

Theoretical Model for Explaining the Ferroelectric Effect in Barium Titanate

W. P. MASON AND B. T. MATTHIAS

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received August 26, 1948)

In order to explain the properties of a barium titanate single domain crystal, a previous theory of the ferroelectric effect in rochelle salt has been extended to the three-dimensional structure of barium titanate. This involves six equilibrium positions and results in significant differences from the single bond type of structure of rochelle salt. The theoretical features considered are a calculation of the spontaneous polarization as a function of temperature, the dielectric constants along the $a=y$ and $c=z$ axes as a function of temperature, the relaxation of the dielectric constant at high frequencies, and the hysteresis loops. All of these features are explained by the three-dimensional model considered here.

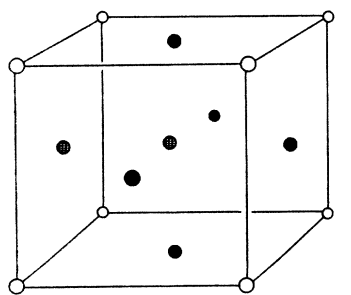
IN a previous paper,¹ a theoretical explanation was given for the ferroelectric effect in rochelle salt, which depended on the motion of a hydrogen nucleus between the two equilibrium positions of a hydrogen bond. It is the purpose of this paper to show that the principal features of the barium titanate single domain crystal can be explained by an extension of this model to the three-dimensional structure of barium titanate involving six equilibrium positions.

I. EXPERIMENTAL DATA

Barium titanate above the transition temperature of 120°C has the cubic cell shown by Fig. 1. The barium atoms occupy the corners of the cell, the oxygens the face-centered positions, while the titanium is usually pictured as being in the center of the cell. As a matter of fact, it probably makes a covalent bond with one of the face-centered

oxygens and is displaced in the direction of that oxygen by about $0.16A^2$ from the center of the cell. Above 120°C the thermal energy is sufficient to cause any one of the six positions to be equally probable and the cell appears to be cubic from x-ray measurements. Below 120°C thermal energy is no longer sufficient to cause any position to be equally probable, and most of the molecules in a given region or domain line up along one of the six directions, a dipole moment develops in that direction and the crystal becomes ferroelectric. The axis along which the titanium has been displaced becomes larger than the other two, as shown by the x-ray measurements of Miss Megaw³ (as shown by Fig. 2) and the crystal changes from cubic to tetragonal form.

The dielectric measurements of multicrystalline ceramics, multi-domain crystals, and single domain crystals all show the presence of a ferroelectric material below 120°C. Dielectric displacement—electric field curves occur in the form of hysteresis loops. The dielectric constant at low field strengths for multicrystal ceramics,⁴ as shown by Fig. 3, rises to a high value at the temperature of 120°C. Above 120 degrees, the dielectric constant follows a Curie-Weiss law approximately, and the dielectric constant decreases inversely as the difference between the tempera-



○ - BARIUM ● - OXYGEN ● - TITANIUM
UNIT CELL FOR BARIUM TITANATE ABOVE 120 C

FIG. 1. Unit cell for barium titanate.

¹ W. P. Mason, *Phys. Rev.* **72**, 854 (1947).

² This value for the displacement of the titanium atom from the center of the unit cell has recently been measured by x-ray methods by Gordon Danielson, *Phys. Rev.* **74**, 986 (1948).

³ H. D. Megaw, *Proc. Roy. Soc.* **189**, 261-283 (1947).

⁴ Von Hippel, Breckenridge, Chesley, and Tisza, *Ind. Eng. Chem.* **38**, 1097-1109 (1946).

ture and the Curie temperature or

$$\epsilon = \epsilon_0 + C/(T - T_0), \quad (1)$$

where ϵ_0 is the constant dielectric constant for temperatures much higher than the Curie temperature. C is a constant, T the temperature, and T_0 the Curie temperature. Below the Curie temperature the dielectric constant decreases from its high value to a value of about 350 near absolute zero. The steady decrease is interrupted at two temperatures 10°C and -70°C . At these temperatures no discontinuities occur in the axis length and hence these points cannot be associated with a change in dipole moment and hence with the position of the titanium nucleus. It has been suggested by Matthias and von Hippel⁵ that these are due to a change from octahedral bonding of the titanium atom to a hybrid type of bonding which may become more probable at the lower temperature. Since this does not involve an appreciable change in the position of the titanium nucleus, this appears to be a reasonable suggestion. As the result is a small second-order change in the dielectric constant, it is neglected in the theory presented here.

The dielectric constant for multi-domain crystals is not too different from those for the multi-crystalline ceramics. Figure 4 shows the measurements of Matthias and von Hippel⁵ for the a and c axes. The dielectric constant along the a axis is higher than that along the c axis. The lowering of the Curie point is probably caused by the impurities introduced. By introducing larger amounts of mineralizers, single domain crystals of a relatively large size have recently been grown, and these show a very marked difference between the dielectric constants along the two axes. As shown by Fig. 5, the dielectric constant along the c axis is less than that for a ceramic material. When the dielectric constant along the a axis is measured over a frequency range, a relaxation occurs at about 15 megacycles and the dielectric constant drops to about 1200 or less, as shown by Fig. 6. A similar relaxation in the dielectric constant of the ceramic occurs at about 10^9 cycles as shown by the measurements of Nash⁶ and Yager

⁵ B. T. Matthias and A. von Hippel, *Phys. Rev.* **73**, 1378-1384 (1948).

⁶ D. E. Nash, Jr., *J. Exper. Theor. Phys. Acad. Sci. U.S.S.R.* **17**, 537 (1947).

Data on Unit Cell Axes of Barium Titanate as a Function of Temperature (Data from H. D. Megaw).

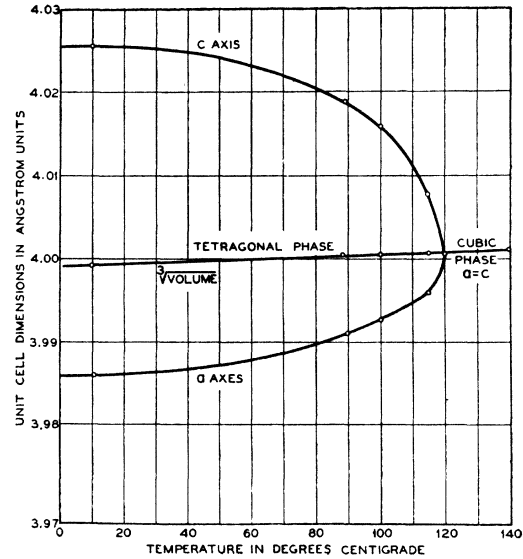


FIG. 2. Cell dimensions as a function of temperature.

(unpublished).⁷ At 23.7-centimeter wave-lengths, the former found a dielectric constant and $\tan \delta$ of

$$\epsilon = 1250 \text{ to } 1420, \quad \tan \delta \doteq 0.2, \quad (2)$$

while at 1.25 centimeters Yager found a dielectric

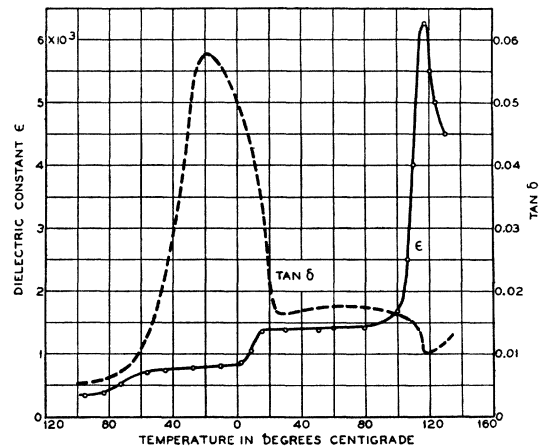


FIG. 3. Dielectric constant of barium titanate ceramic as a function of temperature.

⁷ The dielectric constants of barium titanate ceramics have recently been measured at 1.5 megacycles and 9450 megacycles over a temperature range from 20°C to 160°C by J. G. Powles of Imperial College of Science and Technology. The results are described in a note sent to *Nature*. From the variation of the relaxation frequency with temperature, one can calculate that the activation energy is 3.65 kilocalories per mole in fair agreement with the value found in Eq. (63).

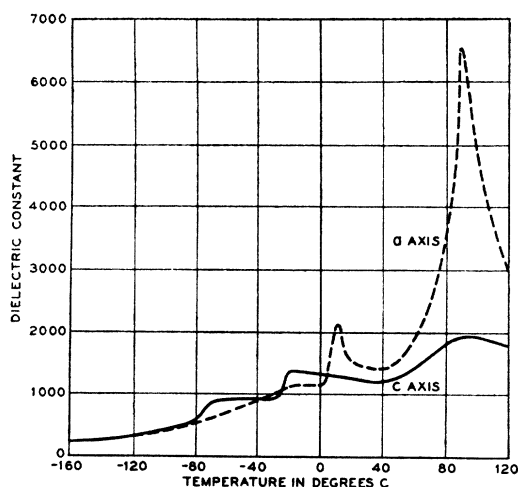


FIG. 4. Dielectric constants for the two crystallographic axes for multi-domain crystals of barium titanate.

constant of approximately

$$\epsilon = 250 \text{ to } 320, \quad \tan \delta \approx 0.70. \quad (3)$$

From these measurements it can be calculated that the dielectric constant has a relaxation frequency of about 6.2×10^9 cycles.

The relaxation of the dielectric constant at these frequencies shows definitely that the high dielectric constant is due to a temperature movable dipole rather than a high dielectric constant of the type due to the near vanishing of the factor $(1 - \beta\gamma)$ in the dielectric equation

$$\frac{\epsilon - 1}{4\pi} = \frac{\gamma}{1 - \beta\gamma}, \quad (4)$$

where γ is the polarizability and β the Lorentz factor, since the polarizability γ due to electrons, ions and atoms should not vary with frequency up to the infra-red frequencies. Hence, a temperature variable dipole of the type discussed in the next section is required to give a relaxation frequency as low as 15 megacycles.

II. SPONTANEOUS POLARIZATION AND DIELECTRIC CONSTANT UNDER EQUILIBRIUM CONDITIONS

The model considered here is the one shown by Fig. 7. Here there are six potential minima in the direction of the six oxygens which are displaced a distance δ from the center of the unit cell. If the titanium nucleus is taken from a position such as

1 to position 2 directly across the unit cell, the form of the potential barrier may be as shown by Fig. 8 in which ΔU represents the height of the potential curve at the center with respect to that at the minima. If the nucleus went directly from position 1 to position 3, it would in general have to cross a higher potential barrier than ΔU , but equilibrium between the two positions can be established by the nucleus jumping to a position slightly to one side of the center in the direction 3 and hence it is thought that the potential barrier determining the relaxation frequency for a 1 to 3 jump will not be much higher than for a 1 to 2 jump, namely ΔU .

For low frequencies, i.e., for frequencies well under the relaxation frequency, equilibrium values can be calculated by using Boltzmann's principle that the equilibrium ratios of numbers of nuclei in two potential wells are in the ratio

$$N_1/N_2 = e^{E/kT} \quad (5)$$

where E is the potential difference between well 2 and well 1, k is Boltzmann's constant and T the absolute temperature.

Suppose now that all the minima of Fig. 7 have initially the same potential, which is set equal to zero. Then if we apply a field E_z in the z direction, a polarization P_z in this direction results. This polarization causes an internal field F of the Lorentz type given by the equation

$$F = E + \beta P \quad (6)$$

where β is $4\pi/3$ for an isotropic material but will be much less than this when the titanium nucleus comes close to the oxygen atom. The total polarization consists of a part P_e due to electrons and atoms and a part P_d due to the dipole caused by the displacement of the titanium nucleus from

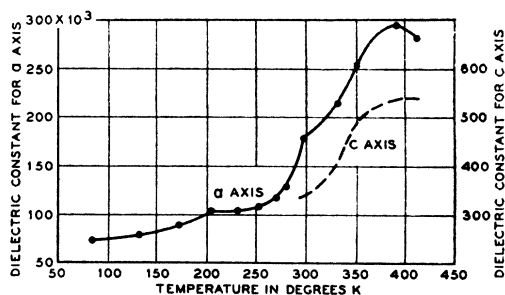


FIG. 5. Dielectric constants for a single domain crystal.

the mid-position of the unit cell. The dipole moment introduced by this change is

$$\mu = 4e\delta, \quad (7)$$

since the valence of the titanium is 4 for the structure, e is the electronic charge, and δ the distance the titanium nucleus moves in going from the center of the unit cell to the equilibrium position. An addition to the dipole may also result from a displacement of the oxygen in the direction of the titanium. The electronic and atomic polarization exerted will be proportional to the local field F , so that

$$F = E + \beta[P_e + P_d] = E + \beta[\gamma F + P_d]$$

or

$$F = \frac{E + \beta P_d}{1 - \beta\gamma} \quad (8)$$

where γ is the polarizability per unit volume due to all polarization except that of the titanium dipoles. The polarizability γ can be determined from the dielectric constant ϵ_0 measured at very low or very high temperatures, for since

$$(\epsilon_0 - 1)/4\pi = P_E/E = \gamma F/E \quad (9)$$

and for P_d suppressed, $F = E/(1 - \beta\gamma)$, hence

$$\frac{\epsilon_0 - 1}{4\pi} = \frac{\gamma}{1 - \beta\gamma} \quad \text{and} \quad 4\pi\gamma = \frac{(\epsilon_0 - 1)}{1 + \frac{\beta}{4\pi}(\epsilon_0 - 1)}. \quad (10)$$

The dielectric constant ϵ_0 near absolute zero is

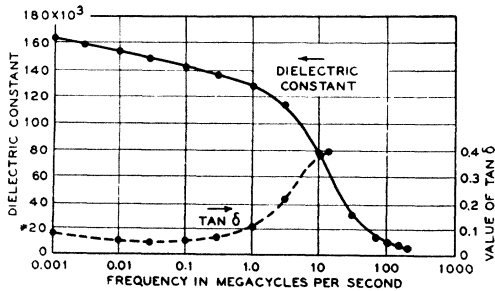


FIG. 6. Dielectric constant of an axis as a function of frequency.

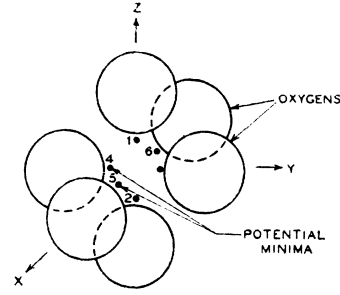


FIG. 7. Theoretical model for barium titanate, showing positions of oxygens and potential minima for the titanium nucleus.

about 350, hence

$$\frac{1}{1 - \beta\gamma} = 1 + \frac{\beta}{4\pi}(\epsilon_0 - 1) = 1 + \beta(27.8). \quad (11)$$

This internal field caused by the applied field E_z causes a decrease in the potential at the minima 1 and an increase in the potential at 2 equal, respectively, to

$$U_1 = -F\mu = -\left(\frac{E_z + \beta P_z}{1 - \beta\gamma}\right)\mu; \quad (12)$$

$$U_2 = +\left(\frac{E_z + \beta P_z}{1 - \beta\gamma}\right)\mu.$$

The potentials for the other four wells are unchanged by this field and hence,

$$U_3 = U_4 = U_5 = U_6 = 0. \quad (13)$$

By Boltzmann's principle (Eq. (5)), the relative number of nuclei in the six potential wells, all expressed relative to N_5 are

$$N_1 = N_5 \exp\left[\left(\frac{E_z + \beta P_z}{1 - \beta\gamma}\right)\frac{\mu}{kT}\right];$$

$$N_2 = N_5 \exp\left[-\left(\frac{E_z + \beta P_z}{1 - \beta\gamma}\right)\frac{\mu}{kT}\right]; \quad (14)$$

$$N_3 = N_4 = N_5 = N_6.$$

Then, since the total number of nuclei is equal to N where N is the number per cubic centimeter, we have

$$N = N_1 + N_2 + N_3 + N_4 + N_5 + N_6. \quad (15)$$

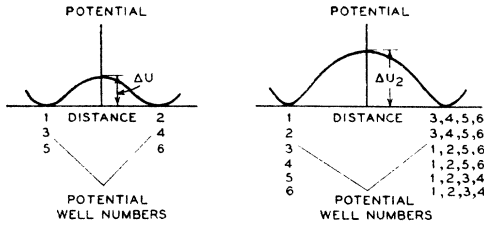


FIG. 8. Potential distribution as a function of distance from the center of the cell.

Substituting in the values from Eqs. (14) we have

$$N_1 = \frac{N \exp \left[\left(\frac{E_z + \beta P_z}{1 - \beta \gamma} \right) \frac{\mu}{kT} \right]}{2 \left[2 + \cosh \left(\frac{E_z + \beta P_z}{1 - \beta \gamma} \right) \frac{\mu}{kT} \right]};$$

$$N_2 = \frac{N \exp - \left[\left(\frac{E_z + \beta P_z}{1 - \beta \gamma} \right) \frac{\mu}{kT} \right]}{2 \left[2 + \cosh \left(\frac{E_z + \beta P_z}{1 - \beta \gamma} \right) \frac{\mu}{kT} \right]};$$

$$N_3 = N_4 = N_5 = N_6$$

$$= \frac{N}{2 \left[2 + \cosh \left(\frac{E_z + \beta P_z}{1 - \beta \gamma} \right) \frac{\mu}{kT} \right]}.$$

The polarization of a dipole nature excited along the Z axis will be then

$$P_z = (N_1 - N_2)\mu$$

$$= \frac{N\mu \sinh \left[(E_z + \beta P_z)/(1 - \beta \gamma) \right] \mu/kT}{2 + \cosh \left[(E_z + \beta P_z)/(1 - \beta \gamma) \right] \mu/kT}. \quad (17)$$

All the equilibrium values of spontaneous polarization, coercive fields, dielectric constants, etc. can be determined from this equation.

Let us first consider the condition for spontaneous polarization and the ferroelectric effect. This can be obtained by setting E_z equal to zero and determining the conditions for which the polarization P_z is different from zero. Setting E_z equal to zero and introducing the substitution

$$A = [\beta N \mu^2 / (1 - \beta \gamma)]^{1/kT}. \quad (18)$$

Equation (17) becomes

$$\frac{P_z}{N\mu} = \frac{\sinh(AP_z/N\mu)}{2 + \cosh(AP_z/N\mu)}. \quad (19)$$

Examining this equation, we see that $P_z/N\mu$ will have a solution different from zero only if A is equal to 3 or greater. If A is greater than 3, $P_z/N\mu$ can have a positive or negative value lying between zero and 1. This represents a spontaneous polarization along the positive or negative Z axis due to the internal field generated by charge displacements of the titanium nuclei from the central position. In general any one of the oxygen atoms can be considered as lying along the Z axis and only chance determines in which direction the spontaneous polarization occurs.

If we solve for $P_z/N\mu$ as a function of A , the relation shown by Fig. 9 results. This is a very much larger increase of $P_z/N\mu$ with increase in A than occurs for a single bond of the hydrogen bond type which is determined by an equation of the type

$$P_z/N\mu = \tanh(AP_z/N\mu). \quad (20)$$

The relative increase for this type is shown by the dashed line of Fig. 9 for the same percentage increase in A . Some confirmation for this sudden increase in polarization is obtained from the cell dimensions shown by Fig. 2. The changes in cell dimension, which are independent of the direction of polarization along the Z axis, can be regarded as due to the electrostrictive effect in barium titanate. The electrostrictive effect for the barium titanate ceramic has been investigated in a previous paper⁸ and it is there shown

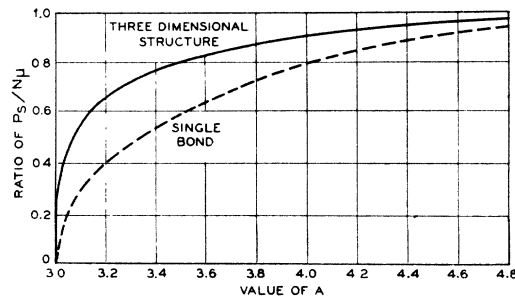


FIG. 9. Theoretical curve for ratio of spontaneous polarization P_s to the total polarization $N\mu$ as a function of the factor A .

⁸ W. P. Mason, "Electrostrictive effect in barium titanate ceramics," *Phys. Rev.* (to be published).

that the ceramic has an increase in thickness and a decrease in radial dimension given by the strain equations

$$S_{33} = Q_{11}(P_z)^2; \quad S_{11} = S_{22} = +Q_{12}(P_z)^2 \quad (21)$$

where

$$Q_{11} = 6.9 \times 10^{-12} \text{ (cm}^2\text{/stat coulomb)}^2;$$

$$Q_{12} = -2.15 \times 10^{-12} \text{ (cm}^2\text{/stat coulomb)}^2.$$

While the value of Q_{11}/Q_{12} is not exactly equal to -2 for the ceramic, a guide to the spontaneous polarization is obtained from these values. At 20°C , S_{33} the longitudinal thickness strain is equal to 6.7×10^{-3} while the radial thickness strain is equal to $S_{11} = S_{22} = -3.3 \times 10^{-3}$ from the measurements of Fig. 2. With these values and the electrostrictive constants of Eq. (21), the indicated spontaneous polarization for the two effects is

$$P_z = 31,500 \frac{\text{stat coulomb}}{\text{cm}^2}$$

$$= 10.5 \times 10^{-6} \frac{\text{coulomb}}{\text{cm}^2} \text{ (long.),} \quad (22)$$

$$P_z = 39,000 \frac{\text{stat coulomb}}{\text{cm}^2}$$

$$= 12.9 \times 10^{-6} \frac{\text{coulomb}}{\text{cm}^2} \text{ (radial).}$$

Taking the average of these

$$P_z = 35,250 \frac{\text{stat coulomb}}{\text{cm}^2}$$

$$= 11.7 \times 10^{-6} \frac{\text{coulomb}}{\text{cm}^2}. \quad (23)$$

This value agrees quite well with that measured electrically by means of the hysteresis loops. For this value Matthias and von Hippel⁶ find a value 12×10^{-6} coulomb/cm² while Hulm⁹ finds a value 16×10^{-6} coulomb/cm². This calibration allows one to obtain the spontaneous polarization as a function of temperature, and this is shown plotted by Fig. 10. The very sudden rise in spontaneous polarization just below the Curie

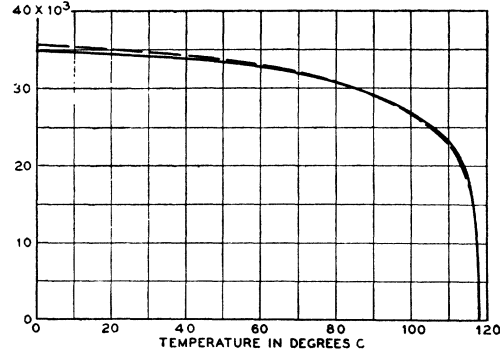


FIG. 10. Measured spontaneous polarization as a function of the temperature.

temperature is evident, and this agrees qualitatively with that shown by Fig. 9.

To find if the spontaneously generated polarization agrees quantitatively with that calculated from Eq. (19) we have to evaluate A and μ by other methods. One method for doing this is to measure the dielectric constants at low field strengths as a function of temperature. The calculated value can be obtained from Eq. (17) by dividing the polarization P_z into the spontaneous part P_s and a very small alternating part $P_0 e^{j\omega t}$. The applied field $E_z e^{j\omega t}$ is assumed very small and hence we have

$$\sinh \left[\frac{(E_z + \beta P_0) e^{j\omega t} + \beta P_s}{1 - \beta \gamma} \right] \frac{\mu}{kT}$$

$$= \sinh \left[\frac{(E_z + \beta P_0) e^{j\omega t}}{1 - \beta \gamma} \right] \frac{\mu}{kT} \cosh \left(\frac{\beta P_s}{1 - \beta \gamma} \right) \frac{\mu}{kT}$$

$$+ \cosh \left[\frac{(E_z + \beta P_0) e^{j\omega t}}{1 - \beta \gamma} \right] \frac{\mu}{kT} \sinh \left(\frac{\beta P_s}{1 - \beta \gamma} \right) \frac{\mu}{kT}$$

$$\doteq \frac{(E_z + \beta P_0) e^{j\omega t} \mu}{(1 - \beta \gamma) kT} \cosh \frac{AP_s}{N\mu} + \sinh \frac{AP_s}{N\mu}. \quad (24)$$

Similarly,

$$\cosh \left[\frac{(E_z + \beta P_0) e^{j\omega t} + \beta P_s}{1 - \beta \gamma} \right] \frac{\mu}{kT} = \cosh \frac{AP_s}{N\mu}$$

$$+ \left[\frac{(E_z + \beta P_0) e^{j\omega t}}{1 - \beta \gamma} \right] \frac{\mu}{kT} \sinh \frac{AP_s}{N\mu}. \quad (25)$$

Inserting Eqs. (24) and (25) in (17) and solving for the constant and time variable parts, we ob-

⁹ F. Hulm, Nature **160**, 126 (1947).

tain Eq. (19) for the constant part, and for the time variable part we have

$$\frac{P_0 e^{i\omega t}}{N\mu^2} = \frac{(E_z + \beta P_0) e^{i\omega t}}{(1 - \beta\gamma)kT} \times \left\{ \frac{2 \cosh(AP_S/N\mu) + 1}{[2 + \cosh(AP_S/N\mu)]^2} \right\}. \quad (26)$$

Solving for P_0 , multiplying by 4π and adding the dielectric constant for electrons and atoms, the dielectric constant for the z axis becomes

$$\epsilon_z = \epsilon_0 + \frac{4\pi A \left[\frac{2 \cosh \frac{AP_S}{N\mu} + 1}{N\mu} \right]}{\beta \left[2 + \cosh \frac{AP_S}{N\mu} \right]} - A \left[\frac{2 \cosh \frac{AP_S}{N\mu} + 1}{N\mu} \right] \left[\frac{2 \cosh \frac{AP_S}{N\mu} + 1}{2 + \cosh \frac{AP_S}{N\mu}} \right]. \quad (27)$$

Above the Curie point, the spontaneous polarization P_S disappears and this equation reduces to

$$\epsilon_z = \epsilon_0 + \frac{(4\pi A/\beta)}{3 - A} = \epsilon_0 + \frac{C}{T - T_0} \quad (28)$$

upon introducing the value of A from Eqs. (18) and (11), where

$$C = \frac{4\pi N\mu^2 [1 + \beta(\epsilon_0 - 1)/4\pi]}{3k}; \quad (29)$$

$$T_0 = \frac{\beta N\mu^2}{3k} \{1 + [\beta(\epsilon_0 - 1)/4\pi]\}.$$

The single domain crystals have so many impurities in them to prevent the breaking up of the crystal into multi-domains that they do not revert to a cubic crystal above the Curie point. This is shown by the different dielectric constant for the two directions above the Curie point. The same is true to a lesser extent for the multi-domain crystals, but the ceramic pieces show a pronounced maximum and a Curie region above 120°C, much in agreement with Eq. (28). Since above the Curie temperature the crystal becomes

cubic and all directions equivalent, it is thought that the best values for C and T_0 will be obtained from a dense ceramic piece. From the dielectric constant above 120°C of Fig. 3, we obtain the values

$$C = 40,000; \quad T_0 = 393^\circ\text{K} \quad (30)$$

and from low temperature measurements

$$\epsilon_0 = 350. \quad (31)$$

Taking the ratio of C/T_0 of Eq. (29) we find

$$\beta = (4\pi T_0/C) = 0.124 \quad (32)$$

upon inserting the experimental values. Then, since the number of dipoles per cubic centimeter (as determined from the size of the unit cell) is $N = 1.56 \times 10^{22}$; $k = 1.38 \times 10^{-16}$, we have

$$C = 40,000 = \frac{4\pi(1.56 \times 10^{22})\mu^2 [1 + 0.124(350/4\pi)]}{3 \times 1.38 \times 10^{-16}}$$

or

$$\mu = 4.34 \times 10^{-18}. \quad (33)$$

This value of μ agrees fairly well with the value one would obtain from the recent x-ray observations that the titanium atom is displaced by 0.16Å from the center of the unit cell. If the oxygen atom moves an equal distance to meet it (which could not be determined by x-ray observations), the dipole moment would be

$$(4e + 2e)(0.16 \times 10^{-8}) = 6 \times 4.8 \times 10^{-10} \times 0.16 \times 10^{-8} = 4.6 \times 10^{-18}. \quad (34)$$

If all the dipoles pointed in one direction, the total polarization would be

$$N\mu = 1.56 \times 10^{22} \times 4.34 \times 10^{-18} = 67,500 \text{ e.s.u.} \\ = 22.5 \times 10^{-6} \text{ coulomb cm}^2. \quad (35)$$

The measured value of approximately 35,500 e.s.u. is 53 percent of this. If all the quantities entering Eq. (18) for A were independent of temperature except T , the absolute temperature, the value of A for 27°C = 300 K would be 3.94, and from Fig. 9 the theoretical value of the polarization $P_S/N\mu$ should be 0.90, rather than the measured value of 0.53, which corresponds to a value of $A = 3.090$. This result indicates that some of the quantities in the expression for A decrease as the temperature is lowered. A similar result is also required for the variation of dielec-

tric constant with temperature. A value of $A = 3.090$, $P_s/N\mu = 0.53$, and β set at 0.096 (in order to give a value of $A = 3.090$), and all the other quantities unchanged, results in a dielectric constant of 1390 which agrees well with the dielectric constant for a ceramic or for a multi-domain barium titanate crystal. The variation may be ascribed to β or to ϵ_0 because the measured temperature expansion coefficients indicate that N and μ should be relatively constant. From the x-ray data of Fig. 2 it is seen that from 120°C to 0°C, N should increase by 0.15 percent. Since the titanium atom is tightly bound to the oxygen, the distance between the center of oxygen and titanium should not change appreciably because of temperature contraction, and hence μ also will not change much with temperature. The value of ϵ_0 , however, may be different for the a and c axes since the a axis ϵ decreases while the c axis increases. Hence, ϵ_c may be smaller and ϵ_a larger than ϵ_0 . The Lorentz factor β , also, may vary considerably depending on the condition of the surrounding electrical charge configurations. For isotropic conditions, the theoretical value is $4\pi/3 = 4.19$. For the case of the titanium surrounded closely by the oxygens the experimental value is only 0.124. As the temperature is decreased, all the oxygen atoms come closer together and hence a decrease in β is to be expected. Assuming all the variation due to β , the values to agree with the dielectric constant measurements are shown plotted by Fig. 11. With these values of β (assuming all the other quantities in A are independent of the temperature), A can be evaluated as a function of temperature and the theoretical values of spontaneous polarization can be determined from Eq. (19). These are shown plotted by the dashed line of Fig. 10, and these agree closely with those determined from the electrostrictive effect. Hence, two independent sets of data are satisfied by the β -curve.

III. DIELECTRIC CONSTANT ALONG a AXIS

Measurements for the dielectric constants along the a axis for single domain crystals show that the dielectric constant along this axis is very

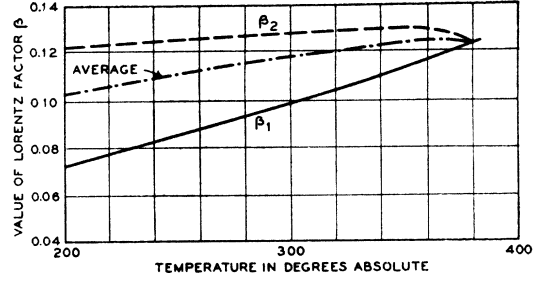


FIG. 11. Value of Lorentz factors β_1 and β_2 for $s=c$ and $y=a$ axes as a function of temperature.

much larger than that along the c axis. To determine the dielectric along the a axis, according to the model shown by Fig. 7, with a field applied along the Y axis, and a spontaneous polarization occurring along Z , the potentials for all six wells are

$$\begin{aligned} U_1 &= -\left(\frac{\beta_1 P_s \mu}{1 - \beta_1 \gamma}\right); & U_2 &= \frac{\beta_1 P_s \mu}{1 - \beta_1 \gamma}; \\ U_3 &= -\frac{[E_y + \beta_2 P_y] \mu}{(1 - \beta_2 \gamma)}; & U_4 &= \left(\frac{E_y + \beta_2 P_y}{1 - \beta_2 \gamma}\right) \mu; \\ U_5 &= U_6 = 0. \end{aligned} \quad (36)$$

We assume that β_2 along the Y axis may be different from β_1 , along the Z axis. Applying the Boltzmann principle and relating N_1, N_2, N_3 and N_4 to $N_5 = N_6$ we find

$$\begin{aligned} N_1 &= N_5 \exp\left[\left(\frac{\beta_1 P_s}{1 - \beta_1 \gamma}\right) \frac{\mu}{kT}\right]; \\ N_2 &= N_5 \exp\left[-\left(\frac{\beta_1 P_s}{1 - \beta_1 \gamma}\right) \frac{\mu}{kT}\right]; \\ N_3 &= N_5 \exp\left[\frac{[E_y + \beta_2 P_y] \mu}{[1 - \beta_2 \gamma] kT}\right]; \\ N_4 &= N_5 \exp\left[-\frac{[E_y + \beta_2 P_y] \mu}{[1 - \beta_2 \gamma] kT}\right]; & N_5 &= N_6. \end{aligned} \quad (37)$$

Since

$$N_1 + N_2 + N_3 + N_4 + N_5 + N_6 = N \quad (38)$$

we find for N_5 , the value

$$N_5 = \frac{N}{2[1 + \cosh[(\beta_1 P_s)/(1 - \beta_1 \gamma)] \mu/kT + \cosh[(E_y + \beta_2 P_y)/(1 - \beta_2 \gamma)] \mu/kT]}. \quad (39)$$

Inserting the value of N_3 , N_4 , and N_6 in the expression for the polarization along the Y axis, we have

$$P_y = (N_3 - N_4)\mu = \frac{N\mu \sinh[(E_y + \beta_2 P_y)/(1 - \beta_2 \gamma)]\mu/kT}{[1 + \cosh[(\beta_1 P_S)/(1 - \beta_1 \gamma)]\mu/kT + \cosh[(E_y + \beta_2 P_y)/(1 - \beta_2 \gamma)]\mu/kT]}. \quad (40)$$

To determine the dielectric constant along Y for small fields, we can replace

$$\sinh\left(\frac{E_y + \beta_2 P_y}{1 - \beta_2 \gamma}\right) \frac{\mu}{kT} \doteq \left(\frac{E_y + \beta_2 P_y}{1 - \beta_2 \gamma}\right) \frac{\mu}{kT}; \quad \cosh\left(\frac{E_y + \beta_2 P_y}{1 - \beta_2 \gamma}\right) \frac{\mu}{kT} \doteq 1. \quad (41)$$

Then

$$P_y = \frac{[N\mu^2/kT][(E_y + \beta_2 P_y)/(1 - \beta_2 \gamma)]}{2 + \cosh[(\beta_1 P_S)/(1 - \beta_1 \gamma)]\mu/kT} = \frac{[N\mu^2/kT][(E_y + \beta_2 P_y)/(1 - \beta_2 \gamma)]}{2 + \cosh(AP_S/N\mu)} \quad (42)$$

where

$$A = \left(\frac{N\mu^2\beta_1}{1 - \beta_1\gamma}\right) \frac{1}{kT} = \frac{N\mu^2\beta_1}{kT} \left[1 + \beta_1 \left(\frac{\epsilon_0 - 1}{4\pi}\right)\right]. \quad (43)$$

Solving for the ratio of P_y to E_y , multiplying by 4π , and adding ϵ_0 the dielectric constant due to other sources than the dipole moment, the dielectric constant along y becomes

$$\epsilon_y = \epsilon_0 + \frac{kT[4\pi N\mu^2/(1 - \beta_2 \gamma)]}{2 + \cosh(AP_S/N\mu) - [N\mu^2\beta_2/(1 - \beta_2 \gamma)kT]}. \quad (44)$$

Now, since the crystal becomes tetragonal due to the distortion caused by the electrostrictive effect, γ may increase along the a axis and cause ϵ_0 to become larger. As before, however, we assume all variation to occur in β_2 and write

$$\frac{1}{1 - \beta_2 \gamma} = 1 + \frac{\beta_2(\epsilon_0 - 1)}{4\pi}. \quad (45)$$

Inserting this value in Eq. (44) for the dielectric constant

$$\epsilon_y = \epsilon_0 + \frac{\frac{4\pi A [1 + (\beta_2/4\pi)(\epsilon_0 - 1)]}{\beta_1 [1 + (\beta_1/4\pi)(\epsilon_0 - 1)]}}{2 + \cosh \frac{AP_S}{N\mu} - A \frac{\beta_2 [1 + (\beta_2/4\pi)(\epsilon_0 - 1)]}{\beta_1 [1 + (\beta_1/4\pi)(\epsilon_0 - 1)]}}. \quad (46)$$

At the Curie temperature where the crystal changes from tetragonal form to cubic form the value of β_2 must be equal to β_1 and hence the dielectric constant along the Y axis will have a Curie temperature at the same temperature as the one along the Z axis. For other temperatures, β_2 will not, in general, equal β_1 on account of the shift in charge due to the electrostrictive effect. One might expect, however, that the shift in charge might to a first approximation produce

additive effects and that, in general

$$2\beta_2 + \beta_1 = 3\beta, \quad (47)$$

where β is the Lorentz factor for the cubic crystal. The factor of 2 is used for β_2 since the charge along the X and Y axis is only half that along the Z axis.

According to Eq. (46) the very high dielectric constants along Y shown on Fig. 5 have to be accounted for by the near vanishing of the de-

nominator of Eq. (46). The values of β_2 to make the denominator vanish, with the experimentally determined values of β_1 are shown by the dashed line of Fig. 11. These values would agree with the above speculation if the average value of β fell off with temperature according to the dot-dash line. Another verification of the near vanishing of the numerator is the very low value of the relaxation frequency for the dielectric constant along the Y axis, shown by Fig. 6. As shown by the next section, this can be accounted for by the same potential barrier for both Y and Z directions, provided that the denominator of Eq. (27) for the dielectric constant along the $c=Z$ axis is about 100 times as large as that of Eq. (46) for the Y axis.

IV. RELAXATION FREQUENCIES FOR THE DIELECTRIC CONSTANTS

To determine the high frequency behavior of the dielectric constants that is predicted by the model of Fig. 7, one can no longer use the Boltzmann equilibrium relation of Eq. (5) to determine the relative number of titanium nuclei in the various potential wells. Instead, one has to relate the time rate of change of the number in a given potential well to the probability of transition for a given time from one potential well to another. $\alpha_{1,2}$ the probability of a nucleus in well 1 jumping to well 2 per unit time is, according to Eyring's reaction rate theory,

$$\alpha_{1,2} = (kT/h)e^{-\Delta U/kT} \quad (48)$$

where h is Planck's constant, k Boltzmann's constant, and ΔU the difference between the maximum height of the potential barrier and the potential of well 1.

The time rate of change of the number N_1 of nuclei in wells of type 1 is obviously

$$\begin{aligned} \frac{dN_1}{dt} = & -N_1(\alpha_{1,2} + \alpha_{1,3} + \alpha_{1,4} + \alpha_{1,5} + \alpha_{1,6}) \\ & + N_2\alpha_{2,1} + N_3\alpha_{3,1} + N_4\alpha_{4,1} \\ & + N_5\alpha_{5,1} + N_6\alpha_{6,1}. \end{aligned} \quad (49)$$

Similarly,

$$\begin{aligned} \frac{dN_2}{dt} = & -N_2(\alpha_{2,1} + \alpha_{2,3} + \alpha_{2,4} + \alpha_{2,5} + \alpha_{2,6}) \\ & + N_1\alpha_{1,2} + N_3\alpha_{3,2} + N_4\alpha_{4,2} \\ & + N_5\alpha_{5,2} + N_6\alpha_{6,2}. \end{aligned} \quad (50)$$

Hence, the rate of change of the polarization along the Z axis is

$$\begin{aligned} \frac{dP_z}{dt} = & \frac{d(N_1 - N_2)\mu}{dt} \\ = & -N_1(2\alpha_{1,2} + \alpha_{1,3} + \alpha_{1,4} + \alpha_{1,5} + \alpha_{1,6})\mu \\ & + N_2(2\alpha_{2,1} + \alpha_{2,3} + \alpha_{2,4} + \alpha_{2,5} + \alpha_{2,6})\mu \\ & + N_3\mu(\alpha_{3,1} - \alpha_{3,2}) + N_4\mu(\alpha_{4,1} - \alpha_{4,2}) \\ & + N_5\mu(\alpha_{5,1} - \alpha_{5,2}) + N_6\mu(\alpha_{6,1} - \alpha_{6,2}). \end{aligned} \quad (51)$$

When a field is applied along the Z axis, the potential minimum U_1 is lowered, and U_2 raised by amounts shown by Eq. (12). Hence,

$$\begin{aligned} \alpha_{1,2} = & \frac{kT}{h} \exp - \left[\Delta U + \frac{(E_z + \beta_1 P_z)}{1 - \beta_1 \gamma} \mu \right] / kT; \\ \alpha_{2,1} = & \frac{kT}{h} \exp - \left[\Delta U - \frac{(E_z + \beta_1 P_z)}{1 - \beta_1 \gamma} \mu \right] / kT. \end{aligned} \quad (52)$$

By the discussion of Section II, it appears that the highest potential barrier in going from 1 to the 3, 4, 5 or 6 potential wells is also nearly ΔU . Hence,

$$\alpha_{1,2} = \alpha_{1,3} = \alpha_{1,4} = \alpha_{1,5} = \alpha_{1,6}. \quad (53)$$

Also,

$$\alpha_{2,1} = \alpha_{2,3} = \alpha_{2,4} = \alpha_{2,5} = \alpha_{2,6}. \quad (54)$$

In going from potential wells 3, 4, 5 or 6 to any of the other wells, the highest potential barrier is ΔU , since these minima are not changed by a field along Z and hence

$$\alpha_{3,n} = \alpha_{4,n} = \alpha_{5,n} = \alpha_{6,n} = \frac{kT}{h} e^{-\Delta U/kT}, \quad (55)$$

where n has all values from 1 to 6 except the one which makes the second index equal to the first.

Therefore, introducing these values in Eq. (51), the time rate of change of polarization along the Z axis becomes, for a simple harmonic field,

$$\begin{aligned} \frac{j\omega h P_z}{kT} e^{\Delta U/kT} = & 6\mu \left\{ N_2 \exp \left[\left(\frac{E_z + \beta_1 P_z}{1 - \beta_1 \gamma} \right) \frac{\mu}{kT} \right] \right. \\ & \left. - N_1 \exp \left[- \left(\frac{E_z + \beta_1 P_z}{1 - \beta_1 \gamma} \right) \frac{\mu}{kT} \right] \right\}. \end{aligned} \quad (56)$$

If ω is zero, this reduces to the Boltzmann condition for determining the ratio of N_2/N_1 .

Since we are dealing only with infinitesimal fields, the sum of N_2 and N_1 can be taken equal to their equilibrium values given by Eq. (16). Since Eq. (56) can be written in the form

$$\frac{j\omega h P_z}{kT} e^{\Delta U/kT} = 6\mu \left[(N_1 + N_2) \sinh\left(\frac{E_z + \beta_1 P_z}{1 - \beta_1 \gamma}\right) \frac{\mu}{kT} - (N_1 - N_2) \cosh\left(\frac{E_z + \beta_1 P_z}{1 - \beta_1 \gamma}\right) \frac{\mu}{kT} \right], \quad (57)$$

this becomes

$$\frac{j\omega h P_z e^{\Delta U/kT}}{6kT \cosh[(E_z + \beta_1 P_z)/(1 - \beta_1 \gamma)] \mu/kT} = \left[\frac{N\mu \sinh[(E_z + \beta_1 P_z)/(1 - \beta_1 \gamma)] \mu/kT}{2 + \cosh[(E_z + \beta_1 P_z)/(1 - \beta_1 \gamma)] \mu/kT} - P_z \right]. \quad (58)$$

Introducing the relations of Eqs. (24) and (25) and solving for the time variable parts of the polarization, P_0 , noting that

$$\frac{\partial P_z}{\partial t} = j\omega P_0 e^{j\omega t},$$

we find for the dielectric constant as a function of frequency, the equation

$$\epsilon_c = \epsilon_0 + \frac{\frac{4\pi A (2 \cosh(AP_S/N\mu) + 1)}{\beta_1 (2 + \cosh(AP_S/N\mu))}}{\left(2 + \cosh\frac{AP_S}{N\mu}\right) - A \left(\frac{2 \cosh(AP_S/N\mu) + 1}{2 + \cosh(AP_S/N\mu)}\right) + \left(\frac{2 + \cosh(AP_S/N\mu)}{\cosh(AP_S/N\mu)}\right) \frac{j\omega h}{6kT} e^{\Delta U/kT}}. \quad (59)$$

When the last term in the denominator equals the sum of the other two, the dipole dielectric constant has equal resistance and reactance values and the corresponding frequency is the relaxation frequency. This frequency f_0 is given by

$$f_0 = \frac{6kT e^{-\Delta U/kT}}{2\pi h} \left[\cosh\frac{AP_S}{N\mu} \left(1 - \frac{A(2 \cosh(AP_S/N\mu) + 1)}{(2 + \cosh(AP_S/N\mu))^2}\right) \right]. \quad (60)$$

For $27^\circ\text{C} = 300^\circ\text{K}$, we found $A = 3.090$; $P_S/N\mu = 0.53$. Introducing these values and the values

$$k = 1.38 \times 10^{-16}; \quad T = 300; \quad h = 6.56 \cdot 10^{-27}, \quad (61)$$

we find for f_0 , the value

$$f_0 = 1.6 \times 10^{12} e^{-\Delta U/kT}. \quad (62)$$

From the data of Eqs. (2) and (3), the relaxation frequency of a ceramic (which probably coincides with that for the c axis direction) is 6.2×10^9 cycles. From this one obtains a value for the potential maximum⁷ of

$$e^{\Delta U/kT} = 260; \quad \Delta U = 3.35 \text{ kilocalories per mole.} \quad (63)$$

This value represents the amount of energy to remove the titanium nucleus from its equilibrium position to a position in the center of the barium titanate unit cell.

The data of Fig. 6 show that the dielectric constant along the a axis is relaxed at a frequency of about 15 megacycles at room temperature. Applying the same process to calculating the dielectric constant along the a axis, one finds

$$\epsilon_a = \epsilon_0 + \frac{\frac{4\pi A \left[1 + (\beta_2/4\pi)(\epsilon_0 - 1)\right]}{\beta_1 \left[1 + (\beta_1/4\pi)(\epsilon_0 - 1)\right]}}{2 + \cosh\frac{AP_S}{N\mu} - \frac{A\beta_2 \left[1 + (\beta_2/4\pi)(\epsilon_0 - 1)\right]}{\beta_1 \left[1 + (\beta_1/4\pi)(\epsilon_0 - 1)\right]} + \left(\frac{2 + \cosh(AP_S/N\mu)}{\cosh(AP_S/N\mu)}\right) \frac{j\omega h}{6kT} e^{\Delta U/kT}}. \quad (64)$$

To obtain a dielectric constant of 150,000 at 27°C = 300°K, the real part of the denominator has to be 0.0028. Hence, the indicated relaxation frequency for this temperature is

$$f_0 = \frac{6kT}{2\pi h} e^{-\Delta U/kT} \frac{\left[2 + \cosh \frac{AP_s}{N\mu} - \frac{A\beta_2}{\beta_1} \left(\frac{1 + (\beta_2/4\pi)(\epsilon_0 - 1)}{1 + (\beta_1/4\pi)(\epsilon_0 - 1)} \right) \right] \cosh \frac{AP_s}{N\mu}}{[2 + \cosh(AP_s/N\mu)]}$$

Introducing the numerical values,

$$e^{\Delta U/kT} = 645 \text{ or } \Delta U = 3.9 \text{ kilocalories.}$$

Thus the indicated activation energy for going from the 1, 2 wells to the 3, 4, 5 or 6 wells is only slightly higher than that between opposite wells such as 1 and 2. This calculation also checks the facts that it is the near vanishing of the denominator of Eq. (64) that causes the very high dielectric constant along the *a* or *X = Y* axes.

V. COERCIVE FIELDS ALONG *a* AND *c* AXES

The coercive fields along the *a* and *c* crystallographic axes and the interaction between a field along *c* and a polarization generated along *a* can be calculated from Eqs. (36) and (40), giving the polarizations along the *c* = *Z* direction and the *a* = *Y* direction. In terms of complete fields and polarizations along the two directions these equations become

$$P_z = \frac{N\mu \sinh[(E_z + \beta_1 P_z)/(1 - \beta_1 \gamma)]\mu/kT}{1 + \cosh[(E_z + \beta_1 P_z)/(1 - \beta_1 \gamma)]\mu/kT + \cosh[(E_y + \beta_2 P_y)/(1 - \beta_2 \gamma)]\mu/kT}, \tag{66}$$

$$P_y = \frac{N\mu \sinh[(E_y + \beta_2 P_y)/(1 - \beta_2 \gamma)]\mu/kT}{1 + \cosh[(E_z + \beta_1 P_z)/(1 - \beta_1 \gamma)]\mu/kT + \cosh[(E_y + \beta_2 P_y)/(1 - \beta_2 \gamma)]\mu/kT}. \tag{67}$$

From these two equations and the constants evaluated previously, the coercive fields for the two directions can be approximately calculated.

The calculations show that it takes considerably more of a negative field along *Z* to reverse the sign of a domain along *Z* than it does to change

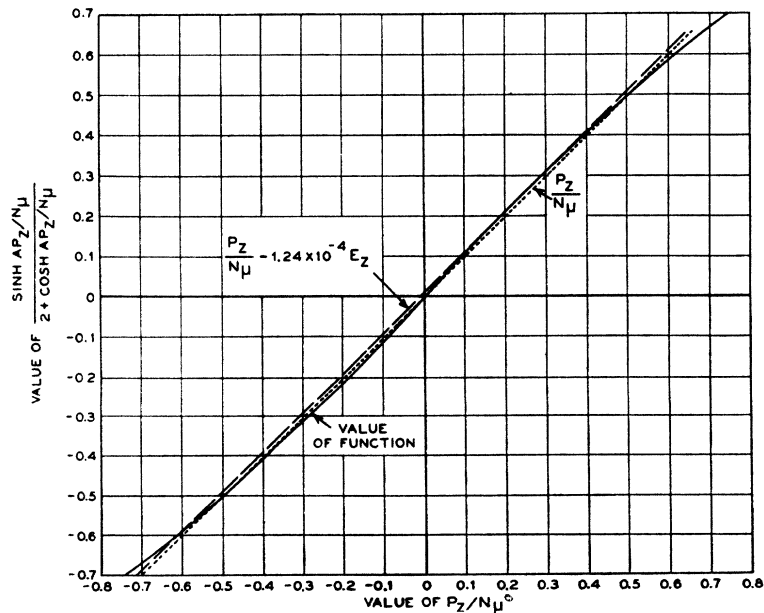


FIG. 12. Method for obtaining spontaneous polarization and coercive field.

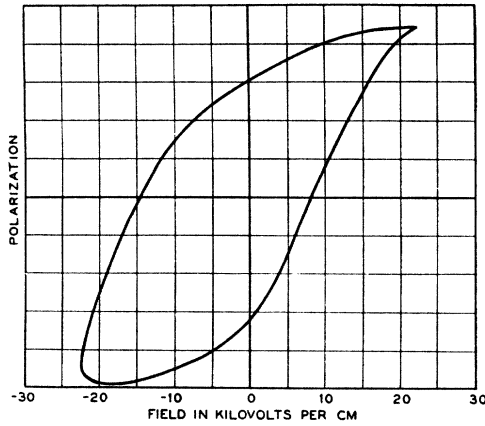


FIG. 13. Hysteresis loop showing relation between polarization along Z and field along Z for a single domain barium titanate crystal.

the direction from Z to Y . To show this, let us assume that no field or polarization exist along Y . Then Eq. (66) can be written in the form

$$\frac{P_z}{N\mu} = \frac{\sinh[(AE_z/\beta N\mu) + (AP_z/N\mu)]}{2 + \cosh[(AE_z/\beta N\mu) + (AP_z/N\mu)]}. \quad (68)$$

Now, since $AE_z/\beta N\mu$ is going to be a very small quantity for any field that can be applied, this can be written as

$$\frac{\sinh(AP_z/N\mu)}{2 + \cosh(AP_z/N\mu)} = \frac{P_z}{N\mu} - \frac{AE_z}{\beta N\mu} \left[\frac{2 \cosh(AP_z/N\mu) + 1}{(2 + \cosh(AP_z/N\mu))^2} \right]. \quad (69)$$

If the applied field E_z is zero, this equation reduces to that for the spontaneous polarization.

If we plot the left hand side of Eq. (69) as a function of $P_z/N\mu$ (assuming $A = 3.090$ for room temperature) the curve of Fig. 12 results. The left hand side is larger than the right, up to a value of $P_z/N\mu = 0.534$ when the two are equal, and this represents the theoretical value of spontaneous polarization for no applied field. If the applied field is positive, a larger ratio of $P_z/N\mu$ is required to satisfy Eq. (69). Since at room temperature, $A = 3.090$; $N\mu = 67,100$ e.s.u.; $\beta = 0.096$; $\cosh(AP_z/N\mu) = 2.68$, the coefficient multiplying E_z is 1.24×10^{-4} . It takes, then, a very high field to increase sensibly $P_z/N\mu$. For example, a field of 30,000 volts per cm = 100 e.s.u.,

will cause the polarization to increase from 35,600 stat coulombs/cm² to 41,500 stat coulombs, an increase of 16 percent. This agrees quite well with the increase measured by Hulm⁹ who found an increase of about 13 percent for this case.

If we put on a negative voltage along the axis the ratio $P_z/N\mu$ will decrease steadily until the difference between the left hand side of Eq. (69) and $P_z/N\mu$ reaches a maximum. This occurs for $P_z/N\mu = 0.405$, and it requires a negative field of

$$E_z = 74 \text{ e.s.u./cm} = 22,200 \text{ volts/cm}. \quad (70)$$

This is the theoretical field strength to switch the direction of a domain along one direction of Z to that along the other. Single domain crystals have been observed to switch at around this value of field strength.

A true single domain crystal, however, will have a hysteresis loop for a considerably smaller field strength than this. For such a crystal a typical field strength polarization curve is as shown by Fig. 13. When the voltage is in the direction of the spontaneous polarization, the curve has a tail toward the right hand side that is considerably different from the rounded relation on the left hand side. This dissymmetrical type of curve occurs down to field strengths of the order of 1000 volts per centimeter and appears to result from the fact that on the application of a negative field along Z , parts of the domain can be spontaneously polarized along Y . To see that this is possible one can examine the conditions for spontaneous polarization along Y given by Eq. (67). Here we set E_y equal to zero and solve for the conditions that will give a finite value of P_y in the presence of a field E_z , and a spontaneous polarization P_z . The onset of P_y will be determined when P_y approaches zero, and thus we can replace the hyperbolic sinh by the argument, and the hyperbolic cosh by unity. Then the equations to solve are

$$\frac{P_y}{N\mu} = \frac{(\beta_2)/(1 - \beta_2\gamma)(\mu/kT)P_y}{2 + \cosh[(E_z + \beta_1 P_z)/(1 - \beta_1\gamma)]\mu/kT}. \quad (71)$$

If $E_z = 0$, this reduces to the case

$$P_y \left(2 + \cosh \frac{AP_z}{N\mu} \right) = \frac{A\beta_2}{\beta_1} \left\{ \frac{1 + [\beta_2(\epsilon_0 - 1)/4\pi]}{1 + [\beta_1(\epsilon_0 - 1)/4\pi]} \right\} P_y.$$

The difference between the left hand side and the right hand side is the denominator of Eq. (44) for the dielectric constant along the Y axis. This denominator is small (about 0.0028 for room temperature) but is always positive, hence no spontaneous polarization can exist along Y as long as there is no static field $-E_z$.

For the addition of a static field, Eq. (71) takes the form

$$P_y \left[2 + \cosh \left(\frac{AE_z}{\beta_1 N \mu} + \frac{AP_z}{N \mu} \right) \right] = \frac{A \beta_2}{\beta_1} \left\{ \frac{1 + [\beta_2(\epsilon_0 - 1)/4\pi]}{1 + [\beta_1(\epsilon_0 - 1)/4\pi]} \right\} P_y. \quad (72)$$

A positive field E_z in the same direction as P_z makes the left hand side still larger than the right, and no possibility exists for polarization along Y . If, however, a negative field E_z is applied, the left hand side can be made equal or less than the right hand side, and spontaneous polarization can exist along Y . Since $AE_z/\beta_1 N \mu$ is a small quantity, this equation can be written in the form

$$\frac{AE_z}{\beta_1 N \mu} = \frac{\left[2 + \cosh \frac{AP_z}{N \mu} - \frac{A \beta_2}{\beta_1} \left\{ \frac{1 + (\beta_2/4\pi)(\epsilon_0 - 1)}{1 + (\beta_1/4\pi)(\epsilon_0 - 1)} \right\} \right]}{\sinh(AP_z/N \mu)}. \quad (73)$$

Since for room temperature the numerator is equal to 0.0028, the denominator to 2.53, the field E_z to cause a domain to switch to the Y direction is

$$E_z = \frac{0.0028}{2.53} \times \frac{0.108 \times 67,100}{3.090} = 2.6 \text{ e.s.u./cm} = 780 \text{ volts/cm}, \quad (74)$$

which is considerably less than the voltage required to shift a domain along Z .

The question arises as to why the whole domain does not go over in the Y direction. This appears to be owing to the fact that when parts of the large domains change direction, they exert an E_y field on the remainder of the domain that is still directed along Z . Then the term $\cosh[(E_y + \beta_2 P_y)/(1 - \beta_2 \gamma)] \times (\mu/kT)$ can no longer be replaced by unity, and the equation for the field to produce a spontaneous polarization along Y becomes

$$\frac{AE_z}{\beta_1 N \mu} = \frac{\left[1 + \cosh \frac{AP_z}{N \mu} + \cosh \left(\frac{E_y + \beta_2 P_y}{1 - \beta_2 \gamma} \right) \frac{\mu}{kT} - A \frac{\beta_2}{\beta_1} \left\{ \frac{1 + (\beta_2/4\pi)(\epsilon_0 - 1)}{1 + (\beta_1/4\pi)(\epsilon_0 - 1)} \right\} \right]}{\sinh(AP_z/N \mu)} \quad (75)$$

and the field E_z becomes larger. There is no definite saturation for the effect which accounts for the rounded shape of the left side of the hysteresis loop of Fig. 13. When a positive E_z voltage is applied, all the Y domains revert back to the Z direction, which accounts for the tail-like shape of the right hand side of the curve of Fig. 13.

When a field is applied along Y , the relation between P_y and E_y is very linear and shows no hysteresis effects up to a field strength of 300 volts per centimeter, at which field the crystal usually breaks down because of the high conduc-

tivity along the a axis. Up to that voltage, no domain shift in the Y direction has occurred. To obtain the field for the shift requires that both Eqs. (66) and (67) shall be solved simultaneously for the P_y and P_z polarizations and this is not attempted here.

VI. SPECIFIC HEAT ANOMALY OF BARIUM TITANATE

The specific heat anomaly of barium titanate ceramics for the 120°C transition has been measured by Harwood, Popper and Rushman,¹⁰ and

¹⁰ Nature **160**, 58 (1948).

Blattner and Merz.¹¹ The former obtain a value of 0.14 cal./gram whereas the latter obtain 0.2 cal./gram. It has been shown by Mueller¹² that the specific heat anomaly is related to the spontaneous polarization by the equation

$$Q = \beta / 2P_s^2 \quad (76)$$

where Q is the specific heat anomaly in ergs/cc, β is the Lorentz factor and P_s the spontaneous

polarization. Since the specific heat anomaly was the integrated increase from about 100°C to a temperature above the Curie temperature we have from Fig. 10, that $P_s = 27,000$ c.g.s. units of charge per square cm. Q , the specific heat anomaly, is 0.2 cal./gram = 1.2 cal./cc = 5×10^7 ergs/cc. This gives a value of β determined by the specific heat anomaly of

$$\beta = 0.138 \quad (77)$$

which agrees reasonably well with the value given in Eq. (32), obtained from dielectric measurements.

¹¹ Helv. Phys. Acta, Vol. XXI, *Fasciculus Tertius et Quartus* (1948).

¹² Annals New York Academy of Sciences, Vol. XL (Art. 5), page 353.