phase of it. The concentration of impurities ^{117}In and ^{117}Sn , which are the decay products of ^{117}Cd , in $\text{Cd}_2\text{Nb}_2\text{O}_7$ and $\text{Cd}_2\text{Ta}_2\text{O}_7$ is estimated to be the order of one part per trillion.

2.2 PAC measurements

The PAC method is mostly applied to an ensemble of nuclei emitting two consecutive γ rays. Figure 2 shows relevant parts of the decay schemes of (a) $^{111m}\text{Cd} \rightarrow ^{111}\text{Cd}$ and (b) $^{117}\text{Cd} \rightarrow ^{117}\text{In}$. The 396-keV excited level of ^{111}Cd , i.e., ^{111m}Cd with a half-life $t_{1/2} = 48.54$ min, decays to the ground level through the 245-keV intermediate level having a spin $I = 5/2$, $t_{1/2} = 85.0$ ns, and an electric quadrupole moment $Q = +0.77(12)$ b.⁶⁾ The 749-keV excited level of ^{117}In is populated by the β^- decay of the parent ^{117}Cd with $t_{1/2} = 2.49$ h, which decays to the 315-keV excited level

through the 660-keV intermediate level having $I = 3/2$, $t_{1/2} = 53.6$ ns, and $Q = (-)0.59(1)$ b.⁶⁾ The intermediate level is split by the interaction of the electric quadrupole moment of the nuclei with an extranuclear electric field gradient (EFG). Detection of the 151-keV (90-keV) γ rays with a detector sorts out a set of ^{111}Cd (^{117}In) nuclei in intermediate states with spin alignments against the direction of the detector from the source. Time-differential measurements of the 245-keV (344-keV) γ rays from the same nuclei with another detector permits a determination of the spin precession frequency of ^{111}Cd (^{117}In) nuclei in intermediate states, and then a determination of the magnitude of the splitting of the level. Thus the PAC of the 151- and 245-keV (90- and 344-keV) γ rays emitted in successive γ transitions reveals an electric quadrupole interaction during the stay of ^{111}Cd (^{117}In) nuclei in intermediate states.

The time dependence of the coincidence counts $N(\theta, t)$ of the 151–245-keV cascade γ rays for samples containing ^{111m}Cd , and that of the 90–344-keV γ rays for samples containing ^{117}Cd , were taken at 77, 290, and 1073 K using a measurement system consisting of four BaF_2 scintillation detectors and standard fast-slow electronic modules. Here θ and t denote the angle and time interval, respectively, between the cascade γ rays. The directional anisotropy $A_{22}G_{22}(t)$ was obtained according to eq. (1):

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

The coefficient A_{22} depends only on the nuclear properties, and the values for ^{111}Cd ($\leftarrow ^{111m}\text{Cd}$) and ^{117}In ($\leftarrow ^{117}\text{Cd}$) are $+0.18$ and -0.36 , respectively.⁷⁾

We give the relevant expressions of $G_{22}(t)$ for a unique static quadrupole interaction. The perturbation factor $G_{22}(t)$ for an ensemble of randomly oriented microcrystals is a function of the electric quadrupole frequency ω_Q and the asymmetry parameter η of EFG through the interaction Hamiltonian. The quantities ω_Q and η are defined as follows: $\hbar\omega_Q = -eQV_{zz}/[4I(2I-1)]$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$. The three components of EFG in the principal-axis system are chosen such that $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, and thus the asymmetry parameter η takes a value between 0 and 1. In case of ^{111}Cd ($I = 5/2$), $G_{22}(t)$ has the form

$$G_{22}(t) = S_0 + S_1 \cos(6\omega_Q C_1 t) + S_2 \cos(6\omega_Q C_2 t) + S_3 \cos(6\omega_Q C_3 t). \quad (2)$$

The S_n and C_n in eq. (2) are numerically calculated for a given value of η . For an axially symmetric case of $\eta = 0$, S_n and C_n can be calculated analytically: $G_{22}(t) = [7 + 13 \cos(6\omega_Q t) + 10 \cos(12\omega_Q t) + 5 \cos(18\omega_Q t)]/35$. In case of ^{117}In ($I = 3/2$),

$$G_{22}(t) = [1 + 4 \cos\{6\omega_Q(1 + \eta^2/3)^{1/2}t\}]/5. \quad (3)$$

It should be noted that in case of ^{111}Cd , the values of ω_Q and η can be determined because S_n and C_n in eq. (2) are each modified in a characteristic way as a function of η , whereas in case of ^{117}In , $G_{22}(t)$ contains only one frequency component and they cannot be determined independently from the spectrum.

Fig. 2 Partial decay schemes of (a) $^{111m}\text{Cd} \rightarrow ^{111}\text{Cd}$ and (b) $^{117}\text{Cd} \rightarrow ^{117}\text{In}$.

Fig. 3 PAC spectra $A_{22}G_{22}(t)$ of $^{111}\text{Cd}(\leftarrow^{111m}\text{Cd})$ in $\text{Cd}_2\text{Nb}_2\text{O}_7$ at 77, 290, and 1073 K with the solid curves representing the least-squares fits of eq. (2) in the text.

Fig. 4 PAC spectra $A_{22}G_{22}(t)$ of $^{117}\text{In}(\leftarrow^{117}\text{Cd})$ in $\text{Cd}_2\text{Nb}_2\text{O}_7$ at 77, 290, and 1073 K with the solid curves representing the least-squares fits of eq. (3) in the text.

3. Results and Discussion

The PAC spectra measured at 77, 290, and 1073 K of ^{111}Cd in $\text{Cd}_2\text{Nb}_2\text{O}_7$ and those of ^{117}In are shown, respectively, in Figs. 3 and 4. At 290 and 1073 K each spectrum is modulated in a manner characteristic of a single quadrupole interaction in polycrystalline samples depending on the spin value of the nuclear level. However, in the ^{111}Cd spectrum at 77 K the oscillation appears to become damped as the time passes. With a careful look at the spectrum beyond $t \sim 140$ ns we can see that there are two quadrupole components with the ω_Q values close to each other and roughly equal amplitudes. In the case of the ^{117}In spectrum at 77 K, it is easy to recognize

Table 1 Absolute values of the quadrupole frequencies of ^{111}Cd and ^{117}In in $\text{Cd}_2\text{Nb}_2\text{O}_7$, as derived from least-squares fits to the PAC spectra.

T/K	$ \omega_Q /\text{Mrad}\cdot\text{s}^{-1}$			
	$^{111}\text{Cd}(\leftarrow^{111m}\text{Cd})$		$^{117}\text{In}(\leftarrow^{117}\text{Cd})$	
77	Site 1(50%)	50.6(1)	Site 1(57%)	188(1)
	Site 2(50%)	49.0(1)	Site 2(43%)	177(1)
290		48.5(1)		188(1)
1073		43.5(1)		183(1)

the beat, which is also due to two close quadrupole frequencies in the spectrum. We analyzed the PAC spectra at 290 and 1073 K with a single quadrupole frequency, and those at 77 K with two quadrupole frequencies, using eqs. (2) and (3) with $\eta = 0$. The least-squares fits were satisfactorily executed. The solid curves in Figs. 3 and 4 are the results of the fits. The derived absolute values of the quadrupole frequencies are summarized in Table 1. Note that site 1, for example, of ^{111}Cd does not necessarily correspond to site 1 of ^{117}In .

The analysis of the ^{111}Cd spectra shows that at temperatures above 290 K (perhaps above T_C), there is one type of Cd sites, as evident from the high-temperature pyrochlore structure. However, at 77 K, *i.e.* below T_C , there are two types of Cd sites. Since the amplitudes corresponding to the two quadrupole frequencies are equal, it seems plausible that the two types of the Cd sites appear alternatively along a Cd-Cd chain. It is natural to consider that the change of the number of Cd types relates to the structural transition at 196 K. Since the fits were successfully carried out with $\eta = 0$, we consider that the coordination around Cd remains axially symmetric below T_C . We are thus confident that PAC is effective for the structural studies of cadmium pyrochlores.

As shown in Figs. 5 and 6, the PAC spectra measured at 77 and 299 K of ^{111}Cd and ^{117}In in $\text{Cd}_2\text{Ta}_2\text{O}_7$ consist of a single quadrupole component below and above the transition temperature. This means that the transition is not accompanied by a structural change around the probe nuclei, which in turn relates to the fact that $\text{Cd}_2\text{Ta}_2\text{O}_7$ is not ferroelectric below the transition temperature. The values of the quadrupole frequencies derived from the least-squares fits with $\eta = 0$ are listed in Table 2.

Fig. 5 PAC spectra $A_{22}G_{22}(t)$ of $^{111}\text{Cd}(\leftarrow^{111m}\text{Cd})$ in $\text{Cd}_2\text{Ta}_2\text{O}_7$ at 77 and 299 K with the solid curves representing the least-squares fits of eq. (2) in the text.

Fig. 6 PAC spectra $A_{22}G_{22}(t)$ of $^{117}\text{In}(\leftarrow^{117}\text{Cd})$ in $\text{Cd}_2\text{Ta}_2\text{O}_7$ at 77 and 299 K with the solid curves representing the least-squares fits of eq. (3) in the text.

Table 2 Absolute values of the quadrupole frequencies of ^{111}Cd and ^{117}In in $\text{Cd}_2\text{Ta}_2\text{O}_7$, as derived from least-squares fits to the PAC spectra.

T/K	$ \omega_Q /\text{Mrad}\cdot\text{s}^{-1}$	
	$^{111}\text{Cd}(\leftarrow^{111m}\text{Cd})$	$^{117}\text{In}(\leftarrow^{117}\text{Cd})$
77	51.0(1)	211(1)
299	49.3(1)	203(1)

Although In seems to behave like Cd in the two oxides, the ratio $|\omega_Q(^{117}\text{In})/\omega_Q(^{111}\text{Cd})|$ is much larger than a value of 2.3 expected from the purely ionic In and Cd ions in the same lattice environment (in case of $\text{Cd}_2\text{Nb}_2\text{O}_7$ at room temperature, for example, the ratio is 3.88(1)). Before considering this anomalous value of the ratio, we first derive the value 2.3.

According to a phenomenological model of Sternheimer,⁸⁾ the largest electric field gradient component V_{zz} is expressed as $V_{zz} = (1 - R)V_{zz}(\text{valence}) + (1 - \gamma_\infty)V_{zz}(\text{lattice})$, where $V_{zz}(\text{valence})$ is due to the non-cubic electron distribution in partially filled valence orbitals of the probe ion and $V_{zz}(\text{lattice})$ to the charges on the lattice ions surrounding the probe ion non-cubic symmetrically. R and γ_∞ are called the Sternheimer shielding and antishielding factors, respectively, both representing the effect of the distortion of the closed-shell electron distributions in the probe ion. In case of the purely ionic In and Cd ions, *i.e.*, In^{3+} and Cd^{2+} , both having the (same) closed-shell electron configuration, $V_{zz}(\text{valence})$ may be neglected, and thus $V_{zz}(\text{lattice}) = V_{zz}/(1 - \gamma_\infty)$. Furthermore, when In and Cd are in the same lattice environment, *i.e.*, the same $V_{zz}(\text{lattice})$, the ratio $\omega_Q(^{117}\text{In})/\omega_Q(^{111}\text{Cd})$ is expressed simply as

$$\begin{aligned} \omega_Q(^{117}\text{In})/\omega_Q(^{111}\text{Cd}) &= (10/3) \cdot [Q(^{117}\text{In})/Q(^{111}\text{Cd})] \\ &\cdot \{[1 - \gamma_\infty(^{117}\text{In})]/[1 - \gamma_\infty(^{111}\text{Cd})]\}, \end{aligned} \quad (4)$$

according to the definition of ω_Q given above eq. (2). Using the calculated values of $\gamma_\infty(\text{In}^{3+}) = -25.8$ and $\gamma_\infty(\text{Cd}^{2+}) = -29.3$, the absolute value of the ratio is evaluated to be 2.3.

This value is actually realized, for example, for ^{117}In and ^{111}Cd substituted at the Li sites of LiNbO_3 and LiTaO_3 at

4.2 K; *i.e.*, 2.26(1) and 2.30(2), respectively.⁴⁾ Since Li in these oxides is considered to be essentially pure-ionic, as indicated by a first-principles calculation on LiNbO_3 ,⁹⁾ it is expected that non-transition elements In and Cd at the Li positions are also highly ionic. These oxides take an ilmenite-related structure and the metal ions are located at interstitial positions in a hexagonal *close-pack* array of oxygen ions. When ^{117}Cd decays to ^{117}In , a structural relaxation seems to be prohibited. Consequently, the two assumptions leading to the value of 2.3 is considered to hold well in LiNbO_3 and LiTaO_3 .

The anomalous values of the quadrupole frequency ratio for $\text{Cd}_2\text{Nb}_2\text{O}_7$ and also $\text{Cd}_2\text{Ta}_2\text{O}_7$ (*e.g.*, 4.120(5) at 299 K) are due to either of the two assumptions being inappropriate. Since the oxygen array of the pyrochlore oxides is not close-packed, a structural relaxation may take place when ^{117}Cd decays to ^{117}In . This relaxation would be such that the distances between an indium ion and some of the surrounding eight oxygen ions become shorter, because of the higher positive charge on In and its smaller ionic size, giving a larger V_{zz} than that expected from a situation where there would be no structural relaxation.

In Fig. 7(a) are plotted the absolute values of $\omega_Q(T)/\omega_Q(\text{room temperature})$ vs temperature T of ^{111}Cd (closed square and closed triangle: 77 K; closed circle: 290 K) and of ^{117}In (open square and open triangle: 77 K; open circle: 290 K) in $\text{Cd}_2\text{Nb}_2\text{O}_7$. Those for $\text{Cd}_2\text{Ta}_2\text{O}_7$ are given in Fig. 7(b). In case of $\text{Cd}_2\text{Ta}_2\text{O}_7$ where there is no structural change around the probe nuclei below and above about 200 K, the ω_Q of ^{111}Cd and that of ^{117}In both decrease with increasing temperature. However, in $\text{Cd}_2\text{Nb}_2\text{O}_7$ where there is a structural phase transition, the ω_Q of ^{117}In rather increases with temperature on the average in contrast to the ω_Q of ^{111}Cd . This difference might be due to a participation of the 5s and 5p electrons in the bonding between In and O in $\text{Cd}_2\text{Nb}_2\text{O}_7$ at 77 K. If this is so, we can speculate that the change of the In-O bonding nature is brought by the structural change.

Fig. 7 Temperature dependences of $|\omega_Q(T)/\omega_Q(\text{room temperature})|$ of ^{111}Cd (closed figures) and ^{117}In (open figures) in (a) $\text{Cd}_2\text{Nb}_2\text{O}_7$ and (b) $\text{Cd}_2\text{Ta}_2\text{O}_7$.

4. Conclusions

In order to examine the applicability of PAC technique to the structural study on cadmium pyrochlore oxides, PAC measurements were performed at 77, 290, and 1073 K on ^{111}Cd arising from ^{111m}Cd in polycrystalline $\text{Cd}_2\text{Nb}_2\text{O}_7$, which is a ferroelectric with $T_C = 196\text{ K}$ and is subject to a structural phase transition at the same temperature. At temperatures above T_C , there is one type of Cd sites. However, at liquid nitrogen temperature, below T_C , there are two types of Cd sites. It is considered that this change reflects the structural phase transition and thus that PAC is effective for the structural studies of cadmium pyrochlores. PAC measurements were also performed at 77 and 299 K on ^{111}Cd in polycrystalline $\text{Cd}_2\text{Ta}_2\text{O}_7$, which is subject to a phase transition near 200 K, but not ferroelectric below the transition temperature. Different from the case of $\text{Cd}_2\text{Nb}_2\text{O}_7$, there is one type of Cd sites above and below the transition temperature, meaning that the transition in $\text{Cd}_2\text{Ta}_2\text{O}_7$ is with no structural change around the probe nuclei. Furthermore, PAC measurements were carried out on ^{117}In arising from ^{117}Cd in the two oxides. The ratio of the electric quadrupole frequency of ^{117}In to that of ^{111}Cd is anomalously deviated from a value expected from the purely ionic In and Cd ions in the same lattice environment. It is considered that a structural relaxation takes place when ^{117}Cd changes to ^{117}In , because the ionic radius of In^{3+} ion is smaller than that of Cd^{2+} , the Coulomb interaction between In and O ions is stronger than that between Cd and O ions, and the oxygen array is not

close-packed. Although on the whole In behaves like Cd, the temperature dependence of ω_Q of ^{117}In in $\text{Cd}_2\text{Nb}_2\text{O}_7$ is rather opposite to the others. This might be due to a participation of the 5s and 5p electrons in the bonding in addition to the ionic bonding.

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