# FERROELECTRICITY

By E. T. JAYNES

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1. FERROELECTRICITY

By E. T. Jaynes

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# PREFACE

This monograph is an extensive revision of a doctoral thesis presented to the Department of Physics of Princeton University in 1950. Numerous errors in the original version have been corrected, detailed calculations have been shortened, and an attempt has been made to bring the discussion up to date. New experimental work has made desirable a change of emphasis in the discussion of theories, and a few ways of improving theoretical treatments are described, although they have not yet been well explored.

In its present form, the work is intended to serve as a general introduction to the subject of ferroelectricity and guide to the literature, with review of various theories of $BaTiO_3$ that have been published, rather than as an exposition of any particular theory. However, the electronic theory developed by the writer is treated in more detail than the others because no other easily available account of it has been published. On the theoretical side, the arrangement of subject matter is not as systematic as would be possible since the various methods are developed as, and to the extent that, they are needed for interpretation of experimental facts. Thus, discussions of thermodynamic properties and internal fields are distributed over several nonconsecutive sections. This may make the work slightly more difficult to use for reference, but for the person who wishes an introduction to the subject there are pedagogical advantages. Since rapid advances are still being made, this work must also be considered as an interim report, with few firm conclusions reached.

# PREFACE

Numerous details have been omitted for brevity, but extensive references to the literature are given. Although the bibliography is long and is believed to be reasonably complete to December 1951, no attempt has been made to include everything that has been written on the subject. The extent of current interest may be judged by the fact that over fifty new references have been added in the last eighteen months.

Thanks are due to Professor E. P. Wigner, who has given valuable advice on all sections of the original thesis and the present revision. Responsibility for statements and conclusions, however, rests entirely with the author.

E. T. Jaynes

Stanford University
February 1952

# NOTE TO FERROELECTRICITY

By E. T. Jaynes

Experimental work since this book was first published has led to some important changes in our knowledge of the behavior of Barium Titanate. This is largely due to the successful production of larger and better crystals than were previously available. Although these new crystals contain impurities which are deliberately introduced to aid the growth process, it is highly probable that the changes in observed behavior are not due to impurities but to the fact that much more perfect crystals result, with a simpler domain structure.

Merz* reports that the observed spontaneous polarization is now considerably higher than was found before, as high as 26 microcoulombs $cm^{-2}$ as against 15.5 as shown in Fig. 1.4. The coercive force is much lower than the value quoted on p. 23; values as low as 500 volts $cm^{-1}$ are reported with the new crystals. Both these changes would be expected as a result of the better domain alignment.

Another important change concerns the order of the transition at the Curie point. As explained in the text, one obtains information about this from the polarization as a function of temperature, existence of thermal hysteresis at the transition, the specific heat anomaly, and the type of dielectric nonlinearity observed just above the Curie point. Experiments and thermodynamic arguments quoted in the text indicate a second-order transition, but other experimental results have sometimes conflicted with these. Merz finds that the new crystals exhibit a sharp rise in polarization at the Curie point, and an upward curvature for the D - E curve just above the Curie point (loc. cit. Fig. 1). The existence of this upward curvature now makes it possible to have a consistent thermodynamic treatment of the type discussed in Chap. 3 even though the transition is first-order. These new results bring the thermodynamic theory into line with experiment in a much more satisfactory way than previously.

E. T. Jaynes

Sept. 1953

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* Phys. Rev. 91, 513 (1953)

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# FERROELECTRICITY

# 1. HISTORICAL INTRODUCTION AND REVIEW OF EXPERIMENTAL FACTS

## 1.0 Rochelle salt

The phenomenon of ferroelectricity is of comparatively recent discovery. In 1917, while investigating the piezoelectric properties of Rochelle salt[1], A. M. Nicolson, J. A. Anderson (A2), and W. G Cady (C4) noted certain anomalies in dielectric behavior, significant among which were the existence of hysteresis between applied electric field and polarization, and a sudden change in the piezoelectric activity at 23°C, now recognized as the first observation of a ferroelectric Curie point.

A few years later the physical properties of Rochelle salt were described in detail in a series of papers by J. Valasek (V3) in which the analogy between the dielectric properties of Rochelle salt and ferromagnetism was stressed. Beginning about 1929, Shulvas-Sorokina and I. Kurchatov (K2) in Russia made numerous contributions to the subject, and more recently it has been studied both experimentally and theoretically by Scherrer, Busch, and collaborators in Zurich, Fowler (F2) in England, and H. Mueller (M8) and W. P. Mason (M13) in the United States.

The experimental facts about Rochelle salt are, briefly, as follows. For electric fields in the crystallographic yz-plane, the dielectric properties are normal at all temperatures. For fields in the x-direction,

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[1] Sodium potassium tartrate tetrahydrate, $(COONa)(CHOH)_2(COOK) \cdot 4H_2O$. This salt forms orthorhombic crystals of class $D_2$ which distort to monoclinic in the ferroelectric range.

however, the susceptibility follows a Curie-Weiss law above $23^{\circ}C$, given by

$$\chi = \frac{C}{T - T_c} \tag{1.01}$$

with the Curie constant $C = 178^{\circ}K$ and $T_c = 23^{\circ}C$. Between $-18^{\circ}C$ and $23^{\circ}C$ there is a spontaneous electric polarization of the order of 0.2 microcoulomb/$cm^2$, or 600 esu, in the x-direction, and in strong alternating fields the relation between displacement and applied field is described by hysteresis loops similar to the B-H curves of ferromagnetic materials, with a coercive force of the order of 100 volts/cm. Below $-18^{\circ}C$, the spontaneous polarization disappears, and from here down to about $-150^{\circ}C$, the susceptibility follows another Curie-Weiss law

$$\chi = \frac{C}{T_c - T} \tag{1.02}$$

with $T_c = -18^{\circ}C$, $C = 93.8^{\circ}K$.

Except for the existence of two Curie points, this behavior is so strongly reminiscent of ferromagnetism that it was natural to try to account for it by a theory built in the image of the classical Langevin-Weiss theory of ferromagnetism. This was attempted by Kobeko and Kurchatov (K1) and by Fowler (F2), using a molecular model in which the $H_2O$ molecules form rotating dipoles, with moments of the order of $10^{-18}$ esu. These theories were deficient in several respects. One was that the effect of piezoelectric interaction, which greatly modifies the behavior of the crystal, was ignored. Secondly, the structure of Rochelle salt had not yet been determined (an X-ray structure analysis was first accomplished by Beevers and Hughes (B1) in 1941), and for this and other reasons the interaction of the dipoles could not be calculated. In this early work the internal field F effective in orienting the dipoles was assumed equal to

$$F = E + \mathscr{P} P, \tag{1.03}$$

where $E$ is the applied field, $P$ is the total polarization, and $\beta$ is a constant, called the Lorentz factor. Lorentz (L1) showed that, neglecting quadrupole and higher moments, an array of point dipoles in a simple cubic lattice, or a random array, with equal dipole moments, leads to the value $\beta = 4\pi/3$, but this value could be greatly different for other structures.

It is easily shown from statistical mechanics that the polarizability of a freely rotating dipole of moment $\mu$, in equilibrium with its surroundings at temperature $T$, is

$$\alpha = \frac{\mu^2}{3kT}, \tag{1.04}$$

so that the polarization in a medium with $N$ dipoles per unit volume is

$$P = N\alpha F = \frac{N\mu^2}{3kT}(E + \beta P).$$

From this we find the susceptibility at high temperatures is given by a Curie-Weiss law

$$\chi = \frac{P}{E} = \frac{N\alpha}{1 - \beta N\alpha} = \frac{1}{\beta}\frac{T_c}{T - T_c}, \tag{1.05}$$

where $T_c = N\mu^2/3k$. When $T < T_c$, we have $\beta N\alpha > 1$, and this relation breaks down. Spontaneous polarization whose magnitude is not determined by the above linear relations can then exist. We see that this argument, which is a greatly simplified form of the early theories, gives the germ of a theory of ferroelectric behavior, but unfortunately one must reject it after a little further study because in fact the internal field has not been taken into account correctly. Since this problem, which lies at the root of many present difficulties in the theory of dielectric properties, has been the subject of some controversy and much misunderstanding, we digress at this point to consider the general problem of internal fields.

## 1.1 Internal fields

The value $\beta = 4\pi/3$ associated with the name of Lorentz corresponds to a random or simple cubic array of point dipoles, plus the physical assumption that each dipole has the same constant moment; indeed, under these conditions Eq. (1.03) gives the rigorously correct value for the total field at the position of one dipole that is produced by all the other dipoles. The Lorentz value is therefore unquestionably the proper one to use in treating a classical model in which polarization is produced by distortion of the ions, each of which remains in a fixed position with no disturbing effects of thermal agitation. Under these conditions, it likewise gives a formally correct value for the internal field when the molecules have a permanent dipole moment. However, this case is without physical interest because in the absence of thermal agitation each permanent dipole will be perfectly aligned with any field, however weak, and we would have the saturation polarization at any field strength; the treatment of dielectric properties arising from permanent dipoles is in principle impossible without consideration of the statistical problem of thermal agitation.

The fact that the validity of the Lorentz value of the internal field must be reexamined when thermal agitation effects are taken into account is easily seen in the case of permanent dipoles. There are two effects that must be considered. In the first place, as was mentioned above, the Lorentz field $4\pi P/3$ is the field at a dipole due to all the other dipoles when all the others are pointing in the same direction. Now let us vary the orientation of dipole A. If it is inclined at an angle $\theta$ to the net polarization direction P, its contribution to P will be proportional to $\cos\theta$, a spherical harmonic of order 1, while each component of its contribution to the field acting on dipole B will vary with its orientation

according to a spherical harmonic of order 2. Thus, in general, there is no longer the same relation between the mean contribution of a dipole to the polarization and the mean value of the field which it produces at other dipoles, and the Lorentz field will be the correct one only when certain symmetry conditions are imposed on the distribution of dipoles in space and on the distribution of orientations of each dipole. This effect exists for dipoles at any distance apart.

The second effect arises from the existence of strong correlations between the orientation of dipoles that are close together. Suppose that initally all dipoles are aligned in the same direction, and then dipole A is rotated to a new position (Fig. 1.1). The field which it

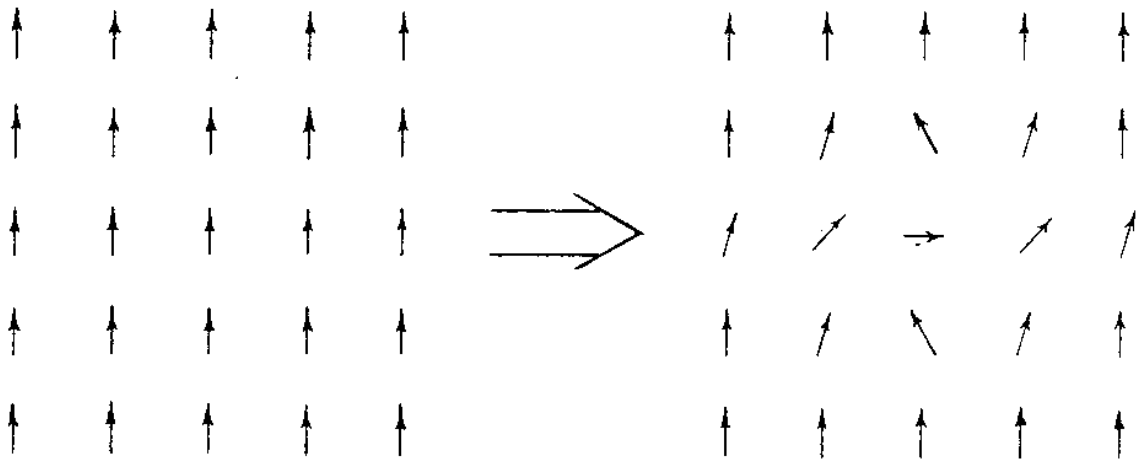

FIG. 1.1

produces at a neighboring dipole is very strong, so its neighbors will also tend to rotate out of their initial positions. As a result of this local distortion of the pattern, the field seen by dipole A is in turn altered; the torque tending to restore it to its original position is different from what it would be if the neighboring dipoles were held fixed. That this effect must always decrease the torque is easily seen as follows. Suppose

that first we rotate dipole A, holding all others fixed. This requires an amount of work $W_1$, determined correctly by the Lorentz field. Then, while holding dipole A fixed, we release the others and allow them to settle into new equilibrium orientations. During the process they can be made to do work $W_2$, and they take up new orientations. Now if we allow dipole A to return slowly to its original orientation, the neighboring ones adjusting themselves continuously to the change, we must get back an amount of work $W_3 = W_1 - W_2 < W_1$, so that when the other dipoles are allowed to adjust themselves freely to changes in orientation of dipole A, the torque on it must always decrease, and the effective field orienting a dipole is less than the Lorentz value. This reasoning also applies to the case where the dipoles are disturbed by thermal agitation, the mean positions of neighboring dipoles dpending on the momentary orientation of dipole A. We also see that the maximum decrease of torque occurs only for slow rotations, since the neighboring dipoles require a finite time to readjust themselves, and that a proper treatment of this point must include relaxation effects.

This correlation effect has been taken into account in first approximation by Onsager (01), using the device of replacing the surrounding dipoles by a homogeneous dielectric material. The dipole under consideration is supposed to be located in a spherical cavity excavated in this dielectric material, the dipole being replaced by a uniformly and permanently polarized sphere which can rotate freely. The field existing in the neighborhood of this sphere is then formed from the superposition of a stationary part due to an externally applied field and a part that rotates with the dipole. Each of these partial fields is found from the solution of a simple boundary-value problem. When the dipole is aligned with the external field and its polarization is equal to that at a large distance in the dielectric medium, the superposition gives again a uniform

field at all points. If the dipole is rotated $90^{\circ}$, the field is distorted to a pattern which corresponds to the distortion pattern of the elementary dipoles in Fig. 1.1.

The torque acting on the rotating sphere in the Onsager model may be calculated from the Maxwell stress tensor due to the fields surrounding the sphere. This tedious but straightforward calculation gives the same result as would be obtained in the case of a dipole of moment $M = 4\pi a^3 P/3$ in a field

$$F = \frac{3\epsilon E}{2\epsilon + 1},$$

where $E$ is the externally applied field and $\epsilon$ is the dielectric constant of the medium. $F$ is the same as the field that would exist in the spherical cavity if the material inside it were removed, and is called the Onsager field. By writing it in the form

$$F = E + \frac{4\pi P}{2\epsilon + 1}$$

where $P$ is the polarization in the external medium, we see that the internal field is still given formally by an expression of the form $F = E + \beta P$, with the difference that the Lorentz factor no longer has the constant value $4\pi/3$, but is a function of the dielectric constant: $\beta = 4\pi/(2\epsilon + 1)$. The Onsager field is always less than the Lorentz field, in agreement with our previous conclusions. In the Onsager model, this weakening is just that due to the fact that the field tends to avoid a cavity in a dielectric medium. It has the consequence of preventing the occurrence of spontaneous polarization; the Onsager model leads to the following expression for the dielectric constant of an assembly of dipoles:

$$\epsilon = 1 + \frac{3}{4}\left\{4\pi N\alpha - 1 + \left(1 + 8\pi N\frac{\alpha}{3} + 16\pi^2 N^2 \alpha^2\right)^{1/2}\right\}, \quad (1.13)$$

where $\alpha = \mu^2/3kT$ is the polarizability of each dipole. Thus, $\epsilon$ cannot become infinite at any finite temperature.

On the other hand, the use of the Lorentz field (which, as we have seen, is illegitimate in the case of rotating permanent dipoles), would lead to the Clausius-Mosotti equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} N\alpha$$

which implies ferroelectricity when $(4\pi/3)N\alpha > 1$, a relation that is satisfied well above the boiling point of many polar liquids (D2). It is this failure, or rather misuse, of the Lorentz formula (called the "$4\pi/3$ catastrophe") which led to the Onsager model, which is in fair, but by no means complete, agreement with experiment.

The Onsager model has the positive virtue of giving a simple definite value for the internal field which can be used in further calculations. Its chief disadvantage from the present point of view is that the model is such an extreme idealization of the actual physical situation that it is very difficult to determine the conditions for its validity, or to make further refinements without abandoning the model entirely and returning to the picture of dipoles as in Fig. 1.1. One small refinement that could be made on the model is to introduce a relaxation time in the external dielectric. Such a generalized model would include both the Lorentz field and the Onsager field as special cases in the limit of very long and very short relaxation times respectively. We see that the true effective field in the case of rotating dipoles lies somewhere between these two extremes, and, since one of them predicts ferroelectricity while the other does not, it remains an open question whether a model based on freely rotating dipoles can lead to spontaneous polarization at low temperatures. Van Vleck (V1) has adduced strong arguments that the answer is in the negative, and Luttinger and Tisza (L2) have proved this for a number of simple cubic lattices. Luttinger and Tisza find that the lowest energy state for such a lattice is one in which alternate strings of dipoles

are oriented in opposite directions. This arrangement gives no macroscopic polarization, and the pheomenon of such a pattern "freezing in" is called antiferroelectricity (K4). It may be expected to occur in more substances than does ferroelectricity, but it is hard to detect experimentally. Tungsten trioxide (K4) and lead zirconate (S7, R8) are believed to be antiferroelectric.

Ferromagnetism is, of course, based on a different type of interaction between dipoles, which is independent of the angle between the direction of the dipoles and the line through their centers.

Other internal field discussions have been given by Fröhlich (F5), Oster (O2), and Kirkwood (K7).

## 1.2 The interaction theory of Mueller

The above considerations, plus the fact that we have no independent evidence that movable dipoles actually exist in Rochelle salt, lead one to conclude that the movable dipole theory is far from being a convincing model to explain its properties, and these early attempts have been almost forgotten. A less ambitious, but more successful, undertaking is the correlation of its properties in terms of a phenomenological thermodynamic treatment. Following a suggestion of Cady (C1) stressing the importance of piezoelectric effect in determining the behavior of Rochelle salt, H. Mueller (M8) has developed in rather complete form his "interaction theory." Granted the validity of thermodynamics, the ultimate success of any such phenomenological theory is of course guaranteed from the start, regardless of the facts to be accounted for. However, a phenomenological theory is of great value in disclosing what thermodynamic properties are needed in order to account for the facts, and therefore what features are to be looked for in some future successful model. For example, Mueller shows that there is a profound difference between the behavior of a crystal which is free to distort under the action of applied electrical and mechanical

stresses and one in which the lattice is held rigidly fixed. Theoretical models of the type discussed describe the latter case, of the "clamped" crystal, while experiments are generally performed on "free" crystals. Mueller shows that the piezoelectric interaction, which in Rochelle salt consists of a strong coupling between the polarization $P_x$ and the shear $e_{yz}$, is great enough to account for ferroelectric behavior in the free crystal even when the clamped crystal has no such properties; the effect of clamping the crystal is found both theoretically and experimentally to cause the two Curie points to come together, and with perfectly rigid clamping they would coalesce and disappear. This makes a very great and unexpected difference in the features to be looked for in a future model. The situation is analogous to that existing between the theoretically simple specific heat of a solid $C_v$ and the experimentally simple one $C_p$, but the difference in the case of Rochelle salt cannot be considered as a small correction.

The basic idea of the interaction theory can be explained by the following argument, which is a generalization of Mueller's.[2] Define a thermodynamic potential which is a quadratic form in the strains $(x_1 \ldots x_6)$ and the polarization components $(P_1 \ldots P_3)$ of the crystal:

$$F(x,P) = \frac{1}{2} \sum C_{ij} x_i x_j + \sum P_i f_{ij} x_j + \frac{1}{2} \sum w_{ij} P_i P_j$$

Then the stresses $(X_1 \ldots X_6)$ and the electric field components $(E_1, E_2, E_3)$ are given by

$$-X_i = \frac{\partial F}{\partial x_i} = \sum_j C_{ij} x_j + \sum_j P_j f_{ji};$$

$$E_i = \frac{\partial F}{\partial P_i} = \sum_j f_{ij} x_j + \sum_j w_{ij} P_j$$

[2] See also W. L. Bond (B9); L. Tisza (T?).

This may be written in matrix form:

$$\begin{pmatrix} -X_1 \\ \vdots \\ -X_6 \\ \hline E_1 \\ \vdots \\ E_3 \end{pmatrix} = \left(\begin{array}{ccc|ccc} C_{11} & \cdots & C_{16} & f_{11} & \cdots & f_{31} \\ \vdots & & \vdots & \vdots & & \vdots \\ C_{61} & \cdots & C_{66} & f_{16} & \cdots & f_{36} \\ \hline f_{11} & \cdots & f_{16} & w_{11} & \cdots & w_{13} \\ \vdots & & \vdots & \vdots & & \vdots \\ f_{31} & \cdots & f_{36} & w_{31} & \cdots & w_{33} \end{array}\right) \begin{pmatrix} x_1 \\ \vdots \\ x_6 \\ \hline P_1 \\ \vdots \\ P_3 \end{pmatrix}$$

or more compactly, as

$$\begin{pmatrix} -X \\ E \end{pmatrix} = \begin{pmatrix} C & \tilde{f} \\ f & w \end{pmatrix} \begin{pmatrix} x \\ P \end{pmatrix} \qquad (1.21)$$

where $\tilde{f}_{ij} = f_{ji}$. By finding the reciprocal of this matrix, we can solve for $(x,P)$:

$$\begin{pmatrix} x \\ P \end{pmatrix} = \begin{pmatrix} S & -\tilde{d} \\ -d & k' \end{pmatrix} \begin{pmatrix} -X \\ E \end{pmatrix} \qquad (1.22)$$

in which the submatrices are related by

$$CS - \tilde{f}d = 1, \quad -C\tilde{d} + \tilde{f}k = 0, \quad fs - wd = 0, \quad -f\tilde{d} + wk' = 1.$$

We see that the susceptibility matrix for a free crystal $(X = 0)$ is $k'$ while for the clamped crystal $(x = 0)$ it is $k = w^{-1}$. These quantities are related by

$$k' = w^{-1}(1 + f\tilde{d}) = k + eS\tilde{e},$$

where we have defined a new set of piezoelectric constants $e_{ij}$ by

$$e = dS^{-1} = kf; \quad d = eS.$$

The quantities $e_{ij}$ were originally designated by Voigt as "the" piezoelectric constants, but it is now believed (M12, C2) that the $f_{ik}$ are more fundamental because the variables $x,P$ are most simply related to the internal state of the crystal, and experiment shows the $f_{ik}$ to be more nearly independent of temperature than the $d_{ik}$ or the $e_{ik}$.

The free susceptibility is always greater than the clamped susceptibility in the sense that the difference $k' - k = e\tilde{S}\tilde{e}$ is a positive semidefinite matrix. To prove this, we note first that $S$ is positive definite since, if $\sum X_i^2 > 0$, the elastic energy stored in the crystal corresponding to the strains $X_i$ is just the quadratic form

$$\sum_{ij} \frac{1}{2} S_{ij} X_i X_j > 0 .$$

If now we write $X_i = \sum_j \tilde{e}_{ij} Y_j$, where the $Y_j$ are arbitrary, we have

$$0 \leq \frac{1}{2} \sum_{ij} S_{ij} X_i X_j = \frac{1}{2} \sum_{ijks} S_{ij} \tilde{e}_{ik} Y_k \tilde{e}_{js} Y_s = \frac{1}{2} \sum_{ks} (e\tilde{S}\tilde{e})_{ks} Y_k Y_s ,$$

which is the condition for $(e\tilde{S}\tilde{e})$ to be positive semidefinite (we must use the inequality sign $\leq$ since the $X_i$ may now all be zero for certain chcices of $e_{ij}$ and $Y_j$).

If the piezoelectric interaction does not alter the principal directions of the susceptibility matrix, we have the result that each principal susceptibility of the free crystal is equal to or greater than the corresponding principal susceptibility of the clamped crystal.

From Eqs. (1.21), (1.22) we see that ferroelectric behavior is possible if the matrix

$$\begin{pmatrix} C & \tilde{f} \\ f & w \end{pmatrix}$$

becomes singular. In the case of Rochelle salt, the only important quantities are $C_{44}$ (the y-z shear modulus), $f_{14}$ (the piezoelectric coupling constant between polarization in the x-direction and shear in the y-z plane), and $w_{11}$, (the reciprocal of the clamped susceptibility in the x-direction). The condition for ferroelectricity then becomes

$$C_{44} w_{11} - f_{14}^2 \leq 0. \tag{1.23}$$

The fact that this condition may be satisfied

"accidentally" without any anomalous values for $C_{44}, f_{14}, w_{11}$ explains the name "interaction theory." Mueller shows that $C_{44}$ and $f_{14}$ exhibit no anomalies, and have values not greatly different from those of other crystals, and that $w_{11}$ goes thru a minimum near $0^{\circ}C$. At that temperature it is very small, but probably does not vanish. The two Curie points then appear as the temperatures at which Eq. (1.23) is satisfied, there being no anomalies in any of the fundamental constants at those temperatures. Between the Curie points there is spontaneous polarization accompanied by spontaneous deformation of the lattice. The magnitude of these effects is determined only when the thermodynamic potential $F(x,P)$ is augmented by terms proportional to $P^4$, and Mueller shows that these lead to a fairly accurate account of the observed properties.

The success of the interaction theory still leaves the question of the mechanism responsible for the behavior of Rochelle salt untouched. The rotating dipole theories first proposed can hardly be accepted today. Mason (M13) has given a theory in which movable hydrogen bonds undergo an order-disorder transition at the upper Curie point, and Ubbelhode and Woodward (U1) have discussed such bonds further. There are two objections to this theory. In the first place, the model would predict a large entropy change and therefore a large specific heat anomaly at this temperature. The observed anomaly is extremely small, and for thermodynamic reasons to be explained in Chapter 3, this means that the model cannot be made to give simultaneously the correct magnitude of polarization in the ferroelectric range and the correct Curie constant for the dielectric constant outside the ferroelectric range. Secondly, Matthias (M19) has stressed the importance of experiments in which the effect of substitution of one atom for another similar one is sought. It is found that replacement of hydrogen by deuterium results in only very minor changes in the ferroelectric behavior,

but aside from this, hardly anything can be done to Rochelle salt without causing the complete disappearance of ferroelectric properties. Replacement of only a few per cent of the potassium by rubidium, for example, removes all dielectric anomalies. Such experiments indicate strongly that hydrogen bonds are not the crucial factor in causing ferroelectricity in Rochelle salt. New evidence about the mechanism may be obtained from the recent discovery (M17, M18) of other ferroelectric tartrates.

One of the chief difficulties in any theoretical explanation of the properties of Rochelle salt is the existence of two Curie points, and a theory which could explain this in a natural way without postulating two independent mechanisms would have a much stronger appeal than do any of the ones thus far proposed. Recently Wigner (W4) has described a model in which mixing of two different electronic states of a crystal unit cell produces an electric moment. This theory was originally proposed in connection with the behavior of barium titanate, to be discussed later, but it was noted that it automatically leads to the existence of two Curie points, with spontaneous polarization between them. In this theory, the unperturbed energy separation of the two possible states passes through zero in the middle of the ferroelectric range, and for temperatures sufficiently near this crossing point, the crystal as a whole has a lower energy if the wave function in each unit cell goes into a linear combination of the two symmetric states, with a resulting dipole moment. Although no attempt has yet been made to fit the constants of this theory to the experimental results on Rochelle salt, this would appear to be a promising possibility.

## 1.3 The $KH_2PO_4$ type ferroelectrics

Another ferroelectric substance, whose structure is not similar to that of Rochelle salt, was discovered in

1935 by Busch and Scherrer (B3) in the salt potassium dihydrogen phosphate, $KH_2PO_4$. Later it was found that the primary phosphates and arsenates of alkalis and ammonium, all forming tetragonal crystals of class $V_d$, also possess ferroelectric properties, but with Curie points at liquid air temperatures. The spontaneous polarization in these crystals is an order of magnitude greater than in Rochelle salt, and they appear to have no lower Curie point, the ferroelectric state extending to absolute zero. They resemble Rochelle salt, however, in that the anomalies are confined to one direction of polarization, and in the existence of strong piezoelectric coupling between polarization in this direction and a shearing strain in the plane at right angles to the polarization.

The crystal structure of $KH_2PO_4$ is much simpler than that of Rochelle salt (W3) and it is therefore to be expected that a molecular theory of its behavior might be easier to develop. Based on the fact that the crystal contains phosphate groups connected by hydrogen bonds, Slater (S2) has described a model in which the hydrogens can take up a number of configurations corresponding to different polarizations of the unit cell. From the total number of arrangements consistent with each value of total polarization, assuming that the energy of a bond depends on the configuration of neighboring bonds rather than on the long range electrostatic interaction, and neglecting those configurations that have high energies, an approximate free energy function is found. This leads to a prediction of a first-order transition at the Curie point instead of the observed second-order one. However, as Slater points out, the observed transition is much sharper than is predicted by the Weiss theory, and is in fact not far from a first-order one.

The fact that replacing hydrogen with deuterium makes only very minor changes in the behavior of Rochelle salt, but raises the Curie temperature of $KH_2PO_4$ consider-

ably (M19), makes it hard to believe that hydrogen bonds are the important things in Rochelle salt, while confirming that they are in $KH_2PO_4$.

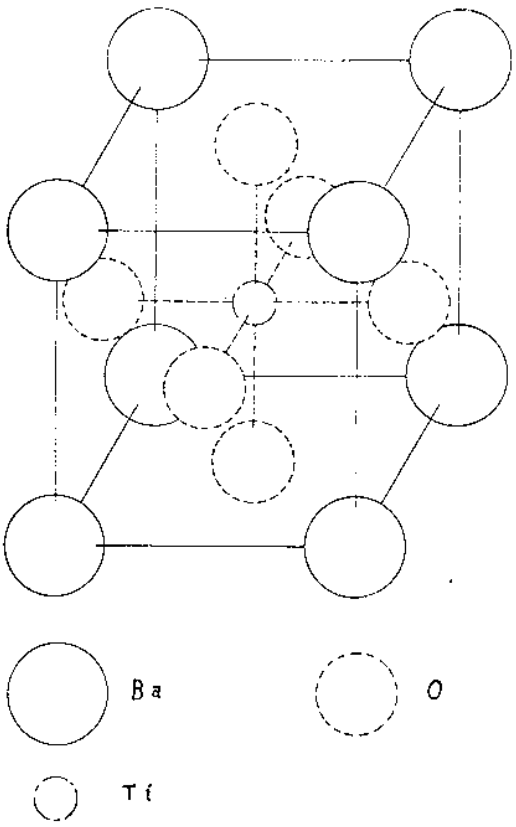


FIG. 1.2

## 1.4 The $BaTiO_3$ type ferroelectrics

A new class of ferroelectrics discovered in the last few years exhibits a behavior in many respects more spectacular and interesting than that of Rochelle salt or the alkali phosphates and arsenates. Anomalies in the dielectric properties of barium titanate ceramic material were first observed by Wainer and Salomon (W1) in 1942, and it was soon established by von Hippel and coworkers at the MIT Laboratory for Insulation Research (H1) and independently by Wul and coworkers in Russia (W2 G1), that $BaTiO_3$ is ferroelectric. $BaTiO_3$ forms in the perovskite lattice (Fig. 1.2), with Ba ions at the corners of the

cubic unit cell, O ions at face centers, and Ti ions at body centers. It also exists in a hexagonal polymorph (B7) which is of no interest in the present study.

In the early work just referred to, the Curie point was located at 120°C, and it was found that the symmetry undergoes a transition from cubic to tetragonal as the temperature is lowered through this point. Megaw (M5) made accurate measurements of the tetragonal c/a ratio in the temperature range 5°C-120°C which suggest that the transition at 120°C is of the $\lambda$-type, with no heat of transition. Roberts (R1) found that a strong piezoelectric effect is induced in the ceramic by a polarizing field. Two other phase transitions were located at 5°C and -80°C. They show up clearly as peaks in the dielectric constant versus temperature measurements of von Hippel, Breckenridge, Chesley, and Tisza (H1).

In 1947, Blattner, Matthias, Merz, and Scherrer (B2) developed a method of growing $BaTiO_3$ crystals from melts, and this opened up the possibility of studying the properties of single crystals. By means of optical, mechanical, and electrical measurements the nature of the changes at the three transition temperatures has been established (F1, M7, M9). Above 120°C, the crystal is cubic, with no spontaneous polarization. From 120°C to 5°C, it is tetragonal, with a spontaneous polarization directed along a (001) direction of the original cube. From 5°C to -80°C, it is orthorhombic with spontaneous polarization in the (011) direction of the original cube, and below -80°C it is rhombohedral with spontaneous polarization along the (111) direction. In each case the crystal is mechanically deformed by an amount proportional to the square of the polarization, being expanded in the direction of the spontaneous polarization and contracted at right angles to it. Optically, the crystals show a birefringence accurately proportional to the mechanical deformation (M7). As the temperature is lowered, the

symmetry classes are in succession $O_h$, $C_{4v}$, $C_{2v}$, $C_{3v}$.

Matthias and von Hippel (M3) and Blattner, Känzig, Merz, and Sutter (B8) observed that in the ferroelectric state the crystals are broken up into domains which can be seen even in unpolarized light, since the birefringence is strong and the optic axes of adjacent domains are perpendicular to each other. The domain walls move smoothly in response to an applied electric field. Forsbergh (F1) has described the various observed domain arrangements and motions in detail, and Kittel (K5) has given a simple theory of their motion. Ferroelectric domains differ from those observed in ferromagnetic materials in that they tend to be larger, with large dimensions comparable to the smallest dimension of the crystal. This is an apparent consequence of the fact that in the electric case the crystal can neutralize external fields by accumulation of surface charges as well as by splitting up into small oppositely directed domains.

Merz (M7) has given a useful summary of the numerical results of electrical and optical experiments on single-domain crystals. Figs. (1.3) and (1.4), taken from this work, give the dielectric constant and the spontaneous polarization, as determined from hysteresis loops, as functions of temperature. The direction of spontaneous polarization in the tetragonal phase is by convention called the [001] or c-direction, and the dielectric constant curves marked c and a refer to fields respectively parallel and perpendicular to this direction. In the case of spontaneous polarization, the quantity plotted is the component of polarization in the [001] direction, which is the quantity measured directly by the charge accumulated on electrodes applied to (001) faces. In the regions $T < -80^{\circ}C$ and $-80^{\circ}C < T < 5^{\circ}C$, the magnitude of the total polarization would be found by multiplying this component by $\sqrt{3}$ and $\sqrt{2}$ respectively, and thus is much more nearly constant than the quantity shown. The magnitude of

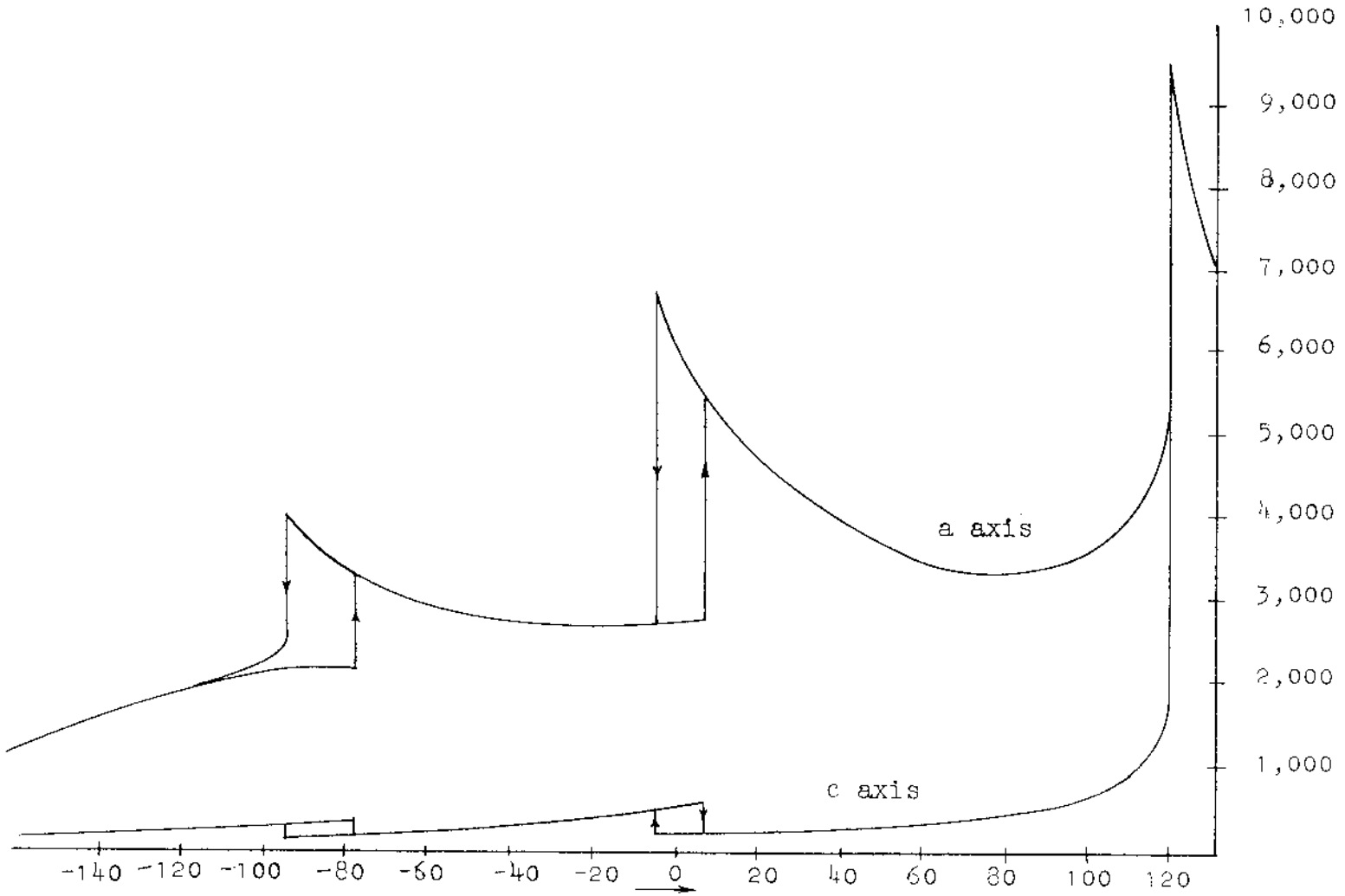


FIG. 1.3

Dielectric constants versus temperature for $BaTiO_3$, according to Merz (M7)

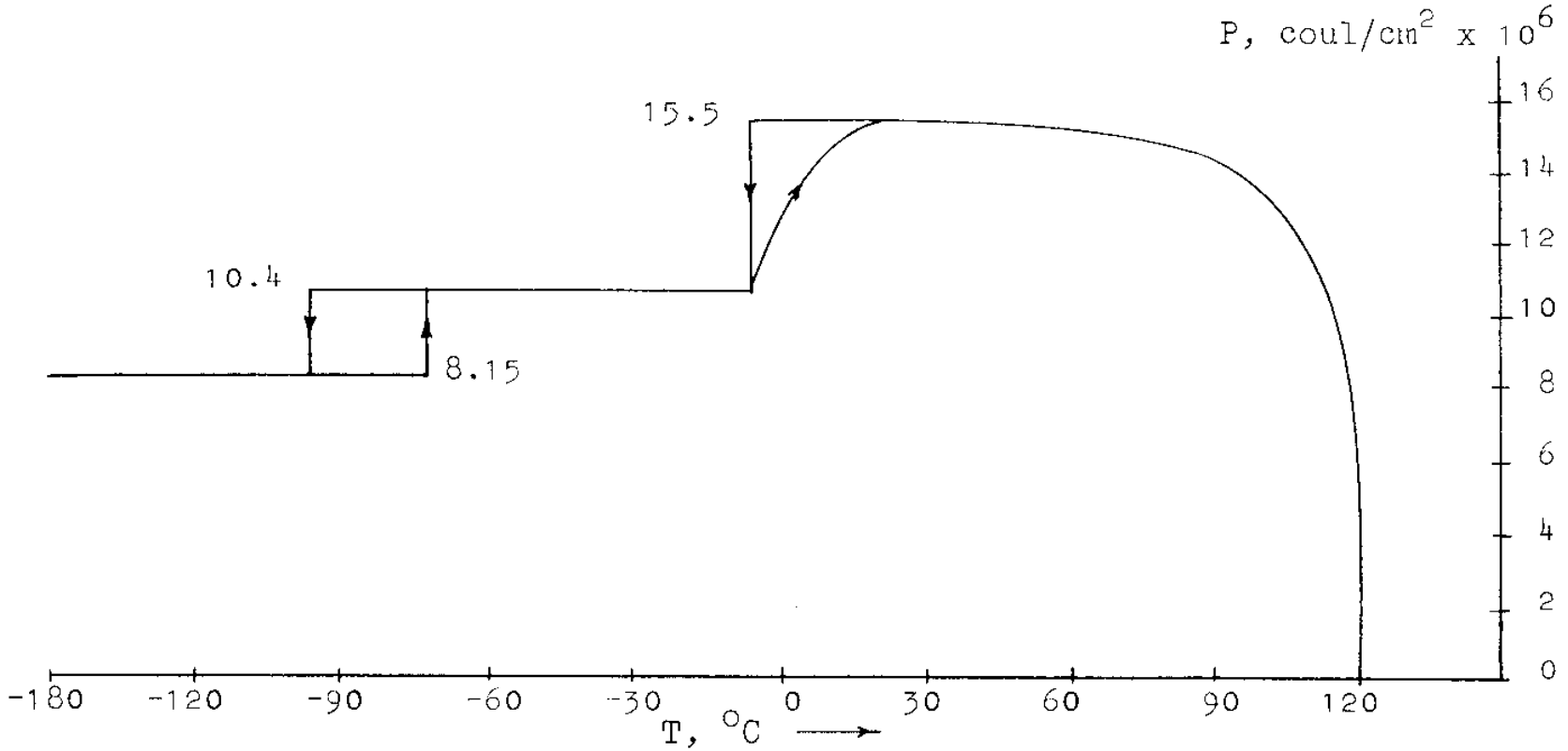


FIG 1.4

Spontaneous polarization versus temperature for $BaTiO_3$, according to Merz (M7)

the spontaneous polarization is about 15.5 microcoulombs/$cm^2$, or 46,500 esu, very much larger than is observed in Rochelle salt or $KH_2PO_4$. $BaTiO_3$ may be described as a very "hard" ferroelectric material, with a coercive force of the order of 25,000 volts/cm (M2, H3), compared to 100 volts/cm for Rochelle salt (C2).

The mechanical deformation accompanying spontaneous polarization in $BaTiO_3$ is unusually large, the extension along the c-axis in the tetragonal phase amounting to nearly 1 per cent of the original length (M5). In the phases in which its symmetry allows a piezoelectric effect, or in any phase if a biasing field is applied (R1, C3), it exhibits a piezoelectric activity comparable to that of Rochelle salt, which has long been the most strongly piezoelectric substance known. This fact, plus desirable mechanical and thermal properties not possessed by Rochelle salt, makes $BaTiO_3$ an important material for a large number of technical applications (T1).

Recent review articles by Matthias (M19), Baumgartner, Jona, and Kaenzig (B11), Lumbroso (L3), and von Hippel (H4) may be consulted for more details.

While the phase changes at -80°C and 5°C are thermodynamically first-order transitions, the tetragonal-cubic transition at 120°C appears to be a $\lambda$-point, or second-order transition involving no latent heat, but a jump in specific heat. The specific heat anomaly, which is an important piece of evidence regarding the molecular mechanism of the transition, has been measured by Wul (W2, Ref. 7), by Blattner and Merz (B6), and by Harwood, Popper, and Rushman (H2). The kind of curve to be expected is illustrated in Fig. 1.5. The smoothly rising curve represents what would be observed if the polarization were held equal to zero. Actually, it is the electric field that is held equal to zero in experiments, so that as we pass into the ferroelectric range, the onset of

spontaneous polarization alters the internal energy of the crystal. According to a naïve form of internal field theory, this increment in energy arises as follows. If a unit volume of the crystal contains $N$ polarizable objects of polarizability $\alpha$, the polarization will be $P = N\alpha F$, where $F$ is the internal field. If the externally applied

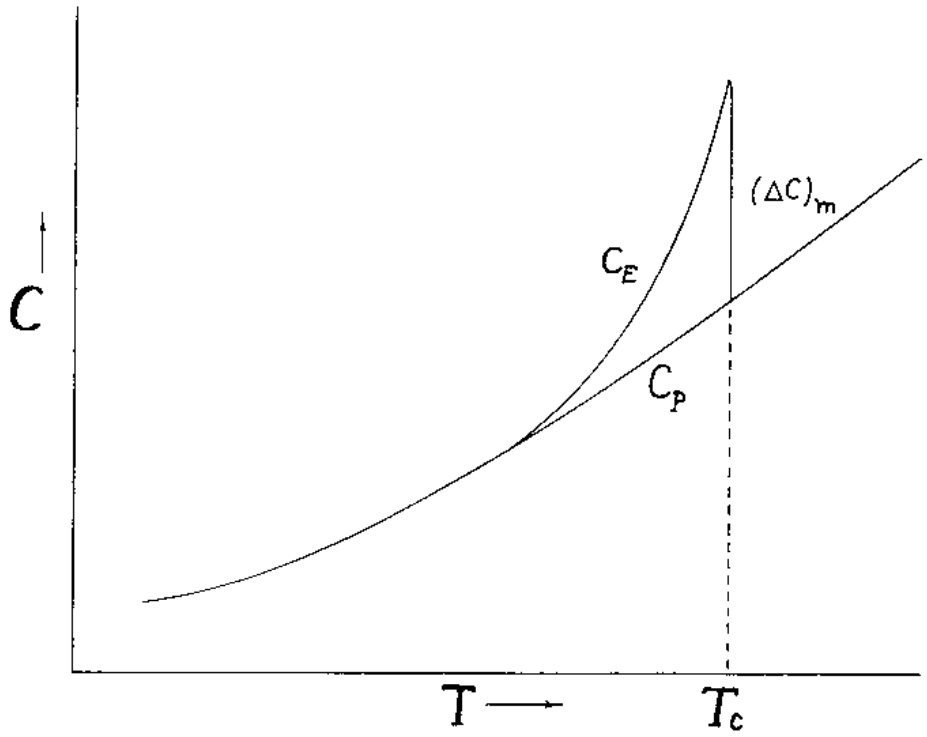


FIG. 1.5

field $E$ is zero, then we also have $F = \beta P$, or $N\alpha\beta = 1$. Now a dipole of moment $M$ in a field $F$ has a potential energy $V = -M \cdot F$, so that the potential energy of a single polarizable object will be $-\alpha F^2$. In getting the total potential energy of interaction of the dipoles per unit volume, we must, however, multiply not by $N$ but by $N/2$, for otherwise the interaction energy of each pair of dipoles will be counted twice. This gives for the change in energy per unit volume due to spontaneous polarization,

$$E = -\frac{1}{2}N\alpha F^2 = -\frac{1}{2}\beta P^2.$$

If the Lorentz factor $\beta$ is a constant, this gives rise to a specific heat anomaly

$$\Delta C = C_E - C_P = -\frac{\beta}{2}\frac{dP^2}{dT} . \qquad (1.41)$$

We see from the experimental polarization curve (Fig. 1.4) that this extra term is zero at low temperatures, where the polarization is constant, then a few degrees below $T_c$ it begins to rise smoothly to a maximum value at $T_c$ where the polarization is decreasing with temperature most rapidly. It then drops abruptly to zero as we enter the "parelectric" range where $P = 0$. Experimental curves are not usually as sharp as this, but show an unsymmetrical peak at the transition temperature.

Two features of the specific heat anomaly are of special interest. The first is the integrated area of the triangular region, which determines the difference in entropy $\Delta S$ associated with the vanishing of polarization, through the relation

$$\Delta S = \int^{T_c} \Delta C \frac{dT}{T} \cong \frac{1}{T_c}\int \Delta C dT$$

The value of $\Delta C$ found in $BaTiO_3$ is very small and difficult to measure, and the three experiments listed give results varying by a factor of five:

| Investigators | $\int \Delta C\, dT$, cal $mol^{-1}$ | $\Delta S$ per unit cell |
|---|---|---|
| BM | 47 | 0.06 k |
| HPR | 9 | 0.011k |
| Wu | 14 | 0.02k |

(k = Boltzmann's constant)

The graph of HPR is the only one revealing a sharp discontinuity in specific heat, but it is also the most difficult one from which to estimate $\Delta S$. In spite of the lack of quantitative agreement, the above values show clearly that the change in entropy is extremely small; interpreting

the entropy as proportional to the logarithm of the volume of phase space available to a system, we see that this value for a unit cell is at most a few per cent higher in the parelectric range, and any explanation of the action of $BaTiO_3$ as an order-disorder transition is quite conclusively ruled out (in contrast, $KH_2PO_4$ exhibits a rather large entropy change at the Curie Point, consistent with an order-disorder transition as treated by Slater). A transition with such a low specific heat anomaly is called a dispacive transition by Tisza (T2).

The value of the parameter $\beta$ in the above oversimplified discussion is found from integrating Eq. (1.41);

$$\frac{1}{2}\beta P_m^2 = \int \Delta C dT \tag{1.42}$$

where $P_m$ is the maximum value of spontaneous polarization reached at low temperatures. From the experimental value $P_m = 4.65 \times 10^4$ esu (M7) we find, taking $\int \Delta C \, dT = 14$ cal/mol,

$$\beta = 0.014,$$

which is a value far lower than could be justified by any electrostatic considerations. It is curious that the value of $\beta$ predicted by the rotating dipole theory, as determined by the susceptibility above the Curie point (Eq. 1.05)

$$\chi = \frac{1}{\beta} \frac{T_c}{T - T_c} \tag{1.43}$$

turns out to be about 0.04 for $BaTiO_3$, in fair agreement with the above value. In spite of this semiquantitative agreement, the theoretical basis of both Eqs. (1.42) and (1.43) is extremely doubtful in the case of ferroelectrics (although both are good approximations in the case of ferromagnetism), and one would at first be inclined to dismiss it as an odd coincidence were it not

for the fact that the same agreement exists to an even better degree for Rochelle salt and for $KH_2PO_4$. Blattner and Merz (B6) have given the following values of $\beta$ as calculated from each formula using experimental values of $\Delta C$, $P_m$, and $\chi$ :

| Substance | from Eq. (1.42) | from Eq. (1.43) |
|---|---|---|
| Rochelle salt | 2.1 | 2.2 |
| $KH_2PO_4$ | 0.37 | 0.48 |
| $BaTiO_3$ | 0.044 | 0.049 |

Their values for $BaTiO_3$ were based on their measurement of $\Delta C$, and are in better agreement that we calculated above. The $\Delta C$ values of Blattner and Merz appear to be higher by a factor of 5 to 10 than the values found by other investigators, and the values predicted indirectly from other experiments. However, we see that there is surprisingly good agreement of these quantities in all cases so that, although we cannot accept the theoretical basis of the two formulas for $\beta$ or their interpretation in terms of internal field constants, we note that it is an experimental fact that for the three types of ferroelectrics the following relation is valid:

$$\frac{1}{2}P_m^2 = C\Delta S \qquad (1.44)$$

where $C$ is the Curie constant and $\Delta S$ is the entropy difference associated with the onset of spontaneous polarization. A theoretical reason for this relation will be presented in Chapter 3.

The second important feature of the specific heat anomaly is the value $(\Delta C)_m$ of the sudden drop in specific heat at the transition point. From the published data, one can estimate the following values:

| Investigators | $(\Delta C)_m$ cal $deg^{-1}$ $gm^{-1}$ |
|---|---|
| BM | 0.02 |
| HPR | 0.0025 |
| Wu | 0.003 |

The importance of $(\Delta C)_m$ lies in the fact that it is connected with the change $\Delta\beta$ in volume expansion coefficient and the derivative $dT/dp$ of the Curie temperature with respect to pressure through the Ehrenfest relation (E3)

$$\frac{dT}{dp} = T_c \frac{\Delta\beta}{\rho}(\Delta C)_m \tag{1.45}$$

in which $\rho$ = density. The effect of hydrostatic pressure on the Curie point of $BaTiO_3$ has been investigated up to pressures of 5000 atm by Merz (M10), who finds a linear decrease $dT/dp = -5.8 \times 10^{-3}$ deg $atm^{-1}$, or $-5.74 \times 10^{-9}$ deg $cm^2$ $dyne^{-1}$. The value $\Delta\beta = -1.8 \times 10^{-5}$ $deg^{-1}$ may be obtained from the X-ray measurements of Megaw (M5). Thus, one can calculate $(\Delta C)_m$ indirectly, and the result is 0.0049 cal $gm^{-1}$ $deg^{-1}$ (M10), which is in fair agreement with the above direct measurements.

From the pressure effect measured by Merz, one can find the dependence of Curie temperature on the lattice constant "a," the result being

$$\frac{dT_c}{da} = 3.3 \times 10^3 \text{ deg } \text{A}^{-1} \quad .$$

This result is of interest because the lattice constant may also be varied without a change of pressure by replacing a fraction of the Ba ions with smaller Sr ions. Rushman and Strivens (R3) find that both the Curie temperature and the lattice constant decrease linearly with the fraction of Sr ions present, at a relative rate

$$\frac{dT_c}{da} = 2.8 \times 10^3 \text{ deg } \text{Å}^{-1} \quad ,$$

in very close agreement with the former value; therefore the Curie temperature depends to a large extent only on the lattice size, and not on the combination of pressure and alkaline earth ionic radii that produces that lattice size.

## 2. REVIEW OF THEORIES OF $BaTiO_3$

Although the behavior of $BaTiO_3$, as described above, is complicated, its basic structure is so simple (in contrast to that of Rochelle salt or $KH_2PO_4$) that there is hope of eventually understanding the mechanism by which these curious effects are brought about. Most of the theoretical attempts to date consider displacement of the Ti ions relative to the rest of the crystal as the cause of the polarization. This point of view originated with Megaw (M6), who pointed out that, if we assume the Goldschmidt ionic radii, the Ba ions are slightly too large to fit into a close-packed perovskite structure. Therefore they cause the lattice to expand with the result that the Ti ions are loosely bound in the octahedra of Oxygen ions, with a resulting large polarizability.

### 2.1 The Mason-Matthias theory

Mason and Matthias (M2) have devloped in considerable detail a theory based on this idea, with a modification apparently originating in a suggestion of Eucken and Büchner (E4), who ascribed the high dielectric constants of TlCl, TlBr, $PbCl_2$, and $TiO_2$ (rutile) to homopolar binding between positive and negative ions, which causes large changes in the electronic distributions as their separation changes. One therefore has the picture of homopolar bonds that shift as an ion is displaced, and as a result an ion might have a number of stable positions at which it is associated with different surrounding ions. An enlarged account of this theory with some modifications is also given in Mason's recent book on piezoelectricity (M16).

We consider the Ti ion to have six stable positions, displaced from the center of the unit cell toward each of the six surrounding oxygens. When an effective field F in the (001) direction acts on this arrangement, it has a partition function

$$Z = 2\left(\cosh \frac{\mu F}{kT} + 2\right)$$

where $\mu$ is the maximum dipole moment per cell. Mason and Matthias (MM) call the polarization due to this displacement of the Ti ion $P_d$, and assume that the effective field F is given by

$$F = E + \beta P = E + \beta(P_d + \gamma F) = \frac{E + \beta P_d}{1 - \beta\gamma} \qquad (2.11)$$

where $\gamma$ is the total polarizability due to all mechanisms other than Ti displacement, divided by the volume of a unit cell. The total experimentally observed polarization is then

$$P = P_d + \gamma F = \frac{P_d + \gamma E}{1 - \beta\gamma} \qquad (2.12)$$

The mean polarization due to the Ti dipoles is given by

$$P_d = NkT \frac{\partial}{\partial F} \log Z, \text{ or } \frac{P_d}{N\mu} = \frac{\sinh(\mu F/kT)}{\cosh(\mu F/kT) + 2} \qquad (2.13)$$

where $N = 1/v$ is the number of unit cells per $cm^3$. From Eqs. (2.13) and (2.11) we see that spontaneous polarization can exist only below the temperature $T_c$ given by

$$\frac{N\mu^2}{3kT_c} = \frac{1 - \beta\gamma}{\beta} \quad .$$

Mason and Matthias evaluate some of the constants by comparison with the experimental dielectric constant above the Curie temperature. This is easily obtained from Eq. (2.13) by observing that for weak applied fields with $T > T_c$, we will have $\mu F/kT \ll 1$, so that Eq. (2.13) becomes

$$P_d = \frac{N\mu^2 F}{3kT} = \frac{T_c}{\beta T}(E + \beta P_d) = \frac{E}{\beta} \frac{T_c}{T - T_c}$$

Using Eq. (2.12), the total polarization is given by

$$\chi = \frac{P}{E} = \frac{1}{\beta(1 - \beta\gamma)} \left\{ \beta\gamma + \frac{T_c}{T - T_c} \right\}$$

and the dielectric constant is

$$\epsilon = \epsilon_o + \frac{4\pi}{\beta(1 - \beta\gamma)} \frac{T_c}{T - T_c} \tag{2.14}$$

where

$$\epsilon_o = 1 + \frac{4\pi\gamma}{1 - \beta\gamma}$$

(In the MM paper, this is given incorrectly as $\epsilon = \epsilon_o + [4\pi/\beta]\ T_c/[T - T_c]$ )

Mason and Matthias have attempted to fit this dielectric constant to the experimental curve, and have taken as an empirical expression:

$$\epsilon = 350 + \frac{40{,}000}{T - 393} \tag{2.15}$$

in which the value $\epsilon_o = 350$ is stated as the dielectric constant near absolute zero. Measurements by Blunt and Love (B4) on ceramic specimens down to about $2^oK$ show a dielectric constant rising smoothly from 95 at $2^oK$ to 140 at $30^oK$. The value $T_c = 393^oK$ is the observed transition temperature, which is not necessarily the value which fits an empirical curve of dielectric constant above $T_c$. The value 40,000 is apparently obtained from a single point on an experimental curve (Fig. 3 in the MM paper), at a temperature of about $130^oC$, which is as high as that curve goes. However, the experimental curve does not follow the above empirical equation, and greatly different values of the parameter "40,000" could be obtained by a different choice of matching point.

These conditions, plus the above-mentioned omission of a factor $(1 - \beta\gamma)$ in the expression for dielectric constant, make it necessary to consider anew the problem of evaluating the constant $\beta$ , $\gamma$ of the theory.

These constants are also considerably revised by Mason in (M16). Measurements by S. Roberts (R2) of the dielectric constant at elevated temperatures supply us with just the information needed to develop an accurate empirical formula. From them we find two equations:

$$\epsilon = \frac{114,000}{T - 106} , \qquad (2.16)$$

which gives an essentially perfect fit to the data above $175^{\circ}C$, and a second one

$$\epsilon = \frac{121,500}{T - 99} , \qquad (2.17)$$

which fits the data better near the Curie point.

We note two facts about this equations. In the first place, there is no constant term. As Roberts has pointed out, if one plots the reciprocal of the dielectric constant against T, the result is a very straight line above $175^{\circ}C$. The constant term, if it exists, is so small in comparison with the temperature-dependent term that it cannot be detected within present experimental error. According to Roberts, the accuracy of the measurement is such that values of $|\epsilon_o - 1|$ greater than 10 are definitely ruled out, while the temperature-dependent part of the dielectric constant is of the order of thousands.

The second point to notice is that the constant $T_c$ which fits the experimental data is not the same as the observed transition temperature but is several degrees lower; this is clear from a glance at any of the several graphs of dielectric constant that have been published. The same effect is found in the other ferroelectrics and in ferromagnetic substances. In all such cases the graph of reciprocal susceptibility versus temperature deviates from a straight line near the Curie point. Becker and Doring (B5) have given qualitative arguments which show that this is undoubtedly due to "Schwarmbildung," or strong correlations between the polarizations of neighbor-

ing dipoles. Such correlations are not taken into account in the usual form of internal field theory, and some correction analogous to that given by Onsager in the case of rotating permanent dipoles, as described in Section 1.1, is needed. However, in this case the internal field theory is not in such catastrophic disagreement with experiment, and the effect of correlations is a small correction important only near the transition point rather than a major change in the theory.

A fundamental objection to the MM theory is found when we try to evaluate the constants of the theory by comparison with experimental data. From the dielectric constant above the Curie point, using Eq. (2.14) and the empirical Eq. (2.16), we have $T_c = 106^\circ C = 379^\circ K$, and

$$\beta(1 - \beta\gamma) = 4\pi \frac{379}{114,000} = 0.0417 .$$

Now consider the maximum polarization at low temperatures. From Eqs. (2.12) and (2.13) this is

$$P_m = \frac{N\mu}{1 - \beta\gamma} .$$

Form the dimensionless quantity

$$\frac{P_m^2}{NkT_c} = \frac{N\mu^2}{kT_c(1-\beta\gamma)^2} = \frac{3}{\beta(1-\beta\gamma)} .$$

Since the left side contains only experimentally measured quantities, we have an independent experimental value of $\beta(1 - \beta\gamma)$. Using the measured values

$$P_m = 15.6 \times 10^{-6} \text{ coulomb cm}^{-2} = 4.68 \times 10^4 \text{ esu}$$
$$N = (4 \times 10^{-8})^{-3} = 1.56 \times 10^{22} \text{ cm}^{-3}; \quad T_c = 379^\circ K,$$

we find

$$\frac{P_m^2}{NkT_c} = 2.68$$

so that

$$\beta(1 - \beta\gamma) = \frac{3}{2.68} = 1.12$$

This differs from the previous value by a factor of 27. Thus there is no way of fitting this theory consistently to the experimental data; the values of the constants vary by an order of magnitude depending on which experiments we use. This discrepancy cannot be attributed to experimental error or to the crude statistical nature of the theory; the experiments involved are relatively easy ones which many investigators have performed with close agreement, and the corresponding theory involves no subtleties of behavior near the critical point. Furthermore, the particular assumptions about other types of polarization than Ti ion displacement contained in Eq. (2.11) are not the source of the discrepancy; if we assume that all the polarization is given by $P_d$, the effect is merely to put $\gamma = 0$ in all the above equations, and we find just the same discrepancy in two independent experimental values of $\beta$.

Another fundamental difficulty concerns the change in entropy as we go through the Curie point. According to the MM theory there are six positions that the Ti ion can assume at random when $T > T_c$, while a few degrees below $T_c$ it will be constrained essentially to a single site. Thus, we expect an entropy change of about $k \log 6 = 1.79\ k$ per unit cell (F1). In Section 1.4 we found that the experimental value of $\Delta S$ is about $0.02\ k$, a discrepancy of a factor of 90. As remarked before, this very low value of $\Delta S$ seems to rule out conclusively any order-disorder explanation of the phenomenon. We note that the above estimate of $1.79\ k$ is too high and would be reduced by consideration of the correlations mentioned earlier; however, the correction could hardly amount to two orders of magnitude.

According to thermodynamic arguments given in Chapter 3, these two discrepancies are closely related. Granted only very general assumptions as to the form of

the free energy function, one can dervie the relation $\frac{1}{2} P^2 = C\Delta S$, where $P$ is the maximum polarization at low temperatures and $C$ is the Curie constant. Thus, if a model does not give the correct entropy change, then it also cannot be made to give both the correct polarization and the Curie constant. Since the entropy change upon polarization can often be found directly from the model by simple physical reasoning, as in the present case, this is a useful point to keep in mind when considering theories.

The internal field assumptions made in this treatment can be greatly improved. In Mason's second form of the theory (M16) two different Lorentz factors are introduced. The electronic part of the polarization $P_e$ is assumed coupled by the classical value $4\pi/3$, while for the ionic part $P_d$ we have an unknown factor $\beta$ ; $F = 4\pi P_e/3 + \beta P_d$. However, as Cohen (C5) has pointed out recently, in a correct treatment we must evaluate the internal field at the position of the displaced ion, not its central position. Since the lattice of Ti ions is uniformly displaced, the internal field due to $P_d$ must be zero. Since the difficulty about entropy would in any event remain, it does not seem worthwhile to reconsider this model by a better internal-field treatment.

## 2.2 The Devonshire theory

A second major attempt to explain the properties of $BaTiO_3$ in terms of ionic displacement has been made by Devonshire (D3), and Slater (S1) has introduced certain modifications. Devonshire first develops a purely phenomenological treatment patterned after Mueller's interaction theory of Rochelle salt. This theory is considerably more complicated in the case of $BaTiO_3$ due to the number of phase changes, and because all components of polarization and all strain components are now coupled together. In the case of Rochelle salt, a major part of the discussion can be carried out in terms of the polarization $P_x$ and the shear $e_{yz}$ only.

The free energy function developed by Devonshire leads to the correct qualitative behavior as regards the successive changes of polarization direction and lattice deformations, but there is no quantitative agreement between theory and experiment on the magnitude of the polarization and dielectric constant as functions of temperature. The phenomenological theory therefore cannot yet be considered as complete as is Mueller's treatment of Rochelle salt.

Devonshire starts with an expression for the Helmholtz free energy of the free crystal per unit volume, expressed as a function of polarization and stress, with the stresses set equal to zero. This function must be invariant under the symmetry group $O_h$ of the undistorted crystal, and the most general function of polarization having this symmetry is an arbitrary symmetric function of $P_x^2$, $P_y^2$, $P_z^2$. If we expand the free energy in powers of the polarization, it will therefore have the form

$$A = \tfrac{1}{2}w'(P_x^2 + P_y^2 + P_z^2) + \tfrac{1}{4}\xi'_{11}(P_x^4 + P_y^4 + P_z^4) + \tfrac{1}{2}\xi'_{12}(P_y^2P_z^2 + P_z^2P_x^2 + P_x^2P_y^2) + \tfrac{1}{6}\zeta'(P_x^6 + P_y^6 + P_z^6) + \cdots . \tag{2.21}$$

The value of $w'$ as a function of temperature may be obtained by comparison with the experimental susceptibility above the Curie point. From the value of the electric field

$$E_x = \frac{\partial A}{\partial P_x} = w'P_x + \xi'_{11}P_x^3 + \cdots$$

we see that for the weak fields used in measuring susceptibility, where the dielectric behavior is linear, the terms in $A$ of order $P^4$ and higher are negligible compared to the second-order term, and $w'$ is in fact just the reciprocal susceptibility,

$$w' = \chi^{-1} = \frac{T - T_c}{C} \tag{2.22}$$

where $C$ is the Curie constant. The basic assumption of the Devonshire theory is that the linear relation Eq.

(2.22) may be extrapolated below the Curie temperature $T_c$, and that the only important temperature effect in the ferroelectric region arises from the temperature variation of $w'$, so that the quantities $\xi'_{11}$, $\xi'_{12}$, $\zeta'$ may be assigned constant values (the primes, according to a notation of Cady (C2), indicate that the constants are for a free crystal). Devonshire shows that the three phase transitions are accounted for, with the observed shifts in polarization direction, if $\xi'_{12}$ and $\zeta'$ are positive while $\xi'_{11}$ is negative, and the numerical values which he estimates from various experimental data are

$$\begin{aligned} \xi'_{11} &= -4.4 \times 10^{-12} \text{ cm}^3 \text{ erg}^{-1} \\ \xi'_{12} &= 5.3 \times 10^{-12} \text{ cm}^3 \text{ erg}^{-1} \\ \zeta' &= 3.7 \times 10^{-21} \text{ cm}^6 \text{ erg}^{-2} . \end{aligned} \tag{2.23}$$

In Devonshire's work, the transition at 120°C was considered to be of first order, the polarization rising discontinuously to a finite value as the temperature is lowered. The measurements of Merz (M7) show no such discontinuity and no hysteresis at 120°C, indicating a second-order transition; however other measurements have sometimes shown a discontinuity in various properties at this temperature, and it is accordingly not certain experimentally whether the transition is of first or second order. Experiments at this temperature are very sensitive to small residual stresses and other departures from ideal conditions so that one should be cautious in drawing conclusions from them. For example, if it should be found that all actual crystals give finite discontinuities but that more perfect crystals tend to have smaller discontinuities, then one would have strong reasons for concluding that the transition is ideally of second order. Theories in the state of development considered here are, of course, concerned with ideal systems: i.e., the limit of actual ones as all imperfections go to zero, and when there is a difference, we would want the model to reproduce the ideal,

rather than the actual, behavior.

One can show as follows that the sign of $\xi'_{11}$ determines the order of the transition. If we consider only polarization in the z-direction, the free energy function may be abbreviated to

$$A = \tfrac{1}{2}w'P^2 + \tfrac{1}{4}\xi'_{11}P^4 + \tfrac{1}{6}\zeta' P^6 \qquad (2.24)$$

and the condition of zero electric field is

$$E = \frac{\partial A}{\partial P} = 0 \ . \qquad (2.25)$$

This can be satisfied by putting $P = 0$, or by having the rate of decrease with $P$ of one of the terms of Eq. (2.24) just balance the rate of increase of the other terms. If $\xi'_{11}$ and $\zeta'$ are positive, it is clear that for positive $w'$ the only solution of Eq. (2.25) is $P = 0$. As the temperature is lowered, $w'$ decreases, and when $w' < 0$ the first term of Eq. (2.24) is negative, and Eq. (2.25) can be satisfied for finite values of $P$, given by

$$P^2 = \frac{-\xi'_{11} + \sqrt{\xi'^2_{11} - 4w'\zeta'}}{2\zeta'} \cong \frac{-w'}{\xi'_{11}} = \frac{T_c - T}{C\,\xi'_{11}} \qquad (2.26)$$

The approximation, being valid near the Curie point, shows that in this case the polarization sets in below the Curie point as $(T_c - T)^{\frac{1}{2}}$, the usual law for a second-order transition.

If $\xi'_{11} < 0$, however, the middle term of Eq. (2.24) is negative for finite polarization, and we see that, for small positive values of $w'$, the free energy will first increase, then decrease, and finally increase again as $P$ is increased from zero. The minimum at a finite value of $P$ will be lower than the minimum at $P = 0$ if $w'$ is sufficiently small so that as the temperature, and therefore $w'$, decreases, the absolute

minimum of A jumps discontinuously from the point P = 0 to a point with a finite value of P, corresponding to a first-order transition.

In this work we assume that the transition is of second order. One argument for this is that no hysteresis is observed at the $120^{\circ}$ in experimental curves of dielectric constant or polarization as functions of temperature (Figs. 1.3, 1.4). From the above discussion of the cause of a first-order transition, we see that for such a change there is an activation energy which must be supplied in order to move the system from a relative minimum of A to an absolute minimum so that, as the temperature is changed, we would not expect the actual transition to take place until the height of the potential hill has been greatly decreased from the value existing at the instant its state ceases to be an absolute minimum. These hysteresis effects are shown in Figs. 1.3 and 1.4 for the two lower transitions, which are definitely of first order. A second reason why it is almost necessary to assume a second-order transition in a treatment of this type is explained in Section 3.3.

Although Devonshire used a negative value for $\xi'_{11}$ it still seems possible to account for the observed transitions and shifts of polarization with $\xi'_{11} > 0$, because, if $\xi'_{12} > \xi'_{11}$, it is still true that the fourth-order terms in A, for a given total polarization, have their minima along the directions of the crystal axes, while the sixth-order term has its minima along cube diagonals. Thus, as the temperature decreases and the polarization increases, its direction will shift from axial to diagonal.

After developing the free energy function for zero stress, Devonshire considers its expression in terms

of polarization and strain. If the strains $(x_1 \ldots x_6) = (e_{11}, e_{22}, e_{33}, e_{23}, e_{31}, e_{12})$ are of order $P^2$, this can be expanded in the form

$$\begin{aligned} A = {} & \tfrac{1}{2}c_{11}(x_1^2 + x_2^2 + x_3^2) + c_{12}(x_2x_3 + x_3x_1 + x_1x_2) \\ & + \tfrac{1}{2}c_{44}(x_4^2 + x_5^2 + x_6^2) + \tfrac{1}{2}w''(P_1^2 + P_2^2 + P_3^2) \\ & + \tfrac{1}{4}\,\xi''_{11}(P_1^4 + P_2^4 + P_3^4) + \tfrac{1}{2}\,\xi''_{12}(P_2^2P_3^2 + P_3^2P_1^2 + P_1^2P_2^2) \\ & + g_{11}(x_1P_1^2 + x_2P_2^2 + x_3P_3^2) \qquad (2.27) \\ & + g_{12}\,[x_1(P_2^2 + P_3^2) + x_2(P_3^2 + P_1^2) + x_3(P_1^2 + P_2^2)] \\ & + g_{44}\,(x_4P_2P_3 + x_5P_3P_1 + x_6P_1P_2) + \ldots \end{aligned}$$

in which all terms through the order $P^4$, that are allowed by the crystal symmetry, are given. By setting the stresses

$$X_i = -\frac{\partial A}{\partial x_i}$$

equal to zero, one can find the following relations between the coefficients of the free energy in Eqs. (2.21) and (2.27), in which double primes indicate that the coefficients are for an unstrained crystal.

$$\begin{aligned} w' &= w'' \\ \xi'_{11} &= \xi''_{11} + 2\,\frac{-g_{11}^2(c_{11} + c_{12}) + 4g_{11}g_{12}c_{12} - 2g_{12}^2c_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \\ \xi'_{12} &= \xi''_{12} + 2\,\frac{g_{11}^2c_{12} - 2g_{11}g_{12}c_{11} + g_{12}^2(-c_{11} + 2c_{12})}{(c_{11} - c_{12})(c_{11} + 2c_{12})}\,. \end{aligned} \qquad (2.28)$$

These relations express the effect of electrostrictive action in causing the free crystal to behave differently from the clamped crystal. If experimental values of the elastic constants $c_{11}, c_{12}, c_{44}$ were available, one could evaluate these corrections numerically, finding $g_{11}, g_{12}, g_{44}$ from the observed deformations of the crystal as a function of

polarization. Mason (M1) has determined the constants for $BaTiO_3$ ceramic material, but they probably would not be a reliable indication of the values for a single crystal.

At this point Devonshire turns to a model theory in which $BaTiO_3$ is regarded as an ionic crystal and the force constants between ions are calculated following Born's treatment (F3). Assuming the Poisson ratio to be 1/3, the elastic constants $c_{11}, c_{12}, c_{44}$ are calculated from the Born-Mayer potential energy function, and the corrections Eq. (2.28) are thus evaluated numerically. Since the ionic character of $BaTiO_3$ appears very doubtful, however, it is not clear that this method of evaluation is more reliable than using Mason's experimental values for ceramics would be. Good measurements of the elastic constants of $BaTiO_3$ single-domain crystals would represent an important step forward from our present experimental knowledge of its properties.

The values of the $\xi$ constants given by Devonshire are, in $cm^3\ erg^{-1}$:

$$\xi''_{11} = 65.6 \times 10^{-12} \qquad \xi'_{11} = -4.4 \times 10^{-12}$$

$$\xi''_{12} = -0.2 \times 10^{-12} \qquad \xi'_{12} = 5.3 \times 10^{-12} \ .$$

The difference between the primed (free) and double primed (clamped) quantities is so great here that the free and clamped crystals would show a completely different behavior; both coefficients have their signs reversed by the electrostrictive action, and the magnitude of $\xi''_{11}$ is reduced by more than a factor of ten, while that of $\xi''_{12}$ is increased by more than a factor of twenty. According to these values the free crystal would show a first-order transition at 120°C with polarization in an axial direction, while the clamped crystal would show a second-order transition about ten degrees lower with polarization along a

cube diagonal. Although we have no experimental disproof of such behavior for the clamped crystal, it seems highly doubtful that the mechanical deformation could lead to such a radical change in properties. We conclude that the numerical values given by Devonshire are probably subject to revision and that with the correct values of the $\xi$ coefficients and the elastic constants, the free and clamped properties will differ by more moderate, although still highly significant, amounts.

The mechanism considered by Devonshire for producing ferroelectric behavior is the cooperation of a rather large polarizability due to ionic displacement and the mechanical deformation effects discussed above. The effective field acting on each ion was assumed given by the Lorentz factor $\beta = 4\pi/3$, and the polarization of ions by distortion was not taken into account. These features have been criticized and modified by Slater, whose work we consider next.

## 2.3 The Slater theory

Slater (S1) has modified the Devonshire theory by taking into account polarization of ions by distortion, and by using values of the internal fields at the ion sites determined from electrostatic calculations based on the actual arrangement of ions rather than on the assumption of a Lorentz factor of $4\pi/3$ for all positions. His model is that of Megaw (M6) who suggested that the small Ti ions could move rather freely in the oxygen octahedra. The displacement of Ba or O ions is not considered, but the electronic polarizability of all ions is taken into account. From the observed index of refraction, optical polarizabilities of the ions are assigned, and Slater shows, as did Jonker and van Santen (J2), that this electronic polarizability is so large that the contribution of ionic displacement need not be large in order to result in ferroelectricity.

In Slater's theory, as in Devonshire's, the

various terms in the expansion of the free energy in powers of the polarization are related to corresponding terms in the expansion of the potential energy of the Ti ion in powers of its displacements from the center of the unit cell. However, Slater considers only Ti displacement, while Devonshire takes into account displacements of all ions. In view of Devonshire's estimate that the oxygen ions are much more loosely bound to their symmetrical positions than are the Ti ions a more general treatment seems necessary. This point will be discussed further in Section 2.4.

Another difficulty with Slater's treatment is that ferroelectricity seems to be explained too easily; there is such a great enhancement of the effect of Ti displacement due to the electronic polarizabilities of the ions that one must then assume an abnormally low value of polarizability due to Ti displacement in order to explain why the Curie point is as low as it is, while the model was originally based on the idea that the Ti ions would be somewhat more freely movable than ions usually are.

Slater finds that ferroelectricity occurs when

$$\frac{4\pi\alpha_{Ti'}}{3v} = 0.062 \tag{2.31}$$

where $\alpha_{Ti'}$ is the polarizability due to Ti displacement, i.e., the ratio of dipole moment to local field at the Ti ion, and $v$ is the volume of a unit cell. All other ionic polarizabilities are assumed equal to zero. If ionic polarizabilities associated with the Ba and O ions had been introduced, the value needed for $\alpha_{Ti'}$ would be even smaller, or more likely negative. On the other hand, Devonshire, following Born's treatment, estimated a restoring force on the Ti ion of $F = -9.4 \times 10^5 z$ dynes, where $z$ is its displacement in cm. This leads to an ionic polarizability of the Ti ion more than four times that given by Eq. (2.31), and comparable values are found for the Ba and O ions.

It is evident that we have here a mild form of the "$4\pi/3$ catastrophe"; the difficulty is not in explaining why $BaTiO_3$ is ferroelectric but in explaining why it is not much more strongly ferroelectric than it is.

This same difficulty was encountered earlier in attempts to account for the dielectric constants of non-ferroelectric crystals in terms of electronic and ionic polarizability. A short review of the work of Fajans and Joos, Heckmann, Hojendahl, and others is given in Chapter I of Mott and Gurney (M14) with the conclusion that the dielectric constants of the alkali halides are best accounted for if we assume a Lorentz factor of zero rather than the "theoretical" value of $4\pi/3$. Mott and Gurney ascribe this apparent weakening of the electrostatic interaction of ions to overlapping of electronic wave functions of adjacent ions, which causes the field at the position of one ion due to polarization of adjacent ions to be greatly reduced. If this explanation is correct, the same effect might lead to considerable changes in the treatments of Devonshire and Slater.

There are three further reasons for expecting a decrease in the apparent internal field in models of the above type. First, we should really apply some correction for the correlations of the instantaneous polarizations of neighboring ions, which would be analogous to that made by Onsager for the case of rotating permanent dipoles, but probably much less drastic. That this could affect the apparent electronic polarizabilities at low frequencies as well as the ionic polarizabilities may be seen as follows. Measurements of dielectric constant at optical frequencies are essentially undisturbed by thermal vibrations, the maximum frequency of which is of the order of a hundred times lower than the optical frequencies. Under these conditions, all similarly situated ions will have the same change in dipole moment per cycle, although the mean dipole moment over a cycle will still fluctuate due to

thermal agitation, and their interaction at optical frequencies will be correctly given by the classical Lorentz theory. For the low frequency case, however, the mean interaction energy of the ions is obtained by averaging over the thermal fluctuations and thus will be affected by correlations between the fluctuations of neighboring dipoles. Similar reasoning to that given in Section 1.1 shows that again this has the effect of reducing the effective internal fields. This effect would be particularly important for ionic displacements.

A second effect reducing the apparent internal field for ionic displacement is the following. The force effective in displacing an ion is not only that arising from the internal electric field at its position but there is also a mechanical force due to displacement of neighboring ions. When the applied electric field tends to displace a positive ion upwards, it will also displace the adjacent negative ions downwards, and as a result mechanical forces will be called into play which will reduce the displacement of all ions. Because of this interaction it is not, strictly speaking, possible to assign values of ionic polarizability to individual ions, as has so often been attempted; the dipole moment of an ion due to its displacement is not merely proportional to the internal electric field which it sees, but is a linear combination of this term and another arising from the motion of neighboring ions.

In connection with this effect a recent theory of Roberts (R4) concerning the dielectric constants of alkali halides is of interest. Although his model is an extremely idealized one, making use of sharp, rigid, and weightless ionic boundaries, this mechanical force appears in the calculations (loc.cit., Eq. 8), and whatever one may think of the actual model, it is clear that a correct treatment would involve equations of a very similar form.

A third reason why the true internal field is

overestimated in treatments of this type has been pointed out in an important recent note by Cohen (C5). He shows that considerable errors are incurred if we merely calculate the internal field at the undisplaced position of an ion. The field actually effective in polarizing an ion is the value at its displaced position, and the difference between the two fields can be comparable to the fields themselves. An example where this is clearly the case is the field at an ion due to displacements of similar ions in other unit cells. In the usual treatments we would calculate a value comparable to the other terms due to other types of ions. However, it is clear that ions of a given type form a sublattice that merely undergoes a uniform displacement, so that the resulting field at the displaced ion due to this lattice is exactly zero. Thus, the expression for the field at a Ti ion should not contain any term arising from displacement of other Ti ions, as it does in the treatments being discussed.

Recent measurements by Mayburg (M15) of the pressure dependence of dielectric constant for a number of ionic crystals show a decrease that according to Mayburg can be explained only if the effective Lorentz factor decreases with increasing pressure. This tends to confirm the above speculations since both the electronic overlapping and the interionic mechanical forces would be expected to become more important as the pressure increases.

The above remarks are not intended to imply that the Ti displacement model is incapable of explaining the action of $BaTiO_3$; the question is left unanswered because even a semiquantitative study of the consequences of the model cannot be carried out until certain fundamental problems in the theory of dielectric properties of ionic crystals are solved. It appears that the resolution of the above "mild catastrophe" must be one of the first steps in this direction. A really satis-

factory treatment would, of course, be extremely complicated. Reasons for doubting the Ti displacement theory, as explained in later sections, concern chiefly the question whether $BaTiO_3$ is an ionic crystal and the fact that displacement of the O ions appears to be a more promising model if it is ionic.

Perhaps the most interesting and generally applicable part of Slater's work is his treatment of internal fields, taking into account the actual arrangement of ions and therefore the actual departures from the $4\pi/3$ theory. This very illuminating treatment, similar to the calculations performed here in Chapters 4 and 5, may be regarded as the basis for a general theory of dielectric constants of crystals.

## 2.4. The oxygen displacement theory

If we regard $BaTiO_3$ as an ionic crystal and use the Goldschmidt radii, we find (M6) that each oxygen ion is squeezed rather tightly between four coplanar Ba ions but is free to move at right angles to this plane toward the Ti ions (Fig. 1.2). Devonshire (D3) shows that the restoring force for small displacements in this direction is near zero and of uncertain sign, while the Ti ion is definitely bound to its symmetrical position. Therefore it appears that any theory of $BaTiO_3$ based on the picture of an ionic crystal with rather freely movable ions must consider motion of oxygen ions as being at least as important as is Ti displacement, and in fact a model in which oxygen displacement is the active cause of ferroelectricity is capable of explaining in a very simple manner the existence of three phase transitions (J1). Each unit cell has three oxygen ions, $O_x$, $O_y$, $O_z$, which are free to move in the x,y,z directions respectively. As the crystal is cooled, the mismatch of ionic sizes successively causes the $O_z$, then the $O_y$, then the $O_x$ ions to be squeezed out of their planes of Ba ions, thus causing a spontaneous polarization first along

a cube edge, then a face diagonal, then a body diagonal, as is observed experimentally. In this model the effect of electromechanical coupling in increasing the rate at which polarization sets in below the Curie point may be seen directly without any thermodynamic analysis; as the $O_z$ ions move out of the plane of the Ba ions, the whole structure can contract in this plane while expanding in the z-direction. This deformation of the crystal reduces the lattice energy, so that the force tending to displace the $O_z$ ion is not merely the electrostatic force due to its interaction with other $O_z$ ions, but there is also a direct mechanical force tending to increase its displacement. The amount of the transverse contraction in the tetragonal phase may be calculated very easily with the oxygen displacement model; a simple geometrical argument based on hard spheres in contact gives for the transverse contraction

$$-\frac{\Delta a}{a} = \left(\frac{z}{a}\right)^2$$

where "a" is the lattice constant and z the displacement of the $O_z$ ion. The resulting polarization is

$$P_{O_z} = 2eza^{-3}$$

so that

$$-\frac{\Delta a}{a} = \frac{a^4}{4c^2} = 3.8 \times 10^{-12} P_{O_z}^2 .$$

Experimentally (M7), $-\Delta a/a$ is found to be accurately proportional to the square of the total polarization, with a coefficient of $1.2 \times 10^{-12}$; therefore, if $P_{O_z}$ represents 56 percent of the total polarization, the transverse contraction is given correctly.

This simple prediction of the correct order of magnitude of the mechanical deformation of the crystal is to be contrasted with the phenomenological treatment,

where one estimates the coefficient by comparison with the observed deformations, no attempt being made to deduce it from the model. We note that a displacement of O is physically equivalent to the opposite displacement of Ba and Ti, and the oxygen displacement theory is a special case of the Devonshire theory with the added feature that electromechanical constants are deduced from the model.

In spite of the apparent promise of this theory and a certain intuitive appeal arising because predictions of the model may be seen qualitatively by very simply physical reasoning without mathematical analysis, it lay dormant for some time because it seemed very doubtful whether $BaTiO_3$ can be regarded as an ionic crystal, an assumption which underlies all of the ionic displacement theories, especially when one uses values of electronic polarizability obtained from refractive indices of other compounds involving a given ion, as Slater does. An ion has a unique polarizability only when its electronic structure is specified, and this polarizability depends critically on the states of those outer electrons which are greatly perturbed unless the crystal is strongly ionic.

However, recent X-ray measurements of Kaenzig (K6) and of Evans and Hutner (E6) have shown that the oxygen nuclei do move (relative to the Ba ions, of course) much more than do the Ti nuclei so that it becomes worthwhile to explore the theory more fully. Schweinler (S8) has described a model patterned after Slater's treatment in which the ionic polarizability of oxygen is assumed several times larger than that of Ti. Results of this work will be awaited with interest.

### 2.5 The electronic theory

The electric moment of ferroelectric and pyroelectric crystals is usually attributed to the displacement of ions from central positions in a lattice cell. In many cases the asymmetrical positions of ions can be

verified directly by X ray analysis; for example, there is no doubt that ionic position is the key to the electrical behavior of tourmaline. In the case of barium titanate, it is usually supposed, as we have just seen, that displacement of the $Ti^{4+}$ ion in the octahedron of $O^{--}$ ions is responsible for the electric moment. This theory received a serious setback by X-ray experiments of Danielson and Rundle (D1) and Kay, Wellard, and Vousden (K2) which failed to find conclusive evidence of any displacement accompanying the onset of spontaneous polarization. The theory described below was first proposed at a time when it seemed doubtful whether any ionic motion occurred. As we have just seen, more recent work has shown that there is some ionic motion, but that oxygens are the active ions. Although this does not in itself invalidate the electronic theory, lack of ionic displacement can no longer be cited as evidence for such a theory. However, there is a considerable amount of other evidence. According to Matthias (M4) all substances are ferroelectric in which an atom or ion with a closed shell is surrounded by an octahedron of O ions, in the manner of the structure of $BaTiO_3$, if the dimension of the octahedron approximates a definite size. Similar conclusions are found by Smolenskii and Kozhevhikova (S9). The substances $LiTaO_3$, $NaTaO_3$, $KTaO_3$, $RbTaO_3$, $LiNbO_3$, $NaNbO_3$, $KNbO_3$, $LaFeO_3$, $PbZrO_3$, $MoO_3$, and $WO_3$ have been shown to be ferroelectric, with Curie points ranging from a few degrees absolute to nearly 1,000°K. Thus it appears to be the oxygen octahedron structure rather than the presence of any specific positive ion that is the necessary element for producing ferroelectricity, and the electronic structure of this arrangement becomes an important question.

There is independent evidence from other properties of ferroelectrics of the titanate type that has already led to suggestions that electronic effects be

investigated. $BaTiO_3$ has an abnormally large refractive index inconsistent with the polarizabilities which its constituents exhibit in other crystals, and van Santen and deBoer (S4) have pointed out that this behavior is exhibited by all compounds containing a Ti ion surrounded by six oxygen ions. Van Santen and collaborators (S4, S5) suggest that the abnormally high polarizability may result from transfer of an electron back and forth between O and Ti ions, and Shockley (S6) has made a similar suggestion in pointing out that the polarizability of O in the presence of Ti appears to be nearly twice as great as in other oxides. (Remember that ions have definite polarizabilities only in strongly ionic crystals.) As a function of temperature the refractive index of $BaTiO_3$ passes through a rather sharp maximum (about $20^\circ$ wide) at the Curie point (M7, B10), suggesting some electronic rearrangement. Furthermore, $TiO_2$ shows a weak temperature-independent paramagnetism (E5) which may indicate that its electronic structure is not a closed-shell arrangement. However, according to Matthias[1] this may also be due to traces of $Ti^{3+}$.

This is disputed - Jonker & Shirane p. 120

We therefore adopt the point of view that $BaTiO_3$ is not a strongly ionic crystal and that its electronic structure is such that the oxygen octahedron must be thought of as a single unit rather than as a structure of several independent parts. Now an octahedron of closely packed, highly polarizable oxygen ions should provide fairly good "shielding" of the internal Ti ion against external conditions so that one could consider each octahedron as possessing, in first approximation, an internal electronic quantum state independent of the state existing in adjacent unit cells. Because of the central symmetry of this unit, in the absence of an electric field each state will have a definite parity and will not give

[1] B. T. Matthias, private communication.

rise to any dipole moment. However, if two states of opposite parity lie close together in energy, interactions between octahedra may have the consequence that the crystal as a whole has a lower energy if the internal state of each octahedron goes over into a linear combination of the symmetrical states. This linear combination of states would have a nonvanishing dipole moment so that a spontaneous polarization and internal electric field would appear.

The electronic theory was first proposed by E. P. Wigner (W4), who developed in some detail a model, already briefly mentioned in Section 1.2, in which the effect of temperature was manifested chiefly in a change in the unperturbed energy separation of the states of the unit cell rather than in the statistical factors as in the model to be described below. Since the original model leads to a prediction of two Curie points with spontaneous polarization between them, it might be considered seriously as a model for Rochelle salt. In that application it would appear to have an advantage over the hydrogen bond model of Mason (M13) because it leads to a low specific heat anomaly. It is, in fact, the only model thus far proposed which gives two Curie points in a completely natural way. All other theories have had to rely on two different mechanisms to give the two transitions.

Formulation of the problem. We give first an outline of a method of attack of the type associated with the names of Clausius, Mosotti, Lorentz, and Langevin which assumes that interaction between octahedra will take place chiefly through the internal electric fields which they generate. In this approach, the problem is broken down in the following way:

1. An applied electric field $E$ produces in a crystal of temperature $T$ a (macroscopic) polarization $P(E,T)$. The present problem is to find this function, in particular $P(0,T)$.

2. The effective field operative in the interior of an oxygen octahedron is then $F = E + \beta P$, where $\beta$ is the Lorentz factor. The correct value of this factor, and even the validity of an expression of this form for the case of interest here, are quite difficult questions which will require a good deal of discussion.

3. The oxygen octahedron, under the influence of the internal field $F$, becomes polarized, the amount due to mixing of electronic states being $P_e(F,T)$.

4. The total macroscopically observed polarization actually consists of the sum of $P_e$, a term $P_i$ due to polarization of the ion cores (including the polarizability of the Ba ions, and possibly of the Ti and O ions, depending on how detailed our treatment of (3) is); and a term $P_d$ due to displacement of the ions from their normal lattice points. In calculating $P_i$ and $P_d$ we may not assume that the local field is the same as that used to calculate $P_e$, but must consider the field seen at each ion site as a separate problem. Thus, we have in all six subproblems, one of type (2) and one of type (3) for each of the three kinds of polarization.

5. The solutions of these subproblems are then "tied together" by the condition that they be simultaneously consistent.

This program, even if carried out in the full detail suggested above, would not be a rigorous treatment of the problem since it assumes that the quantum state of one unit cell is statistically independent of the states of adjacent cells. The average dipole moment is the same in all cells, and this average polarization $P_e$ is then used to calculate the local field acting on the cells. Actually, a given unit cell is more strongly affected by the states of adjacent cells than this would imply, and we expect a rather strong correlation between the dipole moments of cells close together. This correlation may be

taken into account partially by the Bethe-Peierls method, previously used in treatments of order-disorder transitions and ferromagnetism, but the added accuracy does not seem sufficient to justify the work involved.

In order to demonstrate the general type of behavior that would result from the electronic polarization mechanism, consider first a simplified treatment in which we put for the effective field in the oxygen octahedron,

$$F = E + \beta (P_e + P_i + P_d) \qquad (2.5.1)$$

and further assume that $(P_i + P_d) = \gamma F$, where $\beta$ and $\gamma$ are unspecified constants. Elimination of $(P_i + P_d)$ gives us then

$$F = \frac{E + \beta P_e}{1 - \beta\gamma} \quad . \qquad (2.5.2)$$

Making the simplest possible assumptions about the internal states, we postulate that, in the absence of the field $F$, the ground state of the octahedron is invariant under its symmetry group $O_h$ and is therefore of even parity. The polarizability of the octahedron must result from the existence of excited states which are coupled to the ground state by the dipole moment operator. An excited state will belong to one of the ten irreducible representations of $O_h$, described by the character table on page 56.

The multiplication table for product representations is found to be

| $\Gamma_1$ | $\Gamma_2$ | $\Gamma_3$ | $\Gamma_4$ | $\Gamma_5$ |
|---|---|---|---|---|
| $\Gamma_2$ | $\Gamma_1$ | $\Gamma_3$ | $\Gamma_5$ | $\Gamma_4$ |
| $\Gamma_3$ | $\Gamma_3$ | $(\Gamma_1 + \Gamma_2 + \Gamma_3)$ | $(\Gamma_4 + \Gamma_5)$ | $(\Gamma_4 + \Gamma_5)$ |
| $\Gamma_4$ | $\Gamma_5$ | $(\Gamma_4 + \Gamma_5)$ | $(\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5)$ | $(\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5)$ |
| $\Gamma_5$ | $\Gamma_4$ | $(\Gamma_4 + \Gamma_5)$ | $(\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5)$ | $(\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5)$ |

| $O_h$ | I | $8C_3$ | $6C_2$ | $6C_4$ | $3C_4^2$ | $S_2$ | $8S_6$ | $6\sigma_d$ | $6S_4$ | $3\sigma_h$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_1^+$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $\Gamma_1^-$ | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 |
| $\Gamma_2^+$ | 1 | 1 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | 1 |
| $\Gamma_2^-$ | 1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | 1 | -1 |
| $\Gamma_3^+$ | 2 | -1 | 0 | 0 | 2 | 2 | -1 | 0 | 0 | 2 |
| $\Gamma_3^-$ | 2 | -1 | 0 | 0 | 2 | -2 | 1 | 0 | 0 | -2 |
| $\Gamma_4^+$ | 3 | 0 | -1 | 1 | -1 | 3 | 0 | -1 | 1 | -1 |
| $\Gamma_4^-$ | 3 | 0 | -1 | 1 | -1 | -3 | 0 | 1 | -1 | 1 |
| $\Gamma_5^+$ | 3 | 0 | 1 | -1 | -1 | 3 | 0 | 1 | -1 | -1 |
| $\Gamma_5^-$ | 3 | 0 | 1 | -1 | -11 | -3 | 0 | -1 | 1 | 1 |

in which parity signs are added in the obvious way; for example, $\Gamma_3^+ \times \Gamma_4^- + \Gamma_5^-$, $\Gamma_2^- \times \Gamma_5^- = \Gamma_4^+$, etc. Sets of functions which form a basis for five of the representations are:

$$\Gamma_1^+ \quad : \quad (x^2 + y^2 + z^2)$$

$$\Gamma_2^- \quad : \quad (xyz)$$

$$\Gamma_3^+ \quad : \quad (2z^2 - x^2 - y^2),(x^2 - y^2)$$

$$\Gamma_4^- \quad : \quad (x),(y),(z)$$

$$\Gamma_5^+ \quad : \quad (xy),(yz),(zx)$$

in which $x,y,z$ are rectangular coordinates. The dipole moment operator is seen from this to belong to the representation $\Gamma_4^-$, and in order that it may have nonvanishing matrix elements between the ground state $\Gamma_1^+$ and and excited one, the excited state must belong to a representation $\Gamma$ for which the product representation

$$\Gamma_1^+ \times \Gamma_4^- \times \Gamma$$

contains the identical representation $\Gamma_1^+$. From the above multiplication table we see that the only representation which meets this requirement is

$$\Gamma = \Gamma_4^- ,$$

so that the excited state must be triply degenerate. These necessary symmetry conditions are met in the simplest possible way if we write for the excited states

$$\Psi_1 = x\phi(\vec{r}); \qquad \Psi_2 = y\phi(\vec{r}); \qquad \Psi_3 = z\phi(\vec{r})$$

where $\phi(\vec{r})$ is symmetric under $O_h$. We denote the unperturbed energy separation between the ground state $\Psi_o$ and these states by $2\epsilon$ and choose the zero of energy to be midway between these levels. The unperturbed Hamiltonian then becomes

$$H_o = \left(\begin{array}{c|ccc} -\epsilon & 0 & & \\ \hline 0 & \epsilon & & \\ & & \epsilon & \\ & & & \epsilon \end{array}\right)$$

If now the field $F$ in the x-direction is turned on, we get a perturbed Hamiltonian

$$H = \left(\begin{array}{c|ccc} -\epsilon & V & 0 & 0 \\ \hline V & \epsilon & & \\ 0 & & \epsilon & \\ 0 & & & \epsilon \end{array}\right)$$

where $V = -eF \int_v \Psi_o x \Psi_1 dv = \mu F$, $v$ being the volume of a unit cell and $\mu$ the maximum dipole moment due to mixing of states (0,1). States (2,3) do not play any active part in the polarization, but their presence alters the statistics, so they cannot be ignored. $H$ is diagonalized by the transformation matrix

$$S = \left(\begin{array}{cc|cc} \cos\theta & -\sin\theta & & \\ \sin\theta & \cos\theta & & 0 \\ \hline & & 1 & \\ & 0 & & 1 \end{array}\right) \text{ with } \tan 2\theta = \frac{\mu F}{\epsilon}.$$

Then

$$SHS^{-1} = \left(\begin{array}{c|cc} -b\epsilon & 0 & \\ \hline & +b\epsilon & \\ 0 & & \epsilon \quad \epsilon \end{array}\right)$$

where $b = \sec 2\theta = (1 + \mu^2 F^2/\epsilon^2)^{1/2}$. The energy level diagram becomes

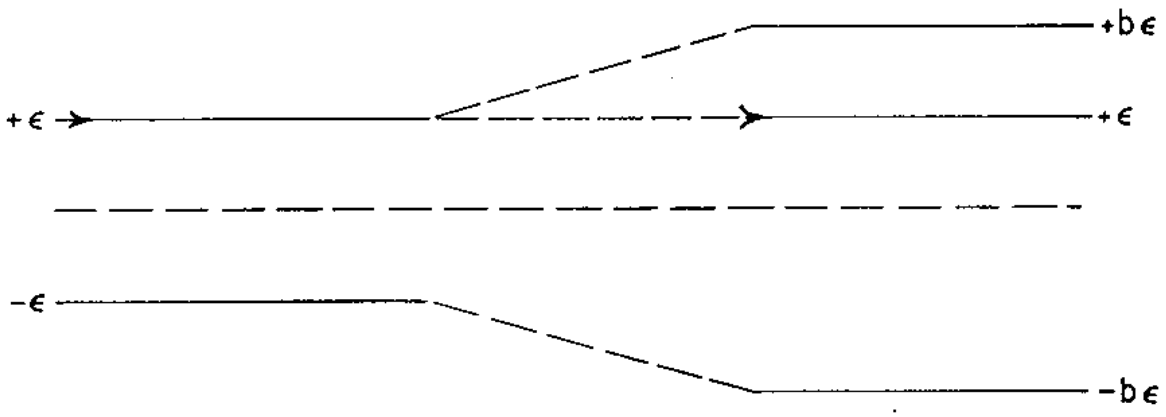


FIG. 2.1

and the perturbed unit cell now has a partition function

$$Z = e^{\frac{b\epsilon}{kT}} + e^{-\frac{b\epsilon}{kT}} + 2e^{-\frac{\epsilon}{kT}} = 2[\cosh b\chi + e^{-\chi}], \chi = \frac{\epsilon}{kT} .$$

The free energy of the cell is $A = -kT \log Z$, and at frequencies low enough so that we have thermal equilibrium at all times, its mean dipole moment is

$$D = -\frac{\partial A}{\partial F} = \frac{kT}{Z}\frac{db}{dF}\frac{\partial Z}{\partial b} = \mu \frac{\sqrt{b^2 - 1}}{b}\frac{\sinh bx}{\cosh b\chi + e^{-\chi}}$$

which gives rise to the polarization term

$$P_e = \frac{\mu}{v}\frac{\sqrt{b^2 - 1}}{b}\frac{\sinh bx}{\cosh bx + e^{-\chi}} . \quad (2.5.3)$$

To make this consistent with Eq. (2.5.2), we write Eq. (2.5.2) in the form

$$(2.5.4)\quad P_e = \frac{F(1 - \beta\gamma) - E}{\beta} = \frac{\epsilon}{\beta\mu}\sqrt{b^2 - 1}\,(1 - \beta\gamma) - \frac{E}{\beta}$$

and equate the two expressions, giving us the fundamental relation

$$(2.5.5)\quad \frac{\sqrt{b^2 - 1}}{b}\left\{Kb - \frac{\sinh bx}{\cosh bx + e^{-x}}\right\} = \frac{vE}{\mu\beta}$$

in which

$$K = \frac{\epsilon v}{\mu^2}\,\frac{(1 - \beta\gamma)}{\beta}\quad .$$

To investigate spontaneous polarization we set $E = 0$, and this reduces to

$$(2.5.6)\qquad Kb = \frac{\sinh bx}{\cosh bx + e^{-x}}\quad .$$

This equation must be solved graphically to give $b$ (and therefore $P_e$) as a function of $K$ and $x$. Since

$$b = \sqrt{1 + \frac{\mu^2 F^2}{\epsilon^2}} = \sqrt{1 + \frac{v^2 P_e^2}{\mu^2 K^2}}\quad ,$$

only values of $b$ greater than unity correspond to physical solutions, and the Curie point is determined by $b = 1$, or

$$(2.5.7)\quad K = \frac{\sinh x_c}{\cosh x_c + e^{-x_c}} = \frac{e^{2x_c} - 1}{e^{2x_c} + 3}\quad ,\ \text{or}\quad \frac{2K}{1+K} = \tanh x_c .$$

At low temperatures ($x \gg 1$), (7) reduces to $Kb = 1$, or

$$(P_e)_{max} = \frac{\mu}{v} \sqrt{1 - K^2} \quad . \qquad (2.5.8)$$

At any temperature, the total experimentally observed polarization is

$$P = P_e + \gamma F = \frac{P_e + \gamma E}{1 - \beta\gamma} = \frac{F - E}{\beta} \qquad (2.5.9)$$

We must now investigate to what extent this simple model is capable of accounting for the experimental results with reasonable values of $\mu$ , $\epsilon$ , $\beta$ , and $\gamma$ . Although the number of parameters is large, they are not all independent, and we will find that nearly all experimental properties can be expressed in terms of $x_c = \epsilon/kT_c$ alone. Furthermore, we must be prepared to find that the finer details of behavior at the Curie point are not given adequately by any model as crude statistically and otherwise as the present one. The sort of situation to be expected is analogous to that occurring in the treatment of the two-dimensional Ising net, in which the rigorous treatment of the statistical problem, only recently achieved by Onsager, revealed new features in the vicinity of the critical point that were qualitatively different from any that could be obtained by various approximate methods. This experience also suggests that we should not try to use experiments on the behavior very near the Curie point for evaluation of our constants.

Experimental values of the dielectric constant above the Curie point and of the maximum spontaneous polarization at low temperatures may be used to fix the values of some of the constants.

The equation of consistency, Eq. (2.5.5), is valid at any temperature. Below the Curie point, b is appreciably different from unity, and the solutions must be found graphically. Above the Curie point, however, there is no spontaneous polarization, and for applied

field strengths less than several thousand volts/cm the polarization is very much less than the values encountered at low temperatures. $b$ is then so extremely close to unity that we can put $b = 1$ everywhere in Eq. (2.5.5) except in the term $\sqrt{b^2 - 1} = \mu F/E$. The equation then reduces to

$$F\left(K - \frac{\sinh x}{\cosh x + e^{-x}}\right) = \frac{KE}{1 - \beta\gamma}$$

in which, as before, $x = \epsilon/kT$. Substituting into Eq. (3.19), we have for the susceptibility

$$(2.5.10)\quad \chi = \frac{P}{E} = \frac{F/E - 1}{\beta} = \frac{1}{\beta(1 - \beta\gamma)} \frac{K}{K - \left(\frac{e^{2x} - 1}{e^{2x} + 3}\right)} - \frac{1}{\beta} .$$

We see from Eq. (2.5.7) that the denominator of the first term vanishes at the Curie point, giving Eq. (2.5.10) the general form of a Curie-Weiss law. To cast it into the usual form we expand in powers of $(T - T_c)$. A tedious but straightforward calculation gives for the susceptibility

$$(2.5.11)\quad \chi = \frac{f_2(x_c)}{\beta(1 - \beta\gamma)} \left[1 - f_1(x_c) + \frac{T_c}{T - T_c} + \ldots\right] - \frac{1}{\beta}$$

where $x_c = \epsilon/kT_c$, and

$$f_1(x) = x\left(\frac{e^{2x} - 3}{e^{2x} + 3}\right)$$

$$f_2(x) = \frac{(e^{2x} - 1)(e^{2x} + 3)}{8x\, e^{2x}} .$$

The remaining terms, being proportional to $(T - T_c)/T_c$, are small near the Curie point, and in fact Eq. (2.5.11) is a good approximation to Eq. (2.5.10) over a fairly wide

range of temperature so that Eq. (2.5.11) may be used for comparison with experiment. In carrying out this comparison the correct procedure is undoubtedly that which is used in ferromagnetism, namely, to assume that the small curvature of the experimental $1/\chi - T$ curve near the Curie point is due to correlation effects neglected in the simple model so that the value of the Curie constant appropriate to the model is that determined by the straight portion of the $1/\chi - T$ curve, which sets in $30^{\circ}$ or so above $T_c$. The model, being adjusted to give this Curie constant, will then predict the extrapolated straight line near $T_c$ rather than the experimental curve. This is the best that one can hope to do as long as there is no refinement of the model which would enable it to follow out the course of the actual curve by taking into account the correlations of polarization between adjacent unit cells.

In our discussion of the Mason-Matthias theory, we found that the experimental susceptibility of ceramic $BaTiO_3$ above the Curie point is well represented by the empirical equation

$$\chi = \frac{23.9T_c}{T - T_c}$$

with $T_c = 379^{\circ}K$. Roberts (R7)[2] has compared the experimental work of six different investigators, considering the correction for porosity of the ceramic, and has concluded that the best present value of the coefficient for single crystals is 31.4. The constant term, if it exists, cannot be much greater than unity. Thus, we have

$$\frac{f_2(x_c)}{\beta(1 - \beta\gamma)} = 31.4 \quad . \qquad (2.5.12)$$

[2] I am indebted to Dr. Roberts for an opportunity to read this manuscript.

Maximum polarization at low temperature. From the previous Eqs. (2.5.8), (2.5.9) the maximum polarization is given by

$$P_m = \frac{1}{1 - \beta\gamma} \frac{\mu}{v} \sqrt{1 - K^2} \quad . \tag{2.5.13}$$

In order to eliminate the unknown $\mu$, we construct a dimensionless expression which is a measure of the amount of polarization energy per unit cell compared to $kT_c$:

$$\frac{vP_m^2}{kT_c} = \frac{v}{kT_c} \frac{\mu^2}{v^2} \frac{1 - K^2}{(1 - \beta\gamma)^2} = \frac{x_c(1 - K^2)}{\beta(1 - \beta\gamma)K}$$

$$= \frac{8}{\beta(1 - \beta\gamma)} \frac{x_c(e^{2x_c} + 1)}{(e^{2x_c} + 3)(e^{2x_c} - 1)} \tag{2.5.14}$$

$$= \frac{2\, g(x_c)}{\beta(1 - \beta\gamma)} \quad .$$

Here we have used the relation

$$K = \left( \frac{e^{2x_c} - 1}{e^{2x_c} + 3} \right)$$

The function $g(x)$ is defined by

$$g(x) = \frac{4x(e^{2x} + 1)}{(e^{2x} + 3)(e^{2x} - 1)}$$

An experimental value of Eq. (2.5.13) may be obtained from the measurements of Merz (M7). He finds $P_{max} = 15.6 \times 10^{-6}$ coulombs/cm$^2$ $= 4.68 \times 10^4$ esu. Therefore we have

$$\frac{vP_m^2}{kT_c} = \frac{(4 \times 10^{-8})^3 \times 4.68^2 \times 10^8}{1.38 \times 10^{-16} \times 393} = 2.59 \quad . \tag{2.5.15}$$

Here we have used the experimental transition temperature $393^{O}K$ for $T_c$ instead of the value that fits the experimental susceptibility above $T_c$. In this case the difference is relatively unimportant.

We now have another relation for the determination of constants;

$$\frac{g(x_c)}{\beta(1-\beta\gamma)} = \frac{2.59}{2} = 1.30 \qquad (2.5.16)$$

Comparing this with the result from the dielectric constant above the Curie point, we have the relation

$$h(x_c) = \frac{f_2(x_c)}{2g(x_c)} = \frac{31.4}{2 \times 1.30} = 12.1 \qquad (2.5.17)$$

From a graph of $h(x)$ we find the value

$$x_c = 2.0.$$

Using this value we find that

$$\frac{1}{\beta(1-\beta\gamma)} = \frac{1.30}{g(x_c)} = 8.3. \qquad (2.5.18)$$

As in the Mason-Matthias theory, the susceptibility above $T_c$ and the maximum polarization depend in the same way on the quantity $\beta(1-\beta\gamma)$ so that we have not yet enough information to fix $\beta$ and $\gamma$ separately. We note that the value of $x_c$ found is very insensitive to the experimental data since $h(x)$ varies as $e^{4x}/64x^2$ for $x > 1$. This means that any future improvements in experimental accuracy will have a negligible effect on the value of $\epsilon$, although refinements in the model could of course effect $\epsilon$ somewhat more. Without a rather drastic change in the model, however, we conclude that

any electronic theory that predicts experimental behavior even qualitatively like that of $BaTiO_3$ must have the initial levels separated not far from $4kT_c$.

The distinguishing feature of the theory developed here is that one odd level (which symmetry arguments show is necessarily triply degenerate) lies within a few kT of the ground state. Conceptually, this theory therefore resembles somewhat the van Vleck-Frank theory of paramagnetism.

The electronic model can account quantitatively for the observed dielectric constant at high temperatures, the magnitude of the polarization at low temperatures, and the entropy change accompanying the transition to the polarized state. Difficulties of the type mentioned in connection with the Mason-Matthias theory do not occur. It is not possible at present to tell whether the rate at which polarization sets in below the Curie point is given quantitatively by the model because this is greatly affected by the tetragonal distortion of the crystal, but estimates based on elastic constants of the ceramic material indicate that there is no difficulty here. Measurements of the elastic constants $c_{11}, c_{12}, c_{44}$ of single-domain crystals would enable an exact check to be made.

A few numerical details may serve to give a general picture of the behavior of the electronic model. The initial level separation, as already mentioned, is fixed not far from $4kT_c = 0.13$ ev., where $T_c = 120^{\circ}C = 393^{\circ}K$ is the Curie temperature. This value is quite insensitive to the experimental data on Curie constant and strength of spontaneous polarization. In the polarized state, the mixing of the ground state $\psi_o$ and the excited state $\psi_1$ is not complete; the ground state goes over into a linear combination

$$\psi_a = \psi_o \cos\theta + \psi_1 \sin\theta ,$$

with $\theta$ about $20^{\circ}$, whereas complete saturation, approached in the limit of infinitely strong internal fields, would correspond to $\theta = 45^{\circ}$. From this, one finds that the mean dipole moment of the unit cell in the spontaneously polarized state rises to only about 40 percent of the saturation value. It is for this reason that the dielectric constant at low temperatures for fields in the direction of spontaneous polarization is still abnormally large, of the order of hundreds, and the experimental hysteresis loops (M7) show the polarization rising considerably above the spontaneous value when a strong supporting electric field is applied. Although the magnitude of the spontaneous polarization (about 16 microcoulombs/$cm^2$) is quite impressively large from a macroscopic point of view, this corresponds to a dipole moment of only about $3 \times 10^{-18}$ esu per unit cell, of which probably not more than half is due to the mixing of electronic states, the remainder arising from polarization of Ba ions and nuclear displacements. From an atomic point of view, therefore, the electronic rearrangement is not drastic, corresponding to motion of one electron through less than a tenth the length of a unit cell. It is for this reason that the entropy change accompanying spontaneous polarization is so small, amounting to only about 0.02 k per unit cell both theoretically and experimentally.

The magnitude of the interaction between unit cells remains an unexplained feature even after lengthy electrostatic calculations of internal fields as described in Chapters 4 and 5, which indicate that the interaction should be even greater than the classical Lorentz value, while in order to fit the data with reasonable values of $\gamma$, we need a L. F. of not more than 0.5 (J3). In this respect the electronic theory is in a position comparable to that of the Langevin-Weiss theory of ferromagnetism before Heisenberg's treatment of exchange forces. It was then realized that, assuming interactions of a certain strength, the behavior of ferromagnetic materials could

be well accounted for, but there seemed to be little justification for such a strong interaction. In the present case, the difficulty is in explaining why the interaction is as weak as it is. The same difficulty is found in other treatments of dielectric properties of crystals and in other attempts to explain the properties of $BaTiO_3$. Mott and Gurney and others have concluded that the actual interactions in crystals are much weaker than one would suppose from electrostatic arguments. A number of effects which tend to weaken the interactions have been discussed, but none is conclusively demonstrated as adequate to the need.

The fact that, strictly speaking, the polarizability matrix $\alpha$ as defined in Section 5 cannot be diagonal, as assumed in the calculations there, should be kept in mind. In fact, the great stability of the $TiO_3$ complex shows that there are directed valence forces, and one cannot simply add polarizabilities as e. g., in NaCl. The latter completely dissociates in solution, while the $TiO_3$ stays together. These considerations may also help to clear up the similar difficulty encountered in the Slater-Devonshire theory.

There are several facts which may be cited as indirect evidence for the electronic theory. The result noted in Section 1.4 that the Curie temperature depends primarily on lattice size rather than on the combination of pressure and ionic radii that produce that size, Matthias' results about the occurrence of $BaTiO_3$ ferroelectricity, and the depolarization of crystals by infrared radiation, all point in this direction. A further qualitative point in favor of the electronic theory is that the behavior of $BaTiO_3$ is so radically different from that of Tourmaline and other pyroelectric substances, for which there is little doubt that movement of ions is the cause of polarization. If one defines pyroelectricity as a condition in which a change of temperature causes a change in the charge distribution within a unit cell, then

ferroelectricity is merely an unusual example of pyroelectricity. However, the fact that $BaTiO_3$ resembles other pyroelectric bodies so little shows that there must be an important difference in the basic mechanisms. It seems hardly likely, for example, that the very great difficulty of flipping the polarity of tourmaline, as compared with $BaTiO_3$, is only accidental.

Fortunately, there are a number of experiments that can easily be performed and that would provide conclusive evidence as to which type of theory is correct. The most decisive ones would be a neutron diffraction study to determine unambiguously the atomic positions of Ti and O below the cubic-tetragonal transition, and a determination of the infrared absorption spectrum, which should reveal a line at about 10 microns, corresponding to the initial level separation of $4kT_c$. Measurements of the elastic constants of single crystals will also enable one to determine whether there is quantitative agreement on the sharpness of the cubic-tetragonal transition.

# 3. THERMODYNAMIC TREATMENTS

## 3.1 General relations

The history of attempts to explain the action of Rochelle salt in terms of an atomic model shows the great value of transcribing the experimental data into a phenomenological model before considering detailed mechanisms, and conversely of transcribing any particular mechanism into a thermodynamic model. Reasons for this are that one obtains a picture of those features that are independent of any particular mechanism, that the requirements of a mechanism being investigated are clearly stated (the interaction theory of Mueller shows that this is not a trivial point), and that the deduction of various results that can be directly compared with experiment is thereby made more systematic in principle. However, such things as susceptibility, specific heat, and magnitude of spontaneous polarization can also be deduced directly from a model, and the amount of manipulation involved is often less than that encountered in the thermodynamic approach, depending on mathematical details. We have therefore not deprived ourselves of a more efficient method of exploring the consequences of different models by postponing the thermodynamic discussion until now.

Various models may be discussed in terms of that energy function $G(T,x_i,P_i)$ for which the independent variables are temperature, polarization, and strain. It is then defined by the equations

$$(3.11) \qquad \frac{\partial G}{\partial T} = -S, \qquad \frac{\partial G}{\partial x_i} = -X_i, \qquad \frac{\partial G}{\partial P_i} = E_i \ .$$

G is determined to within an additive constant by these relations; therefore, if by any means we can construct a function satisfying them, it must be the correct free energy function. In the form of the interaction theory briefly described in Section 1.2, the relations between $P_i, x_i, E_i, X_i$ are linear, and so G must be, in that approximation, a quadratic function of $P_i, x_i$. Nonlinear effects arising at strong polarizations may be described by adding to G further terms proportional to $P^4, P^6, \ldots$, and these terms determine the magnitude of spontaneous polarization.

The free-energy function $G(T, x_i, P_i)$ is the most convenient one for the description of processes involving constant strain (clamped crystals). In the case of a free crystal, for which the streeses $X_i$ are zero, it is more convenient to define a new function

$$A(T, X_i, P_i) = G - \sum_{i=1}^{6} x_i X_i \qquad (3.12)$$

with the properties

$$\frac{\partial A}{\partial T} = -S, \quad \frac{\partial A}{\partial X_i} = x_i, \quad \frac{\partial A}{\partial P_i} = E_i. \qquad (3.13)$$

Further transformations can be carried out to give other thermodynamic potentials in which the independent variables include the electric fields rather than the polarization, the entropy rather than the temperature, internal fields rather than macroscopic ones, the part of the polarization due to a particular atom rather than the total polarization, etc. Most models will give one of the latter types of function directly so that transformations of type (3.12) must then be found before we have a free energy function involving only experimentally measurable quantities.

An example of a way this transformation can be worked out will be given for the case of the electronic

theory discussed in Section 2.5. From the partition function found there, we can define a free energy function

$$G' = - NkT \log 2(\cosh bx + e^{-x})$$

which satisfies the relations

$$(3.14) \qquad \frac{\partial G'}{\partial F} = - P_e, \quad \frac{\partial G'}{\partial T} = - S$$

in which $F$ and $P_e$ are internal field and part of the polarization due to mixing of electronic wave functions respectively. The "theoretical" quantities $P_e, F$ are related, according to our internal field assumptions of Section 2.5, to the experimental quantities $P, E$ through the linear unimodular transformation

$$(3.15) \quad \begin{pmatrix} P \\ E \end{pmatrix} = \begin{pmatrix} 1 & \gamma \\ -\beta & (1 - \beta\gamma) \end{pmatrix} \begin{pmatrix} P_e \\ F \end{pmatrix}, \quad \begin{pmatrix} P_e \\ F \end{pmatrix} = \begin{pmatrix} (1 - \beta\gamma) & -\gamma \\ \beta & 1 \end{pmatrix} \begin{pmatrix} P \\ E \end{pmatrix}$$

From these relations we find the function $G(P,T)$ as follows. We have

$$- \frac{\partial G'}{\partial F} = P_e = P - \gamma F$$

therefore

$$(3.16) \qquad - \frac{\partial}{\partial F} (G' - \tfrac{1}{2}\gamma F^2) = P$$

and $(G' - \frac{1}{2}\gamma F^2)$ is a thermodynamic potential with conjugate variables $P, F$. Now let us carry out a Legendre transformation in which we solve Eq. (3.16) for $F(P)$ and use this value to express

$$(G' - \tfrac{1}{2}\gamma F^2 + PF)$$

as a function of P,T. We will then have

$$\frac{\partial}{\partial P}\left(G' - \frac{1}{2}\gamma F^2 + PF\right) = F = E + \beta P,$$

so that finally

$$\frac{\partial}{\partial P}\left(G' - \frac{1}{2}\gamma F^2 + PF - \frac{1}{2}\beta P^2\right) = E,$$

and the desired thermodynamic potential is

$$G(P,T) = G' - \frac{1}{2}\gamma F^2 + PF - \frac{1}{2}\beta P^2$$

$$= G' + \frac{1}{2}(PE + P_e F) \quad . \qquad (3.17)$$

The added terms represent a Legendre transformation and a correction for the electrostatic interaction of the unit cells, which is counted twice when we multiply the free energy of a single unit cell by N.

For the present model, Eq. (3.16) has the form

$$\left[\gamma + \frac{N\mu^2}{\epsilon b}\,\frac{\sinh bx}{\cosh bx + e^{-x}}\right] F = P$$

which cannot be solved explicitly for F because of the relation

$$b = \left(1 + \mu^2 \frac{F^2}{\epsilon^2}\right)^{1/2} \quad .$$

We may, however, expand in powers of F and P for the case that the internal field is weak. This will give the behavior of the model above the Curie point and for a very short distance below $T_c$. A tedious calculation gives the result

$$G(P,T) = -NkT \log 2(2c - s) + (g^{-1} - \beta)\frac{1}{2}P^2 - \frac{h}{4g^4}P^4 + \ldots$$

where

$$c = \cosh x, \quad s = \sinh x,$$

$$g = \gamma + \frac{N\mu^2}{\epsilon}\frac{s}{2c - s}$$

$$h = \frac{N\mu^4}{2\epsilon^3}\left\{ x\frac{1 - sc + c^2}{(2c - s)^2} - \frac{s}{2c - s}\right\} < 0 .$$

Above the Curie point, the relation between P and E is linear for weak fields, and the susceptibility is then just the reciprocal of the coefficient of $P^2/2$ in G:

$$(3.18)\quad \chi = \frac{P}{E} = \frac{g}{1 - \beta g} = \frac{1}{\beta(1 - \beta\gamma)}\frac{K}{K - f(x)} - \frac{1}{\beta}$$

where

$$f(x) = \frac{s}{2c - s}$$

$$K = \epsilon\frac{1 - \beta\gamma}{N\mu^2\beta} .$$

Then the Curie temperature is determined by

$$f(x_c) = K, \quad x_c = \frac{\epsilon}{kT_c}$$

and the Curie constant is

$$(3.19)\qquad C = \lim_{T\to T_c} \chi (T - T_c) = \frac{kT_c^2}{N\mu^2\beta^2 f'(x_c)}$$

Eqs. (3.18) and (3.19) are the same relations as were derived previously directly from the model.

## 3.2 Specific Heat Anomaly

Using Devonshire's assumption that the linear dependence of the reciprocal susceptibility $w'$ above the Curie point may be extrapolated below this temperature, one can account for the relation (1.44), which was noted before as an unexplained experimental fact. If we write the free energy for zero stress in the form

$$A(P,T) = A_0(T) + \frac{1}{2} w'(T)P^2 + f(P^2) \qquad (3.21)$$

where $A_0(T)$ represents the free energy associated with thermal vibrations and $f(P^2)$ is an unspecified function containing terms of order $P^4$ and higher, we have for the entropy, using Eq. (2.22),

$$S = -\left(\frac{\partial A}{\partial T}\right)_P = -\frac{dA_0}{dT} - \frac{1}{2}\frac{dw'}{dT}P^2 = S_0 - \frac{P^2}{2C}$$

where $C$ is the Curie constant. The entropy difference between the polarized and unpolarized states of the crystal is given by

$$\frac{1}{2}P^2 = C\Delta S = C(S_0 - S) \qquad (3.22)$$

which is just Eq. (1.44). Blattner and Merz (B6) have cited this relation as evidence for the correctness of the internal field theories mentioned in Section 1.4, but we see now that it also follows from much more general assumptions independent of any specific mechanism. Granted these assumptions, discussed below, this means that any model which fails to predict the correct entropy change must also fail to give simultaneously the correct polarization at low temperatures and susceptibility at high temperatures. Conversely, if a model gives the latter two quantities correctly, then it is sure to give also the correct specific heat anomaly so that such agreement cannot

be claimed as an independent confirmation of the theory, as was done erroneously before (J3).

We may also deduce thermodynamically a generalization of the formula (1.41) for the specific heat anomaly $(c_E - c_P)$. The specific heat is given by the temperature derivative of the entropy:

$$c_P = T\left(\frac{\partial S}{\partial T}\right)_P, \qquad c_E = T\left(\frac{\partial S}{\partial T}\right)_E .$$

From the above value of $S$, we find $c_P = TdS_o/dT$, and the specific heat anomaly is

$$(c_E - c_P) = -\frac{T}{2C}\frac{dP^2}{dT} . \tag{3.23}$$

The energy increment associated with this is not $-\frac{1}{2}\beta P^2$ as in the internal field theory, but is

$$-\frac{1}{2C}\int_T^{T_c} T\left(\frac{dP^2}{dT}\right) dT .$$

If the polarization comes in very rapidly below $T_c$, we may replace $T$ by $T_c$ in the integral, leading to the old result. The specific heat anomaly is proportional to $-dP^2/dT$, as in the simple internal field theory described in Section 1.4. In the case of a Langevin-Weiss theory based on rotating permanent dipoles, the internal field constant is equal to $T_c/C$, so that Eq. (3.23) then reduces to Eq. (1.41). However, the validity of Eq. (3.23) does not depend on whether $T_c/C$ can be interpreted as a Lorentz factor. As the temperature decreases and $P^2$ increases, the specific heat anomaly drops below the value that would be expected on the basis of Eq. (1.41).

The results of this section show that two of the relations predicted by the Langevin-Weiss theory are also

true under very general conditions so that their experimental confirmation is not in itself evidence for either the existence of rotating dipoles or the interpretation of $T_c/C$ as an internal field factor. In the electronic model described in Section 2.5, neither of these interpretations is even approximately correct. Our results are, however, not rigorous but depend on the particular form Eq. (3.21) assumed for the free energy function. That expression lacks generality in two respects: We have assumed that $w'(T)$ is given to sufficient accuracy by a linear function of $T$; and the temperature does not appear in the term $f(P^2)$. The first assumption is justified by the experimental fact that a Curie-Weiss law holds for susceptibility above the Curie point and is true to the extent that the graph of reciprocal susceptibility versus temperature is a straight line. Measurements indicate a slight curvature near the Curie point, so errors of the order of a few per cent from this linear simplification of $w'$ might be expected.

## 3.3 First- and second-order transitions

As we have already seen in the discussion of the Devonshire theory (Section 2.2), the sign of the coefficient of $P^4$ in the free energy function determines whether the phase transition is of first or second order. We assume here that we have to deal with a second-order change so that $f(P^2)$ is positive for small polarizations. The attempt to correlate electrical properties on both sides of the Curie point in terms of a single free energy function makes it almost necessary to assume this because the polarization above the Curie point is given by

$$E = \frac{\partial A}{\partial P} = w'P + 2P\frac{\partial f}{\partial P^2} \quad .$$

Since the polarization will be weak unless excessively strong fields are applied, we can replace $f(P^2)$ by

$\xi'_{11}P^4/4$, which leads to the relation

$$E = \left[ w' + \xi'_{11}P^2 \right] P \quad .$$

If now $\xi'_{11} > 0$, corresponding to a first-order transition, the added term represents a nonlinear dielectric behavior which causes the susceptibility $P/E$ to <u>increase</u> as the polarization is increased, a behavior that would be very difficult to understand physically. In any model that has been proposed thus far, the terms of order $P^4$ and higher arise physically from a saturation of the polarization, and their effect is always to cause the polarization to drop below the value given by the linear relation which holds near zero field.

This argument does not say that the physical crystal cannot exhibit a first-order transition; that is purely a matter for experiment to decide. What it does show is that a thermodynamic treatment of the type proposed by Devonshire, in which a single analytical form for the free energy function is used to describe behavior both above and below the transition temperature, probably cannot be made consistent unless the transition is taken to be of second order because in that theory there are necessary connections between the order of the transition and the type of dielectric nonlinearity exhibited above the Curie point.

Thus, if we wish to treat ferroelectric Curie points as first-order, we should go back to the usual conception of the nature of a first-order transition as caused by the more or less accidental crossing of two entirely different free energy functions representing the two phases, each of which can persist a short distance into the temperature range where the other is the stable form, giving rise to hysteresis effects. With this we would lose all of the relations connecting quantities on different sides of the critical point, which made the

proposed type of thermodynamic approach so attractive and useful.

On the other hand, the work of Mueller has amply demonstrated the essential correctness of this type of treatment in the case of Rochelle salt, and the approximate experimental confirmation of Eq. (3.22) for all three classes of ferroelectrics indicates strongly that it is of universal validity, (According to the assumptions that go into the derivation of this relations, we do not expect it to be satisfied more closely than within a few per cent, but even an order of magnitude agreement of the two quantities would be a strange coincidence from the standpoint of a theory using two different free energy functions.)

There is a second prediction of this theory relating behavior above and below the Curie point which has also received experimental confirmation. This concerns the measured susceptibility just below the Curie point. In the determination of susceptibility, electrodes are applied to opposite faces of the crystal, and the capacitance of the unit is measured with an applied alternating voltage. The steady spontaneous polarization thus escapes detection, and what is measured is the "incremental susceptibility" $\chi^{(-)} = dP/dE$. Immediately below the Curie point, where terms of order $P^6$ and higher in A are not yet important, we can derive a simple expression for $\chi^{(-)}$. From the relation

$$E = \frac{\partial A}{\partial P} = w'P + \xi'_{11} P^3$$

we obtain

$$\frac{1}{\chi^{(-)}} = \frac{dE}{dP} = w' + 3\xi'_{11} P^2,$$

while, setting $E = 0$, the spontaneous polarization is determined by

$$w' + \xi'_{11} P^2 = 0.$$

Combining these, we get

$$\chi^{(-)} = -\frac{1}{2w'} = \frac{C}{2(T_c - T)} .$$

Above the Curie point, we have already noted that

$$\chi^{(+)} = \frac{1}{w'} = \frac{C}{T - T_c} .$$

Therefore, the incremental susceptibility just below $T_c$ should satisfy another Curie-Weiss law, with a Curie constant just half that observed above $T_c$. Wul (W2) has shown that $BaTiO_3$ obeys this rule quite accurately.

These results give us great confidence that the Mueller-Devonshire type of approach is correct, and therefore, since Merz (M7) has found that the polarization increases less rapidly than the first power of the applied electric field above the Curie point, the transition must be a second-order one.

# 4. INTERNAL FIELDS IN CRYSTALS

## 4.1 Errors in simplified theories

In each of the theories of ferroelectricity considered above, the predictions of the model were not determined as reliably as we would like because of uncertainty as to the internal fields effective in polarizing the ions. Difficulties already mentioned in Chapter 2 include possible shielding due to overlapping of electronic wave functions, mechanical forces that may also induce polarization as in the oxygen displacement theory, correlations between instantaneous polarizations of adjacent units, and the fact that fields should really be calculated at displaced positions in the lattice.

The part of the polarization due to displacements of ions is usually treated by methods that are much too crude to be realistic, but it is probably true that the polarization due to electronic distortion is taken into account more accurately. However, even here we note that the assignment of definite electronic polarizabilities to individual ions is possible in principle only when the crystal is strongly ionic. Polarizabilities calculated on the basis of a closed-shell electronic structure would be expected to be considerably in error when the wave functions of the outer electrons are distorted only slightly; this critical dependence on the outer electrons is the reason why the Fermi-Thomas model cannot be used to estimate polarizability without elaborate refinements (H5). Thus, a given ion when placed in different chemical compounds will exhibit different polarizabilities as the ionic character of the crystal changes.

One would expect this effect to be especially pronounced in negative ions such as oxygen, and it has already been noted that the observed refractive indices of crystals containing oxygen indicate that its electronic polarizability varies by a factor of two in different compounds.

To these considerations we must add the fact that only dipole moments of the ions are considered in usual treatments. Actually, the ions are of finite size essentially equal to their spacing, and therefore each ion sees a field that is far from uniform. The resulting induced quadrupole and higher order electric moments in turn produce fields at neighboring ions which affect their dipole moments and therefore the observed polarization.

We see that a considerable amount of theoretical work would have to be done before we would be in a position to make reliable interpretations of the experimental facts. However, certain aspects of present theoretical work will certainly retain their importance as the starting-point from which various corrections are made. The problem of calculating electric fields arising from a lattice of dipoles or higher multipoles is one whose solutions will always be needed. About eighty years ago Appell (A3) gave a very interesting treatment of this problem in which the potential function was regarded as a three-dimensional generalization of an elliptic function, many of the fundamental properties of ordinary elliptic functions having three-dimensional analogs which correspond to useful pieces of physical information. A method for numerical evaluation of the fields at specific points in the lattice was later developed by Ewald (E2); this method is described briefly below. Most of the internal field constants which have been used in treatment of dielectric properties of crystals have been obtained by the Ewald method. It has a disadvantage in certain problems because the determination of the field at each point in the lattice is a separate calculation. The recent observation of Cohen (C5) that one

can incur considerable error by using the field at the undisplaced position of an ion as an approximation to the field at the displaced position (this would be even more true of the components of the field that induce higher order moments) makes it appear likely that future theoretical treatments will need values of the field throughout certain regions of the lattice rather than at isolated points. In this chapter we develop a method of calculation based on the fact that in a crystal of sufficiently high symmetry the internal field is the solution of a simple boundary-value problem and can be expressed throughout the lattice in terms of a rapidly converging expansion in orthogonal functions. In Chapter 5, we describe a method of treating the polarization in a crystal that was developed independently by Slater (S1) and the writer (J3), and discussed by Kaenzig (K6).

As we have already noted in Section 2.3, the forces tending to polarize an ion or other structure may not be wholly electrical in nature but may depend on partial overlapping of electronic distributions of adjacent ions (cf. Mott and Gurney, Electronic Processes in Ionic Crystals) as well as on other quantum-mechanical factors, and this is possibly the reason why in the interpretation of experimental dielectric constants one is led so often to ascribing smaller values to the Lorentz factor $\beta$ than would be expected from electrostatic considerations. However, for each particular type of crystal the existence of such a discrepancy can be demonstrated only after the electrostatic calculations have been carried out, and they form a natural starting-point for any discussion of dielectric properties.

## 4.2 The Lorentz factor matrix

It is evident that in general each component of the effective field seen by ion A will be a linear function of each component of the polarization due to each type of ion present, with coefficients which are constants

determined by the geometry of the structure. The proper generalization of the Lorentz factor is therefore a matrix whose dimension is three times the number of ions in a unit cell.

To illustrate this concretely, consider the case of the $BaTiO_3$ structure. Here there are five ions per unit cell: Ba, Ti, $O_x$, $O_y$, $O_z$, where $O_x$ is the oxygen ion in the x-direction from the Ti, etc. Each of these ions, together with other translationally equivalent ones, forms a simple cubic lattice, and the internal field seen by any ion may be expressed as a superposition of the fields due to these five interpenetrating simple cubic arrays of dipoles. In order to build up the internal field at each ion site in a $BaTiO_3$ crystal, we need only calculate the field of a simple cubic array of dipoles at a few points within the unit cell, and then combine these fields in the proper way.

We find that it is necessary to have the field at the following positions, as indicated in Fig. (4.1), when the dipoles are all polarized in the z-direction:

$$P_0 = (000) \quad \text{(corner)}$$
$$P_1 = (\tfrac{111}{222}) \quad \text{(center of cube)}$$
$$P_2 = (\tfrac{1}{2}0\tfrac{1}{2}) \quad \text{(center of xz face)}$$
$$P_3 = (\tfrac{11}{22}0) \quad \text{(center of xy face)}$$
$$P_4 = (\tfrac{1}{2}00) \quad \text{(center of x edge)}$$
$$P_5 = (00\tfrac{1}{2}) \quad \text{(center of z edge)}$$

If each dipole has moment $\mu$, and the volume of the unit cell is $a^3$, the polarization of the simple cubic array is $P = \mu/a^3$ and the field at each of the above points is some factor times P. We see from the symmetry that the field at each of these points is in the z-direction; as a consequence the Lorentz factor matrix will split into three matrices of dimension 5, each re-

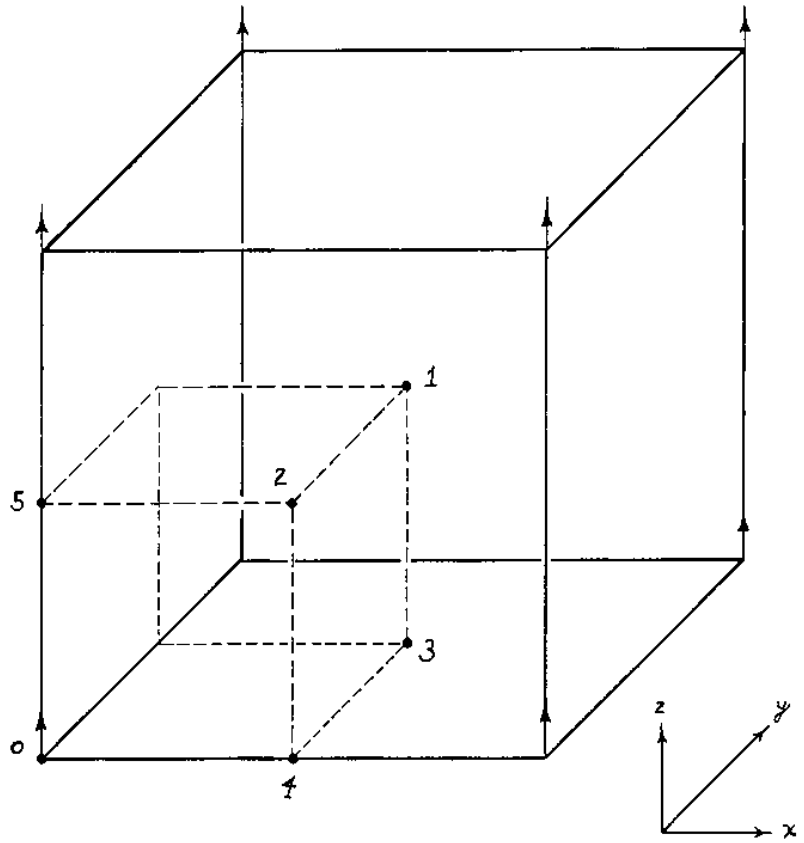


FIG. 4.1

referring to one of the coordinate directions. We denote the field at the i'th position in this simple cubic array of dipoles as

$$F_i = \beta_i P$$

($F_o$ is the field at (000) minus the field of the dipole at that position). The dimensionless factors ($\beta_o \cdots \beta_5$) will be calculated presently, but first we wish to show how they are combined to form the Lorentz factor matrix for the $BaTiO_3$ crystal. Keeping all polarizations and all internal fields in the z-direction, we denote the polarization due to Ba ions as $P_{Ba}$, etc., while the internal field seen by the Ba ion will be $F_{Ba}$, etc. Then by inspection of Fig. (4.1), we can write down the relations

$$F_{Ba} = \beta_0 P_{Ba} + \beta_1 P_{Ti} + \beta_2 (P_{O_x} + P_{O_y}) + \beta_3 P_{O_z} + E$$

$$F_{Ti} = \beta_1 P_{Ba} + \beta_0 P_{Ti} + \beta_4 (P_{O_x} + P_{O_y}) + \beta_5 P_{O_z} + E$$

$$F_{O_x} = \beta_2 P_{Ba} + \beta_4 P_{Ti} + \beta_0 P_{O_x} + \beta_3 P_{O_y} + \beta_2 P_{O_z} + E$$

$$F_{O_y} = \beta_2 P_{Ba} + \beta_4 P_{Ti} + \beta_3 P_{O_x} + \beta_0 P_{O_y} + \beta_2 P_{O_z} + E$$

$$F_{O_z} = \beta_3 P_{Ba} + \beta_5 P_{Ti} + \beta_2 (P_{O_x} + P_{O_y}) + \beta_0 P_{O_z} + E$$

or, in matrix notation,

$$\begin{pmatrix} F_{Ba} \\ F_{Ti} \\ F_{O_x} \\ F_{O_y} \\ F_{O_z} \end{pmatrix}_z = \begin{pmatrix} \beta_0 & \beta_1 & \beta_2 & \beta_2 & \beta_3 \\ \beta_1 & \beta_0 & \beta_4 & \beta_4 & \beta_5 \\ \beta_2 & \beta_4 & \beta_0 & \beta_3 & \beta_2 \\ \beta_2 & \beta_4 & \beta_3 & \beta_0 & \beta_2 \\ \beta_3 & \beta_5 & \beta_2 & \beta_2 & \beta_0 \end{pmatrix} \begin{pmatrix} P_{Ba} \\ P_{Ti} \\ P_{O_x} \\ P_{O_y} \\ P_{O_z} \end{pmatrix}_z + E_z \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

We note that the matrix is symmetric; that this must always be the case is seen from the fact that ion A is necessarily located in the same way relative to the lattice of ions of type B, as B is in the lattice of ions of type A. All this refers only to the z-components of polarization and field; for the x and y components we have similar relations with slightly different matrices:

$$\begin{pmatrix} F_{Ba} \\ F_{Ti} \\ F_{O_x} \\ F_{O_y} \\ F_{O_z} \end{pmatrix}_x = \begin{pmatrix} \beta_0 & \beta_1 & \beta_3 & \beta_2 & \beta_2 \\ \beta_1 & \beta_0 & \beta_5 & \beta_4 & \beta_4 \\ \beta_3 & \beta_5 & \beta_0 & \beta_2 & \beta_2 \\ \beta_2 & \beta_4 & \beta_2 & \beta_0 & \beta_3 \\ \beta_2 & \beta_4 & \beta_2 & \beta_3 & \beta_0 \end{pmatrix} \begin{pmatrix} P_{Ba} \\ P_{Ti} \\ P_{O_x} \\ P_{O_y} \\ P_{O_z} \end{pmatrix}_x + E_x \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

$$\begin{pmatrix} F_{Ba} \\ F_{Ti} \\ F_{O_x} \\ F_{O_y} \\ F_{O_z} \end{pmatrix}_y = \begin{pmatrix} \beta_0 & \beta_1 & \beta_2 & \beta_3 & \beta_2 \\ \beta_1 & \beta_0 & \beta_4 & \beta_5 & \beta_4 \\ \beta_2 & \beta_4 & \beta_0 & \beta_2 & \beta_3 \\ \beta_3 & \beta_5 & \beta_2 & \beta_0 & \beta_2 \\ \beta_2 & \beta_4 & \beta_3 & \beta_2 & \beta_0 \end{pmatrix} \begin{pmatrix} P_{Ba} \\ P_{Ti} \\ P_{O_x} \\ P_{O_y} \\ P_{O_z} \end{pmatrix}_y + E_y \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

In this case, the Lorentz factor is a matrix-vector. If

$$U = \left(\begin{array}{cc|ccc} 1 & 0 & & 0 & \\ 0 & 1 & & & \\ \hline & & 0 & 1 & 0 \\ & 0 & 1 & 0 & 0 \\ & & 0 & 0 & 1 \end{array}\right)$$

is the matrix that interchanges $x$ and $y$, then we have

$$\beta_y = U\beta_x U^{-1}, \text{ etc.}$$

In a more general crystal lattice not containing as many symmetry planes, it would not be possible to separate the equations for the $x,y,z$ components in this manner.

We see that, in the approximation where each ion gives rise to a dipole field but has no quadrupole or higher order electric moments, the internal field is given by an equation of the originally assumed form

$$F = \beta \cdot P + E,$$

provided that the quantities are now interpreted as matrices whose rows and columns refer to the different ions in a unit cell. We turn now to the calculation of the constants $\beta_i$.

## 4.3 Macroscopic and microscopic fields

The calculation of the internal fields at various points in a crystal is commonly done by finding the contribution due to a charge complex at an arbitrary point and summing this expression over all lattice points. This procedure is complicated by the fact that the sums encountered are only conditionally convergent; for example, the series $\sum r^{-n}$ taken over all lattice points is absolutely convergent only for $n \geq 4$(E1). Ewald (E2) has developed a method for converting such sums into rapidly convergent ones. There is one classical case in which one can easily calculate the sum; this is the case of the field due to a simple cubic array of dipoles at a point on a three-fold symmetry axis of the lattice. The z-component of the field of a single dipole of moment $\mu$ pointing in the z-direction is

$$E_z = \mu \frac{2z^2 - x^2 - y^2}{r^5} ,$$

where $x,y,z$ are coordinates of the dipole relative to the point 0 at which the field is sought. If the lattice has a three-fold symmetry axis passing through 0, then there are two other dipoles at points $x'y'z'$; $x"y"z"$, where

$$x = y' = z", \quad y = z' = x", \quad z = x' = y",$$

and the total contribution from these three dipoles vanishes. Therefore, if we describe a sphere of any finite radius $R$ about the point 0, the z-component of the field at 0 due to all the dipoles within the sphere vanishes and the total field is just that due to the material outside. By choosing $R$ to be of macroscopic dimensions, we can apply macroscopic theory to the outside material, which may be assumed to have a uniform polarization $P = \mu/a^3$, where $a$ is the lattice constant. The sphere

then becomes a cavity in a homogeneously polarized dielectric and by solution of a simple boundary-value problem we find the internal field at 0 to be the Lorentz value $F = 4\pi P/3 + E$.

Aside from the fact that this simple method works only when the three-fold symmetry axis is present and is therefore restricted to points on cube diagonals of cubic crystals, one may object to the manner in which macroscopic and microscopic points of view are combined in treating the effect of distant material and/or demagnetization factors, especially since the usual definitions of macroscopic fields in terms of microscopic ones lead to further convergence difficulties if one uses a point charge model. To illustrate this by a simple example, we recall that the macroscopic vectors E,B are customarily defined (V3) as space averages of the corresponding microscopic ones, e,h, while the macroscopic displacement D is defined by $D = E + 4\pi P$. Let us apply this definition to the contribution to E of a cubic array of dipoles of moment $\mu = 2qd$, composed of point charge $\pm q$ separated by a distance 2d small compared to the lattice spacing a. The resulting macroscopic field $E_z$ is then

$$E_z = \frac{1}{a^3} \int e_z dv$$

where the integral is taken over one unit cell. Since the actual field is a superposition of the fields due to the different dipoles, however, this integral taken over a given unit cell must be equal to the integral over the entire crystal of the field $e_z'$ due to the dipole in that cell. Consider the unit cell surrounding the dipole at the center of a spherical crystal of macroscopic radius R, and represent the dipole by two point charges separated by a distance $2d \lll R$. Then there exists an expansion of the form

$$e'_z = \left\{ \begin{array}{ll} \sum_{n=0}^{\infty} A_n \left(\frac{r}{d}\right)^n P_n(\cos\theta), & r < d \\ \sum_{n=2}^{\infty} B_n \left(\frac{d}{r}\right)^{n+1} P_n(\cos\theta); & r > d \end{array} \right\}$$

Terms with $B_0$, $B_1$ do not appear. All terms with $n \geq 1$, however, vanish when integrated over all angles, and the desired integral reduces to

$$\int e'_z dv = A_o \frac{4\pi d^3}{3} .$$

$A_o$ is just the field at the center of the dipole: $A_o = -2q/d^2$, so we get

$$E_z = \frac{1}{a^3} \int e_z dv = -\frac{4\pi}{3} \frac{2qd}{a^3} = -\frac{4\pi}{3} \frac{\mu}{a^3} = -\frac{4\pi P}{3} .$$

The macroscopic field at the center of a uniformly polarized crystal appears to arise entirely from the interior regions of the central dipole, and had we assumed true point dipoles with no internal structure, we would have found zero for the integral if the integration were carried out over angles first, while it would diverge if carried out radially first. On the other hand, we may consider the field of the central dipole as the superposition of the coulomb fields due to the charges $\pm q$, and by being careful about the fields at the surface of the crystal one again obtains the above correct result. In general, space averages can be correctly calculated from a point charge model, but if we use a point dipole model, the results are ambiguous. In order to avoid such troubles, we wish to find new definitions

$$V = V_o - \vec{E} \cdot \vec{r}$$

where $V_o$ has the lattice periodicity and $\vec{E}$ is the macroscopic field. Then the component of E in the z direction is given by

$$E_z = \frac{1}{a} \int_o^a - \left(\frac{\partial V}{\partial z}\right) dz = \frac{1}{a} \int_o^a e_z dz \quad (4.31)$$

where we integrate along a straight line in the z-direction that does not pass through any singularities of the field, and the length is one lattice period. $V_o$ then contributes nothing to the integral, and from the static condition curl (e) = 0, the value of the integral is the same for any such path.

An independent definition of D is obtained from the macroscopic induction law, curl H = $\dot{D}/c$ and its microscopic analog curl h = $\dot{e}/c$; applying Stokes's theorem to a plane surface S passing through the crystal but not intersecting any dipoles, we find that the line integral of H around the entire crystal, which is an experimentally measurable quantity, is

$$\int \vec{H} \cdot \vec{d\ell} = \frac{S}{c} \dot{D}_n = \frac{1}{c} \frac{\partial}{\partial t} \int_s \vec{e} \cdot \vec{ds} \ .$$

The component of D normal to the surface may therefore be put equal to the average of the normal component of the microscopic field over the surface. In the case of a crystal, the average may just as well be taken over the cross-section of a single unit cell, giving us as our definition of the z-component of D,

$$D_z = \frac{1}{a^2} \int_o^a \int_o^a e_z dxdy \ .$$

From the condition div e = 0, the integral is independent of which surface is chosen as long as it is not displaced past an isolated charge. It may be displaced past a point dipole without altering its value. (This change

in the definition of $D$ when the surface is displaced past a charge corresponds to a change in the definition of $P$, discussed by Mason and Weaver[1]; it need not detain us here as we are concerned solely with point dipoles, for which there is no ambiguity in the definitions of $P$ and $D$.)

4.4 Symmetry properties of the $\beta_i$

Let us see how much can be said about the values of $(\beta_0 \ldots \beta_5)$ without actually calculating them. In the first place, we know from the work of Lorentz that $\beta_0 = 4\pi/3$, and since the position $P_1$ lies on a three-fold symmetry axis of the lattice, we expect on the basis of the above arguments that $\beta_1 = 4\pi/3$ also. There are two more relations between the other factors which may be derived by considering the sodium chloride structure, in which each type of ion forms a face-centered cubic lattice. The sodium ions may be divided into four classes, each of which forms a simple cubic lattice; for example, the ions labeled a,b,c,d in Fig. 4.2 may be taken as representative of the four classes. Now the field seen by ion (a) due to polarization of the other sodium ions may be expressed in two different ways. Following our previous method, we have

$$F_a = \beta_0 P_a + \beta_2 P_b + \beta_3 P_c + \beta_2 P_d .$$

On the other hand, each sodium ion is really related to the crystal in the same way as every other one, and each lies on a three-fold symmetry axis of the lattice of sodium ions, therefore

$$P_a = P_b = P_c = P_d = \frac{P}{4} ,$$

[1] The Electromagnetic Field, Univ. of Chicago Press, 1932.

where P is the total polarization due to sodium ions, and

$$F_a = \beta_0 P = \frac{4\pi P}{3} \quad .$$

Comparing these expressions, we have

$$2\beta_2 + \beta_3 = 3\beta_0 = 4\pi . \qquad (4.41)$$

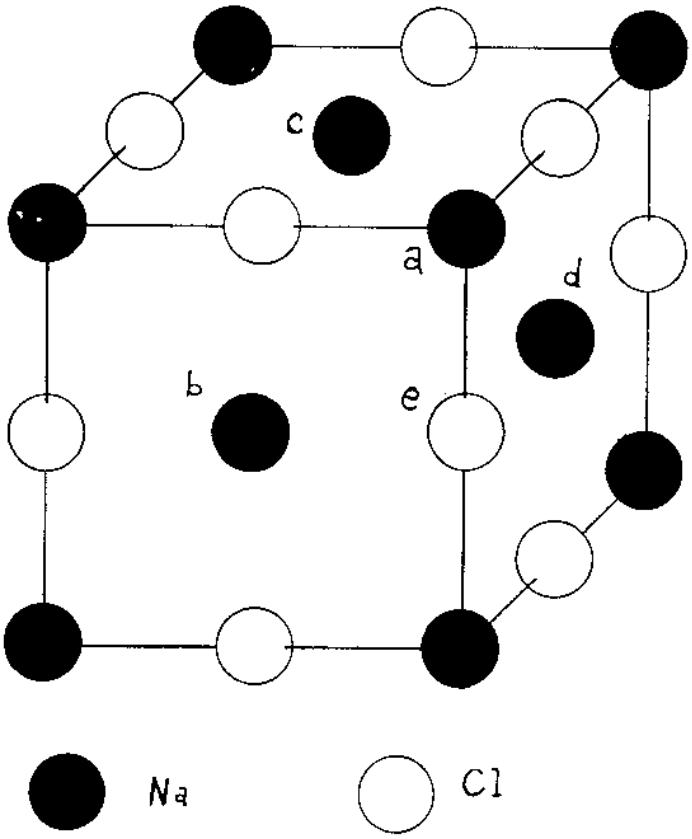


FIG. 4.2

Consider now the field on the chloride ion (e) due to the sodium dipoles. By the first method we have

$$F_{Cl} = \beta_5 P_a + \beta_4 P_b + \beta_1 P_c + \beta_4 P_d ,$$

but the chloride ion also lies on a three-fold symmetry

axis of the sodium lattice, so the second point of view gives us

$$F_{Cl} = \beta_0 P,$$

which leads to the relation

$$2\beta_4 + \beta_5 = 3\beta_0 = 4\pi \quad . \qquad (4.42)$$

Accepting these results, we need calculate only $\beta_2$ and $\beta_4$ in order to determine the Lorentz factor matrix completely. However, we prefer to calculate each of the $\beta_i$ separately and use the above relations as a check on the numerical work.

In setting up suitable expansions of the field the prime consideration is to get rapidly convergent series. This is done, firstly, be expanding the field in a region so chosen that there are no singularities inside the region, and, secondly, by choosing out of various possible sets of "normal modes" those functions which have the greatest resemblance to the actual fields and which in particular become large as we go toward those boundaries on which singularities exist. We find that there is no single region which gives rapidly convergent expressions at all of the points desired but that two different field expansions must be used.

## 4.5 First field expansion

We choose the region $R_1$ indicated in Fig. 4.3, which is a cube displaced by half an xy-face diagonal from the usual unit cell, and use coordinates $x,y,z$ measured from the center of $R_1$. Since the vertical sides of this cube are symmetry planes of the potential, we have the boundary condition

$$\frac{\partial V}{\partial n} = 0.$$

On the top and bottom the potential will be constant except for a $\delta$-function singularity due to the dipole of moment $\mu$ in the center of the face. Thus, on the bottom face, we have

$$V(x,y, -\frac{a}{2}) = 2\pi\mu\ \delta(x)\ \delta(y).$$

Furthermore, from symmetry, the potential is an even function of $x,y$ and an odd function of $z$. Therefore the appropriate expansion is

$$V = \sum_{mn=0}^{\infty} A_{mn} \cos\left(\frac{2\pi mx}{a}\right) \cos\left(\frac{2\pi ny}{a}\right) \sinh\left(\frac{2\pi}{a}\sqrt{m^2+n^2}z\right).$$

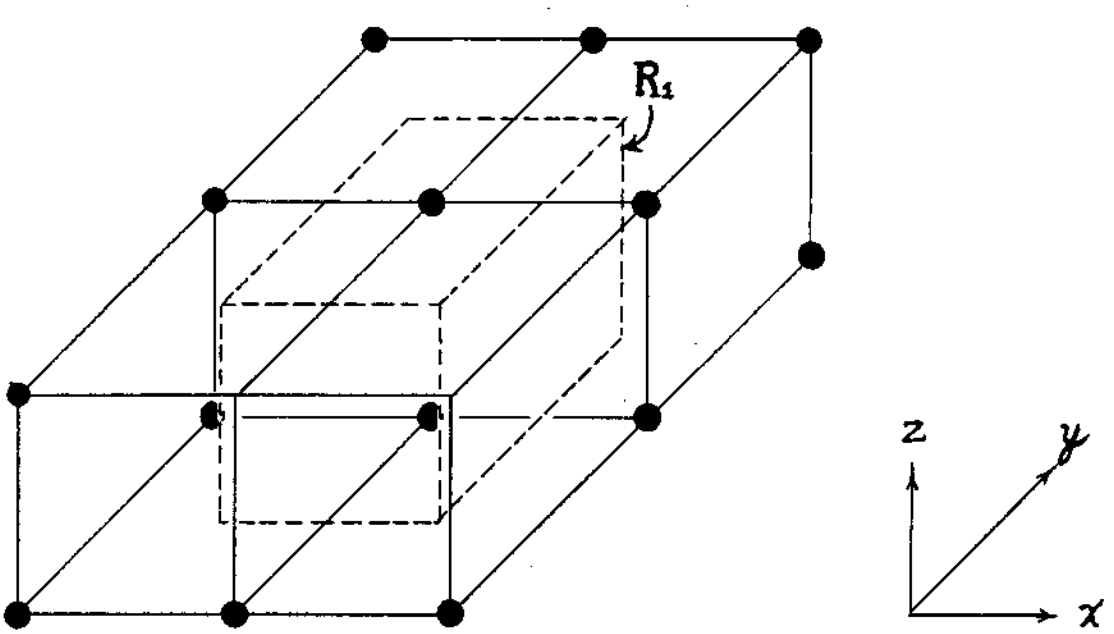


FIG. 4.3

This automatically fits the boundary condition on the vertical sides and becomes large as we approach the planes $z = \pm a/2$. The constants are determined from the condition on the bottom face:

$$\sum_{mn} A_{mn} \cos\left(\frac{2\pi mx}{a}\right) \cos\left(\frac{2\pi ny}{a}\right) \sinh\left(\pi\sqrt{m^2+n^2}\right) = -2\pi\mu\,\delta(x)\,\delta(y)$$

$$\sum_{mn} A_{mn} \sinh \pi\sqrt{m^2+n^2} \int_{-a/2}^{a/2}\int \cos\left(\frac{2\pi mx}{a}\right)\cos\left(\frac{2\pi m'x}{a}\right)\cos\left(\frac{2\pi ny}{a}\right)$$

$$\cdot \cos\left(\frac{2\pi n'y}{a}\right)dxdy$$

$$= A_{m'n'} \cdot \frac{a^2}{4} (1+\delta_{m'o})(1+\delta_{n'o}) \sinh \pi\sqrt{m'^2+n'^2}$$

$$= -2\pi\mu$$

$$A_{oo} = 0$$

$$A_{mn} = -\frac{8\pi\mu}{a^2} \frac{1}{(1+\delta_{mo})(1+\delta_{no}) \sinh \pi\sqrt{m^2+n^2}} .$$

The series converges exponentially, and is therefore well-suited for numerical work. The z-component of the electric field is given by

$$e_z = \frac{16\pi^2\mu}{a^3} \sum_{mn}{}' \frac{\cos\left(\frac{2\pi mx}{a}\right) \cos\left(\frac{2\pi ny}{a}\right) \cosh\left(\frac{2\pi}{a}\sqrt{m^2+n^2}z\right) \sqrt{m^2+n^2}}{(1+\delta_{mo})(1+\delta_{no}) \sinh \pi\sqrt{m^2+n^2}}$$

where the prime indicates that the term $m = n = 0$ is deleted. The factors $\beta_1, \beta_2, \beta_5$ are now found from the values of $e_z$ at the positions $(\frac{1}{2}a, \frac{1}{2}a, 0)$, $(\frac{1}{2}a, 0, 0)$, $(0,0,0)$ respectively.

It is not permissible to set the $\beta_i$ equal to the coefficients of $\mu/a^3$ in the expansions for $e_z$ at these positions because we have not yet investigated the values of the macroscopic fields $E, D = E + 4\pi\mu/a^3$. Using the definition of $D$ developed above and integrating $e_z$ over the plane $z = 0$, we see that $D = 0$ in consequence of the vanishing of $A_{oo}$. Therefore, $E = -4\pi\mu/a^3$, and this must be subtracted from $e_z$ to get the correct

Lorentz factors. (Note that we cannot calculate the macroscopic E directly from this expansion as the resulting series diverges; this is another example of the difficulties inherent in point charge models.) The following expressions for the $\beta_i$ are found:

$$\beta_1 = 4\pi + \frac{a^3}{\mu} e_z(\tfrac{1}{2}a, \tfrac{1}{2}a, 0)$$

$$\beta_2 = 4\pi + \frac{a^3}{\mu} e_z(\tfrac{1}{2}a, 0, 0)$$

$$\beta_5 = 4\pi + \frac{a^3}{\mu} e_z(0, 0, 0)$$

A table of numerical values of

$$\frac{\sqrt{m^2 + n^2}}{\sinh \pi \sqrt{m^2+n^2}}$$

is all that is needed to calculate these three factors.

## 4.6 Second field expansion

The remaining $\beta_i$ may be calculated by expanding the field in the region $R_2$ of Fig. (4.4), which is a cube displaced by half a yz-face diagonal from the usual unit cell. Again choosing coordinates x,y,z measured from the center of $R_2$, we find the following boundary conditions:

$$\frac{\partial V}{\partial n} = 0, y = \pm \frac{a}{2}$$

$$V = 0, z = \pm \frac{a}{2}$$

On the face $x = -a/2$, we have, Fig. (4.5),

$$-\frac{\partial V}{\partial x} = \lim_{\substack{\epsilon \to 0 \\ 2q\epsilon \to \mu}} 2\pi q \delta(y)[\delta(z-\epsilon) - \delta(z+\epsilon)]$$

$$\frac{\partial V}{\partial x} = 2\pi\mu\delta(y)\delta'(z).$$

Furthermore, the potential is an even function of $x$ and $y$ and an odd function of $z$. Since the singularities are now along the x-axis, the expansion which converges rapidly is

$$V = \sum_{mn=0}^{\infty} A_{mn} \cos\left(\frac{2\pi my}{a}\right) \sin\left(\frac{2\pi nz}{a}\right) \cosh\left(\frac{2\pi x}{a}\sqrt{m^2+n^2}\right).$$

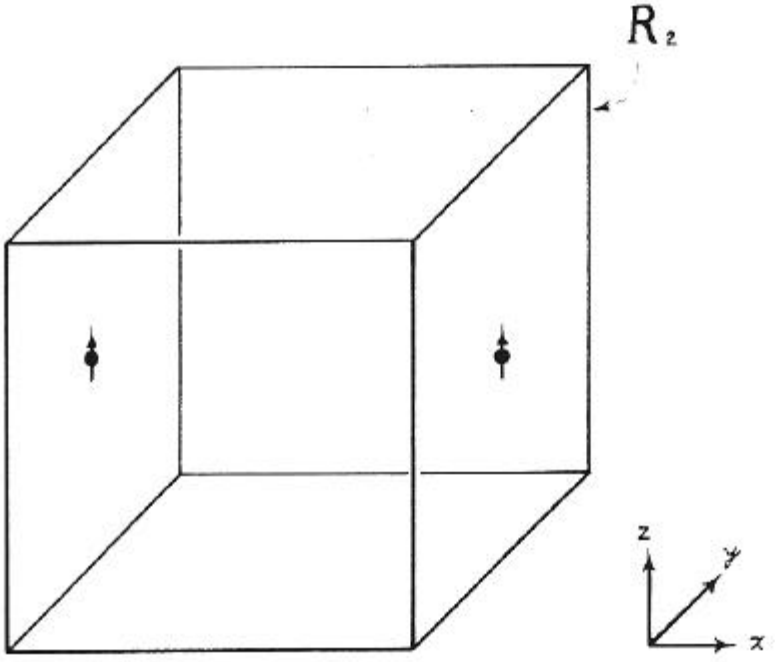


FIG. 4.4

The constants $A_{mn}$ are evaluated as before, with the result:

$$A_{mo} = 0$$

$$A_{mn} = \frac{8\pi\mu}{a^2} \frac{n}{(1+\delta_{mo})\sqrt{m^2+n^2}\sinh \pi\sqrt{m^2+n^2}}, \quad n \neq 0 .$$

The z-component of the field is now given by

$$e_z = -\frac{\partial V}{\partial z} = -\frac{16\pi^2\mu}{a^3} \sum_{mn} \frac{n^2 \cos\left(\frac{2\pi my}{a}\right) \cos\left(\frac{2\pi nz}{a}\right) \cosh\left(\frac{2\pi}{a}\sqrt{m^2+n^2}\, x\right)}{(1+\delta_{mo})\sqrt{m^2+n^2}\sinh \pi\sqrt{m^2+n^2}}$$

and the factors $\beta_1, \beta_2, \beta_3, \beta_4$ are determined by the values of $e_z$ at the positions $(0,\frac{1}{2}a,\frac{1}{2}a)$, $(0,0,\frac{1}{2}a)$, $(0,\frac{1}{2}a,0)$, $(0,0,0)$ respectively. This time the situation with respect to the macroscopic fields is just reversed; using our "line" definition of $E$, we easily see from the expansion of $e_z$ that $E_z = 0$, therefore $D = 4\pi\mu/a^3$.

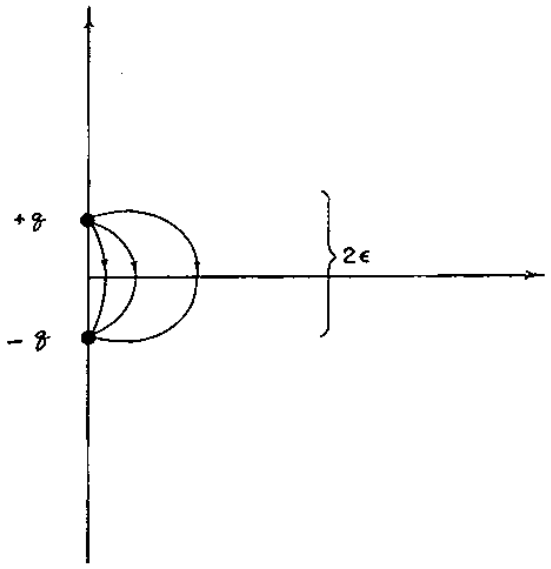


FIG. 4.5

(However, we cannot calculate $D$ directly from this expansion, since the resulting series diverges!) Since $E = 0$, the $\beta_i$ are given directly by the coefficients of $\mu/a^3$ in the expansions for $e_z$ at the four points.

## 4.7 Evaluation of series

Collecting results, we now have the following series to evaluate:

$$\beta_1 - 4\pi = 16\pi^2 \left\{ \sum_{n=1}^{\infty} (-)^n C_{on} + \sum_{mn=1}^{\infty} (-)^{m+n}(C_{mn} + C_{nm}) \right\}$$

$$\beta_2 - 4\pi = 16\pi^2 \left\{ \sum_{n=1}^{\infty} C_{o,2n} + \sum_{mn=1}^{\infty} (-)^m(C_{mn} + C_{nm}) \right\}$$

$$\beta_3 - 4\pi = 16\pi^2 \left\{ \sum_{n=1}^{\infty} C_{on} + \sum_{mn=1}^{\infty} (C_{mn} + C_{nm}) \right\}$$

(from first field exp.)

$$\beta_1 = -16\pi^2 \left\{ \frac{1}{2} \sum_{n=1}^{\infty} (-)^n C_{on} + \sum_{mn=1}^{\infty} (-)^{m+n} C_{mn} \right\}$$

$$\beta_2 = -16\pi^2 \left\{ \frac{1}{2} \sum_{n=1}^{\infty} (-)^n C_{on} + \sum_{mn=1}^{\infty} (-)^n C_{mn} \right\}$$

$$\beta_3 = -16\pi^2 \left\{ \frac{1}{2} \sum_{n=1}^{\infty} C_{on} + \sum_{mn=1}^{\infty} (-)^m C_{mn} \right\}$$

$$\beta_4 = -16\pi^2 \left\{ \frac{1}{2} \sum_{n=1}^{\infty} C_{on} + \sum_{mn=1}^{\infty} C_{mn} \right\}$$

(from second field exp.)

in which

$$C_{mn} = \frac{n^2}{(m^2 + n^2)^{\frac{1}{2}} \sinh \pi (m^2 + n^2)^{\frac{1}{2}}} .$$

The fact that $\beta_1, \beta_2$ are duplicated here plus the relations previously established will provide a good check on the calculations. (Actually, if we assume that the two series given for $\beta_1$ are the same, we can deduce already that $\beta_1 = 4\pi/3$ without directly evaluating the double sums; however, it is preferable to get a direct check on their consistency by summing each series independently.)

It is possible to evaluate the two given series for $\beta_1$ analytically. We first evaluate the sum

$$I = \sum_{n=1} \frac{(-)^n n}{\sinh \pi n} .$$

This is easily done by contour integration as follows. The function $\pi / \sin(\pi n)$ has no singularities in the finite part of the complex plane except a simple pole of residue $(-)^n$ at each integer value of $n$, and it vanishes strongly as $n \to \infty$ everywhere except on the real axis. Therefore

$$I = \frac{1}{2\pi i} \int_C \frac{n}{\sinh \pi n} \frac{\pi dn}{\sin \pi n}$$

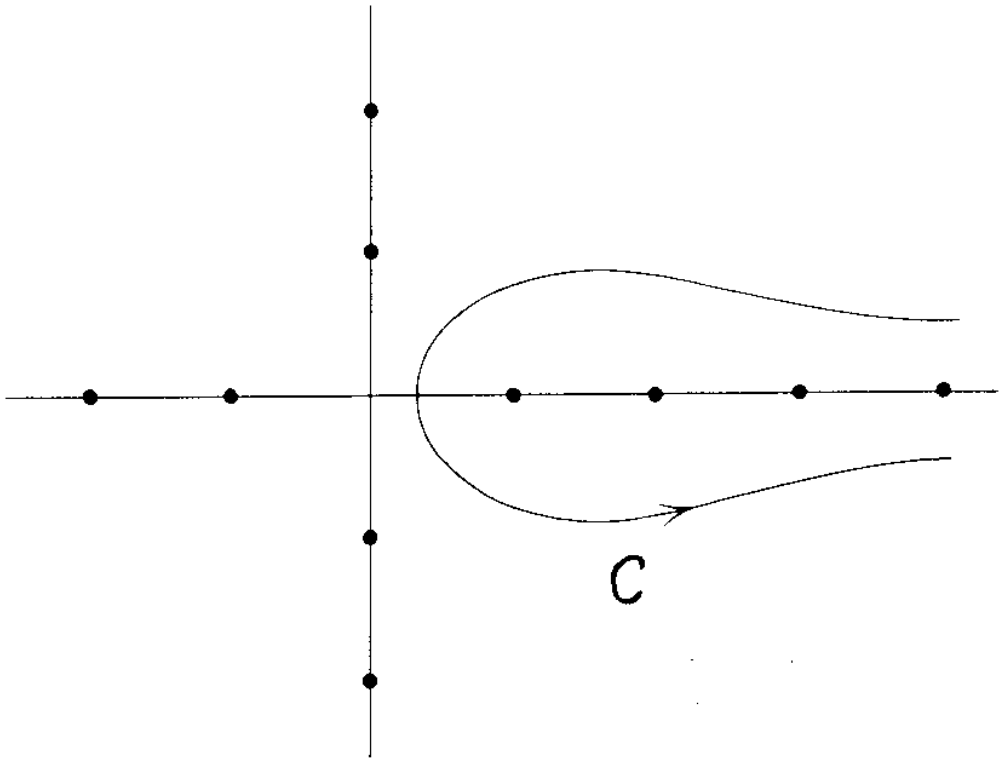


FIG. 4.6

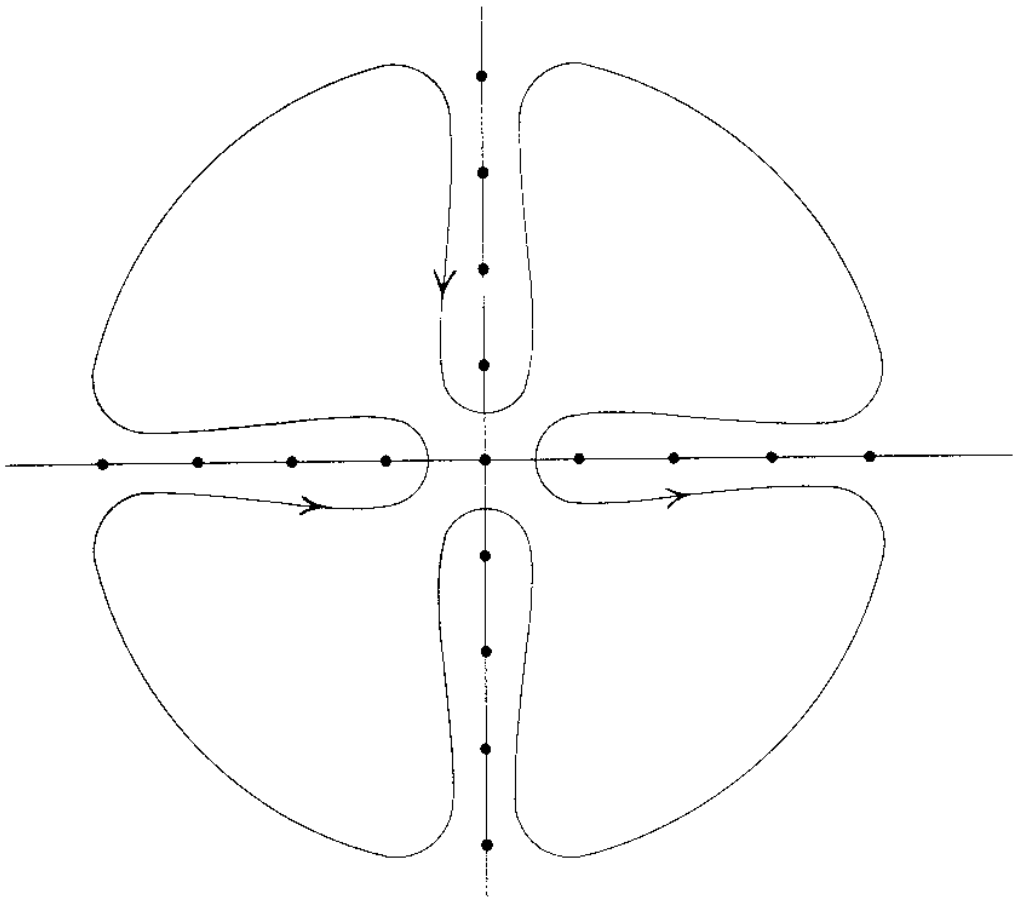

FIG. 4.7

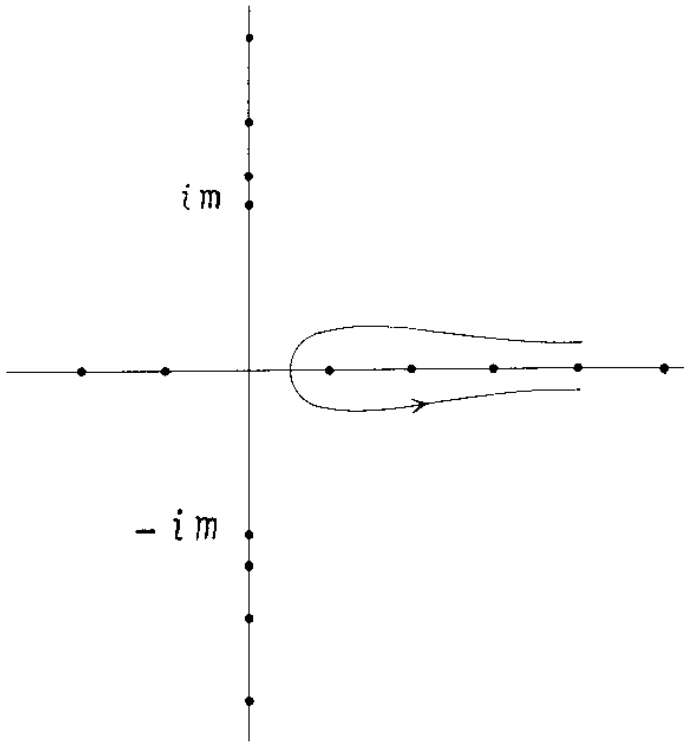


FIG. 4.8

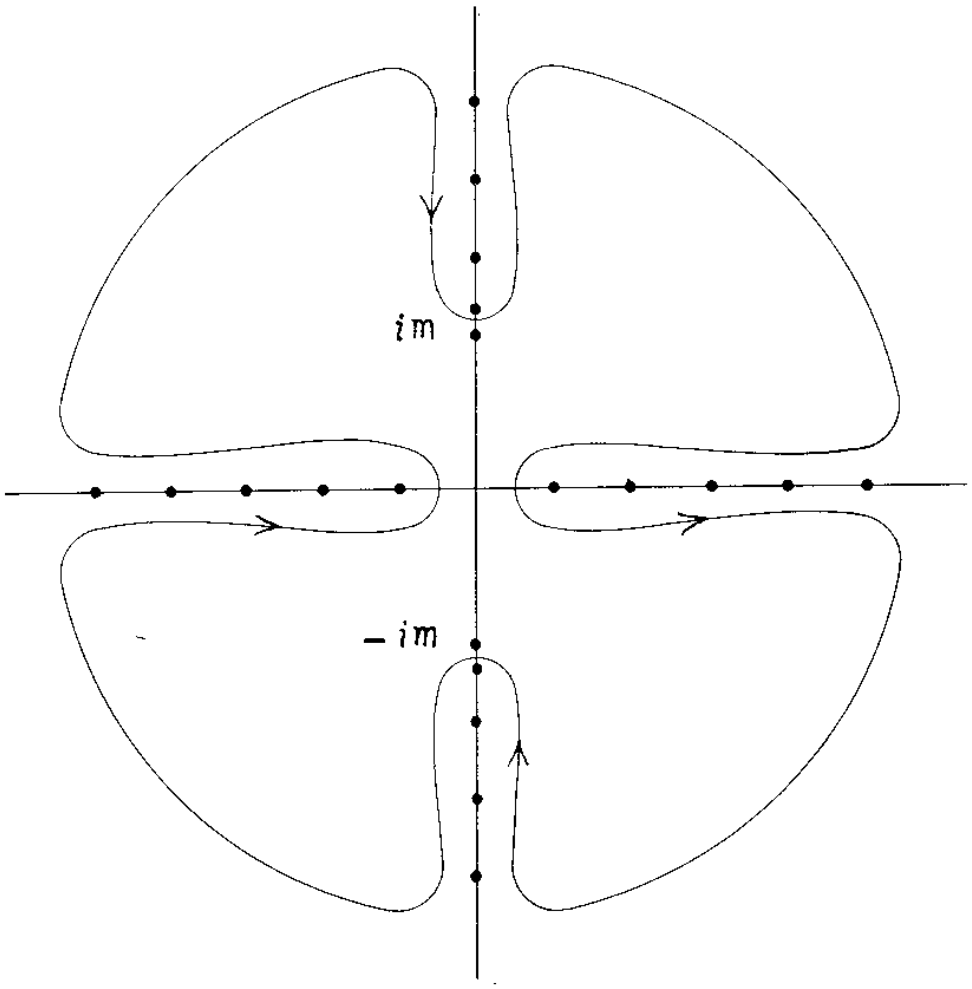


FIG. 4.9

where the contour C is shown in Fig. (4.6). But the integrand is invariant under the substitution $n \longrightarrow in$:

$$\frac{(in)\, d\,(in)}{\sinh(\pi in)\,\sin(\pi in)} = \frac{n\,dn}{\sin(\pi n)\,\sinh(\pi n)} \quad .$$

Therefore 4I is equal to the clover leaf integral of Fig. (4.7) which in turn may be contracted into a single loop about the origin, giving the result

$$-4I = (\text{Residue at } n = 0) = \frac{1}{\pi}$$

$$\therefore \quad \boxed{I = -\frac{1}{4\pi}}$$

We now try to evaluate the two sums:

$$J = \sum_{n=1}^{\infty} \frac{(-)^n n^2}{\sqrt{m^2+n^2}\,\sinh\pi\,\sqrt{m^2+n^2}}, \qquad K = \sum_{n=1}^{\infty} \frac{(-)^n\,\sqrt{m^2+n^2}}{\sinh\pi\,\sqrt{m^2+n^2}} \quad .$$

Consider first the sum J. It is equal to the integral

$$J = \frac{1}{2\pi i} \int_C \frac{n^2}{\sqrt{m^2+n^2}\,\sinh\,\pi\sqrt{m^2+n^2}} \frac{\pi\,dn}{\sin n\pi}$$

with C as shown in Fig. (4.8). There is now no pole at n = 0, but a string of poles along the imaginary axis at

$$n = \pm i\,\sqrt{m^2+k^2}, \qquad k = 0,1,2,\ldots \quad .$$

At n = im, the residue is

$$\frac{-m^2\pi}{2\pi i m \cdot i\,\sinh m\pi} = \frac{m}{2\,\sinh m\pi}$$

and at

$$n = i\sqrt{m^2 + k^2},$$

$$\sqrt{m^2 + n^2} = ik \neq 0,$$

the residue is

$$\frac{-(m^2 + k^2)\pi}{\pi i \sqrt{m^2 + k^2} \cosh \pi ik \cdot i \sinh \pi \sqrt{m^2 + k^2}} = \frac{(-)^k \sqrt{m^2 + k^2}}{\sinh \pi \sqrt{m^2 + k^2}}$$

But this is just the k'th term in the sum $K$, so the integral over the cloverleaf path of Fig. (4.9) is equal to

$$2(J + K) = -2 \operatorname{Res} (n = im)$$

$$= \frac{m}{\sinh m\pi}$$

$$J + K = -\frac{m}{2 \sinh m\pi} .$$

Comparing the definitions of $K, J$ we have

$$\sum_{n=1}^{\infty} \frac{(-)^n (m^2 + 2n^2)}{\sqrt{m^2 + n^2} \sinh \pi \sqrt{m^2 + n^2}} = -\frac{m}{2 \sinh m\pi} .$$

If we multiply by $(-)^m$ and sum over $m$, this gives us

$$\sum_{mn=1}^{\infty} \frac{(-)^{m+n} (m^2 + 2n^2)}{\sqrt{m^2 + n^2} \sinh \pi \sqrt{m^2 + n^2}} = -\frac{1}{2} \sum_{m=1}^{\infty} \frac{(-)^m m}{\sinh m\pi} = \frac{1}{8\pi} .$$

The double sum is taken over a region symmetric in $m$ and $n$ so that it is equal to

$$3 \sum_{mn=1}^{\infty} \frac{(-)^{m+n} n^2}{\sqrt{m^2 + n^2} \sinh \pi \sqrt{m^2 + n^2}} .$$

Therefore we have the result

$$\sum_{mn=1}^{\infty} \frac{(-)^{m+n} n^2}{\sqrt{m^2+n^2}\,\sinh \pi \sqrt{m^2+n^2}} = \frac{1}{24\pi} .$$

Comparing this with the form of K, we have also

$$\sum_{mn=1}^{\infty} \frac{(-)^{m+n}\sqrt{m^2+n^2}}{\sinh \pi \sqrt{m^2+n^2}} = \frac{1}{12\pi} .$$

We have now evaluated all the sums occurring in the two expressions for $\beta_1$. They give the results

$$\beta_1 = 4\pi + 16\pi^2\left(-\frac{1}{4\pi} + \frac{1}{12\pi}\right) = \frac{4\pi}{3}$$

(from first field expansion)

$$\beta_1 = -16\pi^2\left(-\frac{1}{8\pi} + \frac{1}{24\pi}\right) = \frac{4\pi}{3}$$

(from second field expansion).

Thus, the two expansions check in giving the same value to $\beta_1$ that we anticipated on symmetry grounds.

The summation of the other series, which do not have alternating signs, is much more difficult because the functions which have a residue $+1$ at each integer value of $n$ are of the form

$$\frac{\pi}{\tan \pi n}$$

or some essentially equivalent one. The integrands of the resulting contour integrals do not then have the symmetry between sin and sinh that enabled us to sum the alternating series. This does not prevent numerical evaluation to any accuracy desired because of their excellent convergence. Numerical work was done with the aid of the Smithsonian tables of hyperbolic functions

and a Marchant calculator, and is summarized in Appendix I. The results, expressed as multiples of $4\pi/3$, are

$$\beta_0 = \beta_1 = \frac{4\pi}{3} \times 1.00000$$

$$\beta_2 = \frac{4\pi}{3} \times 2.03463$$

$$\beta_3 = \frac{4\pi}{3} \times -1.06927 \qquad (4.71)$$

$$\beta_4 = \frac{4\pi}{3} \times -2.5907$$

$$\beta_5 = \frac{4\pi}{3} \times 8.1813$$

The relations $2\beta_2 + \beta_3 = 3\beta_0 = 2\beta_4 + \beta_5$ are seen to be satisfied to within one unit in the last given decimal place.

Quantities essentially equivalent to the $\beta_i$ have been calculated by McKeehan (M11) and by Luttinger and Tisza (L2), by the Ewald method, and used by J. C. Slater (S1).

It is worthwhile to discuss briefly the relation between the above method of calculation and the one of Ewald (E2) since both methods are available for a large number of other similar problems. The Ewald method is based on transformation properties of the theta function of modulus $\tau$, defined by

$$\theta(\tau,z) = \sum_{n=-\infty}^{\infty} e^{-n^2\tau + 2inz}, \quad R_e(\tau) > 0.$$

By means of an integral representation for $e^{ihr}/r$, a sum of terms

$$\sum_n a_n \frac{e^{ikr_n}}{r_n}$$

over all lattice points may be expressed as an integral

with respect to $\tau$ of a three-dimensional theta function. The transformation formula of Jacobi,

$$\theta(\tau,z) = \sqrt{\frac{\pi}{\tau}}\, e^{-z^2/\tau}\ \theta\left(\frac{\pi^2}{\tau}\,,\ \frac{\pi z}{i\tau}\right)\,,$$

then gives two different series representations of the integrand, one of which converges very rapidly for small $\tau$, the other for large $\tau$. By splitting the region of integration into two parts, $\tau < \tau_0$, $\tau > \tau_0$, and using the appropriate series for each part, one can secure rapid convergence over the entire range of $\tau$, and the expressions may be integrated term by term in terms of error functions, giving a final representation of the desired potential as a sum of two rapidly convergent series taken over all lattice points. The static case is then found as the limit $k \to 0$, and, by forming derivatives, the potentials and field strengths due to various lattices of higher multipoles may be built up. Repeating the calculation for a different value of the splitting point $\tau_0$ provides a check on the numerical work.

The method used here is more elementary and less elegant than the Ewald method, but for the case of interest it offers advantages. We need the values of the internal field not at a single point but at several places. In the Ewald method the evaluation of the field at each point is a separate problem, while in the field expansion method the field is found throughout a certain region. This may be of importance in carrying out treatments along the lines suggested by Cohen (C5) in which the fields are needed at all points along certain lines which represent the loci of possible displaced positions of ions. The fields at points of simple rational coordinates are all compounded out of the same set of basic constants (Appendix I) with different combinations of signs. Thus, while the field at a single point is perhaps found more quickly by the Ewald method, the field expansion method

saves time if a number of evaluations must be made. The tables in Appendix I may be useful for numerical work on other problems similar to the present one.

A second advantage of the field expansion method is that it is readily modified to find how the internal fields vary with lattice parameters; for example, in the tetragonal phase of $BaTiO_3$ the crystal expands along the direction of spontaneous polarization and contracts in the other two directions. This causes a small change in the Lorentz factors which would be rather awkward to find by the Ewald method but is easily evaluated by the field expansion method.

On the other hand, due to the difficulty of formulating boundary conditions, the field expansion method is simple only in crystals with three symmetry planes and is therefore practical only for crystal structures of orthorhombic or higher symmetry, while the Ewald method is completely general.

# 5. ELECTRIC POLARIZATION IN CRYSTALS

## 5.1 General description of polarization

The expression for internal field in matrix notation

$$F = \beta P + E$$

may be augmented to a closed system by an assumption about the polarization which results from the internal field at each ion site. The simplest assumption is that the polarization of the i'th ion is given by $P_i = \alpha_i F_i$, where $\alpha_i$ is a constant equal to the polarizability of the i'th ion divided by the volume of a unit cell. This may be written in matrix form as

$$P = \alpha F \qquad (5.11)$$

where $\alpha = \text{diag}\{\alpha_1 \ldots \alpha_n\}$ is a real diagonal matrix.[1] Then we have

$$P = \alpha(\beta P + E)$$

$$P = (1 - \alpha\beta)^{-1} \alpha E,$$

provided $(\alpha\beta)$ does not have an eigenvalue unity. Thus,

---

[1] However, from the discussion of Section 2.3 we know that such a dependence cannot be strictly correct. The mechanical forces acting between ions could be taken into account by giving $\alpha$ nondiagonal elements.

induced polarization occurs in the pattern corresponding to the rows of the "susceptibility matrix" $\chi$

$$P_i = E \sum_j \chi_{ij}$$

where

$$(5.12) \quad \chi = (1 - \alpha\beta)^{-1}\alpha = \alpha(1 - \beta\alpha)^{-1} = \sqrt{\alpha}\,(1 - \sqrt{\alpha}\,\beta\,\sqrt{\alpha}\,)^{-1}\sqrt{\alpha}$$

the last form being useful because the matrix $(\sqrt{\alpha}\,\beta\,\sqrt{\alpha}\,)$ is real and symmetric. In the absence of spontaneous polarization, all the eigenvalues of $(\sqrt{\alpha}\,\beta\,\sqrt{\alpha}\,)$ are less than unity, and we may expand:

$$\chi = \alpha + \alpha\beta\alpha + \alpha\beta\alpha\beta\alpha + \ldots \quad .$$

The total polarization is $P = \sum P_i$, so that the experimentally observed susceptibility is

$$(5.13) \quad \chi_{exp} = \sum_{ij} \chi_{ij} = \sum_i \alpha_i + \sum_{ik} \beta_{ik}\alpha_i\alpha_k + \cdots$$

which is an expansion in powers of the coupling constants $\beta_{ik}$.

The case of spontaneous polarization requires a more careful physical discussion. When $E = 0$, the connection between polarization and internal fields is given by

$$(5.14) \qquad \begin{aligned} F &= \beta P \\ P &= \alpha F = \alpha\beta P. \end{aligned}$$

We can have a nonvanishing polarization only when the matrix $(\alpha\beta)$ has an eigenvalue equal to unity. As the temperature is decreased, at least one of the components of $\alpha$ increases, and when the greatest eigenvalue of $(\alpha\beta)$ reaches unity a spontaneous polarization can set

in, with the pattern of the corresponding eigenvector. The magnitude of the stable polarization is now determined not by the linear relations but by the fact that at high field strengths the polarization of at least one of the ions is no longer a linear function of applied field, and therefore at least one of the $\alpha_i$'s, which are defined as the ratio of polarization to internal fields, decreases. When the saturation polarization is reached, $\alpha$ goes down as $1/F$. The course of events accompanying spontaneous polarization is then as follows. At high temperatures all eigenvalues of $\alpha\beta$ are less than unity and the only solution of Eq. (5.14) is $P = 0$. When the temperature is lowered, the largest eigenvalue of $\alpha\beta$ will at some point become greater than unity. When this happens, $P = 0$ is still a solution of Eq. (5.14), but it is no longer a stable solution, for any small deviation from $P = 0$ produces an internal field so strong that it further increases the discrepancy. Thus, any small disturbance, such as caused by thermal agitation, produces a rapidly increasing polarization. It continues to increase until nonlinearity sets in and $\alpha$ decreases, and a final steady value of polarization is reached when the field strength is such that the largest eigenvalue of $\alpha\beta$ is just equal to unity. This value is now stable, for any small increase in $P$ decreases ($\alpha\beta P - P$), and vice versa. Thus, the spontaneous polarization as a function of temperature will be determined by the condition that

$$\alpha_i = \frac{P_i}{F_i} = \text{const} = \alpha_i(F_i, T),$$

where $(i)$ refers to the ion whose polarization first becomes nonlinear, and the const is the value which makes

$$\det\,(\alpha\beta - 1) = 0$$

$$\det\,(\alpha\beta - \lambda) \neq 0, \qquad \lambda > 1.$$

The constancy of $P_i/F_i$, however, is just the condition that is imposed in more naive analyses, so the present treatment of internal field does not alter the temperature dependence of polarization, although the magnitude is now determined in a different manner.

5.2 Transition to the spontaneous polarized state

It appears at first as if the pattern of spontaneous polarization would in general be completely different from that of induced polarization since the former corresponds to the eigenvector of $\alpha\beta$ with the greatest eigenvalue while the latter is given by the sum of the elements of the rows of $(1 - \alpha\beta)^{-1}\alpha$. It is true that the polarization pattern changes considerably as we go from one condition to the other, but one can show as follows that the transition is actually continuous. Consider the symmetrical form of the susceptibility matrix:

$$\chi = \sqrt{\alpha}(1 - \sqrt{\alpha}\,\beta\,\sqrt{\alpha})^{-1}\sqrt{\alpha} \quad .$$

Since $\sqrt{\alpha}\,\beta\,\sqrt{\alpha}$ is real and symmetric, it may be diagonalized by an orthogonal matrix O:

$$O^{-1}(\sqrt{\alpha}\,\beta\,\sqrt{\alpha})\,O = \text{diag}\,\{\lambda_1 \ldots \lambda_n\} = D$$

where $\lambda_i$ are the (real) eigenvalues of $(\sqrt{\alpha}\,\beta\,\sqrt{\alpha})$. Since for any function $f(x)$ the matrix function $F(D)$ is

$$F(D) = \text{diag}\,\{f(\lambda_1) \ldots f(\lambda_n)\}$$

we may express $F(\sqrt{\alpha}\,\beta\,\sqrt{\alpha})$ as

$$F(\sqrt{\alpha}\,\beta\,\sqrt{\alpha}) = OF(D)O^{-1}$$

or

$$F(\sqrt{\alpha}\,\beta\,\sqrt{\alpha})_{ik} = \sum_j o_{ij} f(\lambda_j) o^{-1}_{jk} = \sum_j f(\lambda_j) o_{ij} o_{kj} \ .$$

The susceptibility matrix may therefore be expanded in the form

$$\chi_{ij} = \alpha_i \alpha_k \sum_j \frac{o_{ij} o_{kj}}{1 - \lambda_j} \ .$$

As the largest eigenvalue $\lambda_1$ approaches unity, the first term dominates the sum. Then, since the polarization pattern is given by

$$P_i = E \sum_k \chi_{ik}$$

we will have, except for a common factor,

$$P_i \simeq \sqrt{\alpha_i}\ o_{i1} \ .$$

But the quantities $o_{i1}$ are known to be just the components $x_i$ of the eigenvector of $(\sqrt{\alpha}\,\beta\,\sqrt{\alpha})$ belonging to the eigenvalue $\lambda_1$:

$$(\sqrt{\alpha}\,\beta\,\sqrt{\alpha})\ x = \lambda_1 x \ .$$

Multiplying by $\sqrt{\alpha}$, we have

$$(\alpha\beta)(\sqrt{\alpha}\ x) = \lambda_1 (\sqrt{\alpha}\ x)$$

so that $\sqrt{\alpha}\ x = \sqrt{\alpha_i}\, o_{i1}$ is an eigenvector of $(\alpha\beta)$ belonging to the same eigenvalue $\lambda_1$ and therefore represents the pattern of spontaneous polarization.

We conclude that, as we approach the Curie point from above, the induced polarization pattern shifts continuously into that corresponding to spontaneous polarization. This has as a consequence that any "simplified

Lorentz factor," defined as the ratio of internal field at some ion to total polarization, must also be considered to be rapidly varying as the polarization pattern shifts from one regime to the other, and treatments made to date are inadequate in this respect.

## 5.3 Spontaneous polarization

It is evident from the foregoing considerations that the results which we wish to get are bound up with the properties of the matrix $\sqrt{\alpha}\ \beta\ \sqrt{\alpha}$, or what is equivalent, of $\alpha\beta$. The former matrix is real and symmetric; therefore, it can be diagonalized by an orthogonal transformation and all its proper values are real. Since the two matrices differ only by the trivial similarity transformation

$$\alpha\beta = \sqrt{\alpha}\,(\sqrt{\alpha}\,\beta\,\sqrt{\alpha})\,\sqrt{\alpha}^{-1},$$

they have the same proper values, and the proper vectors $x$ and $x'$ of $\alpha\beta$ and $\sqrt{\alpha}\,\beta\,\sqrt{\alpha}$ are related by $x = \sqrt{\alpha}\,x'$.

Two of the proper values may be found immediately; on evaluating its determinant we find that $\beta$, and therefore $\alpha\beta$, is singular, i.e., there exists a non-zero polarization pattern that results in no internal field at any ion site. This pattern is the corresponding proper vector of $\alpha\beta$, whose components are proportional to the cofactors of any row of $\beta$, As is easily verified, this pattern is given by

$$P = \begin{pmatrix} a-3 \\ -a \\ 1 \\ 1 \\ 1 \end{pmatrix} = \begin{pmatrix} -2.11 \\ -0.89 \\ 1. \\ 1. \\ 1. \end{pmatrix} \tag{5.31}$$

where

$$a = \frac{4(\beta_2 - \beta_0)}{\beta_2 - \beta_4} = 0.89.$$

In this pattern the net externally observable polarization $\sum P_i$ also vanishes.

A second proper value is found by noting the symmetry of $(\sqrt{\alpha}\ \beta\ \sqrt{\alpha})$ in $O_x$ and $O_y$. If we transform to a new description of the polarization pattern, using $(P_{O_x} \pm P_{O_y})/\sqrt{2}$ instead of $P_{O_x}$, $P_{O_y}$, i.e., if we transform with the orthogonal matrix

$$S = \left(\begin{array}{cc|ccc} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ \hline 0 & 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 0 & 1 \end{array}\right)$$

we find that

$$S(\sqrt{\alpha}\ \beta\ \sqrt{\alpha})S^{-1} = \left(\begin{array}{ccc|c|c} \alpha_1\beta_0 & \sqrt{\alpha_1\alpha_2}\beta_0 & \sqrt{\alpha_1\alpha_3}\beta_2 & 0 & \sqrt{\alpha_1\alpha_4}\beta_3 \\ \sqrt{\alpha_1\alpha_2}\beta_0 & \alpha_2\beta_0 & \sqrt{2\alpha_2\alpha_3}\beta_4 & 0 & \sqrt{\alpha_2\alpha_4}\beta_5 \\ 2\sqrt{\alpha_1\alpha_3}\beta_2 & \sqrt{2\alpha_2\alpha_3}\beta_4 & \alpha_3(\beta_0+\beta_3) & 0 & \sqrt{2\alpha_3\alpha_4}\beta_2 \\ \hline 0 & 0 & 0 & \alpha_3(\beta_0-\beta_3) & 0 \\ \hline \sqrt{\alpha_1\alpha_4}\beta_3 & \sqrt{\alpha_2\alpha_4}\beta_5 & \sqrt{2\alpha_3\alpha_4}\beta_2 & 0 & \alpha_4\beta_0 \end{array}\right)$$

so that a second proper value is $\alpha_3(\beta_0 - \beta_3)$. The corresponding polarization pattern is

$$P = \begin{pmatrix} 0 \\ 0 \\ 1 \\ -1 \\ 0 \end{pmatrix} .$$

Using the above transformed form of $\sqrt{\alpha}\,\beta\,\sqrt{\alpha}$, the remaining proper values are found from the determinantal equation

$$\det\left(\sqrt{\alpha}\,\beta\,\sqrt{\alpha} - \lambda 1\right) = 0$$

which reduces to

$$\begin{vmatrix} (\beta_0 - \frac{\lambda}{\alpha_1}) & \beta_0 & \sqrt{2}\beta_2 & \beta_3 \\ \beta_0 & (\beta_0 - \frac{\lambda}{\alpha_2}) & \sqrt{2}\beta_4 & \beta_5 \\ \sqrt{2}\beta_2 & \sqrt{2}\beta_4 & (\beta_0 + \beta_3 - \frac{\lambda}{\alpha_3}) & \sqrt{2}\beta_2 \\ \beta_3 & \beta_5 & \sqrt{2}\beta_2 & (\beta_0 - \frac{\lambda}{\alpha_4}) \end{vmatrix} = 0$$

of which we already know that $\lambda = 0$ is a solution. If for the moment we assume all $\alpha_i$ equal; $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = \alpha_0$, the other roots may be found numerically, since the $\beta_i$ are known constants. In this case the above equation reduces to

$$\left(\frac{\lambda}{\alpha_0}\right)^3 - \left[7\beta_0 - 2\beta_2\right]\left(\frac{\lambda}{\alpha_0}\right)^2 - 2\left[4(\beta_0 - \beta_2)^2 + 3(\beta_0 - \beta_4)^2\right.$$

$$\left. - 5\beta_0(\beta_0 - \beta_2)\right]\left(\frac{\lambda}{\alpha_0}\right) + 8\beta_0\left[5(\beta_0 - \beta_2)^2 + 3(\beta_0 - \beta_4)^2\right] = 0$$

or, inserting numerical values, we have for $x = \lambda/\alpha_0\beta_0$:

$$x^3 - 2.93x^2 - 96.32x + 352.48 = 0$$

the roots of which may be found graphically to be

$$x = \{ -10.1, +3.8, +9.232 \} \quad .$$

The proper vector belonging to the largest value $\lambda = 9.232\,\alpha_0\beta_0$ is of principal interest since, under the assumption of equal $\alpha_i$, it would represent the pattern of spontaneous polarization. As might be guessed on physical grounds, this vector represents essentially polarization of the string of Ti and $O_z$ ions, which are placed so that polarization of one produces very strong supporting fields at the other. In fact, we see from the relation

$$\alpha_0 \begin{pmatrix} \beta_0 & \beta_0 & \beta_2 & \beta_2 & \beta_3 \\ \beta_0 & \beta_0 & \beta_4 & \beta_4 & \beta_5 \\ \beta_2 & \beta_4 & \beta_0 & \beta_3 & \beta_2 \\ \beta_2 & \beta_4 & \beta_3 & \beta_0 & \beta_2 \\ \beta_3 & \beta_5 & \beta_2 & \beta_2 & \beta_0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \beta_0 + \beta_3 \\ \beta_0 + \beta_5 \\ \beta_4 + \beta_2 \\ \beta_4 + \beta_2 \\ \beta_5 + \beta_0 \end{pmatrix} = \begin{pmatrix} -0.008 \\ 1.00 \\ -0.06 \\ -0.06 \\ 1.00 \end{pmatrix} \times 9.18\alpha_0\beta_0$$

that the polarization pattern in which Ti and $O_z$ are equally polarized and all other ions are unpolarized is very close to the vector in question. If all $\alpha_i$ were equal, spontaneous polarization would occur when

$$\alpha_0 = \frac{1}{9.23\beta_0} = 0.026.$$

Using the observed volume of a $BaTiO_3$ unit cell, this would mean a polarizability for each ion of

$$\alpha_0 v = 0.026 \times 64 = 1.65 \text{ Å}^3 \quad .$$

When the $\alpha_i$ are different, the proper values of $\sqrt{\alpha}\,\beta\,\sqrt{\alpha}$ are the solutions of a cubic equation involving the $\alpha_i$ in a complicated way. In the present study we describe only the greatest proper value and corresponding polarization pattern, for the case that one polarizability is much greater than the others, and here we may use perturbation theory to get a sufficiently good approximation.

We express the fact that two different orders of magnitude of elements $\alpha_i$ are present by writing

$$\alpha = \alpha' + \epsilon^2 \alpha''$$

where $\alpha'$ is the part of the matrix $\alpha$ containing the large elements, $\alpha''$ contains the small elements, and $\epsilon$ is an expansion parameter that we eventually set equal to unity. If the polarizability $\alpha_2$ at the Ti ion is the only large one, standard perturbation methods give for the largest proper value of $\alpha\beta$:

$$(5.32)\quad \lambda = \alpha_2\beta_0 + \frac{1}{\beta_0}(\alpha_1\beta_0^2 + 2\alpha_3\beta_4^2 + \alpha_4\beta_5^2)\,\epsilon^2 + \ldots \quad .$$

We see that the presence of polarizable ions other than the Ti always increases the largest proper value and makes spontaneous polarization more likely. This expression is valid only if the second term is small compared to the first, and one guesses that it overestimates the largest proper value since, if we put all $\alpha_i = 1$, the above expression reduces to $82\beta_0$, whereas the correct value is the largest proper value of $\beta$, found before to be $9.23\beta_0$. We have, however, the result that the amount by which a given ion helps the spontaneous polarization may vary greatly with its exact position in the unit cell; for example, a given polarizability in the $O_z$ position is $(\beta_5/\beta_0)^2 = 67$ times as effective as in the Ba position, while in the $O_y$ position it is $(\beta_4/\beta_0)^2 = 6.7$

times as effective. Furthermore, since the effectiveness of an ion depends on the square of the Lorentz factor connecting its position with the Ti position, an ion such as $O_x$, located where the field due to polarization at the Ti ions is opposed to the net polarization, still contributes just as effectively to the onset of spontaneous polarization as one in a position where $\beta > 0$, although its dipole moment is now opposed to the Ti moment. This is in contrast to the case of polarization induced by an external field, where two ions coupled by a negative Lorentz factor tend to decrease each other's polarization in the direction of the field, and thus to decrease the experimental susceptibility.

The proper vector of $\alpha\beta$ corresponding to the proper value (5.32) is given to order $\epsilon$ by

$$P = \begin{pmatrix} \alpha_1\beta_0 \\ \alpha_2\beta_0 \\ \alpha_3\beta_4 \\ \alpha_3\beta_4 \\ \alpha_4\beta_5 \end{pmatrix} . \qquad (5.33)$$

Since $\beta_4 < 0$, we find, as expected, that in the spontaneously polarized state the dipole moments of $O_x$ and $O_y$ are opposed to the polarization of Ti.

## 5.4 Simplified Lorentz factors for spontaneous polarization

In our preliminary study of the electronic model we defined a Lorentz factor as the ratio of internal field at the Ti ion to the total experimentally observable polarization. This quantity (denoted by $\beta$ in the first section and by "$\beta$" here) was left as an undetermined constant, but the results just found enable us to make an estimate of its value and to ascertain if it is actually a constant. This factor is given by

$$(5.41) \qquad "\beta" = \frac{\sum_i \beta_{2i} P_i}{\sum_i P_i}$$

where $\beta_{2i}$ is the i'th element in the second row of the matrix $\beta$:

$$\beta_{2i} = |\beta_0\ \beta_0, \beta_4, \beta_4, \beta_5| = \beta_0 |1, 1, -2.6, -2.6, +8.2|$$

"$\beta$" is therefore the average value of $\beta_{2i}$, weighted according to the fraction of the total polarization carried by the i'th ion. Since (Section 4.4) $2\beta_4 + \beta_5 = 3\beta_0$, we have $\sum_i \beta_{2i} = 5\beta_0$, and the average of $\beta_{2i}$ with equal weight is exactly $\beta_0$. In general we see that, if

$$P_{0_x} > P_{0_z}, \quad \text{then} \quad "\beta" < \beta_0 = \frac{4\pi}{3}$$

while if

$$P_{0_x} < P_{0_z} \quad \text{then} \quad "\beta" > \beta_0 .$$

In the case of spontaneous polarization the second condition holds since we have found that $P_{0_x} < 0$, $P_{0_z} > 0$. To order $\epsilon^2$ the value of "$\beta$" may be found from our approximate proper vector Eq. (5.33):

$$"\beta" = \frac{\beta_0^2\alpha_2 + \epsilon^2 \left[\alpha_1\beta_0^2 + 2\alpha_3\beta_4^2 + \alpha_4\beta_5^2\right]}{\beta_0\alpha_2 + \epsilon^2 \left[\alpha_1\beta_0 + 2\alpha_3\beta_4 + \alpha_4\beta_5\right]}$$

$$= \beta_0 \left\{ 1 + 2\frac{\alpha_3}{\alpha_2}\frac{\beta_4}{\beta_0}\left(\frac{\beta_4}{\beta_0} - 1\right) + \frac{\alpha_4}{\alpha_2}\frac{\beta_5}{\beta_0}\left(\frac{\beta_5}{\beta_0} - 1\right) + \cdots \right\}$$

$$(5.42) \qquad = \beta_0 \left[ 1 + 20.6\,\frac{\alpha_3}{\alpha_2} + 58.7\,\frac{\alpha_4}{\alpha_2} + \cdots \right] .$$

In the spontaneously polarized state we must always have $"\beta" > 4\pi/3$, but the difference need not be great if $\alpha_2$ is extremely large compared to $\alpha_3$ and $\alpha_4$. We note that $\alpha_1$ drops out of this expression for $"\beta"$ as it should since the Ba is coupled to the Ti ion by a Lorentz factor $\beta_0$, and therefore the contribution of the Ba ion to the field at the Ti and its contribution to the total polarization are always in the ratio $\beta_0$, so that polarization of the Ba ion cannot cause $"\beta"$ to depart from $\beta_0$ in first order.

In the spontaneously polarized state, $"\beta"$ is essentially a constant independent of temperature since $\alpha_3$ and $\alpha_4$ are not strongly temperature-dependent, and as we have seen the strength of the spontaneous polarization always adjusts itself so that $\alpha_2$ is constant.

## 5.5 Induced polarization

We now wish to find the pattern of induced polarization and the corresponding simplified Lorentz factor $"\beta"$ for the case that $\alpha_2$ is much greater than the other $\alpha_i$. For this, the expansion in terms of proper values and proper vectors of $\alpha\beta$ is not very convenient, as all of these quantities are now important and they are difficult to find, the proper values other than the greatest one being degenerate in zero-order, and the degeneracy is not removed in the first order of $\epsilon$. We use instead a more direct method of expanding the internal field and polarization in powers of $\lambda = \epsilon^2$, making no reference to the proper values of $\alpha\beta$.

We write $\alpha = \alpha' + \lambda\alpha''$ where, as before $\alpha'$ is the part of $\alpha$ containing the large elements and $\alpha''$ is the rest of the matrix. Evidently the matrices $\alpha'$, $\alpha''$ are singular and $\alpha'\alpha'' = 0$. Expanding in powers of $\lambda$, the equations $F = \beta P + E$, $P = \alpha F$ become

$$F^{(0)} + \lambda F^{(1)} + \lambda^2 F^{(2)} + \ldots = \beta\left[ P^{(0)} + \lambda P^{(1)} + \lambda^2 P^{(2)} + \ldots \right] + E$$

$$P^{(0)} + \lambda P^{(1)} + \lambda^2 P^{(2)} + \ldots = (\alpha' + \lambda\alpha'')\left( F^{(0)} + \lambda F^{(1)} + \lambda^2 F^{(2)} + \ldots \right)$$

Equating coefficients of like powers of $\lambda$, we have

$$F^{(0)} = \beta P^{(0)} + E = \beta\alpha' F^{(0)} + E = (1 - \beta\alpha')^{-1} E$$

$$P^{(0)} = \alpha' F^{(0)} = \alpha' (1 - \beta\alpha')^{-1} E$$

$$\left.\begin{aligned} F^{(n)} &= \beta P^{(n)} \\ P^{(n)} &= \alpha' F^{(n)} + \alpha'' F^{(n-1)} \end{aligned}\right\} \qquad n \geq 1$$

The last equations may be rearranged to

$$F^{(n)} = \beta (1 - \alpha'\beta)^{-1} \alpha'' F^{(n-1)}$$

$$P^{(n)} = (1 - \alpha'\beta)^{-1} \alpha'' F^{(n-1)} \quad .$$

In the case that only one of the polarizabilities $\alpha_2$ is large, these expressions may be evaluated without further approximation. We have

$$\alpha' = \left(\begin{array}{cc|c} 0 & 0 & \\ 0 & \alpha_2 & 0 \\ \hline & 0 & 0 \end{array}\right), \qquad \beta\alpha' = \left(\begin{array}{cc|c} 0 & \beta_0\alpha_2 & \\ 0 & \beta_0\alpha_2 & 0 \\ \hline 0 & \beta_4\alpha_2 & \\ 0 & \beta_4\alpha_2 & 0 \\ 0 & \beta_5\alpha_2 & \end{array}\right)$$

We can now easily evaluate $(1 - \beta\alpha')^{-1}$ by noting that $(\beta\alpha')^2 = \beta_0\alpha_2(\beta\alpha')$, and using the method of Appendix B. We find that

$$(1 - \beta\alpha')^{-1} = 1 + \frac{\beta\alpha'}{1 - \beta_0\alpha_2}$$

similarly,

$$(1 - \alpha'\beta)^{-1} = 1 + \frac{\alpha'\beta}{1 - \beta_0\alpha_2}$$

We also note that

$$\alpha'(1 - \beta\alpha')^{-1} = (1 - \alpha'\beta)^{-1}\alpha' = \frac{\alpha'}{1 - \beta_0\alpha_2} \quad .$$

Using these relations, the above equations become

$$P^{(0)} = \frac{\alpha' E}{1 - \beta_0\alpha_2}$$

$$F^{(0)} = E + \frac{\beta\alpha' E}{1 - \beta_0\alpha_2}$$

$$P^{(n)} = \left(1 + \frac{\alpha'\beta}{1 - \beta_0\alpha_2}\right) \alpha'' F^{(n-1)}$$

$$F^{(n)} = \left(1 + \frac{\beta\alpha'}{1 - \beta_0\alpha_2}\right)\beta\alpha'' F^{(n-1)}$$

In zero-order approximation only site 2 is polarized, and the total polarization $P_{tot} = \sum P_i = P_{tot}^{(0)} + \lambda P_{tot}^{(1)} + \ldots$ is

$$P_{tot}^{(0)} = \frac{\alpha_2}{1 - \beta_0\alpha_2} E \qquad (5.51)$$

while the internal field seen at site 2 is just

$$F_2^{(0)} = E + \beta_0 P_{tot}^{(0)} \quad . \qquad (5.52)$$

These are the familiar relations used as the starting point for nearly all treatments of dielectric and optical properties. The first-order corrections to these relations due to other polarizable material are

$$P^{(1)} = \left(1 + \frac{\alpha'\beta}{1 - \beta_0\alpha_2}\right)\alpha'' \left(1 + \frac{\beta\alpha'}{1 - \beta_0\alpha_2}\right) E$$

$$F^{(1)} = \left(1 + \frac{\beta\alpha'}{1 - \beta_0\alpha_2}\right)\beta\alpha'' \left(1 + \frac{\beta\alpha'}{1 - \beta_0\alpha_2}\right) E \qquad (5.53)$$

Using Eq. (5.53), a simple calculation gives, for the first-order correction to the total polarization,

$$P_{tot}^{(1)} = \frac{E}{(1-\beta_0\alpha_2)^2}\left\{\alpha_1 + 2\alpha_3[1 + (\beta_4 - \beta_0)\alpha_2]^2 + \alpha_4[1 + (\beta_5 - \beta_0)\alpha_2]^2\right\},$$

and the first-order correction to the field at the Ti ion is the second component of $F^{(1)} = \beta P^{(1)}$, equal to

$$F_2^{(1)} = \frac{E}{(1-\beta_0\alpha_2)^2}\left\{\alpha_1\beta_0 + 2\alpha_3\beta_4[1 + (\beta_4 - \beta_0)\alpha_2] + \alpha_4\beta_5[1 + (\beta_5 - \beta_0)\alpha_2]\right\},$$

Now to first order in $\lambda$, the simplified Lorentz factor is given by

$$"\beta" = \frac{F_2 - E}{P_{tot}} = \frac{F_2^{(0)} - E + \lambda F_2^{(1)} + \cdots}{P_{tot}^{(0)} + \lambda P_{tot}^{(1)} + \cdots} = \frac{\beta_0 P_{tot}^{(0)} + \lambda F_2^{(1)} + \cdots}{P_{tot}^{(0)} + \lambda P_{tot}^{(1)} \cdots}$$

$$= \beta_0\left[1 + \frac{\lambda}{\beta_0 P_{tot}^{(0)}}(F_2^{(1)} - \beta_0 P_{tot}^{(1)}) + \cdots\right].$$

From previous results we have

$$\beta_0 P_{tot}^{(0)} = \frac{\beta_0\alpha_2 E}{1 - \beta_0\alpha_2}$$

$$F_2^{(1)} - \beta_0 P_{tot}^{(1)} = \frac{E}{1 - \alpha_2\beta_0}\left\{2\alpha_3(\beta_4 - \beta_0)[1 + \alpha_2(\beta_4 - \beta_0)]\right.$$

$$\left. + \alpha_4(\beta_5 - \beta_0)[1 + \alpha_2(\beta_5 - \beta_0)]\right\}$$

Therefore,

$$"\beta" = \beta_0\left[1 + \lambda\frac{(\beta_5-\beta_0)(\alpha_4-\alpha_3)}{\beta_0\alpha_2} + \lambda\frac{(\beta_5-\beta_0)^2}{2\beta_0}(\alpha_3 + 2\alpha_4)\right]$$

$$= \beta_0\left[1 + 7.18\left(\frac{\alpha_4-\alpha_3}{\alpha_2}\right) + 25.8(\alpha_3 + 2\alpha_4)\beta_0\right] \qquad (5.54)$$

## APPENDIX A

Numerical evaluation of Lorentz factors

All of the series developed for various Lorentz factors may be evaluated in terms of the function

$$f(m,n) = \frac{n^2}{\sqrt{m^2 + n^2}\,\sinh \pi \sqrt{m^2 + n^2}}$$

For the series arising from the first field expansion we have

$$\frac{\sqrt{m^2 + n^2}}{\sinh \pi \sqrt{m^2 + n^2}} = f(m,n) + f(n,m).$$

Our first task is therefore the construction of the following table of values of $f(m,n)$.

| m/n | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| 0 | 86589.52 | 7469.81 | 484.20 | 27.84 | 1.50 | 0.06 | 0.004 |
| 1 | 16636.05 | 3182.44 | 275.90 | 18.32 | 1.08 | 0.06 | 0.00 |
| 2 | 795.61 | 391.28 | 60.11 | 5.65 | 0.42 | 0.03 | 0.001 |
| 3 | 30.66 | 26.71 | 6.89 | 0.96 | 0.09 | 0.004 | 0.0004 |
| 4 | 1.14 | 1.41 | 0.54 | 0.11 | 0.02 | | |
| 5 | 0.04 | 0.07 | 0.03 | 0.01 | 0.001 | | |
| 6 | 0.002 | 0.004 | 0.0008 | | | | |

$[10^6 f(m,n)]$

These terms were found as follows: The first few terms are needed to great accuracy, and for these the National Bureau of Standards table of the exponential functions were needed. For intermediate terms the Smithsonian tables of hyperbolic functions were used, while for those terms for

which $10^6 f(m,n) < 1$, slide-rule accuracy is sufficient. Once we have this table the various sums are readily found by addition and subtraction. We find the intermediate results

$$-10^6 \sum_{n=1}^{\infty} \frac{(-1)^n\, n}{\sinh \pi n} = 79577.51 \quad \left(\frac{1}{4\pi} = 0.07957747\right)$$

$$10^6 \sum_{n=1}^{\infty} \frac{n}{\sinh \pi n} = 94572.93$$

$$10^6 \sum_{n=1}^{\infty} \frac{2n}{\sinh 2\pi n} = 7497.71$$

$$10^6 \sum_{m,n=1}^{\infty} \frac{(-1)^{m+n}\, n^2}{\sqrt{m^2+n^2}\, \sinh \pi \sqrt{m^2+n^2}} = 13262.81 \quad \left(\frac{1}{24\pi} = 0.0132629\right)$$

$$10^6 \sum_{m,n=1}^{\infty} \frac{(-1)^{m}\, n^2}{\sqrt{m^2+n^2}\, \sinh \pi \sqrt{m^2+n^2}} = -18922.98$$

$$10^6 \sum_{m,n=1}^{\infty} \frac{(-1)^{n}\, n^2}{\sqrt{m^2+n^2}\, \sinh \pi \sqrt{m^2+n^2}} = -14181.52$$

$$10^6 \sum_{m,n=1}^{\infty} \frac{n^2}{\sqrt{m^2+n^2}\, \sinh \pi \sqrt{m^2+n^2}} = 21435.64$$

$$10^6 \sum_{m,n=1}^{\infty} \frac{(-1)^{m+n}\sqrt{m^2+n^2}}{\sinh \pi \sqrt{m^2+n^2}} = 26527. \quad \left(\frac{1}{12\pi} = 0.026526\right)$$

$$10^6 \sum_{m,n=1}^{\infty} \frac{(-1)^{m}\sqrt{m^2+n^2}}{\sinh \pi \sqrt{m^2+n^2}} = -33104.50$$

$$10^6 \sum_{m,n=1}^{\infty} \frac{\sqrt{m^2+n^2}}{\sinh \pi \sqrt{m^2+n^2}} = 42871.29 \quad .$$

Combining these, we have for the Lorentz factors:

$$\left.\begin{aligned} \beta_1 &= \frac{4\pi}{3} \times 1.00005 \\ \beta_2 &= \frac{4\pi}{3} \times 2.03466 \\ \beta_5 &= \frac{4\pi}{3} \times 8.1813 \end{aligned}\right\} \text{From first field expansion}$$

$$\left.\begin{aligned} \beta_1 &= \frac{4\pi}{3} \times 1.00000 \\ \beta_2 &= \frac{4\pi}{3} \times 2.03461 \\ \beta_3 &= \frac{4\pi}{3} \times -1.06927 \\ \beta_4 &= \frac{4\pi}{3} \times -2.5907 \end{aligned}\right\} \text{From second field expansion}$$

These values should be reliable to at least four significant figures.

## APPENDIX B

### Evaluation of $(1-M)^{-1}$

Let the matrix $M$ be of dimension $n$ and all of its eigenvalues less than unity in absolute magnitude. Then the infinite series representation

$$(1 - M)^{-1} = 1 + M + M^2 + \ldots = \sum_{S=0}^{\infty} M^S$$

is valid. This may be reduced to a sum of a finite number of terms by using the fact that every matrix satisfies its characteristic equation, i.e., if

$$\det (M - \lambda 1) = C \sum_{k=0}^{n} C_n \lambda^k$$

where

$$C = \det (M - 1)$$

then

$$\sum_{k=0}^{n} C_k M^k = 0, \qquad \sum_{k=0}^{n} C_k = 1$$

By repeated application of this relation any function of a matrix may be reduced to a polynomial of degree not exceeding $(n - 1)$:

$$f(M) = \sum_{k=0}^{\infty} a_k M^k = \sum_{k=0}^{n-1} b_k M^k$$

where the $b_k$ are functions of $a_k$ and $C_k$. To carry out this reduction on $f(M) = (1 - M)^{-1}$, we note that

$$(1 - M)^{-1} = (1 - \sum_{k=0}^{n} C_k M^k)(1 - M)^{-1}$$

$$= \sum_{S=0}^{\infty} M^S - \sum_{S=0}^{\infty} \sum_{k=0}^{n} C_k M^{k+S}$$

Put $k + S = \tau$

$$\sum_{S=0}^{\infty} \sum_{k=0}^{n} C_k M^{k+S} = \sum_{\tau=0}^{n-1} \sum_{k=0}^{\tau} C_k M^{\tau} + \sum_{\tau=n}^{\infty} (\sum_{k=0}^{n} C_k) M^{\tau}$$

$$= \sum_{\tau=0}^{n-1} (\sum_{k=0}^{\tau} C_k) M^{\tau} + \sum_{\tau=n}^{\infty} M^{\tau}$$

Therefore we have

$$(1 - M)^{-1} = \sum_{S=0}^{n-1} (1 - \sum_{k=0}^{S} C_k) M^S$$

$$= (1-C_o) + (1-C_o-C_1)M + (1-C_o-C_1-C_2)M^2$$

$$+ \ldots + (1-C_o-C_1 - \ldots -C_{n-1})M^{n-1}$$

The $C_k$ are readily evaluated by writing out the expression $\det (M - \lambda 1)$, so we have a straightforward method of finding $(1 - M)^{-1}$ without having to find the eigenvalues of M. This method has previously been described by R. Dicke (D4).

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