

# Different Crystal Chemistries of the $^{117}\text{Cd}$ $^{117}\text{In}$ and $^{111\text{m}}\text{Cd}$ $^{111}\text{Cd}$ Probes in $\text{LiNbO}_3$ and $\text{LiTaO}_3$ Studied by Time-Differential Perturbed-Angular-Correlation Technique

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# Different crystal chemistries of the $^{117}\text{Cd}\rightarrow^{117}\text{In}$ and $^{111m}\text{Cd}\rightarrow^{111}\text{Cd}$ probes in $\text{LiNbO}_3$ and $\text{LiTaO}_3$ studied by the time-differential perturbed-angular-correlation technique

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The nuclear-electric-quadrupole interactions at  $^{117}\text{In}$  and  $^{111}\text{Cd}$  nuclei arising from  $^{117}\text{Cd}$  and  $^{111m}\text{Cd}$ , respectively, each chemically introduced in ferroelectric  $\text{LiNbO}_3$  ( $T_C=1483\text{ K}$ ) and  $\text{LiTaO}_3$  ( $T_C=938\text{ K}$ ) polycrystals, were studied by measuring the time-differential perturbed angular correlation of  $\gamma$  rays over a temperature range from 4.2 to 1243 K. Well-defined, essentially single, static electric quadrupole frequencies were observed for  $^{117}\text{In}$  and  $^{111}\text{Cd}$  in the oxides. It has been established that both In and Cd occupy the Li sites of  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ . In the case of  $\text{LiTaO}_3$ , the temperature dependences of the quadrupole frequencies  $\omega_Q$  of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  clearly change at around  $T_C=938\text{ K}$ , reflecting the ferroelectric-to-paraelectric phase transition. In both oxides, it might be expected that the temperature dependence of  $\omega_Q$  of  $^{117}\text{In}$  would agree with that of  $^{111}\text{Cd}$ . However, it is so only at low temperatures, including room temperature. There is a significant difference at high temperatures:  $\omega_Q$  of  $^{117}\text{In}$  is strongly dependent on temperature, whereas  $\omega_Q$  of  $^{111}\text{Cd}$  is weakly dependent. It is considered that the Cd ions at the Li sites are in peculiar physicochemical states.

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## I. INTRODUCTION

Lithium niobate,  $\text{LiNbO}_3$ , is a ferroelectric with  $T_C=1483(10)\text{ K}$ ,<sup>1</sup> known as an important nonlinear optic material. Its optical properties are influenced by doping the material with metal impurities.<sup>2</sup> It is reported, for example, that In impurities increase the resistance of  $\text{LiNbO}_3$  to laser damage.<sup>3</sup> Knowledge of the lattice environment and the chemical state of dopants is essential for theoretical understanding of the impurity effects.

Previously, we performed time-differential perturbed-angular-correlation (TDPAC) measurements on  $^{117}\text{In}$  arising from  $^{117}\text{Cd}$  in a temperature range between 4.2 and 873 K and also on  $^{111}\text{Cd}$  arising from  $^{111m}\text{Cd}$  only at 4.2 K, both of which parent nuclides were chemically introduced in polycrystalline samples of  $\text{Li}_{0.995}\text{Cd}_{0.005}\text{NbO}_3$ , in order to obtain information about the valency of In and Cd in  $\text{LiNbO}_3$ .<sup>4</sup> We observed well-defined, essentially single, static electric quadrupole interactions at  $^{117}\text{In}$  and  $^{111}\text{Cd}$  in the samples. It was already reported that a trace amount of Cd and a small amount of In occupy the Li sites in  $\text{LiNbO}_3$ : Hauer *et al.*<sup>5</sup> studied, utilizing the TDPAC technique, the electric quadrupole interactions at  $^{111}\text{Cd}(\leftarrow^{111}\text{In})$  in undoped congruent  $\text{LiNbO}_3$  single crystals and at  $^{111}\text{Cd}(\leftarrow^{111m}\text{Cd})$  in undoped and 6-mol% Mg-doped congruent  $\text{LiNbO}_3$  single crystals after implantation of a maximum concentration of  $2\times 10^{18}$   $^{111}\text{In}/\text{cm}^3$  and of  $1\times 10^{18}$   $^{111m}\text{Cd}/\text{cm}^3$ , respectively. They ob-

served two quadrupole frequencies, differing 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 congruent  $\text{LiNbO}_3$  had been determined by the PIXE (proton-induced x-ray emission) channeling technique to be the Li site,<sup>6</sup> it was concluded that both In (a small amount) and Cd (a trace amount) occupy the Li site in undoped and Mg-doped  $\text{LiNbO}_3$ .<sup>5</sup> By comparing our result on  $^{111}\text{Cd}$  with that obtained by Hauer *et al.*, we confirmed that 0.5 mol% Cd occupy the Li site in  $\text{LiNbO}_3$ . Since the ratio 2.27(2) of the quadrupole frequency  $\omega_Q$  of  $^{117}\text{In}$  to that of  $^{111}\text{Cd}$ , both measured at 4.2 K, coincides with the value of 2.3 estimated on the assumption of purely ionic states of In and Cd, i.e.,  $\text{In}^{3+}$  and  $\text{Cd}^{2+}$ , we concluded that  $^{117}\text{In}$  and  $^{111}\text{Cd}$  at the Li sites in  $\text{LiNbO}_3$  are predominantly ionic in nature. It was observed that the  $\omega_Q$  of  $^{117}\text{In}$  increases gradually as the temperature increases from 4.2 K to room temperature and then increases more and more rapidly as the temperature increases to 873 K. This steep increase above room temperature was then thought not to be explained only in terms of the temperature dependence of the lattice constants and was interpreted as being due most probably to the anisotropic vibrational motions of the  $^{117}\text{In}^{3+}$  ions,<sup>4</sup> as has been argued for the Li ion in  $\text{LiNbO}_3$ .<sup>7</sup>

In this paper, we report the results of the TDPAC measurements on  $^{117}\text{In}$  and  $^{111}\text{Cd}$  in  $\text{Li}_{0.995}\text{Cd}_{0.005}\text{NbO}_3$  in an

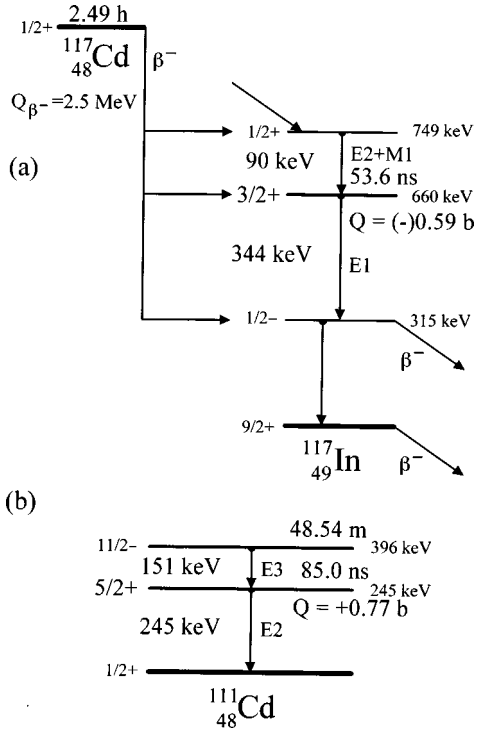


FIG. 1. Partial decay schemes of  $^{117}\text{Cd} \rightarrow ^{117}\text{In}$  and  $^{111m}\text{Cd} \rightarrow ^{111}\text{Cd}$ .

extended temperature range up to 1243 K and also the TDPAC results on polycrystalline samples of  $\text{Li}_{0.99}\text{Cd}_{0.01}\text{TaO}_3$  in the same temperature range. We have observed that in both oxides, although the temperature dependence of  $\omega_Q$  of  $^{117}\text{In}$  agrees with that of  $^{111}\text{Cd}$  at low temperatures including room temperature, they are very much different from each other at high temperatures. In the case of  $\text{LiNbO}_3$ , for example, the  $\omega_Q$  of  $^{117}\text{In}$  continues to increase concavely with increasing temperature, whereas that of  $^{111}\text{Cd}$  even decreases after it increases slowly as the temperature increases up to about 1000 K.

$\text{LiTaO}_3$  is isostructural to  $\text{LiNbO}_3$  and has  $T_C = 938(5)$  K,<sup>8</sup> which is included in the present temperature range. These two oxides belong to the  $R3c$  and  $R\bar{3}c$  space groups below and above their  $T_C$ 's, respectively. Although this oxide system has the  $\text{ABO}_3$  stoichiometry, it does not adopt the perovskite structure, but takes an ilmenite ( $\text{FeTiO}_3$ ) related structure,<sup>9</sup> because of the similar ionic sizes of  $\text{Li}^+$  (76 pm),  $\text{Nb}^{5+}$  (64 pm), and  $\text{Ta}^{5+}$  (64 pm).<sup>10</sup>

Figure 1 shows relevant parts of the decay schemes of  $^{117}\text{Cd} \rightarrow ^{117}\text{In}$  and  $^{111m}\text{Cd} \rightarrow ^{111}\text{Cd}$ . The 749-keV excited state of  $^{117}\text{In}$  is populated by the  $\beta^-$  decay of the parent  $^{117}\text{Cd}$  with a half-life of  $t_{1/2} = 2.49$  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.<sup>11</sup> The 396-keV excited state of  $^{111}\text{Cd}$ , i.e.,  $^{111m}\text{Cd}$  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.<sup>11</sup> 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)  $\gamma$  rays with a detector sorts out a set of  $^{117}\text{In}$  ( $^{111}\text{Cd}$ ) 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)  $\gamma$  rays with another detector permits determination of the spin precession frequency of  $^{117}\text{In}$  ( $^{111}\text{Cd}$ ) nuclei in the intermediate state and then determination of the magnitude of the splitting of the state. Thus the TDPAC of the 90- and 344-keV (151- and 245-keV)  $\gamma$  rays emitted in the successive  $\gamma$  transitions reveals the electric quadrupole interaction during the stay of  $^{117}\text{In}$  ( $^{111}\text{Cd}$ ) nuclei in the intermediate state.

## II. EXPERIMENTAL PROCEDURES

### A. Sample preparation

The parent nuclei  $^{117}\text{Cd}$  and  $^{111m}\text{Cd}$  were separately obtained by irradiating enriched  $^{116}\text{CdO}$  and  $^{110}\text{CdO}$ , respectively, with thermal neutrons at Kyoto University Research Reactor. The irradiated oxide was mixed with appropriate amounts of high-purity powders of  $\text{Li}_2\text{CO}_3$  and  $\text{Nb}_2\text{O}_5$  ( $\text{Ta}_2\text{O}_5$ ) for a chemical composition of  $\text{Li}_{0.995}\text{Cd}_{0.005}\text{NbO}_3$  ( $\text{Li}_{0.99}\text{Cd}_{0.01}\text{TaO}_3$ ). The mixture was pressed into a pellet and heated in air at 1100 °C for about 1 h, and thereby  $\text{Li}_{0.995}\text{Cd}_{0.005}\text{NbO}_3$  ( $\text{Li}_{0.99}\text{Cd}_{0.01}\text{TaO}_3$ ) was obtained. (Occasionally, the process was repeated once after the sample was repowdered. It was confirmed that the TDPAC spectra were independent of the repetition of the process.) Noticeable loss of neither the metals nor the source nuclides was observed during these heating processes. Owing to the short half-lives of  $^{117}\text{Cd}$  and  $^{111m}\text{Cd}$ , samples were prepared for each TDPAC-measurement temperature. As previously examined, the room-temperature x-ray-diffraction pattern of an  $\text{LiNbO}_3$  sample without cadmium prepared by an identical heating process showed a single phase of  $\text{LiNbO}_3$ . The room-temperature x-ray-diffraction pattern of an  $\text{Li}_{0.99}\text{Cd}_{0.01}\text{TaO}_3$  sample after the TDPAC measurement, being naturally similar to that of  $\text{LiNbO}_3$ , coincided with the standard profile of a single phase of  $\text{LiTaO}_3$ .

### B. TDPAC measurements

The time dependences of the coincidence counts  $N(\theta, t)$  of the 90–344-keV cascade  $\gamma$  rays for the samples containing  $^{117}\text{Cd}$  and of the 151–245-keV  $\gamma$  rays for  $^{111m}\text{Cd}$  were taken in a temperature range between 4.2 and 1243 K using a measurement system consisting of standard fast-slow electronic modules and four  $\text{BaF}_2$  scintillation detectors. Here  $\theta$  and  $t$  denote the angle and time interval, respectively, between the cascade  $\gamma$  rays. The directional anisotropy  $A_{22}G_{22}(t)$  was obtained according to Eq. (1):

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

The values of  $A_{22}$  for  $^{117}\text{In}(\leftarrow^{117}\text{Cd})$  and  $^{111}\text{Cd}(\leftarrow^{111m}\text{Cd})$  are  $-0.36$  and  $+0.18$ , respectively.<sup>12</sup>

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  $\omega_Q$  and the asymmetry parameter  $\eta$  of the EFG

through the interaction Hamiltonian. The quantities  $\omega_Q$  and  $\eta$  are defined as follows:  $\hbar\omega_Q = -eQV_{zz}/[4I(2I-1)]$  and  $\eta = (V_{xx} - V_{yy})/V_{zz}$ . The three components of the EFG in the principal-axis system are chosen such that  $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$ , and thus the asymmetry parameter  $\eta$  takes a value between 0 and 1. The perturbation factor  $G_{22}(t)$  has the form

$$G_{22}(t) = [1 + 4 \cos(\omega t)]/5, \quad (2)$$

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

and

$$G_{22}(t) = \sum_{n=0}^3 S_n(\eta) \cos(\omega_n t), \quad (4)$$

$$\omega_0 = 0, \quad \omega_n = 6\omega_Q C_n(\eta) \quad (n=1,2,3) \quad (5)$$

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

The  $S_n$  and  $C_n$  in Eqs. (4) and (5) are numerically calculated for a given asymmetry parameter. It should be noted that in the case of  $^{117}\text{In}$ ,  $G_{22}(t)$  contains only one frequency component and the values of  $\omega_Q$  and  $\eta$  cannot be determined independently from the spectrum, whereas in the case of  $^{111}\text{Cd}$ , they can be determined because the amplitudes  $S_n$  and the frequencies  $\omega_n$  in Eq. (4) are modified in a characteristic way as a function of  $\eta$ .

### III. RESULTS

The TDPAC spectra  $A_{22}G_{22}(t)$  measured at 4.2 and 1173 K of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  in  $\text{LiNbO}_3$  are shown in Fig. 2 and those for  $\text{LiTaO}_3$  are shown in Fig. 3. Note that the time scales for the  $^{117}\text{In}$ - and  $^{111}\text{Cd}$ -TDPAC spectra are different according to the different half-lives of the two probe nuclides in their intermediate states. The anisotropy is modulated in a manner characteristic of the single electric quadrupole interaction in polycrystalline samples depending on the spin value of the intermediate nuclear state. Although Hauer *et al.* analyzed their TDPAC spectra with two quadrupole frequencies [ $\omega_Q$  of the main component (a fraction of about 70%) is different from the minor by only about 5%,<sup>5</sup> as mentioned in the Introduction], we analyzed our TDPAC spectra of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  with a single quadrupole frequency having a Lorentzian distribution around the central value  $\bar{\omega}$ . For the  $^{117}\text{In}$  time spectra, the width of the distribution  $\Delta\omega$  was taken to be 2% of  $\bar{\omega}$  at  $T \leq T_C$  and 0 at  $T \geq T_C$ . In the case of  $^{111}\text{Cd}$  time spectra, it was taken to be 2% at  $T \leq 295$  K and 0 at  $T \geq 573$  K for  $\text{LiNbO}_3$  and was 2% at  $T \leq 773$  K and 0 at  $T \geq 873$  K for  $\text{LiTaO}_3$ . We assume the value of  $\eta$  for  $^{117}\text{In}$  is the same as that obtained for  $^{111}\text{Cd}$ , as assumed in Ref. 13; i.e.,  $^{117}\text{In}$  is subject to the same asymmetry of the EFG as  $^{111}\text{Cd}$  in the sample. The  $^{111}\text{Cd}$  time spectra are consistent with small values of  $\eta$ . Since the value of  $\omega_Q$  is not very sensitive to the value of  $\eta$  in a limited range, we set  $\eta=0$  for all the  $^{111}\text{Cd}$  and  $^{117}\text{In}$  spectra, which conforms to the fact that the Li site has a threefold symmetry axis and the EFG at this site is therefore axially symmetric. Equations (2) and (3) were fitted using the least-squares method to the observed time spectra for  $^{117}\text{In}$  in time ranges between 7 and 157 ns

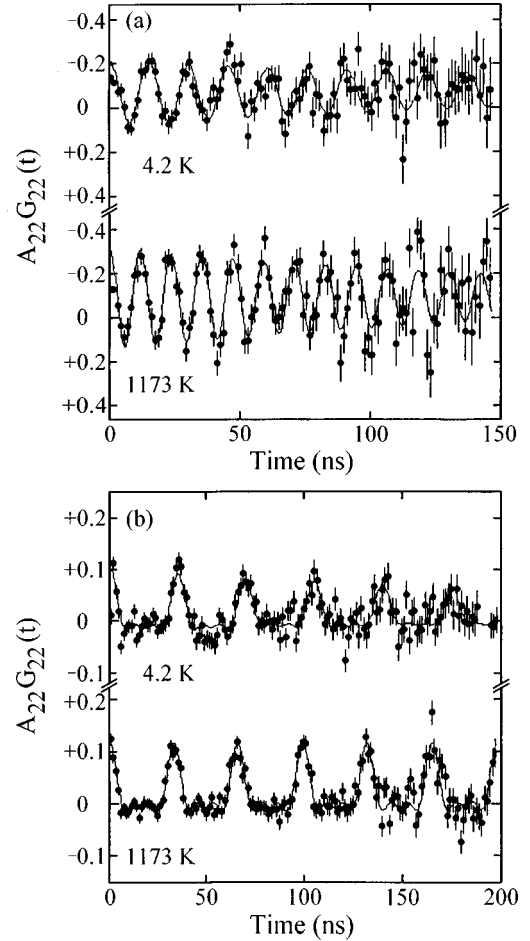


FIG. 2. (a) TDPAC spectra  $A_{22}G_{22}(t)$  of  $^{117}\text{In}(\leftarrow^{117}\text{Cd})$  in  $\text{Li}_{0.995}\text{Cd}_{0.005}\text{NbO}_3$  at 4.2 and 1173 K with the solid curves representing the least-squares fits of Eqs. (2) and (3) in the text and (b) the corresponding spectra of  $^{111}\text{Cd}(\leftarrow^{111m}\text{Cd})$  with the solid curves representing the fits of Eqs. (4) and (5) in the text.

and Eqs. (4) and (5) to those for  $^{111}\text{Cd}$  in time ranges between 0 and 180 ns. [In the case of  $^{117}\text{In}$ , the experimental points at  $t < 7$  ns were not used in the fit to avoid the influence of the huge prompt peak of  $N(\theta, t)$  at  $t=0$ .] The solid curves in Figs. 2 and 3 are the results of the fits.

In Fig. 4 are plotted the  $\omega_Q(T)/\omega_Q(0)$  values of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  in  $\text{LiNbO}_3$  vs temperature  $T$  as open squares and solid circles, respectively. The values of  $\omega_Q(0)$  were determined by a linear extrapolation. Those for  $\text{LiTaO}_3$  are shown in Fig. 5. The quadrupole frequency of  $^{117}\text{In}$  in  $\text{LiNbO}_3$  increases concavely by about 33% as the temperature increases from 4.2 to 1243 K, whereas the  $\omega_Q$  of  $^{111}\text{Cd}$  in the oxide increases in step with that of  $^{117}\text{In}$  at temperatures up to about 550 K, then increases very slowly, and at temperatures above around 1000 K tends to even decrease. As for  $\text{LiTaO}_3$ , the  $\omega_Q$  of  $^{117}\text{In}$  also increases concavely by about 45% with increasing temperature in the range from 4.2 to about 940 K, and then decreases gradually. The quadrupole frequency of  $^{111}\text{Cd}$  in this oxide increases in step with that of  $^{117}\text{In}$  at temperatures only up to room temperature, keeps increasing slowly at temperatures up to about 940 K, and then decreases linearly and rapidly. The temperature dependences of  $\omega_Q$  of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  in  $\text{LiTaO}_3$  clearly change at around  $T_C$

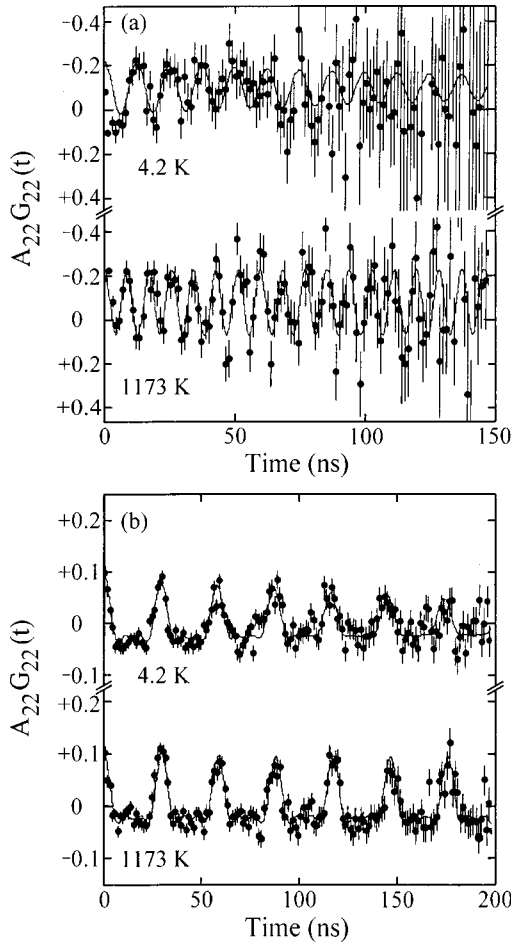


FIG. 3. (a) TDPAC spectra  $A_{22}G_{22}(t)$  of  $^{117}\text{In}(\leftarrow^{117}\text{Cd})$  in  $\text{Li}_{0.99}\text{Cd}_{0.01}\text{TaO}_3$  at 4.2 and 1173 K and (b) the corresponding spectra of  $^{111}\text{Cd}(\leftarrow^{111m}\text{Cd})$ . The solid curves represent the fits (see the caption of Fig. 2).

=938 K, reflecting the ferroelectric-to-paraelectric phase transition. In both oxides, the temperature dependence of  $\omega_Q$  of  $^{117}\text{In}$  agrees with that of  $^{111}\text{Cd}$  only at low temperatures, including room temperature. There is a significant difference at high temperatures. In the next section, this difference is discussed in terms of the anisotropic vibration of the probe nuclei, the chemical bonding, and also a lattice distortion owing to the large ionic radius of  $^{111}\text{Cd}^{2+}$ .

#### IV. DISCUSSION

As described in the Introduction, it has been established that a small amount of Cd occupies the Li sites in  $\text{LiNbO}_3$  from the combined experimental results of PIXE channeling<sup>6</sup> and TDPAC.<sup>4,5</sup> Considering that  $\text{LiTaO}_3$  is isostructural to  $\text{LiNbO}_3$  and that a well-defined  $\omega_Q$  of  $^{111}\text{Cd}$  was also observed in  $\text{LiTaO}_3$ , the temperature dependence of which being similar to that in  $\text{LiNbO}_3$  at temperatures below  $T_C$  of  $\text{LiTaO}_3$ , we conclude that a small amount of Cd also occupies the Li sites in  $\text{LiTaO}_3$ . Although the maximum recoil energy of  $^{117}\text{In}$  given in the  $\beta^-$  decay of  $^{117}\text{Cd}$  amounts to being as large as 22 eV (the recoil energies of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  given in the  $\gamma$  emissions are negligibly small), we

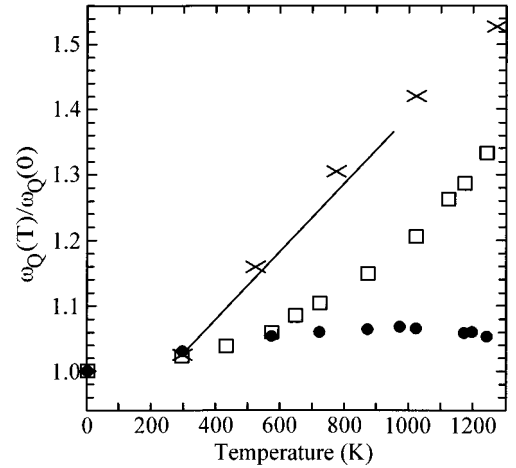


FIG. 4. Temperature dependences of the electric quadrupole frequencies  $\omega_Q$  of  $^{117}\text{In}$  (open squares) and  $^{111}\text{Cd}$  (solid circles) in  $\text{Li}_{0.995}\text{Cd}_{0.005}\text{NbO}_3$  together with that of the quadrupole coupling constant  $\nu_Q$  of  $^7\text{Li}$  (Ref. 7) (solid line) in  $\text{LiNbO}_3$ . The crosses represent the temperature dependence of  $V_{zz}$  at the Li site in  $\text{LiNbO}_3$  calculated by a simple point-charge model. The  $\nu_Q$  of  $^7\text{Li}$  and the calculated  $V_{zz}$  are scaled so as to coincide with our TDPAC data at room temperature.

consider that most of  $^{117}\text{In}$  remain at the Li sites where their parent nuclei  $^{117}\text{Cd}$  originally occupy, because if the nuclear recoil effect were significant, we should have observed several values of or extensively distributed  $\omega_Q$  of  $^{117}\text{In}$  in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ , but as a matter of fact we observed essentially single well-defined  $\omega_Q$  of  $^{117}\text{In}$  in the two oxides.

The electric quadrupole frequencies  $\omega_Q$  of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  at the Li sites in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  exhibit very interesting temperature dependences. As shown in Figs. 4 and 5, they first increase with increasing temperature, which temperature dependence is the opposite of those for  $ABO_3$  ferroelectric perovskites such as  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  (Ref. 14); together with the spontaneous polarization,  $V_{zz}$  for these perovskites

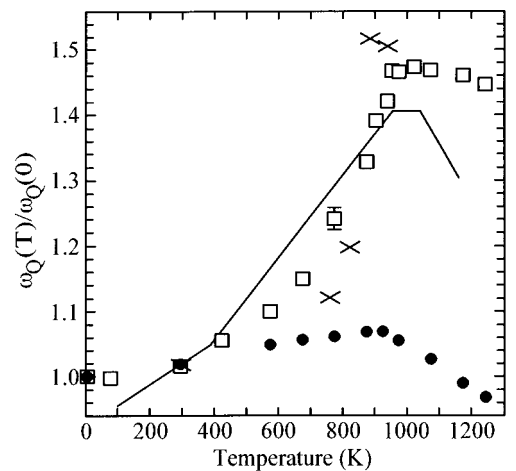


FIG. 5. Temperature dependences of the electric quadrupole frequencies  $\omega_Q$  of  $^{117}\text{In}$  (open squares) and  $^{111}\text{Cd}$  (solid circles) in  $\text{Li}_{0.99}\text{Cd}_{0.01}\text{TaO}_3$  together with that of the quadrupole coupling constant  $\nu_Q$  of  $^7\text{Li}$  (Ref. 15) (solid line) in  $\text{LiTaO}_3$ . The crosses are due to the point-charge calculation (see the caption of Fig. 4).

decreases as the temperature increases to  $T_C$ . For  $\text{LiNbO}_3$ , the  $\omega_Q$  of  $^{117}\text{In}$  continues to increase in the present temperature range, whereas that of  $^{111}\text{Cd}$  starts to decrease at a temperature about 1000 K. For  $\text{LiTaO}_3$ , the  $\omega_Q$ 's of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  reach maxima at around  $T_C$ , and then decrease, clearly indicating the ferroelectric-to-paraelectric phase transition at  $T_C$ . At temperatures above  $T_C$ , the  $\omega_Q$  of  $^{111}\text{Cd}$  in  $\text{LiTaO}_3$  more rapidly decreases with increasing temperature than that of  $^{117}\text{In}$ , which might be due to the same cause as that makes the  $\omega_Q$  of  $^{111}\text{Cd}$  in  $\text{LiNbO}_3$  decrease. In both oxides, the temperature dependence of  $\omega_Q$  of  $^{117}\text{In}$  agrees with that of  $^{111}\text{Cd}$  at low temperatures, including room temperature. However,  $\omega_Q$  of  $^{117}\text{In}$  is strongly temperature-dependent, whereas that of  $^{111}\text{Cd}$  is weakly dependent. We first note that the nuclear recoil of  $^{117}\text{In}$  is irrelevant to the specimen temperature and thus to the diverging temperature dependences of  $\omega_Q$  of  $^{117}\text{In}$  and  $^{111}\text{Cd}$ . In our previous paper,<sup>4</sup> we interpreted the steep increase of  $\omega_Q$  of  $^{117}\text{In}$  in  $\text{LiNbO}_3$  with increasing temperature as being most probably to the anisotropic vibrational motions of the  $^{117}\text{In}^{3+}$  ions. Therefore, if the anisotropic vibration is really the major reason for the temperature dependences of  $\omega_Q$  of both  $^{117}\text{In}$  and  $^{111}\text{Cd}$ , it will be able to explain the diverging temperature dependences of  $\omega_Q$  of the two probe nuclides. However, the anisotropic vibration<sup>7</sup> predicts the opposite:  $\omega_Q$  of  $^{111}\text{Cd}$  should be more strongly temperature dependent than that of  $^{117}\text{In}$  because of the smaller charge and mass of  $^{111}\text{Cd}^{2+}$  than those of  $^{117}\text{In}^{3+}$ . Therefore, the anisotropic vibration cannot be the major cause of the observed diverging temperature dependences of  $\omega_Q$ . It does not seem that the anisotropic vibration is also the right reason for the steep increase of  $\omega_Q$  of  $^{117}\text{In}$  in  $\text{LiNbO}_3$ .

In Figs. 4 and 5 are also shown as solid lines the  $^7\text{Li}$ -nuclear magnetic resonance (NMR) quadrupole coupling constant  $\nu_Q (=eV_{zz}Q/h)$  for  $\text{LiNbO}_3$  in the temperature range between 297 and 953 K (Ref. 7) and for  $\text{LiTaO}_3$  in the range between 100 and 1160 K (Ref. 15), both normalized to our respective data at room temperature. Roughly speaking, the temperature dependences of  $\nu_Q$  of  $^7\text{Li}$  in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  are much more similar to the corresponding ones of  $\omega_Q$  of  $^{117}\text{In}$  than to those of  $^{111}\text{Cd}$ . We have observed that at low temperatures, including room temperature, the temperature dependence of  $\omega_Q$  of  $^{117}\text{In}$  agrees with that of  $^{111}\text{Cd}$ . From these comparisons we guess that the In ions at the Li sites are more or less in similar physicochemical states to the Li ions themselves in the present temperature range, whereas the Cd ions at the Li sites are in different states at high temperatures, although they are in identical states as Li and In at low temperatures. For example, the chemical bonding of Cd with O could be different from those of Li and In with O at high temperatures or Cd could be in a different lattice environment at high temperatures, although they occupy the Li sites. Here we should note the following. By saying that the In ions at the Li sites are more or less in similar physicochemical states to the Li ions, we do not mean that heavy In ions jump from their original Li sites into other sites, as some of the Li ions are considered to jump into normally vacant metal sites, forming interstitials, or jump back to the normal Li sites (a little more detail about the jumping motion of Li is described below). We

suppose that the normal Li site is equivalent or similar to the interstitial site, so that the value of  $V_{zz}$  at  $^7\text{Li}$  at the normal Li site is identical to that at the interstitial site. We thus mean that the In ions at the normal Li sites or those that happen to be placed at the interstitial sites are more or less in similar physicochemical states to the Li ions at the normal Li sites or at the interstitial sites.

The electric quadrupole interactions at the Li sites in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  have also been studied by Catchen *et al.*<sup>16,17</sup> over a wide temperature range from 295 to about 1700 K, using the TDPAC method on the  $^{181}\text{Ta}$  ( $\leftarrow^{181}\text{Hf}$ ) probe. It is interesting to compare our results on  $\omega_Q$ , the asymmetry parameter  $\eta$  of the EFG and the width  $\Delta\omega$  of the Lorentzian distribution of  $\omega_Q$  (our  $\Delta\omega/\bar{\omega}$  corresponds to their  $\delta$ ) with their results. The value of  $\omega_Q$  of  $^{181}\text{Ta}$  at the Li site in  $\text{LiNbO}_3$  increases monotonically by several percent in the temperature range from 295 to about 1700 K, whereas the  $\omega_Q$  of  $^{117}\text{In}$  increases by 30% in the temperature range from 295 to 1243 K, but that of  $^{111}\text{Cd}$  increases by 2% in the temperature range from 295 to about 1000 K and above it decreases. The  $\omega_Q$  of  $^{181}\text{Ta}$  in  $\text{LiTaO}_3$  increases concavely by about 12% as the temperature increases from 295 K to  $T_C$  ( $=938$  K) and above  $T_C$  decreases slowly, whereas those of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  increase by 44% and 5%, respectively, in the temperature range from 295 K to  $T_C$ , and above  $T_C$  they decrease slowly and much rapidly, respectively. Although the rate of change is very different among  $^{181}\text{Ta}$ ,  $^{117}\text{In}$ , and  $^{111}\text{Cd}$ , these qualitative features for  $^{181}\text{Ta}$  look more like those for  $^{117}\text{In}$  than for  $^{111}\text{Cd}$ , indicating that In and Ta may be in similar states, and indicating again that the Cd ions at the Li sites are in distinctive physicochemical states at high temperatures. The  $\eta$  values for  $^{181}\text{Ta}$  in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  are relatively large at room temperature, each about 0.25, in spite of the fact that the Li site has a threefold symmetry axis and the EFG at this site is thus axially symmetric. Those  $\eta$  values for  $^{181}\text{Ta}$  decrease with increasing temperature. For  $\text{LiTaO}_3$ , it reaches values of less than 0.1, reasonably close to zero, at temperatures above  $T_C$ . On the other hand, in our case of  $^{117}\text{In}$  and  $^{111}\text{Cd}$ , the  $\eta$  values are considerably small in the whole temperature range studied; the  $\eta$  value for  $^{117}\text{In}$  was actually assumed to be equal to that for  $^{111}\text{Cd}$ , but the  $\eta$  value for  $^{117}\text{In}$  at low temperatures could be as large as that for  $^{181}\text{Ta}$  because, as considered above, In and Ta may be in similar physicochemical states. The  $\Delta\omega/\bar{\omega}$  values for  $^{181}\text{Ta}$  in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  are large at room temperature, each about 0.1, and decrease with increasing temperature, whereas the  $\Delta\omega/\bar{\omega}$  values for  $^{117}\text{In}$  and  $^{111}\text{Cd}$  in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  are small, 0.02, even at 4.2 K, and for  $\text{LiTaO}_3$  they are zero at temperatures above  $T_C$ .

Catchen and Spaar<sup>16</sup> pointed out the abnormality of the increasing temperature dependence of  $\omega_Q$  of  $^{181}\text{Ta}$ , comparing with the temperature dependences seen for  $ABO_3$  ferroelectric perovskites, but did not give an explanation to it. However, they gave a reasonable explanation to the temperature dependences of  $\eta$  and  $\Delta\omega/\bar{\omega}$  in terms of an order-disorder model. This model suggests that some of the Li ions occupy normally vacant metal sites, i.e., there are interstitial Li sites, and the existence of the interstitials breaks the axial symmetry associated with the Li sites in the ordered ferroelectric phase where the number of Li atoms in the normal Li sites exceeds the number of the interstitials. In the disordered

paraelectric phase those numbers are equal and the axial symmetry is recovered. [A pair of Li and Nb (Ta) forms an electric dipole. The dipoles formed by the normal-site Li ions and Nb (Ta) ions are oriented in a particular direction, whereas those formed by the interstitial Li ions and Nb (Ta) ions are oriented in the opposite direction. In the disordered phase, those two types of dipoles cancel with each other because of the equal number of the normal-site and interstitial Li ions. In the ordered phase, some of the dipoles formed with the normal-site Li ions remain and the spontaneous polarization exists.] Only with this model, however, it does not seem possible to understand the difference between the small  $\eta$  and  $\Delta\omega/\bar{\omega}$  values for  $^{117}\text{In}$  and  $^{111}\text{Cd}$  and those large values for  $^{181}\text{Ta}$ .

We now discuss the valency of In and Cd at the Li sites in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ . One of the results of a first-principles calculation on  $\text{LiNbO}_3$  by Ching *et al.*<sup>18</sup> is that the derived valence state of the oxide is  $\text{Li}^{0.98}\text{Nb}^{3.67}(\text{O}^{-1.55})_3$ , showing that Li is essentially pure ionic, although there is a significant covalent bonding character between Nb and O. From the conjecture that the In ions are in similar physicochemical states to the Li ions and so are the Cd ions at low temperatures, we expect that In is also highly ionic, and so is Cd at least at low temperatures, although there might be a significant covalent bonding character between Cd and O at high temperatures.

In order to examine this expectation about the valency of In and Cd, we evaluate the ratio of  $\omega_Q$  of  $^{117}\text{In}$  to that of  $^{111}\text{Cd}$ ,  $\omega_Q(^{117}\text{In})/\omega_Q(^{111}\text{Cd})$ , employing the phenomenological model of Sternheimer.<sup>19</sup> In his model,  $V_{zz}$  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 noncubic 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 noncubic symmetrically. The quantities  $R$  and  $\gamma_\infty$  are 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 a situation where In and Cd exist as being purely ionic, i.e.,  $\text{In}^{3+}$  and  $\text{Cd}^{2+}$ , both having the (same) closed-shell electron configuration, and furthermore where In and Cd are in the same lattice environment, the ratio  $\omega_Q(^{117}\text{In})/\omega_Q(^{111}\text{Cd})$  is expressed simply as

$$\frac{\omega_Q(^{117}\text{In})}{\omega_Q(^{111}\text{Cd})} = \frac{10}{3} \frac{Q(^{117}\text{In})}{Q(^{111}\text{Cd})} \frac{1 - \gamma_\infty(^{117}\text{In})}{1 - \gamma_\infty(^{111}\text{Cd})}. \quad (6)$$

Using the calculated values of  $\gamma_\infty(\text{In}) = -25.8$  and  $\gamma_\infty(\text{Cd}) = -29.3$ ,<sup>4,20</sup> the absolute value of the ratio is evaluated to be 2.3. The values of the experimental ratio for  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  in the temperature ranges from 4.2 to about 550 K and from 4.2 K to room temperature, respectively, are within  $\pm 0.03$  of 2.27, and thus at low temperatures, including room temperature, agree very well with this calculated value. These agreements support the indicated highly ionic nature of In and Cd at low temperatures and moreover indicate that In and Cd are in the same lattice environment at low temperatures. Corresponding to the diverging temperature dependences of  $\omega_Q$  of  $^{117}\text{In}$  and  $^{111}\text{Cd}$ , their ratio  $\omega_Q(^{117}\text{In})/\omega_Q(^{111}\text{Cd})$  for  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  at high tem-

peratures deviates from the calculated value of 2.3; for example, the experimental ratio for  $\text{LiTaO}_3$  at 1243 K is 3.43(1).

We can ascribe the characteristic temperature dependence of  $\omega_Q$  of  $^{111}\text{Cd}$  to an appearance of covalency in the Cd-O at high temperatures or to a lattice relaxation around Cd at high temperatures. At present, however, we are not certain which is the right reason, provided that there is no other cause. As for the former possibility, covalent bonding effects on the EFG at  $^{111}\text{Cd}$  were in fact proposed<sup>21</sup> in order to explain significant differences found in the values of  $V_{zz}$  and  $\eta$ , and their temperature dependences for the two TDPAC-probe nuclei,  $^{111}\text{Cd}(\leftarrow^{111}\text{In})$  and  $^{181}\text{Ta}(\leftarrow^{181}\text{Hf})$ , both at the Ti sites in  $\text{TiO}_2$ . Accordingly, covalency in the Cd-O bonding may play an important role in changing the temperature dependence of  $\omega_Q$  of  $^{111}\text{Cd}$  in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ . However, there are two indirect objections to this interpretation. One is that the diffraction-derived structural data on  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  (Refs. 22–25) show that, roughly speaking, the distance between a Li ion and each oxygen in the octahedron surrounding it becomes larger with increasing temperature, indicating the covalency between Cd at the Li site and O, if it exists at all, may become less important at high temperatures. Another is that in the TDPAC studies of hyperfine magnetic interactions at  $^{117}\text{In}(\leftarrow^{117}\text{Cd})$  (Ref. 26) and  $^{111}\text{Cd}(\leftarrow^{111}\text{In})$  (Ref. 27), both at the tetrahedral sites in a spinel  $\text{Fe}_3\text{O}_4$ , a slightly larger value of the hyperfine magnetic field at  $^{117}\text{In}$  than at  $^{111}\text{Cd}$  has been observed and qualitatively explained as due to the covalency of  $\text{In}^{3+}$  being larger than that of  $\text{Cd}^{2+}$ .<sup>26</sup>

We next consider the temperature dependence of  $\omega_Q$  of  $^{111}\text{Cd}$  in terms of a structural relaxation around the Cd ion. We note the large ionic radius of  $\text{Cd}^{2+}$ , 95 pm, compared to those of  $\text{Li}^+$ , 76 pm, and of  $\text{In}^{3+}$ , 80 pm (the ionic radii are effective ones).<sup>10</sup> The sum of the two ionic radii of  $\text{Cd}^{2+}$  and  $\text{O}^{2-}$  (140 pm) (Ref. 10) is 235 pm, which is quite larger than the shortest Li-O distances in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  at room temperature, 206.8 pm (Ref. 22) and 204.1 pm (Ref. 25), respectively, though the sum of the ionic radii of  $\text{Li}^+$  and  $\text{O}^{2-}$ , 216 pm, is already larger than either of them. We thus imagine that Cd is compelled to be situated in a narrow space formed by the surrounding oxygens: Owing to the tight close-packed arrangement of oxygen ions, Cd seems not to be able to push the surrounding oxygens away at low temperatures. However, as the temperature increases, the crystal is softened and a structural relaxation around Cd would take place. If each oxygen surrounding Cd is pushed away maintaining the axial symmetry around Cd, the value of  $V_{zz}$  at  $^{111}\text{Cd}$  and thus  $\omega_Q$  of  $^{111}\text{Cd}$  reduce.

Finally, we comment on the unusual temperature dependence of  $\omega_Q$  of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ , i.e., the increasing nature of the temperature dependence of  $\omega_Q$ . We estimate the temperature dependences of  $V_{zz}$  at the Li sites in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  by means of their diffraction-derived structural data<sup>22–25</sup> and a point-charge model, which takes into account the charges on only the first nearest-neighbor ions surrounding the probe nucleus.<sup>28</sup> This model was quite successful in reproducing the variation of  $V_{zz}$  at the Nb site in the  $\text{LiNbO}_3$ - $\text{LiTaO}_3$  solid-solution system with composition and the temperature dependence of  $V_{zz}$  at the

Nb site in  $\text{LiNbO}_3$ , both measured with the  $^{93}\text{Nb}$ -NMR.<sup>29</sup> By a consideration of Catchen and Spaar<sup>16</sup> that  $V_{zz}$  may not be strongly coupled to the order parameter for the phase transition in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ , use of the point-charge model with the diffraction-derived structural data that do not reflect the existence of the interstitial Li ions might be justified for the calculation of  $V_{zz}$ . The present calculation reproduces the order of magnitude of  $V_{zz}$  and an important feature that the value of  $V_{zz}$  at the Li site in  $\text{LiNbO}_3$  is smaller than that for  $\text{LiTaO}_3$ . In Figs. 4 and 5 are shown as crosses the calculated  $V_{zz}$  at the Li sites in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ , respectively, normalized to our corresponding TDPAC data at room temperature. The point-charge calculation roughly reproduces the temperature dependences of the  $^7\text{Li}$ -NMR  $\nu_Q$  for  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ . Although the present calculation is too simple and its results should not be taken seriously, it suggests that the temperature dependence of the lattice constants is very much related to the increasing nature of the temperature dependence of  $\omega_Q$ . However, for the clear understanding of the generally increasing temperature dependence of  $\omega_Q$  and also of the distinctive temperature dependence of  $\omega_Q$  of  $^{111}\text{Cd}$ , accurate theoretical calculations are certainly desired.

## V. CONCLUSIONS

The nuclear-electric-quadrupole interactions at  $^{117}\text{In}$  and  $^{111}\text{Cd}$  nuclei arising from  $^{117}\text{Cd}$  and  $^{111m}\text{Cd}$ , respectively, each chemically introduced in ferroelectric  $\text{LiNbO}_3$  ( $T_C = 1483\text{ K}$ ) and  $\text{LiTaO}_3$  ( $T_C = 938\text{ K}$ ) polycrystals, were studied by measuring the time-differential perturbed angular correlation of  $\gamma$  rays over the temperature range from 4.2 to 1243 K. Well-defined, essentially single, static electric quadrupole frequencies were observed for  $^{117}\text{In}$  and  $^{111}\text{Cd}$  in the oxides. It has been established that both In and Cd occupy the Li sites of  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ . In the case of  $\text{LiTaO}_3$ ,

the temperature dependences of the quadrupole frequencies  $\omega_Q$  of  $^{117}\text{In}$  and  $^{111}\text{Cd}$  clearly change at around  $T_C = 938\text{ K}$ , reflecting the ferroelectric-to-paraelectric phase transition.

In both oxides, the temperature dependence of  $\omega_Q$  of  $^{117}\text{In}$  agrees with that of  $^{111}\text{Cd}$  only at low temperatures including room temperature. At high temperatures there is a significant difference:  $\omega_Q$  of  $^{117}\text{In}$  is strongly dependent on temperature, whereas  $\omega_Q$  of  $^{111}\text{Cd}$  is weakly dependent. From the highly ionic nature of the Li ion, suggested by a first-principles calculation<sup>18</sup> on  $\text{LiNbO}_3$ , it is considered that In and Cd are also highly ionic. However, the comparison among the temperature dependences of  $\nu_Q$  of  $^7\text{Li}$  (Refs. 7 and 15),  $\omega_Q$ 's of  $^{117}\text{In}$  ( $\leftarrow^{117}\text{Cd}$ ) and  $^{111}\text{Cd}$  ( $\leftarrow^{111m}\text{Cd}$ ), and  $\omega_Q$  of  $^{181}\text{Ta}$  ( $\leftarrow^{181}\text{Hf}$ ) (Refs. 16 and 17), all probes at the Li sites in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ , indicates that there may be a significant covalent bonding character between Cd and O at high temperatures and/or there may be a structural relaxation around Cd starting to take place at a temperature above room temperature, because of the large ionic radius of  $^{111}\text{Cd}^{2+}$ .

A simple point-charge model calculation with the diffraction-derived structural data<sup>22-25</sup> suggests that the temperature dependence of the lattice constants is very much related to the increasing nature of the temperature dependence of  $\omega_Q$ . However, for the clear understanding of the generally increasing temperature dependence of  $\omega_Q$  and also of the characteristic temperature dependence of  $\omega_Q$  of  $^{111}\text{Cd}$ , accurate theoretical calculations are needed.

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The value in Ref. 23 would change the results of point-charge calculations in Ref. 7 very much.

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