where

$$\tan\theta_1 = -E_{g0}/2\mathcal{J}\alpha^2. \quad \text{(B11)}$$

$\mathcal{H}_2'$ mixes $|\, g_0\rangle$ with only one of the three excited two-ion states of $\mathcal{H}_{20}$, viz.,

$$|\, e_0\rangle = (1/\sqrt{2})\,(|\, 0_c, 1_c\rangle + |\, 1_c, 0_c\rangle), \quad \text{(B12)}$$

which has energy

$$E_{e0} = \Delta[1 - 2(\mathcal{J}/\Delta)\alpha^2]. \quad \text{(B13)}$$

Treating the mixing of $|\, e_0\rangle$ into $|\, g_0\rangle$ by perturbation theory gives

$$\bar{M}_2 = \frac{2g^2\mu_B^2 H'(z-1)\alpha^2}{E_{e0} - E_{g0}}\,(1 + \sin 2\theta_1). \quad \text{(B14)}$$

Then using (B4) and (B14) in (B3) gives the critical condition for magnetic ordering to occur with infinitesimal moment at zero temperature.

$$\frac{z}{z-1} = \frac{1 + \sin 2\theta_1}{[1 + (A/2z)^2]^{1/2} - A/2z}, \quad \text{(B15)}$$

with

$$\tan\theta_1 = -2z\{1 - [1 + (A/2z)^2]^{1/2}\}/A. \quad \text{(B16)}$$

We have the result that for given z in the constant-coupling approximation (B15) and (B16) are a set of transcendental equations determining the critical value of A and the value of θ_1 when A has this critical value. The values of A_{crit} shown in Table I were obtained by numerical solution of this set of equations.

It is interesting to note that the percentage increase in the critical value of $\mathcal{J}(0)/\Delta$ necessary for magnetic ordering on going from the molecular-field approximation to the constant-coupling approximation is much smaller for the two-singlet-level problem than in the case where the excited state is a triplet.[4] (For example, with $z=6$, the critical value increases by 12% for the singlet-singlet and by 23% for the singlet-triplet case.) This occurs because the excited state of $\mathcal{H}_{20}$ mixed into the ground state by $\mathcal{H}_2'$ has a much stronger mixing with the ground state in the singlet-triplet case.

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Atomic Displacement Relationship to Curie Temperature and Spontaneous Polarization in Displacive Ferroelectrics

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The phase transition from nonpolar to polar in displacive ferroelectric crystals is accompanied by the displacement Δz of certain atoms from their higher-temperature symmetry positions. A study of all displacive ferroelectrics in which atomic positions have been determined has shown that a fundamental relationship exists between Δz and the Curie temperature T_C. This relation has the form $T_C = (\mathcal{K}/2k)(\Delta z)^2$, where $\mathcal{K}$ has the dimensions of a force constant, k is Boltzmann's constant, and T_C is in absolute units. A least-squares fit, based on Δz and T_C for ten different ferroelectrics, gives $\mathcal{K}/2k = (2.00 \pm 0.09) \times 10^4$ °K Å^{-2}. In addition, the spontaneous polarization P_s is found to be related to Δz by the equation $P_s = (258 \pm 9)\,\Delta z\,\mu$C cm^{-2}. $\mathcal{K}$ is discussed in terms of the interatomic force constant along the polar axis.

THE phase transition from nonpolar to polar in displacive ferroelectric crystals is accompanied by the displacement of certain atoms from their higher-temperature symmetry positions. Until recently, very few reliable determinations of the detailed atomic arrangement in displacive ferroelectrics have been available,[1] making comparisons with ferroelectric theories inconclusive. In this article, we report for the first time a simple experimental relationship between atomic displacement and the macroscopic ferroelectric properties of Curie temperature and spontaneous polarization, valid over a wide range of materials. From simple physical considerations, it is shown that this experimental relationship may be interpreted as an equivalence between the lattice vibrational energy and the displacive energy of the ferroelectric state.

We define Δz as the displacement developed by the "homopolar" metal atom, as listed in Table I, along the polar direction at $T \ll T_C$. The values of atomic displacement Δz, Curie temperature T_C, and spontaneous polarization P_s for a group of twelve compounds are given in Table I, together with their estimated standard deviations. We derive Δz for one material as an illustrative example. In the case of $LiNbO_3$ above T_C, the oxygen atoms most probably[2] are arranged in planes with $z = \frac{1}{12}(2n+1)$, where n is integral. The homopolar Nb atom is at $z=0$, the position with point symmetry $\bar{3}$. At $T \ll T_C$, the oxygen framework may be

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TABLE I. Properties of some displacive ferroelectrics.[a]

No.	Compound	T_c (°K)	Space group transformation	Point symmetry[b]	Origin shift (Å)	Homopolar atom	Atomic displacement (Å)	Measured spontaneous polarization (μC cm^{-2})
1	$NaNbO_3$	73±10	monoclinic→*Pbma*[c]			Nb	[0.060]	11.7±5[d]
2	SbSI	296±2	$Pna2_1$→*Pnam*	*m*	0.041	Sb	0.144±0.040[e]	25±3[f]
3	$Ba_{5/4}Sr_{15/4}Nb_{10}O_{30}$	348±15	$P4bm$→$P\bar{4}b2$	222	0.013	Nb	0.106±0.022[g]	
4	$Pb_{10}Fe_5Nb_5O_{30}$	388±15	$R3m$→$R\bar{3}m$	$\bar{3}m$	0.118	Nb	0.091±0.100[h]	
5	$BaTiO_3$	399±5	$P4mm$→$Pm3m$	$m3m$	0.075	Ti	0.132±0.009[i]	25±1[j]
6	$Ba_6Ti_2Nb_8O_{30}$	505±15	$P4bm$→$P\bar{4}b2$	222	0.052	Ti, Nb	0.174±0.100[k]	
7	$KNbO_3$	708±5	$Bmm2$→$Pm3m$	$m3m$	0.160	Nb	0.160±0.014[l]	30±3[m]
8	$PbTiO_3$	763±15	$P4mm$→$Pm3m$	$m3m$	0.465	Ti	0.299±0.040[n]	
9	$LiTaO_3$	891±5	$R3c$→$R\bar{3}c$	$\bar{3}$	0.197	Ta	0.197±0.008[o]	50±2[p]
10	$Bi_4Ti_3O_{12}$	949±5	$Fmm2$→$Fmmm$	mm		Ti	[0.215]	50±10[q]
11	$LiNbO_3$	1468±15	$R3c$→$R\bar{3}c$	$\bar{3}$	0.269	Nb	0.269±0.006[r]	71±2[p]
12	$Ba_{10}Cu_5W_5O_{30}$	1473±15	$P4mm$→$Pm3m$	$m3m$	0.431	W	0.328±0.100[h]	

[a] Error values are assumed if not given in the primary references. Magnitudes in square brackets are derived values.

[b] Paraelectric or antipolar point symmetry of homopolar atom.

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[r] References 5 and 6.

regarded as unchanged in z, but the Nb atom is displaced through a distance of $0.0194c$ (the mean of the x-ray[3] and neutron[4] diffraction values). In the diffraction studies, the origin was arbitrarily taken at the Nb atom; hence this origin must be shifted by $0.0194c = 0.269$ Å, equal to the Nb displacement along the trigonal polar axis.

The experimental values of Δz and T_C for ten displacive ferroelectrics are shown in Fig. 1. These points have been fitted by the method of least squares[5] to give the equation

$$T_C = (2.00 \pm 0.09) \times 10^4 (\Delta z)^2 \text{ °K}, \quad (1)$$

indicated in the figure by the solid line.[6] The maximum difference between any experimental value and Eq. (1) is 2.6 standard deviations in Δz for $PbTiO_3$. The probability of such a difference occurring by chance is estimated, by the Student t test, to be 3%.

The empirical relation of Eq. (1) may be expressed in energy terms as

$$kT_C = \tfrac{1}{2}\mathcal{K}(\Delta z)^2, \quad (2)$$

where k is the Boltzmann constant and $\mathcal{K}$ has the dimensions of a force constant. The magnitude of this force constant may be evaluated from Eqs. (1) and (2) as

$$\mathcal{K} = (5.52 \pm 0.25) \times 10^4 \text{ dyn cm}^{-1}. \quad (3)$$

This value is similar in magnitude to the force constant between atoms in a crystalline solid, suggesting that $\mathcal{K}$ may be interpreted as an average force constant between the homopolar atom and the oxygen framework along the polar direction.[7] Further support for this point of view is obtained by considering the atomic array in the polar direction as consisting of the sequence $-A-B-A-B-A-$, where A is oxygen (or the equivalent anion) and B is the homopolar atom. In this approximation, we have

$$\mathcal{K}' = \bar{r}_e c, \quad (4)$$

where $\bar{r}_e$ is the average equilibrium interatomic separation between atoms A and B, and c is the elastic con-

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[5] The weights used in the observational equations are the inverse variances derived from the standard deviations in Table I.

[6] An equally good fit to the experimental values is given by the linear equation $T_C = 7.14 \times 10^3 \Delta z - 493$°K. The intercept at 0°K together with the lack of a theoretical basis for a linear relation led us to discard this equation.

[7] A similar relationship to Eq. (2) can be found in the theories of various authors, for example, Y. Takagi, in *Proceedings of the International Conference on Theoretical Physics, Kyoto and Tokyo, 1953.* (Science Council of Japan, Tokyo, 1954), p. 824. Other predictions of these early theories, such as specific-heat magnitudes, are not in good agreement with experiment.

stant associated with the polar direction.[8] For example, in $BaTiO_3$ the experimental value of $\bar{r}_e=2.018$ Å and $c_{33}=17.8\times10^{11}$ dyn cm^{-2}, resulting in $\mathcal{K}'=3.59\times10^4$ dyn cm^{-1}, which compares favorably with the experimental value in Eq. (3). Equation (2) may, in consequence, be given a simple physical interpretation. At T_C, the amplitude of thermal motion of the homopolar atom becomes equal to Δz, resulting in an average displacement of zero for this atom. Below T_C, as the thermal amplitude progressively decreases, the average displacement increases to its asymptotic value Δz, at which point the low-temperature displacive energy is equal to the thermal energy at the Curie point.

There are only five displacive ferroelectric compounds for which reliable values of both P_s and Δz have been measured, as given in Table I. However, Fig. 2 shows these experimental points together with a least-squares fit to a straight line passing through the origin with equation

$$P_s=(258\pm9)\Delta z\ \mu\text{C cm}^{-2}. \quad (5)$$

A recent theoretical study[9] by Lines has also shown that $T_C\propto(P_s)^2$ for any one compound, implying from Eq. (1) that $P_s\propto\Delta z$. This theory does not predict a universal constant. More than one value for the constant in Eq. (5) is in fact likely, depending on the class of material. It is improbable that such values will differ by as much as a factor of 2. Spontaneous polarizations for compounds 1 and 10 in Table I may now be estimated from their Curie temperatures, based on the above relationships, and are found to be in fair agreement with experiment.

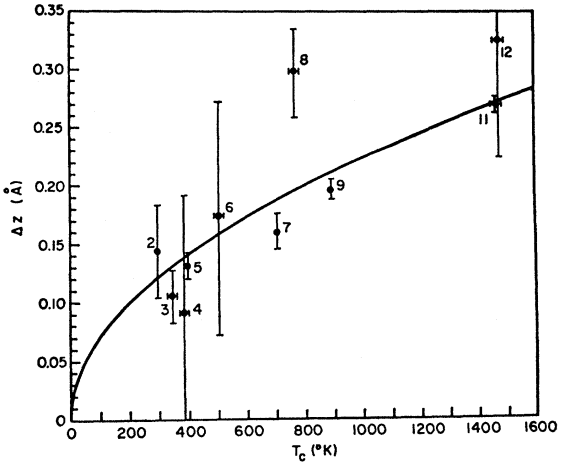

FIG. 1. The solid line represents the equation $T_C=2.00\times10^4(\Delta z)^2$ °K, and the numbered points are the Δz and T_C values for ten of the materials in Table I. The low Δz values for compounds 3, 4, and 5 may be related to the large T/T_C ratio at which the measurements were made. No experimental point significantly differs from the solid line. It may be noted that $\Delta z=0.08$ Å for phosphorus in potassium dihydrogen phosphate [G. E. Bacon and R. S. Pease, Proc. Roy. Soc. (London) **A230**, 359 (1955)], for which $T_C=$ 123°K, fits this equation very well.

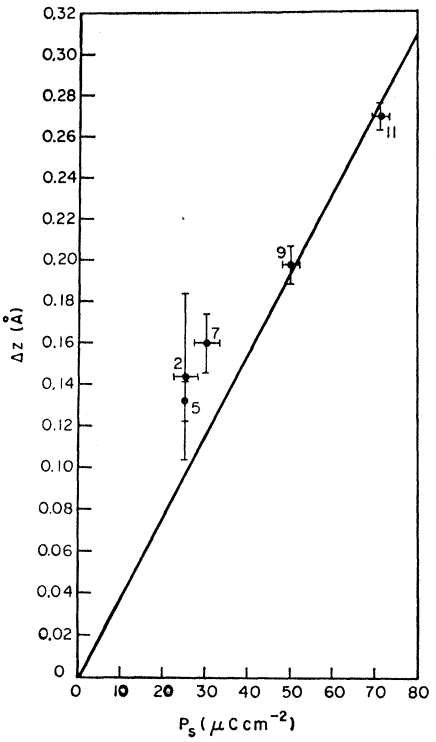

FIG. 2. The solid line represents the equation $P_s=258\Delta z\ \mu$C cm^{-2}, and the numbered points are P_s and Δz values from Table I. P_s for compounds 5 and 7 are probably low since an additional low-temperature phase prevents measurement at $T\ll T_C$.

The equation $T_C=(0.303\pm0.018)\ P_s^2$ °K (when P_s is in μC cm^{-2}) may be derived directly from the experimental quantities given in Table I, which compares with a value for the proportionality constant of 0.300 ± 0.020 obtained from Eqs. (1) and (5). A similar linear relationship between spontaneous polarization and atomic displacements has recently been derived by Axe,[10] based on the infrared dielectric response above T_C. It may be noted that his predicted value of $P_s=$ 70.3 μC cm^{-2} for $LiNbO_3$ is in excellent agreement with the measured value quoted in Table I.

In conclusion, we have demonstrated the existence of two equations applicable to a large range of ferroelectrics. Further experimental and theoretical studies are necessary to establish the full range of validity of these equations.

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