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Time-differential perturbed-angular-correlation studies on ^{117}In and ^{111}Cd in $Li_{0.995}Cd_{0.005}NbO_3$

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The nuclear-electric-quadrupole interactions at ^{117}In and ^{111}Cd nuclei arising from ^{117}Cd and ^{111m}Cd, respectively, chemically introduced in $Li_{0.995}Cd_{0.005}NbO_3$ polycrystals were studied using the time-differential perturbed angular correlation of γ rays. The $|V_{zz}^{\text{lattice}}|$ values derived for ^{117}In and ^{111}Cd coincided with each other, i.e., $3.4(1)\times10^{20}$ V/m^2 and $3.4(5)\times10^{20}$ V/m^2, respectively, meaning that the In and Cd ions are in the same lattice environment in the forms of In^{3+} and Cd^{2+}. Although these probes are considered to occupy the Li sites, the above values of V_{zz}^{lattice} are substantially different from the previously reported value for ^{7}Li, 0.7×10^{20} V/m^2, which is ascribable to the structural relaxation around the probe atoms. The temperature dependence of ω_Q of ^{117}In indicates that the In ion vibrates anisotropically about its equilibrium position at high temperatures, as has been argued for the Li ion in $LiNbO_3$. [S0163-1829(97)04942-4]

Lithium niobate, $LiNbO_3$, is a ferroelectric with $T_C = 1483$ K.[1] Because of the similar sizes of Li^+ (76 pm) and Nb^{5+} (64 pm),[2] this oxide while having the ABO_3 stoichiometry (A and B stand for metal elements) does not adopt the perovskite structure, but takes an ilmenite ($FeTiO_3$)-related structure.[3] The oxide is an important nonlinear optic material. Its optical properties are influenced by doping the material with metal impurities.[4] It is reported, for example, that In impurities increase the resistance of $LiNbO_3$ to optical damage.[5] Knowledge of the lattice environment and the chemical state of dopants is essential for theoretical understanding of the impurity effects.

In the present study, we performed time-differential perturbed-angular-correlation (TDPAC) measurements on ^{117}In arising from ^{117}Cd and on ^{111}Cd arising from ^{111m}Cd in polycrystalline samples of a chemical composition $Li_{0.995}Cd_{0.005}NbO_3$, both of whose parent nuclides were chemically introduced in order to obtain information about the valency of In and Cd. The assumption of purely ionic states of In and Cd, i.e., In^{3+} and Cd^{2+}, leads to the ratio of the electric quadrupole frequency for $^{117}In^{3+}$ to that for $^{111}Cd^{2+}$ being 2.3.[6] A deviation of the measured ratio from 2.3 may indicate a participation of the $5s$ and $5p$ electrons in the bonding.[6]

Figure 1 shows decay schemes of $^{117}Cd\rightarrow^{117}In$ and $^{111m}Cd\rightarrow^{111}Cd$. The 749 keV excited state of ^{117}In is populated by β^- decay of the parent ^{117}Cd with a half-life $t_{1/2} = 2.49$ h and decays to the 315 keV excited state through the 660 keV intermediate state having a spin $I=\frac{3}{2}$, $t_{1/2} = 53.6$ ns, and an electric quadrupole moment $Q = (-)0.59(1)$ b.[7] Here and hereafter, the number in the parentheses represents the uncertainty in the least significant digit(s). The 396 keV excited state of ^{111}Cd, i.e., ^{111m}Cd with $t_{1/2} = 48.54$ min decays to the ground state through the 245 keV intermediate state having $I=\frac{5}{2}$, $t_{1/2} = 85.0$ ns, and $Q = +0.77(12)$ b.[7] The intermediate state is split by the interaction of the electric quadrupole moment of the nuclei with an extranuclear electric-field gradient (EFG). Detection of the 90 keV (151 keV) γ rays with a detector sorts out a set of ^{117}In (^{111}Cd) nuclei in the intermediate state with spin alignment against the direction of the detector from the source. Then, time-differential measurements of the 344 keV (245 keV) γ rays with another detector permits determination of the spin precession frequency of ^{117}In (^{111}Cd) nuclei in the intermediate state and then determination of the magnitude of the splitting of the state. Thus, TDPAC of the 90 and 344 keV (151 and 245 keV) γ rays emitted in the successive γ transitions reveals the electric quadrupole interaction during the stay of ^{117}In (^{111}Cd) nuclei in the intermediate state.

The parent nuclei ^{117}Cd and ^{111m}Cd were separately obtained by irradiating enriched ^{116}CdO and ^{110}CdO, respectively, with thermal neutrons at Kyoto University Research Reactor Institute. The irradiated oxide was mixed with appropriate amounts of high-purity powders of Li_2CO_3 and Nb_2O_5 for a chemical composition of $Li_{0.995}Cd_{0.005}NbO_3$. The mixture was pressed into a pellet and heated in air at 1100 °C. The same process followed after the sample was repowdered and thereby $Li_{0.995}Cd_{0.005}NbO_3$ was obtained. We tentatively use the formula $Li_{0.995}Cd_{0.005}NbO_3$ for our samples, use of which will be justified below. Loss of neither the metals nor the source nuclides was observed during these heating processes. The room-temperature x-ray-diffraction pattern of a sample without cadmium prepared by an identical heating process showed a single phase of $LiNbO_3$. TDPAC measurements were performed in the temperature region between 4.2 and 873 K for the samples containing ^{117}Cd by means of a conventional fast-slow setup and four BaF_2 scintillation detectors. For the sample containing ^{111m}Cd, a TDPAC measurement was performed at 4.2 K

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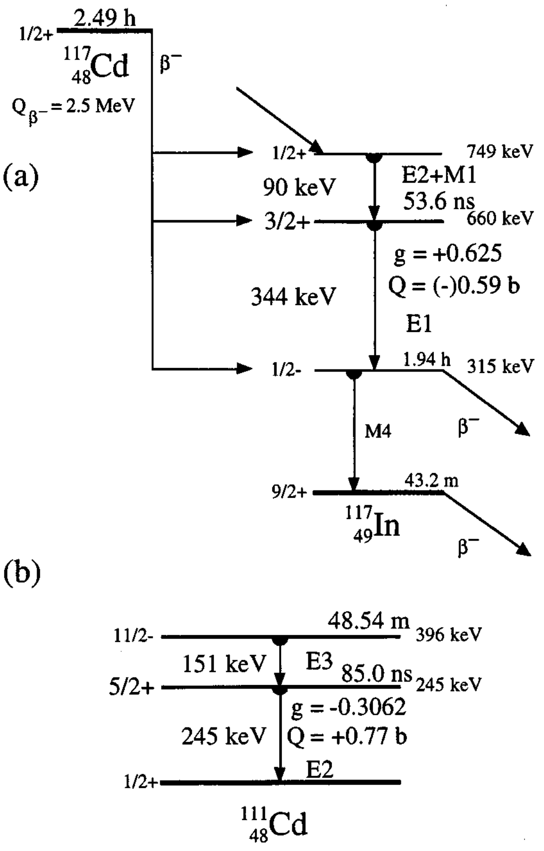

FIG. 1. Partial decay schemes of ^{117}Cd→^{117}In and ^{111m}Cd→^{111}Cd.

using the same detection system. For the details of the experimental method, refer to Ref. 8.

Here, we give the expressions of directional anisotropy, $A_{22}G_{22}(t)$, for a unique static quadrupole interaction. The coefficient A_{22} depends only on the nuclear transitions. 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 the 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 asymmetry parameter η takes a value between 0 and 1. The perturbation factor $G_{22}(t)$ has the form

$$G_{22}(t) = [1 + 4\cos(\omega^{(0)}t)]/5, \tag{1}$$

$$\omega^{(0)} = 6\omega_Q\left(1 + \frac{\eta^2}{3}\right)^{1/2} \quad \text{for the case of } ^{117}\text{In}, \tag{2}$$

and

$$G_{22}(t) = \sum_{n=0}^{3} S_n(\eta)\cos(\omega_n t), \tag{3}$$

$$\omega_0 = 0, \quad \omega_n = 6\omega_Q C_n(\eta) \quad (n = 1,2,3)$$

$$\text{for the case of } ^{111m}\text{Cd}. \tag{4}$$

The S_n and C_n in Eqs. (3) and (4) are numerically calculated for a given asymmetry parameter. It should be noted that for the case of ^{117}In, $G_{22}(t)$ contains only one frequency component and the values of ω_Q and η cannot be determined independently from the spectrum, whereas for the case of ^{111}Cd, they can be determined because the amplitudes S_n and the frequencies ω_n in Eq. (3) are modified in a characteristic way as a function of η.

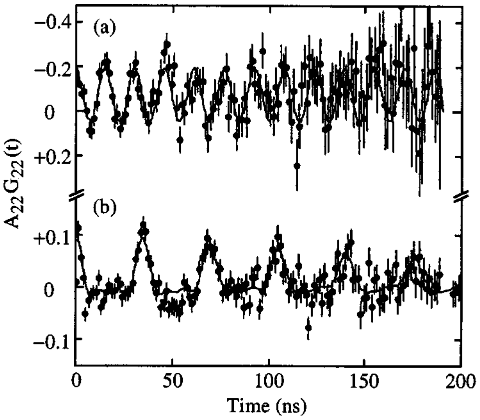

FIG. 2. (a) TDPAC spectrum, $A_{22}G_{22}(t)$, of ^{117}In (←^{117}Cd) in $Li_{0.995}Cd_{0.005}NbO_3$ at 4.2 K with the solid curve showing the result of fitting with Eqs. (1) and (2) in the text, and (b) the corresponding spectrum of ^{111}Cd (←^{111m}Cd) with the solid curve showing the result of fitting with Eqs. (3) and (4) in the text.

The $A_{22}G_{22}(t)$ measured at 4.2 K of ^{117}In and ^{111}Cd in $Li_{0.995}Cd_{0.005}NbO_3$ are shown in Figs. 2(a) and 2(b), respectively. The anisotropy is modulated in a manner characteristic of the electric quadrupole interaction in polycrystalline samples depending on the spin value of the intermediate nuclear state. They were analyzed with an expression assuming that the electric quadrupole frequency ω_Q has a Lorentzian distribution around the central value $\overline{\omega}$. The width of the Lorentzian distribution $\Delta\omega$ was taken to be 0 for the ^{117}In time spectra at $T \leqslant 433$ K, and to be 3% of $\overline{\omega}$ for the ^{117}In time spectra at $T \geqslant 573$ K and for the ^{111}Cd time spectrum at 4.2 K. We assume that the value of η for ^{117}In is the same as that obtained for ^{111}Cd as assumed in Ref. 6. The solid curves in Fig. 2 are the results of the fitting.

In order to examine the site of 0.5 mol% Cd in $LiNbO_3$, we compare our result on ^{111}Cd with that obtained by Hauer *et al.*[9] They studied the electric quadrupole interactions at ^{111}Cd (←^{111}In) in undoped $LiNbO_3$ single crystals and at ^{111}Cd (←^{111m}Cd) in undoped and 6 mol% Mg-doped $LiNbO_3$ single crystals after implantation of ^{111}In and ^{111m}Cd employing the TDPAC method. They observed two electric quadrupole frequencies that differ from each other by only about 5% in each of the above three systems, and each electric quadrupole frequency was the same in the three systems. Since the lattice site of 0.59 mol% In in 6 mol% Mg-doped $LiNbO_3$ had been determined by the PIXE (proton-induced x-ray emission)/channeling technique to be the Li site,[10] it was concluded that both In and Cd occupy the Li site of undoped and Mg-doped $LiNbO_3$.[9] From Table II and Fig. 5 of Ref. 9, showing the room-temperature values of the quadrupole interaction at ^{111}Cd (←^{111m}Cd) and the temperature variation of the two quadrupole frequencies of ^{111}Cd (←^{111}In), respectively, the weighted average of quadrupole frequency of ^{111}Cd (←^{111m}Cd) at 4.2 K is estimated to be

30.3(3) Mrad/s, which essentially coincides with our value of 29.7(2) Mrad/s. Our η value of 0.08 is considered to be eventually the same as the η value of the main component in Ref. 9, i.e., 0.11(2). This observation means that 0.5 mol% Cd occupy the Li site of $LiNbO_3$ and that the chemical formula $Li_{0.995}Cd_{0.005}NbO_3$ is justified.

Since the Li site has a three-fold symmetry axis, the EFG's at ^{117}In and ^{111}Cd at the sites may provisionally be expected to be axially symmetric. Hauer *et al.* interpreted the obtained nonzero η values as being due to the influence of the considerable concentration of Nb vacancies in congruent $LiNbO_3$.[9] On the other hand, Catchen *et al.* interpreted the asymmetry of the EFG at ^{181}Ta ($\leftarrow^{181}$Hf) at the Li site in stoichiometric $LiNbO_3$ and $LiTaO_3$, isostructural to $LiNbO_3$ with $T_C = 938$ K, using an order-disorder model.[11] In both $LiNbO_3$ and $LiTaO_3$, it was observed that η decreases from the value of about 0.25 at room temperature to less than 0.1 above T_C. Catchen *et al.* considered that in the ferroelectric phase some of the Li ions occupy the interstitial sites (normally vacant metal-ion sites in oxygen octahedra) and break the axial symmetry of the Li site, whereas in the paraelectric phase equal occupancy of the normal and interstitial Li sites gives effectively zero asymmetry of the EFG. The observation by Hauer *et al.* of the two electric quadrupole interactions are consistent with this argument. As an additional cause of the nonzero η value, we consider that impurity probe ions with the electric charges larger than +1 are displaced from the normal Li position and deform the surroundings, as described later on.

We now move to the discussion on the valency of In and Cd in $LiNbO_3$. We calculate the ratio of the electric quadrupole frequency of ^{117}In to that of ^{111}Cd, $\omega_Q(^{117}\mathrm{In})/\omega_Q(^{111}\mathrm{Cd})$, assuming that In and Cd exist as purely ionic states, In^{3+} and Cd^{2+}, and are in the same lattice environment. Employing the phenomenological model of Sternheimer,[12] V_{zz} is expressed as $V_{zz} = (1-\gamma_\infty)V_{zz}^{\mathrm{lattice}}$ under the former assumption. Here, $V_{zz}^{\mathrm{lattice}}$ is due to the charges on the lattice ions surrounding the probe atom noncubic symmetrically. The quantity γ_∞ is the Sternheimer antishielding factor representing the effect of the distortion of the closed-shell electron distributions in the probe atom. The latter assumption means that $V_{zz}^{\mathrm{lattice}}$ is the same for both probe nuclei. Then,

$$\frac{\omega_Q(^{117}\mathrm{In})}{\omega_Q(^{111}\mathrm{Cd})} = \frac{10}{3}\,\frac{Q(^{117}\mathrm{In})}{Q(^{111}\mathrm{Cd})}\,\frac{1-\gamma_\infty(^{117}\mathrm{In})}{1-\gamma_\infty(^{111}\mathrm{Cd})}. \quad (5)$$

Using the calculated values of −29.3 as γ_∞(Cd) and −25.8 as γ_∞(In),[13] $|\omega_Q(^{117}\mathrm{In})/\omega_Q(^{111}\mathrm{Cd})|$ is evaluated to be 2.3, where the value of γ_∞(In) was taken to be the average value of $\gamma_\infty(\mathrm{Cd}) = -29.3$ and $\gamma_\infty(\mathrm{Sn}) = -22.3$.[13] The observed ratio of 2.27(2) at 4.2 K agrees reasonably with the above calculated value of 2.3. Putting it in another way, the values of $V_{zz}^{\mathrm{lattice}}$ derived for ^{117}In and ^{111}Cd by dividing the observed EFG's by the corresponding values of $1-\gamma_\infty$ excellently coincide with each other, i.e., $3.4(1)\times10^{20}$ V/m^2 and $3.4(5)\times10^{20}$ V/m^2, respectively. We then consider that when $^{117}Cd^{2+}$ decays to $^{117}In^{3+}$, no observable structural relaxation takes place, In and Cd being in the same lattice environment, and that both In and Cd are predominantly ionic, i.e., they have the identical electronic configuration.

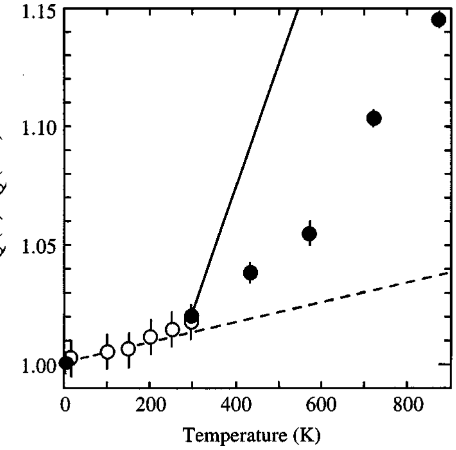

FIG. 3. Temperature dependence of the electric quadrupole frequency ω_Q of ^{117}In in $Li_{0.995}Cd_{0.005}NbO_3$ (solid circles) together with those of ^{111}Cd ($\leftarrow^{111}$In) (Ref. 9) (open circles) and of ^{7}Li (Ref. 15) (solid line) in $LiNbO_3$. The dashed line represents the temperature dependence of $V_{zz}^{\mathrm{lattice}}$ at the Li site in $LiNbO_3$ calculated by the point-charge model with no anisotropic vibration effect (Refs. 9 and 15). The ω_Q of ^{7}Li is scaled so as to be equal to our ^{117}In data at 295 K.

In Ref. 9, room-temperature $V_{zz}^{\mathrm{lattice}}$ values are compared among three TDPAC probes, ^{44}Sc ($\leftarrow^{44}$Ti), ^{111}Cd ($\leftarrow^{111}$In), and ^{181}Ta ($\leftarrow^{181}$Hf) (Ref. 14) all occupying the Li site of $LiNbO_3$. The $|V_{zz}^{\mathrm{lattice}}|$ values are 2.7(3) $\times10^{20}$ V/m^2, $3.1(5)\times10^{20}$ V/m^2, and $3.1(2)\times10^{20}$ V/m^2, respectively, for ^{44}Sc, ^{111}Cd, and ^{181}Ta.[9] The value for ^{117}In obtained in the present study is $3.4(1)\times10^{20}$ V/m^2. The uncertainties in the parentheses include both the uncertainties of the quadrupole frequencies and the electric quadrupole moments. These values of the $V_{zz}^{\mathrm{lattice}}$'s are remarkably similar to each other. However, the $|V_{zz}^{\mathrm{lattice}}|$ value for ^{7}Li in $LiNbO_3$ at room temperature, 0.7×10^{20} V/m^2, calculated from the ^{7}Li-NMR quadrupole coupling constant,[15] is 4–5 times as small as those for the above TDPAC probes. The large difference seen in the $V_{zz}^{\mathrm{lattice}}$ value is not ascribable to the ionic size because the ionic radius of Li^+ at the octahedral site is 76 pm, which is among the ionic radii of Sc^{3+} (74.5 pm), Cd^{2+} (95 pm), In^{3+} (80 pm), and Ta^{5+} (64 pm).[2] In the TDPAC study of electric quadrupole interactions at the Ti site in TiO_2 using the ^{111}Cd ($\leftarrow^{111}$In) and ^{181}Ta ($\leftarrow^{181}$Hf) probes, where significant differences were found in the values of V_{zz} and η, and their temperature dependence, directional bonding effects on EFG were proposed to explain the differences.[16] However, in the present case where all the involved atoms are ionic, a reasonable explanation would be that the TDPAC probe ions, all with the electric charges larger than +1, cause a structural relaxation: they deform the surroundings and are substantially displaced from the inherent Li position. This structural relaxation could also be a cause of the nonzero η, described earlier. As seen in the decay of $^{117}Cd^{2+}$ to $^{117}In^{3+}$, where no further observable structural relaxation takes place, the TDPAC probes with the electric charge +2 and with +3 are considered to be in an essentially identical lattice environment.

In Fig. 3 is plotted the $\omega_Q(T)/\omega_Q(0\ \mathrm{K})$ value of ^{117}In ($\leftarrow^{117}$Cd) vs temperature T, as solid circles. The electric quadrupole frequency ω_Q of ^{117}In increases by about 15% with increasing temperature in the range from 4.2 to 873 K. In the figure is also shown, as open circles, the $\omega_Q(T)/\omega_Q(0\ \text{K})$ for the weighted average of the two ω_Q's of ^{111}Cd ($\leftarrow^{111}$In) obtained by Hauer *et al.*[9] Temperature dependence of ω_Q of ^{117}In agrees with that of ^{111}Cd in the range between 4.2 and 295 K. This agreement supports the above stated consideration on the lattice environment and valency of In and Cd. The dashed line in the figure represents the $\omega_Q(T)/\omega_Q(0\ \text{K})$ calculated with the lattice parameters based on the point charge model.[9,15] This calculation reproduces the temperature dependence of ω_Q for ^{117}In only below room temperature. The ω_Q of ^{117}In above room temperature clearly deviates upward from the dashed line. As discussed below, we consider that there is another cause of increasing ω_Q of ^{117}In.

The ^{7}Li quadrupole coupling constant, eQV_{zz}/h, for LiNbO$_3$ between 297 and 953 K increases linearly as the temperature increases from 297 to 953 K.[15] The solid line in Fig. 3 represents the scaled temperature dependence of the ^{7}Li coupling constant. Obviously, the large gradient of the line cannot be explained by the changes of the lattice parameters. Halstead interpreted this large linear increase of the quadrupole coupling constant as being due to the anisotropic vibration of Li. We consider that the upward deviation of ω_Q of ^{117}In from the dashed line in Fig. 3 is also due to the anisotropic vibration of In. There is a large difference between the rates of change for ^{7}Li and ^{117}In as seen in Fig. 3. It implies that the effect of the anisotropic vibration is much smaller for In. We can qualitatively understand this difference to be due to the fact that the mass of In is much larger than that of Li and the ionic bond between In^{3+} and O^{2-} is stronger than that between Li$^+$ and O^{2-}. In the case of ^{181}Ta ($\leftarrow^{181}$Hf) at the Li site of LiNbO$_3$, the quadrupole frequency increases by only a few percent in the temperature range from 295 to 1100 K,[11] different from the present case of ^{117}In. The mass of Ta is larger than that of In and, moreover, the ionic bond between Ta^{5+} and O^{2-} is stronger than that between In^{3+} and O^{2-}, resulting in essentially no anisotropic vibration effect. Finally, we note that the ω_Q of ^{181}Ta ($\leftarrow^{181}$Hf) at the Li site of LiTaO$_3$ increases by about 11% as temperature increases from 295 K to about T_c (=938 K).[11] For a better understanding of the observed temperature dependence, the present study should be extended to measurement of ω_Q of ^{117}In and ^{111}Cd in LiNbO$_3$ and LiTaO$_3$ at high temperatures.

Well-defined static electric quadrupole interactions were observed at ^{117}In at the Li site in LiNbO$_3$ employing the TDPAC method. From the comparison of the quadrupole frequency ω_Q of ^{117}In with that of ^{111}Cd, both measured at 4.2 K, it is concluded that ^{117}In at the Li site in LiNbO$_3$ is predominantly ionic in nature. It was observed that the ω_Q of ^{117}In increases about 15% with increasing temperature in the range from 4.2 to 873 K, which is not explained only in terms of the temperature dependence of the lattice constants. The steep increase above room temperature is most probably ascribed to an increase of anisotropic vibration of ^{117}In^{3+} ions.

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