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## Author's Accepted Manuscript

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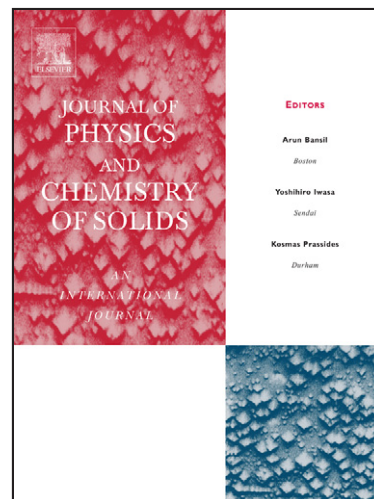
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# Anelastic and dielectric study of the phase transformations of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ around the morphotropic phase boundary

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(Dated:)

A revival of the interest on the morphotropic phase boundary of the  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  started after a neutron diffraction study revealed the existence of a monoclinic phase (M) bridging the tetragonal (T) and rhombohedral (R) ones. In addition, the M phase has been found to exhibit a low temperature transformation, possibly involving rotations of the oxygen octahedra, raising a debate on its nature. Finally, the rotational instability has been predicted to extend also in the T phase. We present measurements of the complex dielectric susceptibility and elastic compliance of  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  with  $0.455 \leq x \leq 0.53$  which bring new information on the low temperature phase transformations. The T–M transition gradually changes from first- to second-order increasing the Ti content from the boundary with the R phase to  $x = 0.48$ , confirming that the coexistence of T and M phases found by neutron diffraction is intrinsic and not due to compositional fluctuations. Strikingly, the T-M transformation causes a peak in the elastic compliance, whose amplitude may even exceed that of the jump at the cubic-to-tetragonal transition, as if it were a ferroelastic transformation; it is shown that indeed there is linear coupling between shear strain and order parameter, when the T-M transition mainly consists of a rotation of the polarization. The instability involving rotation of the octahedra below 200 K is visible both in the dielectric and anelastic losses, and it extends in the tetragonal phase, as predicted by recent first-principle calculations.

Key words: A. oxides, C. ultrasonic measurements, D. phase transitions

## I. INTRODUCTION

The  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  perovskite (PZT) is widely adopted in applications requiring materials with high piezoelectric constant or dielectric permittivity, such as electromechanical actuators and sensors, capacitors or non volatile memories, and its phase diagram has been known for over 40 years. The compositions displaying the highest values of the dielectric and electromechanical constants are around the so-called morphotropic phase boundary (MPB) separating the Ti-rich tetragonal phase (T with space group  $4mm$ ) from the Zr-rich rhombohedral phase (R =  $R3m$ ) at  $0.44 < x < 0.52$ . In the last decade numerous X-ray, neutron and electron diffraction studies focused on this issue [1,2] and the old phase diagram [3] has been enriched with new features. The picture of R and T domains coexisting near the MPB has been substituted with a new monoclinic (M =  $Cm$ ) phase, bridging the two ferroelectric phases [4]. The M phase has an intermediate direction of the polarization and its only symmetry element is the mirror plane common to the T and R structures and containing these three directions of polarization. After the discovery of the M phase, new features have been found from diffraction and theoretical studies. Thus Noheda *et al.* [5] reported a region of coexistence of M and T structures. Other models have also been proposed interpreting the local structures of R, M and T phases of PZT across the MPB in terms of progression from short-range, long-range and again short-range M order [1] or assuming that the observation of an M phase in X-ray diffraction spectra is due to a nanodomain structure in the MPB region [6]).

At low temperatures, superlattice spots in powder neutron diffraction patterns evidenced a doubled elementary perovskite cell with antiphase rotations of oxygen octahedra about [001] direction (space group  $Pc$ ) [7]. This new instability ( $Cm \rightarrow Pc$ ) has been seen as a continuation in the M phase of the well known instability  $R3m \rightarrow R3c$  in the R phase related to the octahedra rotating about the ternary axis. While there is a general agreement on the existence of a new low temperature phase in the MPB, its nature is still under strong debate. Thus a coexistence of two monoclinic structures with  $Cm$  and  $Cc$  space groups at liquid He temperatures has been proposed by Noheda *et al.* [8] and Woodward *et al.* [9] while coexistence of  $Cm$  and  $R3c$  [10] or the existence of a  $Pc$  symmetry [7] have been alternatively postulated.

On the theoretical side, microscopic descriptions confirming the M phase have been provided, based on first principle calculations [11,12]. Evidence for a continuation of rotational instability below a certain low temperature (hereafter called  $T_3$ ) in Ti-rich compositions is provided by first principle calculations [12,13]. A new phase diagram of PZT near MPB from first principle calculations, including antiferrodistortive degrees of freedom, has been proposed, with a low temperature rotational instability whose space group changes from  $R3c$  to  $Cc$  and further to  $I4cm$  when  $x$  increases [13]. Models for the description of the PZT phase diagram based on the Landau expansion of the free energy in powers of the polarization up to the sixth order [14], beyond the sixth order [15,16] or by introducing an additional order parameter [17] or an additional tetragonal invariant [18] have also been proposed.

In a previous paper [19] we have presented anelastic and dielectric spectroscopy measurements of PZT with  $0.455 < x < 0.53$ , providing evidence about the nature of T-M transformation and the existence of a further low temperature transformation in the M phase and even in the T one beyond the MPB region. Here we present more extensively results and discussion of these investigations.

## II. EXPERIMENTAL METHODS

PZT samples with  $x = 0.455, 0.465, 0.48$  and  $0.53$  have been prepared by the conventional mixed oxide method. The starting oxides (PbO, ZrO<sub>2</sub> and TiO<sub>2</sub>) are wet mixed, dried and heat treated at 800 °C for 4 h to obtain the perovskitic phase. The powder is then uniaxially pressed at 60 MPa to obtain pellets and bars and finally sintered at 1200 °C for 2 h. In order to avoid the loss of PbO, which is very fast at temperatures above 1000 °C, the sintering processes were carried out with the samples placed on a ZrO<sub>2</sub> disk, covered with an Al<sub>2</sub>O<sub>3</sub> crucible and sealed with PbZrO<sub>3</sub> + 5 wt% ZrO<sub>2</sub> pack to keep a constant PbO activity at the sintering temperature [20].

Powder X-ray diffraction evidenced the formation of pure perovskite phase and the absence of pyrochlore or other spurious phases. The grain size was always larger than 10 μm, enough to avoid the coexistence of tetragonal and rhombohedral phases that may be induced by internal strains present in small crystallites [5,21]. The densities were all higher than 96% of the theoretical ones. The samples have been cut into bars 4–5 cm long, 4 mm wide and 0.5-0.6 mm thick. Silver paint electrodes were applied on the major surfaces for anelastic and dielectric measurements. A heating treatment at 750 °C allowed both the electrode consolidation and elimination of possible strains induced by cutting.

Dielectric measurements were carried out between 100 and 530 K using a Hewlett-Packard impedance bridge (model HP 4194A) with a four wire probe and a signal level of 0.5 V/mm, between 200 Hz and 200 kHz. The measurements were made on heating/cooling at 1–1.5 K/min in a Delta Design climatic chamber (model 9023A). The dielectric susceptibility  $\chi = \chi' - i\chi''$  was obtained from the measured values of capacitance and loss.

The elastic compliance  $s = s' - is''$  is the mechanical analogue of  $\chi$  and was measured between 50 and 750 K by electrostatically exciting the flexural modes of the bars suspended in vacuum on thin thermocouple wires in correspondence with the nodal lines. The compliance was therefore given by  $s = E^{-1}$ , where  $E$  is the Young's modulus and is related to the fundamental resonance frequency by  $\omega/2\pi = 1.028h/l^2(E'/\rho)^{1/2}$  where  $h$ ,  $l$  and  $\rho$  are the sample thickness, length and density [22]. The temperature dependence of the latter quantities is negligible with respect to that of  $E$  or  $s$ , so that  $s(T)/s_0 = \omega^2(T_0)/\omega^2(T)$ , where we choose  $T_0 = 750$  K. The fundamental frequencies of the various samples were  $\omega(T_0)/2\pi \cong 1.0-1.6$  kHz and the resulting Young's mod-

uli, uncorrected for porosity, were  $E_0(T_0) = 138, 139, 134$  and 125 GPa for  $x = 0.455, 0.465, 0.48$  and  $0.53$ , respectively. During a same run it was possible to measure also the 3rd and 5th flexural modes, whose frequencies are 5.4 and 13.3 times higher than the fundamental one.

## III. RESULTS AND DISCUSSION

Figure 1 shows the dynamic compliance normalized to  $s_0 = s'(750 \text{ K})$  and dielectric susceptibility curves for the sample  $x = 0.48$ , measured on cooling at two frequencies: 1.2 and 17 kHz for the compliance and 1 and 20 kHz for the dielectric susceptibility.

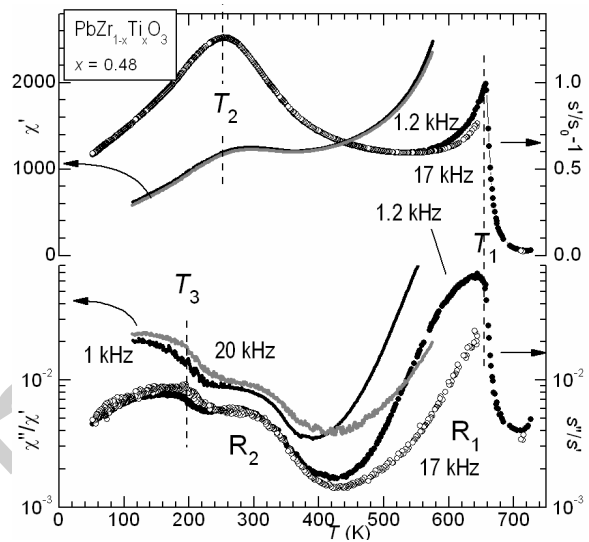


FIG. 1: Real parts and losses of the compliance (circles) and dielectric susceptibility (lines) of PZT with 48% Ti; in each case measurements at two frequencies are shown.

The peaks in the real parts at  $T_1$  and  $T_2$  are related to the paraelectric cubic-ferroelectric tetragonal, and tetragonal-monoclinic transitions. In the dielectric curves only the tail of the huge Curie-Weiss maximum at  $T_1$  is visible, due to limitations in the temperature range of the climatic chamber. Our measurements can nonetheless be compared with those of Zhang *et al.* [23] on a similar sample, where the peak at  $T_1$  could be measured (Fig. 2). The slightly less marked maxima in that curve may be due to the presence of 0.61% Nb in Zhang's composition.

Below  $T_1$  both dielectric and anelastic losses in Fig. 1 show frequency dispersion. This is due to space charge relaxation [24] (for dielectric case) and to the mobile charges contribution to anelastic relaxation (migration to the 90° domain walls that become charged by piezoelectric effect during the sample vibration [25]).

The dielectric and anelastic maxima at  $T_2$  are not accompanied by any clear anomaly in the losses. The  $R_2$  broad dissipation maximum, visible in both anelastic and

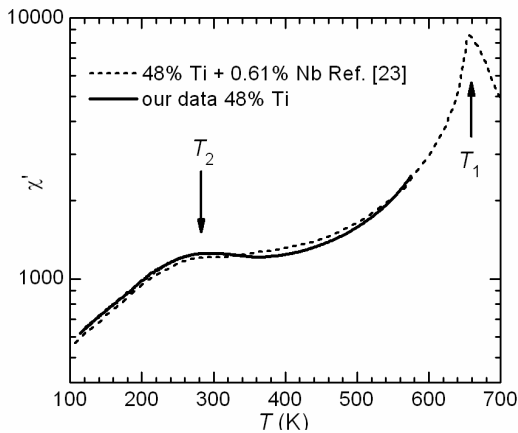


FIG. 2: Comparison between  $\chi(T)$  on the  $x = 0.48$  sample and a measurement on a similar sample over a more extended temperature range from Ref. [23].

dielectric losses, is observed also at  $x = 0.53$  where no T-M transition occurs, and is mainly due to relaxational dynamics of domain walls (DW).

At low temperature there is no clear anomaly in  $s'$  or  $\chi'$ , while those in the losses, connected with the octahedral rotational transformation at  $T_3$ , will be described below.

### A. Cubic-to-tetragonal transition

Figure 3 presents the heating/cooling dynamic compliance curves for all samples at 1–1.6 kHz, near  $T_1$ , where the transition between paraelectric cubic (C) and ferroelectric T phase occurs. The C-T transition is second order, and, indeed, only a small hysteresis ( $\Delta T < 3$  K) is observed between cooling and heating (more evident for  $x = 0.455$  and  $x = 0.465$ ). The temperature of this transition matches well the corresponding boundary line in the PZT phase diagram (see Fig. 6 below).

The step-like behavior of  $s'$  at  $T_1$  is a consequence of the coupling between strain  $\varepsilon$  and the primary order parameter, polarization  $P$ , involving terms that are linear in  $\varepsilon$  and quadratic in  $P$  (bilinear terms are not allowed because violate the inversion symmetry). Indeed, the second derivative of this term, written below for the parent cubic symmetry

$$Q_{11} \sum_{i=1}^3 \varepsilon_{ii} P_i^2 + Q_{12} \sum_{i=1}^3 \varepsilon_{ii} (P_j^2 + P_k^2) + Q_{44} \sum_{i=1}^3 \varepsilon_{ij} P_i P_j \quad (1)$$

( $Q_{ij}$  = electrostrictive coupling constants), taken with respect to strain, gives the change of the elastic constants at the phase transition, which is a step. We would obtain a peak in the compliance in case of bilinear coupling, because in that case the spontaneous strain is proportional to polarization and therefore indistinguishable

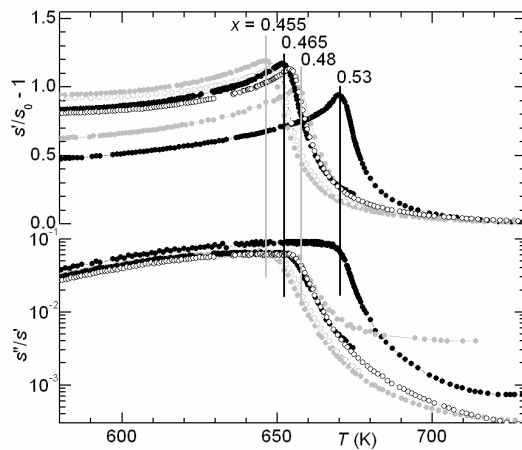


FIG. 3: Elastic compliance and loss at the C-T transition measured on the four tested samples on cooling (filled symbols) and heating (open symbols).

from the order parameter; then the corresponding compliance would follow the dielectric susceptibility.

Superposed to the step at  $T_1$ ,  $s'$  presents a peak with strong frequency dispersion below  $T_1$  (Fig. 1); this is due to relaxation  $R_1$  produced by the thermally activated motion of the domain walls and contributing also to the real part; the rounding of the step in the high temperature side is due to pretransitional fluctuations in the cubic phase. At much higher frequencies,  $R_1$  would be shifted to higher temperatures and one would observe a step in the real part, and a narrow fluctuation peak in the losses.

### B. Tetragonal-to-monoclinic transition

We consider now anelastic and dielectric spectra around  $T_2$ , corresponding to the T-M transition. Figure 4 shows  $s'(T)$  (at 1-1.6 kHz) and  $\chi'(T)$  (at 1 kHz) heating/cooling curves for all the samples.

The T-M transition at  $T_2$  is mainly associated with a peak in  $s'$  and temperature hysteresis in all the susceptibilities. This peak does not change with frequency (see Figure 1); thus it corresponds to a phase transition. Peaks and temperature hysteresis connected with the T-M transformation in the  $\chi'(T)$  curves are much less pronounced than in  $s'$ , also because they are masked by the rise of  $\chi'$  on approaching the ferroelectric transition at  $T_1$ .

The thermal hysteresis is almost zero for  $x = 0.48$ , and gradually increases with decreasing the Ti content. Nothing is observed at  $x = 0.53$ , where no M phase is formed. This behavior is not trivial. In fact, Vanderbilt and Cohen [15] analysed the PZT phase diagram in terms of Landau expansion up to the eighth order of polarization, and found that the T-M transition should be second order. For this reason, they proposed that the coexistence

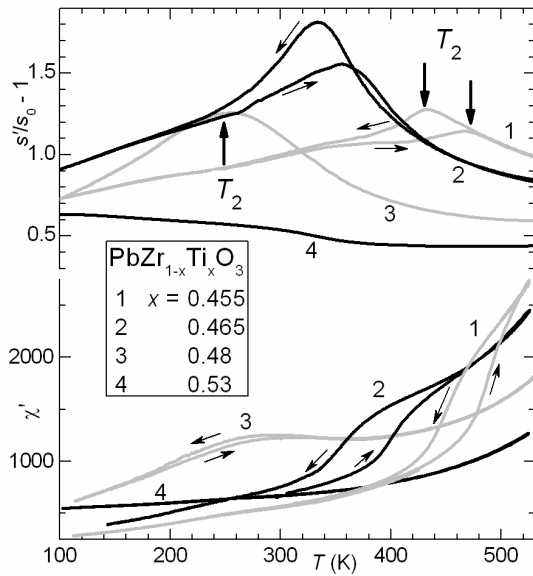


FIG. 4: Real parts of the compliance and dielectric susceptibility measured on cooling and heating in the region of the M-T transition at  $\sim 1$  kHz.

region M+T observed by Noheda [5] (the hatched region in Fig. 6 below) was in fact due to inhomogeneities in the Zr/Ti ratio over the sample. Indeed, the slope of this line is very high, and a change of just 1% Ti content produces a change of 80 K in the transition temperature. However sample inhomogeneities would produce broadening of the anelastic and dielectric curves rather than hysteresis between heating and cooling; therefore our results indicate that the change to 2nd order behavior is gradual, and there is a genuine coexistence region between T and M phases; the hysteresis narrows gradually, and at 48% Ti we have a 2nd order phase transition. Below  $x = 0.455$  there is only the T-R transition, which must be of the first order, lacking a group-subgroup relationship between the T and R space groups.

We comment now on the significance of the peak intensity in the  $s'(T)$  curves at  $T_2$  (Figs. 1 and 4). In fact, the T-M transition produces an enormous effect in the compliance, compared to the ferroelectric transition at  $T_1$  (Figs. 1 and 3). We have seen that, once excluded the frequency dependent domain wall contribution, one remains with a step in the compliance at the ferroelectric transition, as expected with linear-quadratic coupling between strain and polarization; but what appears at  $T_2$  is a peak and certainly not a step. This anomaly is even more evident if we compare with the dielectric susceptibility. In the dielectric response the T-M transition is much less important than the C-T transition (Fig. 2). The reason for the large elastic response could be a nearly linear coupling between strain and the order parameter of the T-M transition. We show that this could be obtained from the accepted linear-quadratic coupling term (Eq. 1). Indeed, in the monoclinic phase there is mainly a tilting

of the polarization away from the [001] direction toward the rhombohedral [111] direction, with little change of the magnitude [13,18]. Thus near the T-M transition we can suppose that

$$\begin{aligned} P_3 &= P \cos \theta \simeq P_0 \\ P_{1,2} &= P \sin \theta \simeq P_0 \theta \end{aligned} \quad (2)$$

which means that the monoclinic angle  $\theta$  behaves now as the order parameter, being null in the parent tetragonal phase and progressively growing in the monoclinic phase. With these approximations the last term in Eq. (1), which couples  $T_{2g}$ -type shears  $\varepsilon_i$  ( $i = 4 - 6$ , Voigt notation  $\varepsilon_4 = \varepsilon_{23}$ , etc.) with polarization, becomes

$$Q_{44} P_0^2 (\varepsilon_4 \theta + \varepsilon_5 \theta + \varepsilon_6 \theta^2) \quad (3)$$

which is just a bilinear coupling between the two shears  $\varepsilon_4, \varepsilon_5$  and the order parameter; this implies that the corresponding susceptibilities, the compliances  $s_{44}$  and  $s_{55}$ , are Curie-Weiss-like, and explains the large effect on the compliance at transition.

### C. Octahedral rotations

A low temperature anomaly ( $T_3$ ) appears as a step or sharp edge in the anelastic losses (Fig. 5). This is observed also in the dielectric losses (see Fig. 1) although the dielectric case is more difficult to assess because of the limit in the temperature range. The curves shown in Fig. 5, measured at the first flexural mode on cooling, are perfectly reproducible on heating; as shown for the samples with  $x = 0.455$  and 0.53. Moreover, an increase of frequency slightly increase the overall dissipation level, leaving unchanged the shape and temperature of the anomalies (see Fig. 1). This means that  $T_3$  is the temperature of a second order phase transformation that occurs at low temperature in all samples. We have attributed these anomalies to octahedral rotational instabilities, which are responsible for the well-known  $R3m - R3c$  transformation in the rhombohedral phase, with rotations of the O octahedra about [111] directions. Its extension into the M phase ( $Cm-Cc$  or  $Cm-R3c$ ) is controversial [2,10,26], and that in the T phase ( $4mm-I4cm$ ) is only theoretical [13]. Yet, it should be noted that cell doubling due to antiferrodistortive rotations of the octahedra at low temperature is found in all the diffraction measurements in the M region, whether occurring homogeneously in the M phase or in the coexisting R domains, and is also consistent with Raman studies [27,28]. In addition, such cell doubling has been found also in the tetragonal composition  $x = 0.80$  under pressure, indicating that it is a general tendency of the PZT lattice under pressure, whether externally applied, chemical (larger Zr substituting Ti) or due to thermal expansion [27].

Our findings show that a second order structural transformation indeed exists in the M region ( $x = 0.465, 0.48$ ) and extends far into the T phase ( $x = 0.53$ ) also in the

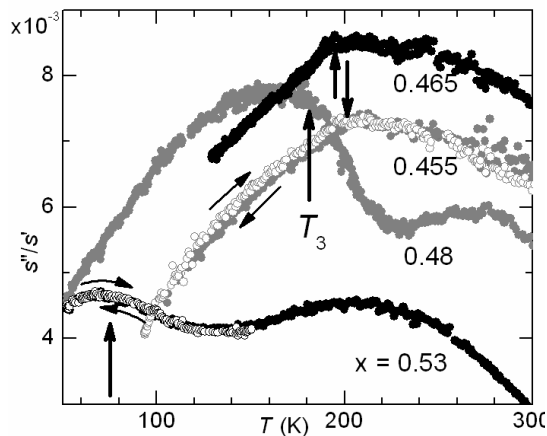


FIG. 5: Elastic energy loss of the four PZT samples measured on cooling; the vertical arrows indicate  $T_3$  and the empty symbols at  $x = 0.455$  and  $0.53$  are measured on heating.

absence of external pressure; although no indication on the symmetry change can be obtained from anelastic and dielectric measurements on ceramics, it is obvious to associate it with the antiferrodistortive rotations of the octahedra found by other techniques.

#### D. Phase diagram

The transition temperatures  $T_1$ ,  $T_2$  and  $T_3$  deduced from the present study are added to the established experimental phase diagram [2,3] complemented with the recently calculated one [13] in Fig. 6. There is perfect agreement between  $T_1$  and the C-T transition line, but also between the region of coexistence of M and T phases below  $T_2$ , and the region where we observe hysteresis between heating and cooling. The filled symbols are from the anelastic measurements and the open symbols from the dielectric ones, while the error bars indicate the difference in temperature between heating and cooling of the maxima in  $s'(T)$  and  $\chi'(T)$ . Even though the maxima in  $s'(T)$  are rather well defined near  $T_2$ , the onset of the T-M transition does not necessarily coincide exactly with these maxima; in order to make definite statements, one should work out completely the contributions of the various phase transitions on all the elastic constants and take the appropriate polycrystalline averages, which is a rather complicated task [18]. Also the maxima in  $\chi'(T)$  do not determine  $T_2$  sharply, since they are rather shallow and superimposed on the steeper maximum at  $T_1$ . We therefore consider that there is good agreement between  $T_2$  deduced from the anelastic and dielectric curves and  $T_2$  deduced from diffraction experiments.

At lower temperature, the filled points in the phase diagram are from the edge of the step in the elastic losses (Fig. 5), while the empty symbols from the dielectric curves, and they are very close to the prosecution of the

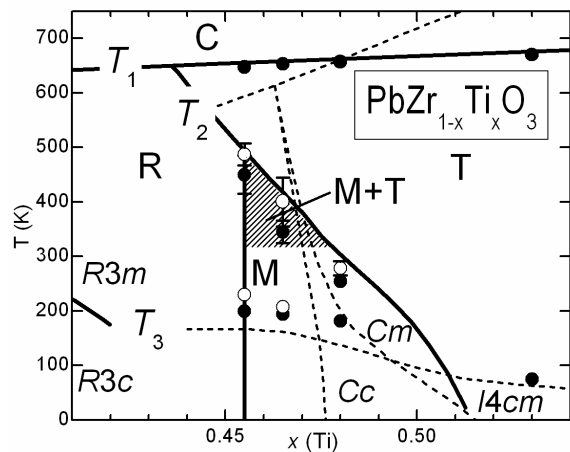


FIG. 6: Phase diagram of PZT around the MPB. Continuous lines and dashed region: experimental from Refs. [2,3]; dashed lines: calculated [13]. The full symbols are the transition temperatures deduced from the anelastic spectra:  $T_1$  and  $T_2$  from the maxima in  $s'$  (the error bars indicate the hysteresis between cooling and heating) and  $T_3$  from the kink in  $s''$ . The open symbols are from the  $\chi'$  curves. The line  $T_3$  is the onset of transitions involving rotations of the O octahedra.

experimental  $T_3$  line in the rhombohedral phase and to that calculated in the M and T phases. Thus these data provide evidence of the prosecution of the  $T_3$  line into the M phase, and further into the T phase, as predicted by the recent work of Kornev and coworkers [13]. Up to now the experimental evidence of a transformation involving the rotation of the octahedra had been found in the R phase, while the interpretations of the superlattice diffraction peaks in the M phase are still controversial, and no indication at all existed in the T phase.

#### IV. CONCLUSIONS

We presented measurements of the dynamic elastic compliance  $s(\omega, T)$  and dielectric susceptibility  $\chi(\omega, T)$  of  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  at compositions near the MPB, providing new information on the phase transformations between the cubic, tetragonal and monoclinic phases. In particular, the hysteresis between cooling and heating in both the  $s'(T)$  and  $\chi'(T)$  curves demonstrate that the character of the T-M transition gradually passes from first order at the border with the rhombohedral region at  $x = 0.455$  to second order at  $x = 0.48$ , well within the M region. Such a transition is accompanied by a large maximum of the compliance, that appears anomalous if compared to the step at the C-T transition. This effect can be explained noting that, even though the coupling between strain and polarization is linear-quadratic, for the shear components  $\varepsilon_4$  and  $\varepsilon_5$  it becomes almost bilinear in the M phase where the polarization starts deviating from the tetragonal direction toward the rhombohedral

one, inducing a Curie-Weiss-like behavior of the  $s_{44}$  and  $s_{55}$  compliances. At lower temperature, signatures of an additional transformation are found in both the elastic and dielectric losses at all the compositions we tested up to  $x = 0.53$ ; this is evidence that the instability involving antiferrodistortive rotations of the octahedra exists also in the M phase and extends even in the T phase, as recently predicted [13].

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