

# Low-temperature polarity in antiferroelectric $\text{PbZrO}_3$ and $\text{PbHfO}_3$ driven by dynamical covalency in the $\text{ZrO}_6$ and $\text{HfO}_6$ substructures

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At low temperatures, additional phase transitions have been detected in the antiferroelectric crystals  $\text{PbZrO}_3$  and  $\text{PbHfO}_3$  near 270 K. In this paper we investigate these transitions theoretically and experimentally and arrive at the conclusion that it is of first order, using the free energy expanded to a sixth order in the order parameter. In addition to recently published pyroelectric and dielectric properties, the presence of this transition has been proven by measuring the temperature dependence of the specific heat and natural absorbance, and compared with the literature data of the structural investigations by neutron scattering. Opposite to the previous articles, the origin of this transition is not connected with the Pb ion displacements, but it is solely caused by the p-d interaction in the transition metal-oxides  $\text{ZrO}_6$  and  $\text{HfO}_6$  substructures, typical for a broad number of ferroelectric oxide perovskites.

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## I. INTRODUCTION

In recent work, the title compounds have been in the focus of intense experimental investigations and theoretical modelling, where especially their low-temperature properties have been explored. In both compounds, anomalies in their dielectric permittivity and pyroelectric current have been observed around 270 K and below, accompanied by huge hysteretic effects. Here, we concentrate on the possibility of a ferroelectric/polar phase emerging below 270 K and investigate this within Landau theory with two coupled order parameters. In a rather small parameter window of the coupling parameter, the possibility of a phase transition to a polar phase exists, which is accompanied by an unusually large hysteresis. The transition temperature of  $\approx 270$  K is derived from the expansion parameters of a sixth-order potential. Importantly, we ascribe the low temperature properties to the oxygen ions and their dynamical covalency with the transition metal ions and corroborate this by experimental observations.

More than 50 years ago, Holakovskiy [1] proposed that a new type of ferroelectric phase transition might occur, which is triggered by a foregoing instability signaling new phase transition sequences. Indeed, these have been observed in a rather large number of ferroelectric materials, such as  $\text{BaTiO}_3$  (BTO) [2],  $\text{KNbO}_3$  (KNO) [3],  $\text{NaNbO}_3$  (NNO) [4], and more related perovskite oxides. Mostly, these successions start from

a cubic structure, followed by a tetragonal, orthorhombic, or rhombohedral one at a lower temperature.  $\text{PbTiO}_3$  (PTO) [5],  $\text{SrTiO}_3$  (STO) [6], and  $\text{KTaO}_3$  (KTO) [7] appear to be exceptions since in PTO, a single phase transition to a ferroelectric phase is observed. In contrast, in STO, an antiferrodistortive transition takes place, characterised by the oxygen octahedral rotations [8]. Simultaneously, a long-wavelength transverse optic (TO) mode softens, indicating the possibility of a ferroelectric phase transition; however, this is inhibited by quantum fluctuations, defined as quantum paraelectricity [9]. In KTO, a rather analogous softening of a TO mode is observed, but the concept of quantum paraelectricity is not applicable here since the extrapolated phase transition temperature lies not at a finite temperature but well below. Correspondingly, this was termed incipient ferroelectricity [7]. Rather analogous to STO related sequences have been observed in  $\text{EuTiO}_3$  (ETO) [10] where around 270 K a structural phase transition driven by a soft zone boundary transverse acoustic mode takes place accompanied by a long wave length polar transverse optic indicating possible ferroelectric order, but its extrapolation to zero takes place only at  $T < 0$  K, classifying the compound as incipient ferroelectric.

While the homologous relatives of PTO, namely  $\text{PbZrO}_3$  (PZ) and  $\text{PbHfO}_3$  (PH), have primarily been suggested to be prototype antiferroelectrics (AFE) [11] with pronounced transverse acoustic (TA) zone boundary soft mode behavior, intense research efforts have demonstrated that much more complex dynamics are involved in their phase transitions. In close proximity to the TA mode, also a TO mode softens with an extrapolated phase transition temperature  $T_C$  only a few degrees below the TA mode freezing temperature  $T_A$  [12–14]. In both compounds, a transient region follows the phase of the first transition at  $T_A$ , which is narrower in PZ

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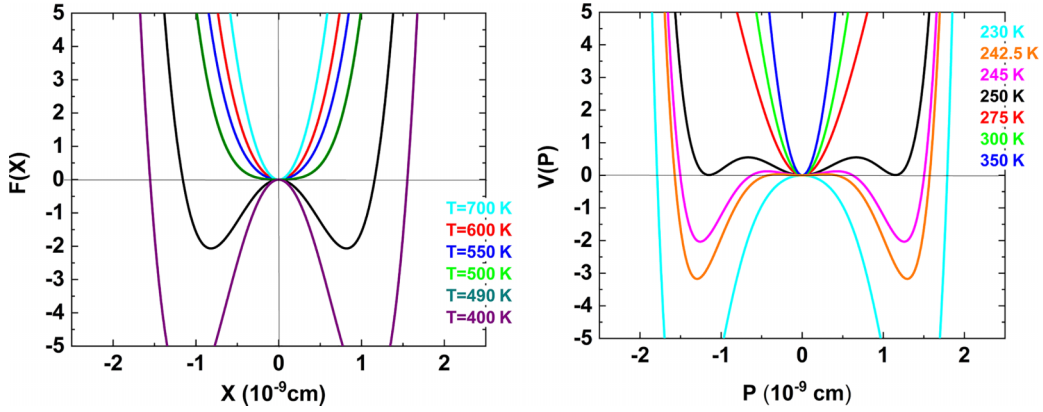


FIG. 1. The potentials  $V(X)$  and  $V(P)$  as a function of temperature related to the transition at  $T_A = 490$  K with parameters  $\alpha = -6.171 \cdot 10^4 \text{ gs}^{-2}$ ,  $\beta = 4.606 \cdot 10^{22} \text{ gs}^{-2} \text{ cm}^2$  (left) and the one around  $T_P = 250$  K (right) with parameters  $a = 27.9859 \cdot 10^4 \text{ gs}^{-2}$ ,  $b = -4.216 \cdot 10^{22} \text{ gs}^{-2} \text{ cm}^2$ ,  $c = 1.5922 \cdot 10^{40} \text{ gs}^{-2} \text{ cm}^6$ . The color codes of the lines correspond to the temperature given in the inset.

than in PH [15,16]. The symmetry of this intermediate state is not yet resolved, probably caused by the coexistence of the symmetry-lowering related to  $T_A$  and  $T_C$ . A true transition to antiferroelectric order has been established at lower temperatures  $T < T_{A,C}$  [17,18]. It is important to note that the soft TO mode is accompanied by an almost dispersion-free, very low-energy acoustic mode, indicating that only the chains of heavy atoms, namely the transition metals Zr and Hf, are involved in it [19]. This mode folds back to the zone center at  $T_A$  because of the symmetry-lowering caused by the phase transition. An interaction with the soft TO mode is restricted to very small momentum values, with the possibility of enabling a “local mode” softening. Very recently, indications of a further phase transition have been obtained from dielectric permittivity data and pyroelectric current measurements, where anomalies in both suggest possible polar (ferroelectric) order below 270 K [20]. From Raman and infrared data, multiple soft modes have been detected, and potential evidence for a polar instability has been explored [21]. In the work by Tagantsev and coworkers, speculations on polar order have been raised where, through flexoelectric coupling, a connection between the antiferroelectric displacement pattern has been established [22]. A similar study was performed by Aramberri *et al.*, where first-principles and density functional results suggest that some kind of ferroelectric order might be realized [23]. Patel *et al.* [24] indicated that antiferrodistortive modes are essential in understanding the complex phase transition sequences in PZ. Here, in contrast, we investigate the possibility of ferroelectric order within Landau theory with two coupled order parameters, namely, polarization  $P$ , which eventually appears below  $T_P = 270$  K, and displacement field  $X$ , which is related to the antiferroelectric order. Opposite to the other above-mentioned approaches [21–24], we associate the polarization not with displacements arising from the Pb substructure but with the one caused by the polarisable  $\text{ZrO}_6$  and  $\text{HfO}_6$  units, which, analogous to many related perovskites, is the decisive building element for the appearance of polar order. Its electronic properties are intimately related to the transition metal  $d^0$  configuration and the instability of the oxygen ion  $2p^6$ . This enables dynamical covalency [25] and the formation of a local double-well potential, giving rise

to the spontaneous polarization [26–28]. In this approach, the Pb skeleton plays only a minor role, mostly relevant through the lone pair formation at the Pb site. Thereby, the lead perovskites adopt analogies to BTO, STO, and KNO, where the A-site lattice in  $\text{ABO}_3$  remains rather meaningless with respect to the essential dynamics.

## II. THEORETICAL APPROACH

The methodology is closely related to the one suggested by Holakovsky [1], however, with the explicit allowance for ferroelectric order. The coupling proportional to  $\gamma$  between the order parameters  $P$  and  $X$  arises from the fact that both possible phase transitions at  $T_A$  and  $T_P$  are enabled by the dynamical polarizability of the transition metal oxygen octahedra, which has been shown in STO [25] and ETO [26] to consistently describe their phase transitions. The free energy density in powers of both order parameters is given by

$$F = \frac{1}{2}\alpha X^2 + \frac{1}{4}\beta X^4 - \frac{1}{2}\gamma X^2 P^2 + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 - EP \quad (1)$$

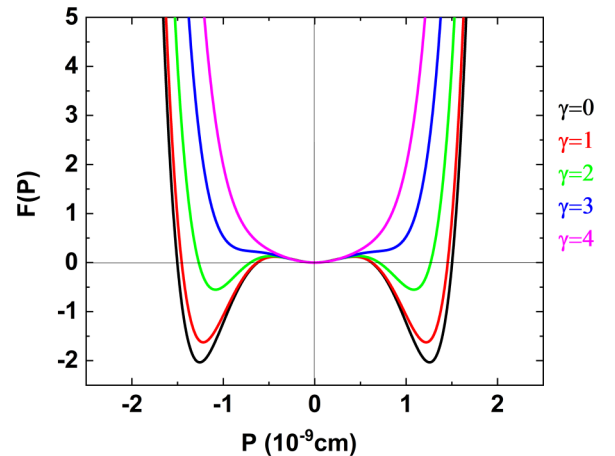


FIG. 2. The potential  $V(P)$  as a function of the coupling constant  $\gamma$ . The temperature is  $T = 240$  K. The color code of the lines corresponds to the coupling constants as indicated in the figure.

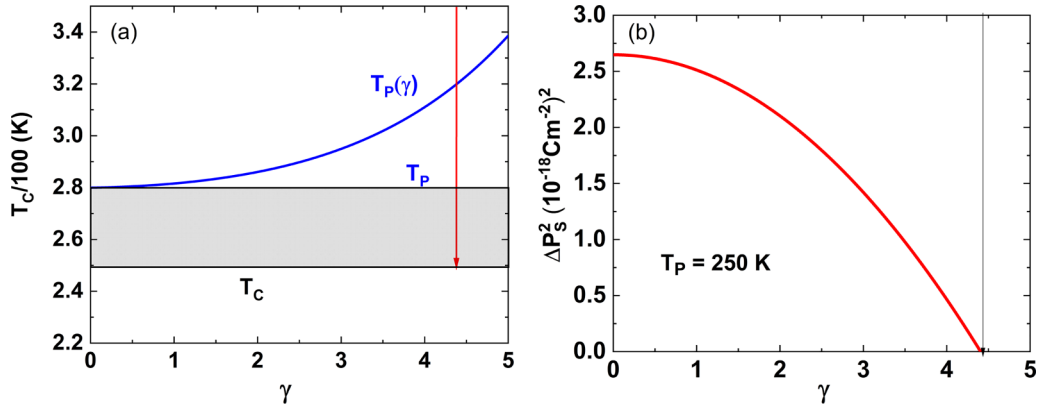


FIG. 3. (a)  $T_c = T_P + \frac{b'^2}{4a'c}$  as a function of the coupling constant  $\gamma$ . The increase of  $T_c$  to  $T_P$  at  $\gamma = 0$  is almost 30 K (shaded area). With finite  $\gamma$ , a nonlinear increase takes place. The vertical arrow indicates the stability limit where the coupling has no stable solution any more. (b) shows the squared polarization as a function of  $\gamma$ , where the vertical arrow indicates the stability limit. With increasing  $T_P(\gamma)$ , the polarization decreases and vanishes at the critical coupling strength.

with  $E$  being an external electric field, and the coefficients  $\alpha$ ,  $\beta$  self-consistently determined from the lattice dynamics of PH within the polarizability model [27–31]. The remaining coefficients  $a$ ,  $b$ , and  $c$  have been obtained similarly, however, using a variational methodology in order to guarantee a possible phase transition around 250 K, i.e., the starting assumption is that another phase transition at  $T_P$  can occur, emerging from the one at  $T_A$ . The quantities  $\alpha$  and  $a$  explicitly depend on temperature like  $\alpha = \alpha_0(T - T_A)$ ,  $a = a_0(T - T_P)$ , with  $T_P \approx 250$  K being the Curie-Weiss temperature and  $T_A = 490$  K. This is different from Ref. [1] where the temperature dependence of  $a$  is not included. It is added here to guarantee the phase transition in the vicinity of  $T_P$  and investigate this in the presence of a coupling to the potential in  $X$ . Minimizing Eq. (1) with respect to  $X$  yields straightforwardly the solutions  $X = 0$  and  $X^2 = \frac{1}{\beta}(\gamma P^2 - \alpha)$ . Because  $P = 0$  for  $T > 250$  K, the temperature dependence of  $X^2$  is given by  $\alpha$  and is correspondingly linear in  $T$ . At  $T < T_A$ ,  $\alpha = -2\alpha_0(T_A - T)$ . The two uncoupled potentials are shown in Fig. 1 as a function of temperature.

As expected, the potential in  $X$  exhibits a single minimum for  $T > T_A$  and adopts a double-well character below  $\approx 490$  K. The one related to a possible transition around  $T_P \approx 250$  K gradually changes from single-well to triple well, indicating a first-order transition with hysteretic features.

By inserting the finite solution for  $X^2$  in the Eq. (1), the coefficient of the squared and fourth order parameters  $a$ ,  $b$  are modified like

$$a' = a + \frac{\alpha\gamma}{\beta}, \quad b' = b - \frac{\gamma^2}{\beta}, \quad (2)$$

whereby an additional temperature dependence appears in  $a'$  stemming from  $\alpha$ , and a new transition temperature can be defined once  $a' < 0$  in the paraelectric phase ( $P = 0$ ), which is unstable in this region. The crucial quantity is  $b'$ , which triggers the order of the phase transition, and for  $0 < b'$ , a second-order transition is expected. Using the actual numbers this can be excluded and together with the condition:  $-4\sqrt{\frac{ac}{3}} < b - \frac{\gamma^2}{\beta} < 0$ , which is fulfilled as long as  $\gamma^2 < 19.42$ , a first-order phase transition takes place. The renormalized potential  $V(P)$  in the presence of the coupling is shown in Fig. 2 for temperatures around  $T_P$  (corresponding to the black line in Fig. 1(b) and various coupling constants  $\gamma$  as given in the Figure.

With increasing  $\gamma$ , the potential gets narrower, and the metastable minima away from  $P = 0$  smoothly vanish. The coupling thus appears to act like a heating bath.

Since the potential in  $P$  can now be rewritten, using the above definitions, as

$$F = \frac{1}{2}a'P^2 + \frac{1}{4}b'P^4 + \frac{1}{6}P^6 - EP \quad (3)$$

and assuming the external field to be zero, two conditions need to be satisfied simultaneously in order to obtain the true transition temperature, namely,

$$\frac{a'}{2} + \frac{b'}{4}P_S^2 + \frac{c}{6}P_S^4 = 0 \quad (T = T_P), \quad (4)$$

$$a' + b'P_S^2 + cP_S^4 = 0. \quad (5)$$

The three real solutions to Eq. (4) are

$$P_S^2 = 0, \quad P_S^2 = -\frac{b'}{2c} \pm \frac{1}{2c}\sqrt{b'^2 - 4a'c} \quad (6)$$

and with  $a' = a + \frac{\alpha\gamma}{\beta}$ ,  $b' = b - \frac{\gamma^2}{\beta}$ :

$$P_S = 0, \quad P_S = \pm \sqrt{-\frac{b - \gamma^2/\beta}{2c} \pm \frac{1}{2c}\sqrt{\left(b - \frac{\gamma^2}{\beta}\right)^2 - \left[4a_0(T - T_P) + \frac{\alpha\gamma}{\beta}\right]c}} \quad T < T_P, \quad (7)$$

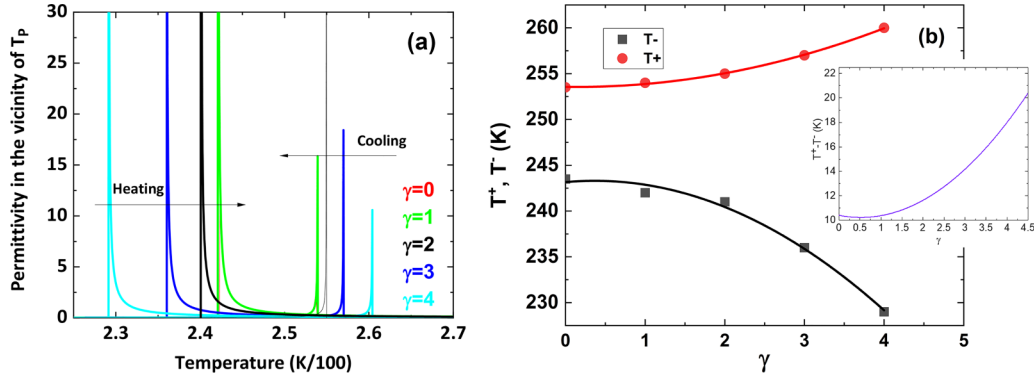


FIG. 4. (a) The temperature-dependent zero field permittivity in the vicinity of  $T_P$  as a function of  $\gamma$  upon cooling and heating, with the color code as given in the figure. (b) shows the difference in the spontaneous polarization as a function of  $\gamma$  upon approaching  $T_P$  from above or below. The difference between the two is shown in the inset, from which the corresponding hysteresis can be defined.

which yields,  $T = T_c = T_P + \frac{b'^2}{4d'c}$ , which is always enhanced as compared to the Curie-Weiss temperature and defines a hysteresis behavior and a regime of metastability around  $T_P$  by  $\Delta P_S = \sqrt{-\frac{b-\gamma^2/\beta}{2c}}$  (see the inset to Fig. 3). An additional increase in  $T_C$  occurs in the presence of a finite coupling  $\gamma$  between the two order parameters which is shown in Fig. 3 and which simultaneously expands the metastability region.

While the Curie-Weiss temperature is increased by a constant value of  $\approx 30$  K for  $\gamma = 0$  corresponding to the expected hysteresis (shaded area in Fig. 3), with finite  $\gamma$  the increase becomes nonlinear and can amount to almost 60 K with increasing  $\gamma$  which appears to be unphysical but, as can be seen in the inset, it has a physical origin since the spontaneous polarization at  $T = T_C$  rapidly decreases with increasing coupling strength and vanishes at the stability limit given above. This implies that a large hysteretic increase in  $T_C$  may indeed occur (area under the blue line in Fig. 3), but at the expense of the polarization.

From the above the zero field permittivity can be derived:

$$\chi^T = \frac{3b'^2}{4c} + 8a'(T_C - T) \quad T \rightarrow T_C^-$$

$$\chi^T = \frac{3b'^2}{16c} + a'(T - T_C) \quad T \rightarrow T_C^+$$

which demonstrates a discontinuity in  $\chi^T$  at  $T_C$ . With increasing coupling the discontinuity grows (Fig. 4) and the hysteresis gets larger [inset to Fig. 4 together with  $\Delta(T^+ - T^-)$ , inset.]

As has been emphasized already by Lines and Glass [32], the form of the potential [Fig. 1(b), Fig. 2] the low-temperature phase can exist above  $T_C$  as a metastable state in analogy to the high temperature phase, which persists for  $T < T_C$ , since local minima appearing in the potential are, however, higher in energy than the stable one. Nevertheless, tunnelling processes between the local and global minima might occur, where inhomogeneous states may be a consequence.

Experimentally, the transition around  $\approx 270$  K was detected by dielectric and pyroelectric [20], and second harmonic generation measurements [33]. A large hysteresis, of about 40 K, in the data upon cooling and heating has also been seen, comparable to the predictions made here (see Fig. 7). Since

the first-order character of the transition is accompanied by an entropy change, anomalies at the phase transition should be observable in the specific heat, thermal expansion and further thermodynamic quantities, since the discontinuity at  $T_C$  causes a change in the entropy, where the resulting latent heat is given by  $T_C \Delta S = \frac{1}{2} T_C a' P_C^2$ , i.e., dependent on  $\gamma$ . This causes anomalies in the above-mentioned quantities, which differ upon heating and cooling. Note that for zero coupling, the hysteresis in the thermodynamic quantities would be absent, and also the anomaly in  $c_p(T)$  would disappear. Correspondingly, any anomaly in  $c_p(T)$  is direct evidence for the presence of the coupled order parameters.

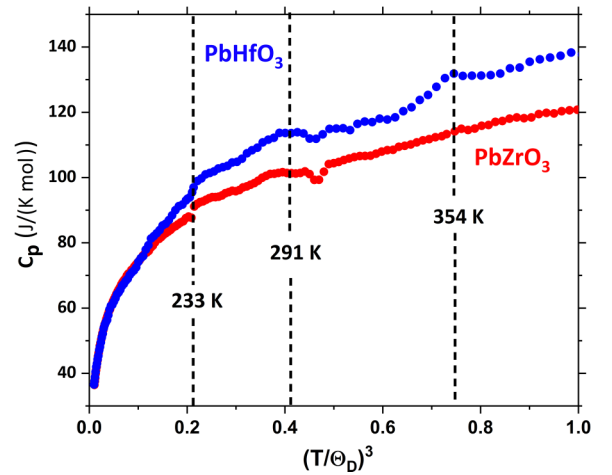


FIG. 5. (a) Specific heat  $c_p$  as a function of temperature  $(T/\Theta_D)^3$  for PZ (red) and PH (blue) single crystals on heating, where  $\Theta_D = 391$  K is the Debye temperature [35]. The dashed lines indicate anomalies in the  $c_p$  run, which correspond to changes in pyroelectric measurements observed near the low-temperature transition [20,34]. These anomalies appear in the  $c_p$  run stemming from the phonon mode contributions to the specific heat based on the Debye model. However, in the present case, the contribution from the phonon modes is distinctly larger as compared to the electronic bands and thus allows the use of the Debye model. Interestingly, in the case of PH, the distinct anomaly near 354 K (dashed black line) corresponds to anomalies in oxygen,  $O_{x,y}$  structural positions presented in Fig. 6(c).

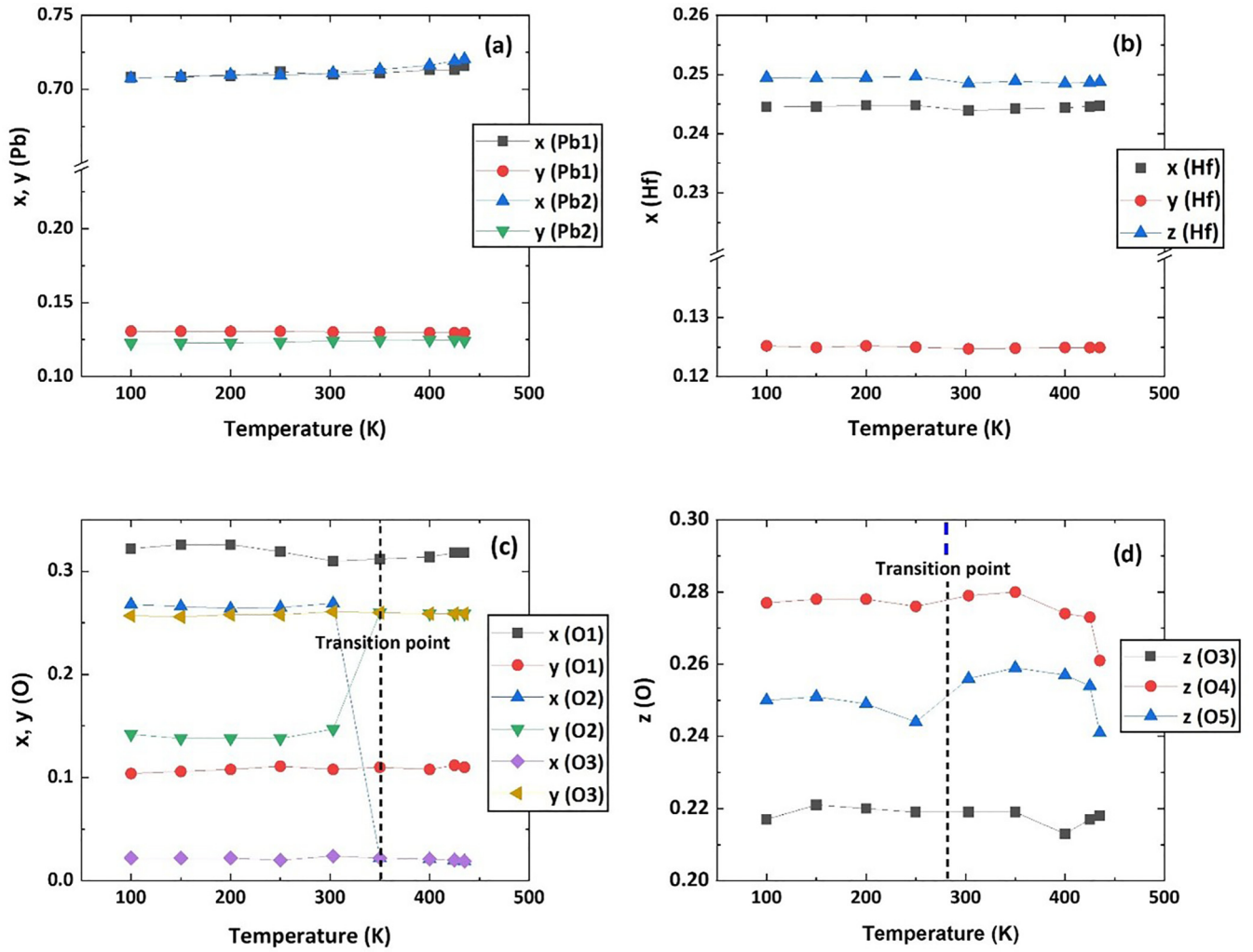


FIG. 6. Structural parameters of PH in the temperature range from 100 to 435 K separated according to the substructure of Pb (a), Hf (b),  $O_{x,y}$  (c) and  $O_z$  (d) taken from Ref. [36]. A clear change in the positions of oxygen ions (O2), (O3), (O4), and (O5) is seen. The dashed line marks the temperature at which anomalies in dielectric and pyroelectric properties are very pronounced, together with the disappearance of Raman lines and domain structure changes were observed [20].

### III. EXPERIMENTAL

In order to confirm this prediction, we have performed specific heat measurements, a thermodynamic tool which is often used to detect phase transitions as pointed out above. The specific heat  $c_p(T)$  was measured in the 83–395 K temperature range using a physical property management system platform with a heat capacity option (Quantum Design, San Diego, California, USA). The sample was first cooled down to 83 K at the maximum cooling rate of 12 K/min. It was then maintained at this temperature for 1 h to reach thermal equilibrium. After this stabilization, the specific heat measurement was initiated, with the temperature increasing linearly up to 395 K at a rate of 1 K/min. Small but distinct anomalies on the  $c_p(T)$  run have indeed been observed in PZ and PH single crystals, as shown in Fig. 5, which suggest the first-order nature of the low-temperature transition in these compounds. Moreover, such specific heat anomalies are in accordance with the volume changes in the crystals' structure rather than a

transition inside the domain boundaries or related to changes in vortices, as observed in PZ [34].

Further evidence for the structural instability was obtained from x-ray diffraction and neutron scattering data [33], where disorder in the oxygen ion displacements has been observed. However, this must be taken with care since the experimental resolution was most likely insufficient. Since our starting point was the assumption that not the Pb ordering is the essential ingredient for a transition to a polar phase, but the relative oxygen-transition metal displacement, we have replotted the structural parameters of  $PbHfO_3$  as obtained by x-ray diffraction below 435 K [36]. A space group  $Pbam$  was used in which fractional coordinates have the following values:  $z(Pb1) = z(O1) = x(O4) = x(O5) = 0$ ,  $z(Pb1) = z(O2) = y(O4) = 0.5$ . Instead of showing these values in a single figure, as done in Ref. [33], we have split the values for Pb and Hf only, together with those related to planar and c-axis related oxygen ions. The results are shown in Fig. 6.

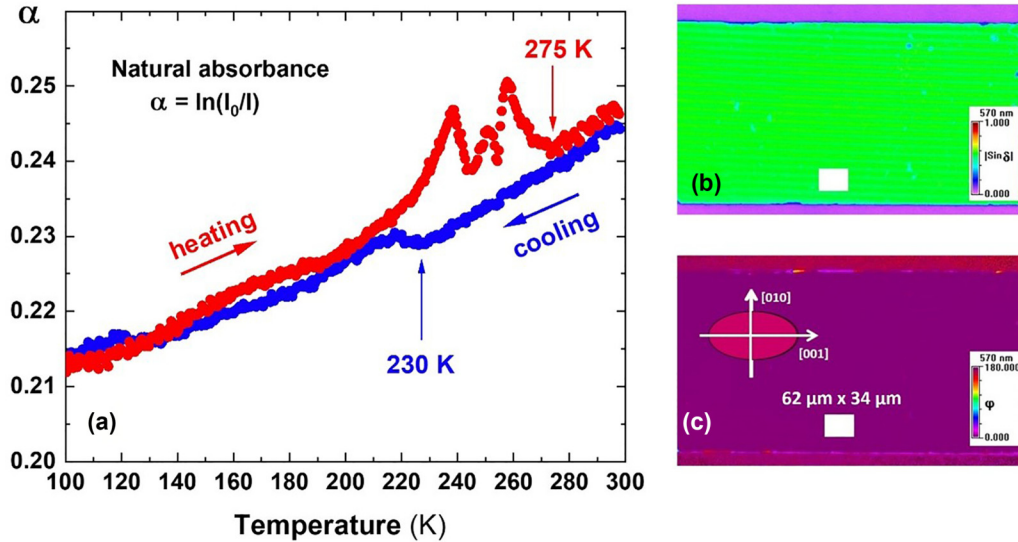


FIG. 7. Temperature dependence on heating (red curves) and cooling (blue curves) of the natural absorbance (a) for  $\text{PbZrO}_3$  single crystal. The optical retardation  $\delta$ , expressed in  $|\sin\delta|$ , and (c) the orientation of the optical indicatrix  $\phi$ , show the single domain state of the crystal represented by homogeneous colors according to the included labels. The large thermal hysteresis is well visible, and its order of magnitude is comparable to the theoretical predictions for large coupling  $\gamma$ ; the arrows mark the transition temperatures on heating and cooling. In (b) and (c), the white rectangle represents a part of the crystal for which the data were calculated. This rectangle was chosen close to the crystal edge to calculate the natural absorbance (extinction)  $\alpha = \ln(I_0/I)$ , where  $I_0$  and  $I$  are the light intensity entering and going out of the crystal, respectively.

Most amazing in Fig. 6 is the fact that the structural parameters of neither the Pb (6a) nor the Hf (6b) ions show any anomalous temperature dependence, opposite to the oxygen ions (c), (d), which exhibit gross anomalies around 350 K, especially well visible for the x (O2) and y (O2) parameters. The structural parameters along the z axis related to (O4) and (O5) also trace a transition around 290 K, and are extremely well visible near 433 K, the onset of the antiferroelectric (AFE) phase. These data directly highlight the roles of the different ions for the phase transition at 433 K and a possible one around 290 K, namely, the only players are the oxygen ions. This finding is in contrast to related theoretical and experimental work [23,24], where it was assumed that the Pb substructure is decisive for possible antiferroelectric, ferroelectric or even ferrielectric properties of PH and PZ, but in support of our picture that the polarizability of the oxygen ion triggers the dynamical behavior of these perovskite compounds.

More evidence for a low-temperature transition in PZ and PH is obtained from measuring the natural light absorbance in single crystals of these two materials. This methodology has the advantage of being extremely sensitive to structural changes, even at a local scale, and of providing unique evidence of structural phase transitions. We used the Metropol technique, described elsewhere [37,38], to detect the birefringence and optical indicatrix orientation, which establishes precise detections of the lattice geometry. This was done for pristine single-domain crystals, which were not exposed to external factors like electric, magnetic field, or pressure, but only low-intensity light with a wavelength of 570 nm. This means that we have detected the sensitivity of the electronic structure of PZ and PH, which is the same as is responsible for the data registered by x-ray spectroscopy (Fig. 6).

Because there are literature data for structural investigations for  $\text{PbHfO}_3$ , it is possible to connect these results with those experiments we have performed for single crystals. This is presented in Fig. 8, where the chosen structure parameters taken from Ref. [36] and specific heat data are directly compared to each other. Evidently, the combination of both experiments undermines the existence of structural instabilities pronouncedly near the temperatures 291 and 354 K.

#### IV. CONCLUSIONS

In summary, we have assumed that the phase transition at  $T_A = 490$  K can be described by a local double-well potential, which admits the possibility of observing a first-order as well as a second-order phase transition. However, in recent experimental and theoretical studies, it has been clarified that the transition is of first order [27] with a temperature region where high and low-temperature dynamics coexist. The transition, which takes place at  $T_P \approx 291$  K for  $\text{PbZrO}_3$  and  $\text{PbHfO}_3$  due to the coupling to the first transition, is ascribed to a sixth-order expansion in the order parameter, inducing a first-order phase transition with thermal hysteresis and a small spontaneous polarization. The difference between the theoretically predicted transition at 250 K and the experimentally observed one in the range 275 K (optical properties) and 291 K (thermal properties) is acceptable, since in the theoretical approach external factors like strains stemming from point defects, extended defects, presence of the electrode and thermal gradients being different in different stages with different sample mountings are not taken into account. Coupling both potentials by a biquadratic term in the order parameters provides an inherent connection between the order parameters in terms of a common origin through the

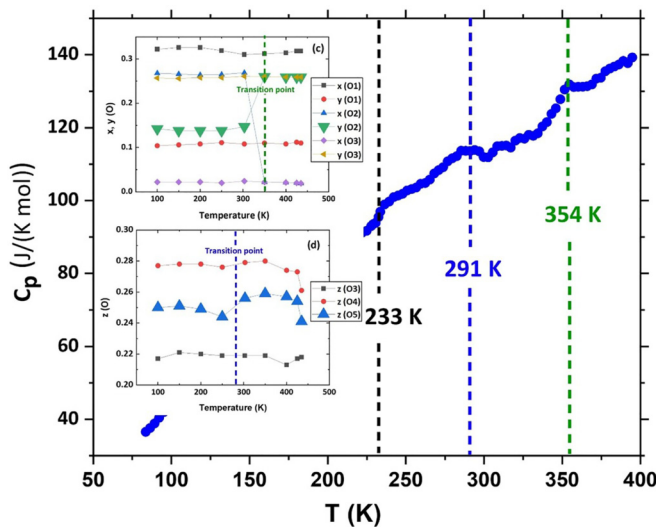


FIG. 8. The figure shows the correspondence of anomalies detected on the run  $c_p(T)$  and those obtained from x-ray diffraction and neutron scattering data shown in Fig. 6 as (c) and (d), with enlarged experimental points in green and blue connected with the y coordinate of oxygen O2 and the z coordinate of oxygen O5, respectively. It would mean that low-temperature transitions in  $\text{PbHfO}_3$  are connected with the deformation in the oxygen octahedra. The difference is that the transition at 354 K in  $\text{PbHfO}_3$  is not observed in  $\text{PbZrO}_3$  (see Fig. 7). Our preliminary experiments showed that the region between 291 and 354 K in  $\text{PbHfO}_3$  is also connected with the polar properties, but much weaker than that found below 291 K and described in Ref. [33].

polarization. Consequently, the thermal hysteresis at the lower transition is broadly enlarged; however, it is at the expense of the polarization, which vanishes completely at a critical coupling strength. The question arises about the role of the

coupling constant, and we suggest that this depends, e.g., on doping, since doping at the transition metal site does not grossly change the transition sequences [39–44]. This can, however, be tested by probing the appearance of the above-described phenomena. Our analysis shows that PH and PZ can undergo a low-temperature phase transition to a ferroelectric state (below 290 K), where the metastable states around the transition temperature, i.e., within the hysteretic region, can obscure their presence. From a lattice dynamical perspective, the flat back-folded TA mode could couple with the zone center optic TO mode at finite momentum values, leading to ferroelectric order in confined spatial regions. Importantly, this instability is not connected with the Pb ion displacements but is solely due to the transition metal-oxygen  $\text{ZrO}_6$  and  $\text{HfO}_6$  substructures, which are typical for a broad number of ferroelectric perovskite oxides. It is important to emphasize that in thin films, a true ferroelectric order has been detected at low temperature [45,46] when the films are oriented. In the unoriented case, coexistence of ferro- and antiferroelectricity has been reported. This apparently controversial result might be related to stress or strain naturally arising in films, which favours one or the other ground state at the expense of the other. An excellent review on the potential of film engineering has been given in Ref. [46].

#### ACKNOWLEDGMENT

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#### DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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