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Thermodynamic Theory of Ferroelectric Ceramics

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A review of theories of ferroelectricity and of experimental data on ferroelectric ceramics leads to the conclusion that an analytic theory of such ceramics on microscopic basis does not seem feasible. A thermodynamic continuum theory is developed here, which is based on the postulated isomorphism, relevant to small signals only, between a polarized ceramic and one under bias fields near the limit of its nonpolar state; this bears analogy to Mueller's classical theory of Rochelle salt. The results of the theory include an elastic relation, which supplements existing experimental data, and a piezoelectric one, which relates to retained polarization and which agrees with measurements.

INTRODUCTION

MAJOR advances in ferroelectricity have been made recently, particularly, in structure exploration (for a recent comprehensive review, see Shirane *et al.*[1]); but a definitive atomic theory is not yet extant. The most comprehensive treatments are thermodynamic[2–4]; model and special mechanism theories[2,5–9] tend to cover particular aspects and are in part mutually conflicting. (A critical review is presented by Jaynes.[10]) Even the thermodynamic approaches, where the intrinsic parameters are adjusted to fit experimental data, are not entirely satisfactory. When thermodynamic potentials are expanded in terms of polarization P, at least the terms $O(P^6)$ and corresponding thermo- and elasto-dielectric terms must be included in view of the number of energetically competing states; it has been shown[11,12] that otherwise the theory will not accommodate all sequences of ferro- and antiferroelectric transitions and types of upper transitions[13,14] possible in pervoskite-type ferroelectrics.[15,16] An apparent consequence of incompleteness due to omission of significant terms in Devonshire's theory[3] is the observed rapid variation with temperature of one of the thermodynamic "constants": B.[17] Thermodynamic theory should be able to account for the rapid changes in the transition regions solely through the cooperative effect of the different slowly varying intrinsic parameters if all of them are suitably adjusted; but existing data are often insufficient for this purpose.[11,12,18] Other disagreements relating to Curie shifts under stress[19] are still in doubt.[20]

The present concern is with polycrystalline ferroelectric ceramics. It is well known that these are permanently polarizable by means of externally applied fields; this makes them useful as electromechanical transducers in complex shapes, not possible with single crystals. Even if a definitive theory of ferroelectrics existed, derivation of the macroscopic properties of ceramics with acceptable precision would still be a formidable task. The inadequacy of known averaging methods was early recognized.[2] Even such simple quantities as dielectric constants of isotropic mixtures depend intrinsically on microscopic detail,[21] and the simplest elastic moduli are intractable except for grossly simplified geometries.[22] In regard to electromechanical properties the task is still more complex due to their more intimate connection with the ferroelectric domains. The patterns present in single crystals[23–26] are also found in ceramics[27,28]; but while application of a poling field can convert multidomain crystals into single domains through nucleation and growth phenomena whose dynamics are fairly well understood,[29–32] this is not the case in ceramics. Domain switching mechanisms in ceramic

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[1] Shirane, Jona, and Pepinsky, Proc. Inst. Radio Engrs. **43**, 1738 (1955).

[2] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949); **42**, 1065 (1951).

[3] A. F. Devonshire, Phil. Mag. Quart. Suppl. **3**, 85 (1954).

[4] C. Kittel, Phys. Rev. **82**, 729 (1951).

[5] W. P. Mason and B. T. Matthias, Phys. Rev. **74**, 1622 (1948); H. J. Wellard, Phys. Rev. **76**, 565 (1949).

[6] S. Roberts, Phys. Rev. **76**, 1215 (1949).

[7] J. C. Slater, Phys. Rev. **78**, 748 (1950).

[8] E. T. Jaynes, Phys. Rev. **79**, 1008 (1950); E. T. Jaynes and E. P. Wigner, Phys. Rev. **79**, 213 (1950).

[9] H. C. Schweinler, Phys. Rev. **82**, 313 (1951).

[10] E. T. Jaynes, *Ferroelectricity* (Princeton University Press, Princeton, 1953).

[11] M. Ya. Shirobokov and L. P. Kholodenko, Zhur. Eksptl. i Teort. Fiz. **21**, 1239 (1951).

[12] L. P. Kholodenko and M. Ya. Shirobokov, Zhur. Eksptl. i Teort. Fiz. **21**, 1250 (1951).

[13] L. Tisza, in *National Research Council Conference on Phase Transitions in Solids, 1948* (John Wiley and Sons, Inc., New York, 1951), pp. 1–37; M. J. Klein and L. Tisza, Phys. Rev. **76**, 1861 (1949).

[14] A. de Bretteville, Phys. Rev. **98**, 1563(A) (1955).

[15] See reference 1, pp. 1743-46, 1756-61.

[16] A recent paper [L. E. Cross, Phil. Mag. Ser. 8, **1**, 76 (1956)] came subsequently to the writer's attention, in which it is shown that for such complex situations as in $NaNbO_3$ and related mixed compounds at least one term $O(P^8)$ is essential.

[17] E. J. Huibregtse and D. R. Young, Bull. Am. Phys. Soc. Ser. II, **1**, 50 (1956); Phys. Rev. **103**, 1705 (1956), see Fig. 9.

[18] L. E. Cross, Phil. Mag., Ser. 8, **1**, 76 (1956).

[19] P. W. Forsbergh, Jr., Phys. Rev. **93**, 686 (1954).

[20] E. Sawaguchi, Busseiron Kenkyu, No. 74, 27 (1954).

[21] W. F. Brown, J. Chem. Phys. **23**, 1514 (1955).

[22] D. A. G. Bruggeman, Z. Physik **92**, 561 (1935); Ann. Physik **29**, 160 (1937).

[23] P. W. Forsbergh, Jr., Phys. Rev. **76**, 1187 (1949).

[24] W. J. Merz, J. Appl. Phys. **25**, 1346 and cover (1954).

[25] J. A. Hooton and W. J. Merz, Phys. Rev. **98**, 409 (1955).

[26] D. S. Campbell, Phil. Mag. **46**, 1261 (1955).

[27] F. Kulcsar, J. Am. Ceram. Soc. **39**, 13 (1956).

[28] W. R. Cook, Jr., J. Am. Ceram. Soc. **39**, 17 (1956).

[29] W. J. Merz, Phys. Rev. **95**, 690 (1954).

[30] Drougard, Funk, and Young, J. Appl. Phys. **23**, 1106 (1954).

[31] M. E. Drougard and D. R. Young, Phys. Rev. **94**, 1561 (1954).

[32] Landauer, Young, and Drougard, Bull. Am. Phys. Soc. Ser. II, **1**, 191 (1956).

grains leading to the right order of magnitude for aging[33,34] and fast relaxation[35] have been proposed, but they do not bear on the macroscopic piezoelectric coefficients. These can be expressed in terms of polarization and electrostriction.[36] Some pertinent experimental data,[37,38] to which reference is made, are available.

Considering polarization, the simpler item, let us assume temporarily that under a strong poling field each randomly oriented crystallite became a single domain polarized in the closest of 6, 12, or 8 directions possible in the tetragonal, orthorhombic, or rhombohedral state, respectively; this is certainly a gross oversimplification, but gives an upper bound for P. The associated statistic is elementary[39] and leads to the respective percentages: $\frac{3}{8}\sqrt{2}\arctan(1/\sqrt{2})=0.831$, $(3/\pi)\arctan\sqrt{2}=0.912$, and $\frac{1}{2}\sqrt{3}=0.866$ of single domain polarization: ~ 0.3 coul/m^2.[29,31] Actually, at most $\sim 50\%$ can be reached with strong maintained poling fields and only 20–35% is retained permanently.[37,38] As to electrostriction, the lateral coefficient in ceramics[37] amounts to about 25% of the single crystal value[2,3,36,40,41] or about 30% of its orientational average.[37]

Qualitatively, the causes of such deficiency are well understood: Though 99% of theoretical density may be achieved in ceramics,[42] there are interstices[27]; if a poling field is applied their presence and the misorientations between adjacent grains lead to local intergranular charges which counteract alignment: not even the simple head-to-tail arrangement[24,25] will exist across grain boundaries. These are the loci of high local stresses engendered electrostrictively upon cooling, which likewise counteract permanent alignment. Impurities interfering with dislocation movements will play a part. The complexity of these and related effects defies analytical approach.

While prospects for a theory on microscopic basis thus seem remote, electromechanical applications of ferroelectric ceramics call for numerical data of considerable precision on the adiabatic elastodielectric coefficients relating to small-signal ac phenomena. Not all of these parameters lend themselves readily to measurement[43]; considerable errors accrue, in particular, for elastic cross-ratios as a consequence of local inhomogeneities. A dynamic method in which Poisson ratios are obtained in terms of frequency ratios[44] overcomes this difficulty, but has not yet been developed to the point of general applicability. The large anisotropy of recently developed lead zirconate-titanate ceramics[45,46] makes determination of the complete set of coefficients particularly timely. Any pertinent theoretical contribution would thus be welcome. This motivated the present approach, which was the subject of a previous preliminary communication.[47] It is straight continuum theory, not based on any mechanism, but on mildly speculative inferences from the general macroscopic properties of poled ferroelectric ceramics, which transcend the relations inherent in axial isotropy. Its most relevant result is an elastic relation which fills the gap in experimental data. Another prediction relates to piezoelectric coefficients; this lends itself to experimental test and has been verified recently.[45]

SKETCH OF THE THEORY

The basic assumption is an isomorphism, pertinent to small-signal phenomena, between a ferroelectric ceramic in a polar state, permanently poled, and one in the nonpolar state, but under an externally applied field E_0, slightly above the temperature $\theta_1[=\theta_0+(3B^2/5AC)$, according to Merz[48]]; θ_1 is the upper limit of that region above the Curie point θ_c in which the polar (tetragonal) state can be induced (see reference 3, Fig. 8; reference 48, Fig. 3). In either case the ceramic behaves substantially conservatively for small signals, that is, disregarding dielectric[38] and elastic losses[45,49] and piezoelectric phase angles,[50] which are $O(10^{-2})$ or less, and conductivity, thermal and electrical, which would set a lower limit to the frequency range considered. The neglect is a mere matter of convenience, as such dissipative phenomena obey reciprocity relations[51]; their consideration would make the otherwise real constant matrix elements complex relation-type functions of frequency (these may be obtained readily following, e.g., Biot's ideas[52]), but would not affect interrelations, which are the present objective.

One may then describe ceramics above θ_1 in terms of positive definite thermodynamic potentials, which must be invariant under the group I_3 of three-dimensional rotations. Sets of linear small-signal equations for the

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[33] W. P. Mason, Proceedings of the Symposium on Barium Titanate Accelerometers, NBS Report 2654, 1953; Acustica **4**, 200 (1954).

[34] W. P. Mason and R. F. Wick, Proc. Inst. Radio Engrs. 1606 (1954).

[35] T. F. Hueter and D. P. Neuhaus, J .Acoust. Soc. Am. **27**, 292 (1955).

[36] H. F. Kay, Repts. Progr. in Phys. **18**, 230 (1955).

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[39] H. G. Baerwald, Clevite Research Center Memorandum.

[40] H. F. Kay and P. Vousden, Phil. Mag. **40**, 1019 (1949).

[41] W. J. Merz, Phys. Rev. **75**, 1221 (1949); **78**, 52 (1950).

[42] E. J. Brajer, J. Am. Ceram. Soc. Ceram. Abstr. **38**, 146 (1955), and to be published.

[43] W. P. Mason and H. Jaffe, Proc. Inst. Radio Engrs. **42**, 921 (1954).

[44] H. G. Baerwald and C. Libove, Office of Naval Research, Technical Report No. 8, December 12, 1955 (unpublished).

[45] D. Berlincourt, Proc. Natl. Electronics Conf. **11**, 777 (1955).

[46] D. Berlincourt, Office of Naval Research Twelfth Quarterly Progress Report, October 26, 1955 (unpublished).

[47] H. G. Baerwald, J. Acoust. Soc. Am. **25**, 834 (1953).

[48] W. J. Merz, Phys. Rev. **91**, 513 (1953).

[49] D. A. Berlincourt, Office of Naval Research Technical Report No. 2, November 30, 1954 (unpublished).

[50] H. G. Baerwald, Brush Laboratories Report No. 555, February, 1955 (unpublished); J. M. McKee, Brush Laboratories Memorandum, September, 1954 (unpublished).

[51] S. R. DeGroot, *Thermodynamics of Irreversible Processes* (North Holland Publishing Company, Amsterdam, 1952), Chaps. 2–4, pp. 13–53.

[52] M. A. Biot, J. Appl. Phys. **27**, 240 (1956); Phys. Rev. **97**, 1463 (1955).

variables of state are obtained by differentiation with the material parameters as coefficients. Though keeping to the continuum concept, appeal to a molecular scale of magnitude must be made at this point: It is well known that an ordinary material breaks down (electrically or mechanically) whenever one of the variables such as electric field or strain reaches values about three orders of magnitude below the "molecular scale," characterized by elementary distortions or displacements of the order of molecular diameters; in a ferroelectric, however, one variable, the dielectric polarization P, may approach this scale: electronic charge/(lattice constant)^2 ~ 1 coul/m^2. For instance, in case of $BaTiO_3$, the polarization of single domain crystals is $P_0 \sim 0.3$ coul/m^2,[29,31] of ceramics under bias: $\sim \frac{1}{2} P_0$ and in remanence: $(\frac{1}{4}$ to $\frac{1}{3})P_0$,[37,38] while remanent charge densities of ~ 0.5 coul/m^2 are observed in some lead titanate-zirconate ceramics.[53]

This difference bears directly on the thermodynamics: In ordinary continua, thermodynamic potential changes are adequately approximated by homogeneous positive quadratic forms in the state variables; terms of higher order are negligible below breakdown. Invariance under I_3 then means reduction of the number of independent thermo-elasto-dielectric invariants to five; they are related to specific heat, dielectric constant, Young's and shear modulus, and the coefficient of thermal expansion. In case of a ferroelectric ceramic near θ_1, however, a thermodynamic potential involves all seven isotropic invariants as general functions of P^2, though terms of higher than second order, not counting P, may again be neglected. In particular, the dielectric behavior under, for instance, stress-free isothermal conditions depends on the single invariant P^2; differentiation with respect to P gives the associated electric field E. As P can reach molecular scale, but not E, the dielectric behavior is generally nonlinear, but hysteresis-free with effective numerical dielectric constants $K \sim 10^4$: $P \sim 10^{-\frac{1}{2}}$ coul/m^2 for $E \sim 10^{6\frac{1}{2}}$ v/m. For $E \sim 0$ such that $P \lesssim 10^{-3}$ and small signals in general, isotropy in the usual sense obtains; this condition will be called "0-state." Similarly, the "E_0-state" relates to a bias field E_0 producing large-scale polarization P_0, and to superposed small thermo-elasto-dielectric signals. With respect to these, the continuum is no longer three-dimensionally, but only axially isotropic (invariance under the group I_1 of rotations about one axis); symmetry-wise, it is equivalent to the crystallographic classes 4 mm and 6 mm, as the highest tensor rank involved is four. The analysis then shows that the E_0-state does not possess the full generality of invariance under I_1 which admits 14 independent parameters, but satisfies additional relations. In the sense of Mueller's classical theory of Rochelle salt,[54] these express the "morphic" character of the E_0-state.[55]

What is the extent of relevancy of these morphic relations to a poled ceramic below θ_c? It is readily shown[56,57] that assumption of complete isomorphism between the two cases, justifiable for weak polarization where terms of higher than third order may be neglected, leads to the relation

$$g_{15} = g_{33} - g_{31}; \tag{1}$$

the g_{mn} denote the adiabatic piezoelectric field-stress constants (the notations are in accord with the I.R.E. Standards on Piezoelectric Crystals, 1949,[58] and with Mason[59]; mks-units are used). Measurements[45] show that under slight poling (1) is substantially correct, but that for fully polarized ceramics consistently:

$$g_{15} > g_{33} - g_{31}. \tag{2}$$

The relation (1) corresponds to the morphic expressions of Mueller[54] and is a direct consequence of the fact that invariance under I_3 reduces the number of independent elements of the electrostriction tensor to two.

(2) Indicates that complete isomorphism as assumed in reference 56 does not exist for strong poling. This is not surprising, as the thermodynamic approach implies conservative behavior; relevance to those aspects of poled ceramics which are grossly irreversible, in particular, associated with hysteresis, cannot be expected. At subaudio frequencies, these aspects come to the fore even at small signals as high dielectric loss (see reference 38, Fig. 1), mechanical creep[60] and aging,[33,45] large excess of static over dynamic values of piezoelectric moduli,[61] etc., all typical of the polar state and absent above θ_c. The large-signal behavior in this range is entirely nonconservative: during the poling process, virtually all electrical energy is converted into heat, and only a negligible part of the charge is recoverable pyroelectrically or piezoelectrically by stress application.[45] Thus such quantities as E_0 or the entropy change associated with isothermal application of E_0 are certainly not relevant and hardly meaningful in regard to poled ceramics. They are, accordingly, called "fictitious." Considering a poled ceramic below θ_c as the "object" of

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[53] Unpublished measurements by D. A. Berlincourt, Clevite Research Center.

[54] H. Mueller, Phys. Rev. **47**, 175 (1935); **57**, 829–39 (1940); **58**, 563, 805 (1940); Ann. N. Y. Acad. Sci. **40**, 321 (1940).

[55] Comparison with the case of Rochelle salt is relevant although both the types of symmetry: orthorhombic *versus* isotropic, monoclinic *versus* axially isotropic and the thermodynamic character of the transition are different; the "morphic" relations in case of Rochelle salt are first-order expressions of the "new" monoclinic parameters in terms of P^2 and of the orthorhombic ones.[54]

[56] W. P. Mason, Phys. Rev. **74**, 1134 (1948).

[57] H. Jaffe, Phys. Rev. **73**, 1261 (1948).

[58] Institute of Radio Engineers, Standards on Piezoelectric Crystals, 1949, Proc. Inst. Radio Engrs. **37**, 1378 (1949).

[59] W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics* (D. Van Nostrand and Company, Inc., New York, 1950), pp. 29–40.

[60] H. Krueger, Phys. Rev. **93**, 362 (1954).

[61] D. A. Berlincourt, Proceedings of Symposium on Barium Titanate Accelerometers, National Bureau of Standards Report 2654, 1.7.4, 53, 1953.

the theory and one near $\theta_1 > \theta_c$ as its "morphic analog," we then postulate our basic assumption:

Small-signal thermo-elasto-dielectric properties of the morphic analog in the E_0-state are relevant to those of the object, with complete isomorphism; large-signal properties of the analog are fictitious.

ANALYSIS

The pertinent extensive variables of state are: accretion of entropy density $\Delta\sigma$, $\mathbf{P}$, and strain dyadic $\|S\|$[58] and the associated intensive ones: accretion of temperature $\Delta\theta$, electric field $\mathbf{E}$, and stress dyadic $\|T\|$.[58] $\mathbf{P}$ and dielectric displacement $\mathbf{D}$ are used interchangeably as in the mks system their relative difference is $K^{-1} \sim 10^{-3}$ to 10^{-4}; in order to accommodate usages in physics[3] and engineering,[58] $\mathbf{D}$ will be used in the signal equations and $\mathbf{P}_0$ to indicate the state of polarization. The matrix scheme of material parameters is

$$\begin{array}{lll} \text{thermoelectric } (1\times 1;0) & \text{pyroelectric } (1\times 3;1) & \text{thermoelastic } (1\times 6;2) \\ \text{pyroelectric } (3\times 1;1) & \text{dielectric } (3\times 3;2) & \text{piezoelectric } (3\times 6;3) \\ \text{thermoelastic } (6\times 1;2) & \text{piezoelectric } (6\times 3;3) & \text{elastic } (6\times 6;4), \end{array} \tag{3}$$

with the orders of the submatrices and tensor ranks written parenthetically; the tensors in the diagonal are symmetric. As E_0 is applied to the morphic analog under isothermal stress-free conditions, corresponding to poling, the appropriate thermodynamic potential is the elastic Gibbs function $G_e(\Delta\theta;\mathbf{D};\|T\|)$. It is related to the densities of accretion of energy and free energy, U and A, respectively, by[59]

$$\begin{gathered} G_e = U - \Delta\sigma\Delta\theta - S_{jk}T_{jk} = A - S_{jk}T_{jk}, \\ S_{jk} = \tfrac{1}{2}\left(\frac{\partial u_j}{\partial x_k} + \frac{\partial u_k}{\partial x_j}\right) \end{gathered} \tag{4}$$

(u displacement), using the summation convention with (i,j,k) running from 1 to 3. Invariance under I_3 requires that G_e depend on the isotropic invariants only. These are homogeneous and isobaric,[62] and the easiest way to find the complete set is to try such polynomial combinations of D^2 and the well-known stress invariants; it is sufficient to do this for the infinitesimal elements of I_3.[63] One has, in addition to the scalar $\Delta\theta$,

$$\left.\begin{array}{l} \text{one dielectric invariant: } D^2, \\ \text{three stress invariants:} \\ \qquad \tau_1 = T_{ii}, \quad \tau_2 = \tilde{T}_{ii}, \quad \tau_3 = \det(T_{jk}), \\ \text{two electrostrictive invariants:} \\ \qquad \vartheta_3 = D_jD_kT_{jk}, \quad \vartheta_4 = D_jD_k\tilde{T}_{jk}; \end{array}\right\} \tag{5}$$

here $\tilde{T}_{jk} \equiv$ minor of T_{jk} in the determinant: $\det(T_{jk})$. The subscripts indicate the degree of the polynomial. Thus,

$$G_e = G_e(\Delta\theta; D^2; \tau_1,\tau_2,\tau_3; \vartheta_3,\vartheta_4,). \tag{6}$$

It is preferable to substitute the technical strain and stress components:

$$S_i \equiv S_{ii}, \quad S_\alpha \equiv 2S_{jk}, \quad T_i \equiv T_{ii}, \quad T_\alpha \equiv T_{jk}, \tag{7}$$

where

$$(i,j,k) = (1,2,3), \quad (\alpha,\beta,\gamma) = (4,5,6), \quad j+k+\alpha = \cdots = 9$$

and

$$(l,m,\cdots) = (1,2,\cdots 6),$$

which leaves the strain energy density

$$S_{jk}T_{jk} = S_nT_n \tag{7a}$$

invariant. The direction of P_0 is taken as z or 3 axis; orientation of the 1 and 2 axes in the z plane is arbitrary. If Roman letters denote the order of magnitude in terms of small-signal quantities and terms of order higher than the second (h.o.t.), P_0 aside, are neglected, one obtains from (5)

$$\begin{aligned} &D^2 = P_0^2 + 2P_0D_3 + (D_1^2 + D_2^2) \equiv (0) + (\mathrm{I}) + (\mathrm{II}), \\ &\tau_1 = T_3 + (T_1 + T_2) \equiv (\mathrm{I}) + (\mathrm{I}), \\ &\tau_2 = \frac{T_1+T_2}{2}\left(T_3 + \frac{T_1+T_2}{2}\right) \\ &\qquad - \left\{\left(\frac{T_1-T_2}{2}\right)^2 + T_6^2 + T_4^2 + T_5^2\right\} \equiv (\mathrm{II}) + (\mathrm{II}), \\ &\tau_3 = \text{h.o.t.}, \\ &\vartheta_3 = P_0^2T_3 + 2P_0(D_3T_3 + D_1T_5 + D_2T_4) \\ &\qquad + \text{h.o.t.} \equiv (\mathrm{I}) + (\mathrm{II}) + \cdots, \\ &\vartheta_4 = P_0^2\left\{\left(\frac{T_1+T_2}{2}\right)^2 - \left[\left(\frac{T_1-T_2}{2}\right)^2 + T_6^2\right]\right\} \\ &\qquad + \text{h.o.t.} \equiv (\mathrm{II}) + \cdots. \end{aligned} \tag{8}$$

Appreciable simplification accrues from the definitions:

$$\begin{gathered} (T_1+T_2)/2 \equiv T_pV, \quad (T_1-T_2)/2 \equiv \hat{T}_6; \\ S_1+S_2 \equiv S_p, \quad S_1-S_2 \equiv \hat{S}_6, \end{gathered} \tag{9}$$

with

$$\begin{aligned} S_nT_n = {} & [S_3T_3 + S_pT_p] \\ & + [(S_6T_6 + \hat{S}_6\hat{T}_6) + (S_4T_4 + S_5T_5)]. \end{aligned} \tag{7b}$$

T_p and S_p represent "planar" (two-dimensionally isotropic) stress and strain in the z plane, $\hat{T}_6$ and $\hat{S}_6$ shear in this plane ("face shear") relative to axes bisecting those to which T_6, S_6 refer. The first two terms of (7b) represent the contribution of the normal components: axial and planar; the last four, the distortion com-

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[62] M. Bôcher, *Introduction to Higher Algebra* (The Macmillan Company, New York, 1907), Chap. XVII.

[63] E. L. Ince, *Ordinary Differential Equations* (Dover Publications, New York, 1944), Chap. IV.

ponents, with two face shear and two meridianal shear terms. Each normal term and each shear term in parentheses is invariant under I_1.

If (8), (9) are substituted in (6) and the terms are arranged according to order of magnitude:

$$G_e=[0]+[I]+[II]+\text{h.o.t.}, \tag{6a}$$

they may be written with complete generality in the following form, where the integrals are all taken from 0 to P_0^2:

$$[0]=\tfrac{1}{2}\left[\beta_0 P_0^2+\int (P_0^2-x)\beta_1^{T,\theta}(x)dx\right], \tag{10a}$$

$$\begin{aligned}[I]=&\left[\beta_0+\int\beta_1^{T,\theta}(x)dx\right]P_0\cdot D_3\\ &-\tfrac{1}{2}\int\pi_1^T(x)dx\cdot\Delta\theta-\tfrac{1}{2}\int\gamma_{a1}^\theta(x)dx\cdot T_3\\ &-\int(\gamma_{a1}^\theta(x)-\gamma_{s1}(x))dx\cdot T_p,\end{aligned} \tag{10b}$$

$$\begin{aligned}[II]=&\tfrac{1}{2}\Bigg[\left\{\beta_0+\int\beta_1^{T,\theta}(x)dx\right\}\\ &\cdot(D_3^2+D_1^2+D_2^2)+2P_0^2\beta_1^{T,\theta}(P_0^2)\cdot D_3^2\Bigg]\\ &-\tfrac{1}{2}\Bigg[\left\{s_{n0}^\theta+\int s_{a1}^{D,\theta}(x)dx\right\}\cdot T_3^2\\ &+\left\{(4s_{n0}^\theta-s_{s0})+\int s_{p1}^{D,\theta}(x)dx\right\}\cdot T_h^2\\ &+\Big\{(2s_{n0}^\theta-s_{s0})+\int(s_{a1}^{D,\theta}(x)-s_{m1}(x)\\ &+\tfrac{1}{4}s_{p1}^{D,\theta}(x))dx\Big\}\cdot 2T_3T_h+\left\{s_{s0}+\int s_{f1}(x)dx\right\}\\ &\cdot(T_6^2+\hat{T}_6^2)+\left\{s_{s0}+\int s_{m1}^D(x)dx\right\}\cdot(T_4^2+T_5^2)\Bigg]\\ &-\tfrac{1}{2}\left[\Gamma_0^T+\int\Gamma_1^{D,T}(x)dx\right]\cdot(\Delta\theta)^2\\ &-\left[\alpha_0+\int\alpha_1^D(x)dx\right]\cdot(T_3+T_h)\Delta\theta\\ &-P_0\pi_1^T(P_0^2)\cdot D_3\Delta\theta\\ &-P_0\{\gamma_{a1}^\theta(P_0^2)\cdot T_a+2(\gamma_{a1}^\theta(P_0^2)-\gamma_{s1}(P_0^2))\cdot T_p\}\\ &\cdot D_3+P_0^{-2}\int\gamma_{s1}(x)dx\cdot(D_1T_5+D_2T_4).\end{aligned} \tag{10c}$$

The subscript 0 refers to the isotropic state ($P_0\sim 0$) and 1 implies: incremental with P_0^2; subscripts n and s refer to the isotropic normal and shear elastic parameters, a, p, and f, m to axial, planar normal, and face, meridianal shear, respectively; the superscripts denote nonvariation, i.e., T: stress-free, θ: isothermal, D: open-circuit, and their omission connotes absence of the corresponding coupling in the second-order approximation; finally, β denotes dielectric stiffness, s—elastic compliance, Γ—incremental specific heat times mass density, π—pyroelectric, γ—electrostrictive, and α—thermoelastic parameters, essentially in accord with I.R.E. Standards.[58]

According to Eq. (4), the signal equations are, symbolically:

$$\Delta\sigma=-\partial G_e/\partial\Delta\theta,\quad \mathbf{E}=+\partial G_e/\partial\mathbf{D},\quad \|S\|=-\partial G_e/\partial\|T\|. \tag{11}$$

The term (10a) contributes nothing. The term (10b) yields the biased E_0 state alone:

$$\begin{aligned}(\Delta\sigma)_0&=\tfrac{1}{2}\int\pi_1^T(x)dx;\\ E_0&=\left[\beta_0+\int\beta_1^T(x)dx\right]P_0;\\ S_{a0}&=\tfrac{1}{2}\int\gamma_{a1}^\theta(x)dx;\\ S_{p0}&=\int[\gamma_{a1}^\theta(x)-\gamma_{s1}(x)]dx;\end{aligned} \tag{12a-c}$$

where as before the integrals are all taken from 0 to P_0^2. Equations (12a-c) thus give the free accretion of entropy density, the free bias field, and the isothermal axial and planar electrostrictive strains in terms of P_0^2. The small-signal equations of the E_0 state are obtained from (10c), (11):

$$\begin{aligned}E_3&=\beta_{33}^{T,\theta}D_3-g_{33}^\theta T_3-g_{3p}^\theta T_p-\pi^T\Delta\theta,\\ S_3&=g_{33}^\theta D_3+s_{33}^{D,\theta}T_3+s_{3p}^{D,\theta}T_p+\alpha_3^D\Delta\theta,\\ S_h&=g_{3p}^\theta D_3+s_{3p}^{D,\theta}T_3+s_{pp}^{D,\theta}T_p+\alpha_p^D\Delta\theta,\\ \Delta\sigma&=\pi^T D_3+\alpha_3^D T_3+\alpha_p^D T_p+\Gamma^{D,T}\Delta\theta,\end{aligned} \tag{13}$$

$$\begin{aligned}(E_1;E_2)&=\beta_{11}^T\cdot(D_1;D_2)-g_{15}\cdot(T_5;T_4),\\ (S_5;S_4)&=g_{15}\cdot(D_1;D_2)+s_{55}^D\cdot(T_5;T_4),\\ (S_6;\widehat{S}_6)&=s_{66}\cdot(T_6;\hat{T}_6),\end{aligned}$$

with

$$\beta_{11}^T=\beta_0+\int\beta_1^{T,(\theta)}(x)dx,$$

$$\beta_{33}^{T,\theta}=\beta_{11}^T+2P_0^2\cdot\beta_1^{T,\theta}(P_0^2);$$

$$s_{66}=s_{s0}+\int s_{f1}(x)dx,\quad s_{55}^D=s_{s0}+\int s_{m1}^D(x)dx,$$

$$
\begin{aligned}
s_{33}{}^{D,\theta} &= s_{n0}{}^{\theta} + \int s_{a1}{}^{D,\theta}(x)dx,\\
s_{pp}{}^{D,\theta} &= 4s_{n0}{}^{\theta} - s_{s0} + \int s_{p1}{}^{D,\theta}(x)dx,\\
s_{3p}{}^{D,\theta} &= 2s_{n0}{}^{\theta} - s_{s0} + \int \{s_{a1}{}^{D,\theta}(x) - s_{m1}{}^{D}(x)\\
&\qquad + \tfrac{1}{4}s_{p1}{}^{D,\theta}(x) + \tfrac{1}{4}s_{f1}(x)\}dx;\\
\Gamma^{D,T} &= \Gamma_0{}^T + \int \Gamma_1{}^{D,T}(x)dx; \quad \pi^T = P_0\cdot\pi_1{}^T(P_0{}^2);\\
g_{33}{}^{\theta} &= P_0\cdot\gamma_{a1}{}^{\theta}(P_0{}^2), \quad g_{3p}{}^{\theta} = 2P_0\cdot(\gamma_{a1}{}^{\theta}(P_0{}^2) - \gamma_{s1}(P_0{}^2)),\\
g_{15} &= \frac{1}{P_0}\int \gamma_{s1}(x)dx;\\
\alpha_3{}^D &= \alpha_0 + \int \alpha_1{}^D(x)dx, \quad \alpha_p{}^D = 2\alpha_3{}^D,
\end{aligned}
\tag{14}
$$

the integrals being taken from 0 to $P_0{}^2$.

We compare the system (13) with the corresponding equations relating to a crystal of class 4 mm or 6 mm,[64–66] noting that retraction of (9) yields the identities:

$$
s_{pp} = 2(s_{11}+s_{12}), \quad s_{66} = 2(s_{11}-s_{12}), \quad s_{3p} = 2s_{31}; \quad g_{3p} = 2g_{31}; \quad \alpha_p = 2\alpha_1. \tag{15}
$$

As related to the crystal, (13) involves 14 independent constant parameters. As related to the morphic analog, one notes that aside from being functions of $P_0{}^2$ with β, s, Γ, and α finite for $P_0=0$, but g and π of $O(P_0)$, the parameters are not mutually independent; there are four relations, identities in $P_0{}^2$:

$$
\beta_{33}{}^{T,\theta}(P_0{}^2) \equiv \beta_{11}{}^T(P_0{}^2) + 2P_0{}^2\frac{d\beta_{11}{}^T}{dP_0{}^2}\text{—dielectric;} \tag{16a}
$$

$$
\begin{aligned}
s_{33}{}^{D,\theta}(P_0{}^2) + \tfrac{1}{4}s_{pp}{}^{D,\theta}(P_0{}^2) - s_{3p}{}^{D,\theta}(P_0{}^2)&\\
- s_{55}{}^D(P_0{}^2) + \tfrac{1}{4}s_{66}(P_0{}^2) &\equiv 0,
\end{aligned}
\tag{16b}
$$

or

$$
s_{33}{}^{D,\theta} + s_{11}{}^{D,\theta} - 2s_{31}{}^{D,\theta} \equiv s_{55}{}^D\text{—elastic;}
$$

$$
\alpha_p{}^D(P_0{}^2) \equiv 2\alpha_3{}^D(P_0{}^2), \tag{16c}
$$

or

$$
\alpha_1{}^D(\equiv\alpha_2{}^D) \equiv \alpha_3{}^D\text{—thermoelastic;}
$$

$$
\frac{1}{P_0}[g_{33}{}^{\theta}(P_0{}^2) - \tfrac{1}{2}g_{3p}{}^{\theta}(P_0{}^2)] \equiv \frac{d(P_0g_{15})}{dP_0{}^2}, \tag{16d}
$$

or

$$
\frac{g_{33}{}^{\theta} - g_{31}{}^{\theta}}{P_0} \equiv \frac{d(P_0g_{15})}{dP_0{}^2}\text{piezoelectric.}
$$

According to the basic postulate, (12) is irrelevant: $(\Delta\sigma)_0$ and E_0 are fictitious; strain gauge measurements[53] show that the spontaneous electrostrictive strains S_{a0}, S_{p0} in ceramics are only about 10% of the x-ray values. By the same token, the small-signal relations (16) are relevant. (16c) states that open-circuit thermal expansion is isotropic, and (16b) connotes elastic quasi-isotropy under isothermal open-circuit conditions.

Ac phenomena involve the adiabatic rather than the isothermal elastodielectric parameters. This transition affects (16a) only: (16b) and (16d) remain unchanged because in the second-order approximation the right sides are not thermally coupled. The adiabatic dielectric relation follows from elimination of $\Delta\theta$, setting $\Delta\sigma=0$ in (13):

$$
\begin{aligned}
\beta_{33}{}^{T,\sigma} &\equiv \beta_{11}{}^T + 2P_0{}^2\frac{d\beta_{11}{}^T}{dP_0{}^2} + \frac{[P_0\cdot\pi^T(P_0{}^2)]^2}{\Gamma^{D,T}(P_0{}^2)},\\
s_{33}{}^D + s_{11}{}^D - 2s_{31}{}^D &\equiv s_{55}{}^D,\\
\alpha_1{}^D \equiv \alpha_2{}^D &\equiv \alpha_3{}^D,\\
(g_{33} - g_{31})/P_0 &\equiv d(P_0g_{15})/dP_0{}^2.
\end{aligned}
\tag{17a-d}
$$

APPLICATION AND COMPARISON WITH MEASUREMENTS

The relation (17a) has scant practical significance. The last term, which is positive, involves a pyroelectric function which is associated with entropy accretion (12a) and thus not relevant. As an inequality:

$$
\beta_{33}{}^{T,\sigma} > \beta_{11}{}^T + 2P_0{}^2(d\beta_{11}{}^T/dP_0{}^2), \tag{17a'}
$$

(17a′) is relevant, but hardly useful as it involves both the value and the derivative of $\beta_{11}{}^T$; measurement of P_0 in poled ceramics over an extended range under reversible conditions is difficult and inaccurate. (16c) is likewise relevant, but not useful as it would be hard to maintain isothermal and open-circuit conditions simultaneously. Avoidance of charge leakage would also be a serious problem in verifying (17c); the corresponding short-circuit relation [$E_3=0$ in (13)] again involves π^T.

The elastic relation (17b) represents a result of practical significance, as s_{31} is difficult to measure whereas the other three compliances can be readily and accurately determined by resonance methods.[43,45,46] There are indirect ways of obtaining s_{31}, but they involve cascaded errors. A recent collation[67] of data thus derived from different commercial batches of BaTiO$_3$ ceramics shows agreement with (17b) within less than 3% for both open- and short-circuit. For isotropy: $s_{33}=s_{11}$, (17b) is an identity; it connotes "quasi-isotropy" if $\frac{1}{2}(s_{33}+s_{11})$ is considered as "mean" normal compliance.

Products of polarization and electrostriction,[36,56] piezoelectric coefficients are odd functions of P_0, as (14) shows. By formal expansion

$$
g_{mn} = P_0(g_{mn}{}^1 + g_{mn}{}^2P_0{}^2 + g_{mn}{}^3P_0{}^4\cdots), \tag{18}
$$

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[64] See reference 59, pp. 41–45.

[65] W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946), pp. 54, 55, 162, 191, 192.

[66] W. L. Bond, Bell System Tech. J. 22, 1 (1943).

[67] R. Bechmann, J. Acoust. Soc. Am. 28, 347 (1956).

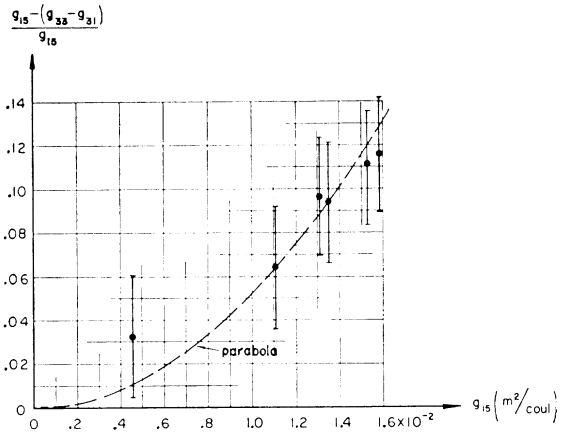

FIG. 1. Excess-g ratio *versus* g_{15}.

and substitution in (17d) one obtains for small P_0:

$$g_{15}^1 = g_{33}^1 - g_{31}^1 \text{ (first approximation)}: \tag{1re}$$

this is known to hold for weakly polarized ceramics or unpolarized ones under weak bias fields. In order of magnitude, the first term of (18) corresponds in $G_e(6)$ to the term P_0^4 which produces the lowest order of dielectric nonlinearity; the two are considered jointly in.[56] Correspondingly, the terms with $g_{mn}^2(18)$ parallel those $O(P^6)$ in (6). For the single crystal, the latter are positive definite due to stability requirements, whereas those $O(P^4)$ are in the main negative because θ_c is a first-order transition.[2,3] One would, therefore, expect

$$g_{mn}^2/g_{mn}^1 < 0, \tag{19}$$

which is also in line with the expected saturation character of the γ functions [(10), (14)]. Noting that $g_{33} > 0$, $g_{31} < 0$, $g_{55} > 0$,[45] this means: $g_{15} - (g_{33} - g_{31}) = |g_{15}^2| P_0^2 \cdots > 0$, i.e.,

$$g_{15} > g_{33} - g_{31}, \tag{2re}$$

confirmed experimentally for well-polarized specimens, or rewritten

$$\frac{[g_{15} - (g_{33} - g_{31})]}{g_{15}} \propto g_{15}^2 \propto P_0^2 \text{ (second approximation)}. \tag{20}$$

The factors of proportionality would depend on the particular ceramic material; for a given material, the relative excess of g_{15} over $(g_{33} - g_{31})$ would represent a comparative measure of the effective polarization squared. Some experimental results[68] from a batch of commercial $BaTiO_3$ ("Brush Ceramic A") of good reproducibility are shown in Fig. 1. They were obtained with bars about 3×3×8 mm polarized to various degrees in the long dimension; g_{33} is obtained from longitudinal resonance, g_{31} by means of the open-circuit response under low-frequency hydrostatic pressure, with electrodes on the end faces, while g_{15} is measured by means of an ac force applicator producing simple shear with the samples mounted on one long face and electroded on this and the opposite face. As electrodes must be changed without disturbing remanent polarization and close temperature control is required, the probable accuracy of the single measurements is at best ±2%, which accounts for the comparatively large estimated error limits of the difference (20) indicated in Fig. 1.

One may rewrite (17d) in the form

$$\frac{g_{15} - (g_{33} - g_{31})}{g_{15}} = \frac{1}{2}\left[1 - \frac{d \ln g_{15}}{d \ln P}\right], \tag{21}$$

which indicates that $\frac{1}{2}$ would represent an upper bound as g_{15} "saturates." Noticeably weaker than parabolic growth may then be expected starting at values half an order of magnitude below $\frac{1}{2}$ due to the third-order terms in (18) or those $O(P_0^8)$ in (6), which have the same sign as $O(P_0^6)$.[18] The two highest points of Fig. 1 indicates this tendency.

The following table[45] represents averages over four samples each of laboratory-made $BaTiO_3$ ceramic (I) and one with 5 molar % $CaTiO_3$ (II) as well as over two samples of an experimental lead zirconate-titanate (III).

Ceramic:	I	II	III
$1-(g_{33}-g_{31})/g_{15}$:	0.12	0.09	0.04

According to the present theory, this would indicate that I shows the highest retained polarization relative to its saturation. Measurements of the relative increase of electromechanical coupling under an applied bias field confirm that the relative remanence of I is somewhat higher than II.

III represents a material basically different from I and II; the respective factors of proportionality thus cannot be compared, as pointed out following (20). As the relative difference given in the table is small and based on the only two samples available, its relative accuracy is bound to be low. Comparison of compositional variations and examination of the validity and range of (20) for this type of ceramic material are planned.

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[68] The writer is indebted to Mr. D. Berlincourt who performed these rather intricate measurements.