Piezoelectricity in nominally centrosymmetric phases

O a A a \bullet

 T e $\frac{1}{2}$ and $\frac{1}{2}$ data and 4 be and 4 f 4 f ex 4 e ectricity in $n = \frac{1}{2}$ π α b α are a are broad dided π α are causes. *a. Ferroelastic domains within ferroelastic phases and ferroelastic local domains in the paraphase*. Tee a e e a ed t_A e t_A de t_B af a t_B and t_B strain in ferroelastic materials, c a evector cannot analog of $\frac{4}{5}$ are mechanical analog of $\frac{4}{5}$ (see Fig. 4.1 are 4. \mathcal{A} a za 4F) and ferramagnetication (spontaneous magnetication) and ferromagnetic magnetic $[16 \t20]$ $[16 \t20]$ $[16 \t20]$. Iⁿ e fe^{re} ferroelastic phase, twin walls, i.e., b^{oundaries} e aatif fe \mathcal{A} e a cd \mathcal{A} af (\mathcal{A} strain), ee \mathcal{A} f 4 be eleq $\begin{pmatrix} 4 & a & 6 \end{pmatrix}$. Above the temperature, signature $4f$ eferred paragonale (also called equality equality equality equal provided provided provided provided provided provided 4) 4°cco a alucta4°l (leadeac, ae), eadi \mathcal{A} ici a ee \mathcal{A} eⁿe [\[16](#page-10-0) [18](#page-10-0)[,21\]](#page-11-0). These include tweed a e \mathbb{P} a a electron experiments are seen in the set of \mathbb{R} energies as c 4 - a c ed a e Fard e e 4 b e ed 4 a e er 4 f 100 $\sqrt{4}$ 2000 (19). Such ee $\sqrt{4}$ eⁿe ee can be a et 4 ffeaca $^\mathbb{F}_1$. 4 4 4 , e leac $_\mathbb{F}_1$ 4 f $_\mathbb{F}_2$ 4 2 $_\mathbb{C}$ and $_\mathbb{C}$ \mathbb{C} 4 d. 4 e., ica 4 caeda. F.F.4 e.e.4 e α de and a_i de , a_i a za a_i ⁿ in incipent ferree c, 4 c4 4 d7 4 e fe 4 e ec c4 fe 4 a fe c a e **i** a^fe4 fe 4e a c [\[16](#page-10-0)[,19,20,22\]](#page-11-0).

b. Ferroelectriclike local polar structures within the para-
 electric phase. T e e e e 4 *intrinsic*, exe e c *electric phase.* The end end *a intrinsic* ex⁴e ectricity a 4 4 e defec-induced $4a$ a a a a $4e$ a extrinsic stimulus [\[16](#page-10-0) [18](#page-10-0)[,23](#page-11-0) [25\]](#page-11-0). In the context of the also include ferredectric equipped and precursors, which occursos and paraelectric precursors, which occur in the paraelectric ρ a eald e ρ by 4 called the structural feature. The state leads when e fe ℓ eccc a e [\[16](#page-10-0) [18](#page-10-0)[,23](#page-11-0) [25\]](#page-11-0). L ℓ ca ℓ a cue a e ece^{f} been 4b e ed by electron minimal electron minimal method in the electron minimal model of 4c a ae ectric paraelectric ectric BaTiO₃ and its solid solution and its solution \mathcal{L} and its solution \mathcal{L} $\lceil \cdot \rceil$ 4 m incipient ferroelectric or incipient ferroelectric STO3 with $\lceil \cdot \rceil$ and $\lceil \cdot \rceil$ with $\lceil \cdot \rceil$ ends are contained substitute $\lceil \cdot \rceil$ and $\lceil \cdot \rceil$ and $\lceil \cdot \rceil$ and $\lceil \cdot \rceil$ and $\lceil \cdot \rceil$ an se $4f$ 2 44 $\sqrt{26,27}$. This class includes local polarization structures in relaxors (or relaxor ferroelectrics), which remain α b.c.d 4 β 4 absolute $28,29$]. I β lee e a 4 leare, e ae eleastiefered $4a$, $4a$ lall 4 e 4 ll (PNR) [\[7](#page-10-0)[,28,29\]](#page-11-0). The size $4f$ PNRs and end of $4f$ and end a 420 nm in e case $4f$ elles elle $4f$ elles as $4PMN$ [\[29,30\]](#page-11-0).

Leⁿgth cales 4 f ab 4 e $\frac{1}{2}$ ength 4 red 4 ca_{l a} 4 al polar structures ca let e Id from some cases, in some cases, nearly some cases, nearly Id a c 4° c 4° [\[6,](#page-10-0)[19,26,27\]](#page-11-0). We efer 4° all 4° erection 4° c t e a $4a$ $\frac{a}{2}a$ \ldots e.

Extrinsic versus intrinsic reasonings. A_{\perp} effec (a) and (b) c $4 \,$, d, include in the \mathbb{R} ecanisms (i.e., characeric \mathcal{L} the ideal, pristing effects) and equal equations as \mathbb{R} or ecanisms, and it is not always possible 4 distinguishment between the experimental them extrinsic effects i^nc_i de defect ad eⁿ f² ed during high-temperature syne $4f - 4c$ a (ceramics) [\[1\]](#page-10-0). Indeed, in 4 de 4 4b e e a macroscopic perfecteur effect under the local effects under the local $4ca$ p_1 , p_2 is necessary it is necessary that the local piezoelec- $\begin{bmatrix} \cdot & c & d \\ c & e & g \end{bmatrix}$ of $\begin{bmatrix} 4 & e & d \\ 4 & e & g \end{bmatrix}$ () do not set $\begin{bmatrix} 4 & e & f \\ 4 & e & g \end{bmatrix}$ are self-compensate instance in the self-competence in the self-compete instance in the self-compete in the self-compete the sample; e.g., e.g., $\sqrt{2}$ e.g., e.g., $\frac{1}{2}$ all $\frac{1}{2}$ be $\frac{1}{2}$ $\frac{1}{2}$ e.g. T_{c} can be pictured by an effective bias field. The eend $e \equiv e \pmod{4}$, end a 4π , which would be expected in the $\text{c} \times 4$ d fa $\text{c} \times 4$ and and $\text{d} \times 4$ distributions of the tensor c^2 , d rent [\[1,](#page-10-0)[31,32\]](#page-11-0). Current understanding is the this bias that the this bias the this bias that the this bias that the this bias that the $\parallel a \parallel c \parallel$ ef \parallel defec ad entrance from defect as an extra formed during $\frac{1}{2}$ eare fem 4 f 4 c a (ceal c) [\[1\]](#page-10-0). The same mechanism has been proposed to occur during the same mechanism of \mathbb{F}_2 \mathcal{A} 4f fecal [\[1\]](#page-10-0). Other cafe and mechanisms that substantials that substantials that substantial substantials that substantial substantial substantial experimental substantial experimental substantial experimental su

ale elayecal mea 4 beel e 4 ed [\[2,3,](#page-10-0)[33\]](#page-11-0). H²¹ ee, ee, al 4 alce $\left[\begin{smallmatrix}a&0\end{smallmatrix}\right]$ a $\left[\begin{smallmatrix}a&0\end{smallmatrix}\right]$ eafa $\left[\begin{smallmatrix}c&0\end{smallmatrix}\right]$ a xal 4 f e eⁿ fe α α α are entity are not subjected to an effective ba ed. Such a events and \mathbb{R} that \mathbb{R} and \mathbb{R} a collections and a collections an lec $4\mathbb{I}'4\mathbb{f}$, $4\mathbb{a}$ e \mathbb{I}' entities $(1\mathbb{e}, \frac{1}{2}, 4\mathbb{a})$ and \mathbb{I}^n and \mathbb{I}^n are \mathbb{I}^n and \mathbb{I}^n \Box $^{p}4e$ e^{rter}a defectoral also ead q a ^{p}e a net q a net q . In this case, nucleation of the first polar nanostructure biases the first polar nanostructure biases to examine the first polar nanostructure biases to examine the first polar nanostructure biases to examine the first polar e $4f$ evaca, elde f 4 a ald ex $4e$ ecc. C² $\mathbb{F}_{\mathbb{Q}}$ dering that \mathbb{Q} exactly (a) and (b) and edge previously edge previously edge provided previously edge provided provi regard \mathbb{P} region effective loss of inversion symmetry leading to the effective loss of inversion symmetry leading to the effective loss of inversion symmetry leading to the effective loss of inversion symmetry leadi pez electricity in the cubic and alleve electricity in the general line of the cubic paraphases were generic to and $n4$ specifically data are $n4$ also and $n4$ always unitors are not always unit alwa ce a $\lceil \text{a} \rceil d$, a $\lceil \text{c} \rceil$ de ea. $\lceil \text{a} \rceil$, $\lceil \text{a} \rceil$ \mathcal{A} systematically easing the piez \mathcal{A} e ectric effect in \mathcal{A} in \mathcal{A} ceⁿ $4 \sqrt{2}$ e'c $\sqrt{2}$ a e q . Whereas per $4e$ echo change $4d$ effec (d₁ c4 e ed₁ ⁿ 1880 by e G₁ e b⁴ e₁) and $\lceil \ln \ln \frac{1}{2} \rceil$ a vast $\lceil \ln \ln \frac{1}{2} \rceil$ be 4f ec $\lceil \ln \frac{1}{2} \rceil$ case, ca- \mathbb{R} ⁿ [\[34,35\]](#page-11-0), fd \mathbb{R} a \mathbb{R} \mathbb{N} \mathbb{R} \mathbb{R} \mathbb{N} is \mathbb{R} and exciting physics. We measured the equality c and c resonant piezoelectric spectrum c , \overline{c} or c and \overline{c} and (RPS) [\[5,10](#page-10-0)[,36\]](#page-11-0) $4f$ en $4g$ ed fer $4g$ ec c c $4g$ $4g$ $4g$ (c a acterized by ferred and c domains) and the same and the same sectric phases (α as α and α and α and α are α including ferroelectric contributions in α eq 4), fe 4e a c LaA_lO₃ (with polar twin 4e a m c 4e e a 4 fe $\text{deg}(c, \emptyset)$ PNR) ab \emptyset e feezing tem- α_1 e, incipent ferreelectrics KTaO3 and STO3 with no k ⁿ A P ₁, P _a c_{luster} at r q ₁, q $\frac{4\pi}{\pi}$ called a 4ⁿ 4f defects, namely, NaC_l, CaF₂, and silica a B is p be \sqrt{a} exercises. c is a \sqrt{a} single crysa a a a standard, we find the strain generated as a strain generator of a is a strain generator. in resonant ultrasound spectroscopy (RUS) and calibrate the piez $4e$ ectric $4^{\frac{n}{2}}$ ede ected by RPS $4^{\frac{n}{2}}$, $4^{\frac{n}{2}}$ ed fe $4^{\frac{n}{2}}$ ectrics ead τ' c4 α e titalate (PZT-5H) and L NbO₃, aⁿd L_a ae ec $t_{\rm c}$ CSTO₃. Then, \mathbb{R} show that non-tag nominally centrally \mathbb{R} of \mathbb{R} values of $\mathbb{$ phase 4f materials and materials with local polar entities and chemical polar enti defects, ed A and A even in a piezoelectric effects a a beel 4 de 4 fl a l de l compa \mathbb{R}^n a 4 \mathbb{N} p ed ferred ferroelectric that have high piez p ectric coefficients. T e e are alef \mathcal{A} e c \mathcal{A} a abe \mathcal{A} a $\mathcal{A}\mathrm{f}$ are 4 10 $\frac{1}{2}$. Y, which is the examed of $\frac{1}{2}$ and $\frac{1}{2}$ a de ec 4^p , \mathbb{Y} aff can electric measurements. F is equiled in detail in the individual in the energy of the term of the term of these q er \mathbb{R} e ad 4 cate the idea that ex4 e common a common \mathbb{R} 4 f phenomenon in 14 minutes in the nominal central materials and un- $\frac{1}{2}$ ed fer $\frac{4}{5}$ ectrics. Previous structural probes applied $\frac{4}{5}$ ed $\frac{4}{5}$ ed $\frac{4}{5}$ ed $\frac{4}{5}$ α aelecc α' , a.e. α e. ed α a. deviations from crystal- A a c ie A i we een in the a even in a (f^{α} e a_{nd}e_xRef. [\[38](#page-11-0) [40\]](#page-11-0)). He elect in contrate such structural \mathcal{A} be a \mathcal{A} ^p \mathcal{A} ec \mathcal{A} c \mathcal{A} e a \mathcal{A} ^p \mathcal{A} fⁿ ea ex \mathcal{A} eecc, and ϕ early ade ϕ be eard narrow the extraordinary extr \mathcal{S} ensits of the advanced equal techniques \mathbb{R} is equal RUS. Te \mathbf{v} a de a 4^p f \mathbf{v} centrosymmetry are ecced by ex $4e$ ectric coefficients that are as 4π and 0.1% to 0.01% $4f$ a $4f$, ex $4e$ ec c i a x.

II. METHODS

Measurements were performed 4^n 15 compounds with \mathcal{A} and \mathcal{A} 18 different samples. Fig. α , end are ferred are ferroelectricial BaT O_3 , \parallel e c \parallel a, a BaT O_3 ce a c, e arec.5(BaT)35.5(3Tc([)T

TABLE I. Change in the \mathbb{Z} of compounds in the compounds used efeez^{ng} or slowing or slowing or set P and P are from Refs. [\[41](#page-11-0) [43\]](#page-11-0).

 \mathbb{Z} \mathbb{F} F. [2.](#page-4-0) These e \mathbb{Z} and a peaks in \mathbb{Z} both \mathbb{Z} RPS $a \nvert d$ RUS \lvert ec a.

B. How to extract the piezoelectric response from the spectra

Iⁿ RPS, because the excitati^al 4f each elastic resonances requi[res](#page-10-0) to α be example to be perfected to be a called the area of res[onanc](#page-11-0)e

FIG. 2. Eace \mathcal{L}^{A} and \mathcal{L}^{B} and \mathcal{L}^{C} and \mathcal{L}^{C} and \mathcal{L}^{A} and ca_l (by RUS). (a) Schematic of RUS and RPS measurements. The sample is lightly held between two transmusses of entry held between two transmusses of $e^{\frac{1}{2}}$, $e^{\frac{1}{2}}$, $e^{\frac{1}{2}}$, $e^{\frac{1}{2}}$, $e^{\frac{1}{2}}$, e^{\frac V_{AC} =

4 e ex $4e$ ecc f $4f$ e 4 , $4e$ e face. This $4d$ cause a material $\frac{a}{b}$ a e material to be $\frac{b}{c}$ face perfective is the expected vertex of e f_1^2 e f_2 in abef f_3 inverse flexoelectricity (this has if factored and discussed in the literature), and the same \Box ze-dependent e \Box e Υ entries \Box and $\$ \mathbb{F}_1 ca \mathbb{F}_2 \mathbb{F}_2 of \mathbb{F}_2 excludes \mathbb{F}_2 and \mathbb{F}_2 excludes a $\mathbb{F$ $4f_{11}$ face ex $4e$ ectectricity. In relation to the this is the end of the to the to-this is a been \mathbb{R} and face effects are not the dominant method. \mathbb{R} if \mathbb{Z} is the formulation detected in parameter in parameter in parameters in par a e $4f$ fe $4e$ ec c $[1]$. Ne e ee, surface ex $4e$ ecic \mathbb{V} a \mathbb{V} a'e \mathbb{N} e \mathbb{V} (m²) c² \mathbb{P} b \mathbb{P} ⁿ \mathbb{P} e the de ec ed in ex $4e$ ec c weasted en T e e effects are lie en anced in ecase of 4 rough surfaces, as so 4 in by $\binom{1}{1}$ a 4^p [\[61\]](#page-12-0).

IV. PIEZOELECTRICITY IN NOMINALLY CENTROSYMMETRIC PHASES OF COMPOUNDS

A. RPS and RUS spectra of nominally centrosymmetric and bulk-centrosymmetric materials

E $\frac{1}{2}$, e 4f RPS and RUS sec a f4 $\frac{1}{2}$ ed fe 4eeccald centrosymmetric area are $4.1 FF.4$ $4.1 FF.4$ (ee F_{igs.} S1–S3 in the S_{upple}rial Material [\[45\]](#page-11-0) f² e spectra 4 f 4 other compounds and samples). Similar 4 external to piezoelectric quartz, poled LNbO₃, and poled PZT-5H, a_{ll} samples show elastic elastic resonances in RPS special Due 4 to dia- $\frac{3}{4}$ ed $\frac{1}{4}$ ed $\frac{1}{4}$ ed $\frac{1}{4}$ ed $\frac{1}{4}$ ed ferroelectrics in $\frac{1}{4}$ ed ferroelectrics in $\frac{1}{4}$ and n \mathbb{Z}_p nature centrosymmetric compounds, the piez \mathbb{Z}_p compounds of \mathbb{Z}_p c Per cell \mathbb{V}_1 , be \mathbb{V}_2 all electric effects of intensity effects of intensity or intensity of \mathbb{R} . \mathcal{A}^{F} a ad e $^{\text{F}}$ (e.g., e $^{\text{F}}$ e a ed by e e \mathcal{A} e $^{\text{F}}$ e \mathcal{A} celemical calculations calculations chemical chemica ed c 4π) a e ab e π [\[62,63\]](#page-12-0). B a_{rc} *et al.* [\[1\]](#page-10-0) ea ed $t_{\rm e,d_33}$ c 4 ef cel^t 4f a BaT $\rm O_3$ ce and clear the ferred energy c a^{p} , 4^{p} d^{p} eare a^{p} d f 4^{p} d a ec 4 ef ce $^{\text{p}}$. The e 4° e 4 de 4f 0.1–0.3 C N (4)

FIG. 4. Pez \mathcal{P} ectricity in \mathcal{P} ballcent \mathcal{P} (ferroelectric materials and unpoled ferroelectric ferroelectric ferroelectric materials of \mathcal{P} aea F4Pfd4, aFaFdaF(a2ee eSuppleFaMaea[\[45\]](#page-11-0)). RUS eca4Pfac4, AFFd4F4 - 4Fe4FaFceY e 4Fe de ec ed in RPS and e f4 to 10⁻³ $\frac{1}{4}$ ∼10⁻⁸ V, demonstration and broken 4 V e centros

V. CURRENT UNDERSTANDING OF SPONTANEOUS ATOMIC-SCALE SYMMETRY BREAKING IN PARAPHASES

 $T e$, ℓ , abeita e , ℓ 4f a a ae ecc c a e acc 4 dⁿ $4'$ a nde any e a nate 4 ba xe 4 d β e because each site a a ze β dipole. This "nonelectric contractor" and a zero dipole. This indicate α contract α $\frac{d}{dx}$ 4de $\frac{d}{dx}$ are $\frac{d}{dx}$ electricity has been $\frac{d}{dx}$ electricity has been $\frac{d}{dx}$ electronic $\frac{d}{dx}$ electronic $\frac{d}{dx}$ electronic $\frac{d}{dx}$ electronic $\frac{d}{dx}$ electronic $\frac{d}{dx}$ electronic $\frac{d$ $\frac{1}{\pi}$ it cle calculations as $\frac{1}{2}$ and $\frac{1}{2}$ allows on the smallest the smallest smallest,

 h_{e} = $\sum_{n=1}^{\infty}$ crystallogicallogicallogical unit cell. Analogous Analogous approximations were common for describing paramagnets as a *p*hime e cappi all fat de c b ^{pi}, a d a le a
a e e each e a re 4 M el Becae
c a 4 e e a al 4 f A d e d 4 e l e a ca^peca aⁿ 4 ^p f² if $\frac{1}{4}$ ed 4 e ^pe

4 - $\frac{1}{4}$ ear efe 4 ecc_ca e $\frac{1}{4}$ re 4 d $\frac{1}{4}$ e ^peaa- \mathcal{A} -dectric phase ferroelectric phase to \mathcal{A} as \mathcal{A} of \mathcal{A} e. \mathcal{B} e. a ae ecc cae, a bete a , $4 \sqrt{a}$ a 4^{β} a been edg, ace $\frac{d}{dx}$ de 4 f a ae ectric paraelectric phases $[76]$ that still uses the minimal uses of $\frac{d}{dx}$ $\mathfrak{g}\restriction \mathfrak{h}$ but $\mathfrak{g}\restriction \mathfrak{m}$ for finite polar displacements in a single d^{oubl}e-well picture. H^{ow} electric experiments of the restriction of 4^{p}

FIG. 5. Comparison of RPS spec a 4f fe ℓ ectric BZT20 c_1^2 ec ed 32 and 84 K ab c_1^2 e te c_2^2 ec c Curie temperature $T_c = 296$ K.

 \mathcal{A} a minimal unit cell in the displace \mathcal{A} depends \mathcal{A} excellent model. \mathbb{F} e a ae'ectric phase must be all field in tandem, lead- \mathbb{F}_1 4 a 4^p - a^p e-4 de ed \mathbb{F}_2 4de f⁴, a ae ectricity. In $v_{\rm e}$ ie atoms are $v_{\rm e}$ are potentially in a single potentially in a single potential \log_{10} a \approx \log_{10} around the Wickoff $\frac{4}{3}$ and $\frac{4}{3}$. Therefore, $\frac{4}{3}$ e $\text{ca} \mathbb{P}$ always a time average $\mathbb{P} \mathbb{P}$ and $\mathbb{P} \mathbb{P}$ are $\mathbb{P} \mathbb{P}$ and $\mathbb{P} \mathbb{P}$ erties. Reciprocal-space calculation of \mathbb{R}^n and \mathbb{R}^n or \mathbb{R}^n based \mathbb{R}^n such a symmetry-unbroken monomorphous structure for the content of the theorem is a structure for the theorem paraphase following the softening the softening of the paraphonons are the paraphonons as the paraphonons as the paraphonons are the paraphono \lceil all $4\lceil$ $4\lceil$ $4\lceil$ e. $4\lceil$ e. $4\lceil$ e. a. e. a. e. e. a a 4 ac ed. Iⁿ the alternative of a details of a and a for the model of a and b and a and b and a $\left[\begin{array}{cc} a^p & 4^p & [77], \end{array} \right]$ $\left[\begin{array}{cc} a^p & 4^p & [77], \end{array} \right]$ $\left[\begin{array}{cc} a^p & 4^p & [77], \end{array} \right]$ and $\left[\begin{array}{cc} a & a^p & a^p \end{array} \right]$ and $\left[\begin{array}{cc} a & a^p & a^p \end{array} \right]$ \Box ce f4² dec bⁿ e aa ae 4² ad 4 de ed 4 ca p , q a d , q acements are q , q be p equations are paraelectric phase; i.e., e.e., $a \cdot 4 e^{\beta}$ a γ e. γ a few minima (f4 β e) but e^a co_n a 4^{π} hype a e a abe, a 4^{π} ^p le polarity. Phase transition occurs when occupational symmetry ib $4e^{\frac{\pi}{2}}$. H $4e$ ee, e $^{\pi}$ ed $4e$ $^{\pi}$ e $^{\pi}$.

The electric equality of \mathbb{R}^n are been recently challenged [\[78\]](#page-12-0). Indeed, there are $e^{i\theta}$ are recent theoretical reasons are recently and the example that $[79'83]$ $[79'83]$ $[79'83]$ 4 believe that \mathbb{F} intrinsic mechanisms must mean interval \mathbb{F} and \mathbb{F} be responsible for the formation \mathbb{F} 4 f a $\frac{1}{2}$, c-cae $\sqrt{2}$ e bea in parae, manifest- \mathbb{F}_1 \mathbb{F}_2 \mathbb{F}_3 = aⁿ e-4 de ed (SRO) 4ca \mathbb{F}_4 f (\mathbb{F}_4 \mathbb{F}_4 \mathbb{F}_4 \mathbb{F}_5 \mathbb{R}^N (4) [\[79\]](#page-12-0). Such \mathbb{N} breaking was argued theoretca_l 4 4 e e^{nerg} eⁿergy under the internal energy under the internal energy and energy under the internal energy and the internal energy and internal energy and the internal energy and internal energy and interna a "a 4ⁿ" e F, ead ^p '4 e f4 a 4ⁿ 4f a *distribution* of local motifs in all paraphases. This includes *paraelectric*, a.e. (where the pertinent degree 4f freed4_{the se}ven α d₁ α _e), *paramagnetic* a e α e e e α ⁻¹ ca de ee 4f feed $\frac{d}{dx}$ e 4ca $\frac{d}{dx}$ a Fe c $\frac{d}{dx}$ e i), $\frac{d}{dx}$ *paraelastic*₁, a e (e e e e ^pertient de ee²ff freed² can be a eA e c-e ceffect c a 4 c a ed a 4 a 4 m). $S \nightharpoonup^{\text{R}} c$ a R , e e R *static minimization* 4f , e R e R density file 4 $\frac{1}{2}$ elergy of supercells constraints of $\frac{1}{2}$ \mathcal{A} ba \mathbf{W} e a ead \mathbf{A}'' ed a f caf ab za \mathcal{A} f f f^2 is network that f^2 is network that f^2 is a letter different local \parallel 4 f c4e ii \parallel 4 f e a e iece. Naturally, as $\frac{1}{2}$ e - at e.e. $\mathbb{P} \subseteq \mathbb{P}$ 4de ed value functional theory (DFT) $\frac{1}{2}$ eq a d $\frac{1}{2}$ c. (MD) [\[80,83\]](#page-12-0)), add $\frac{1}{2}$ and aces ef. $a e$, ace. S_{ign}ificantly, both e , \mathbb{F}_q internally, \mathbb{F}_q and \mathbb{F}_q internal of the internal of the internal set of the inter ene U (in DFT) and that of the energy U-TS (via DFT-MD) ead 4 We bea F FcrdF e d 4 a 4 f \therefore \mathbb{R} e \mathbb{R} **i** \mathbb{R} e \therefore T_{rus}, a 4 e *average* $\langle S \rangle$ *A* e \langle ² ca $\{A, f, \{S\}, a$, we can be centrosymmetric), d \mathcal{A} e \mathcal{A} \mathcal{A} all measured physical \mathcal{A} e e $\ket{\mathbb{S}}$

coefficients in the paraelectric phase of ferreelectrics were experienced as α f $\mathbb A$ id $\mathbb A$ be comparable $\mathbb A$ defined to the top of $\mathbb A$ and up $\mathbb A$ ed ference Γ events in the angle $\frac{4d}{d}$ can $\frac{4d}{d}$ and $\frac{4d}{d$ c 4 ec 4 4 4 f 4 f a a a a a a c c c a a ead 4 a a c c a c c a^{\dagger} ca devel. Such and attended to be proved example, in Ref. [\[63\]](#page-12-0), Nee in 4d c41 4f ee4 ele4 . c d_{is} calculation 4° ed $4d_{33} = 321$ pm/V in Na_{0.5}B_{i0.5}T_iO₃- $Bar\ O_3$, $\begin{bmatrix} 0 & c & e \end{bmatrix}$ coefficients of most most coefficients of $\begin{bmatrix} 4 & 4 \end{bmatrix}$ fe Re ec c and c Im a ab e Im a Tr ead z c Tr t_i al^pa'e (PZT) [\[89\]](#page-12-0). M4² e because the intervalse of f_i and f_i and g_i $\lceil \text{a} \rceil$ $\frac{4}{\pi}$ i c i e $\frac{4}{\pi}$ e f^o be for definition the form of $\lceil \text{a} \rceil$ be $\text{seV } 4 \text{ e}$ in V d ed 4 f de ee ab 4 e fe $\text{'} 4$ e ec curie d ' eare and feezing temperatures as $4c$ and c and d associated with r $h = e_{n+1}$ e ar energ e_n ez e_n echectrications, including energy a e \int , can be envisible ded via the ged via the growth or syne $4f$ ae a ace ca, e, e, $\frac{1}{2}f$ and e ecca ad $e^{\frac{1}{2}}$ [\[34](#page-11-0)[,63,90\]](#page-12-0).

The scenario of intrinsic symmetry breaking short-range order in paraphases without defects and polar nanostructures. We \mathbb{R}^4 a *positional* \oint c \bigcup **b** ea \bigcap i c a displacements and c and c and a rotations are seen by a cal structural p ⁴bes in p ⁿ, p ⁿ p ⁿ, p ₁ q obc₂, e 4 q e (p ¹ z ., add b¹ 4 ⁿ function (PDF) [\[79\]](#page-12-0)), $\sqrt{ }$ e ease 4 f e^{β} e ca e de ec 4^{β} by 4^{γ} e-a e a β ecos β i equiper a $c4$ ^r, $e^{\frac{t}{2}} 4^{\frac{t}{2}}$ - a diff $ac^2 4^{\frac{t}{2}}$. Indeed, 4 *local* \bullet e-

reversaling predicted theoretical predicted theoretical predicted theoretical problems in paraa $\lceil e \rceil$ [\[79,81\]](#page-12-0), even $\lceil e \rceil$ e $\lceil e \rceil$ e $\lceil e \rceil$ a $\lceil e \rceil$ (ec 4 \mathbb{S} sum of \mathbb{S} and \mathbb{S} we see in the set in the set in the set in the second second set in the seco α e^{nvo} \mathcal{A} a. e.g. e.g. α dipole in a accept c \mathcal{A} , d be \mathcal{Y} a_n \mathcal{A} and \mathcal{A} ⁿ, \mathcal{Y} \mathcal{Y} e' -b ea \mathcal{P} ca c a \mathcal{A} ⁿ. [\[79,83\]](#page-12-0) $\lceil \cdot \rceil$ dicate a *local* dipoles $\lceil \cdot \rceil$ eed $\lceil \cdot \rceil$ a Remarkably, e.g., eanliee 4 f r c 4 cal 4 f a elergy-local motion \mathbf{S} symmetry-breaking features in paramagnets, paramagnets, \mathbf{S} and a agectric can lead $4 \sqrt{ }$ across consequences, abent in the effections and \mathbb{R}^n act in the \mathbb{R}^n act in the \mathbb{R}^n $\sqrt{4}$ f.

ACKNOWLEDGMENTS

O.A. acknowledges the support of the Natural National Alta Scielce F4 Fdat4F 4f C Fa (Graf N4. 51850410520). E.K.H.S.^N a fiⁿded b EPSRC (G aⁿ N4. EP/P024904/1) and eEU's H^2 , \mathcal{A}^p , 2020 \mathcal{A} and ennance Marie Marie S 4d² a-Curie Grant Agreement N4. 861153. G.C. fi $\left[\text{Med } b \right]$ MINECO G a $\left[\text{N4. SEV-2017-0706} \text{a}\right]$ e Ge $\left[\text{Fe} \right]$ e a_{re}a de Caar^ra Graⁿ N4. 2017 SGR 579. The ^we 4 4 4 4 4 4 4 \pm

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h_{a.} *h h*²*n*</sup>₁ ez²e ec_tre materials, Na. C²₁**V**₁ *h*₂ 10, 1266 (2019).

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