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Dipolar theory of ferroelectrics revisited

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An analysis of experimental data has been done for various ferroelectrics within the framework of the dipolar theory, along the same lines of the recent work on triglycine sulfate (TGS) and triglycine fluoberillate (TGFB). A simple method is applied which, using solely dielectric data near T_C, leads to the determination of the main parameters of the theory. The resulting numbers N of elementary dipoles per unit volume appear to be close to the numbers of unit cells per unit volume as determined from crystallographic data. The elementary dipole moments μ are reasonably consistent with obervations of low-temperature spontaneous polarization. The mean-field coefficients β appear to be consistent with an independent evaluation of the "reaction" field in cases for which quasi-point-dipoles in the lattice can be assumed. The relative contribution of the dipolar polarization to the total (dipolar plus atomic) polarization appears to be larger in the more ionic ferroelectrics. The transition entropy due to the order-disorder process can account for the observed values in most (but not all) cases. No adjustable parameters have been used.

A recently proposed mean-field equation of state,[1,2] describing the relationship of polarization P, external field E, and temperature T, has been shown to give a satisfactory account of the ferroelectric behavior near T_C for triglycine sulfate (TGS) and tryglycine fluoberillate (TGFB). In this paper, a similar analysis is made of data pertaining to other ferroelectric transitions.

Since the discovery of ferroelectricity in the early twenties, several attempts were made to apply the mean-field concept to the physical description of this phenomenon. Among them, the model of Mason[3] (in its revised version) takes into account the distinction between dipolar and ionic as well as electronic polarization. The application of this model to perovskites was subsequently subject to strong criticism.[4] Cochran's[5] new model for ferroelectricity, based upon anomalous lattice dynamical behavior (soft modes), confirmed afterwards by experiment, contributed to shift the theoretical interest away from the mean-field concept. However, recent experimental observations[1,2] which support the validity of this concept to explain the critical behavior of some ferroelectrics of the TGS family, suggest that other ferroelectric families should be examined.

The mean-field (dipolar-theory) equation of state is given[2] by

$$\frac{\kappa P}{N\mu} = \tanh\left(\kappa \frac{E+\beta P}{\beta N\mu}\,\frac{T_C}{T}\right), \quad T_C = \frac{\beta N\mu^2/\kappa}{k}, \tag{1}$$

where N is the number of unit dipoles per unit volume, μ is the dipole moment of a unit dipole, β is the mean-field coefficient $[F = E + \beta P = E + \beta(P_a + P_d)]$, and $\kappa \equiv (1-\beta\gamma)$ is a coefficient which establishes a *linear relationship* ($P_d = \kappa P$) between the total polarization P and the dipolar polarization P_d. The linear relationship is valid as long as the mean field is small in comparison with the spontaneous field at saturation ($T = 0$ °K or very large E), and the linearity should break down for large values of F. Note that the approximation[2] made in the right-hand side of Eq. (7), Ref. 2 to obtain the above equation of state, i.e., $P_d = \kappa P - \gamma E \simeq \kappa P$, becomes

TABLE I. Dielectric data for various representative ferroelectrics. T_C is the Curie temperature; C is the Curie constant; $\epsilon_0 = \epsilon_{obs} - C/(T - T_C)$; P_s is the spontaneous polarization.

Crystal	Order of transition	T_C (°K)	Ref.	C (°K)	Ref.	ϵ_0	Ref.	$(T_c/3)\,(P_s^2/\Delta T)$ (e.s.u.)	Ref.
TGS	2nd	322.5	1	3.56×10^3	4	65	2	410×10^6	5
colemanite	2nd	266.0	6	0.5×10^3	6	2	6	23×10^6	6
KDP	1st	123.0	7	3.3×10^3	7	26	7	432×10^6	8
$NaNO_2$	1st	437.0	9	6.6×10^3	9	25	10	3.87×10^9	9
SbSI	1st	290.0	11	2.33×10^5	11	266	11	20.62×10^9	12
$BaTiO_3$	1st	(399.0)[a]	13	1.5×10^5	13	145	14	16.66×10^9	13
$LiTaO_3$	2nd	890.	15	1.6×10^5	15	246	15	21.67×10^9	15

[a] Extrapolated from double hysteresis loops.

TABLE II. Mean-field parameters. β is the mean-field coefficient; $\kappa = (1-\beta\gamma)$, γ is the atomic polarizability; N is the number of dipoles per unit volume; μ is the dipole moment of elementary dipole.

Crystal	β ($T > T_C$)	β ($T < T_C$)	κ	$N \times 10^{-22}$ (dip./cm^3)	$\mu \times 10^{18}$ (esu)
TGS	1.14	0.98	0.169	0.152	2.26
colemanite	6.68	•••	0.499	0.209	1.14
KDP	0.460	0.365	0.579	0.540	2.23
$NaNO_2$	0.832	•••	0.386	2.061	1.16
SbSI	0.0156	•••	0.752	0.604	17.8
$BaTiO_3$	0.0335	•••	0.728	1.436	8.93
$LiTaO_3$	0.069	•••	0.423	0.522	11.9

rigorously valid near T_C for small fields. This is the case with small field dielectric constant measurements and spontaneous polarization measurements from hysteresis loops at $E = 0$, since for those cases $P \gg E$, κ, and γ being usually comparable in magnitude. No approximation is needed in the right-hand side of the same equation, since it is already an explicit function of P.

By means only of dielectric data [Curie temperature T_C, Curie constant C, $\epsilon_0 = \epsilon$ ($T \gg T_C$), and $P_s^2/\Delta T$] all the fundamental constants entering Eq. (1) can be determined[2] as follows:

$$\beta = 4\pi T_C/C \text{ (for } T \gtrsim T_C), \qquad \beta = (P_s^2 E/P^3 \Delta T) T_C \text{ (for } T \lesssim T_C), \tag{2}$$

$$\kappa = 1 - [4\pi/\beta(\epsilon_0 - 1) + 1]^{-1}, \tag{3}$$

$$N = \kappa(\beta P_s/3k\Delta T), \tag{4}$$

$$\mu = \kappa N^{-1}[P_s^2/3(T/T_C)]^{1/2}. \tag{5}$$

Some considerations should be made regarding the evaluation of the dielectric data. The Curie constant should be determined from the slope of ϵ^{-1} vs ΔT *immediately* above T_C. ϵ_0 can be determined either from the low-frequency dielectric constant data somewhat far above T_C (where domain-wall-motion effects are absent) as $\epsilon_0 \equiv \epsilon_{obs} - C^+/T - T_C$), or from high-frequency (above-relaxation) data, also at $T > T_C$. The ratio $P_s^2/\Delta T$ should be determined from hysteresis loops (or pyroelectric) measurements *immediately* below T_C and using sweeping external fields large enough to ensure full reversal of the spontaneous polarization P_s.

A representative sample of ferroelectrics, of molecular as well as of ionic type, for which all the necessary experimental information is available is listed in Table I. All the first-order-transition ferroelectrics listed, except perhaps $BaTiO_3$, are very nearly second order, in the sense that they are almost completely disordered when the high-temperature phase sets in. References 1 and 2 and 6–15 for the sources of experimental information are identified in the table. The application of Eqs. (2)–(5) permits a direct evaluation of the relevant mean-field parameters (Table II). If one assumes point dipoles located at the center of the primitive unit cell, one can compute β from the "*reaction*" field of successive dipole lattice "shells" on a given dipole. For instance, for $BaTiO_3$,[16] one obtains $\beta = -0.051 + 0.002 + 0.006 - 0.006 \cdots \simeq -0.049$, which appears to be compatible with the value in Table II.

A meaningful comparison can be made between N

TABLE III. Primitive unit cells and low-temperature spontaneous polarizations. Z is the number of molecules per unit cell; n is the number of primitive unit cells per full unit cell; v_c is the unit cell volume; P_{so} is the low-temperature spontaneous polarization.

Crystal	Space group ($T < T_C$)	Space group ($T > T_C$)	Z	n	$v_c \times 10^{22}$ (cm^{-3})	Ref.	P_{so} (μC/cm^2)	Ref.
TGS	$P2_1$	$P2_1/m$	2	1	6.77	18	4.3	19
colemanite	$P2_1$	•••	2	1	5.64	20	0.7	6
KDP	Fdd_2	$I\bar{4}2d$	4	2	$\frac{1}{2}$ (3.83)	21	5.0	22
$NaNO_2$	$Im2m$	$Immm$	2	2	$\frac{1}{2}$ (1.06)	23	12.0	9
SbSI	$Pna2_1$	$Pnam$	4	2	$\frac{1}{2}$ (3.54)[a]	24	27.0	12
	($P2_1$)	($P2_1/m$)	(2)	(1)		25		
$BaTiO_3$	$P4mm$	$Pm3m$	1	1	0.641	16	29.0	26
$LiTaO_3$	$R3c$	($R\bar{3}c$)	2	1	1.06	27	48.0	15

[a] The simplified unit cell has been used, with $Z = 2$, corresponding to a transition $P2_1 \rightarrow P2_1/m$ (see Ref. 25).

TABLE IV. Comparison of calculated physical parameters and related experimental data. N is the number of unit dipoles per unit volume; μ is the dipole moment of unit dipole; and ΔS is the transition entropy.

Crystal	$N\times 10^{22}$ (u. dip./cm^3)	$v_c^{-1}\times 10^{22}$ (u. dip./cm^3)	$\mu\times 10^{18}$ (esu)	$P_{s0}v_c\times 10^{18}$ (esu)	ΔS (cal.) o.d. (cal./mol °C)	ΔS (obs.) (cal./mol °C)	Ref.
TGS	0.152	0.155	2.26	8.7	0.688	1.1	28
colemanite	0.209	0.177	1.14	1.2	0.688	···	···
KDP	0.540	0.522	2.23	2.9	0.688	0.69	29
$NaNO_2$	2.061	1.878	1.16	1.9	1.377	1.26	30
SbSI	0.604	0.564	17.8	14.3	0.688	0.2	31
$BaTiO_3$	1.436	1.558	8.9	5.6	1.377	0.12	32
$LiTaO_3$	0.522	0.943	11.9	15.3	0.688	> 0.51	15

the number of elementary dipoles per unit volume, as determined from dielectric data only, and $N_{uc} = v_c^{-1}$, the number of primitive unit cells per unit volume. A similar comparison for the elementary dipole moments μ is more difficult, since it would require a complete knowledge of the spatial charge distribution, but we can take instead as a reference the saturation spontaneous moment per primitive cell. Finally, a comparison can be made between the calculated (order-disorder) contributions to the transition entropy and the experimental observations.[17] The number of independent dipoles per mole is $N_m = N_A(Z/n)^{-1}$, where Z/n is the number of molecules per primitive unit cell, Z being the number of molecules in the full unit cell (see Table III), and N_A is Avogadro's number. Then, one has

$$\Delta S = N_m k \ln 2 \tag{6}$$

for the order-disorder transition entropy. Of course, associated changes in the lattice dynamics of the crystal in going through the transition can make independent contributions.

Table IV gives a comparison of calculated (dipolar theory) and pertinent experimental data. The first conclusion which can be drawn is that the calculated (dipolar theory) number of elementary dipoles per unit cell is close (within 10% except for colemanite and $LiTaO_3$) to the number of primitive unit cells per unit volume. Second, the calculated dipole moments are reasonably consistent with the total saturation moments as deduced from the low-temperature spontaneous polarization ($P_{s0}v_c = \mu/\kappa_0$). It should be noted, however, that $\kappa_0(T \sim 0\,°\mathrm{K})$ is in general different from $\kappa(T \sim T_C)$, and one may expect deviations from linearity for large fields (i.e., anharmonicity), as it is the case for the spontaneous field at low temperatures, leading to an increase in $\kappa \equiv 1 - \beta\gamma$ towards κ_0 as γ decreases. The effective ratio κ/κ_0 ranges from 0.46 ($BaTiO_3$) to 0.74 [potassium dihydrogen phosphate (KDP)] and is consistent with the observed low-temperature flattening of the spontaneous polarization with respect to the pure mean-field behavior. Finally, the calculated order-disorder transition entropy can account fairly well in most cases for the observed values. The difference is substantial, however, for SbSI and especially for $BaTiO_3$. The observed values for these two cases correspond to power data (inherently less accurate) but probably large contributions due to phonon frequency shifts must be invoked.

Considering that no adjustable parameters have been used, the overall consistency can be said to be better than anticipated for such a varied sample of ferroelectrics as those examined (note that the agreement can be extended to other crystals belonging to these ferroelectric families, such as TGFB, isomorphous with TGS). A closer analysis of the temperature dependence of the parameter κ is under way. Preliminary calculations show that it can be linked with anomalous anharmonicity and can correlate, at least semiquantitatively, such phenomena as anomalous thermal expansion, soft modes and pressure dependence of the ferroelectric behavior.

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[1] J. A. Gonzalo, Phys. Rev. B 1, 3125 (1970).

[2] A. Mercado and J. A. Gonzalo, Phys. Rev. B 7, 3074 (1973). Note "erratum": it should be $T_C = \beta N\mu^2/\kappa k$, instead of $T_C = \beta N\mu^2/\kappa^2 k$. This gives for TGS and TGFB $n \sim 1$ (instead of 6) and $n \sim 1$ (instead of 12), respectively.

[3] W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics* (Van Nostrand, New York, 1950).

[4] E. T. Jaynes, *Ferroelectricity* (Princeton U. P., Princeton, N. J., 1953).

[5] W. Cochran, Adv. Phys. 9, 387 (1960).

[6] H. H. Wider, J. Appl. Phys. 30, 1010 (1959).

[7] G. Busch, Helv. Phys. Acta 11, 269 (1938).

[8] J. A. Gonzalo and I. Nazario (unpublished).

[9] Y. Takagi and K. Gesi, J. Phys. Soc. Jap. 22, 979 (1967); K. Hamano, J. Phys. Soc. Jap. 35, 157 (1973).

[10] I. Hatta, J. Phys. Soc. Jap. 24, 1043 (1968).

[11] T. Mori and H. Tamura, J. Phys. Soc. Jap. 19, 1247 (1965).

[12] K. Imai, S. Kawada, and M. Ida, J. Phys. Soc. Jap. 21, 1855 (1966).

[13] J. A. Gonzalo and J. M. Rivera, Ferroelectrics 2, 31 (1971).

[14] Y. Makita, J. Phys. Soc. Jap. 19, 576 (1964).

[15] A. M. Glass, Phys. Rev. 172, 564 (1968).

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

[17] Landolt-Bornstein, *Crystal and Solid State Physics* (Springer-Verlag, New York, 1969), Vol. 3.

[18] S. Hoshino, Y. Okaya, and R. Pepinsky, Phys. Rev. 115, 323 (1959).

[19] S. Triebwasser, IBM J. Res. Develop. 2, 212 (1958).

[20] C. L. Christ, J. R. Clark, and H. T. Evans, Jr., Acta Crystallogr. 11, 761 (1958).

[21] B. C. Frazer and R. Pepinsky, Acta Crystallogr. 6, 273 (1953).

[22] A. von Arx and W. Bantle, Helv. Phys. Acta 16, 211 (1943).

[23] M. Kay and B. C. Frazer, Acta Crystallogr. 14, 56 (1961).

[24] R. Arndt and A. Niggli, Naturwiss. 51, 158 (1964).

[25] D. K. Agrawal and C. H. Perry, *Light Scattering in Solids* (Flammarion, Paris, 1971).

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

[27] S. C. Abrahams and J. L. Bernstein, J. Phys. Chem. Solids 28, 1685 (1967); S. C. Abrahams, W. C. Hamilton, and A. Sequeira, J. Phys. Chem. Solids 28, 1693 (1967).

[28] B. A. Strukov, Fiz. Tverd. Tela 6, 2862 (1964) [Sov. Phys.-Solid State 6, 2278 (1965)].

[29] B. A. Strukov, M. Amin, and V. A. Kopchik, Solid State Phys. 27, 741 (1968).

[30] M. Sakiyama, A. Komoto, and S. Seki, J. Phys. Soc. Jap. 20, 2180 (1965).

[31] T. Mori, H. Tamura, and E. Sawaguchi, J. Phys. Soc. Jap. 20, 281 (1965).

[32] G. Shirane and A. Takeda, J. Phys. Soc. Jap. 7, 1 (1952).