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.

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.

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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,

---

[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 a-
bove 23°C, given by

$$(1.01) \qquad \chi = \frac{C}{T - T_c}$$

with the Curie constant $C = 178°K$ and $T_c = 23°C$. Between
$-18°C$ and $23°C$ there is a spontaneous electric polariza-
tion 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 des-
cribed by hysteresis loops similar to the B-H curves of
ferromagnetic materials, with a coercive force of the order
of 100 volts/cm. Below $-18°C$, the spontaneous polariza-
tion disappears, and from here down to about $-150°C$, the
susceptibility follows another Curie-Weiss law

$$(1.02) \qquad \chi = \frac{C}{T_c - T}$$

with $T_c = -18°C$, $C = 93.8°K$.

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 be-
havior of the crystal, was ignored. Secondly, the struc-
ture 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

$$(1.03) \qquad F = E + \beta P,$$

where E is the applied field,   P is the total polariza-
tion, and β 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 μ ,   in equilibrium with its surroundings at temper-
ature T, is

(1.04) $\alpha = \dfrac{\mu^2}{3kT}$,

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

(1.05) $\chi = \dfrac{P}{E} = \dfrac{N\alpha}{1 - \beta N\alpha} = \dfrac{1}{\beta}\dfrac{T_c}{T - T_c}$,

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 unfortunate-
ly 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 prop-
erties, 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 <u>when all the others are pointing in the same direction</u>. Now let us vary the orientation of dipole A. If it is inclined at an angle θ 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 dis-
tance 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
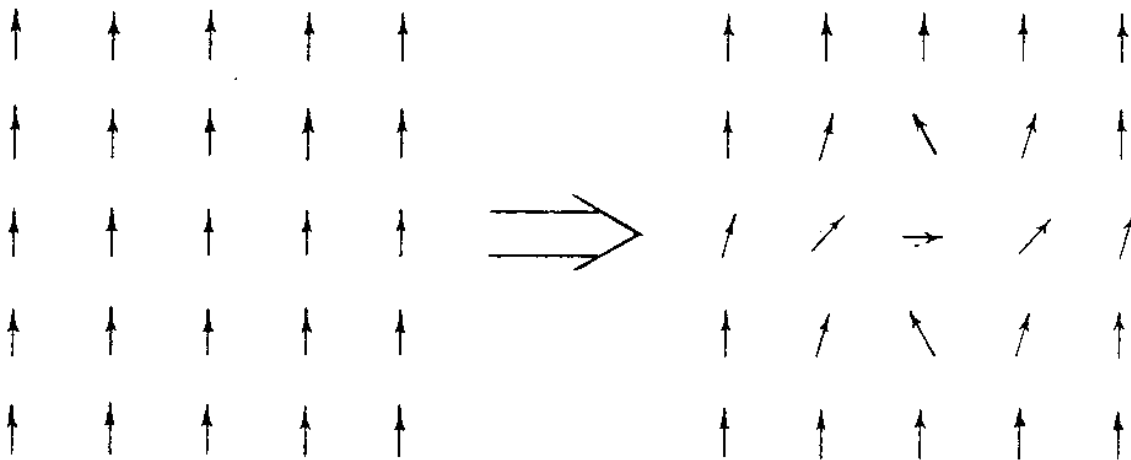
FIG. 1.1

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 correct-
ly 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 con-
tinuously 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 orienta-
tion 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 re-
adjust 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 (O1), 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 station-
ary 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°, 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 ϵ 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:

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

where $\alpha = \mu^2/3kT$ is the polarizability of each dipole. Thus, ϵ 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 a-
bandoning 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 effec-
tive 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 tempera-
tures. 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 experi-
mentally. Tungsten trioxide (K4) and lead zirconate
(S7, R8) are believed to be antiferroelectric.

Ferromagnetism is, of course, based on a differ-
ent type of interaction between dipoles, which is independ-
ent 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 success-
ful, undertaking is the correlation of its properties in
terms of a phenomenological thermodynamic treatment.
Following a suggestion of Cady (C1) stressing the import-
ance of piezoelectric effect in determining the behavior
of Rochelle salt, H. Mueller (M8) has developed in rather
complete form his "interaction theory." Granted the val-
idity 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. How-
ever, a phenomenological theory is of great value in dis-
closing 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 (T2).

This may be written in matrix form:

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

or more compactly, as

$$
\begin{pmatrix} -X \\ E \end{pmatrix}
=
\begin{pmatrix} C & \widetilde{f} \\ f & w \end{pmatrix}
\begin{pmatrix} x \\ P \end{pmatrix}
\tag{1.21}
$$

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

$$
\begin{pmatrix} x \\ P \end{pmatrix}
=
\begin{pmatrix} S & -\widetilde{d} \\ -d & k' \end{pmatrix}
\begin{pmatrix} -X \\ E \end{pmatrix}
\tag{1.22}
$$

in which the submatrices are related by

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

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

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

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

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

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

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

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 choices 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

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

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 ferro-
electric 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 ex-
istence of two Curie points, and a theory which could ex-
plain this in a natural way without postulating two in-
dependent 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 pro-
duces an electric moment. This theory was originally pro-
posed 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 unperturb-
ed 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 possi-
bility.

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$_2$PO$_4$. 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 re-
semble Rochelle salt, however, in that the anomalies are
confined to one direction of polarization, and in the ex-
istence of strong piezoelectric coupling between polari-
zation in this direction and a shearing strain in the plane
at right angles to the polarization.

The crystal structure of KH$_2$PO$_4$ 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 approxi-
mate free energy function is found. This leads to a pre-
diction 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$_2$PO$_4$ consider-

ably (M19), makes it hard to believe that hydrogen bonds
are the important things in Rochelle salt, while confirm-
ing that they are in KH_2PO_4.
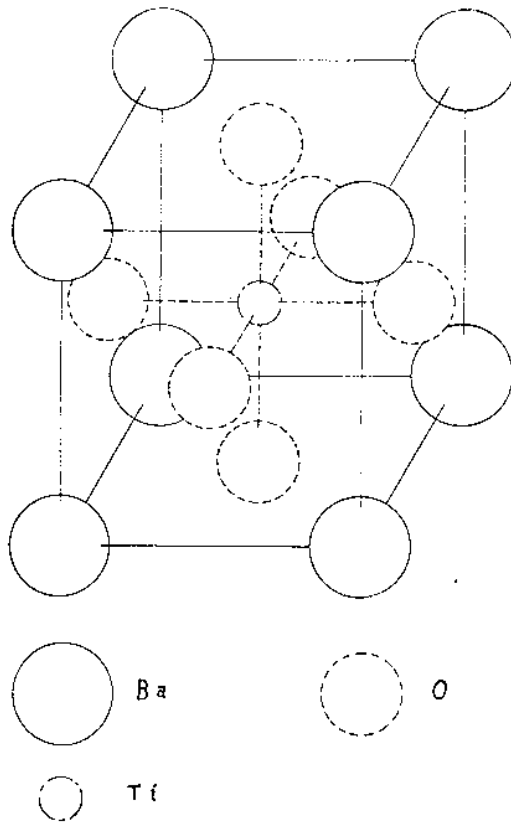
FIG. 1.2

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 λ-type, with no
heat of transition. Roberts (R1) found that a strong
piezoelectric effect is induced in the ceramic by a polar-
izing field. Two other phase transitions were located at
5°C and -80°C. They show up clearly as peaks in the di-
electric 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, mech-
anical, and electrical measurements the nature of the
changes at the three transition temperatures has been es-
tablished (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 direc-
tion 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 $T < -80°C$ and $-80°C < T < 5°C$, 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
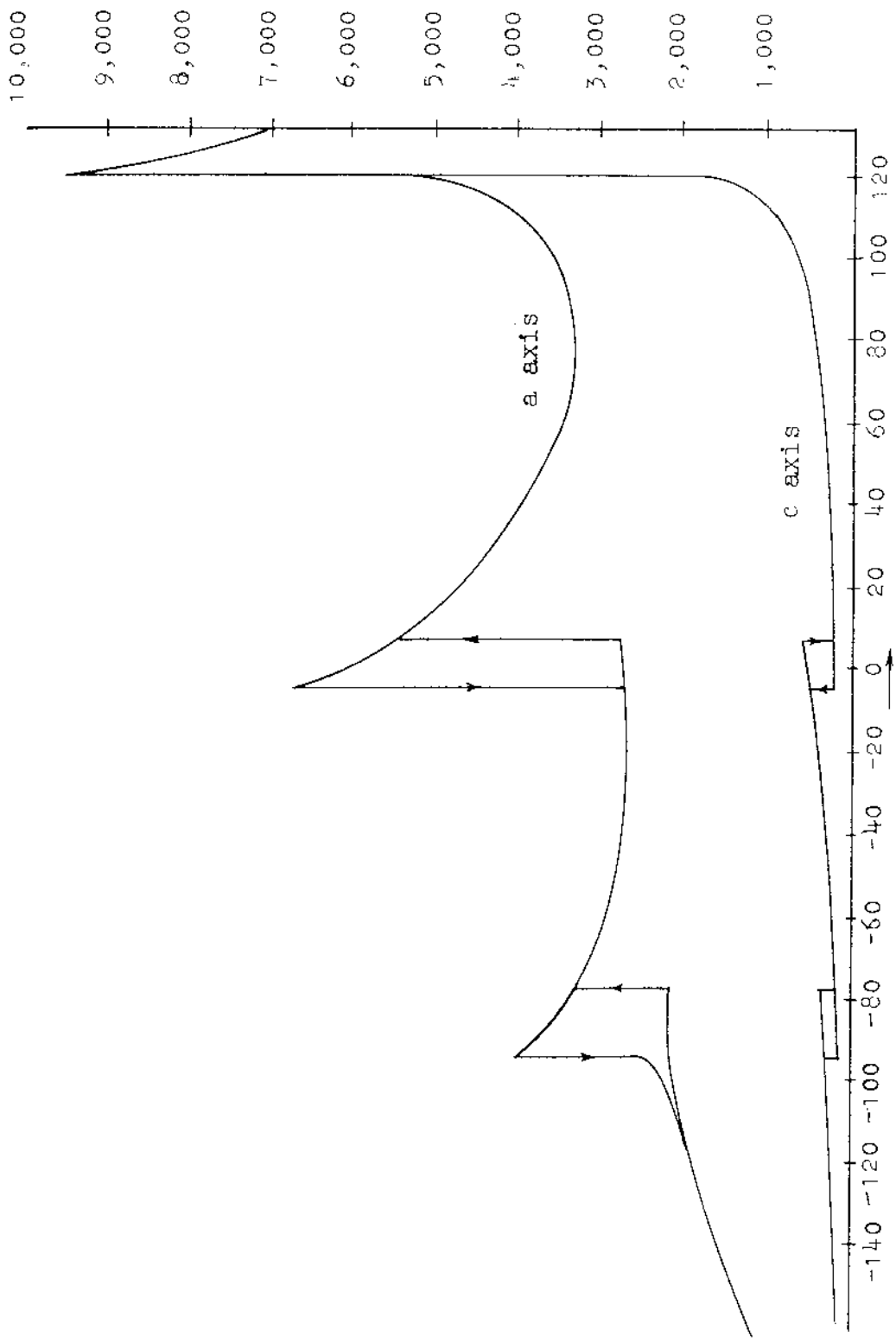
FIG. 1.3

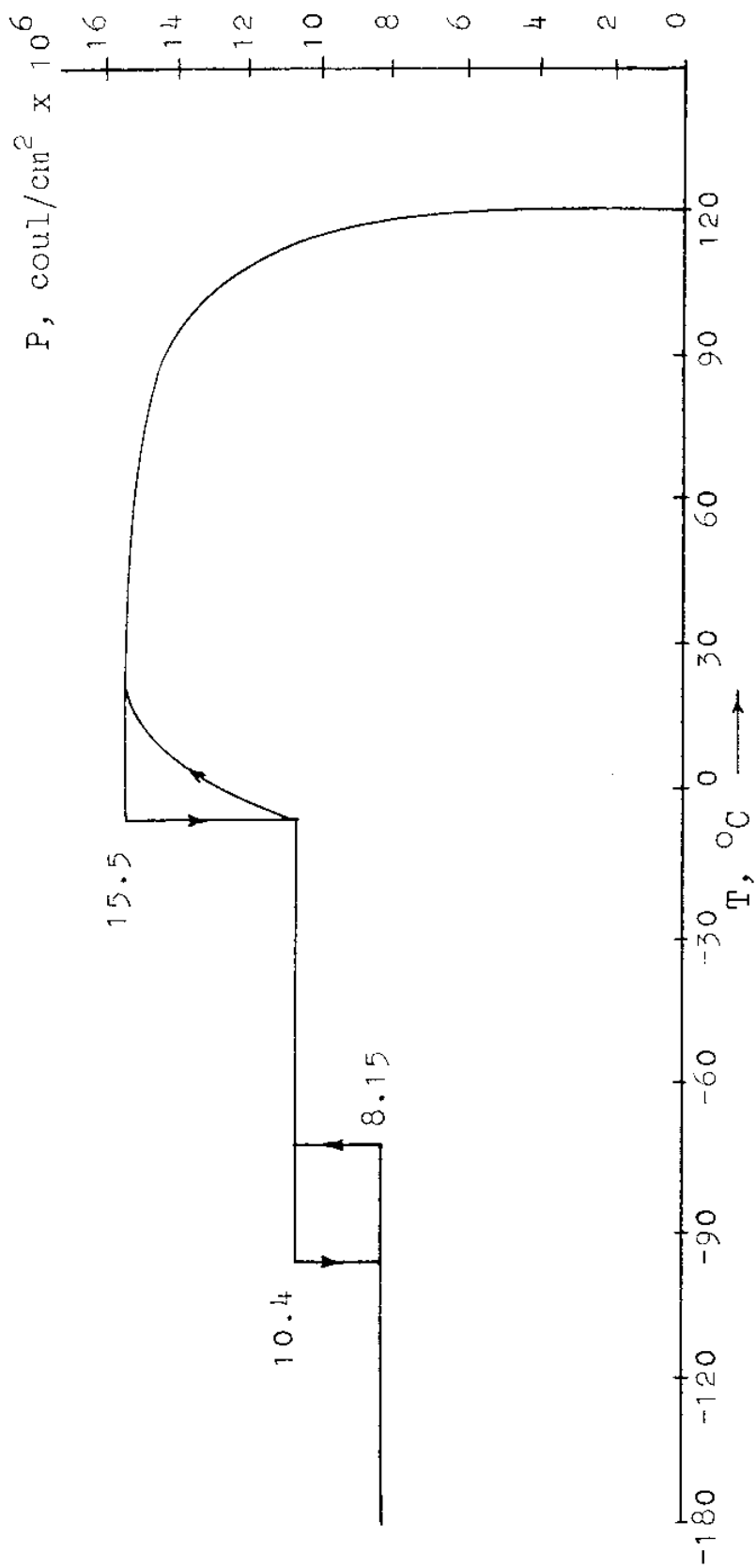Dielectric constants versus temperature for BaTiO$_3$, according to Merz (M7)

FIG 1.4

Spontaneous polarization versus temperature for BaTiO$_3$, according to Merz (M$_7$)

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$_2$PO$_4$. 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 λ-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 α , the polarization will be $P = N\alpha F,$'
where F is the internal field. If the externally applied
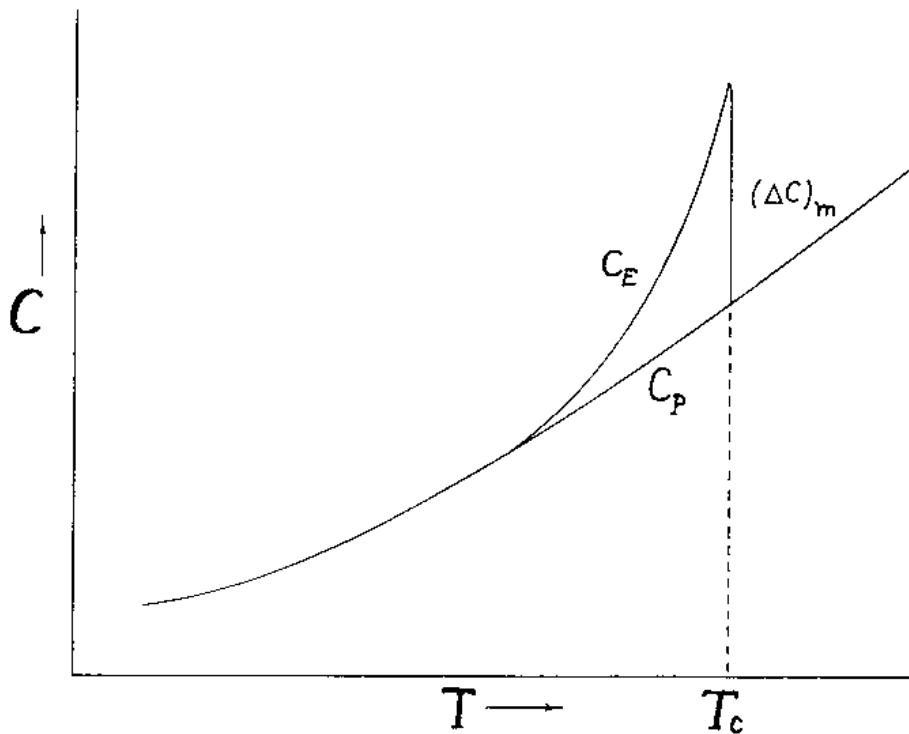
FIG. 1.5

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 en-
ergy 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 β 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 rapid-
ly. 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 ΔS associated with the vanishing of polariza-
tion, 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 ΔC 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}	ΔS 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 dis-
continuity in specific heat, but it is also the most diffi-
cult one from which to estimate ΔS. 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 β in the above oversimplified discussion is found from integrating Eq. (1.41);

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

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 β predicted by the rotating dipole theory, as determined by the susceptibility above the Curie point (Eq. 1.05)

$$(1.43) \qquad \chi = \frac{1}{\beta}\frac{T_c}{T - T_c}$$

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$_2$PO$_4$. Blattner
and Merz (B6) have given the following values of β as
calculated from each formula using experimental values of
ΔC, P$_m$, and χ :

Substance	from Eq. (1.42)	from Eq. (1.43)
Rochelle salt	2.1	2.2
KH$_2$PO$_4$	0.37	0.48
BaTiO$_3$	0.044	0.049

Their values for BaTiO$_3$ were based on their measurement
of ΔC, and are in better agreement that we calculated

above. The ΔC 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 β or their interpretation
in terms of internal field constants, we note that it is
an experimental fact that for the three types of ferro- ,
electrics the following relation is valid:

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

where C is the Curie constant and ΔS 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 publish-
ed 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 co-efficient and the derivative dT/dp of the Curie temperature with respect to pressure through the Ehrenfest relation (E3)

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

in which ρ = 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 -5.74×10^{-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

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

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

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

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$_2$PO$_4$) 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).

30

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 μ 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 γ 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

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

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

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

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

(2.14) $\epsilon = \epsilon_0 + \frac{4\pi}{\beta(1 - \beta\gamma)} \frac{T_c}{T - T_c}$

where

$$\epsilon_0 = 1 + \frac{4\pi\gamma}{1 - \beta\gamma}$$

(In the MM paper, this is given incorrectly as
$\epsilon = \epsilon_0 + [4\pi/\beta] T_c/[T - T_c]$)

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

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

in which the value $\epsilon_0 = 350$ is stated as the dielectric
constant near absolute zero. Measurements by Blunt and
Love (B4) on ceramic specimens down to about $2^{\circ}K$ show a
dielectric constant rising smoothly from 95 at $2^{\circ}K$ to
140 at $30^{\circ}K$. The value $T_c = 393^{\circ}K$ is the observed
transition temperature, which is not necessarily the value
which fits an empirical curve of dielectric constant a-
bove 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 $130^{\circ}C$, which is as high
as that curve goes. However, the experimental curve does
not follow the above empirical equation, and greatly differ-
ent 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 β, γ 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:

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

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

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

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 measure-
ment 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 im-
portant 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

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

Form the dimensionless quantity

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

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

$$P_m = 15.6 \times 10^{-6} \text{ coulomb cm}^{-2} = 4.68 \times 10^4 \text{ esu}$$

$$N = (4 \times 10^{-8})^{-3} = 1.56 \times 10^{22} \text{ cm}^{-3}; \ T_c = 379^\circ K,$$

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 β .

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 ΔS is about $0.02 k$, a discrepancy of a factor of 90. As remarked before, this very low value of ΔS 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 β; $F = 4\pi P_e/3 + \beta P_d$. 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

$$A = \frac{1}{2}w' (P_x^2 + P_y^2 + P_z^2) + \frac{1}{4} \xi_{11}' (P_x^4 + P_y^4 + P_z^4)$$

$$+ \frac{1}{2} \xi_{12}' (P_y^2 P_z^2 + P_z^2 P_x^2 + P_x^2 P_y^2) + \frac{1}{6} \zeta' (P_x^6 + P_y^6 + P_z^6) + \cdots .$$

(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,

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

(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 ξ'_{11}, ξ'_{12}, ζ' 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 ξ'_{12} and ζ' are positive while ξ'_{11} is negative, and the numerical values which he estimates from various experimental data are

$$\xi'_{11} = -4.4 \times 10^{-12} \text{ cm}^3 \text{ erg}^{-1}$$

(2.23)
$$\xi'_{12} = 5.3 \times 10^{-12} \text{ cm}^3 \text{ erg}^{-1}$$

$$\zeta' = 3.7 \times 10^{-21} \text{ cm}^6 \text{ erg}^{-2} .$$

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 ξ'_{11} determines the order of the transition. If we consider only polarization in the z-direction, the free energy function may be abbreviated to

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

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 ξ'_{11} and ζ' 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° 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
ξ'_{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

$$A = \tfrac{1}{2}c_{11}(x_1^2 + x_2^2 + x_3^2) + c_{12}(x_2 x_3 + x_3 x_1 + x_1 x_2)$$

$$+ \tfrac{1}{2}c_{44}(x_4^2 + x_5^2 + x_6^2) + \tfrac{1}{2}w''(P_1^2 + P_2^2 + P_3^2)$$

$$+ \tfrac{1}{4}\,\xi''_{11}(P_1^4 + P_2^4 + P_3^4) + \tfrac{1}{2}\,\xi''_{12}(P_2^2 P_3^2 + P_3^2 P_1^2 + P_1^2 P_2^2)$$

$$+ g_{11}(x_1 P_1^2 + x_2 P_2^2 + x_3 P_3^2) \qquad\qquad (2.27)$$

$$+ g_{12}\,[x_1(P_2^2 + P_3^2) + x_2(P_3^2 + P_1^2) + x_3(P_1^2 + P_2^2)]$$

$$+ g_{44}\,(x_4 P_2 P_3 + x_5 P_3 P_1 + x_6 P_1 P_2) + \ldots$$

in which all terms through the order P^4, that are allow-
ed 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 be-
tween the coefficients of the free energy in Eqs. (2.21)
and (2.27), in which double primes indicate that the co-
efficients are for an unstrained crystal.

$$w' = w''$$

$$\xi'_{11} = \xi''_{11} + 2\,\frac{-g_{11}^2(c_{11} + c_{12}) + 4g_{11}g_{12}c_{12} - 2g_{12}^2 c_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})}$$

$$(2.28)$$

$$\xi'_{12} = \xi''_{12} + 2\,\frac{g_{11}^2 c_{12} - 2g_{11}g_{12}c_{11} + g_{12}^2(-c_{11} + 2c_{12})}{(c_{11} - c_{12})(c_{11} + 2c_{12})}\;.$$

These relations express the effect of electrostrictive ac-
tion 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 ξ constants given by
Devonshire are, in cm^3 erg^{-1}:

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

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

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 electro-
strictive action, and the magnitude of ξ_{11}'' is reduced
by more than a factor of ten, while that of ξ_{12}'' is in-
creased 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 tran-
sition 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 sub-
ject to revision and that with the correct values of the
ξ 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 pro-
ducing 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 ex-
plain 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

$$(2.31) \qquad \frac{4\pi\alpha_{Ti'}}{3v} = 0.062$$

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 small-
er, 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 fre-
quencies 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 effec-
tive 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 neighbor-
ing ions. When the applied electric field tends to dis-
place a positive ion upwards, it will also displace the
adjacent negative ions downwards, and as a result mechani-
cal 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 calcu-
late 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 con-
tain 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 elec-
tronic 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 funda-
mental 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 compli-
cated. 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 in-
ternal 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 respec-
tively. 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 1.2×10^{-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 de-
duce 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 struc-
ture is specified, and this polarizability depends criti-
cally 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 worth-
while 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 pyro-
electric 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 elec-
trical 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 pro-
posed 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 $1,000^{\circ}K$. Thus it appears
to be the oxygen octahedron structure rather than the
presence of any specific positive ion that is the nec-
essary element for producing ferroelectricity, and the
electronic structure of this arrangement becomes an
important question.

There is independent evidence from other prop-
erties 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 surround-
ed 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°
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+} .

We therefore adopt the point of view that
BaTiO$_3$ is not a strongly ionic crystal and that its elec-
tronic 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 in-
ternal 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

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

(margin note, left side:) This is disputed — Jona + Shirane P. 126

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 β 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 β and γ 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

Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
Γ_2	Γ_1	Γ_3	Γ_5	Γ_4
Γ_3	Γ_3	$(\Gamma_1 + \Gamma_2 + \Gamma_3)$	$(\Gamma_4 + \Gamma_5)$	$(\Gamma_4 + \Gamma_5)$
Γ_4	Γ_5	$(\Gamma_4 + \Gamma_5)$	$(\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5)$	$(\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5)$
Γ_5	Γ_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_d	$6S_4$	3_h
Γ_1^+	1	1	1	1	1	1	1	1	1	1
Γ_1^-	1	1	1	1	1	-1	-1	-1	-1	-1
Γ_2^+	1	1	-1	-1	1	1	1	-1	-1	1
Γ_2^-	1	1	-1	-1	1	-1	-1	1	1	-1
Γ_3^+	2	-1	0	0	2	2	-1	0	0	2
Γ_3^-	2	-1	0	0	2	-2	1	0	0	-2
Γ_4^+	3	0	-1	1	-1	3	0	-1	1	-1
Γ_4^-	3	0	-1	1	-1	-3	0	1	-1	1
Γ_5^+	3	0	1	-1	-1	3	0	1	-1	-1
Γ_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 Γ_4^-, and in order that it may have nonvanishing matrix elements between the ground state Γ_1^+ and and excited one, the excited state must belong to a representation Γ for which the product representation

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

contains the identical representation Γ_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

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

where $\phi(\vec{r})$ is symmetric under O_h. We denote the un-
perturbed energy separation between the ground state Ψ_0
and these states by 2ϵ and choose the zero of energy
to be midway between these levels. The unperturbed
Hamiltonian then becomes

$$H_0 = \begin{pmatrix} -\epsilon & & 0 & \\ & \epsilon & & \\ 0 & & \epsilon & \\ & & & \epsilon \end{pmatrix}$$

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

$$H = \begin{pmatrix} -\epsilon & V & 0 & 0 \\ V & \epsilon & & \\ 0 & & \epsilon & \\ 0 & & & \epsilon \end{pmatrix}$$

where $V = -eF \int_v \Psi_0 x \Psi_1 dv = \mu F$, v being the volume
of a unit cell and μ 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 diagonal-
ized by the transformation matrix

$$S = \begin{pmatrix} \cos\theta & -\sin\theta & & 0 \\ \sin\theta & \cos\theta & & \\ & & 1 & \\ 0 & & & 1 \end{pmatrix} \quad \text{with } \tan 2 = \frac{\mu F}{\epsilon} .$$

Then

$$
SHS^{-1} = \begin{pmatrix} \begin{array}{c|c} -b\epsilon & 0 \\ \hline & +b\epsilon \\ 0 & \epsilon \\ & & \epsilon \end{array} \end{pmatrix}
$$

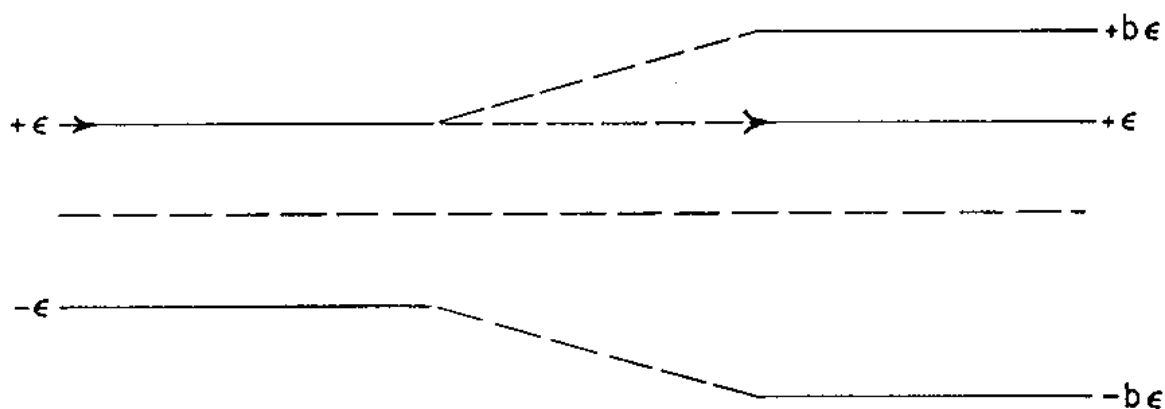where $b = \sec 2\theta = (1 + \mu^2 F^2/\epsilon^2)^{1/2}$. The energy level diagram becomes

FIG. 2.1

and the perturbed unit cell now has a partition function

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

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

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

which gives rise to the polarization term

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

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

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

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

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

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 μ , ϵ , β , and γ . 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

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

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° 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

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

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

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

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[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

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

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

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

$$(2.5.14)$$

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

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

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

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

Here we have used the experimental transition temperature $393^{\circ}K$ 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 β and γ 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 ϵ, although refinements in the model could of course effect ϵ 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 devel-
oped 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 there-
fore 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 affect-
ed by the tetragonal distortion of the crystal, but esti-
mates 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°C =
393°K is the Curie temperature. This value is quite
insensitive to the experimental data on Curie constant
and strength of spontaneous polarization. In the polar-
ized state, the mixing of the ground state ψ_0 and the
excited state ψ_1 is not complete; the ground state
goes over into a linear combination

$$\psi_a = \psi_0 \cos \theta + \psi_1 \sin \theta ,$$

with θ about 20°, whereas complete saturation, approach-
ed in the limit of infinitely strong internal fields,
would correspond to $\theta = 45^O$. From this, one finds that
the mean dipole moment of the unit cell in the spontaneous-
ly 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 im-
pressively large from a macroscopic point of view, this
corresponds to a dipole moment of only about 3×10^{-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 displace-
ments. From an atomic point of view, therefore, the elec-
tronic 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, amount-
ing 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
γ, 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 polariza-
bility matrix α as defined in Section 5 cannot be diagon-
al. as assumed in the calculations there, should be kept
in mind. In fact, the great stability of the TiO$_3$ com-
plex 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$_3$ ferro-
electricity, and the depolarization of crystals by infrared
radiation, all point in this direction. A further quali-
tative 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 pyro-electricity. 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 clear-
ly 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 ex-
periment 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 manipu-
lation 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 dis-
cussion 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

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

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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

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

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

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

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

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

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

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

and $(G' - \frac{1}{2}\gamma F^2)$ is a thermodynamic potential with con-
jugate 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

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

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

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

so that finally

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

and the desired thermodynamic potential is

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

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

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

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

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

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

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

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

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 generali-
zation 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:

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

From the above value of S, we find $c_P = T dS_0/dT$, and
the specific heat anomaly is

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

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 in-
terpreted as a Lorentz factor. As the temperature de-
creases 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 tran-
sition, 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 polari-
zation, 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 pro-
posed 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 polariza-
bility 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 re-
sulting 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 funda-
mental 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 disad-
vantage in certain problems because the determination of
the field at each point in the lattice is a separate cal-
culation. The recent observation of Cohen (C5) that one

can incur considerable error by using the field at the un-
displaced 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 theo-
retical treatments will need values of the field through-
out certain regions of the lattice rather than at isolated
points. In this chapter we develop a method of calcula-
tion 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 β
than would be expected from electrostatic considerations.
However, for each particular type of crystal the exist-
ence 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 func-
tion 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:

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

If each dipole has moment μ, 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-
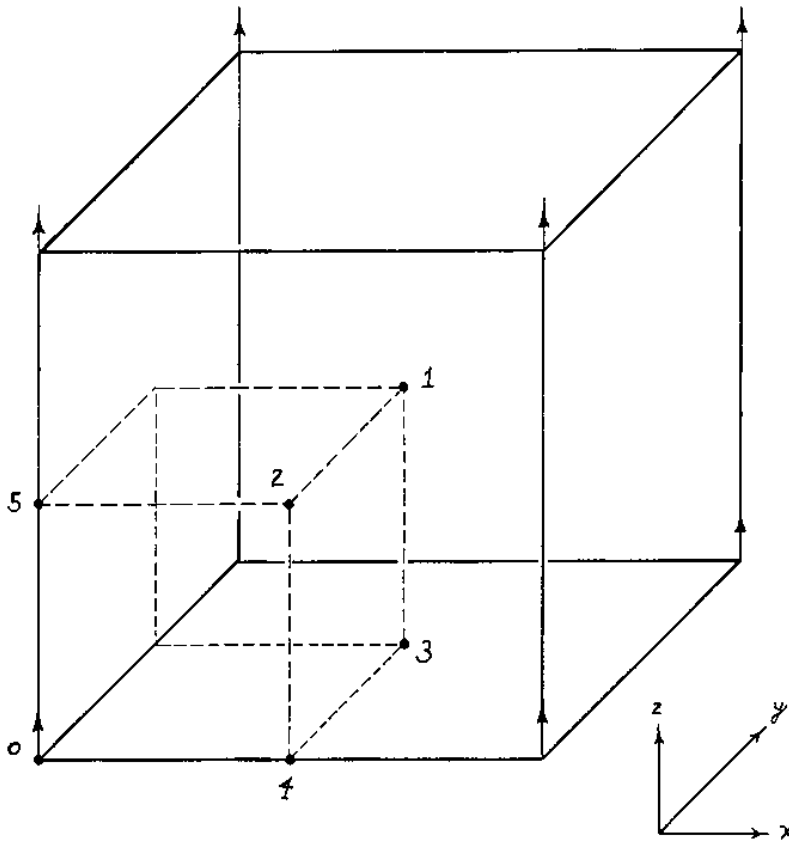
FIG. 4.1

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_0 is the field at (000) minus the field of the dipole
at that position). The dimensionless factors ($\beta_0 \cdots \beta_5$)
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 polariza-
tion 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

$$U = \begin{pmatrix} 1 & 0 & & & & \\ 0 & 1 & & 0 & & \\ & & 0 & 1 & 0 \\ & 0 & 1 & 0 & 0 \\ & & 0 & 0 & 1 \end{pmatrix}$$

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 β_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 μ 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 di-
electric and by solution of a simple boundary-value prob-
lem 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 macro-
scopic 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

$$e_z' = \left\{ \begin{array}{l} \displaystyle\sum_{n=0}^{\infty} A_n \left(\frac{r}{d}\right)^n P_n(\cos\theta), \quad r < d \\[4ex] \displaystyle\sum_{n=2}^{\infty} B_n \left(\frac{d}{r}\right)^{n+1} P_n(\cos\theta); \quad r > d \end{array} \right\}$$

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

$$\int e_z' dv = A_0 \frac{4\pi d^3}{3} .$$

A_0 is just the field at the center of the dipole:
$A_0 = -2q/d^2$, 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

$$V = V_0 - \vec{E} \cdot \vec{r}$$

where V_0 has the lattice periodicity and $\vec{E}$ is the macroscopic field. Then the component of E in the z direction is given by

$$E_z = \frac{1}{a} \int_0^a - \left(\frac{\partial V}{\partial z}\right) dz = \frac{1}{a} \int_0^a e_z dz \quad (4.31)$$

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_0 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,

$$D_z = \frac{1}{a^2} \int_0^a \int_0^a e_z dx dy \ .$$

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 de-
tain 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 βi

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 representa-
tive of the four classes. Now the field seen by ion (a)
due to polarization of the other sodium ions may be ex-
pressed 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] <u>The Electromagnetic Field</u>, 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

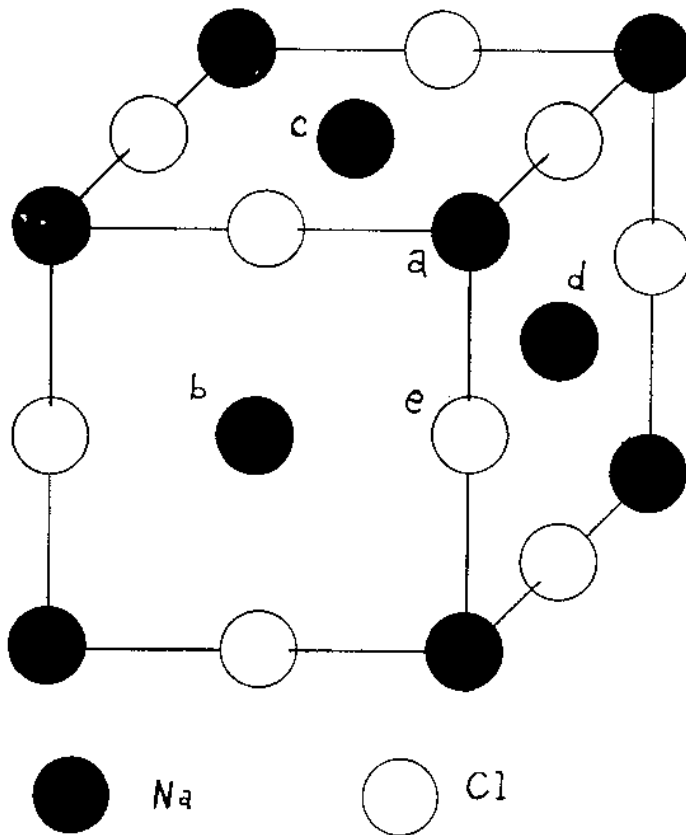$$2\beta_2 + \beta_3 = 3\beta_0 = 4\pi . \qquad (4.41)$$

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

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

Accepting these results, we need calculate only
β_2 and β_4 in order to determine the Lorentz factor
matrix completely. However, we prefer to calculate each
of the β_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 con-
vergent 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 con-
stant except for a δ-function singularity due to the
dipole of moment μ 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 func-
tion of x,y and an odd function of z. Therefore the
appropriate expansion is

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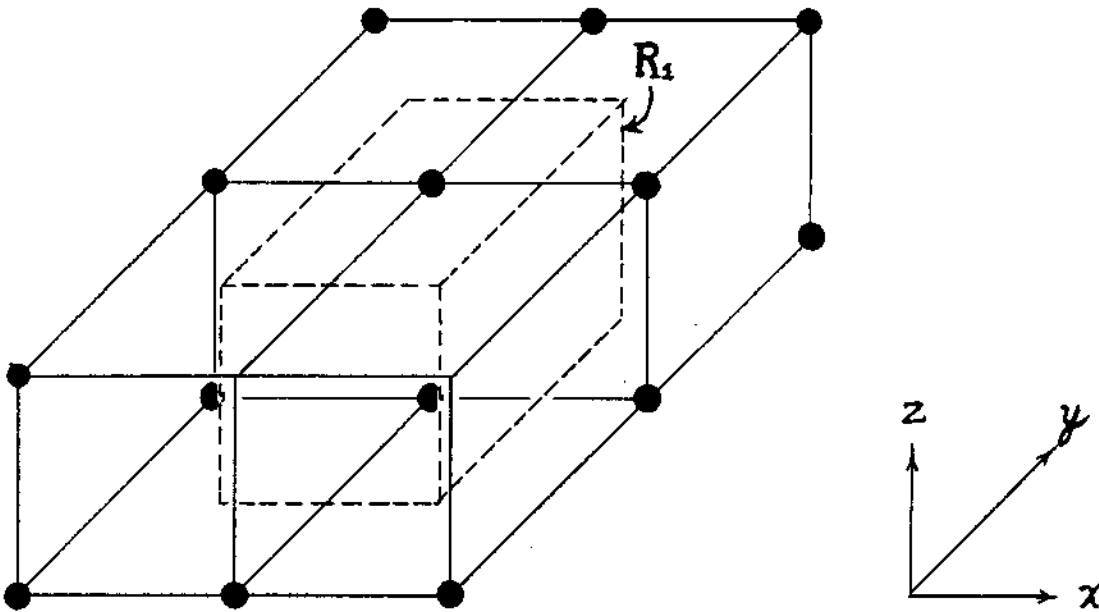

FIG. 4.3

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 con-
dition on the bottom face:

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

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

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

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

$$= -2\pi\mu$$

$$A_{oo} = 0$$

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

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 β_i equal to the coefficients of μ/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 β_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 β_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

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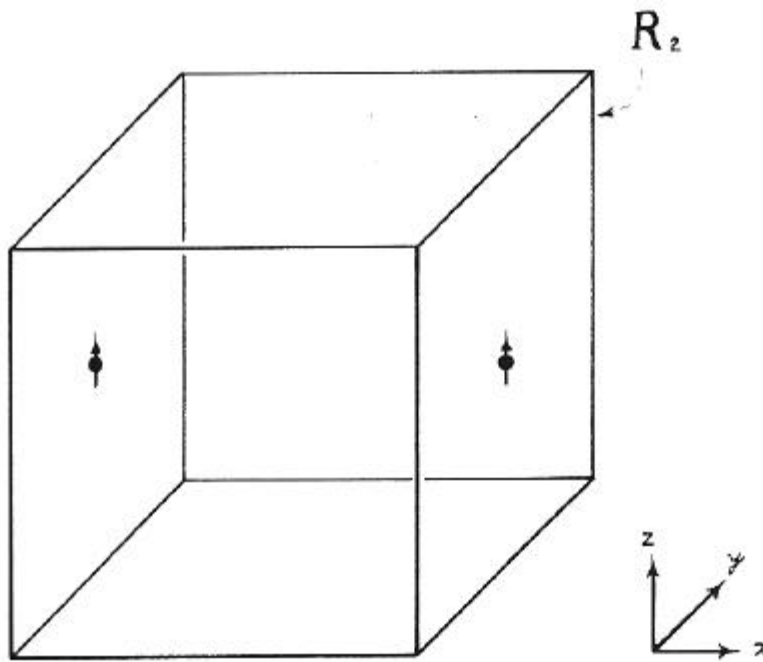

FIG. 4.4

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 $D = 4\pi \mu/a^3$.
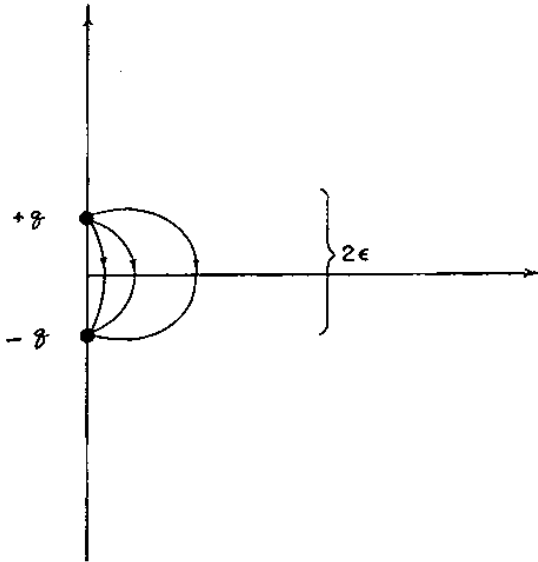

FIG. 4.5

(However, we cannot calculate D directly from this expansion, since the resulting series diverges!) Since $E = 0$, the β_i are given directly by the coefficients of μ/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 β_1, β_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 β_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 β_1 analytically. We first evaluate the sum

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

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 $n \rightarrow \infty$ everywhere except on the real axis. Therefore

$$I = \frac{1}{2\pi i} \int_C \frac{n}{\sinh \pi n} \frac{\pi dn}{\sin \pi n}$$
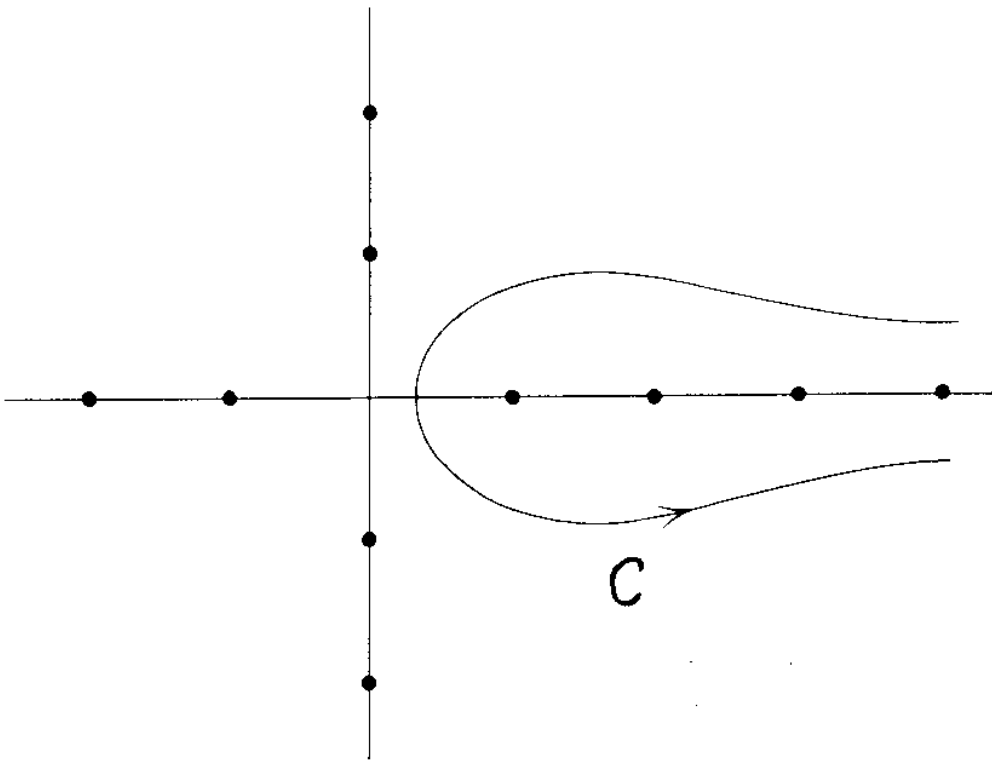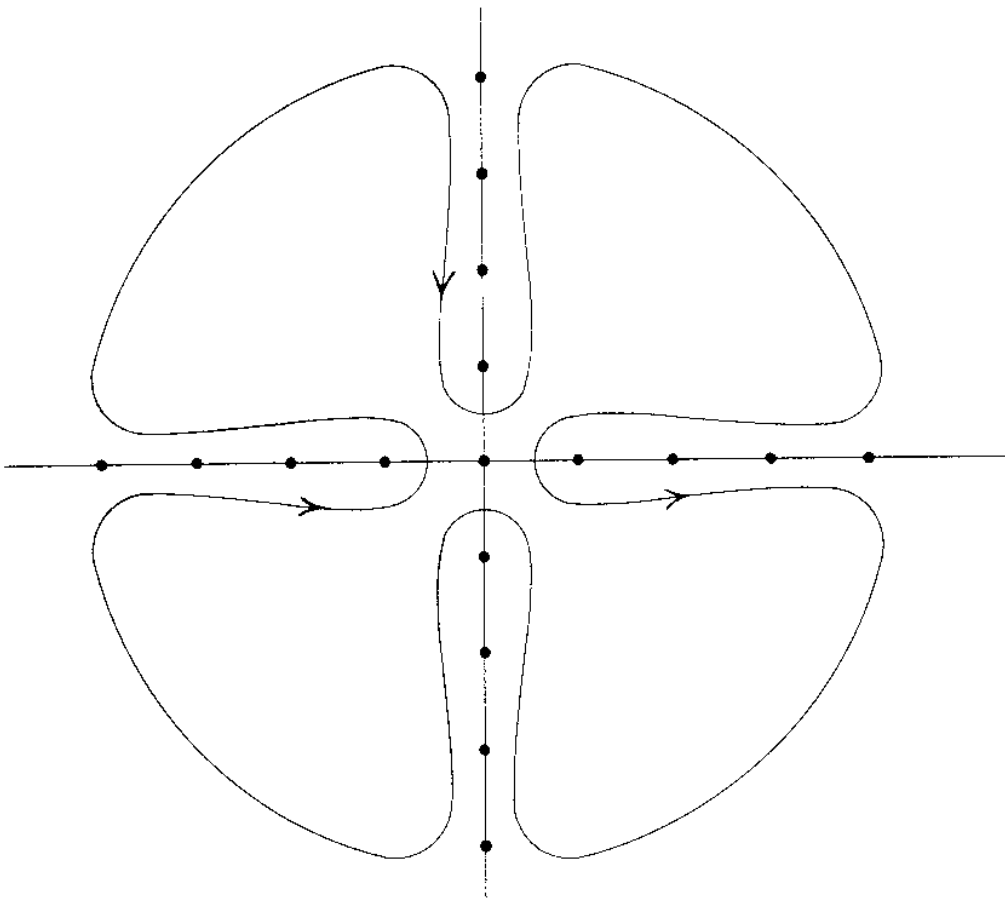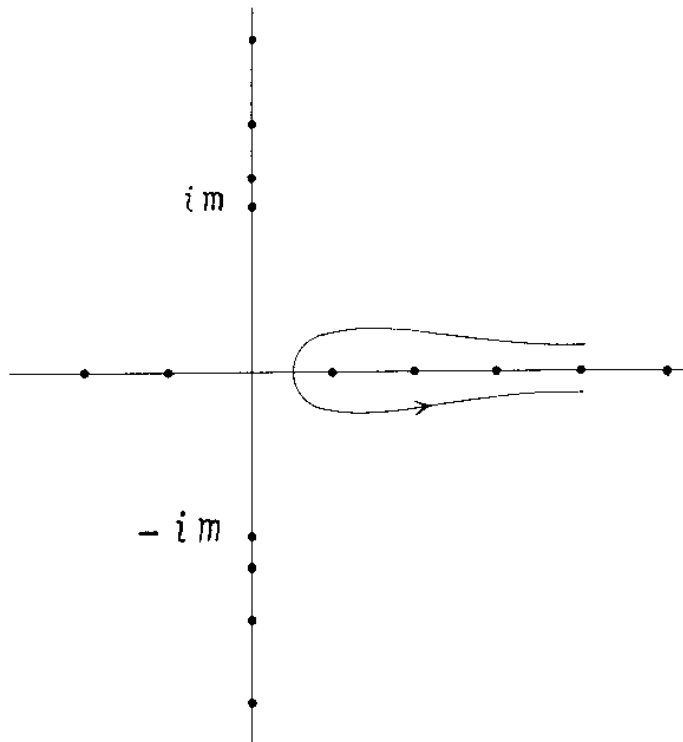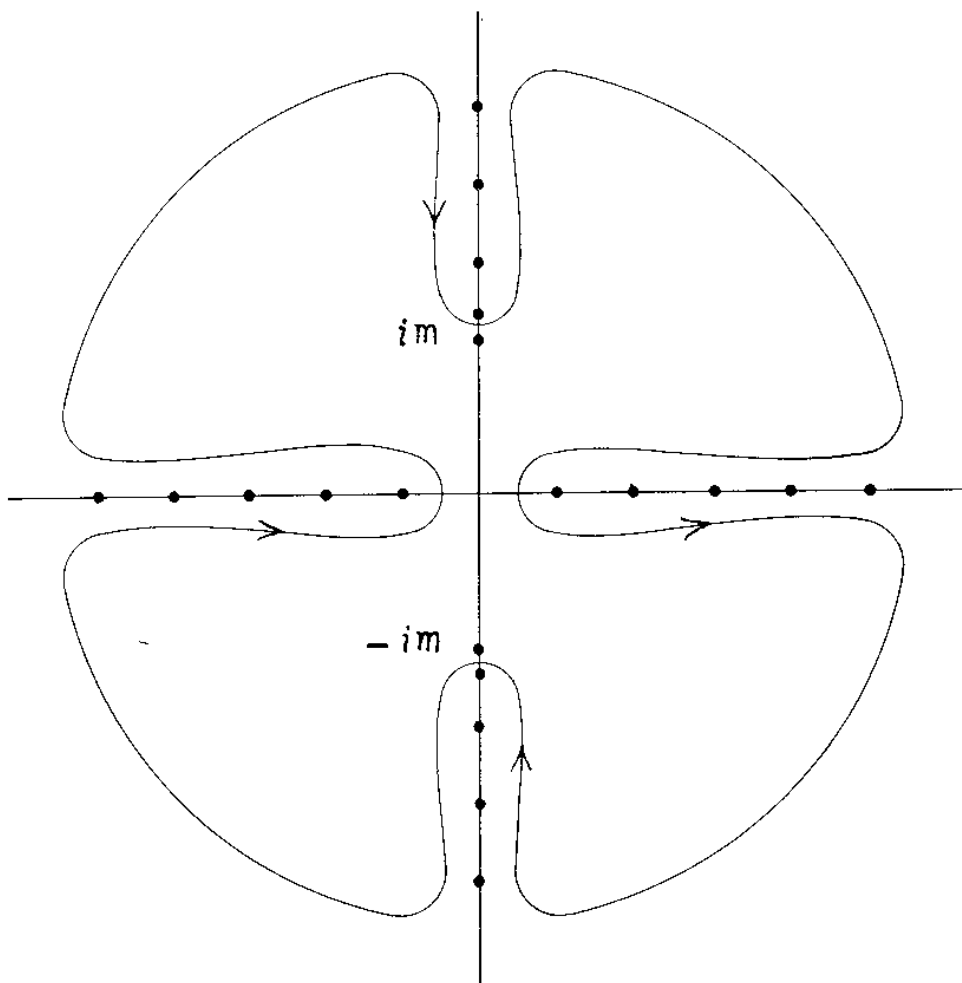
FIG. 4.6

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 $n \rightarrow in$:

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

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:

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

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

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

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

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

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

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

Comparing the definitions of K,J we have

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

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

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

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 β_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 β_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 ex-cellent 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

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

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

(4.71)

$$\beta_3 = \frac{4\pi}{3} \times -1.06927$$

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

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

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 β_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 τ, defined by

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

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 τ 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 τ, the other for large τ. By splitting the region of integration into two parts, $\tau < \tau_o,\; \tau > \tau_o$, and using the appropriate series for each part, one can secure rapid convergence over the entire range of τ, 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 $k \rightarrow 0$, 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 τ_o 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 formu-
lating boundary conditions, the field expansion method is
simple only in crystals with three symmetry planes and is
therefore practical only for crystal structures of orth-
orhombic 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 α_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 α nondiagonal elements.

induced polarization occurs in the pattern corresponding
to the rows of the "susceptibility matrix" χ

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

where

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

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 ex-
perimentally observed susceptibility is

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

which is an expansion in powers of the coupling constants
β_{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)
$$F = \beta P$$
$$P = \alpha F = \alpha\beta P.$$

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 α 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 deter-
mined 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 α_i's, which are
defined as the ratio of polarization to internal fields,
decreases. When the saturation polarization is reached,
α goes down as $1/F$. The course of events accompany-
ing 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
α 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 de-
creases $(\alpha\beta P - P)$, and vice versa. Thus, the spon-
taneous 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

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

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

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

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 λ_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 λ_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 λ_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 consider-
ed 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 orth-
ogonal transformation and all its proper values are real.
Since the two matrices differ only by the trivial similar-
ity 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 immediate-
ly; on evaluating its determinant we find that β , 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 β , As is easily verified,
this pattern is given by

$$(5.31) \qquad P = \begin{pmatrix} a - 3 \\ - a \\ 1 \\ 1 \\ 1 \end{pmatrix} \quad = \quad \begin{pmatrix} -2.11 \\ -0.89 \\ 1. \\ 1. \\ 1. \end{pmatrix}$$

where

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

In this pattern the net externally observable polarization $\sum_i P_i$ 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

$$S = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 \\ 0 & 0 & -\dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

we find that

$$S(\sqrt{\alpha}\ \beta\ \sqrt{\alpha})S^{-1} = \begin{pmatrix} \alpha_1\beta_0 & \sqrt{\alpha_1\alpha_2}\beta_0 & \sqrt{\alpha_1\alpha_3}\beta_2 & 0 & \sqrt{\alpha_1\alpha_4}\beta_3 \\ \sqrt{\alpha_1\alpha_2}\beta_0 & \alpha_2\beta_0 & \sqrt{2\alpha_2\alpha_3}\beta_4 & 0 & \sqrt{\alpha_2\alpha_4}\beta_5 \\ 2\sqrt{\alpha_1\alpha_3}\beta_2 & \sqrt{2\alpha_2\alpha_3}\beta_4 & \alpha_3(\beta_0+\beta_3) & 0 & \sqrt{2\alpha_3\alpha_4}\beta_2 \\ 0 & 0 & 0 & \alpha_3(\beta_0-\beta_3) & 0 \\ \sqrt{\alpha_1\alpha_4}\beta_3 & \sqrt{\alpha_2\alpha_4}\beta_5 & \sqrt{2\alpha_3\alpha_4}\beta_2 & 0 & \alpha_4\beta_0 \end{pmatrix}$$

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

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

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

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

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 α_i equal; $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = \alpha_0$, the other roots may be found numerically, since the β_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

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

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 α_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 α_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

$$\alpha_0 v = 0.026 \times 64 = 1.65 \ \overset{o}{A}^3 \ .$$

When the α_i are different, the proper values
of $\sqrt{\alpha}\,\beta\,\sqrt{\alpha}$ are the solutions of a cubic equation in-
volving the α_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 α_i are present by writing

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

where α' is the part of the matrix α containing the
large elements, α'' contains the small elements, and
ϵ is an expansion parameter that we eventually set equal
to unity. If the polarizability α_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 ex-
pression is valid only if the second term is small com-
pared 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 β , 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 po-
sition, 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 ϵ by

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

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 β in the first section and by "β" 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)
$$"\beta" = \frac{\sum_i \beta_{2i} P_i}{\sum_i P_i}$$

where β_{2i} is the i'th element in the second row of the matrix β :

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

$"\beta"$ is therefore the average value of β_{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 β_{2i} with equal weight is exactly β_0. In general we see that, if

$$P_{O_x} > P_{O_z}, \quad \text{then} \quad "\beta" < \beta_0 = \frac{4\pi}{3}$$

while if

$$P_{O_x} < P_{O_z} \quad \text{then} \quad "\beta" > \beta_0 .$$

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

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

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

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

In the spontaneously polarized state we must always have $"\beta" > 4\pi/3$, but the difference need not be great if α_2 is extremely large compared to α_3 and α_4. We note that α_1 drops out of this expression for $"\beta"$ as it should since the Ba is coupled to the Ti ion by a Lorentz factor β_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 β_0, so that polarization of the Ba ion cannot cause $"\beta"$ to depart from β_0 in first order.

In the spontaneously polarized state, $"\beta"$ is essentially a constant independent of temperature since α_3 and α_4 are not strongly temperature-dependent, and as we have seen the strength of the spontaneous polarization always adjusts itself so that α_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 α_2 is much greater than the other α_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 ϵ. 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 α' is the part of α containing the large elements and α'' is the rest of the matrix. Evidently the matrices α', α'' are singular and $\alpha'\alpha'' = 0$. Expanding in powers of λ, 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 λ, we have

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

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

$$\left.\begin{array}{l} F^{(n)} = \beta P^{(n)} \\[2mm] P^{(n)} = \alpha' F^{(n)} + \alpha'' F^{(n-1)} \end{array}\right\} \quad n \geq 1$$

The last equations may be rearranged to

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

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

In the case that only one of the polarizabilities α_2 is large, these expressions may be evaluated without further approximation. We have

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

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

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

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

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

$$\qquad (5.53)$$

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

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 λ, 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

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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

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

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

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

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

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

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

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

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

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

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

Combining these, we have for the Lorentz factors:

$$\beta_1 = \frac{4\pi}{3} \times 1.00005$$

$$\beta_2 = \frac{4\pi}{3} \times 2.03466$$

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

From first field expansion

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

$$\beta_2 = \frac{4\pi}{3} \times 2.03461$$

$$\beta_3 = \frac{4\pi}{3} \times -1.06927$$

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

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 $(n - 1)$:

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

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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 $k + S = \mathcal{T}$

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

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

Therefore we have

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

$$= (1-C_0) + (1-C_0-C_1)M + (1-C_0-C_1-C_2)M^2$$

$$+ \dots + (1-C_0-C_1 - \dots -C_{n-1})M^{n-1}$$

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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