PHYSICAL REVIEW B VOLUME 48, NUMBER 1 1 JULY 1993-I

Raman-scattering study of the II-III phase transition in TlH_2AsO_4

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(Received 29 January 1993)

The Raman spectra of polycrystalline TlH_2AsO_4 were measured between 15 and 300 K. There was a strong analogy between the Raman spectrum of TlH_2AsO_4 ($T_L = 250$ K) and that of TlH_2PO_4 (space group $P2_1/a\text{-}C_{2h}^5$ at room temperature, $T_L = 230$ K) in their paraelectric phase-II structures (above T_L). This similarity persists for their respective phase-III structures (below T_L), indicating that we have observed the equivalent transition at T_L in both compounds. The number of low-lying vibrational modes above and below T_L reveals that the II-III transition in TlH_2AsO_4 and TlH_2PO_4 is accompanied by a multiplicative increase of the size of the primitive unit cell, probably doubling of the cell. This result shows that the II-III transition in the TlH_2PO_4 family of crystals is not a ferroelectric [T. Fernandez-Diaz, A. de Andres, and C. Prieto, Ferroelectrics **92**, 71 (1989)], but an antiferroelectric [N. Yasuda, S. Fujimoto, and T. Asano, Phys. Lett. **76A**, 174 (1980); R. J. Nelmes, Solid State Commun. **39**, 741 (1981)].

INTRODUCTION

Thallium dihydrogen phosphate, TlH_2PO_4 (TDP), undergoes a structural phase transition at 357 K (the upper phase-transition point T_U)[1-3] and at 230 K (the lower phase-transition point T_L).[4-16] The crystal in the high-temperature phase-I structure ($T > T_U$) is orthorhombic with the space group of $Pcan\text{-}D_{2h}^{14}$ ($Z = 4$).[3] The ferroelastic phase transition occurs at T_U with decreasing temperature.[1-3] The crystal in the ferroelastic phase-II structure ($T_U > T > T_L$) is monoclinic with a space group of $P2_1/a\text{-}C_{2h}^5$ ($a = 14.308$ Å, $b = 4.518$ Å, $c = 6.516$ Å, $\beta = 91.76°$, and $Z = 4$ at room temperature).[12] The phase-III structure appears below T_L, where the crystal is monoclinic and the space group has been suggested to be $Pa\text{-}C_S^2$,[12] but reported to be a C-centered cell ($Z = 16$ in the crystallographic unit cell; $Z = 8$ in the primitive unit cell).[13] Raman-scattering studies[6] and x-ray-diffraction measurements[13] have shown that the transitions at 230 K in TDP and around 353 K in TlD_2PO_4 (DTDP) are structurally equivalent. Direct evidence for antiferroelectricity, in the form of double hysteresis loops, has been obtained for DTDP III (at 222 K), while in TDP III only antipolar characteristics were reported due to the dielectric breakdown before undergoing the field-enforced transition from the antiferroelectric to the ferroelectric state.[11] Therefore, the state of TDP III had been believed to be antiferroelectric. On the contrary, Fernandez-Diaz, de Andres, and Prieto claimed that the TDP III is ferroelectric by measuring the released charge.[15] Raman spectra on polycrystal and nonoriented single-crystal TDP and DTDP have been reported in the temperature range 77–400 K by Huong *et al.*[5] and Vignalou *et al.*,[6] but no assignment of the vibrational modes was made.[5,6] de Andres and Prieto performed the Raman scattering on oriented single-crystal TDP at temperatures between 80 and 300 K.[14] Based on the factor group analysis of TDP II, they obtained the Raman spectra of symmetry species of A_g and B_g modes above 230 K, but the group-theoretical analysis was not made for the Raman spectra of TDP III.

On the other hand, thallium dihydrogen arsenate, TlH_2AsO_4 (TDA), has been little investigated. Milia has found the structural phase transition of TDA at 249 K.[17] He regarded the transition as a ferroelectric from the observation of the presence of two ^{75}As NQR frequencies below 249 K. Blinc *et al.* studied proton spin-lattice relaxations and pointed out the order-disorder nature of the protons on the O—H $\cdots$ O bonds in the transition at 251 K.[18] The x-ray-diffraction measurement indicated that TDA is monoclinic ($a = 14.544$ Å, $b = 4.645$ Å, $c = 6.626$ Å, and $\beta = 92.47°$) and is nearly isomorphous with TDP at room temperature, but full structural analyses have not been performed.[19] Narasaiah *et al.* have studied the heavy-atom structure of TlD_2AsO_4 (DTDA), which was found to be isomorphous with TDP at room temperature.[20] Recently, Lee and Kim studied the dielectric properties of TDA from 80–433 K and found that TDA undergoes two structural phase transitions at 250 K (T_L) and around 390 K (T_U).[21] Comparing the temperature dependence of the dielectric constant of TDA with that of TDP, they suggested an antiferroelectric phase transition at 250 K and a ferroelastic phase transition around 390 K. Lee *et al.* confirmed the antipolar characteristic below 250 K by hysteresis loop study.[22] Recent calorimetric studies of TDA from 10–300 K showed only one lower transition around 250 K.[23] However, the upper phase transition of TDA around 390 K has been reported to be strongly dependent on the experimental conditions.[21]

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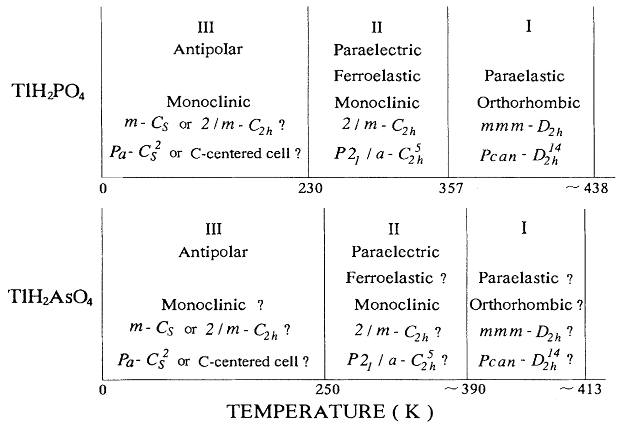

	III	II	I
TlH_2PO_4	Antipolar Monoclinic m-C_s or $2/m$-C_{2h} ? Pa-C_s^2 or C-centered cell ?	Paraelectric Ferroelastic Monoclinic $2/m$-C_{2h} $P2_1/a$-C_{2h}^5	Paraelastic Orthorhombic mmm-D_{2h} $Pcan$-D_{2h}^{14}

0 230 357 ~438

	III	II	I
TlH_2AsO_4	Antipolar Monoclinic ? m-C_s or $2/m$-C_{2h} ? Pa-C_s^2 or C-centered cell ?	Paraelectric Ferroelastic ? Monoclinic $2/m$-C_{2h} ? $P2_1/a$-C_{2h}^5 ?	Paraelastic ? Orthorhombic ? mmm-D_{2h} ? $Pcan$-D_{2h}^{14} ?

0 250 ~390 ~413

TEMPERATURE (K)

FIG. 1. Phase-transition sequences of TlH_2PO_4 and TlH_2AsO_4. See text about the lower and the upper phase transitions for TlH_2PO_4 and TlH_2AsO_4. Thermal decomposition takes place around 438 K for TlH_2PO_4 and around 413 K for TlH_2AsO_4 (Refs. 19 and 21). The onset temperature of the decomposition process is very strongly dependent on the experimental conditions.

Figure 1 shows the present experimental situations about the phase-transition sequences of TDP and TDA. Judging from the analogy of the temperature dependence of dielectric constants in TDP and TDA and from the antipolar character below T_L, it is believed that TDP and TDA belong to the same family.[21,22] However, it is uncertain whether or not the II-III transition of TDA is equivalent to that of TDP, because the complete determination of the structure of TDA above and below 250 K has not appeared in the literature. In this paper we will show by Raman spectroscopy that the structural phase transition of TDA at 250 K is equivalent to that of TDP at 230 K.

EXPERIMENT

Small TDA single crystals of good optical quality were grown by slow evaporation from an aqueous solution as described previously.[21,22] They were quite thin and very brittle, and so were ground to form a disk-shaped pellet for Raman-scattering studies. Raman excitation was induced via the 5145 Å line of an argon-ion laser which was focused through a cylindrical lens to avoid local heating of the sample. The scattered light was dispersed by a double-grating monochromator (Spex 1403) and detected by a GaAs PM tube (Hamamatsu R943-02). The bandpass was 2 $\mathrm{cm^{-1}}$ for every measurement. Raman spectra were obtained from polycrystalline samples which were mounted on the cold finger of a closed cycle He refrigerator with Crycon grease. The temperature was measured using a silicon diode and stabilized within ± 0.5 K during each measurement.

RESULTS AND DISCUSSION

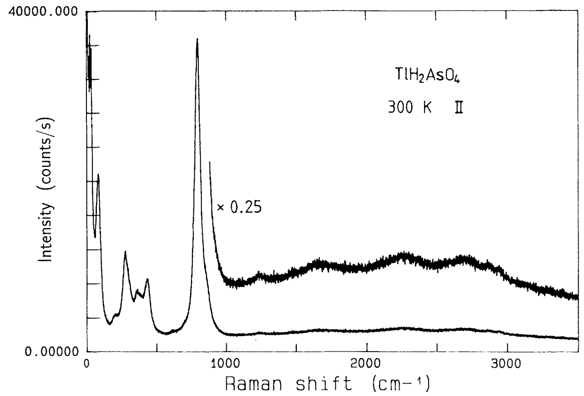

FIG. 2. Raman spectrum of polycrystalline TlH_2AsO_4 at 300 K (phase II). See the Raman spectrum of polycrystalline TlH_2PO_4 at 300 K (phase II) in Fig. 1 of Ref. 5 and compare.

Figure 2 shows the Raman spectrum of polycrystalline TDA in the frequency range 10–3500 $\mathrm{cm^{-1}}$ at 300 K. Comparison of the Raman spectrum of TDA at 300 K (Fig. 2) with that of TDP at 300 K (Fig. 1 in Ref. 5) reveals a strong analogy in their paraelectric phase-II structures, indicating more definitely that TDA II is isomorphous with TDP II. Isomorphism between the two compounds is manifested more clearly when we compare the Raman spectrum of TDA in the frequency range to 500 $\mathrm{cm^{-1}}$ (Fig. 3) with that of TDP in the frequency range to 600 $\mathrm{cm^{-1}}$ (Fig. 3 in Ref. 5). Since there is a one-to-one correspondence between the spectral lines of TDA and those of TDP in the paraelectric phase-II structure, the spectral lines of TDA are thus assigned with reference to those of TDP. In TDP, the internal modes of PO_4^{3-} ions correspond to the intermediate range from 300 to 1200 $\mathrm{cm^{-1}}$, and at lower frequencies below 300 $\mathrm{cm^{-1}}$ the external vibrations (lattice modes) appear.[5,14] In TDA, the AsO_4^{3-} internal vibrations (250–1000 $\mathrm{cm^{-1}}$) and the lattice modes (0–250 $\mathrm{cm^{-1}}$) in which AsO_4^{3-} groups are involved, shift to lower frequencies when As is substituted for P. Frequency changes are summarized in Table I. The vibrational frequencies of intramolecular and intermolecular motions in TDP are almost harmonically shift-

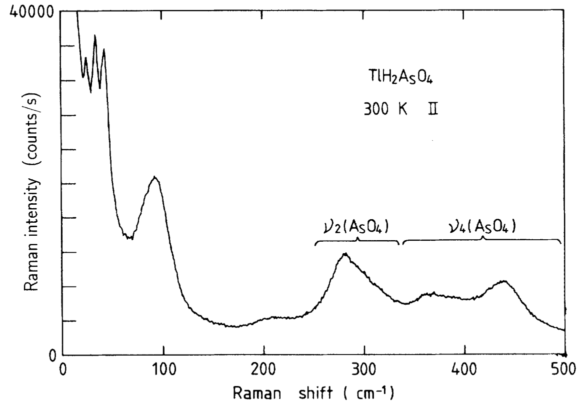

FIG. 3. Low-frequency Raman spectrum of polycrystalline TlH_2AsO_4 at 300 K (phase II). See the Raman spectrum of polycrystalline TlH_2PO_4 at 298 K (phase II) in Fig. 3 of Ref. 5 and compare.

TABLE I. Assignment of Raman-active mode frequencies in $\mathrm{TlH_2PO_4}$ and $\mathrm{TlH_2AsO_4}$ at 300 K.

	Mode frequency ($\mathrm{cm^{-1}}$)				
$\mathrm{TlH_2PO_4}$ II[a]	$\mathrm{TlH_2PO_4}$ II[b]		$\mathrm{TlH_2AsO_4}$ II[c]		
	A_g	B_g			Assignment
28		27	25		
36	36	36	34		
47	45	45	43		Lattice vibrations of $\mathrm{Tl^{+}\text{-}H_2PO_4^{-}/H_2AsO_4^{-}}$
		58			
88	85.5				
105	105	102	92		
238	242	242	209		
360	362	365	280	ν_2	Internal vibrations of $\mathrm{PO_4^{3-}/AsO_4^{3-}}$
480	483	487	370	ν_4	
550	546	544	440	ν_4	
570	568			ν_4	
920	920	920	799	ν_1	
1105	1085	1107	~863	ν_3	
			~1229		OH vibrations
~1690			~1664		
~2220			~2267		
~2600			~2731		

[a] Mode frequencies are taken from Figs. 1, 3, and 5 of Ref. 5.

[b] From Ref. 14.

[c] This work.

ed in TDA, whereas the three broad hydrogen-mode frequencies (1400–3500 $\mathrm{cm^{-1}}$) seem to remain almost the same, if we take into consideration the broad bandwidth of OH vibrations. This fact indicates that the hydrogen motions are strongly anharmonic. Because TDP II belongs to monoclinic $P2_1/a\text{-}C_{2h}^5$, we can say with certainty that TDA II also belongs to monoclinic $P2_1/a\text{-}C_{2h}^5$. In addition, the elastic state of TDA II can be considered as a ferroelastic. The space group $P2_1/a\text{-}C_{2h}^5$ is included in the point group $2/m\text{-}C_{2h}$, whose Raman-active irreducible representations are classified by nonpolar A_g and B_g modes.[14,15,24] Therefore, Raman spectra of polycrystalline TDA II include A_g and B_g modes. According to the factor group analysis of TDP II by de Andres and Prieto, there are 18 ($9A_g+9B_g$) Raman-active optic lattice modes.[14] In TDP II, all of the predicted modes were not observed, probably due to the very closeness of several distinct modes and the accidental similarity between A_g and B_g modes.[14] In TDA II, five optic lattice modes at 25, 34, 43, 92, and 209 $\mathrm{cm^{-1}}$ clearly appear. The broad peak at about 92 $\mathrm{cm^{-1}}$ may be a superposition of at least four modes, as will be shown in the Raman spectrum at 15 K.

Figure 4 shows the Raman spectra of TDA in the frequency range 10–130 $\mathrm{cm^{-1}}$ from 15 to 300 K. They evolve very similarly as observed in TDP in the frequency range to 150 $\mathrm{cm^{-1}}$ (see Fig. 5 in Ref. 5). In other words, the strong similarity of Raman spectra between TDA and TDP persists even for the respective phase-III structures, proving that we have observed the equivalent transition in both compounds. Therefore, TDA III is confirmed to be isomorphous with TDP III, although the structural information on TDA III is not available as yet. The following facts are noted from Fig. 4.

(i) The evolution of Raman spectra changes smoothly around the transition temperature 250 K, so it is difficult to determine the order of the II-III phase transition, in spite of the weak first-order nature from the dielectric constant measurements.[21] The II-III transition point in TDA at atmospheric pressure seems to be close to a tricritical point, as pointed out in the II-III transition of TDP by Matsuo and Suga.[7]

(ii) Each spectral line or band shifts or splits into two or more lines on passing through 250 K, indicating the multiplicative increase of the size of the primitive unit cell in the II-III phase transition. Below 65 $\mathrm{cm^{-1}}$, three peaks at 25, 34, and 43 $\mathrm{cm^{-1}}$ were observed at 300 K. Six peaks at 32, 38, 45, 50, 55, and 60 $\mathrm{cm^{-1}}$ clearly appeared at 15 K, so the counting of the numbers of low-lying vibrational modes indicates that the doubling of the primitive unit cell takes place. Similarly, the broad peak at about 92 $\mathrm{cm^{-1}}$ at 300 K may be considered as a superposition of four modes. As a result of cell doubling, eight peaks at 70, 79, 86, 90, 96, 101, 107, and 116 $\mathrm{cm^{-1}}$ seem to appear at 15 K. The spectroscopic evidence for the doubling of the primitive unit cell in the II-III transition of TDP-family crystals is in good agreement with the x-ray-diffraction measurements that show the crystallographic unit cell of TDP III and DTDP III is a C-centered cell ($Z=16$), and so the primitive unit cell contains eight formula units ($Z=8$).[13] Fernandez-Diaz, de Andres, and Prieto reported that TDP III is ferroelectric with the lowest spontaneous polarization.[15] This is inconsistent with the D-E hysteresis loop[11,22] and the x-ray-

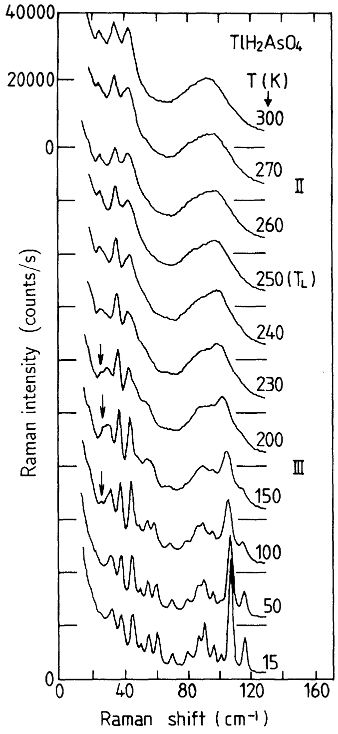

FIG. 4. Temperature effect on the Raman spectra in the II-III phase transition of polycrystalline TlH_2AsO_4. See Raman spectra of nonoriented single-crystal TlH_2PO_4 in Fig. 5 of Ref. 5 and compare. In the Raman spectra of powdered TDA recorded with a double monochromator in this figure, additional uncertain peaks (denoted by an arrow) are often detected in the frequency range 25–30 cm^{-1} below the transition temperature 250 K. However, no overdamped mode has been observed in the nonoriented single-crystal TDP Raman spectra recorded with a triple monochromator in Fig. 5 of Ref. 5. Therefore, a low-lying mode of TDA from the Rayleigh wing to 25 cm^{-1} may result from the elastic scattering due to the static defects and/or surface of the powdered specimen.

diffraction study,[13] which support the antiferroelectric phase transition. Our Raman spectra of TDA show that the II-III transition in TDP-family crystals is accompanied by the multiplicative increase of the size of the primitive unit cell, probably cell doubling ($Z=4 \rightarrow Z=8$). This means that TDP-family crystals undergo antiferrodistortive transition. Therefore, the ferroelectricity of phase-III structures is denied. This is consistent with the fact that the A_g and B_g modes are nonpolar modes, i.e., these vibrations do not carry an electric dipole moment, so that the soft mode responsible for the ferroelectricity of phase-III structures is not expected. Then the soft mode above T_L in the TDP-family crystals may be associated with an optical phonon at the Brillouin-zone boundary.

(iii) Recently, Lee proposed that for the state of phase-III structures to become antiferroelectric, the point group of phase III is not $m\text{-}C_s$, but must be $2/m\text{-}C_{2h}$, in which the six space groups $P2/m\text{-}C_{2h}^1$, $P2_1/m\text{-}C_{2h}^2$, $C2/m\,(B2/m, A2/m)\text{-}C_{2h}^3$, $P2/c\,(P2/b, P2/a)\text{-}C_{2h}^4$, $P2_1/c\,(P2_1/b, P2_1/a)\text{-}C_{2h}^5$, and $C2/c\,(B2/b, A2/a)\text{-}C_{2h}^6$ are included.[25] If the point group in phase III is $2/m\text{-}C_{2h}$, then the II-III transition may be *nonferroic,* i.e., a crystal-class-preserving transition, according to the definition of nonferroic phase transition by Tolédano and Tolédano.[26] Then vibrational symmetry species in phase-III structures are also composed of A_g and B_g modes.[24] In order to demonstrate this possibility, x-ray-diffraction or neutron-diffraction experiments must be carried out to determine one of the six space groups given above. Here, we want to point out Lee's proposal[25] that the II-III transitions in the TDP-family crystals may be nonferroic with the change of space group as $P2_1/a\text{-}C_{2h}^5 \rightarrow P2_1/a\text{-}C_{2h}^5$ with cell doubling.

SUMMARY

In conclusion, the present work clearly shows that the II-III phase transition at 250 K in TDA is equivalent to that at 230 K in TDP, and supports our contention that the phase-III structure of TDP-family crystals is antiferroelectric rather than ferroelectric.

ACKNOWLEDGMENT

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the Science Research Center (SRC) of Excellence Program.

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[1] H. Yoshida, M. Endo, T. Kaneko, T. Osaka, and Y. Makita, J. Phys. Soc. Jpn. **53**, 910 (1984).

[2] M. Arai, T. Yagi, A. Sakai, M. Komukae, T. Osaka, and Y. Makita, J. Phys. Soc. Jpn. **59**, 1285 (1990).

[3] K. Hanazawa, M. Komukae, T. Osaka, Y. Makita, M. Arai, T. Yagi, and A. Sakai, J. Phys. Soc. Jpn. **60**, 188 (1991).

[4] S. Le Montagner and L. Le Donche, in *Proceedings of the First International Meeting on Ferroelectricity, Prague,* edited by V. Dvořák, A. Fouskova, and P. Glogar (Institute of Physics of the Czechoslovak Academy of Sciences, Prague, 1966), p. 244.

[5] P. V. Huong, M. Couzi, J. R. Vignalou, and A. Tranquard, in *Proceedings of the Third International Conference on Light Scattering in Solids, Campinas, Brazil,* edited by M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Wiley, New York, 1975), p. 845.

[6] J. R. Vignalou, A. Tranquard, M. Couzi, and P. V. Huong, in *Proceedings of the Fifth International Conference on Raman Spectroscopy, Freiburg,* edited by E. D. Schmid, J. Brandmüller, W. Kiefer, B. Schrader, and H. W. Schrötter (Hans Ferdinand Schulz Verlag, Freiburg im Breisgau, 1976), p. 594.

[7] T. Matsuo and H. Suga, Solid State Commun. **21**, 923 (1977).

[8] J. Bousquet, M. Diot, A. Tranquard, G. Coffy, and J. R. Vignalou, J. Chem. Thermodyn. **10**, 779 (1978).

[9] N. Yasuda, S. Fujimoto, T. Asano, H. Shimizu, K. Yoshino, and Y. Inuishi, Jpn. J. Appl. Phys. **18**, 1607 (1979).

[10] N. Yasuda, S. Fujimoto, T. Asano, K. Yoshino, and Y. Inuishi, J. Phys. D **13**, 85 (1980).

[11] N. Yasuda, S. Fujimoto, and T. Asano, Phys. Lett. **76A**, 174 (1980).

[12] R. J. Nelmes and R. N. P. Choudhary, Solid State Commun. **38**, 321 (1981).

[13] R. J. Nelmes, Solid State Commun. **39**, 741 (1981).

[14] A. de Andres and C. Prieto, Phase Transitions **14**, 3 (1989).

[15] T. Fernandez-Diaz, A. de Andres, and C. Prieto, Ferroelectrics **92**, 71 (1989).

[16] R. Mizeris, J. Grigas, R. N. P. Choudhary, and T. V. Narasaiah, Phys. Status Solidi (A) **113**, 597 (1989).

[17] F. Milia, Ferroelectrics **20**, 229 (1978).

[18] R. Blinc, M. Rožmarin, F. Milia, and M. Melisaropoulou, Solid State Commun. **27**, 999 (1978).

[19] A. S. Luyt, J. B. Clark, and A. M. Heyns, S. Afr. Tydskr. Fis. **7**, 65 (1984).

[20] T. V. Narasaiah, R. N. P. Choudhary, G. D. Nigam, and G. Mattern, Acta Crystallogr. Sec. C **43**, 388 (1987).

[21] K. S. Lee and K. L. Kim, J. Phys. Soc. Jpn. **60**, 3207 (1991).

[22] K. S. Lee, S. M. Ju, K. L. Kim, S. K. Lee, J. H. Kim, J. B. Kim, B. C. Choi, and J. N. Kim, Ferroelectrics **137**, 123 (1992).

[23] D. J. Bae, I. K. Moon, Y. H. Jeong, and K. S. Lee (unpublished).

[24] R. Loudon, Adv. Phys. **13**, 423 (1964).

[25] K. S. Lee (unpublished).

[26] P. Tolédano and J. C. Tolédano, Phys. Rev. B **25**, 1946 (1982).