

The mean error of  $\pm 850 \text{ cm}^{-1}$  on a configuration width of  $22000 \text{ cm}^{-1}$  constitutes an accuracy of four percent.

For a further comparison we show in Table II the differences between theoretical and experimental term values in V I and their parents in V II as taken from Many.<sup>1</sup> It is important to note that, for related terms, the differences in question are mostly of the same order of magnitude and have the same signs.

### III. Cr II

The recent classification of this spectrum by Kiess appears to be still unpublished. Therefore, we had to compile the experimental term values from the classification of the Cr II spectrum as given by Moore.<sup>5</sup>

Since Moore did not assign the terms to specific configurations, the problem of assignments naturally arose. After several calculations best agreement was reached by ascribing all of the 29 terms given by Moore to  $d^5$  and  $d^4s$ ,  $d^3s^2$  being apparently too high.  $d^5$  and  $d^4s$  combined should theoretically contain 40 different terms. Our most powerful means for testing these assignments was the check-up on the Landé splittings, which, according to theory, should vanish for all  $d^5$  terms and all doublets of  $d^4s$  which are based on singlets. In Table III we evaluated  $\zeta_{3d}$  from the experimental splittings of each term assigned to  $d^4s$ .

It should be noted that the values of  $\alpha$  shown against the last six terms in Table III, which are non-linear, are approximate only. As the average, resulting from

<sup>5</sup> C. E. Moore, *A Multiplet Table of Astrophysical Interest* (Princeton University Press, Princeton, New Jersey, 1945).

this calculation, we obtained roughly  $\zeta_{3d} = 220 \text{ cm}^{-1}$ . Most of the poor agreements can be explained. With  $(^3D)^4D$ , it suffices to use instead of an average value of  $18 \text{ cm}^{-1}$  the least one, namely,  $12.5 \text{ cm}^{-1}$ , in order to reach agreement with the above-quoted value of  $\zeta_{3d}$ . The unsatisfactory values in the cases of  $(^3G)^2G$  and  $(^3F^-)^2F$  can be explained qualitatively by spin interactions with neighboring terms.

On the other hand, we can make, starting from  $\zeta_{3d} = 220 \text{ cm}^{-1}$ , rough calculations for the presumably not weak spin interactions in the two cases of  $d^5(^2D_{5/2}^- - ^2F_{5/2})$  and  $d^5(^2G_{9/2}^- - ^2H_{9/2})$ . The results obtained are  $270$  and  $170 \text{ cm}^{-1}$ , respectively, in pretty good agreement with the actual splittings found in these four  $d^5$  terms; according to theory the latter, belonging to a half-filled shell, should show no splittings at all. The agreement is very bad in the case of  $c^4F$ , and it is interesting to note here that, taking the hypothetical case of  $c^4F$  as the lowest term of  $d^3s^2$ , we should receive the much better result,  $\zeta_{3d} = 240 \text{ cm}^{-1}$ .

Finally, the usual calculations have been carried out, first disregarding electrostatic interactions and, thereafter, taking them into account. In both cases  $c^4P$  has been neglected because of its uncertainty. The results are compiled in Table IV. The improvement, when allowing for electrostatic interactions, is but insignificant. The mean error of  $\pm 1076 \text{ cm}^{-1}$  on a configuration width of  $53000 \text{ cm}^{-1}$  constitutes an accuracy of two percent.

I am deeply grateful to Professor G. Racah for suggesting this problem and for his constant assistance throughout my work.

## The Electromechanical Behavior of BaTiO<sub>3</sub> Single-Domain Crystals\*

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The electromechanical response of BaTiO<sub>3</sub> single-domain crystals was investigated as a function of temperature from room temperature to above the Curie point. It was found that when we eliminate domain effects, either by using a perfect single-domain crystal or by aligning the domains by an external electric field, we are dealing with a true linear piezoeffect. The linear piezoeffect was measured by both a static and a dynamic method. The values of the  $d_{31}$  piezoelectric coefficient were compared with those calculated from the dielectric constant and the spontaneous polarization. The behavior of the piezoelectric resonance frequency was observed also through the same temperature range. Although the crystal is cubic above the Curie point and has a center of symmetry, the piezoelectric response persisted under the application of an external d.c. field because the external field will induce a tetragonal crystal structure through the electrostrictive effect, so that the crystal becomes piezoelectric again above the Curie point. Optical and dielectric measurements were found to verify these results.

### I. INTRODUCTION

THE practical importance of BaTiO<sub>3</sub> as transducers makes it essential to know the electromechanical response of this substance. A number of

measurements of the electromechanical coupling have been made on ceramics and also on multidomain crystals by Mason,<sup>1</sup> Jaffe,<sup>2</sup> and RzhanoV.<sup>3</sup> However,

<sup>1</sup> W. P. Mason, *Phys. Rev.* **74**, 1134 (1948).

<sup>2</sup> H. Jaffe, *Ind. Eng. Chem.* **42**, 264 (1950), and a private communication.

<sup>3</sup> A. V. RzhanoV, *J. Exp. Theor. Phys. U.S.S.R.* **19**, 502 (1949).

\* Sponsored by the ONR, the Army Signal Corps, and the USAF.

for a true understanding of BaTiO<sub>3</sub>, the electromechanical behavior of single-domain crystals must be investigated in detail. Such experiments have been carried out from room temperature through the Curie region with static and dynamic methods. Since the interpretation of the electromechanical effects of BaTiO<sub>3</sub> crystals in the ferroelectric region is more complicated than for ordinary piezoelectric crystals, a brief discussion of the electromechanical coupling of ferroelectrics follows.

## II. ELECTROMECHANICAL COUPLING OF FERROELECTRIC CRYSTALS

The relation between strain ( $x_h$ ), stress ( $X_h$ ), electric field ( $E_h$ ), and electric polarization ( $P_h$ ) for nonferroelectric, piezoelectric crystals is given by the following equations:

$$x_h(E, X) = \sum_{i=1}^3 d_{ih}E_i + \sum_{i=1}^3 g_{ih}E_i^2 - \sum_{i=1}^6 s_{ih}X_i + \dots, \quad h=1 \dots 6, \quad (1)$$

$$P_h(E, X) = \sum_{i=1}^3 \chi_{ih}E_i - \sum_{i=1}^6 d_{hi}X_i + \dots, \quad h=1, 2, 3. \quad (2)$$

Here,  $\chi_{ih}$  are the components of the electric susceptibility,  $s_{ih}$  the elastic compliance coefficients, while  $d_{ih}$  and  $g_{ih}$  are known as the first- and second-order piezoelectric coefficients, respectively. The first term on the right-hand side of Eq. (1) represents the linear converse piezoeffect, while the second term represents the second-order effect, which is quadratic and is called the electrostrictive effect. In our experiments we are concerned with the converse effect without external stress, where the external field is applied in the  $z$ -direction (along the polar axis).

For a crystal of tetragonal symmetry such as BaTiO<sub>3</sub> in the ferroelectric region between 5° and the Curie temperature  $\theta$  at 120°C, Eq. (1) reduces to

$$x_x = d_{31}E_{z, \text{ext.}} + g_{31}E_{z, \text{ext.}}^2, \quad (3)$$

$$z_z = d_{33}E_{z, \text{ext.}} + g_{33}E_{z, \text{ext.}}^2, \quad (4)$$

where  $x_x$  and  $z_z$  are the strain components along the  $x$ - and  $z$ -axes, respectively. These equations hold also for BaTiO<sub>3</sub> above the Curie point; however, in this cubic range the  $d_{ih}$  coefficients are zero, since the crystal structure has a center of symmetry. The ferroelectricity of barium titanate complicates the situation, as compared with other piezoelectric crystals, in two ways. In the first place, there is now a spontaneous polarization, the magnitude of which depends on the temperature and the applied external field; and thus the piezoelectric coefficients are dependent on these parameters. Secondly, a domain structure exists in these crystals, which changes with the applied field and thus causes additional changes in the strain components.

The effect of the spontaneous polarization can be taken into account in the following way: calling  $P_0$  the spontaneous polarization which is directed along the  $z$ -axis of the crystal and  $(z_z)_0$  and  $(x_x)_0$  the spontaneous

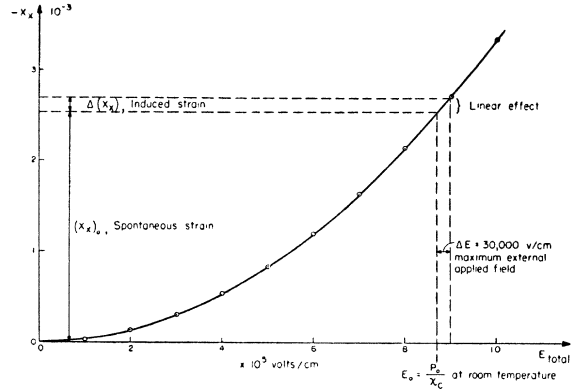


FIG. 1. Total strain as function of total field.

strain components along the  $z$ - and  $x$ -directions, respectively, taken relative to the dimensions of the crystal at the Curie point, it has been demonstrated<sup>4</sup> that the following relations hold:

$$(x_x)_0 = \mu P_0^2, \quad (5)$$

$$(z_z)_0 = \rho P_0^2, \quad (6)$$

where  $\mu$  and  $\rho$  are constants. Here  $(x_x)_0$  corresponds to a contraction and  $(z_z)_0$  to an elongation. Using the values of  $(x_x)_0$  and  $(z_z)_0$  calculated from Megaw's x-ray measurements,<sup>5</sup> and our values<sup>4</sup> of  $P_0$  as a function of temperature, we obtain the following values for  $\mu$  and  $\rho$ :

$$\mu = -10.5 \times 10^6 \text{ cm}^4/\text{coul}^2 = -1.17 \times 10^{-12} \text{ c.g.s.},$$

$$\rho = +24.0 \times 10^6 \text{ cm}^4/\text{coul}^2 = +2.67 \times 10^{-12} \text{ c.g.s.}$$

When an external field is applied along the  $z$ -axis, resulting in an additional "external" polarization  $P_{z, \text{ext.}}$ , we obtain a further change  $\Delta(x_x)$  and  $\Delta(z_z)$  in the respective strain components. Then Eqs. (5) and (6) become

$$x_x = (x_x)_0 + \Delta(x_x) = \mu(P_0 + P_{z, \text{ext.}})^2, \quad (7)$$

$$z_z = (z_z)_0 + \Delta(z_z) = \rho(P_0 + P_{z, \text{ext.}})^2. \quad (8)$$

Expanding the first of these equations, we have

$$x_x = (x_x)_0 + \Delta(x_x) = \mu P_0^2 + (2\mu P_0)P_{z, \text{ext.}} + \mu P_{z, \text{ext.}}^2. \quad (9)$$

Thus

$$\Delta(x_x) = (2\mu P_0)P_{z, \text{ext.}} + \mu P_{z, \text{ext.}}^2. \quad (10)$$

For  $P_{z, \text{ext.}}$  we can write  $\chi_c E_{z, \text{ext.}}$ , where  $\chi_c$  is the susceptibility in the  $z$ -direction. Thus, the additional contraction strain component in the  $x$ -direction becomes

$$\Delta(x_x) = (2\mu\chi_c P_0)E_{z, \text{ext.}} + (\mu\chi_c^2)E_{z, \text{ext.}}^2. \quad (11)$$

Similarly, the additional  $z$ -component of the strain caused by the external field in the  $z$ -direction is

$$\Delta(z_z) = (2\rho\chi_c P_0)E_{z, \text{ext.}} + (\rho\chi_c^2)E_{z, \text{ext.}}^2. \quad (12)$$

<sup>4</sup> W. J. Merz, Phys. Rev. **76**, 1221 (1949).

<sup>5</sup> H. D. Megaw, Proc. Roy. Soc. **A189**, 261 (1947).

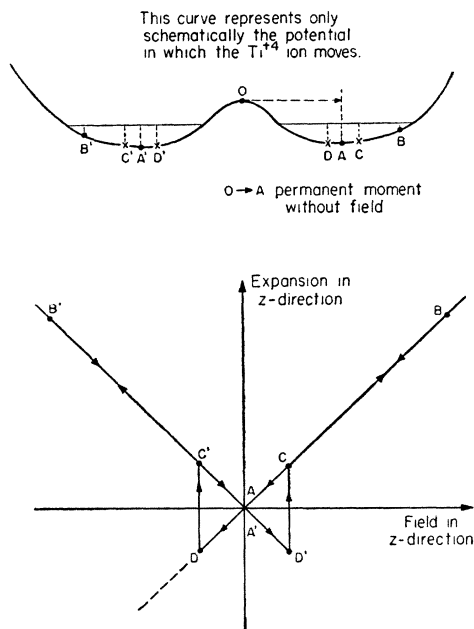


FIG. 2. Piezoelectric response of ideal  $BaTiO_3$  "single-domain" crystal.

Comparison with Eqs. (3) and (4) shows that

$$d_{31} = 2\mu\chi_e P_0, \quad d_{33} = 2\rho\chi_e P_0;$$

while

$$g_{31} = \mu\chi_e^2, \quad g_{33} = \rho\chi_e^2. \quad (13)$$

If we take for  $\chi_e$  the initial electric susceptibility as measured earlier,<sup>4</sup> we can calculate the coefficients from Eqs. (13) at any temperature. At room temperature we have ( $\chi_e = 16$ ;  $P_0 = 15.5 \times 10^{-6}$  coul/cm<sup>2</sup>)

$$\begin{aligned} d_{31} &= -173 \times 10^{-8} \text{ c.g.s.}, & d_{33} &= +396 \times 10^{-8} \text{ c.g.s.}, \\ g_{31} &= -300 \times 10^{-12} \text{ c.g.s.}, & g_{33} &= 683 \times 10^{-12} \text{ c.g.s.} \end{aligned}$$

Since, at the field strength which we have applied (max. 30,000 v/cm), the quadratic effect is much smaller than the linear, it can be neglected.

In the above argument we have tacitly assumed that the spontaneous polarization does not depend on the "external" polarization; that is, when the external field is applied, the spontaneous polarization remains constant as long as the temperature is kept constant. This is not strictly true, of course, since there is no inherent difference between the two types of polarization. The assumption is justified, however, since the internal field is very much larger than the externally applied field. The internal field is of the order of  $P_0/\chi_e$ . Taking the values of the initial susceptibility for  $\chi_e$ , we get for the internal field at room temperature  $8.7 \times 10^5$  v/cm, which is about 30 times the largest applied field. Again, using Megaw's<sup>5</sup> value of the lattice constant *vs.* temperature, we find that a spontaneous polarization at room temperature of the value of  $15.5 \times 10^{-6}$  coul/cm<sup>2</sup> produces, according to Eq. (5), a spontaneous strain component in the *x*-direction of about  $-2.65 \times 10^{-3}$ ,

while the strain component produced by an externally applied field of 20,000 v/cm is about  $-7 \times 10^{-5}$ . It is thus justifiable to speak of a linear piezoeffect at any specified temperature, at least at temperatures not too near the Curie temperature, when an external field is applied (Fig. 1).

The effect of the domains on the electromechanical response is quite complicated. The alignment of the domains by an external field contributes towards the total strain effect. This, as we shall show later, is at least of the same order of magnitude as the true linear piezoeffect. Without an external field not all domains are parallel, and thus their polar axes do not point in the same direction throughout the crystal. When the domains are aligned and these axes turned into the same direction, the dimensions of the crystal will change, since the polar axis is about 1 percent longer than the other axes at room temperature. In order to minimize domain effects, we have worked consistently with single-domain crystals grown by the method first used by Matthias *et al.*<sup>6</sup> It is known that these crystals consist of closely spaced parallel and antiparallel domains<sup>4,7</sup> which can be aligned parallel by an external field.

In this truly aligned state the situation is as follows (Fig. 2): without an external field the  $Ti^{+4}$  ions rest in their equilibrium positions, *A*, somewhat off-center in the  $TiO_6$  octahedra, thus forming permanent electric dipoles. An external field will vary the moments of these

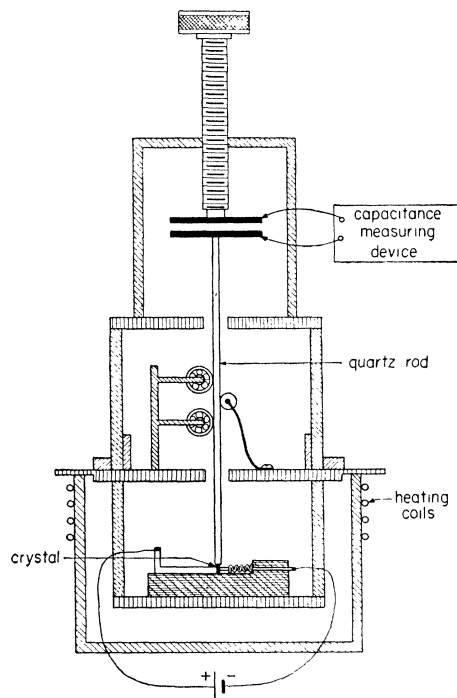


FIG. 3. Apparatus for static measurement of the electromechanical response of  $BaTiO_3$  single-domain crystals.

<sup>6</sup> Danielson, Matthias, and Richardson, *Phys. Rev.* **74**, 986 (1948).

<sup>7</sup> W. J. Merz, *Phys. Rev.* **78**, 52 (1950).

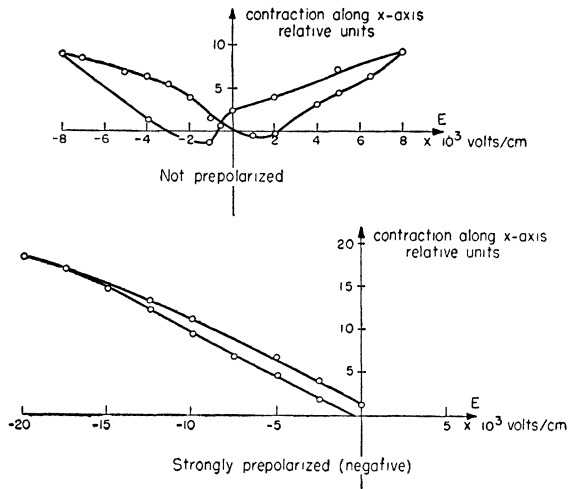


FIG. 4. Piezoelectric contraction of actual BaTiO<sub>3</sub> single-domain crystals.

dipoles by moving the Ti<sup>4+</sup> ions to *B* and thus cause an elongation in the *z*-direction. As explained above, this effect is almost linear when the applied fields are much smaller than the internal field. In a normal piezoelectric material, when the field along the *z*-direction is reduced to zero and then increased in the opposite direction, the crystal will contract along the line *B-C-D* and beyond *D*. Since in our ferroelectric crystal the domain can be turned through an angle of 180°, the permanent dipole moments will at some point *D* reverse their directions and the Ti<sup>4+</sup> ions will jump from *D* to *C'* on the other side of the octahedron center. This will cause a sudden expansion, as indicated in the graph, followed by a continuous expansion *C'* to *B'* as the reverse field is increased. Similarly, when the field is again reversed, another domain switch will take place at *D'* to *C*. If the Ti<sup>4+</sup> ions jump from *A* to *A'*, no change of length would be observed; but, since under the action of the field the jump carries the Ti<sup>4+</sup> ions from *D* to *C'* or from *D'* to *C*, a sudden expansion in the *z*-direction and a sudden contraction in the *x*-direction results. In an actual crystal where parallel and antiparallel domains can exist, not a single abrupt change will take place, but small jumps distributed over a wide field-strength range. To eliminate domain effects, one has therefore to operate at high field strengths or have a truly single-domain crystal when measurements of the true piezoelectric effect are observed.

We may thus summarize the situation: besides the spontaneous strain caused by the spontaneous polarization (expressed in the tetragonality of the crystal),

FIG. 5. Equivalent circuit of a piezoelectric crystal.

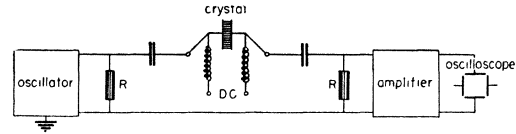
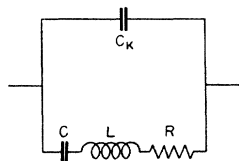


FIG. 6. Apparatus for measuring resonance and antiresonance frequencies.

which is a quadratic effect, we have, under the influence of an external field, a linear piezoeffect and a second-order piezoeffect, which is quadratic. The latter is much smaller than the former and can be neglected. We are allowed to speak of a linear piezoeffect, since the external polarization produced by the applied field is always much smaller than the spontaneous polarization. In addition, we have strains caused by domain changes, which can be very large, even in our so-called single-domain crystals.

### III. STATIC MEASUREMENT OF THE *d*<sub>31</sub> COEFFICIENT

The piezoelectric coefficient *d*<sub>31</sub> of BaTiO<sub>3</sub> was measured statically by the converse piezoeffect. An electric field was applied in the *z*-direction; and the resulting contraction, and thus the strain component in the *x*-direction, was measured. Apart from the strain caused by the linear piezoeffect, there is a contribution to the strain from the domains. Thus, the total strain component in the *x*-direction at zero external stress is given by the equation,

$$\Delta(x_x)_{total} = \Delta(x_x)_{piezo} + \Delta(x_x)_{domain}, \quad (14)$$

$$= d_{31}E_{z, ext.} + \Delta(x_x)_{domain},$$

from which *d*<sub>31</sub> can be evaluated as soon as domain effects can be eliminated. The strain component  $\Delta(x_x)$  was measured as a capacity change produced by the change in spacing of a parallel plate condenser (Fig. 3). The crystals used were single-domain crystal plates *ca.* 3 mm<sup>2</sup> in area and 0.2 mm thick, the polar axis (*z*-direction) of which was perpendicular to the plate. A very light quartz rod with a thin aluminum plate attached to its upper end rested on the crystal. When the crystal contracted, the capacity of the condenser formed by the two aluminum plates changed.

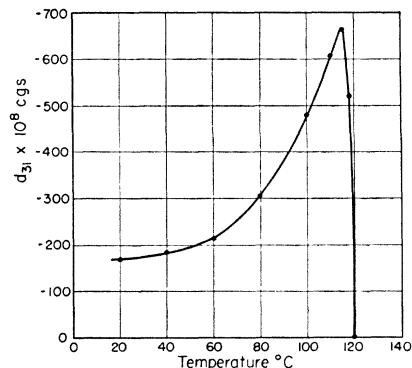


FIG. 7. *d*<sub>31</sub> coefficient as a function of temperature (calculated).

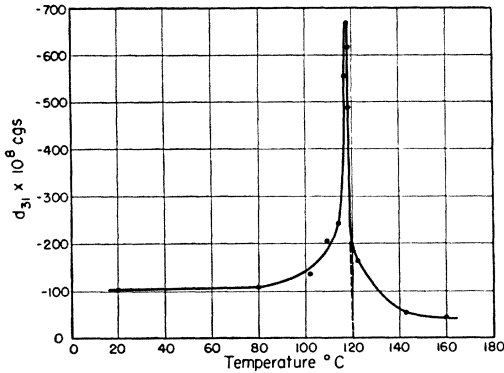


FIG. 8.  $d_{31}$  coefficient as a function of temperature by the static method.

This change was measured on a beat frequency apparatus.<sup>8</sup> This apparatus has an ultimate sensitivity of better than  $0.001 \mu\mu\text{fd}$  and about the same accuracy. By converting this sensitivity to measurable changes of length it is found that over-all displacements up to  $1 \times 10^{-7}$  cm can be accurately measured by using condenser plates 1 in. diam. and a spacing of 0.1 mm.

Figure 4 shows graphs of field strength *vs.* actual contraction for two different crystals. The values given for the contraction are only relative; they are of the order of magnitude of  $10^{-6}$  to  $10^{-5}$  cm. The upper graph is the characteristic of a non-prepolarized crystal taken through a complete cycle at relatively low field strengths. We can here recognize the well-known butterfly hysteresis loop.<sup>1,2</sup> This can be explained on the basis of the arguments pertaining to Fig. 2 in Section II if it is borne in mind that our crystals consist of many parallel and antiparallel domains which can be turned at various field strengths. The lower graph shows the curve of a strongly prepolarized crystal (10,000 v/cm applied for 2 days); the curve is much smoother, and the loop is repeatedly reproducible. Although some hysteresis effects are still present at high field strengths, a reversible behavior is found when the field strength is taken up and down between 17 and 20 kv/cm. At these fields all effects of domains are minimized, and the magnitude of the  $d_{31}$  coefficient can be measured. All good crystals

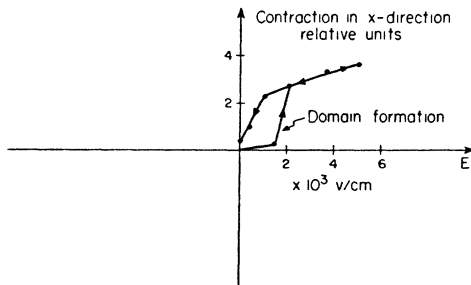


FIG. 9. Hysteresis characteristics of good crystal above the Curie point.

<sup>8</sup> J. G. Jelatis, Tech. Rep. VII, Lab. Ins. Res., M.I.T., September, 1947.

gave almost the same value for the  $d_{31}$  coefficient, indicating that the domains were nearly 100 percent aligned. It is seen from the graph that, even when the domains are aligned, the curve is not a straight line, owing to the finite conductivity of the crystal, which is troublesome since it produces a temperature expansion tending to nullify the electromechanical contraction. A correction for this must be applied; the value of the  $d_{31}$  coefficient can then be determined to an accuracy of within 10 percent. The value obtained from measurements of six crystals is  $-110 \times 10^{-8}$  statcoul/dyne.

This value is somewhat smaller than that derived from the spontaneous polarization and electric susceptibility ( $d_{31} = -173 \times 10^{-8}$ , Section II). This difference arises mainly from the fact that we have taken the initial electric susceptibility in Eq. (13) instead of the susceptibility for the state of complete alignment (saturation). This value could not be obtained directly from the hysteresis loops with satisfactory accuracy. However, it is evident that the values of the initial susceptibility are larger than those of true saturation susceptibility, and hence the measured electromechanical coefficients must be smaller than the calculated ones.

#### IV. DYNAMIC METHOD

It is known that a vibrating piezoelectric crystal can be represented by the equivalent network of Fig. 5. From the resonance frequency, the antiresonance frequency, and the dielectric constant of the crystal, it is possible, by using this equivalent network, to calculate the piezoelectric coefficients.

In order to carry out this experiment, the conventional apparatus was used, which consists of a generator, an amplifier, and a cathode-ray oscilloscope (Fig. 6).

In terms of the elements of the equivalent network, the resonance frequency can be expressed by the formula,

$$\nu_R = 1/2\pi(LC)^{\frac{1}{2}}, \quad (15)$$

and the antiresonance frequency by

$$\nu_A = (C + C_k)^{\frac{1}{2}}/2\pi(LCC_k)^{\frac{1}{2}}. \quad (16)$$

The capacitances,  $C$  and  $C_k$ , are related to the piezoelectric coefficients by the following equations:

$$C = \alpha d_{31}^2 a / s d, \quad (17)$$

$$C_k = \kappa' a / 4\pi d, \quad (18)$$

where  $\alpha$  is a constant,  $d_{31}$  is the piezoelectric coefficient,  $a$  the area,  $s$  the elastic compliance coefficient,  $d$  the thickness of the crystal plate, and  $\kappa'$  the dielectric constant in the  $z$ -direction.

Letting

$$\nu_R = \beta(1/s\rho)^{\frac{1}{2}}, \quad (19)$$

where  $\beta$  is a constant and  $\rho$  the density, we obtain the following expression for the  $d_{31}$  piezoelectric coefficient:

$$d_{31}^2 = G\Delta\nu \cdot \kappa_c' / \nu_R^3. \quad (20)$$

Here,  $\Delta\nu$  is the difference between the resonance and antiresonance frequencies, and  $G$  a constant which contains  $\alpha$ ,  $\beta$ ,  $\rho$ ,  $a$ , and  $d$ .

Unfortunately, the crystals used were small rectangular plates and the width of the crystal could not be neglected. Hence it was impossible to determine the exact mode of vibration of the crystal and the constant,  $G$ . An absolute value of the  $d_{31}$  coefficient could therefore not be determined by this method. However, the temperature dependence of the coefficient could be measured.

#### V. THE TEMPERATURE DEPENDENCE OF THE ELECTROMECHANICAL RESPONSE

The temperature dependence was measured as a function of temperature from room temperature to above the Curie point (120°C). By using Eq. (13) it is possible to calculate the  $d_{31}$  coefficient as a function of temperature from the measured  $P$  and  $\chi_e$  characteristics. The result is shown in Fig. 7, where we have taken our values of  $P_0$  for the spontaneous polarization and  $\chi_e$  for the initial susceptibility from our data.<sup>4</sup> It can be seen that the  $d_{31}$  coefficient increases slowly at first and at higher temperatures more rapidly towards a sharp maximum a few degrees below the Curie point. It then drops suddenly to zero at the Curie point since the crystal is not piezoelectric above this temperature. The maximum value obtained lies between  $-600$  and  $-700 \times 10^{-8}$  statcoul/dyne.

A direct measurement by the static method (Fig. 8) shows a very similar behavior. This experimental characteristic was obtained at field strengths between 5000 and 6000 v/cm. It is important to use such high fields, since near the Curie point even good single-domain crystals tend to break up into many domains if the external field does not keep them aligned.

The maximum values in Figs. 7 and 8 agree well. This closer agreement near the Curie point is to be expected because in this region the value of the electric susceptibility does not change much with field strength. However, the experimental value does not go to zero at the Curie point. There is a definite piezoelectric response above the Curie point which decreases only slowly as the temperature increases. At 160°C the value is still about half that at room temperature.

The electromechanical response of the crystal above the Curie point is indicated in detail in Fig. 9. As the field strength is raised, the response is at first small; but at some critical field strength a sudden contraction takes place. At higher field strengths the characteristic flattens out again. The better the crystal, the higher the critical field strength and the smaller this contraction.

The dynamic method leads to the following results: the piezoelectric resonance frequency,  $\nu_R$ , stays constant for a considerable range of temperature and drops to a sharp minimum a few degrees below the Curie point, as already seen by earlier observers.<sup>9</sup> At the same tem-

<sup>9</sup> Blattner, Känzig, and Merz, *Helv. Phys. Acta* **22**, 35 (1949).

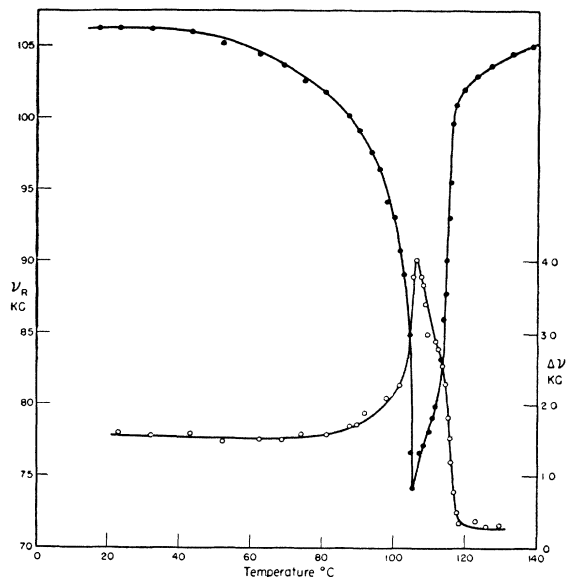


FIG. 10. Resonance frequency  $\nu_R$  and  $\Delta\nu = \nu_A - \nu_R$  vs. temperature.

perature the difference  $\Delta\nu$  between resonance frequency  $\nu_R$  and antiresonance frequency  $\nu_A$  reaches a maximum (Fig. 10). The better the crystal, the nearer the extrema approach the Curie temperature as determined by the maximum of the dielectric constant. The crystals also show a slight piezoelectric response above the Curie point. However, when very good crystals are used with a minimum of internal strains and absolutely free of domains perpendicular to the thickness of the crystal plate, the behavior becomes different. The resonance frequency again drops sharply near the Curie point, but shows no minimum. It does not rise again, and there is no piezoelectric response above the Curie point (Fig. 11).

From the results for  $\nu_R$  and  $\Delta\nu$  and the values of the

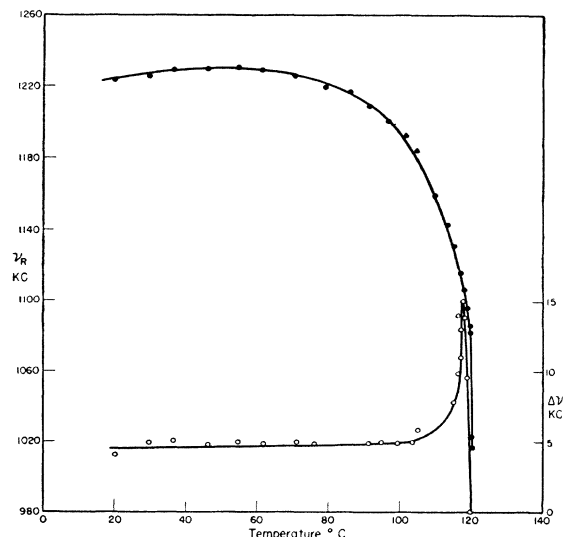


FIG. 11. Resonance frequency  $\nu_R$  and  $\Delta\nu = \nu_A - \nu_R$  vs. temperature.

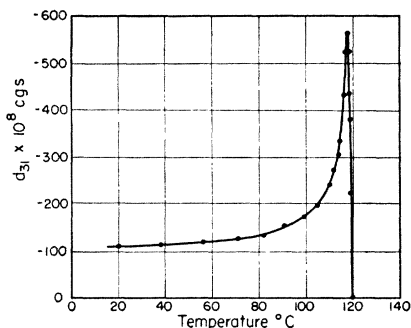


FIG. 12.  $d_{31}$  coefficient as a function of temperature by the dynamic method.

dielectric constant  $\kappa'$  for the good crystals,<sup>4</sup> one obtains the  $d_{31}$  piezoelectric coefficient as a function of temperature, as shown in Fig. 12. A value for  $d_{31}$  of  $110 \times 10^{-8}$  c.g.s. at room temperature has been assumed for this curve. The behavior agrees well with both the calculated curve (Fig. 7) and the characteristic obtained from static measurements (Fig. 8). However, there is no piezoelectric response above the Curie point, in contrast to the static method.

#### VI. OPTICAL AND DIELECTRIC OBSERVATIONS

Optical observations have shown that at and immediately above the Curie temperature the cubic BaTiO<sub>3</sub> crystals become birefringent when an external d.c. field is applied. We observed that when the field strength is increased, the crystal lighted up and at somewhat higher field strengths domain patterns could be observed that are similar to those below the Curie point. At even higher field strengths the domain pattern again disappeared because of the alignment of the domains, but the crystal remained birefringent. This is in agreement with the hysteresis curve obtained by the static method above  $\theta$  (Fig. 9). The lighting up of the crystal at low field strengths corresponds to the initial flat portion of the curve, the formation of the domains to the steep increase, while the alignment of the domains corresponds to the flat portion of the curve at higher field strengths. We must thus deduce that the crystal, under the influence of the electric field, becomes tetragonal above  $\theta$ . The field strength at which the domains appear and disappear is dependent on the temperature and the quality of the crystal. The temperature of disappearance of the domains in a crystal was about 1°C above the zero field Curie point when a field of 1 kv/cm was applied. When the field was removed, the crystal reverted back to its cubic structure with a time constant which decreases with the increasing temperature.

One can observe also a shift of the maximum of the dielectric constant to higher temperatures when a d.c. field is applied, as previously observed on ceramic samples. This shift is of the order of a few tenths of a degree for 1 kv/cm, and is accompanied by flattening out of the peak of the characteristic.

#### VII. DISCUSSION

The drop in the resonance frequency with increasing temperature can be explained in the following way: it is known that, apart from the geometry of the crystal, the resonance frequency depends on the elastic constants ( $s_{ih}$ ) such that  $\nu_R \sim s^{-1/2}$ . However, it is necessary to distinguish between the compliance coefficients of a shorted and of an insulated crystal. The former,  $s_{ih}^E$ , corresponds to the condition of constant field, while in the latter  $s_{ih}^P$  corresponds to that of constant polarization. The relation between the various coefficients in the two cases is<sup>10</sup>

$$s_{ih}^E = s_{ih}^P + (4\pi d_{ni} d_{nh} / \kappa_n'), \quad (21)$$

with  $\kappa_n'$  the dielectric constant. For BaTiO<sub>3</sub> we have

$$\begin{aligned} s_{11}^E &= s_{11}^P + (4\pi d_{31}^2 / \kappa_c'), \\ s_{12}^E &= s_{12}^P + (4\pi d_{31}^2 / \kappa_c'), \end{aligned} \quad (22)$$

since  $d_{31} = d_{32}$ . By replacing one of the  $d_{31}$  coefficients according to Eq. (13),

$$\begin{aligned} s_{11}^E &= s_{11}^P + 2\mu P_0 d_{31}, \\ s_{12}^E &= s_{12}^P + 2\mu P_0 d_{31}. \end{aligned} \quad (23)$$

The elastic coefficient,  $s_{ih}^P$ , of the insulated crystal changes only slightly and almost linearly with temperature. Thus, when  $d_{31}P_0$  has a maximum value,  $s_{ih}^E$  will have a maximum, and hence the resonance frequency of the plated crystals will drop to a minimum. Since  $P_0$  decreases much more slowly than  $d_{31}$  increases with temperature very near the Curie point, the maximum of  $d_{31}$  and of  $\Delta\nu$  occurs at nearly the same temperature as the minimum of the resonance frequency.

Optical observations showed that most of the crystals split up into many domains immediately below the Curie temperature. It could be verified that the maximum in the  $d_{31}$  coefficient, and thus also the minimum in the resonance frequency, occurs exactly at this temperature where the single-domain state of the crystal breaks up into multiple domains. Crystals with much internal strain show this domain change at a lower temperature than do good crystals, since the formation of these domains is the result of residual strain effects. In most of the crystals used, some domains were present even at room temperature, which is substantiated by the fact that such poor crystals have a dielectric constant along the thickness ( $z$ -direction) of the order of 1200, while in a very good crystal this value is 200 to 300 at room temperature. An ideal crystal completely free of strains changes suddenly at the Curie temperature from the tetragonal to the cubic crystal structure, and then there is no more piezoeffect. In poor crystals we can expect that owing internal strains the various domains of the crystal become cubic at different temperatures, so that the transitions take place over a wide temperature range. It seems likely that the cubic re-

<sup>10</sup> W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, New York, 1946), p. 271.

gions of the crystal are harder and have smaller compliance coefficients. In this case the resonance frequency of the plated crystal should increase again above the minimum, as was observed. Since in this case there is no really sharply defined Curie temperature, and the Curie temperature which we have indicated is determined from the maximum of the dielectric constant (which measures an average behavior over all domains), it is to be expected that even above this temperature a slight piezoelectric response can be obtained. Thus, the peculiar behavior obtained from most of our crystals (Fig. 10), in contrast to that of a very good crystal (Fig. 11), may be explained by domain effects.

That a piezoelectric response is obtained by the static method even for the very best crystals is caused by the tetragonality induced by the external field. This must be explained by the fact that even in the best crystal some Ti<sup>4+</sup> ions are shifted to an eccentric position by the external field through the electrostrictive effect, which thus induces a piezoelectric effect, at least in parts of the crystal. As the temperature is increased, this effect is greatly reduced; but, up to about 180°C in fields of 6 kv/cm, it was never found to disappear completely.

It is now possible to compare our results with those of Mason<sup>1</sup> and Jaffe.<sup>2</sup> Both obtained the butterfly hysteresis characteristics similar to our Fig. 4. They interpreted their results as a quadratic effect which they call electrostrictive. This quadratic effect is caused by the domain changes and is not electrostrictive in the usual sense. As soon as the domain effect is suppressed by prepolarization with an external field, the behavior becomes linear, as can be seen for single-domain crystals in Fig. 4, and for multi-domain crystals and ceramics<sup>3</sup> when all the domains are aligned. Thus, we can speak of a true linear piezoeffect. Our absolute values are smaller than those obtained by Mason and Jaffe, presumably because we have been able to eliminate domain effects to a large extent. They are in rather close agreement, however, with the values obtained by Rzhano<sup>3</sup> on ceramics.

It is interesting to compare the electromechanical behavior of BaTiO<sub>3</sub> with that of Rochelle salt and KH<sub>2</sub>PO<sub>4</sub>. The latter two show no butterfly characteristics, but have the usual hysteresis loops. There, the domain effects (Barkhausen jumps) are much larger compared with the linear piezoeffect<sup>11,12</sup> (saturation branch of the hysteresis loop). Rochelle salt and KH<sub>2</sub>PO<sub>4</sub>, on the other hand, have only parallel and antiparallel domains, unlike BaTiO<sub>3</sub>, which may also have perpendicular domains. However, the domain jumps from antiparallel to parallel positions in Rochelle salt and KH<sub>2</sub>PO<sub>4</sub> cause a shear strain of about half a degree and, therefore, a considerable change in length will result. On the other hand, in BaTiO<sub>3</sub> the domain change from antiparallel to parallel will give no change in length without an external field (Section II); and perpendicular domains are not present in our single-domain crystals. In ceramics only a relatively small percentage (about 10 percent according to Mason<sup>1</sup>) of the domains switch into the parallel position.

The shape of the curve of the temperature dependence of the  $d_{31}$  piezoelectric coefficient obtained by Rzhano<sup>3</sup> on ceramics is very similar to ours. His values have been obtained by static measurements of the direct piezoeffect, and thus no response above the Curie temperature could be observed.

We have confined our measurements to those on the  $d_{31}$  coefficient. The temperature dependence of the  $d_{33}$  coefficient should be, according to Eq. (13), identical to that of the  $d_{31}$  coefficient, while its absolute value should be about 2.3 times as large as the  $d_{31}$ . This value is in agreement with the measurements of Jaffe.<sup>2</sup>

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<sup>11</sup> H. Hinz, reference 10, p. 541.

<sup>12</sup> A. von Arx and W. Bantle, *Helv. Phys. Acta* **17**, 298 (1944).