

## SENSITIVITY

An attempt was made to measure direct photoconductivity of an argon photocell, of the type shown in Fig. 1, in terms of current change per incident number of photons. These measurements indicated a quantum efficiency of approximately 10, which indicates that considerable multiplication must occur in the process. Since this type of measurement is probably not reliable, a better theoretical estimate of the efficiency can be obtained by considering the absorption cross-section for a photon by a metastable in the cell, the density of metastables, and the branching ratio for decay back to the metastable state vs decay to other states. All of these considerations suggest that a quantum efficiency of 0.7 to 0.8 should be obtainable in the helium photocell for a cell whose depth in the direction of the light beam is of the order of 10 cm. The noise level of such a device is difficult to assess theoretically. Experimentally it has been determined that the helium detector of the form shown in Fig. 1 has about the same

signal-to-noise ratio as a Kodak Ektron detector 2 cm<sup>2</sup> in area filtered to observe only the 2- $\mu$  radiation.

Experiments with light attenuators placed in the chopped-light beam in an argon experiment indicate that the response of the photocell is linear over three orders of magnitude variation in light intensity.

No attempt has been made to assess in detail the frequency response of this instrument, although its response to details of the chopping mechanism of mechanically chopped light suggests that response extends from dc up to several kilocycles at least. It appears possible that there is a gain-bandwidth relationship such that the response for extremely weak discharges and high sensitivity is rather poor at high frequencies and may depend on a slow buildup and recovery of metastable populations.

## ACKNOWLEDGMENTS

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## Variation of Permittivity with Electric Field in Perovskite-Like Ferroelectrics.\*

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A model is considered for the case of polycrystalline ferroelectrics in which each crystallite is presumed to behave according to a free-energy function of the type formulated by A. F. Devonshire [Advances in Phys. 3, 85 (1954)] for BaTiO<sub>3</sub>. The Curie temperatures for the individual grains are taken in a Gaussian distribution about some chosen temperature. The permittivity is obtained by averaging with this distribution over all of the crystallites. In accordance with the free-energy function, it is assumed that the electric field induces a ferroelectric axis in those crystallites of the distribution which are not ferroelectric at a given temperature. On the basis of experimental evidence, 90° reorientation of domains in the ferroelectric part of the distribution is presumed to be negligible for semistatic and dynamic fields. Despite the seemingly severe restriction imposed by the latter assumption, a large field sensitivity is predicted. Agreement between the theory and experimental data is excellent for both parallel and transverse fields. It is concluded that the variation of incremental permittivity is associated with an induced ferroelectric state rather than being directly a property of domain processes, and that a large variation with field must necessarily be accompanied by strong thermal sensitivity.

## I. INTRODUCTION

CERTAIN ferroelectric compositions exhibit a change of incremental (small-signal) permittivity when placed in a strong electric field. In this paper the effect will be called "dielectric nonlinearity." It is our objective here to investigate the mechanism for this property in a special class of ferroelectrics under the influence of semistatic and dynamic electric fields. Here we specialize to the case of the perovskite-like polycrystalline substances such as BaTiO<sub>3</sub> and to mixed compositions of the type Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> and

Pb<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>, etc., but it will be evident that the analysis can be extended to other systems whose thermodynamic properties are similar to those of the perovskites.

First, the experimental situation with regard to the nonlinearity of these ferroelectrics will be discussed. It will be shown that if the variation in permittivity with electric field is held to be in some way associated with domain alignment or rotation processes (as is the case for magnetic substances) one is led to contradictions with the experimental data. Then we consider a ferroelectric composed of an ensemble of crystallites in which the domains may be considered immobile for

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the purpose of analysis. Such a material can exhibit large dielectric nonlinearities if one allows for a field-induced phase transition<sup>1,2</sup> near the Curie temperature (the temperature of transition between ferroelectric and nonferroelectric phases) of the crystallites. The model of such a polycrystalline dielectric using a Gaussian distribution for the Curie temperatures of the individual crystallites leads to theoretical results for the nonlinearity which are in excellent agreement with the experimental data.

## II. EXPERIMENTAL SITUATION

Figures 1 and 2 show typical data for the permittivity of polycrystalline samples of  $\text{BaTiO}_3$  and  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ , respectively, as a function of both a 0.5-cps electric field and temperature. Despite the fact that in the room-temperature region the pure  $\text{BaTiO}_3$  is ferroelectric, and in this state many domains are known to exist, the sample does not show a large change in incremental permittivity with electric field. On the other hand, the  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  composition, which has a rather broad Curie region or a broad region of peak permittivity, shows very strong nonlinearity. One may presume with Isupov<sup>3</sup> that the broadening may be due to a distribution of Curie temperatures among the grains which compose the polycrystalline sample. Such a distribution can occur as a result of chemical inhomogeneities or strains or both. It is noted that the nonlinearity is greatest in the region of peak permittivity, not in a lower-temperature region where one would expect a greater number of grains to be ferroelectric and hence contain domains. These results

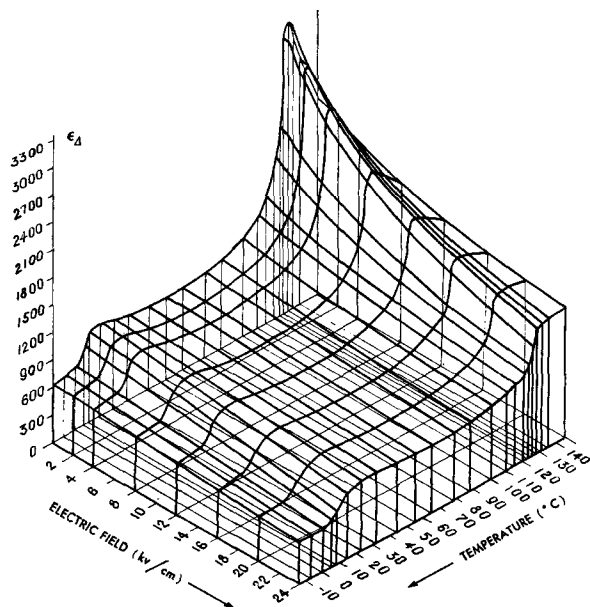


Fig. 1.  $\epsilon_dTE$  surface for a pure  $\text{BaTiO}_3$  ceramic.

<sup>1</sup> A. F. Devonshire, *Advances in Phys.* **3**, 85 (1954).

<sup>2</sup> W. J. Merz, *Phys. Rev.* **91**, 513 (1953).

<sup>3</sup> V. A. Isupov, *Soviet Phys.—Tech. Phys.* **1**, 1846 (1956).

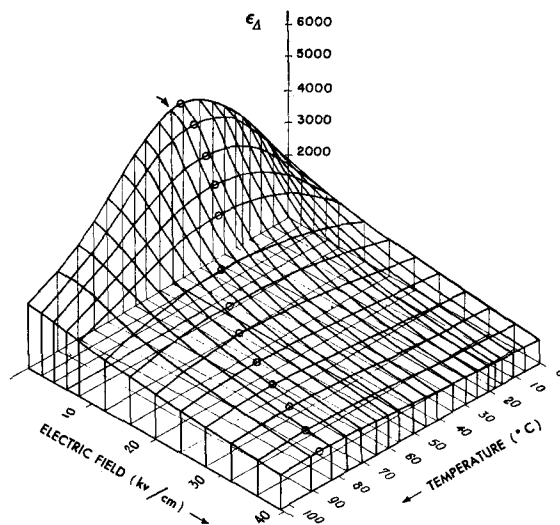


Fig. 2.  $\epsilon_dTE$  surface for a typical  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  ceramic.

are also typical for other perovskite-like polycrystals such as, for example,  $\text{PbTiO}_3$  and  $\text{Pb-Sr-TiO}_3$ . The failure of the more strongly ferroelectric samples to show large changes in incremental permittivity appears to contradict the well-known behavior of these materials in regard to their hysteresis properties.<sup>2,4</sup> The pure  $\text{BaTiO}_3$  samples show wide rectangular hysteresis loops near room temperatures. Mixed compositions such as the  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  example cited are characterized by rather thin loops which become wider as the temperature is lowered (cf. Fig. 3; as more grains become ferroelectric, a greater number of domains are being switched). However, it becomes clear why such domain switching does not produce changes in the *incremental permittivity* when one considers the experimental results of Burke and DeVries.<sup>5</sup> These investigators have given evidence that polarization reversal in  $\text{BaTiO}_3$  ceramic grains takes place mainly by  $180^\circ$  switching. Since a ferroelectric domain is symmetric about its axis of spontaneous polarization, a reversal of the polarization direction by  $180^\circ$  would not be expected to produce a change in the incremental permittivity, but nonetheless would give rise to hysteresis.

More recent experiments by Berlincourt and Krueger<sup>6</sup> have indicated that some  $90^\circ$  domain alignment does take place in  $\text{BaTiO}_3$  and  $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$  ceramics (10% and 50% of the possible  $90^\circ$  alignment, respectively). It is important to note that these investigators did not observe  $90^\circ$  domain reorientation directly, but interpreted observed transverse strains as being due to domain reorientation. The possibility of an induced ferroelectric state contributing to these strains was not treated. Furthermore, the permanent part of the trans-

<sup>4</sup> W. J. Merz, *Phys. Rev.* **95**, 690 (1954).

<sup>5</sup> J. E. Burke and R. C. DeVries, *J. Am. Ceram. Soc.* **40**, 200 (1957).

<sup>6</sup> D. Berlincourt and H. H. A. Krueger, *J. Appl. Phys.* **30**, 1804 (1959).

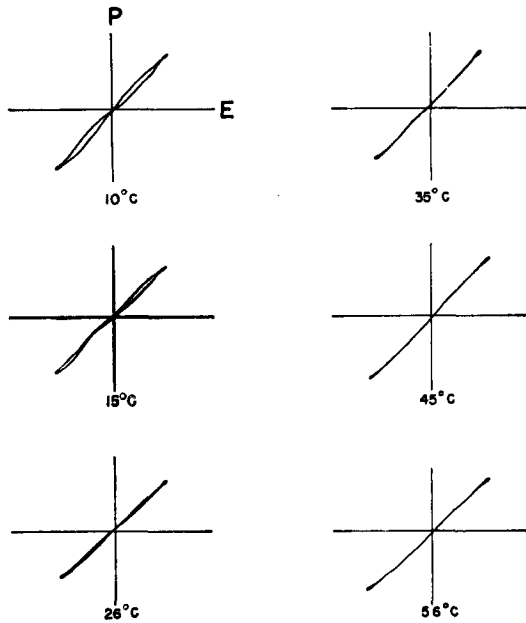


FIG. 3. Hysteresis loops for a  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  ceramic at various temperatures.

verse strain (i.e., the strain that remains after the field is removed and the sample short circuited) appears to require rather long periods of time to develop—from a matter of several minutes up to several hours, for some compositions. On the other hand, it is known that strong dielectric nonlinearity exists in certain ferroelectrics at rapid cycling rates. For example, the data of Fig. 2 were obtained with 0.5-cps sweeping field and a 10 000-cps incremental measuring field. The author has obtained similar results with only slightly diminished nonlinearity when the sweeping field is 60 cps.

It may be argued that the reason that the ferroelectrics show large changes in the incremental permittivity with electric field only in the vicinity of the peak in permittivity is that there may be a thermal activation energy associated with domain alignment. That is, one may say that the domains cannot align with the electric field unless sufficient thermal energy is supplied. This point of view, however, does not hold up when the results of a crossed-field experiment are considered. In this experiment two pairs of electrodes, at right angles to each other, were placed on cubical samples of  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  ceramic. The permittivities were measured with strong electric fields both parallel and normal to the measuring fields. It is seen in Fig. 4 that the permittivity decreases for *both* parallel and transverse fields. Now a ferroelectric domain in  $\text{BaTiO}_3$  is extremely anisotropic with regard to the permittivity.<sup>7</sup> Along the polar direction  $\epsilon_e \cong 200$  at room temperatures, whereas for directions normal to this axis  $\epsilon_a \cong 2000$ . For a polycrystalline sample of  $\text{BaTiO}_3$  one would expect to measure an average value of permittivity  $\epsilon_{av}$  because

of the random orientation of domains. That is,  $\epsilon_{av}$  could be expected to lie within the limits

$$\epsilon_c < \epsilon_{av} < \epsilon_a. \quad (1)$$

If an electric field were applied parallel to the small measuring fields one would expect on the basis of a domain-alignment concept that  $\epsilon_{av}$  approaches  $\epsilon_c$  as larger and larger electric fields are applied. This represents a decrease in permittivity. On the other hand, if the permittivity is viewed transverse to strong electric fields, one expects that if domains are being aligned by the strong field,  $\epsilon_{av}$  approaches  $\epsilon_a$ , an *increase* in permittivity. The experimental results already cited in which the permittivity decreases for both parallel and transverse fields is taken as further evidence, but not the only evidence, that domain alignment along the direction of the strong electric field does not make a major contribution to the change in permittivity of the polycrystalline samples.

To recapitulate, the results of Burke and DeVries<sup>5</sup> and the experiments discussed in connection with Figs. 1, 2, and 4 all indicate very strongly that such domain processes as  $90^\circ$  reorientation or alignment do not satisfactorily account for the nonlinear behavior in polycrystalline ferroelectrics of the  $\text{BaTiO}_3$  type. Moreover, the observed  $180^\circ$  switching in these ferroelectrics, while explaining the hysteresis properties, does not account for the nonlinearity in incremental permittivity. In the next section we consider a model for a ferroelectric which predicts both qualitatively and quantitatively the results of the experiments described above.

### III. MODEL FOR NONLINEAR BEHAVIOR

In order to allow for a tractable analysis which would still retain most of the qualitative features of the ferroelectric behavior, the following assumptions and idealizations are made:

- (a) The polycrystalline ferroelectric is composed of

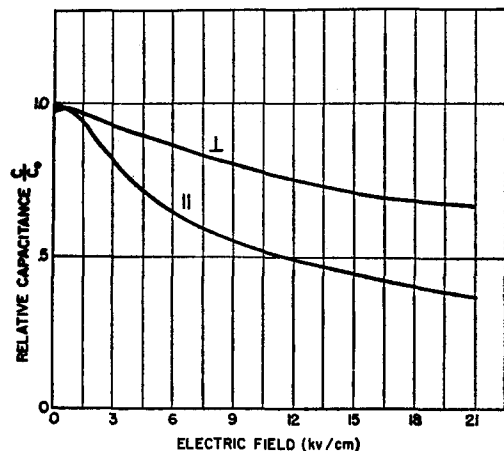


FIG. 4. Relative capacitance for a  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  sample measured transverse (I) and parallel (II) to a biasing field.

<sup>7</sup> See, for example, Helen Megaw, *Ferroelectricity in Crystals* (Methuen and Company, Ltd., London, 1957), Chap. 4.

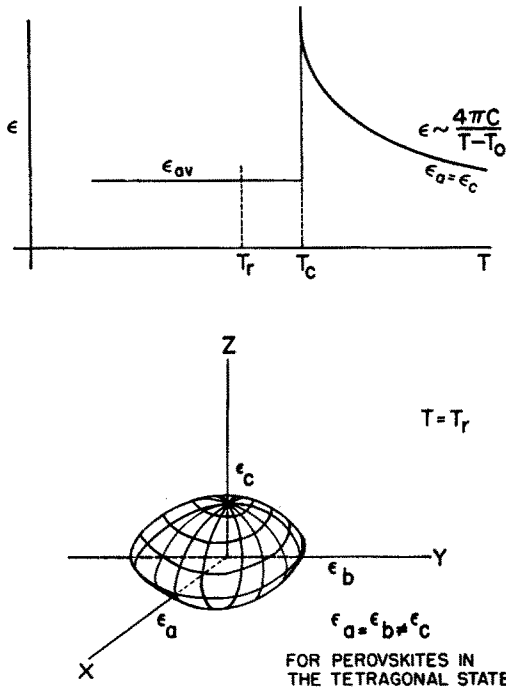


FIG. 5. The average characteristic of a ceramic grain and the permittivity ellipsoid at zero field.

an ensemble of grains containing, in the absence of an external field, many randomly oriented domains.

(b) The Curie temperatures for the grains are taken in a Gaussian distribution about some conveniently chosen temperature  $T_r$ . (Experimentally one may, for example, adjust  $T_r$  by the addition of Sr or Pb to a  $\text{BaTiO}_3$  ferroelectric.)

(c) Only the upper Curie transition (tetragonal to cubic) is to be considered. Above this transition, a Curie-Weiss law is presumed to hold for the permittivity, and below the transition the permittivity is some constant average value for any given grain.

(d) All domains in those grains of the distribution which are ferroelectric are treated as if "frozen in." That is, it is assumed that  $90^\circ$  domain alignment does not exist and that  $180^\circ$  domain switching does not affect the *incremental permittivity* because of symmetry about the polar axis for  $180^\circ$  reversals.

(e) For the grains in the distribution which are nonferroelectric, the effect of the strong external electric field is to induce in these grains a ferroelectric state. This is in accordance with Devonshire's free-energy function<sup>1,8</sup> and with experiments performed on single crystals of  $\text{BaTiO}_3$ , as has been already noted. It is presumed that the field induces a polar axis along the field direction.

The model based on these postulates neglects several other possible effects. For example, mechanical stresses are neglected. On the other hand, the stresses would

contribute to the existence of a Gaussian distribution of Curie temperatures in the first place, so that in this way, stresses may be partially taken into account. Also, to the approximation of this model, the possibility of depolarizing fields at grain boundaries and field inhomogeneities within the grains is not treated. Another point to be mentioned is that, strictly speaking, a tensor relationship would exist between the electric field direction and the induced polar axis. The simplification implied by (e) does not qualitatively affect the results, however. Indeed, as will be shown, reasonable quantitative agreement between experiment and the predictions of the model is attained as well.

The following is broken up into three parts; first, the average permittivity  $\epsilon_{av}$  for a grain in the ferroelectric state is computed. Then a Gaussian distribution for Curie temperatures is considered for the zero field situation, and finally we examine the effect of an electric field on this distribution and hence on the incremental permittivity.

In accordance with assumption (a), let us imagine a collection of grains containing, in the absence of electric fields, many randomly oriented domains. The dielectric characteristic for any one grain is presumed to behave ideally according to Fig. 5, where below the Curie temperature  $T_c$  the permittivity has some constant average value  $\epsilon_{av}$ , and above  $T_c$  a Curie-Weiss law is presumed to hold. Only the cubic-to-tetragonal phase transition is to be considered. If each ferroelectric grain contains a large number of randomly oriented domains, the permittivity  $\epsilon_{av}$  may be computed by averaging over the ellipsoid associated with the permittivity tensor for a single domain or crystallite (cf. Fig. 5). That is, we say that

$$\epsilon_{av} = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \epsilon(\phi, \theta) d\phi d\theta / \int_{\phi=0}^{2\pi} d\phi \int_{\theta=0}^{\pi} d\theta. \quad (2)$$

The ellipsoid becomes a sphere in the Curie-Weiss region; i.e., the grain in the region  $T \geq T_c$  is cubic and  $\epsilon_a = \epsilon_c$ . For  $T < T_c$ ,  $\epsilon_{av}$  is computed from Eq. (2) with

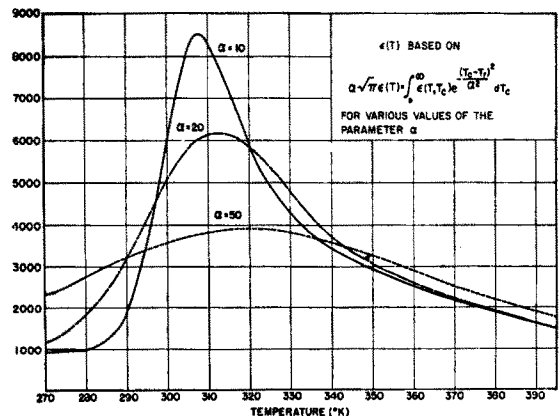
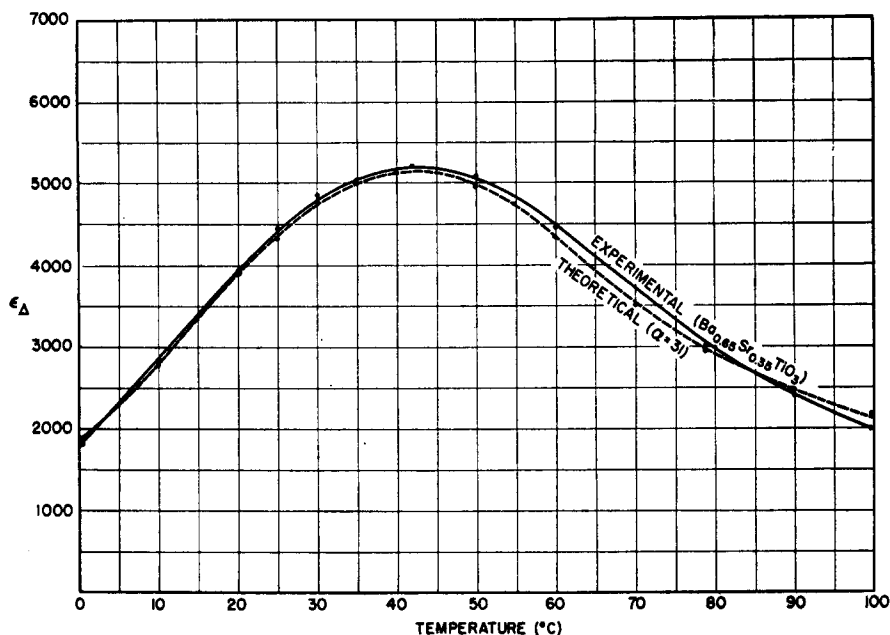


FIG. 6. Theoretical values of permittivity vs temperature.

<sup>8</sup> E. J. Huibregste and D. R. Young, Phys. Rev. 103, 1705 (1956).

FIG. 7. Comparison of experimental and theoretical permittivities.



the measured values of  $\epsilon_a$  and  $\epsilon_c$  for a single crystal at temperatures slightly less than  $T_c$ . The equation of the ellipsoid in polar form is

$$\frac{\epsilon^2 \sin^2\theta \cos^2\phi}{\epsilon_a^2} + \frac{\epsilon^2 \sin^2\theta \sin^2\phi}{\epsilon_b^2} + \frac{\epsilon^2 \cos^2\theta}{\epsilon_c^2} = 1. \quad (3)$$

Hence

$$\epsilon(\theta, \phi) = \left( \frac{\cos^2\theta}{\epsilon_c^2} + \frac{\sin^2\theta}{\epsilon_a^2} \right)^{-\frac{1}{2}} = \frac{\epsilon_c}{(1 - k^2 \sin^2\theta)^{\frac{1}{2}}}, \quad (4)$$

for  $\epsilon_a = \epsilon_b \neq \epsilon_c$  (tetragonal), and where  $k^2 = 1 - \epsilon_c^2/\epsilon_a^2$ . By substituting Eq. (4) into Eq. (2) we obtain

$$\epsilon_{av} = \frac{\epsilon_c}{2\pi^2} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \frac{d\theta d\phi}{(1 - k^2 \sin^2\theta)^{\frac{1}{2}}} = \frac{2\epsilon_c}{\pi} \int_0^{\frac{1}{2}\pi} \frac{d\theta}{(1 - k^2 \sin^2\theta)^{\frac{1}{2}}}, \quad (5)$$

an elliptic integral which may be evaluated from the tables. As an example, published data<sup>9</sup> for a single crystal of  $\text{BaTiO}_3$  in the tetragonal form just below  $T_c$  are

$$\epsilon_a \cong 4000, \quad \epsilon_c \cong 400,$$

or

$$k^2 = 1 - (\epsilon_c/\epsilon_a)^2 = 0.990.$$

Applying this to Eq. (5) and evaluating the integral one obtains

$$\epsilon_{av} = 940,$$

in excellent agreement with the experimental results for polycrystalline tetragonal  $\text{BaTiO}_3$  (cf. Fig. 1 for  $T < 120^\circ\text{C}$ ).

This value of  $\epsilon_{av}$  is used in obtaining the dependence of the zero-field dielectric constant on temperature.

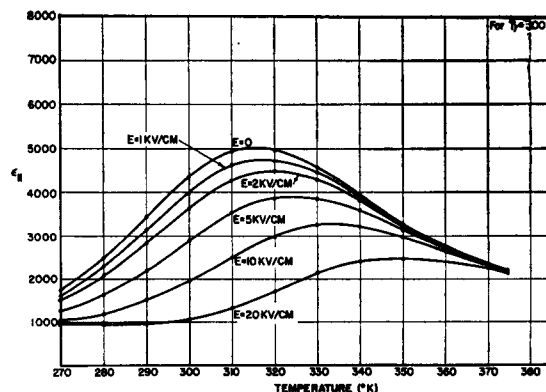
Supposing a Gaussian distribution for the Curie temperatures of the individual crystallites, one obtains the average dielectric constant by use of the expression for the mean in such a distribution:

$$\langle \epsilon(T) \rangle = \int_0^\infty \epsilon(T, T_c) \exp[-(T_c - T_r)^2/\alpha^2] dT_c / \int_0^\infty \exp[-(T_c - T_r)^2/\alpha^2] dT_c, \quad (6)$$

where

$$\epsilon(T, T_c) = \begin{cases} \epsilon_{av} & \text{for } T \leq T_c \\ \frac{4\pi C}{T - T_0} & \text{for } T > T_c \end{cases}. \quad (7)$$

In Eq. (6),  $T_r$  is some chosen temperature about which the distribution is taken. As has been already noted, this can be controlled experimentally, for example, by cation substitutions in the perovskite structure (Sr


 FIG. 8. Theoretical parallel permittivity vs temperature and electric field (for  $\alpha = 31$ ).

<sup>9</sup> W. J. Merz, Phys. Rev. 76, 1221 (1949).

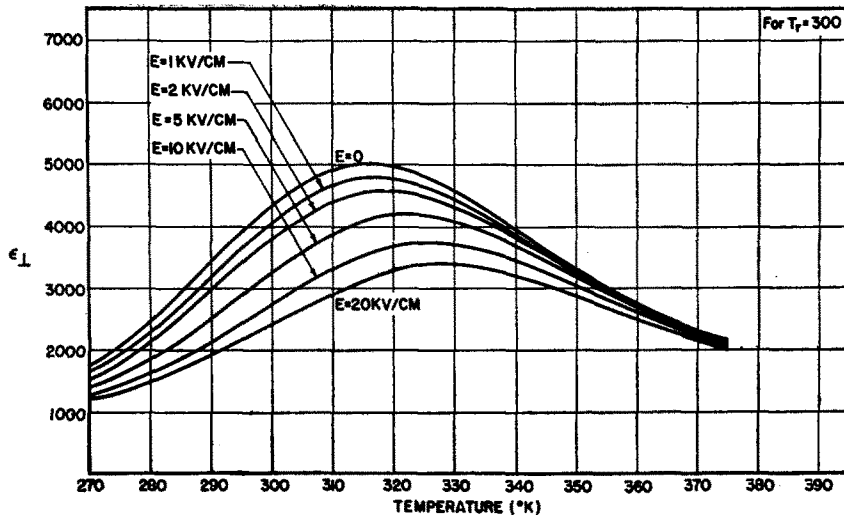


FIG. 9. Theoretical transverse permittivity vs temperature and electric field (for  $\alpha=31$ ).

or Pb substituted for Ba in  $\text{BaTiO}_3$  will lower or raise, respectively, the temperature  $T_r$ ). The  $\alpha$  determines the variance of the distribution and is another factor under experimental control. The permittivity  $\epsilon$  of any given grain is assumed to be  $\epsilon_{av}$  for  $T \leq T_c$  and  $4\pi C/(T-T_0)$  for  $T > T_c$ , where  $C$  is the Curie constant. It is important to note that  $T_0$  is not the same as  $T_c$ , but is related to  $T_c$  through the Devonshire free-energy function. The latter factor,  $T_c$ , is the actual transition temperature. For  $\text{BaTiO}_3$ ,  $T_0$  may be about 10 deg Centigrade lower in temperature than  $T_c$ , depending on the crystal. The fact that  $T_0$  is distinct from  $T_c$  results from the nature of the first-order thermodynamic transition at the Curie temperature for  $\text{BaTiO}_3$ -like crystals.<sup>2,8,10</sup>

The integrals may be evaluated in closed form except for the interval  $T_c < T$ , where  $\epsilon(T, T_c) = 4\pi C/(T-T_0)$  and  $T_0 = T_0(T_c)$ . To obtain some typical qualitative results for a wide range of temperatures and for many

values of the parameter  $\alpha$ , the integral (6) was evaluated numerically by means of an electronic digital computer. Results are shown in Fig. 6 for barium titanate-like mixed compositions for  $\alpha$  equal 10, 20, and 50, and for  $T_r$  equal 300°K with  $T_c = T_0 + 10$  and with the Curie constant  $C = 1.4 \times 10^4$  as measured by Merz.<sup>2</sup> The curves for  $\alpha$  equal 20 and 50 bear a marked resemblance, respectively, to currently available so-called K6000 and K3000 titanate ceramic bodies. A remarkably good fit between experimental data for a  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  composition and a theoretical curve is obtained by choosing  $\alpha$  equal 31. This is shown in Fig. 7.

To show that the mechanism of an induced ferroelectric state in the originally nonferroelectric grains in the Gaussian distribution can account for the observed nonlinear properties, Eq. (6) must be modified to include electric field effects. In accordance with the assumptions (a) through (e) we may write

$$\langle \epsilon(T, E) \rangle = \int_0^\infty \epsilon(T_c^*, T, E) \exp[-(T_c^* - \gamma E - T_r)^2 / \alpha^2] dT_c^* / \int_0^\infty \exp[-(T_c^* - \gamma E - T_r)^2 / \alpha^2] dT_c^*, \quad (8)$$

where  $T_c^*$  is a modified (by the field) Curie temperature for a crystallite and one may show<sup>1,2</sup> that  $T_c^* = T_c + \gamma E$ . Since we are at this time only considering the approximation of uniform electric fields within the different grains, the factor  $\gamma$  is taken as a proportionality constant. A more detailed treatment must take into account the fact that the paraelectric grains just above the Curie point have a higher permittivity than the ferroelectric grains, so that the electric field in each type of grain would be different. As a result,  $\gamma$  would itself be, strictly speaking, a function of the state of polarization of the sample. On the other hand, it is seen from Fig. 2 that the shift in peak permittivity with

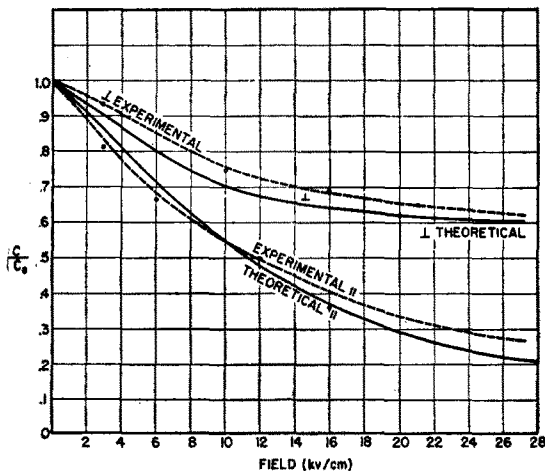


FIG. 10. Theoretical and experimental relative variation of capacitance for a  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  sample.

<sup>10</sup> M. E. Drougard and D. R. Young, Phys. Rev. **95**, 1152 (1954).

electric field for the  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  ceramic is almost the same as that for a  $\text{BaTiO}_3$  single crystal (the shift for both is about  $1.3^\circ\text{K}/\text{kv}/\text{cm}$ ). Hence it is doubtful that much is to be gained, from the point of view of what we are trying to demonstrate here, by using in the analysis the precise dependence of  $\gamma$  on the field  $E$ .

Also,

$$\epsilon(T_c^*, T, E) = \begin{cases} \epsilon_{av} & \text{for } T < T_c \\ \left\{ \begin{array}{l} \epsilon_c \text{ for } \parallel \text{ fields} \\ \epsilon_a \text{ for } \perp \text{ fields} \end{array} \right\} & \text{for } T_c \leq T \leq T_c^* \\ 4\pi C / (T - T_0) & \text{for } T > T_c^* \end{cases} \quad (9)$$

That is, on the basis of assumption (d), we may say that from the point of view of incremental permittivity, the domains are treated as if immobile in a grain for which  $T < T_c$ . For the interval  $T_c \leq T \leq T_c^*$  the electric field induces a ferroelectric state in a grain which in the absence of the field is nonferroelectric. For  $T > T_c^*$  the field is not sufficiently strong to induce a ferroelectric state in the grain, and the Curie-Weiss law is presumed to hold. Here  $T_0 = T_0(T_c^*)$ .

Typical behavior of the permittivity vs electric field and temperature may be demonstrated by a numerical evaluation of the integrals in Eq. (8) with Eq. (9). Results are shown in Figs. 8 and 9 for  $\alpha = 31$ ,  $T_r = 300^\circ\text{K}$ ,  $\gamma = 1.3^\circ\text{K}/\text{kv}/\text{cm}$  (which was determined experimentally with a  $\text{BaTiO}_3$  single crystal), and  $T_0 = T_c - 10 = T_c^* - \gamma E - 10$ . The values for  $\epsilon_c$  and  $\epsilon_a$  used with Eq. (9) were those for a single crystal of  $\text{BaTiO}_3$ . Figure 8 shows the behavior of the incremental permittivity when the biasing fields are parallel to the signal fields. Note the resemblance of these results with those of Fig. 2, both in magnitude of the change in permittivity and in the shift of the peak permittivity to higher temperatures with electric fields. Figure 9 shows the results for biasing fields perpendicular to the signal fields. It is seen here that the transverse field produces a decrease in the permittivity (cf. the experimental data of Fig. 4), but the relative decrease is not so pronounced as for parallel fields. A comparison of theoretical vs experimental relative change in permittivity for both parallel and transverse fields is shown in Fig. 10 for  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  at  $315^\circ\text{K}$ . The theoretical data are obtained from Figs. 8 and 9, which were obtained from the integral (8).

#### IV. CONCLUSIONS

It has been shown in the above that it is possible to account for the nonlinearity in permittivity with electric field without appealing to a domain alignment or rotation concept. This is done by assuming that the ferroelectric consists of a collection of grains or crystal-

lites whose Curie temperatures are given by some distribution law as, for example, a Gaussian distribution. In this way the polycrystalline composition, at the temperature about which the Gaussian distribution is taken, has half of its grains in a paraelectric (nonferroelectric) state. The electric field acts on the nonferroelectric grains in such a way as to induce a ferroelectric state in these grains. The analysis for a polycrystalline ferroelectric leads to results which correlate well with experimental data. It has been shown that a domain rotation effect would lead to an increase in the transverse permittivity with field, whereas both the experiments and the analysis have indicated that a decrease in the transverse permittivity is obtained.

One may also conclude from this model that the electric field nonlinearity in the barium titanate or mixed titanate-type ferroelectrics must be necessarily accompanied by strong thermal sensitivity. This is simply because the free-energy function demands that the thermal and electric field effects go hand in hand. Stated another way, in order for the ferroelectric to display a large electric field sensitivity, a large percentage of the paraelectric grains of the distribution must be susceptible to induction into a ferroelectric state by the field. The percentage of grains which are in this way susceptible will, however, depend on the operating temperature of the material relative to the temperature of the peak in the distribution law [cf. Eqs. (8) and (9) and the attendant discussion].

It is of practical significance to note that the nonlinear mechanism envisaged here allows for the signal fields themselves to effect a change in the permittivity, perhaps even at uhf or microwave frequencies. Indeed, it has recently been brought to the writer's attention<sup>11</sup> that a parametric amplifier using a  $\text{BaSrTiO}_3$  ferroelectric as the nonlinear element has been successfully operated at 1000 Mc with a pump frequency of 2000 Mc.

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<sup>11</sup> T. W. Butler, University of Michigan Department of Electrical Engineering EDG Quart. Progr. Rept. 1 (August, 1959), p. 37.