MERZ, M. J., 1948, *Phys. Rev.*, **75**, 687.
RUSHMAN, D. F., and STRIVENS, M. A., 1946, *Trans. Far. Soc.*, **42**, 231.
UBBELOHDE, A. R., and WOODWARD, H., 1947, *Proc. Roy. Soc.* A, **188**, 358.
MASON, W. P., and MATTHIAS, B. T., 1948, *Phys. Rev.*, **74**, 1622.
HULM, F., 1947, *Nature*, **160**, 126.
DEVONSHIRE, A. F. In this issue.
SAUER, J. A., 1940, *Phys. Rev.*, **57**, 142.
BETHE, H. A., 1935, *Proc. Roy. Soc.* A, **150**, 552.
SZIGETI, B., 1949, *Trans. Far. Soc.*, **45**, 155.
DANIELSON, G. C., MATTHIAS, B. T., and RICHARDSON, J. M., 1948, **74**, 986.
MOTT, N. F., and GURNEY, R. W., 1940, *Electronic Processes in Ionic Crystals*,
    (Oxford : University Press).
FRÖHLICH, H., 1949, *Theory of Dielectrics*. (Oxford : University Press).

XCVI. *Theory of Barium Titanate.*—Part I.

By A. F. DEVONSHIRE,

H. H. Wills Physical Laboratory, University of Bristol*.

SUMMARY.

The theory of the dielectric and crystallographic properties of barium titanate is considered. By expanding the free energy as a function of polarization and strain and making reasonable assumptions about the coefficients, it is found possible to account for the various crystal transitions. Calculations are made of the dielectric constants, crystal stains, internal energy, and self polarization as functions of temperature. Finally relations are obtained between the coefficients in the free energy and the ionic force constants. These are used to estimate some of the coefficients which are not completely determined by experimental data.

§1. INTRODUCTION.

IN the last few years the properties of a number of substances known as ferroelectrics or seignette-electrics have been much studied. At present three groups of these substances are known, typical members of the three groups being Rochelle salt, potassium dihydrogen phosphate, and barium titanate. All these substances have certain properties in common. At sufficiently high temperatures their properties are normal, though the dielectric constants are usually rather high. As the temperature falls the dielectric constant increases and reaches a peak at a transition temperature. At this temperature there is a change of crystal form to one of lower symmetry. Below this temperature each crystal breaks up into domains and there is clear evidence that these domains are polarized. The substance shows the properties of hysteresis and saturation that one would expect from such a structure. There may be lower

transition temperatures. Rochelle salt becomes normal again at still lower temperatures, and barium titanate has two lower transition temperatures at which there are further changes of crystal form. The crystal changes are always small, the shears involved being usually less than a degree. There are also small specific heat changes at the transition temperature.

In this paper we shall consider only the most recently discovered group of ferroelectrics, the third, and in particular barium titanate. This is the only known pure substance in the group, though solid solutions of barium titanate with lead or strontium titanate show similar properties.

We shall first review the experimental evidence on the crystal structure, specific heat, saturation polarization and dielectric constant for small fields. We shall then discuss the theory of the substance, first on a phenomenological basis and then in terms of a molecular model. This will include a discussion of theories already put forward. We shall not consider the dielectric constant at large fields, nor any of the time-dependent phenomena, such as hysteresis or the dependence of dielectric constant on frequency of field. We hope to deal with some of these in a later paper.

§ 2. Crystal Structure

Above the transition temperature barium titanate $BaTiO_3$ has a cubic structure. The barium ions lie at the corners of a cubic lattice, the titanium ions at the body centres, and the oxygen ions at the face centres. Below 120° C. it was shown by Megaw (1946) that the substance becomes tetragonal ; one of the axes (usually taken to be the c-axis) becomes lengthened, and the other two shortened. The axial lengths as a function of temperature are shown in fig. 1. It will be seen that the change appears to set in rather abruptly. This was verified by Harwood, Popper and Rushman (1947), who showed that in a given crystallite c/a changed discontinuously from 1 to 1·005. There is a range of a few degrees, however, in which the substance is a mixture of cubic and tetragonal forms. Optical studies by Kay (1948) Matthias and Von Hippel (1948) and Blättner, Kanzig and Merz (1949) show that each crystal has broken up into a number of domains. In the simplest type the domains are arranged in the way shown in fig. 2. The domain extends from one face to a parallel one and the directions of the tetragonal axes are as shown.

More recent optical and X-ray studies by Kay, Vousden and Wellard (1949) show that there is a further transition at about −10° C. Below this temperature the crystal is orthorhombic. At the transition the c-parameter shortens slightly and the a-parameter increases so that the two become equal and there is a shear of about 14′ in the ca plane. The polar axis, which was formerly in the c-direction is now along a diagonal in the ca plane. The above authors also report that there is a further transition at about −70°.C. Below this temperature the crystal is probably rhombohedral with the polar axis along the [111] direction.

Fig. 1.
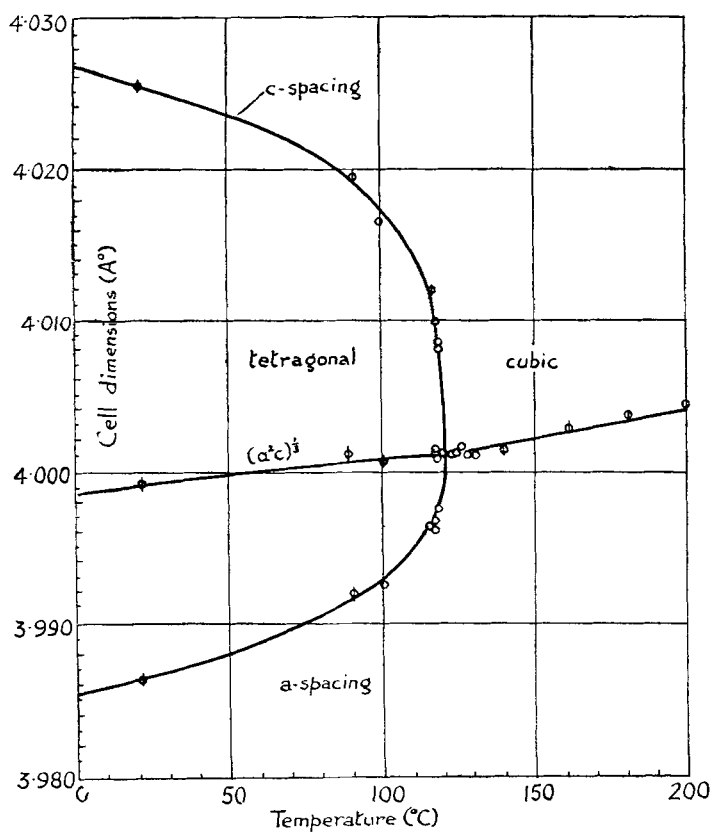
Lattice spacing of $BaTiO_3$ as a function of temperature (Megaw 1946).

Fig. 2.
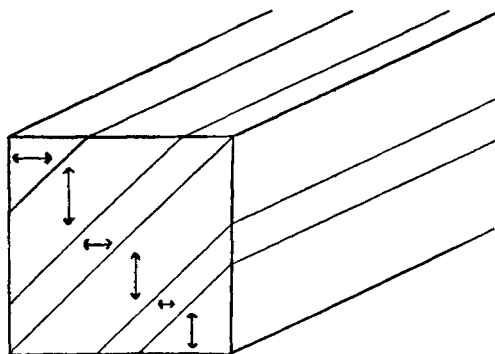
§3. Specific Heat and Spontaneous Polarization.

It has been found by Wul (1946) and also by Harwood, Popper and Rushman (1947) that there is a hump in the specific heat curve in the neighbourhood of 120° C. Blattner, Kanzig and Merz (1949) found a hump in the neighbourhood both of 120° C. and of 0° C. The additional specific heat is only a small fraction of the normal specific heat so it is difficult to separate the two, but Blattner, etc. found that the total additional heat was about 47 cals./mole at the higher transition, and about 16 cals./mole at the lower transition. The other authors' results are not stated in their papers, but estimating very roughly from their curves the total additional heat appears to be about 20 or 30 cals./mole.

There is only a limited amount of evidence on the spontaneous polarization. A field which is strong enough to orientate all the domains in the same direction will produce considerable induced polarization since the domains are themselves highly polarizable. It is difficult, therefore, to separate the spontaneous from the induced polarization. For sufficiently strong fields, however, the polarization becomes a linear function of field strength, and by extrapolating back to zero field Hulm (1947) estimated that the spontaneous polarization at room temperature was about 16 microcoulombs per cm.^{2}. Matthias and Von Hippel (1948) estimated it to be about 12 microcoulombs/cm.^{2}. Unfortunately we do not know the spontaneous polarization as a function of temperature, but Hulm (1947) has given the total polarization for large fields as a function of temperature. As the temperature falls it rises rather rapidly in the neighbourhood of 120° C. and then increases slowly. The measurements do not go below 0° C.

§4. Dielectric Constant for Small Fields.

Numerous measurements of the dielectric constant for small fields have been made, usually with alternating current. Papers by various Russian authors have been summarized by Wul (1946). Jackson and Reddish (1945) and Rushman and Strivens (1946) have studied the effect of varying the composition. Von Hippel, Brockenridge, Chesley and Tisza (1946) have published many measurements for various compositions, field strengths, and frequencies. All the authors agree that above the highest transition temperature the dielectric constant obeys a Curie-Weiss law ; that is

$$\epsilon = \frac{A}{T - T_a} + \epsilon_0,$$

where ϵ_0 may or may not be zero and A is very large, about 10^5 degrees. Below this temperature the dielectric constant drops to about 1000–2000, and as the temperature decreases remains constant or slowly decreases. There are small peaks at lower temperatures. These almost certainly correspond to the lower crystal transitions. All the above measurements were made with powders.

Now, above the highest transition temperature the substance has complete cubic symmetry and therefore a single dielectric constant ;

but below this temperature the dielectric constants along the different axes will be different and experiments on powders will only give a mean value. Matthias and Von Hippel (1948) have carried out experiments on single crystals ; but even a single crystal may contain several differently orientated domains. However, they made measurements on a crystal in which all the domains had been made parallel by applying a strong electric field, and they found a dielectric constant of 500 along the c-axis and 1700 along the a-axis. Mason and Matthias made measurements on single domain crystals and found dielectric constants along the a-axis

Fig. 3.
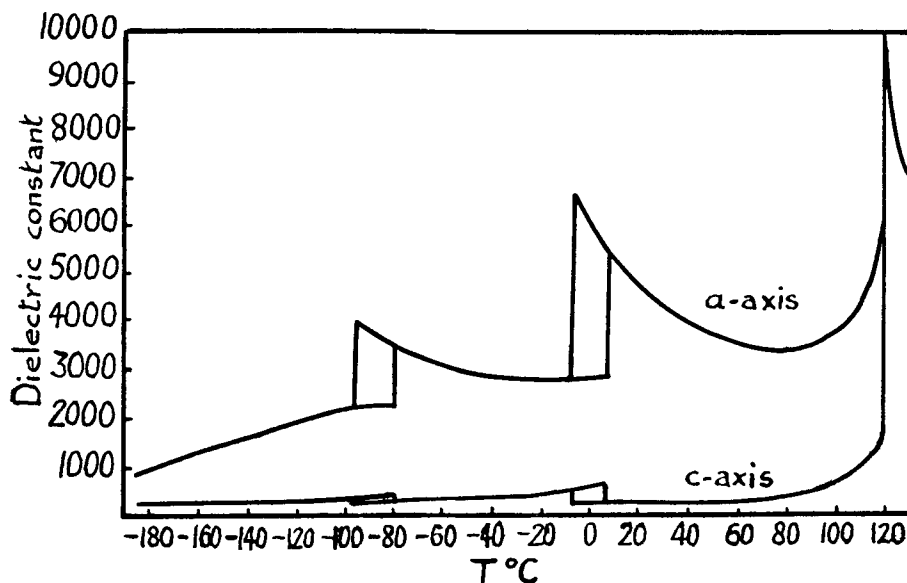
Dielectric constant of $BaTiO_3$ single domain crystals (Merz 1949).

of the order of 10^5. Merz, however, found more moderate values. His results are shown in fig. 3. The discontinuities at the lower transition temperatures are very well marked.

§5. THEORIES.

Suggestions put forward to account for the behaviour of barium titanate are usually based on the assumption that the titanium ion can move rather easily. Miss Megaw (1946) has pointed out that if the ions are all assumed to have the Goldschmidt radii they cannot be fitted together exactly to make a cubic structure but that they have a certain amount of free space. Rushman and Strivens (1946) have developed this idea by suggesting that the titanium ions are slightly displaced from the symmetrical position and therefore form dipoles which can rotate. It is known that such a set of dipoles have a Curie temperature above which they rotate freely, but below which they are parallel to one another. This latter state, of course, corresponds to the ferroelectric region.

Mason and Matthias have developed in considerable detail a rather different model. They assume that the titanium ion has six equilibrium positions slightly displaced in the axial directions from the symmetrical one. In the cubic state the ions occupy the positions at random. In the tetragonal state they occupy mainly positions along one axis. The transition from cubic to tetragonal symmetry therefore corresponds to a transition from a disordered to an ordered state. By assuming suitable values for the ionic shift, the polarizability of the rest of the material, and the Lorentz factors, they have accounted for the dielectric constant in the cubic region, and the two dielectric constants in the tetragonal region. They have also considered hysteresis and frequency effects.

The greater part of this paper considers the theory of barium titanate in a phenomenological way. We expand the free energy in terms of the strains and polarization of the crystal, use certain properties of the crystal to determine the coefficients, and then predict other properties. Results obtained in this way are of course, independent of any atomic model. This method has been applied to Rochelle salt with considerable success by Mueller (1940), but owing to the very different symmetry of barium titanate we cannot make any direct use of his results. Mason (1948) has applied this method to the electrostrictive effect in barium titanate; Ginsburg (1946) has applied it to the highest transition, but only a limited amount of experimental evidence was available when his paper was published. We have been able to show that by assuming reasonable values for the coefficients we can explain the successive transitions through the cubic, tetragonal, orthorhombic and rhombohedral forms. In determining the coefficients we use the observed transition temperatures, the value of the dielectric constant in the cubic region, and the observed strain and saturation polarization at a single temperature in the tetragonal region. We are then able to predict the various dielectric constants in the tetragonal, orthorhombic and rhombohedral regions. We also predict values for the strain and saturation polarization in these regions. It is not possible to verify all these predictions as many of these quantities have not yet been observed.

Finally we consider an atomic model for barium titanate. Following the method used by Born for ionic crystals we treat the ions mainly as point centres of force, though also taking into account their polarizability. After checking the force constants by calculating the interatomic distance we make an estimate of the elastic constants. In conjunction with the results already obtained this enables us to calculate the electrostrictive constants. We then attempt to calculate directly the field in which each ion moves, the other ions being in the symmetrical positions. These calculations clearly indicate that the stable position of the titanium ion is the symmetrical one. It seems just possible that the oxygen ions might have two unsymmetrical equilibrium positions displaced towards the nearest Ti ions, but the calculations are not accurate enough to make a definite prediction. We have, however, assumed that an ion moving individually has only one position of equilibrium, and that the spontaneous polarization

is caused by the Lorentz field, in other words, it is a cooperative effect, since this field only exists when ions of one sign move together.

The Lorentz field requires some consideration since it plays an important part in the theory of ferroelectrics. When a body becomes polarized an ion or dipole in the body will experience a force due to the polarization of the rest of the body. We may assume this force to be proportional to the polarization and put it equal to βP where β is the Lorentz factor. Owing to the slow fall off with distance of the dipole force it is a "long range" one, that is dipoles in distant parts of the body have an appreciable effect. Hence for an insulated body β is dependent on external shape and reaches its maximum value for a needle or plate polarized parallel to a long axis. But for an uninsulated body β always has this value whatever the external shape. A maximum value of β corresponds to a minimum polarization energy since this is $-\frac{1}{2}\beta P^2$ per unit volume, and hence the uninsulated body will always collect surface charges in such a way as to make β a maximum, say β_m. For point dipoles in a cubic or random array β_m can be shown to be $4\pi/3$ (Fowler 1936). If the array is regular but not cubic β_m will vary somewhat with direction though its mean value will still be $4\pi/3$. If the dipoles are not point dipoles β_m will have a different value.

Mason and Matthias have found it necessary to assume that β_m is slightly different for the tetragonal and the other directions and also varies slowly with the temperature. These assumptions are reasonable, but the values they have found it necessary to assume for β_m are near 0·10. This differs considerably from the theoretical value of 4·19 even taking into account the fact that the dipoles are far from being point dipoles. Physically it means that the cooperative effect between the dipoles is rather small.

We have assumed that β_m has the value $4\pi/3$, and that the Lorentz field approximately balances the short range restoring force. By taking into account thermal vibrations, including anharmonic terms, we are able to show that the restoring force increases with temperature, and hence explain the existence of a transition temperature.

For the properties we are dealing with in this paper there is no important difference between the predictions of the two models. The Mason Matthias model would need a little modification to account for the lower transitions, but this could certainly be done. There are bigger differences in other phenomena, but these will be dealt with in a later paper.

§6. PHENOMENOLOGICAL THEORY : INTRODUCTION.

We shall consider the substance as a strained cubic crystal. All the changes from cubic symmetry are small, so this is quite legitimate. We shall use the notation given by Cady in his "Piezoelectricity", as far as possible. For barium titanate, however, it is necessary to consider higher order terms in the free energy than any used by Cady, so we shall have to introduce some new notation.

Now the free energy of a crystal can be expressed in several different forms. We can take as our independent variables polarization and stress,

polarization and strain, field and stress or field and strain. We shall start by expressing the free energy as a function of polarization and stress with the stresses equated to zero. We then have

$$A = \tfrac{1}{2}\chi'\{P_x^2 + P_y^2 + P_z^2\} + \tfrac{1}{4}\xi'_{11}\{P_x^4 + P_y^4 + P_z^4\} + \tfrac{1}{2}\xi'_{12}\{P_y^2 P_z^2 + P_z^2 P_x^2 + P_x^2 P_y^2\}$$
$$+ \tfrac{1}{6}\zeta'\{P_x^6 + P_y^6 + P_z^6\}. \qquad . \quad . \quad (6.1)$$

The zero of free energy is taken to be that of the unpolarized, unstressed crystal. All the terms of the second and fourth orders are included and some of the terms of the sixth order. We shall find it necessary to take into account all these terms to account for the behaviour of the crystal. The derivatives of A with respect to P_x give the field-components for the free, that is unstressed, crystal. Hence we have

$$E_x = \chi' P_x + \xi'_{11} P_x^3 + \xi'_{12} P_x (P_y^2 + P_z^2) + \zeta' P_x^5. \qquad . \quad . \quad (6.2)$$

In the absence of a field the right-hand side of (6.2) must be zero and for stability A must be a minimum.

We shall find that we can account satisfactorily for the observed facts if we assume that ζ' and ξ'_{12} are positive, ξ'_{11} is negative, and χ' is a decreasing function of temperature which passes through a zero value in the neighbourhood of the upper transition temperature. Since χ' is the reciprocal susceptibility for zero polarization we can obtain its value from experiment directly above the upper transition temperature where there is zero polarization for zero field. We find, in fact, that it is a linear decreasing function of temperature which, if extrapolated, passed through zero a little below the transition temperature. With these assumptions A will clearly be always positive for sufficiently large χ', that is, at sufficiently high temperatures. The minimum value of A will then correspond to zero polarization. For χ' small or negative, however, the minimum value of A will correspond to a finite polarization. The second order term is independent of direction. But for a given resultant polarization the fourth order term has its minima along the axes and the sixth order term has its minima along the diagonal directions. Hence as the temperature falls and the magnitude of the polarization increases the direction will be likely to change from an axial to a diagonal one.

For zero field, equation (6.2) and the similar equations become

$$\left.\begin{array}{l} P_x = 0, \text{ or } \zeta' P_x^4 + \xi'_{11} P_x^2 + \xi'_{12}(P_y^2 + P_z^2) + \chi' = 0, \\ P_y = 0, \text{ or } \zeta' P_y^4 + \xi'_{11} P_y^2 + \xi'_{12}(P_z^2 + P_x^2) + \chi' = 0, \\ P_z = 0, \text{ or } \zeta' P_z^4 + \xi'_{11} P_z^2 + \xi'_{12}(P_x^2 + P_y^2) + \chi' = 0. \end{array}\right\} \quad . \quad . \quad (6.3)$$

There are four sets of solutions of these equations which may correspond to minima of A, namely

$$\left.\begin{array}{ll} P_x = P_y = P_z = 0, & (a) \\ P_x = P_y = 0, \; \zeta' P_z^4 + \xi'_{11} P_z^2 + \chi' = 0, & (b) \\ P_x = 0, \; P_y = P_z, \; \zeta' P_z^4 + (\xi'_{11} + \xi'_{12})P_z^2 + \chi' = 0, & (c) \\ P_x = P_y = P_z, \; \zeta' P_z^4 + (\xi'_{11} + 2\xi'_{12})P_z^2 + \chi' = 0, & (d) \end{array}\right\} \quad . \quad . \quad (6.4)$$

with, of course, the corresponding solutions obtained by interchanging P_x, P_y, and P_z. The corresponding values of A are given by

$$
\begin{aligned}
&\text{A}=0, &(a)\\
&\text{A}=\tfrac{1}{6}\zeta'P_z^6+\tfrac{1}{4}\xi'_{11}P_z^4+\tfrac{1}{2}\zeta'P_z^2, &(b)\\
&\text{A}=\tfrac{1}{3}\zeta'P_z^6+\tfrac{1}{2}(\xi'_{11}+\xi'_{12})P_z^4+\chi'P_z^2, &(c)\\
&\text{A}=\tfrac{1}{2}\zeta'P_z^6+\tfrac{3}{4}(\xi'_{11}+2\xi'_{12})P_z^4+\tfrac{3}{2}\chi'P_z^2. &(d)
\end{aligned}
\qquad (6.5)
$$

The necessary conditions for A to be a minimum are

$$
\begin{aligned}
&\chi'>0, &(a)\\
&\chi'+\xi'_{12}P_z^2>0, \quad \tfrac{1}{2}\xi'_{11}+\zeta'P_z^2>0, &(b)\\
&\chi'+2\xi'_{12}P_z^2>0, \quad \tfrac{1}{2}\xi'_{11}+\zeta'P_z^2>0, &(c)\\
&\qquad\qquad\quad \tfrac{1}{2}\xi'_{11}+\zeta'P_z^2>0. &(d)
\end{aligned}
\qquad (6.6)
$$

It is possible for A to have more than one minimum, and we then have to determine which is the least. If we plot the values of A given by (6.4) and (6.5) as a function of χ', taking ζ' and ξ' to be constant then we find that for χ' positive and large enough the least minimum of A is zero, but as χ' decreases the least minimum is successively given by equations (b), (c) and (d). When the minimum given by (b) is equal to that given by (a) we have

$$
\tfrac{1}{6}\zeta'P_z^4+\tfrac{1}{4}\xi'_{11}P_z^2+\tfrac{1}{2}\chi'=0, \qquad \cdots \cdots \quad (6.7)
$$

and from (6.4 b) we have

$$
\zeta'P_z^4+\xi'_{11}P_z^2+\chi'=0. \qquad \cdots \cdots \cdots \quad (6.8)
$$

Let us denote by χ'_0 the value of χ' which satisfies these equations and by P_1 the corresponding value of P_z. Then we have

$$
\zeta'=3\chi'_0/P_2^4, \qquad \cdots \cdots \cdots \quad (6.9)
$$

$$
\xi'_{11}=-4\chi'_0/P_1^2. \qquad \cdots \cdots \cdots \quad (6.10)
$$

If we assume that ζ' and ξ'_{11} are constants, independent of temperature, and therefore always given by (6.9) and (6.10), and if we also put

$$
P_z^2=zP_1^2, \ P_x^2=xP_1^2, \ P_y^2=yP_1^2, \qquad \cdots \cdots \quad (6.11)
$$

$$
\chi'=t\chi'_0, \qquad \cdots \cdots \cdots \cdots \quad (6.12)
$$

$$
\xi'_{12}=-\alpha\xi'_{11}, \qquad \cdots \cdots \cdots \quad (6.13)
$$

then equations (6.4) and (6.5) become

$$
\begin{aligned}
&x=y=z=0, &(a)\\
&x=y=0, \ 3z^2-4z+t=0, &(b)\\
&x=0, \ y=z, \ 3z^2+4(-1+\alpha)z+t=0, &(c)\\
&x=y=z, \ 3z^2+4(-1+2\alpha)z+t=0, &(d)
\end{aligned}
\qquad (6.14)
$$

and
$$A=0,$$
$$A=\chi_0' P_1^2 \{\tfrac{1}{2}z^3 - z^2 + \tfrac{1}{2}zt\},$$
$$A=\chi_0' P_1^2 \{z^3 + 2(-1+\alpha)z^2 + zt\},$$
$$A=\chi_0' P_1^2 \{\tfrac{3}{2}z^3 + 3(-1+2\alpha)z^2 + \tfrac{3}{2}zt\}. \qquad \right\} \quad \dots \quad (6.15)$$

The equations are now in a convenient form for calculation, since they are now in the form of a relation between two variables z and t with a single parameter α. The other constants of the equation enter only as scale factors. The variable t is related to the temperature, and the relation is probably approximately linear. We have seen this is the case experimentally for t positive, since χ' is proportional to t. In fig. 4 we plot z and $A/\chi_0' P_1^2$ as functions of t for α equal to 1·2. As already stated the minimum value of A is given in turn by equations (a), (b), (c) and (d). The value of z will therefore change discontinuously at three transition temperatures as z is given in turn by equations (a), (b), (c) and (d). The polarization, which was originally zero, will in turn point along a cube edge, a face diagonal, and a body diagonal. The corresponding effect on the crystal symmetry will be to change it from the original cubic successively to tetragonal, orthorhombic and rhombohedral. In the Schönflies notation the symmetry of the crystal will be in turn O_h, C_{4v}, C_{2v} and C_{3v}.

§7. Phenomenological Theory : Dielectric Constant.

In the high temperature region where the crystal has cubic symmetry the dielectric constant is independent of direction and is given by

$$\epsilon = 1 + 4\pi/\chi', \quad \dots \dots \quad (7.1)$$

but in the temperature regions where the crystal has less symmetry the dielectric constant is no longer independent of direction and has to be described by a tensor. It is, in practice, more convenient to work in terms of the susceptibility η_{rs} and the reciprocal susceptibility χ_{rs}. For small fields and polarization they are defined by the relations

$$E_x = \chi_{11}P_x + \chi_{12}P_y + \chi_{13}P_z,$$
$$\dots \dots \dots$$
$$P_x = \eta_{11}E_x + \eta_{12}E_y + \eta_{13}E_z, \qquad \dots \dots \quad (7.2)$$
$$\dots \dots \dots \dots,$$

and are connected by the equation

$$\eta_{rs} = \chi_{rs}/\Delta, \quad \dots \dots \dots \quad (7.3)$$

where Δ is the determinant of the χ's and X_{rs} is the minor of χ_{rs} in that determinant. When the relation between field and polarization is no longer linear we define χ by the equation

$$\chi_{sr} = \chi_{rs} = \frac{\partial E_r}{\partial P_s} = \frac{\partial E_s}{\partial P_r} = \frac{\partial^2 A}{\partial P_r \partial P_s}. \quad \dots \dots \quad (7.4)$$

Fig. 4.
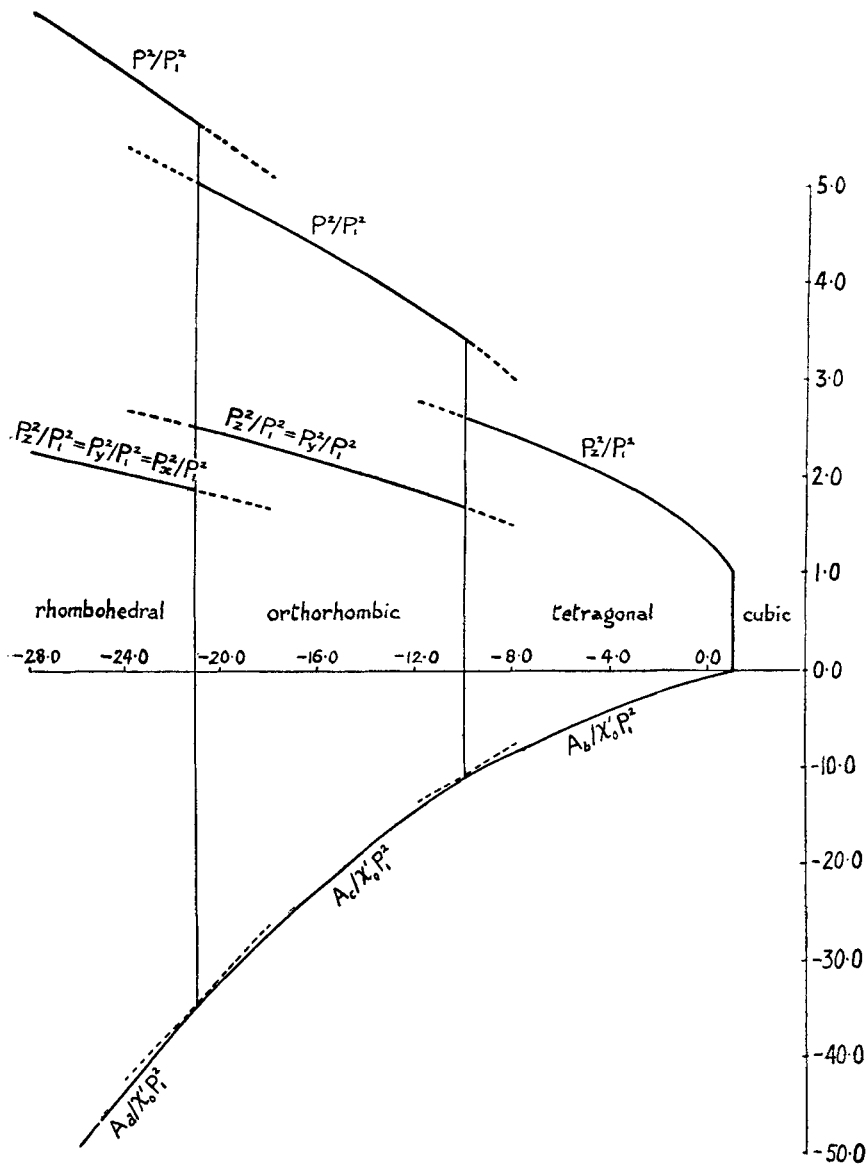
Free energy and polarization of $BaTiO_3$ as a function of temperature
(theoretical).

Hence from (6.1) we have

$$\begin{rcases} \chi_{zz} = \chi' + 3\xi'_{11}P_z^2 + \xi'_{12}(P_x^2 + P_y^2) + 5\zeta'P_z^4, \\ \chi_{xy} = \xi'_{12}P_xP_y, \end{rcases} \quad \ldots \ldots \quad (7.5)$$

with similar expressions for χ_{xx} etc. Using the equations (6.9) to (6.13) we have

$$\begin{rcases} \chi_{zz} = \chi'_0\{t - 12z + 4\alpha(x+y) + 15z^2\}, \\ \chi_{xy} = 4\alpha\chi'_0 x^{\frac12}y^{\frac12}. \end{rcases} \quad \ldots \ldots \quad (7.6)$$

If we now consider our four cases in turn we find that

$$\begin{rcases} \begin{rcases} \chi_{xx} = \chi_{yy} = \chi_{zz} = \chi' = {}^r\chi'_0, \\ \chi_{yz} = \chi_{zx} = \chi_{xy} = 0, \end{rcases} (a) \\[2mm] \begin{rcases} \chi_{xx} = \chi_{yy} = \chi'_0(t + 4\alpha z), \\ \chi_{zz} = \chi'_0(t - 12z + 15z^2), \\ \chi_{yz} = \chi_{zx} = \chi_{xy} = 0, \end{rcases} (b) \\[2mm] \begin{rcases} \chi_{xx} = \chi'_0(t + 8\alpha z), \\ \chi_{yy} = \chi_{zz} = \chi'_0(t - 12z + 4\alpha z + 15z^2), \\ \chi_{xy} = \chi_{zx} = 0, \quad \chi_{yz} = \chi'_0 4\alpha z, \end{rcases} (c) \\[2mm] \begin{rcases} \chi_{xx} = \chi_{yy} = \chi_{zz} = \chi'_0(t - 12z + 8\alpha z + 15z^2), \\ \chi_{yz} = \chi_{zx} = \chi_{xy} = \chi'_0 4\alpha z. \end{rcases} (d) \end{rcases} \quad \ldots \quad (7.7)$$

For cases (a) and (b) χ_{xx}, χ_{yy} and χ_{zz} are the principal values of the reciprocal susceptibilities, but for (c) and (d) they are not. For case (c) the principal directions are the x-axis and the two face diagonals in the yz-plane. The reciprocal susceptibilities in these directions are

$$\begin{rcases} \chi_{xx} = \chi'_0(t + 8\alpha z), \\ \chi_{\beta\beta} = \chi_{zz} + \chi_{yz} = \chi'_0(t - 12z + 8\alpha z + 15z^2), \\ \chi_{\gamma\gamma} = \chi_{zz} - \chi_{yz} = \chi'_0(t - 12z + 15z^2). \end{rcases} \quad \ldots \ldots \quad (7.8)$$

$\chi_{\beta\beta}$ gives the reciprocal susceptibility in the direction of polarization. For case (d) the principal directions are a body diagonal and any direction perpendicular to it. The reciprocal susceptibilities are given by

$$\begin{rcases} \chi_{\alpha\alpha} = \chi_{zz} + 2\chi_{xy} = \chi'_0(t - 12z + 16\alpha z + 15z^2), \\ \chi_{\delta\delta} = \chi_{zz} - \chi_{xy} = \chi'_0(t - 12z + 4\alpha z + 15z^2). \end{rcases} \quad \ldots \quad (7.9)$$

$\chi_{\alpha\alpha}$ gives the reciprocal susceptibility in the direction of polarization. The reciprocal susceptibility in all perpendicular directions is the same and is given by $\chi_{\delta\delta}$.

We must now compare our results with experiment and determine the parameters we have used. These are χ'_0, $\beta_0 P_1$, and the relation between t and the temperature. Now in the non-ferroelectric region we have

$$\chi = t\chi'_0,$$

and experimentally χ is a linear function of temperature. We can therefore reasonably assume that t is a linear function of temperature throughout, and since by definition it is 1 at the upper transition temperature, which we shall call T_1, we can conveniently write

$$t = (T - T_0)/(T_1 - T_0), \quad \ldots \ldots \quad (7.10)$$

where T_0 is a parameter to be determined. Since T_0 is the temperature at which t and therefore χ vanishes we can determine it by extrapolating χ to zero. Unfortunately it is only slightly less than T_1, and since the transition is spread over a few degrees this means that $T_1 - T_0$ is rather uncertain. From the measurements of Harwood, Popper and Rushman (1947) we estimate that T_0 is $118°$ C. and $T_1 - T_0$ about $10°$ C., making T_0 $128°$ C. Since

$$\chi = t\chi_0' = \chi_0'(T - T_0)/(T_1 - T_0), \quad \ldots \ldots \quad (7.11)$$

we can determine $\chi_0'/(T_1 - T_0)$ from the observed slope of χ plotted against temperature. The measurements of different observers agree fairly well and we find that

$$\chi_0'/(T_1 - T_0) = 1 \cdot 0 \times 10^{-4} (\text{degrees})^{-1}, \quad \ldots \ldots \quad (7.12)$$

and hence if we take $T_1 - T_0$ equal to $10°$, then

$$\chi_0' = 1 \cdot 0 \times 10^{-3}. \quad \ldots \ldots \ldots \quad (7.13)$$

P_1 can be determined by making the calculated saturation polarization agree with the observed value at a given temperature. If we take P_1 to be 10 microcoulombs/cm.², then from (6.11), (6.14) and (7.10) we can show that the saturation polarization is about 16 microcoulombs/cm.² at room temperature in agreement with Hulm's result (1947).

α is best determined by choosing it so that one of the lower transition temperatures agrees with the observed value. We find, in fact, that if we take α to be $1 \cdot 2$ both transition temperatures agree fairly well with the observed values.

If we substitute the above values in (6.9), (6.10) and (6.13) we find that

$$\xi_{11}' = -4 \cdot 4 \times 10^{-12}, \quad \ldots \ldots \ldots \quad (7.14)$$

$$\xi_{12}' = 5 \cdot 3 \times 10^{-12}, \quad \ldots \ldots \ldots \quad (7.15)$$

and

$$\zeta' = 3 \cdot 7 \times 10^{-21}. \quad \ldots \ldots \ldots \quad (7.16)$$

We can now plot the principal dielectric constants as a function of temperature. The dielectric constants in the principal directions are related to the reciprocal susceptibilities by the relation

$$\epsilon = 1 + 4\pi\chi^{-1}.$$

The results are shown in fig. 5. If we compare them with the results of Merz given in fig. 3 we see that the theoretical curves have the same form,

but there is no exact numerical agreement. In the tetragonal region our ϵ_{xx} and ϵ_{zz} correspond to Merz's ϵ_a and ϵ_c. In the orthorhombic region ϵ_a and ϵ_c are no longer principal dielectric constants ; and the crystal is no longer a single domain. However, ϵ_c must be a mean of $\epsilon_{\beta\beta}$ and $\epsilon_{\gamma\gamma}$, and ϵ_a must be a mean of all three dielectric constants. In the rhombohedral case we should expect

$$\epsilon_a = \epsilon_c = \tfrac{1}{3}(\epsilon_{\alpha\alpha} + 2\epsilon_{\gamma\gamma}).$$

However, Merz found ϵ_a to be much larger than ϵ_c. This may be the result of domain boundaries shifting under the application of a field. This would not affect the polarization in the c-direction since, presumably all domains have a positive component of polarization in that direction as

Fig. 5.
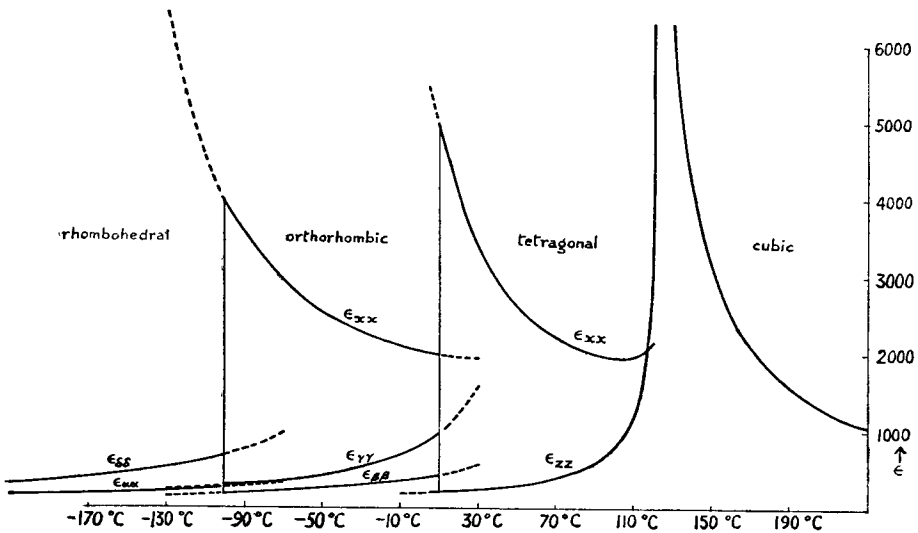
Principal dielectric constants of $BaTiO_3$ (theoretical).

the crystal had in the tetragonal region. On the other hand, the components in the α-direction would be randomly positive or negative, so a shift in boundary with fields might alter the net polarization and hence increase ϵ_α.

§ 8. Phenomenological Theory : Heat of Polarization.

The polarization will be accompanied by a change of internal energy, which will be given by the usual formula

$$E = T \left(\frac{\partial A}{\partial T} \right)_p - A, \quad \ldots \ldots \quad (8.1)$$

where A is given by (6.1). Now A depends on temperature partly through

the polarization, so we can write

$$\left(\frac{\partial A}{\partial T}\right)_p = \left(\frac{\partial A}{\partial T}\right)_{p,P} + \sum_{x,y,z} \left(\frac{\partial A}{\partial P_x}\right)_{p,T} \left(\frac{\partial P_x}{\partial T}\right)_p . \quad \cdots \quad (8.2)$$

$$= \left(\frac{\partial A}{\partial T}\right)_{p,P} + \sum E_x \left(\frac{\partial P_x}{\partial T}\right)_p , \quad \cdots \cdots (8.3)$$

and hence for zero field

$$\left(\frac{\partial A}{\partial T}\right)_p = \left(\frac{\partial A}{\partial T}\right)_{p,P} . \quad \cdots \cdots \cdots (8.4)$$
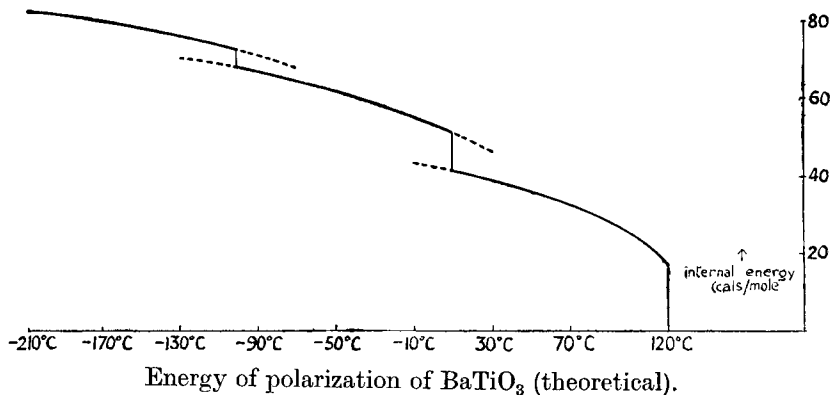
Now we have assumed all the coefficients to be independent of temperature except χ', which is given by

$$\chi' = \chi_0'(T-T_0)/(T_1-T_0). \quad \cdots \cdots (8.5)$$

Hence

$$T\left(\frac{\partial A}{\partial T}\right)_p = \tfrac{1}{2}\frac{\chi_0' T}{T_1-T_0}\{P_x^2+P_y^2+P_z^2\}. \quad \cdots \cdots (8.6)$$

Fig. 6.

Energy of polarization of $BaTiO_3$ (theoretical).

We can now calculate the energy of polarization as a function of temperature using the values of the parameters we have already determined. The result is shown in fig. 6. Since the polarization is discontinuous at the transition temperatures there will be latent heats at these points. The calculated latent heats at the three transition temperatures, starting from the highest, are about 17 cals/mole, 10 cals/mole, and 5 cals/mole. These are lower than the experimental values. The latter, however, include some of the change in polarization energy which takes place below the transition temperatures.

§ 9. PHENOMENOLOGICAL THEORY : CRYSTAL FORM.

In order to study the strain which accompanies self polarization we must express the free energy as a function of polarization and strain. As before, we take the zero of free energy to be that of the unpolarized

cubic crystal. Then we have

$$A = \tfrac{1}{2}c_{11}(x_x^2 + y_y^2 + z_z^2) + c_{12}(y_y z_z + z_z x_x + x_x y_y) + \tfrac{1}{2}c_{44}(x_y^2 + y_z^2 + z_x^2)$$
$$+ \tfrac{1}{2}\chi''(P_x^2 + P_y^2 + P_z^2) + \tfrac{1}{4}\xi_{11}''(P_x^4 + P_y^4 + P_z^4) + \tfrac{1}{2}\xi_{12}''(P_y^2 P_z^2 + P_z^2 P_x^2 + P_x^2 P_y^2)$$
$$+ g_{11}(x_x P_x^2 + y_y P_y^2 + z_z P_z^2) + g_{12}\{x_x(P_y^2 + P_z^2) + y_y(P_z^2 + P_x^2) + z_z(P_x^2 + P_y^2)\}$$
$$+ g_{44}(y_z P_y P_z + z_x P_z P_x + x_y P_x P_y). \quad \ldots \ldots \ldots \ldots \quad (9.1)$$

All the terms of order P^4 or lower order are given, where it has been assumed that the strain is of the order of the square of the polarization. This will shortly be verified. Terms not given vanish because of the crystal symmetry.

The components of field and stress are given by the equations

$$X_x = \frac{\partial A}{\partial x_x}, \ldots \qquad E_x = \frac{\partial A}{\partial P_x}, \ldots \qquad \ldots \quad (9.2)$$

If we assume that the six components of stress are zero, then we get six relations between strain and polarization, namely

$$\left.\begin{aligned} 0 &= c_{11}x_x + c_{12}(y_y + z_z) + g_{11}P_x^2 + g_{12}(P_y^2 + P_z^2), \\ &\qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ 0 &= c_{44}y_z + g_{44}P_y P_z. \\ &\qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \end{aligned}\right\} \quad \ldots \quad (9.3$$

If we solve these equations for the strain in terms of the polarization we find that

$$\left.\begin{aligned} (c_{11} - c_{12})(c_{11} + 2c_{12})x_x &= P_x^2\{-g_{11}(c_{11} + c_{12}) + 2g_{12}c_{12}\} \\ &\quad + (P_y^2 + P_z^2)(g_{11}c_{12} - g_{12}c_{11}), \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot &\quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ c_{44}y_z &= -g_{44}P_y P_z, \\ &\quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \end{aligned}\right\} \quad . \quad (9.4)$$

If we substitute these values for the strain in equation (9.1) then we get an expression for the free energy in terms of polarization for zero stress, that is, we obtain equation (6.1) except for terms of higher order than P^4. Comparing the coefficients of P^2 etc., we find that

$$\left.\begin{aligned} \chi' &= \chi'', \\ \xi_{11}' &= \xi_{11}'' + 2 \frac{-g_{11}^2(c_{11} + c_{12}) + 4g_{11}g_{12}c_{12} - 2g_{12}^2 c_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})}, \\ \xi_{12}' &= \xi_{12}'' + 2 \frac{g_{11}^2 c_{12} - 2g_{11}g_{12}c_{11} + g_{12}^2(-c_{11} + 2c_{12})}{(c_{11} - c_{12})(c_{11} + 2c_{12})} - \frac{g_{44}^2}{c_{44}}. \end{aligned}\right\} \quad . \quad (9.5)$$

From (9.4) we can see that the strains are proportional to the square of the polarization as already stated.

In the temperature ranges where the crystal is respectively cubic, tetragonal, orthorhombic and rhombohedral equations (9.4) become

$$\left.\begin{array}{l} x_x = y_y = z_z = 0, \\ y_z = z_x = x_y = 0, \end{array}\right\} \quad (a)$$

$$\left.\begin{array}{l} x_x = y_y = P_z^2 \dfrac{g_{11}c_{12} - g_{12}c_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})}, \\[2mm] z_z = P_z^2 \dfrac{-g_{11}(c_{11} + c_{12}) + 2g_{12}c_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})}, \\[2mm] y_z = z_x = x_y = 0, \end{array}\right\} \quad (b)$$

$$\left.\begin{array}{l} x_x = P_z^2 \dfrac{2(g_{11}c_{12} - g_{12}c_{11})}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \\[2mm] y_y = z_z = P_z^2 \dfrac{-g_{11}c_{11} - g_{12}(c_{11} - 2c_{12})}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \\[2mm] z_x = x_y = 0, \qquad y_z = -g_{44}^2 P_z^2/c_{44}, \end{array}\right\} \quad (c)$$

$$\left.\begin{array}{l} x_x = y_y = z_z = P_z^2 \dfrac{-g_{11} - 2g_{12}}{c_{11} + 2c_{12}}, \\[2mm] y_z = z_x = x_y = -g_{44}P_z^2/c_{44}. \end{array}\right\} \quad (d)$$

$$\quad \cdots \quad (9.6)$$

From the observed strains and polarizations we can get some information about the constants. The most convenient quantity to use is the difference between the strains along the c and a-axes, that is $z_z - x_x$, which is given by

$$z_z - x_x = P_z^2(g_{12} - g_{11})/(c_{11} - c_{12}), \quad \cdots \quad (9.7)$$

in either the tetragonal or the orthorhombic region. This is about 0·01 at room temperature when P_z is about 16 microcoulombs. Hence we have

$$g_{12} - g_{11} = (c_{11} - c_{12}) \times 4 \times 10^{-12}. \quad \cdots \quad (9.8)$$

Similarly in the tetragonal region we have for the volume expansion

$$x_x + y_y + z_z = P_z^2(-g_{11} - 2g_{12})/(c_{11} + 2c_{12}). \quad \cdots \quad (9.9)$$

The volume expansion is more difficult to determine since we have to estimate the unstrained volume by extrapolation from the cubic region. However, we have approximately

$$-(g_{11} + 2g_{12}) = (c_{11} + 2c_{12}) \times 0·8 \times 10^{-12}. \quad \cdots \quad (9.10)$$

The shear y_z just below the second transition temperature is about 14′. Hence we have

$$-g_{44} = c_{44} \times 2·7 \times 10^{-12}. \quad \cdots \quad (9.11)$$

In the orthorhombic region we have

$$x_x + y_y + z_z = 2P_z^2(-g_{11} - 2g_{12})/(c_{11} + 2c_{12}). \quad \cdots \quad (9.12)$$

Hence in all regions the strains can be evaluated in terms of P_z^2 and the ratios $(g_{12} - g_{11})/(c_{11} - c_{12})$ and $(g_{11} + 2g_{12})/(c_{11} + 2c_{12})$ given empirically

by (9.8) and (9.10). The calculated strains are given in fig. 7. A term representing the thermal expansion is added so that the figure shows the total variation of axial length with temperature.

By considering the observed piezoelectric resonances Mason (1948) has been able to calculate the g's and c's independently for the ceramic. These quantities might, however, be very different for the single crystal, so we are not able to make use of his results.

Fig. 7.
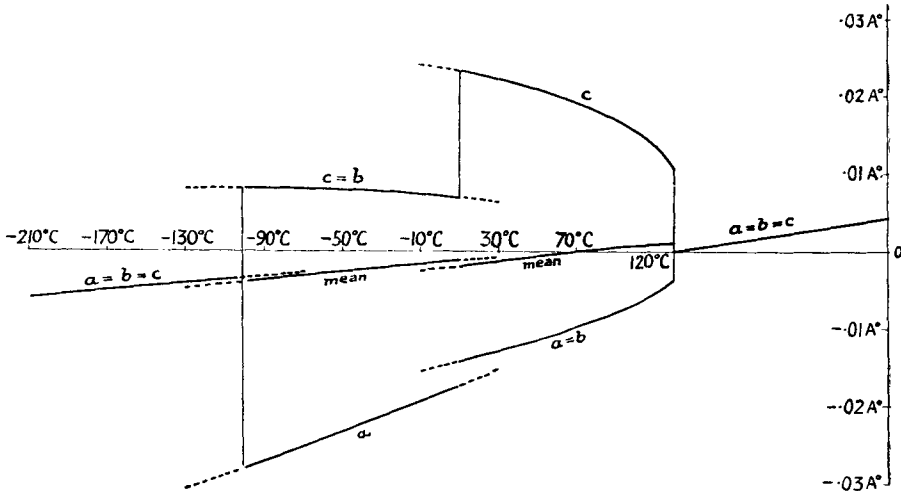
Lattice spacing of BaTiO$_3$ relative to spacing at 120° C. (theoretical).

§ 10. MODEL THEORY.

Our picture of barium titanate is that it is an ionic crystal, and we shall follow Born's treatment of such crystals as given by Fowler (1936). The ions are regarded as point centres of force, and the potential energy of two ions with charges ϵ_1 and ϵ_2 at a distance r apart is assumed to have the form

$$\epsilon_1\epsilon_2 r^{-1} - \mu r^{-6} + \lambda r^{-9}.$$

The second term represents the Van der Waals attraction, and the third term the repulsive forces. The potential energy of BaTiO$_3$ per unit cell is then given by the expression

$$\phi(R) = \frac{-49\cdot1\epsilon^2}{R} + \frac{3\cdot31(\lambda_{TT}+\lambda_{BB}+3\lambda_{OO})}{R^9} + \frac{8\cdot07\lambda_{BT}}{(2R/\sqrt{3})^9} + \frac{6\cdot07\lambda_{OT}}{(R/2)^9}$$

$$+ \frac{12\cdot30(\lambda_{OB}+\lambda_{OO})}{(R/\sqrt{2})^9} - \frac{4\cdot20(\mu_{TT}+\mu_{BB}+3\mu_{OO})}{R^6} - \frac{8\cdot71\mu_{BT}}{(2R/\sqrt{3})^6}$$

$$- \frac{6\cdot24\mu_{OT}}{(R/2)^6} - \frac{13\cdot29(\mu_{OB}+\mu_{OO})}{(R/\sqrt{2})^6}, \qquad \ldots \ldots \ldots \quad (10.1)$$

where we have assumed the unit cell to be cubic with an edge of length R,

and the charges on the Ba, Ti and O ions to be 2ϵ, 4ϵ and -2ϵ respectively, $-\epsilon$ being the electronic charge. The values of λ_{BB}, λ_{OO}, λ_{OB}, μ_{BB}, μ_{OB}, and μ_{OO} have been given by Fowler (1936). We have used his methods to estimate λ_{OT} and μ_{OT}, and the contributions of the terms containing λ_{TT}, λ_{BT}, μ_{TT} and μ_{BT} are negligible. The complete set of values used is given in Table I.

<div align="center">

TABLE I.

Force constants between ions in c.g.s. units.
</div>

λ_{BB}	$82{\cdot}7 \times 10^{-82}$	μ_{BB}	$239{\cdot}0 \times 10^{-60}$
λ_{OB}	$99{\cdot}0 \times 10^{-82}$	μ_{OB}	$162{\cdot}0 \times 10^{-60}$
λ_{OO}	$113{\cdot}5 \times 10^{-82}$	μ_{OO}	$135{\cdot}0 \times 10^{-60}$
λ_{OT}	$15{\cdot}6 \times 10^{-82}$	μ_{OT}	$31{\cdot}3 \times 10^{-60}$

If we choose R so that $\phi(R)$ is a minimum this will give us the side of the unit cell at zero temperature. Using the force constants from Table I. we find that R is 4·04 Å. as compared with the extrapolated observed value of 3·99 Å. This suggests that our force constants are reasonably accurate, and we can now use equation (10.1) to estimate the compressibility.

The change in potential energy of the unit cell when we alter R by a small amount ΔR is $\frac{1}{2}(\Delta R)^2 \phi''(R)$, and hence the change per unit volume is $\frac{1}{2}(\Delta R)^2 \phi''(R) R^{-3}$. But the change in free energy is

$$\tfrac{1}{2}c_{11}(x_x^2+y_y^2+z_z^2)+c_{12}(x_x y_y+y_y z_z+z_z x_x),$$

where

$$x_x=y_y=z_z=\Delta R/R.$$

If we neglect the difference between free and potential energy these two quantities can be equated, and we have

$$c_{11}+2c_{12}=\tfrac{1}{3}R^{-1}\phi''(R), \qquad \cdots \cdots \quad (10.2)$$

Putting in the values for the force constants from Table I. we have

$$c_{11}+2c_{12}=1{\cdot}2\times 10 \text{ dynes/cm.}^2. \qquad \cdots \cdots \quad (10.3)$$

As our assumption that the ions are point centres of force can only be a rough approximation to the truth we shall not attempt to calculate c_{11} and c_{12} separately but shall assume c_{11} to be equal to $2c_{12}$. This is equivalent to be taking Poisson's ratio to be $\frac{1}{3}$, which is not far from the value for most substances. This makes

$$\left.\begin{array}{l} c_{11}=6{\cdot}0\times 10^{12} \text{ dynes/cm}^2., \\ c_{12}=3{\cdot}0\times 10^{12} \text{ dynes/cm}^2., \end{array}\right\} \quad \cdots \cdots \quad (10.4)$$

and hence from (10.8) and 10.10),

$$\left.\begin{array}{ll} g_{11}+2g_{12}= & -\ 9{\cdot}6, \\ g_{11} & =-11{\cdot}2, \\ g_{12} & =-\ 0{\cdot}8. \end{array}\right\} \quad \cdots \cdots \cdots \quad (10.5)$$

If we assume central forces between the ions c_{44} should have the same value as c_{12}. This makes

$$g_{44} = -8.$$

Substituting the above values in equations (9.5) we get

$$\xi'_{11} = \xi''_{11} - 70 \times 10^{-12},$$

and

$$\xi'_{12} = \xi''_{12} + 26 \cdot 8 \times 10^{-12} - 21 \cdot 3 \times 10^{-12}$$
$$= \xi''_{12} + 5 \cdot 5 \times 10^{-12}.$$

Putting in the values of ξ'_1 and ξ'_{12} from (7.14) and (7.15) this gives

$$\left.\begin{array}{l} \xi''_{11} = -4 \cdot 4 \times 10^{-12} + 70 \times 10^{-12} = 65 \cdot 6 \times 10^{-12}, \\ \xi''_{12} = 5 \cdot 3 \times 10^{-12} - 5 \cdot 5 \times 10^{-12} = -0 \cdot 2 \times 10^{-12}. \end{array}\right\} \quad \text{. .} \quad (10.6)$$

We shall now examine the field in which each ion moves. We assume all the ions except one to be fixed, and then it is a straightforward matter to calculate the field in which that ion moves in terms of the force constants. If the ion is displaced a distance r from its symmetrical position then its potential energy can be expanded in the form

$$r^2 a(\theta, \phi) + r^4 b(\theta, \phi),$$

where θ and ϕ are polar coordinates referred to some suitable axis. For barium and titanium, which are symmetrically placed, a is independent of θ and ϕ and is given by

$$a_{\mathrm{B}} = 1 \cdot 2 \times 10^5 \text{ ergs/cm.}^2,$$
$$a_{\mathrm{T}} \quad 4 \cdot 7 \times 10^5 \text{ ergs·cm.}^2.$$

The contribution to a_{B} and a_{T} from the short range repulsive forces, which is positive, is several times larger than the contribution from the electrostatic and Van der Waal's forces. Thus a_{B} and a_{T} are bound to be positive. The case is different for the oxygen ion. This lies in a much less symmetrical field, and if we take the initial line to be the line joining the O ion to a neighbouring Ti ion we find that

$$a_{\mathrm{O}} = 0 \cdot 6 \times 10^5 [(7 \cdot 4 \cos^2 \theta + 4 \cdot 2 \sin^2 \theta) - \alpha R^{-3} 196 \cdot 4 (\cos^2 \theta + \tfrac{1}{4} \sin^2 \theta)] \text{ ergs/cm.}^2,$$

$$\text{. . . (10.7)}$$

where α is the polarizability of the oxygen ion, and R is the edge of the unit cell. The term in α is there because if the ion is displaced there will be an electrostatic field acting on it propoitional to its displacement. This will polarize the ion and there will be a lowing of potential energy proportional to the square of the displacement. There is no similar term for the barium or titanium ions because, owing to the symmetrical arrangement of the ions round them, the electrostatic field acting on a displaced ion is proportional to the cube of the displacement. Various values have been given for α. A value of about $2 \cdot 4 \times 10^{-24}$ gives the correct value for the refractive index of $CaTiO_3$, after allowing for the polarizability of the Ca and Ti ions. This value makes a_{O} about zero along $\theta = 0$, and positive for other directions. The value of α given above, however, is only a mean value and is likely to be different for different

directions since the oxygen ion must be very distorted. Hence we cannot predict with certainty whether a_0 will be always positive or may have negative values in certain directions. In the latter case, of course, the symmetrical position of the oxygen ion will be unstable, and there will be positions of equilibrium off centre. These are likely to be in the direction $\theta = 0$, that is, in the direction of the neighbouring Ti ions.

We must now consider the relation between the constants a, b, etc., and the free energy. This involves studying the thermal vibrations of the substance. We assume that the vibrations of each ion are independent. Let

$$a_x x^2 + a_y y^2 + a_z z^2 + b_{xx} x^4 + b_{yy} y^4 + b_{zz} z^4 + 2b_{yz} y^2 z^2 + 2b_{zx} z^2 x^2 + 2b_{xy} x^2 y^2$$

be the potential energy of an ion when displaced to a point (x, y, z) relative to the symmetrical position as origin, the substance being unpolarized. The above expression includes all terms of lower order than the sixth. The displaced ion is equivalent to a dipole which we assume to have components $(\gamma_x x, \gamma_y y, \gamma_z z)$ where the γ's are constants of the order of the ionic charge. Now if the substance is polarized there will be a force acting on the ion having components $(\beta P_x, \beta P_y, \beta P_z)$, where β is the Lorentz factor, and hence an additional term in the potential energy of magnitude

$$-\beta(\gamma_x x P_x + \gamma_y y P_y + \gamma_z z P_z).$$

Then the partition function f for a single ion is given by

$$f = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \{ [\beta\gamma_x x P_x + \ldots - a_x x^2 - \ldots - b_{xx} x^4 - \ldots$$

$$-2b_{yz} y^2 z^2 - \ldots]/kT \} dx\, dy\, dz. \quad . \quad . \quad . \quad (10.8)$$

We shall assume that bkT/a^2 is small. Then terms in b^2 can be neglected and we have

$$f = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left(1 - \frac{b_{xx} x^4 \ldots + 2b_{yz} y^2 z^2 + \ldots}{kT} \right)$$

$$\exp \left[\frac{\beta\gamma_x x P_x + \ldots - a_x x^2 - \ldots}{kT} \right] dx\, dy\, dz. \quad . \quad . \quad (10.9)$$

If we now put

$$x = \tfrac{1}{2}\beta\gamma_x P_x a_x^{-1} + x', \quad . \quad . \quad . \quad . \quad . \quad (10.10)$$

then

$$f = \exp \left\{ \frac{1}{4} \frac{\beta^2 \gamma_x^2 P_x^2}{a_x kT} + \ldots \right\}$$

$$\times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left\{ 1 - \frac{b_{xx}}{kT} \left(\frac{\beta^4 \gamma_x^4 P_x^4}{16 a_x^4} + \frac{3}{2} \frac{\beta^2 \gamma_x^2 P_x^2 x^2}{a_x^2} + x^4 \right) - \ldots \right.$$

$$\left. - \frac{2b_{yz}}{kT} \left(\frac{\beta^4 \gamma_y^2 \gamma_z^2 P_y^2 P_z^2}{16 a_y^2 a_z^2} + \frac{\beta^2 \gamma_y^2 P_y^2 z^2}{4 a_y^2} + \frac{\beta^2 \gamma_z^2 P_z^2 y^2}{4 a_z^2} + y^2 z^2 \right) \right\}$$

$$\times \exp \left\{ \frac{-a_x x^2 - \ldots}{kT} \right\} dx\, dy\, dz$$

$$= \frac{(\pi k\mathrm{T})^{3/2}}{(a_x a_y a_z)^{1/2}} \exp\left\{ \frac{1}{4}\frac{\beta^2 \gamma_x^2 \mathrm{P}_x^2}{a_x k\mathrm{T}} + \dots \right\}$$

$$\times \left\{ 1 - \frac{3}{4}\frac{b_{xx}k\mathrm{T}}{a_x^2} - \dots - \frac{1}{2}\frac{b_{yz}k\mathrm{T}}{a_y a_z} - \dots - \frac{3}{4}\frac{b_{xx}\beta^2\gamma_x^2\mathrm{P}_x^2}{a_x^3} - \dots \right.$$

$$- \tfrac{1}{4}b_{yz}\left(\frac{\beta^2\gamma_y^2\mathrm{P}_y^2}{a_y^2 a_z} + \frac{\beta^2\gamma_z^2\mathrm{P}_z^2}{a_y a_z^2} \right) - \dots - \frac{b_{xx}}{k\mathrm{T}}\frac{\beta^4\gamma_x^4\mathrm{P}_x^4}{16 a_x^4} - \dots$$

$$\left. - \frac{b_{yz}}{k\mathrm{T}}\frac{\beta^4\gamma_y^2\gamma_z^2\mathrm{P}_y^2\mathrm{P}_z^2}{8 a_y^2 a_z^2} - \dots \right\}. \qquad \dots \dots \dots \dots \dots \quad (10.11)$$

The free energy per unit volume is given by

$$A = -N k\mathrm{T}\Sigma \log f + \tfrac{1}{2}\beta(\mathrm{P}_x^2 + \mathrm{P}_y^2 + \mathrm{P}_z^2), \qquad \dots \quad (10.12)$$

where N is the number of unit cells per unit volume, and the summation is over the different ions in the unit cell. The term in P^2 arises because in summing over the unit cells we have reckoned twice over the equilibrium potential energy of the ions, which is $-\tfrac{1}{2}\beta(\mathrm{P}_x^2 + \mathrm{P}_y^2 + \mathrm{P}_z^2)$. Hence we have

$$A = N\Sigma\left[-\tfrac{1}{2}k\mathrm{T}\log\frac{(\pi k\mathrm{T})^3}{a_x a_y a_z} + (k\mathrm{T})^2\left(\tfrac{3}{4}\frac{b_{xx}}{a_x^2} + \dots + \tfrac{1}{2}\frac{b_{yz}}{a_y a_z} + \dots \right) \right]$$

$$+ \mathrm{P}_x^2\left[\tfrac{1}{2}\beta - \tfrac{1}{4}N\beta^2\Sigma\left(\frac{\gamma_x^2}{a_x} - 3k\mathrm{T}\frac{b_{xx}\gamma_x^2}{a_x^3} - k\mathrm{T}\frac{b_{xy}\gamma_x^2}{a_x a_y} - k\mathrm{T}\frac{b_{xz}\gamma_x^2}{a_x^2 a_z} \right) \right] + \dots$$

$$+ \mathrm{P}_x^4 N\beta^4\Sigma\frac{b_{xx}\gamma_x^4}{a_x^4} + \dots + \mathrm{P}_y^2\mathrm{P}_z^2 N\beta^4\Sigma\frac{b_{yz}\gamma_y^2\gamma_z^2}{a_y^2 a_z^2} + \dots \dots \dots \quad (10.13)$$

If we compare this expression with equation (9.1) we have

$$\chi'' = \beta - \tfrac{1}{2}N\beta^2\Sigma\left\{ \frac{\gamma_x^2}{a_x} - \frac{k\mathrm{T}\gamma_x^2}{a_x^2}\left(3\frac{b_{xx}}{a_x} + \frac{b_{xy}}{a_y} + \frac{b_{xz}}{a_z} \right) \right\}, \quad \dots \quad (10.14)$$

$$\xi'_{11} = \frac{N\beta^4}{4}\Sigma\frac{b_{xx}\gamma_x^4}{a_x^4}, \qquad \dots \dots \dots \dots \quad (10.15)$$

$$\xi'_{12} = \frac{N\beta^4}{4}\Sigma\frac{b_{xy}\gamma_y^2\gamma_z^2}{a_z^4}. \qquad \dots \dots \dots \quad (10.16)$$

As before, the summation is over the different ions in the unit cell, and when this summation is carried out the quantities involved will be the same for all axes (or pairs of axes) owing to the crystal symmetry. It is possible to make rough estimates of the b's and a's in terms of the force constants in the way already described, and we find that the term involving T in (10.14) is small compared with the other terms at constant temperatures. Now we have already found that χ'' has to vanish at a temperature T_0, so that approximately

$$1 = \tfrac{1}{2}N\beta\Sigma\frac{\gamma_x^2}{a_x}. \qquad \dots \dots \dots \dots \quad (10.17)$$

Now from (9.1) we see that the coefficients g_{11} and g_{12} measure the variation of $\tfrac{1}{2}\chi''$ with strain. Now as we have already stated the third

term in χ'' is small and β, being the Lorentz factor, will not depend much on strain, and hence we have approximately

$$g_{11} = \tfrac{1}{4}N\beta^2 \Sigma \frac{\gamma_x^2}{a_x} \frac{\partial}{\partial x_x} \log\left(\frac{a_x}{\gamma_x^2}\right), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10.18)$$

and

$$g_{12} = \tfrac{1}{4}N\beta^2 \Sigma \frac{\gamma_x^2}{a_x} \frac{\partial}{\partial y_y} \log\left(\frac{a_x}{\gamma_x^2}\right). \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10.19)$$

Hence $\quad g_{11} + 2g_{12} = \tfrac{1}{4}N\beta^2 \Sigma \frac{\gamma_x^2}{a_x}\left(\frac{\partial}{\partial x_x} + \frac{\partial}{\partial y_y} + \frac{\partial}{\partial z_z}\right) \log\left(\frac{a_x}{\gamma_x^2}\right), \quad \cdot \quad (10.20)$

where R is the side of the unit cell. Now a_x decreases as about the tenth power of R, and γ_x will not vary much with R. Hence from (10.20) and (10.17) we have

$$g_{11} + 2g_{12} \approx -5\beta \approx -20, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10.21)$$

if we take β, the Lorentz factor, to have the value $4\pi/3$. This differs from the value given in (10.5) by a factor of 2. In view of the approximate nature of both calculations this is however, not surprising. From (10.19) we see that the small value of g_{12} given in (10·5) means that a_x is little changed by a strain in the y-direction. This is what we should expect. Again we found that χ'' was given by an equation of the form

$$\chi'' = \chi' = \chi_0'(\mathrm{T} - \mathrm{T}_0)/(\mathrm{T}_1 - \mathrm{T}_0),$$

under conditions of zero stress, that is $\chi_0'/(\mathrm{T}_1 - \mathrm{T}_0)$ is the rate of variation of χ'' with temperature, when the stress is zero. Hence

$$\frac{\chi_0'}{\mathrm{T} - \mathrm{T}_0} = \frac{\partial \chi''}{\partial \mathrm{T}} + g_{11}\frac{dx_x}{d\mathrm{T}} + g_{12}\left(\frac{dy_y}{d\mathrm{T}} + \frac{dz_z}{d\mathrm{T}}\right)$$

$$= \frac{\partial \chi''}{\partial \mathrm{T}} + \alpha(g_{11} + 2g_{12}), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10.22)$$

where α is the coefficient of thermal expansion and the partial differentiation with respect to T is for constant strain. This follows because g_{11} and g_{12} give the variation with strain. Hence from (11.14) it follows that

$$\frac{\chi_0'}{\mathrm{T}_1 - \mathrm{T}_0} = \tfrac{1}{2}N\beta^2 k\Sigma \frac{\gamma_x^2}{a_x^2}\left(\frac{3b_{xx}}{a_x} + \frac{b_{xy}}{a_y} + \frac{b_{xz}}{a_z}\right) + \alpha(g_{11} + 2g_{12}). \quad (10.23)$$

The thermal expansion coefficient α can be obtained from the X-ray data above the highest transition temperature and is about 10^{-5}. Hence, since $g_{11} + 2g_{12}$ is approximately -10, the value of $\alpha(g_{11} + 2g_{12})$ is approximately -10^{-4}, and since the left-hand side is 10^{-4} the first term on the right-hand side must be 2×10^{-4}. It can be verified that it is of this order. Physically the whole expression in (10.23) gives the rate of decrease of polarizability with temperature. The second term gives the indirect effect of temperature change through the medium of lattice expansion. It corresponds to an increase in polarizability, as is physically obvious since lattice expansion must allow the ions to move more easily. The first term gives the direct effect of thermal vibrations. We see that they cause the polarizability to decrease, and this term is comparable with, though larger than, the other.

This work is part of a project carried out with the financial assistance of the Electrical Research Association, and is published with their permission.

REFERENCES.

BLATTNER, KANZIG, and MERZ, 1949, *Helv. Phys. Acta*, **22**, 35.
CADY, *Piezoelectricity* (New York : McGraw-Hill & Co.).
FOWLER, 1936, *Statistical Mechanics* (2nd ed.), (Oxford : University Press).
GINSBERG, 1946, *J. Phys. U.S.S.R.*, **10**, 107.
HARWOOD, POPPER, and RUSHMAN, 1947, *Nature*, **160**, 59.
HULM, 1947, *Nature*, **160**, 127.
KAY, 1948, *Acta Cryst*, **1**, 229.
KAY, VOUSDEN, and WELLARD, 1949, *Nature*, **163**, 637.
JACKSON, and REDDISH, 1945, *Nature*, **156**, 717.
MASON, 1948, *Phys. Rev.*, **74**, 1134.
MASON, and MATTHIAS, 1948, *Phys. Rev.*, **74**, 1622.
MATTHIAS, and VON HIPPEL, 1948, *Phys. Rev.*, **73**, 1378.
MEGAW, 1946, *Trans. Faraday Soc.*, **42A**, 224.
MERZ, 1949, *Phys. Rev.*, **75**, 687.
MUELLER, 1940, *Phys. Rev.*, **57**, 829 ; **58**, 565, 805.
RUSHMAN, and STRIVENS, 1946, *Trans. Faraday Soc.*, **42A**, 231.
VON HIPPEL, BROCKENRIDGE, CHELSEY, and TISZA, 1946, *Ind. & Eng. Chem.*, **38**, 1097.
WÜL, 1946, *J. Phys. U.S.S.R.*, **10**, 95.

XCVII. *Theory of the High Pressure Helium Discharge.*

By V. J. FRANCIS, B.Sc., F.Inst.P., M.I.E.E., A.R.C.S.

(Communication from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England.)

SUMMARY.

The method developed in recent papers for calculating the characteristics of the high pressure discharge is extended to helium. The properties of the helium discharge derived in this way are compared with those of high pressure mercury vapour, and it is shown that a loading of the order of 10^4 watts per cm. of arc is required in the former to produce conditions usually associated with the normal operation of the high pressure mercury vapour discharge at 10 to 100 watts per cm. of arc.

---

§1. INTRODUCTION.

IN some recent papers a method has been developed for calculating approximately the properties of the high pressure discharge (Francis 1946 a, b, 1949). The nomenclature and symbols employed in these publications are used also in the present paper. The method is approximate only since it is assumed (*a*) that all the energy is evolved within a certain radius r_1 of the discharge column and that over that area it is uniformly distributed. The radius r_1, is, of course, a function of the operating conditions of the discharge. It is assumed also that (*b*) heat losses from