O_3 tilt and the Pb/(Zr/Ti) displacement order parameters in Zr-rich PbZr_{1-x}Ti_xO₃ from 20 to 500 K

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Neutron diffraction and dielectric data have been collected from a polycrystalline sample of $PbZr_{1-x}Ti_xO_3$ (x=0.035) to determine the temperature dependence of the two-order parameters associated with the oxygen octahedral tilt and the Pb/(Zr/Ti) displacement, respectively, through the sequence of phase transitions F_{RL} - F_{RH} - P_{C} present in this mixed system. The weak coupling between tilt and polarization (displacements) is satisfactorily described within the framework of a two-order-parameters statistical theory in which the respective effective fields involve two higher-order terms in addition to a linear term. [S0163-1829(97)01709-8]

I. INTRODUCTION

Perovskite structures, which are cubic at high temperatures, frequently display a rich variety of phase transitions at lower temperatures¹ that usually involve cation shifts and/or oxygen octahedra tilts, with respect to the high-symmetry phase. These shifts and tilts are basically independent, in the sense that one can appear in the absence of the other, but they can couple weakly to each other. The mixed perovskite system PbZr_{1-x}Ti_xO₃ (generally denoted PZT) is especially interesting,² not only because it can be prepared over the entire compositional range ($0 \le x \le 1$), with a variety of distorted structures at room temperature, e.g., tetragonal ($F_{\rm T}$), zero-tilt rhombohedral high-temperature ($F_{\rm RL}$), and antiferroelectric orthorhombic ($AF_{\rm O}$) phases, but also because³ of its important technological applications.

The basic features of the phase diagram of PZT solid solutions were established by Shirane, Suzuki, and Takeda.² Barnett⁴ pointed out the existence of an additional lowtemperature phase change for Zr-rich compositions, later characterized as the F_{RL} - F_{RH} transition. Michel *et al.*⁵ determined the space groups of the two rhombohedral phases as R3c ($F_{\rm RI}$) and R3m ($F_{\rm RH}$) by means of x-ray and neutron powder diffraction at room temperature using two compositions x=0.10 ($F_{\rm RL}$, with two formula units per unit cell, involving oxygen octahedra tilts), and x=0.42 ($F_{\rm RH}$, with one formula unit per unit cell and zero tilt). In summary, the sequence of phase transitions in Zr-rich PZT is F_{RL} (rhombohedral $R3c) \rightarrow F_{RH}$ (rhombohedral $R3m) \rightarrow P_{C}$ (cubic). Later, Glazer, Mabud, and Clarke⁶ made a further neutron powder study on PZT with x=0.10, characterizing the $F_{\rm RL}$ phase in terms of the tilting of oxygen octahedra⁷ and the expansion or contraction of the octahedra triangles neighboring the shifted B cation (Zr/Ti).

Glazer⁷ has also made a general classification of tilted octahedra in perovskites. He pointed out that the cation dis-

placements, which are directly related to the ferroelectric character of the perovskites, have only a small effect on the lattice parameters and that, generally, the overall symmetries follow those of the tilts.

Research has been done to describe the possible relations between the atomic displacements in these materials. Megaw and Darlington⁸ described the perovskite structures in terms of four structural parameters, classifying them by their space groups to allow comparisons. They found no correlation between the cation displacements and the octahedra tilts in the space groups R3c and R3m, to which rhombohedral PZT belongs. A study of such a correlation, if it exists, is important to determine which parameters are the cause of the deformations and which parameters are only consequences. Nevertheless, even if displacement and tilt are independent, they may be coupled, mainly because of the shared-corner linkage between octahedra, which is required by the packing.

We have recently reported some preliminary neutron diffraction measurements⁹ on a ceramic sample of PZT with x = 0.035 over a limited temperature region around the phase transition between the two ferroelectric rhombohedral phases, $F_{\rm RL}$ and $F_{\rm RH}$ which occurs at a temperature $T_{\rm LH} \approx 323$ K. This work allowed a detailed description of the structural parameters which characterize the transition, namely, the cation displacements along the [111] axis, s (Pb) and t (Zr, Ti), the distortion of the oxygen octahedra d, and a parameter e, which describes the rotation of the oxygen octahedra around the [111] axis with a tilt angle, ω , in the (111) plane such that $\tan \omega = 4\sqrt{3}e^{.6}$ We have also reported some measurements on the dielectric response of Zr-rich PZT (Ref. 10) in the temperature region around the rhombohedral-cubic phase transition, $F_{\rm RH}$ - $P_{\rm C}$, which occurs at \approx 510 K and is shown to be first order.

The weak coupling between tilt and displacements has been recently studied by Dai, Lie, and Viehland¹¹ in PZT (x=0.35) by means of dielectric constant, hysteresis loops, and dilatometric and electron diffraction techniques. They

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proposed that the inability of the oxygen octahedra to rotate coherently within a rigid lattice generates random internal stresses which constrain the polarization. They found doubled hysteresis loops for this composition, which appear to be relaxed with La and Nb doping.

To analyze in depth the coupling between tilt and displacements, it is very convenient to use neutron diffraction data, especially to measure the tilt angle, which is difficult to determine by other techniques. In the present work, we investigate the temperature dependence of the two-order parameters associated with the octahedral tilting and the cation displacements over a wide temperature range spanning both the F_{RL} - F_{RH} and F_{RH} - P_{C} transitions, with special emphasis on the weak coupling between polarization, directly associated with the cation shifts, and tilt in a Nb-doped PbZr_{1-x}Ti_xO₃ ceramic sample with x=0.035. Nb doping is important, among other things, to reduce the electrical conductivity and to facilitate dielectric constant and polarization measurements.

The squared structure factor of the first superstructure peak, $\frac{1}{2}(3\overline{1}1)$, which can be expressed as

$$|F|^2 = 8[\sin^2(4\pi \mathbf{e})][1 + \cos(24\pi \mathbf{d})] \approx 16 \sin^2(4\pi \mathbf{e}),$$

is, in practice, directly proportional to the squared rotation parameter e^2 . This allows us to define the temperature dependence of the tilt order parameter as

$$\eta_s(T) = [I_{\rm RL}(T)/I_{\rm RL}(0)]^{1/2}$$

where I_{RL} is the integrated intensity of the superstructure $\frac{1}{2}(\overline{311})$ Bragg reflection. We have accurately measured $\eta_s(T)$ between 20 and 375 K by neutron diffraction.

Dielectric constant data, which show a small anomaly at $T_{\rm LH}$, and pyroelectric charge measurements through $T_{\rm LH}$, were used to characterize the small decrease in spontaneous polarization which accompanies the $F_{\rm RL}$ - $F_{\rm RH}$ transition. Measurements of hysteresis loops, which were previously used to characterize the behavior of the polarization order parameter $p_s(T) = P_s(T)/P_s(O)$ at the $F_{\rm RH}$ - $P_{\rm C}$ (ferroelectric-paraelectric) transition, were attempted at $T \leq T_{\rm LH}$, but were unsuccessful because of the high values of the coercive field for the sample in this temperature range.

The combined neutron diffraction and dielectric data were used for a theoretical analysis of the weak tilt-polarization coupling. Prior work by Halemane *et al.*^{12,13} made use of Landau's theory to describe the simultaneous temperature dependence of tilt and polarization in PZT with a different composition, x=0.10, but no detailed information on the temperature dependence of the tilt order parameter was available at this time. We describe below an analysis of our data for PZT with x=0.035 by means of a simple two-orderparameters statistical theory, in which the effective fields¹⁴ for both tilt and polarization involve linear, cubic, and fifth power terms in the conjugate variable. In spite of its simplicity, this theoretical approach produces a simple relationship between tilt and polarization which is borne out quantitatively by the experimental data.

II. EXPERIMENT

The samples were high quality polycrystalline ceramics prepared at the Shanghai Institute of Ceramics, with nominal



FIG. 1. Tilt order parameter vs temperature obtained from neutron diffraction measurements on a ceramic sample of Nb-doped PbZr_{1-x}Ti_xO₃ with x=0.035. The tilt order parameter is defined as $\eta_s = [I_{\rm RL}(T)/I_{\rm RL}(0)]^{1/2}$, where $I_{\rm RL}$ corresponds to the integrated intensity of the first superstructure peak $(hkl) = \frac{1}{2}(3\overline{11})$ of the rhombohedral unit cell. Dashed line indicates calculated metastable region between low-temperature and high-temperature phases. The theoretical curves (full and dashed lines) are calculated from Eq. (7) with x=0.

composition $Pb_{1-y/2}(Zr_{1-x}Ti_x)_{1-y}Nb_yO_3$, with x=0.035 and y=0.039, confirmed by chemical analysis. The constituent oxides were ground, pressed into pellets, and fired at 1350 °C for 2 h. Cylinders of about 1 cm in height and 1 cm in diameter were sintered and hot pressed for the neutron diffraction runs, and thin plates of about 1 mm in thickness and 1 cm in diameter were used for the dielectric measurements. Data were collected with neutrons of 14.7 meV energy for several low angle peaks, including the superstructure peak $\frac{1}{2}(311)$ (Ref. 9) at one of the triple-axis diffractometers at the Brookhaven National Laboratory HFBR between 20 K and $T_{LH} \cong 323$ K. The dielectric constant data, capacitance and dissipation factor, were measured at regular intervals of about 0.1 K by means of an automatic Hewlett-Packard Precision LCR Meter (Model 4284A) with a field amplitude of 8.3 V/cm to an accuracy better than 1 part in 10⁴ at a frequency of 1 KHz. The rate of temperature change was ~ 20 K/h for both heating and cooling runs. The pyroelectric charge released through the $F_{\rm RL}$ - $F_{\rm RH}$ transition was measured with a Keithley Electrometer (Model 610C), and measurements of hysteresis loops data were made with a modified Diamant-Pepinsky-Drenck circuit with a Nicolet Digital Scope (Model NIC-310). The temperature for the electrical measurements was measured in all cases by a chromel-alumel thermocouple with a Keithley Digital Multimeter (Model 196).

III. RESULTS

Figure 1 depicts the tilt order parameter $\eta_s(T)$ obtained directly from the neutron diffraction data. It can be seen that $\eta_s(T)$ decreases gradually with increasing temperature, reaches a value of $\eta_s(T_{\text{LH}})\cong 0.59$, and then drops fairly abruptly to nearly zero for $T > T_{\text{LH}} \cong 323$ K. As shown below, a good fit of the data for $\eta_s(T)$ between 20 K $< T < T_{\text{LH}}$ is obtained with an extrapolated Curie temperature $T_{\text{ct}}\cong 178.2$ K, much lower than the transition temperature T_{LH} , and in-



FIG. 2. (a) Inverse dielectric constant vs temperature (heating and cooling) for Nb-doped PbZr_{1-x}Ti_xO₃ (x=0.035) showing the $F_{\rm RL}-F_{\rm RH}$ transition associated with the O3 tilt and the $F_{\rm RH} - P_{\rm C}$ transition to the cubic paraelectric phase. (b) Spontaneous polarization vs temperature for Nb-doped PbZr_{1-x}Ti_xO₃ (x=0.035). Since hysteresis loops data show an increasingly large coercive field as T decreases and approaches T_{LH} , making measurements near this temperature impossible, pyroelectric charge measurements were made. It may be noted that in ceramic rhombohedral perovskites, the saturation polarization is substantially lower than in single crystals, the ratio being P_s (s.c) $\approx 1.15 \times P_s$ (ceramic) (see text). Dashed line indicates calculated metastable region. The theoretical curves (full and dashed lines) are calculated from Eq. (4) with e = 0.

dicative of the pronounced first-order character of the transition. The fit is done by varying the tilt saturation value, $\eta_s(0) \equiv \eta_{s0}$, and the effective Curie temperature, T_{ct} , from estimated initial values to optimize the agreement between available experimental data and the equation of state arrived at in Sec. IV. It may be noted that, in our case, $\eta_s(0) \approx \eta(20$ K) is well defined beforehand, while $T_{ct} < T_{LH} = 323$ K (transition temperature) is not, because it is inaccessible experimentally. In Sec. V the fitting process is described in more detail.

Figure 2(a) shows the inverse dielectric constant as a function of temperature over a wide range, from slightly below $T_{\rm LH}$ =323 K to well above $T_{\rm FP}$ =509.6 K, the ferroelectric-paraelectric transition temperature. In this case, the extrapolated Curie temperature, T_c =489.9 K, is relatively close to the transition temperature. A small anomaly in $\epsilon^{-1}(T)$ at $T \cong T_{\rm LH}$ marks the onset of the tilting of the oxygen octahedra.

Figure 2(b) presents the behavior of the spontaneous polarization (displacement order parameter) P_s as a function of temperature over the same wide range as in Fig. 2(a). Data of the hysteresis loops for $T \ge T_{\rm LH}$ in the region of $T_{\rm FP}$ are combined with pyroelectric charge measurements made around $T_{\rm LH}$. They indicate, as expected, a small change in spontaneous polarization at the onset of the tilting transition. It may be noted that the numerical values for T_c and $T_{\rm FP}$ are not identical to those in Fig. 2(a) but appear slightly shifted towards lower temperatures. This may be due to the fact that in the measurements of the hysteresis loops, extra heating of the sample under the relatively high driving field is known to take place. The thermocouple, which is not in good thermal contact with the sample, may register a temperature closer to that within the furnace than that of the sample. The data, read automatically from the digital scope, include extra polarization just above the true transition temperature. As is well known, at first-order discontinuous transitions in ferroelectric perovskites, the single hysteresis loops evolve towards double loops which, when imperfectly compensated due to the high conductivity of the sample, may give rise to tails in the apparent spontaneous polarization above the transition temperature, whose precise value may become blurred. It should be pointed out that the estimated ratio between the true (single-crystal) polarization and the apparent (ceramic) polarization is about 1.15,¹⁵ which has been used to correct the data shown in Fig. 2(b).

IV. THEORETICAL ANALYSIS

To analyze the phase transition sequence

$$F_{\text{RL}}(\eta_s > 0; p_s > 0; \Delta p_s > 0) \rightarrow F_{\text{RH}}(\eta_s = 0; p_s > 0; \Delta p_s = 0)$$
$$\rightarrow P_C(\eta_s = p_s = \Delta p_s = 0),$$



we first examine separately the polarization order parameter (p_s) and the tilt order parameter (η_s) using a common orderdisorder statistical approach, and then we investigate the weak coupling between both order parameters, which gives rise to the increase in the polarization order parameter (Δp_s) apparent at $T \leq T_{\text{LH}}$ [see Fig. 2(b)].

A. Polarization

If there are N interacting elementary dipoles per unit volume in the solid, of which N_2 are pointing one way and N_1 in the opposite way, $(N_1+N_2)=N$, in thermal equilibrium we have

$$N_{2}(k_{B}\Theta_{D}/h)e^{-\phi_{d}/k_{B}T}e^{-E_{\text{eff}}\mu/k_{B}T}$$
$$=N_{1}(k_{B}\Theta_{D}/h)e^{-\phi_{d}/k_{B}T}e^{E_{\text{eff}}\mu/k_{B}T},$$
(1)

where $(k_B \Theta_D / h) e^{-\phi_d / k_B T}$ is the jump probability per unit time per unit dipole, μ , for an effective field $E_{\text{eff}}=0$, and ϕ_d is the height of the energy barrier between the two potential minima corresponding to the two possible orientations $(E_{\text{eff}}=0)$. The net dipolar polarization (practically identical to the total polarization, P) would then be

$$P_d = (N_2 - N_1)\mu = N\mu \tanh(E_{\text{eff}}\mu/k_BT), \qquad (2)$$

where μ , as before, is the elementary dipole moment per unit cell.

The effective field may be expanded in powers of the polarization, taking into account that, for an external field E=0, $E_{\text{eff}}(P_d) = -E_{\text{eff}}(-P_d)$. Thus,

$$E_{\rm eff} = E + \beta P_d + \gamma P_d^3 + \delta P_d^5 + \cdots, \qquad (3)$$

where β, γ, δ are constant (i.e., temperature independent) coefficients.

Using the dimensionless variables, $e=E/\beta N\mu$, $p=P_d/N\mu=P/N\mu$, and substituting $T_c=\beta N\mu^2/k_B$, $g\equiv(\gamma/\beta)N^2\mu^2$, $h\equiv(\delta/\beta)N^4\mu^4$, we obtain the equation of state

$$e = (T/T_c) \tanh^{-1} p - p(1 + gp^2 + hp^4 + \cdots),$$
 (4)

FIG. 3. Calculated temperature dependence of the tilt and polarization order parameters for PZT (x=0.035) indicating that the extra polarization associated with the tilt Δp_s is well described, below T_{LH} by $p_s = (1+p_s \eta_s)^{-1}(1-p_s^{-2}) \eta_s$, Eq. (9). [See text for details on the fitting procedure for $\eta_s(T)$ and $p_s(T)$]. Dashed lines indicate calculated metastable region between lowtemperature and high-temperature phases. The dotted line for $p_s(T)$ below T_{LH} is the calculated polarization in the absence of tilt.

which specifies completely the temperature dependence of the spontaneous (e=0) order parameter $p(0) \equiv p_s$. (This dimensionless field *e* should not be confused, obviously, with the structural parameter **e**, which describes the O₃ rotation.)

The temperature dependence of the inverse dielectric constant can also be obtained easily from the equation of state, Eq. (4), as $\epsilon^{-1}(T) = (T_c/C)(de/dp)$.

B. Tilt

Similarly, we can try to describe the temperature dependence of the tilt order parameter in the $F_{\rm RL}$ ferroelectric antiferrodistortive phase, in which the unit cell is doubled, using a statistical approach as follows. If there are N' interactive unit cells per unit volume, consisting of N'₁ with the two oxygen octahedra within the unit cell tilted in the sequence $(+\omega, -\omega)$, and N'₂ with the two oxygen octahedra tilted in the opposite sequence $(-\omega, +\omega)$, the net "staggered" tilt per unit volume θ_t of the pseudocubic threedimensional arrangement of cells is

$$\theta_t = (N'_2 - N'_1) 2 |\omega| = N' 2 |\omega| \tanh(|X_{\text{eff}}|2|\omega|/k_B T),$$
(5)

where

$$|X_{\text{eff}}| = X + \beta' \,\theta_t + \gamma' \,\theta_t^3 + \delta' \,\theta_t^5 + \cdots \tag{6}$$

is the generalized (torsional) field and $|\omega|$ is the absolute value of the rotation angle of a single oxygen octahedron in the unit cell (the other oxygen octahedron within the unit cell will have, automatically, a rotation angle with the same value in the opposite direction). Because the $F_{\rm RL}$ phase presents an antiferrodistortive deformation with respect to the higher temperature rhombohedral phase, $F_{\rm RH}$, $X_{\rm eff}$ is an effective staggered field (torsional field in our case), conjugate with the staggered tilt strain.

The equation of state in dimensionless variables is

$$x = \left(\frac{T}{T_{\rm ct}}\right) \tanh^{-1} \eta - \eta (1 + g_t \eta^2 + h_t \eta^4 + \cdots), \qquad (7)$$



FIG. 4. (a) Plot of $(g'_t)_{exp} \equiv f_t[T/T_{ct}\eta_s^2]$ vs η_s^2 , where T_{ct} and $I_{RL}(0)$ are adjusted by a least-squares fit to get the best linear dependence of g'_t vs η_s^2 . $I_{RL}(T)$ are the actual measured values of temperature and integrated intensity. It may be noted that $[I_{RL}(0)]^{1/2}$ comes out very close to $[I_{RL}(20 \text{ K})]^{1/2}$. (b) Plot of $(g')_{exp} \equiv f(T/T_c, p_s^2 \equiv P_s/P_{so})$ vs p_s^2 , where T_c and P_{so} are similarly adjusted. In this case P_{so} is still somewhat larger than $P_s(T \approx 450 \text{ K})$ which is the maximum value actually measured. Points corresponding to $T > T_{FP}$ (transition temperature) have been omitted.

where $x = X/\beta' N' 2|\omega|$; $\eta = \theta_t/N' 2|\omega|$, which can also be interpreted as $\langle \mathbf{e}(T) \rangle / \langle \mathbf{e}(0 \text{ K}) \rangle$, due to the fact that $\mathbf{e} = \tan \omega / 4\sqrt{3} \approx \omega/4\sqrt{3}$; $T_{ct} = \beta' N' (2|\omega|)^2 / k_B$, $g_t \equiv (\gamma'/\beta') N'^2 (2|\omega|)^2$ and $h_t \equiv (\delta'/\beta') N'^4 (2|\omega|)^4$. Here $T_{ct} < T_{LH}$ is the effective Curie temperature for the transition involving O₃ tilting, which is different from $T_c < T_{FP}$, the Curie temperature for the ferroparaelectric transition involving Pb and Zr/Ti displacement or order-disorder orientations.

The spontaneous (x=0) tilt order parameter $\eta(0) \equiv \eta_s \equiv \mathbf{e}_s / \mathbf{e}_{so}$ is therefore given by Eq. (7) with x=0. Note that \mathbf{e} can be interpreted, in general, as a common tilt for all unit cells (displacive transition) at any given temperature, or as an average tilt $\langle \mathbf{e} \rangle$ for a statistical distribution of the tilts through the lattice (order-disorder transition). Very often, transitions have a mixed displacive/order-disorder character which should, to some extent, be taken into account by a generalized effective field which includes terms with higher order powers, as in Eq. (6).

C. Polarization-tilt coupling

Let us assume that there is a weak coupling between tilt and polarization, or, in other words, that a unit cell tilted in one specific direction favors atomic displacements in one of the two opposite directions perpendicular to the plane of the tilt. In this case, the total interaction energy to be substituted into Eq. (2) is $W_d + W_t = E_{eff} \mu + X_{eff} 2\omega$, instead of W_d $= E_{eff} \mu$ only, and we therefore have

$$p_{s} + \Delta p_{s} = \tanh\left[\frac{W_{d}}{k_{B}T} + \frac{W_{t}}{k_{B}T}\right] = \frac{\tanh\left[\frac{W_{d}}{k_{B}T}\right] + \tanh\left[\frac{W_{t}}{k_{B}T}\right]}{1 + \tanh\left[\frac{W_{d}}{k_{B}T}\right] \tanh\left[\frac{W_{t}}{k_{B}T}\right]}.$$
(8)

Taking into account that for E=0, $tanh[W_d/k_BT]=p_s$ and $tanh[W_t/k_BT]=\eta_s$, we obtain directly from Eq. (8)

$$\Delta p_{s} = (1 + p_{s} \eta_{s})^{-1} (1 - p_{s}^{2}) \eta_{s}, \qquad (9)$$

which relates the increase in polarization to the tilt in a very simple way. The prefactor $(1+p_s\eta_s)^{-1}$ varies smoothly from 0.5 at T=0 K to 1.0 at $T=T_{LH}$. The second factor $(1-p_s^2)$ is zero at T=0 K and is still much less than unity at $T=T_{LH}$ if T_{LH} is substantially lower than T_{FP} as in the present case.

Figure 3 shows the temperature dependence of the spontaneous polarization and the tilt, in excellent agreement with the observed behavior.

V. DISCUSSION AND CONCLUSIONS

As mentioned above, the temperature dependence of the tilt order parameter, $\eta_s(T)$, and the polarization order parameter, $p_s(T)$, are well described by Eqs. (7) and (4) with x=0 and e=0, respectively. In Figs. 1, 2(b), and 3, which display Eqs. (7) and (4), full line indicates equilibrium states (heating) and dashed line corresponds to ideal metastable behavior (cooling). The fitting procedure was the following: the experimental values for $\eta_s(T) = [I_{\rm RL}(T)/I_{\rm RL}(0)]^{1/2}$ and $p_s(T) = P_s(T)/P_s(0)$, with initial values for $I_{\rm RL}(0)$, $T_{\rm ct}$ and $P_s(0)$, T_c chosen as discussed below, were substituted, respectively, into

$$g_t' = \frac{\left(\frac{T}{T_{\rm ct}}\right) \tanh^{-1} \eta_s(T) / \eta_s(T) - 1}{\eta_s^2(T)} \approx g_t + h_t \eta_s^2 \qquad (10)$$

and

$$g' = \frac{\left(\frac{T}{T_c}\right) \tanh^{-1} p_s(T) / p_s(T) - 1}{p_s^2(T)} \approx g + h p_s^2.$$
(11)

Here the experimental values for g'_t , defined by the actual value of the tilt at a given temperature, are plotted vs η_s^2 , using as normalized parameters $I_{\text{RL}}(0)$ and T_{ct} . If Eqs. (7) and (4) describe correctly the observed behavior, g'_t vs η_s^2 and g' vs p_s^2 should result in linear plots, giving automatically (g_t, h_t) and (g, h). The quality of these least-square-

fitted linear plots was assessed through $R_t = |\Delta g'_t/g'_t|^2$ and $R = |\Delta g'/g'|^2$, respectively, summing up over all data points, where $|\Delta g'_t|$ and $|\Delta g'|$ are the differences between experimental and calculated values. The values of $I_{\rm RL}(0 \text{ K})$, $T_{\rm ct}$ needed to obtain $\eta_s(T)$ and $T/T_{\rm ct}$, and P_{so} , T_c to get $P_s(T)$ and T/T_c in Eqs. (10) and (11), are not known experimentally, so the fitting procedure is carried out by changing them to get the best linear fit. The initial values are chosen from the experimental data knowing that $I_{\rm RL}(0 \text{ K}) \approx I_{\rm RL}(20 \text{ K})$, $T_{\rm ct} \leq T_{\rm LH} = 323 \text{ K}$, $P_{so} \geq P_s$ (430 K) and $T_c \leq T_{\rm FP} = 501.0 \text{ K}$.

Then, varying T_{ct} and $I_{RL}(0 \text{ K})$ [fixed in practice because the neutron data include points for $I_{RL}(20 \text{ K}) \approx I_{RL}(0 \text{ K})$ with very small statistical error], we proceed to minimize the least-square error of the fit to get a final T_{ct} [see Fig. 4(a)]. Likewise, experimental values for g', defined by the actual value of the spontaneous polarization at a given temperature, are plotted vs p_s^2 , using as normalized parameters initial estimates for P_{so} and T_c . Varying again (within narrow limits) T_c and P_{so} and optimizing the linear fit, we get final values for P_{so} and T_c [see Fig. 4(b)].

This procedure leads to $R \le 10^{-4}$ for $I_{\rm RL}(20 \text{ K})/I_{\rm RL}(0 \text{ K})$ =0.985 and $T_{\rm ct}$ =178.2 K (with estimated uncertainties of the order of 1%), and to $R \le 10^{-3}$ for P_{so} =33.0 μ C/cm², T_c =480.0 K (with estimated uncertainties of the order of 5%). These fits resulted in linear plots giving g_t =5.1±0.1, h_t =-5.8±0.2 for the tilt order parameter, and g=0.62 ±0.25, h=-(0.15^{+1.10}_{-0.15}) for the polarization order parameter. It should be noted that the set of experimental data for $\eta_s(T)$ covered the range 0.06 \le T/T_{LH} \le 1.00, while the available set for $p_s(T)$ covered only 0.85 \le T/T_{FP} \le 1.00. This is the main reason for the larger uncertainties in the latter.

The occurrence of nonvanishing values $g_t > \frac{1}{3}$, $h_t < 0$, and $g > \frac{1}{3}$, h < 0 in the expressions for $\eta_s(T)$ and $p_s(T)$ implies a first-order (discontinuous) character for the transitions, in agreement with the observed behavior. Physical meaning can be attributed to the effective field coefficients β_t , $\gamma_t(g_t)$, $\delta_t(h_t)$ and β , $\gamma(g)$, $\delta(h)$ in Eqs. (6) and (3), considering the

effective field expressions as multipolar expansions. These expansions include successive dipolelike (long-range), quadrupolelike (short-range), octupolelike (shorter-range) terms, summing up the contributions over the whole lattice. However, detailed calculations of this kind in rhombohedral perovskites are nontrivial.

The temperature dependence of the weak peak in $\epsilon(T)$ at $T \approx T_{\rm LH}$ can be described only in a semiquantitative manner within the theoretical approach used here to describe $p_s(T)$ at the $F_{\rm RL}$ - $F_{\rm RH}$ transition. The presently available information on the trend of $\Delta p_s(T_{\rm LH})$ with composition (x) for x=0.035, $^9 x=0.10$, 6 and x=0.40 (Ref. 16) indicates a tendency to smooth out the discontinuity with increasing x. This behavior might also be masked by the increasing compositional inhomogeneity of the samples. It would be interesting to be able to predict theoretically the composition dependence of $T_{\rm LH}(x)$ and $\Delta p_s(T_{\rm LH}(x))$ in terms of $g_t(x)$ and $h_t(x)$, but this is not possible at present.

In summary, the temperature dependence of the tilt order parameter of PZT with x=0.035, previously investigated in a narrow range near⁹ $T_{\rm LH}$, has been determined by means of neutron diffraction in the whole temperature range from T=20 K to $T_{\rm LH}=323$ K. The associated polarization change $P_s(T)$ at $T \approx T_{\rm LH}$ has been determined.

It may be concluded that the simple two-order-parameters statistical theory outlined in Sec. IV accounts well for the coupling between tilt and polarization determined by neutron diffraction and dielectric measurements, especially in view of the fact that the data were obtained not from single crystals, but from ceramic samples.

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- ¹See for instance, *Ferroelectric and Related Substances: Oxides*, Landolt-Börnstein, New Series, Group 3, Vol. 16, Pt. a (Springer-Verlag, Berlin, 1981).
- ²G. Shirane, K. Suzuki, and A. Takeda. J. Phys. Soc. Jpn. 7, 12 (1952).
- ³J. C. Burfoot and G. W. Taylor. *Polar Dielectrics and Their Applications* (McMillan, London, 1979).
- ⁴H. Barnett, J. Appl. Phys. **33**, 1606 (1962).
- ⁵C. Michel, J. M. Moreau, G. D. Achenbach, R. Gerson, and W. J. James, Solid State Commun. 7, 865 (1969).
- ⁶A. M. Glazer, S. A. Mabud, and R. Clarke, Acta Crystallogr. B 34, 1060 (1978).
- ⁷A. M. Glazer, Acta Cryst. B 28, 3384 (1972).
- ⁸H. D. Megaw and C. N. W. Darlington, Acta Cryst. A **31**, 161 (1975).

- ⁹B. Noheda, T. Iglesias, N. Cereceda, J. A. Gonzalo, H. T. Chen, Y. L. Wang, D. E. Cox, and G. Shirane, Ferroelectrics **184**, 251 (1996).
- ¹⁰B. Noheda, N. Cereceda, T. Iglesias, G. Lifante, J. A. Gonzalo, H. T. Chen, and Y. L. Wang, Phys Rev. B **51**, 16 388 (1995).
- ¹¹X. Dai, J-F. Lie and D. Viehland, J. Appl. Phys. 77, 3354 (1995).
- ¹²T. R. Halemane, M. J. Haun, L. E. Cross, and R. E. Newnham, Ferroelectrics **62**, 149 (1985).
- ¹³T. R. Halemane, M. J. Haun, L. E. Cross, and R. E. Newnham, Ferroelectrics **70**, 153 (1986).
- ¹⁴J. A. Gonzalo, *Effective Field Approach to Phase Transitions and Some Applications to Ferroelectrics* (World Scientific, Singapore, 1991).
- ¹⁵D. Berlincourt and H. A. Krueger, J. Appl. Phys. **30**, 1804 (1959).
- ¹⁶A. Amin, R. E. Newnham, L. E. Cross, and D. E. Cox, J. Solid State Chem. **37**, 248 (1971).