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The Lorentz Correction in Barium Titanate

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It is assumed, following Devonshire, that the ferroelectric behavior of $BaTiO_3$ arises because of the Lorentz correction, leading to a vanishing term in the denominator of the expression for dielectric constant. If the polarizability varies slowly with temperature, the temperature variation of dielectric constant follows. This temperature variation is assumed to come from that part of the polarization resulting from the displacement of the Ti ion, in a field whose potential energy has fourth-power as well as second-power terms in the displacement. The main object of this paper is to compute the Lorentz correction exactly, not assuming spherical symmetry, but taking account of the precise crystal structure. When this is done, it is found that the Ti ions, and those oxygen ions which are in the same line with them, the line being parallel to the electric field, exert very strong fields on each other, the resulting local field at the Ti ion being much greater than if computed on the assumption of spherical symmetry. This enhanced field makes it clear that even a relatively small ionic polarizability for the Ti ions will be enough to lead to ferroelectricity. The polarization of the Ti ions is however an essential feature of the theory; if they are not polarized, the Lorentz correction is profoundly modified, leading almost exactly to the value given by the approximate theory assuming spherical symmetry, and not resulting in ferroelectricity. Detailed formulas are given for comparison of the present theory with Devonshire's results, so that the present methods can be incorporated in his treatment of the effect of elastic strain energy on the stability of the various phases below the Curie point.

I. INTRODUCTION

THE ferroelectric properties of barium titanate have aroused much interest in recent years, particularly because its structure is so simple that there is good hope of understanding it fairly completely Enough progress has been made very recently so that we begin to have a satisfactorily consistent theory of its behavior, but this theory has hardly advanced far enough so that direct numerical comparisons with experiment can be made with complete success. The present paper fills in one missing gap in this theoretical treatment. To explain what this gap is, we give in the present introductory section a discussion of some aspects of the present state of understanding of the problem.

Barium titanate has a ferroelectric Curie point at about 118°C. Above that point, the dielectric constant is of the form $[\text{constant}/(T-T_c)]$, where the constant is very large, of the order of 150,000°K, and where T is the temperature, T_c the Curie temperature.[1] The dielectric constant even of a single crystal does not literally become infinite at the Curie point; the curve is rounded off somewhat, but the Curie law holds to within a very few degrees of the Curie point, so that there are very large dielectric constants. Below the Curie point,[2] there is a permanent polarization and the dielectric constant decreases from the very high values close to the Curie point, but remains high, of the order of several thousand, around room temperature. At about 5°C there is a phase change, and at about −70°C another phase change, the dielectric constant becoming very large near each phase change, and permanent polarization persisting in each phase. The nature of the phase changes is well understood. Above the Curie point at 118°C the crystal is cubic. A unit cell holds a Ba ion at each corner of the cube, an O ion at the center of each face, and a Ti ion at the center of the cube. The permanent polarization in the range between 118° and 5°C is along a 100 direction in the crystal. There is a slight mechanical deformation associated with this polarization: the crystal axis in the direction of the polarization slightly expands, whereas the two axes at right angles to it contract, the amount of mechanical deformation being proportional to the square of the polarization, so that the crystal becomes tetragonal in this range. In the range between 5° and −70°C the polarization is along a 110 direction; here again the crystal stretches along the axis of polarization and shrinks at right angles, producing an orthorhombic symmetry. Below −70°C the polarization is along a 111 direction, again with crystal deformation, resulting now in rhombohedral symmetry. The phase changes from tetragonal to orthorhombic, and from orthorhombic to rhombohedral, are changes of the first order, with latent heats. It is not quite certain experimentally whether the change from cubic to tetragonal is of the first order or is a second-order transition of the lambda-point variety; if it is the latter, however, the increase of polarization just below the transition point occurs much more rapidly than would be expected from elementary theories of lambda-point transitions.

At the various transitions, the free energies of the two phases in equilibrium with each other must be equal. Since these phases correspond to different polarizations, it is clear that it requires a negligible external effect (that is, a negligible electric field) to shift from one phase to the other, or to modify the magnitude or direction of the polarization. This is the qualitative explanation of the very large dielectric constant near the transition temperatures, and it explains as well the directional dependence of dielectric effect. Thus near

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[1] S. Roberts, Phys. Rev. **75**, 989 (1949); **76**, 1215 (1949).

[2] P. W. Forsbergh, Jr., Phys. Rev. **76**, 1187 (1949) gives an extensive set of references relating to the phase transition.

the transition between tetragonal and orthorhombic form, where the spontaneous polarization is shifting from the 100 to the 110 direction, it is particularly easy to rotate the polarization from the one direction to the other, so that the dielectric constant related to polarizing the crystal at right angles to the existing spontaneous polarization becomes very large, though that associated with changing the magnitude of the polarization, without change of direction, is not unusually large.

With this sketch of some of the observed facts in mind, we naturally ask what is responsible for the abnormally large polarization of the crystal. There are in general two types of possible polarization: electronic polarization, or distortion of the electronic structure of one of the ions, and ionic polarization, arising from the displacement of the ions as a whole. They can be distinguished on the basis of the frequency dependence: in the optical part of the spectrum, where the frequency is too high for whole ions to follow the oscillations, only the electronic polarization remains. The dielectric constant of $BaTiO_3$ as found from the index of refraction in the visible spectrum is no larger than one would expect from the electronic polarizabilities of its constituents, and is[3] in fact about $(2.40)^2=5.76$. Thus it is clear that the abnormality in the low frequency dielectric constant arises from ionic displacement. It is generally considered that it is the Ti ion which is responsible for the effect. The reason is that the Ti ion is surrounded octahedrally by six oxygens; the Ba ions, being rather large, stretch the structure enough so that the hole in the middle of the octahedron occupied by the Ti is slightly too large for that ion, if we compute using conventional ionic radii; and as a result the Ti ion is rather loosely held, with a small restoring force, or large ionic polarizability.[4] This seems to be the qualitative reason for the effect, but it is clear that the ionic polarizability arising in this way is not larger in order of magnitude than that usually found. To explain the enormous effect which this has on the dielectric constant, it is usually to invoke the Lorentz correction in the theory of the Clausius-Mossotti formula. According to the Lorentz correction, we assume that the field acting on a dipole to polarize it is not really $\mathbf{E}$, but is $\mathbf{E}+\mathbf{P}/3\epsilon_0$ (in rationalized m.k.s. units) or $\mathbf{E}+4\pi\mathbf{P}/3$ (in non-rationalized Gaussian units). Let us assume that the dipole moment induced in a volume v is α times the field, where α is the polarizability. We then have $\mathbf{P}=(\alpha/v)(\mathbf{E}+\mathbf{P}/3\epsilon_0)$, so that the dielectric constant is

$$\kappa=1+\frac{P}{\epsilon_0 E}=1+\frac{\alpha/\epsilon_0 v}{1-\alpha/3\epsilon_0 v} \tag{1}$$

in rationalized m.k.s. units; here, as elsewhere throughout the paper, we obtain the corresponding formula in non-rationalized Gaussian units by replacing ϵ_0 wherever it appears by $1/(4\pi)$. From (1) we see that the dielectric constant becomes infinite when $\alpha/3\epsilon_0 v$ (in m.k.s. units) or $4\pi\alpha/3v$ (in Gaussian units) becomes unity. This is the so-called "$4\pi/3$ catastrophe." The ferroelectricity of barium titanate, then, can arise from a quite finite value of the ionic polarizability, and does not demand infinite polarizabilities.

We next ask why the dielectric constant shows the temperature dependence which it does, and why it has a Curie point. We can explain this if we assume that the quantity $\alpha/3\epsilon_0 v$ shows a slow decrease with temperature, being slightly greater than unity at absolute zero, and going through the value unity at a certain temperature T_c, which then must be the Curie temperature. Thus if we have

$$\alpha/3\epsilon_0 v=1-C(T-T_c), \tag{2}$$

where C is a constant, we find at once that

$$\kappa=-2+[3/C(T-T_c)]. \tag{3}$$

This simple hypothesis, then, is enough to result in a Curie law for the dielectric constant; in the region we are interested in, the second term is very large compared to the additive constant, -2, which can be neglected. If, then, the constant in Curie's law is known to be of the order of 150,000°, C is of the order of 2×10^{-5}, indicating a very slow change of the quantity (2) with temperature. What physical mechanism, we may ask, is responsible for this slow decrease of α/v with temperature?

The first suggestion, which has been made by certain writers,[5] is that the change arises from the obvious increase of volume with temperature, coming from the thermal expansion. The volume coefficient of expansion of $BaTiO_3$ is about 3×10^{-5}, so that this alone is more than capable of explaining the whole effect. But this neglects an important fact: as the volume increases, the atoms get farther apart, the repulsive forces between them get smaller, the elastic restoring forces consequently decrease, and the ionic polarizability increases. In fact, there is evidence that α increases faster than v, under these conditions. Thus it is found that either application of pressure,[6] or substitution[4] of smaller ions for Ba, resulting in a decrease of volume at constant temperature, results in a decrease of the Curie temperature. That is, α/v is smaller at a given temperature, for a smaller v, so that we have to go to a lower temperature for the quantity $\alpha/3\epsilon_0 v$ to become equal to unity.

This argument shows that an increase of volume at constant temperature will make α/v increase, rather than decrease. Since we have seen that α/v nevertheless decreases with increasing temperature, there must be an additional influence making α decrease with increasing temperature, at constant volume. Such a possible effect is of course known. The familiar Langevin theory

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[3] W. J. Merz, Phys. Rev. **76**, 1221 (1949).

[4] See, for instance, G. H. Jonker and J. H. van Santen, Science **109**, 632 (1949).

[5] For instance, Jonker and van Santen, reference 4.

[6] W. J. Merz, Phys. Rev. **78**, 52 (1950).

of rotating permanent dipoles leads to an average polarization inversely proportional to the absolute temperature. Such a temperature dependence leads to a temperature coefficient C equal to $1/T_c$, very much larger than we are looking for. The rotating dipole is not the only model leading to this temperature dependence. We get it whenever we have an ion which can move in a region of arbitrary shape and size in which the potential energy is constant, surrounded by infinitely high walls; that is, when we have an ion in a potential well. The rotating dipole is the case in which the available region for motion is a thin spherical shell. Other shapes of potential wells which have been discussed are those in which the ion has several alternative locations allowed to it, all with identical energy.[7] Any such model, then, will lead to the same temperature coefficient C, of the order of 100 times as great as the value we are looking for, provided we assume the ordinary Lorentz correction. Such a model is probably approximately correct for rochelle salt,[8] in which C is in fact not far from $1/T_c$; but not for $BaTiO_3$. At the other extreme is an ion held by a linear restoring force; in this case the polarizability α is independent of temperature, so long as the volume, and hence the force constant, remains constant.

Between these two extremes, we should be able to find a model capable of explaining the facts, and in fact we can. If we start with a linear restoring force, but modify the potential by adding a term in the potential energy in the fourth power of the displacement, as well as in the square, we introduce, as Devonshire[9] has shown, a linear decrease of polarizability with temperature whose coefficient C is proportional to the coefficient of the fourth-power term in the potential energy. A reasonable value of this fourth-power term leads to a value of C of the order of magnitude of that observed. It seems highly probable that this is the explanation of the observed temperature variation, and hence of the occurrence of Curie's law. A difficulty arises when we use this model, however. The same fourth-power term in the potential energy of the ion leads not only to a temperature dependence of the polarizability (that is, to a temperature dependence of the coefficient of the term proportional to P^2, where P is the polarization, in the free energy), but leads also to a fourth-power term in the free energy, a term proportional to P^4. Such a term is essential in calculating the spontaneous polarization below the Curie point. If we calculate the spontaneous polarization from this term, however, choosing the coefficient to describe the temperature dependence of polarizability correctly, we find that the polarization increases much more slowly below the Curie point than is observed. This discrepancy between observation and theory is removed, as Devonshire has shown, by including the electromechanical terms in the free energy, the ones which lead to the piezoelectric effect and electrostriction. When the crystal is allowed to distort itself, in the tetragonal phase below the Curie point, the free energy is decreased by a term proportional to the square of the elastic strain. We have already seen that this strain is proportional to the square of the polarization; thus the effect of the electromechanical coupling is to introduce into the free energy a term, with negative coefficient, proportional to P^4. The effect of this term is to make the crystal polarize much more rapidly below the Curie point; in fact, as Devonshire has shown, it is easy for the term to be great enough to lead to a first-order phase change at the Curie point. This mechanical effect does not alter the temperature dependence of the polarizability, however, and hence leaves Curie's law unaffected. Devonshire has shown that, by a complete expansion of the free energy in powers of the polarization and strain, one can arrive at constants for the various coefficients which lead to a rather complete understanding of the successive changes from one type of polarization to another, as the temperature goes down.

This argument seems convincing, and in its broad outlines it is. However, there is a feature missing in it, which we shall supply in the present paper. We have not taken account of the contribution to the polarizability made by the electronic polarization of the various ions of the crystal. The optical value of the dielectric constant shows that the value of $\alpha/3\epsilon_0 v$ arising from the electronic polarization is about 0.61. Thus a further contribution of only about 0.39 must be made to this quantity by the ionic polarizability of the Ti ion, in order to produce ferroelectricity. This fact was entirely neglected in the treatment of Devonshire mentioned above, the most elaborate treatment of the problem to date. Not only this, but our formula (1), on which our discussion has been based, is correct only if the Lorentz correction in its simple form is valid. But it has been pointed out by several writers[4,10] that there are large deviations from the Lorentz formula in the $BaTiO_3$ crystal. If the polarization is along a 100 direction, a third of the oxygens will fall into linear arrays, in the same lines in which the Ti ions are located; these we shall call oxygens of type *a*. The other two-thirds, which we shall call type *b*, do not fall in line with the Ti ions. We now find that in the presence of the Ti ions, the type *a* oxygens are much more strongly polarized than the type *b* ions. Furthermore, these type *a* oxygens are very close to the Ti ions, and are oriented in such a way as to be able to polarize the Ti ions with maximum effect. The result is that the Ti ions are really in a field

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[7] W. P. Mason and B. T. Matthias, Phys. Rev. **74**, 1622 (1948). These writers explain the temperature variation by use of an artificially low value for the Lorentz correction which, in the light of the present paper, seems to have no physical justification.

[8] W. P. Mason, Phys. Rev. **72**, 854 (1947).

[9] A. F. Devonshire, Phil. Mag. (Series 7) **40**, 1040 (1949). Such calculations regarding the effect of a fourth-power term in the energy were made independently by P. W. Anderson, Phys. Rev. **78**, 341 (1950), and by the present writer, before the work of Devonshire came to their attention.

[10] H. F. Kay and P. Vousden, Phil. Mag. (Series 7) **40**, 1019 (1949).

much greater than the Lorentz value $E+P/3\epsilon_0$. The field is, so to speak, enhanced at the location of the Ti ion by a considerable factor. Thus, in order to result in ferroelectricity, we do not need nearly as great an ionic polarizability on the part of the Ti as we should otherwise suppose. In fact, we shall find that the quantity $\alpha/3\epsilon_0 v$ arising from the ionic polarizability of the Ti need be only 0.06 in order to produce ferroelectricity, rather than the value 0.39 mentioned above. The perovskite structure met in the ferroelectric form of $BaTiO_3$ is thus particularly favorable for the production of ferroelectricity. It has already been pointed out[11] that the other polymorphic forms of $BaTiO_3$, which do not have these rows of alternating Ti and O ions, do not have this favorable predisposition toward ferroelectricity, and in fact they show quite ordinary dielectric behavior.

The main point of the present paper, then, is to work out the Lorentz correction in detail, and to show how it is to be incorporated into calculations of the dielectric constant and the free energy of the type made by Devonshire. As a preliminary to this, we take up in the next section the calculation of the free energy of the crystal, as arising from the displacement of the Ti ion in the field of its neighbors, including a fourth-power term, following to a considerable extent the calculations of Devonshire. We adopt a rather different statistical method, however, which seems more straightforward than his. Then we pass on to the treatment of the Lorentz correction, taking account of the actual crystal structure of $BaTiO_3$.

II. THE FREE ENERGY OF Ti IONS IN A NON-LINEAR FIELD

In our first discussion we shall treat the Ti ions as being independent of each other; later we shall consider their interactions. Let the potential energy of an ion at position (x, y, z) (measured from the position of equilibrium of the ion) in the absence of an external field be $\phi(x, y, z)$. When it is displaced to position x, y, z, let the resulting dipole moment have components (qx, qy, qz), q being the effective charge on the ion. We shall assume ϕ to have cubic symmetry, on account of the symmetry of the field surrounding the Ti ions. In this respect we introduce greater specialization than does Devonshire, who assumes a general potential energy. That assumption is necessary if, for instance, we are interested in the displacement of an oxygen ion, since these are not in positions of cubic symmetry in the lattice, but it is not necessary for the Ti ions, which we assume make the principal contribution to the ionic polarization. Now let there be a local electric field E, of components (E_x, E_y, E_z), acting on the ion. (We postpone until later the question as to how this depends on the external applied field.) Then the additional potential energy of the ions in this local field is $-q(E_x x+E_y y+E_z z)=-q\mathbf{E}\cdot\mathbf{r}$, where $\mathbf{r}$ is the radius vector.

We shall now proceed to treat this system by statistical mechanics. We shall operate entirely with classical statistical mechanics; this should be suitable at the temperatures concerned in the $BaTiO_3$ problem, though our results would need correction at fairly low temperatures. Then the first step in handling the problem statistically is to compute the partition function, Z. If we were dealing with a single polarizable ion, this would be $(2\pi mkT/h^2)^{\frac{3}{2}}w$, where m is the mass of the ion, and

$$w=\int \exp(-\phi+q\mathbf{E}\cdot\mathbf{r})/kTdv. \tag{4}$$

If our system contains N identical ions, the whole partition function is the value above, raised to the Nth power, divided by $N\,!$; or, using the Stirling formula for the factorial, we have

$$Z=[(e/Nh^3)(2\pi mkT)^{\frac{3}{2}}]^N w^N.$$

The free energy A_E is then given by the equation $A_E=-kT\ln Z$. That is,

$$A_E=-NkT\ln[(e/Nh^3)(2\pi mkT)^{\frac{3}{2}}]-NkT\ln w.$$

This free energy is expressed as a function of T and E; it is for this reason that we have denoted it by the subscript E. The entropy is given by $-(\partial A_E/\partial T)_E$, and hence is

$$S=Nk\ln[(e/Nh^3)(2\pi mkT)^{\frac{3}{2}}]+(3/2)Nk+Nk\ln w \\ +NkT(\partial \ln w/\partial T)_E.$$

By differentiation of (4), the last term may be rewritten

$$NkT(\partial \ln w/\partial T)_E=N\langle\phi-q\mathbf{E}\cdot\mathbf{r}\rangle/T,$$

where $\langle\phi-q\mathbf{E}\cdot\mathbf{r}\rangle$ signifies the average value of this quantity over the distribution given by the Boltzmann factor $\exp[(-\phi+q\mathbf{E}\cdot\mathbf{r})/kT]$. The total dipole moment of the distribution is given by $-(\partial A_E/\partial E_x)_T$, etc., so that its x-component is

$$(\text{Moment})_x=NkT(\partial \ln w/\partial E_x)_T=Nq\bar{x}, \tag{5}$$

where again the last form comes by differentiating (4). The internal energy U is given by $U=A_E+TS$; thus it is

$$U=(3/2)NkT+N\langle\phi-q\mathbf{E}\cdot\mathbf{r}\rangle,$$

the sum of the kinetic energy as given by equipartition, and the mean potential energy of the ions as displaced by the field $\mathbf{E}$. In all these formulas if we are dealing with unit volume of the material, so that N becomes the number of ions per unit volume, our expressions give the values of free energy, entropy, moment, and so on, per unit volume. Thus in particular the moment per unit volume, given by (5), is the polarization vector $\mathbf{P}$. If the volume per ion, or the volume of unit cell, is v, as in the preceding section, we then have the number of atoms per unit volume, or N, equal to $1/v$, so that we can express the quantities properly by replacing N by $1/v$.

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[11] R. D. Burbank and H. T. Evans, Jr., Acta Crys. **1**, 330 (1948); H. T. Evans, Jr., and R. D. Burbank, J. Chem. Phys. **16**, 634 (1948).

If we are dealing with unit volume, we then have $S=-(\partial A_E/\partial T)_E$, $P_x=-(\partial A_E/\partial E_x)_T$. Then we have at once

$$(\partial S/\partial E_x)_T=(\partial P_x/\partial T)_E, \tag{6}$$

analogous to the Maxwell relations of thermodynamics. This shows us that if the polarization depends on temperature, the entropy must depend on the field, or polarization. If, for instance, we assume that the polarizability depends on temperature as in Eq. (2), we then find from (6) that at the Curie point

$$S=S_0-\tfrac{1}{2}\,3\epsilon_0CE^2=S_0-CP^2/6\epsilon_0,$$

where S_0 is the value of entropy when E or P is zero. We therefore see that if C is small, the change of entropy with polarization is also small, so that there is only a small increase of entropy in going from the ferroelectric state at low temperature to the unpolarized state at high temperature.

The free energy A_E which we have computed, like the Helmholtz free energy in ordinary problems of statistical mechanics, is the one which is simplest to find, from the partition function. More convenient for most purposes, however, is a free energy A_P, analogous to the Gibbs free energy, expressed in terms of the polarization and temperature, rather than in terms of the field and temperature. This is defined by the relation

$$A_P=A_E-E_x\left(\frac{\partial A_E}{\partial E_x}\right)_T-E_y\left(\frac{\partial A_E}{\partial E_y}\right)_T-E_z\left(\frac{\partial A_E}{\partial E_z}\right)_T$$

and is to be expressed as a function of P and T. That is, it is $A_P=A_E+\mathbf{E}\cdot\mathbf{P}$, if we are dealing with unit volume of material. When expressed in terms of the proper variables, it has the properties that

$$S=-(\partial A_P/\partial T)_P,\quad E_x=(\partial A_P/\partial P_x)_T. \tag{7}$$

In many ways the most convenient way to approach the problem is to find A_P as a function of P and T; we shall discuss the results later. We note that in the absence of an electric field E, the free energy A_P will have a minimum value as far as changes of polarization are concerned, at constant temperature. Corresponding to this, A_P will be unchanged when there is a change of phase, involving change of polarization, at constant temperature, so that the equality of the values of A_P for the two phases is the condition for equilibrium. It is this free energy A_P which Devonshire considers in his paper, but his method of finding it is less straightforward.

We now have the necessary statistical and thermodynamic background for our calculations of free energy. Following Devonshire, but modifying his results for the special case of cubic symmetry, we shall assume that the potential energy of a displaced ion is

$$\phi(x,y,z)=a(x^2+y^2+z^2)+b_1(x^4+y^4+z^4)+2b_2(y^2z^2+z^2x^2+x^2y^2).$$

For the case of spherical symmetry, b_1 will equal b_2, and ϕ will reduce to ar^2+br^4. We must now insert this expression into (4), and compute the partition function. This cannot be carried out exactly, and we therefore use series expansion methods, treating b_1 and b_2 as small quantities, and disregarding all terms of higher powers than the first in these quantities. We expand the quantity $-\phi+q\mathbf{E}\cdot\mathbf{r}$ appearing in the exponent of (4) in power series in the coordinates about the point where it is a minimum, and it then becomes the sum of a term independent of the b's, and a term linear in the b's. We expand the exponential function of this linear term in power series, retaining only the term in the series linear in the b's. The integration then becomes straightforward, and we find

$$w=(\pi kT/a)^{\frac{3}{2}}\exp(q^2E^2/4akT)\left\{1-\tfrac{3}{4}(3b_1+2b_2)(kT/a^2)-\frac{q^2(3b_1+2b_2)}{4a^3}(E_x^2+E_y^2+E_z^2)-\frac{q^4}{16a^4kT}[b_1(E_x^4+E_y^4+E_z^4)+2b_2(E_y^2E_z^2+E_z^2E_x^2+E_x^2E_y^2)]\right\}.$$

This agrees with the result of Devonshire [reference 9, Eq. (10.11)], provided we consider the differences in notation. The free energy A_E is then

$$A_E=-NkT\ln[(e/Nh^3)(\pi kT)^3(2m/a)^{\frac{3}{2}}]-Nq^2E^2/4a+\frac{3N(kT)^2}{4a^2}(3b_1+2b_2)+NkT(3b_1+2b_2)q^2E^2/4a^3+\frac{Nq^4}{16a^4}[b_1(E_x^4+E_y^4+E_z^4)+2b_2(E_y^2E_z^2+E_z^2E_x^2+E_x^2E_y^2)].$$

From this free energy, we can use our general equations to calculate various other quantities. Thus we find

$$S=Nk\ln[(e/Nh^3)(\pi kT)^3(2m/a)^{\frac{3}{2}}]+3Nk-\frac{3}{2}\frac{Nk^2T}{a^2}(3b_1+2b_2)-Nk(3b_1+2b_2)q^2E^2/4a^3, \tag{8}$$

$$P_x=\frac{Nq^2E_x}{2a}\left[1-\frac{kT(3b_1+2b_2)}{a^2}\right]-\frac{Nq^4}{4a^4}E_x[b_1E_x^2+b_2(E_y^2+E_z^2)], \tag{9}$$

$$U=3NkT-Nq^2E^2/4a+\frac{Nq^4}{16a^4}[b_1(E_x^4+E_y^4+E_z^4)+2b_2(E_y^2E_z^2+E_z^2E_x^2+E_x^2E_y^2)],$$

$$A_P = -NkT\ln[(e/Nh^3)(\pi kT)^3(2m/a)^{\frac{3}{2}}] + \frac{3N(kT)^2}{4a^2}(3b_1+2b_2) + \frac{aP^2}{Nq^2}\left[1+\frac{kT}{a^2}(3b_1+2b_2)\right] + \frac{1}{N^3q^4}[b_1(P_x{}^4+P_y{}^4+P_z{}^4) + 2b_2(P_y{}^2P_z{}^2+P_z{}^2P_x{}^2+P_x{}^2P_y{}^2)]. \quad (10)$$

At this point our treatment has differed significantly from that of Devonshire (who introduces the Lorentz correction before making these steps), so that (10) does not agree with Devonshire's Eq. (10.13) (which, in addition, contains several misprints).

Let us now call attention to a number of aspects of these results. From (9), giving the polarization as a function of the field, we see, as we mentioned in the preceding section, that the polarization decreases linearly with temperature, for constant local field. It is this decrease of polarizability with temperature which we have seen in Eqs. (2) and (3) to be responsible for the temperature dependence of the dielectric constant in the neighborhood of the Curie point. In order to get a small temperature dependence of polarization, we clearly need only assume a small value of the quantity $(3b_1+2b_2)$, determining the non-linear behavior of the law of force. We shall return later to the necessary value of this quantity, and show that it is reasonable. Associated with this decrease of polarizability with temperature is a decrease of entropy, as given in (8), with electric field; we immediately verify that Eq. (6) is satisfied. It is interesting to look into the physical reason for this change of entropy with polarization, for by (6) this will then tell us why the polarizability decreases with temperature. Let us consider the entropy for a linear oscillator, in which the b's are zero. From (8), we have in this case

$$S = Nk\ln[(e/Nh^3)(\pi kT)^3(2m/a)^{\frac{3}{2}}]+3Nk.$$

Let us particularly observe the dependence on a: S contains a term $-(3/2)Nk\ln a$. This dependence is fundamental, and has a simple explanation. For a large restoring force constant a, the particle at a given energy, or temperature, is confined to a small volume; but we know that the smaller the effective volume available to a particle, the smaller is its entropy. Or alternatively, for a large value of a, the frequency of oscillation of the particle will be large, its stationary states as given by the quantum condition will be far apart, and at a given temperature there will be fewer occupied states than for a smaller value of a; this again leads to small entropy. Now let us return to our case of the non-linear restoring force, where the b's are different from zero, and positive. If we polarize the ion by a local field, so that its position of equilibrium is displaced from the origin of our (x, y, z) coordinates, the fourth-power terms will have the effect of increasing the restoring force constant for this new position of equilibrium, increasing the vibration frequency about that point, and hence decreasing the entropy. It is this effect which results in the term in E^2, in (8). At the same time, as the temperature goes up, the particle spends more time in a region of high amplitude, where the restoring force constant is larger; this results in the decrease of entropy with temperature described by the term $-(Nk^2T/a^2)3(3b_1+2b_2)/2$ in (8). In this way we understand the effect of the fourth-order terms on the entropy, and hence on the polarizability. It is interesting to see that the effect is very simple and elementary, and quite different from any order-disorder explanation of entropy change, such as is invoked in some other phenomena leading to lambda-points.

III. THE NATURE OF THE LORENTZ CORRECTION

In Section II, we assumed that the various Ti ions vibrated quite independently of each other. This assumption is incorrect, since actually they exert forces on each other, rather than having an external force acting on them which depends only on their displacement. This situation is well known from the theory of the specific heat of solids. We know that if we treat the vibrations of the atoms separately, we arrive at a specific heat theory of the Einstein type. On the other hand, if we consider their interactions, we must introduce normal coordinates, describing the various standing waves which can be set up in the crystal, and arrive at a specific heat theory of the Debye type. If there are several types of atoms or ions, then as Born and others have shown, there will be various branches to the vibration spectrum, some being of the so-called acoustical type, and having frequencies extending down to acoustical ranges, while others are of the so-called optical type, with frequencies in the infra-red. These optical vibrations are the ones in which the ions of different type oscillate in opposite directions; they are connected with the residual rays or *Reststrahlen.* In our case, the vibrations of the Ti ions with respect to the rest of the lattice will be of this optical type. And in general it is found that the spectrum of frequencies in an optical branch is not widely spread out, so that the correct theory is not greatly different from an Einstein-type theory, in which all frequencies are assumed to be identical. For this reason, in the present treatment we shall not consider the interactions of the ions, but shall treat them as being independent. The writer has been informed by Dr. P. A. Anderson, of the Bell Telephone Laboratories, that he is working on a more elaborate treatment, in which the normal coordinates are properly introduced.

This simple discussion is correct in some respects; but it neglects a very important aspect of the problem, the Lorentz correction. The ordinary theory of elastic vibrations of the ions deals with short-range forces, only interactions between nearest neighbors ordinarily being considered. When the ions by their displacements produce electric dipoles throughout the interior of the solid, however, these dipoles produce long-range electric forces acting on each dipole of the system, and these dipole forces must be considered separately. We can make a first approximation to a theory including these Lorentz forces if we proceed in the following way. We introduce as coordinates representing the motion of the Ti ions first the coordinate of the average displacement, or center of gravity, of all the ions; then, as additional coordinates, the displacements of the separate ions from the displaced position which they would take up if the whole Ti lattice were displaced bodily. The displacement of the whole lattice will be equivalent to the polarization produced by the ions, and there will be a term in the energy coming from the Lorentz interaction of the field produced by the resulting dipoles, with the dipoles themselves. There will be further terms in the energy arising from the displacements of the separate ions from this average position, and these will be treated essentially as in the preceding section. This is admittedly only a partially satisfactory way of handling the complete problem of the interactions of the displaced ions, including their electrostatic interactions, but it should give a satisfactory first approximation.

Let us see how it would work out, if the Lorentz assumption of spherical symmetry were correct. In that case, if there were a polarization $\mathbf{P}$, the local field acting on a given ion would be $\mathbf{E}+\mathbf{P}/3\epsilon_0$. If the ions were displaced in such a way as to produce the polarization $\mathbf{P}$, each ion would make a negative contribution to the electrostatic energy, since it is displaced in the direction of the field $\mathbf{P}/3\epsilon_0$. The total electrostatic energy per unit volume arising in this way will be $-P^2/6\epsilon_0$, the factor $\frac{1}{2}$ (leading to $-P^2/6\epsilon_0$ rather than $-P^2/3\epsilon_0$) arising because we are really dealing with interactions of forces between pairs of dipoles, and we must count each pair only once, not twice. We can then take care of the Lorentz correction by supplementing the free energy A_P of (10) by this correction term $-P^2/6\epsilon_0$, where we are dealing specifically with unit volume of material.

We can now take this revised free energy, and inquire what is the polarization as a function of field arising from it, and consequently what effect the Lorentz correction has on the dielectric constant. From (7) we find

$$E_x=\frac{2aP_x}{Nq^2}\left[1+\frac{kT}{a^2}(3b_1+2b_2)\right]-\frac{P_x}{3\epsilon_0}+\frac{4P_x}{N^3q^4}[b_1P_x^2+b_2(P_y^2+P_z^2)]. \quad (11)$$

If we disregard the cubic term, to get the dielectric behavior above the Curie point, in a small field, and solve for P_x, treating the b's as small quantities, we have

$$P_x=\frac{Nq^2}{2a}\left[1-\frac{kT}{a^2}(3b_1+2b_2)\right]\left(E_x+\frac{P_x}{3\epsilon_0}\right)\cdot$$

This agrees with the assumption leading to Eq. (1), and when we remember that $N=1/v$, we see that the polarizability α is given by

$$\alpha=\frac{q^2}{2a}\left[1-\frac{kT}{a^2}(3b_1+2b_2)\right], \quad (12)$$

showing a linear decrease with temperature proportional to the b's, qualitatively agreeing with (2). Thus our addition of the correction term $-P^2/6\epsilon_0$ has correctly taken care of the Lorentz correction. We note that the entropy expressed as a function of the P's, by (7), is unaffected by the presence or absence of the Lorentz correction; it is

$$S=Nk\ln[(e/Nh^3)(\pi kT)^3(2m/a)^{\frac{3}{2}}]+3Nk-\frac{3Nk^2T}{2a^2}(3b_1+2b_2)-\frac{P^2k}{Naq^2}(3b_1+2b_2).$$

This shows the quadratic decrease of entropy with polarization, proportional to the b's, which we have already discussed.

We can discuss the spontaneous polarization below the lambda-point from the expression (11). Let the applied field $\mathbf{E}$ be zero. Then we have various possibilities for spontaneous polarization. Let us consider the simple case where P_x is different from zero, P_y and P_z equal to zero. Then we have from (11)

$$\frac{P_x^2}{\epsilon_0}=\frac{N^2q^2a}{2b_1\epsilon_0}\left[\frac{Nq^2}{6\epsilon_0 a}-1-\frac{kT}{a^2}(3b_1+2b_2)\right]\cdot \quad (13)$$

The spontaneous polarization will be zero at the Curie point; hence we have

$$Nq^2/(6\epsilon_0 a)=1+[kT_c(3b_1+2b_2)/a^2]. \quad (14)$$

We may then rewrite (13), correct to linear terms in the b's, in the form

$$(P_x^2)/\epsilon_0=3Nk(3b_1+2b_2)(T_c-T)/b_1. \quad (15)$$

This indicates that P is proportional to $(T_c-T)^{\frac{1}{2}}$ below the Curie point, the usual type of dependence for a lambda-point theory. If the actual transition is a lambda-point transition rather than a phase change of the first order, however, the temperature dependence of polarization given by (15) is much too slow. Thus if we have something not far from spherical symmetry for the Ti ion, so that b_1 and b_2 are comparable in size, and (15) reduces to 15 $Nk(T_c-T)$, comparison with observed curves shows that if the real variation of polarization with temperature is to be fitted to a curve of the form (15), the coefficient must be something like 60 times as large as that given above. This situation, as we indicated in the introductory section, can be corrected by considering elastic distortion of the crystal, as we shall describe in a later section.

IV. THE LORENTZ CORRECTION FOR THE ACTUAL CRYSTAL

In the preceding section, we have considered the way in which the Lorentz correction affects the free energy, and hence the expression for dielectric constant. Now we are ready to ask how this argument is modified if we take account of the polarizability of the other ions in the crystal. In the present section we shall deal only with the polarization above the Curie point, where the polarization is proportional to the field. In the next section we extend the argument to a calculation of the effect of the Lorentz correction on the free energy, so as to treat the problem below the Curie point.

In the $BaTiO_3$ crystal, each unit cell contains five ions. Let us assume that the crystal is polarized along the z axis; symmetry demands that each of the ions be polarized along the z axis. Let us then write the total polarization in the crystal as the sum of five terms: the polarizations arising from each type of ion. When we consider the whole crystal, each of these types of ions will form a simple cubic lattice. We then visualize for each type of ion a simple cubic lattice of equal dipoles, and we wish to find the field of these dipoles at one of the lattice points. It is well known that the field of a simple cubic lattice of dipoles at one of its lattice points is $\mathbf{P}/3\epsilon_0$, where $\mathbf{P}$ is the polarization resulting from this lattice alone. Thus, for instance, if we had only the polarization arising from the displacement of the Ti ions, as we were considering in the preceding section, the Lorentz correction as treated in that section would be correct. However, the field of a simple cubic lattice of dipoles is not equal to $\mathbf{P}/3\epsilon_0$ at most points within the unit cell. Thus for instance the field exerted by the lattice of Ti ions is not equal to $\mathbf{P}/3\epsilon_0$ at the position of one of the oxygen ions, but is quite a different amount. What we must do is to examine the field actually exerted at the position of each ion, by the lattices of the dipoles of all types of ions.

Fortunately the necessary calculations have been performed in papers by McKeehan[12] and by Luttinger and Tisza.[13] Luttinger and Tisza give the field exerted at various points through the lattice by a lattice of dipoles whose polarization is unity, polarized along the z direction. They express their results in the nonrationalized Gaussian units, and the fields which they give are those in addition to the value $4\pi\mathbf{P}/3$. Thus they find that the additional field at a point (ξ, η, ζ) in the unit cell, where ξ, η, ζ are the ratios of the displacement from a lattice point to the lattice spacing, are given by expressions $S_z(\xi, \eta, \zeta)$, where

$$\begin{aligned} &S_z(0,0,0)=S_z(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})=0\\ &S_z(0,\tfrac{1}{2},\tfrac{1}{2})=4.334, \qquad S_z(\tfrac{1}{2},\tfrac{1}{2},0)=-8.668,\\ &S_z(\tfrac{1}{2},0,0)=-15.040, \quad S_z(0,0,\tfrac{1}{2})=30.080. \end{aligned} \tag{16}$$

Let us see what these mean. The first statements show that the ordinary Lorentz correction $4\pi\mathbf{P}/3$ (in Gaussian units) is correct not only at a lattice point, but at a point in the center of the unit cell. Thus this ordinary correction is valid for the actions of the Ba and Ti ions on themselves and on each other. On the other hand, for interactions between the oxygens and the other ions, the ordinary correction is entirely incorrect. Thus if we ask for the action of the Ti ions on those oxygens which lie along the same line parallel to the polarization (or z axis), which we have previously called oxygens of type a, we find that the Lorentz correction is really $(30.080+4\pi/3)\mathbf{P}$, or approximately 8.2 times the ordinary value $4\pi\mathbf{P}/3$. The action of the oxygens of type a on the Ti ions contains this same greatly enhanced Lorentz factor. It is this fact which we shall find operating to make the field at the position of the Ti ions so much greater than we should get from a simple Lorentz argument, as we mentioned in the introductory section.

Let us now write the polarization of the Ti ions as P_{Ti}, that of the Ba ions as P_{Ba}, that of the oxygens of type a as $P_{\mathrm{O}a}$, and that associated with the two lattices of oxygens of type b as $P_{\mathrm{O}b1}$ and $P_{\mathrm{O}b2}$. By symmetry, we shall find that $P_{\mathrm{O}b1}=P_{\mathrm{O}b2}$, but it will simplify our procedure to keep them separate. These polarizations are assumed to arise from electronic polarization, except in the case of P_{Ti}, where we shall sometimes assume that it is the sum of that arising from electronic and ionic polarizations. Then from the relations (16) we can write the effective or local fields acting on each type of ion to polarize it. We shall write these fields in the m.k.s. system; to get the corresponding formulas in the Gaussian system, we replace ϵ_0 by $1/(4\pi)$, as usual. We shall then want to use the quantities $8.668/4\pi$ and $30.080/4\pi$. We shall abbreviate these as

$$8.668/4\pi=0.690=p, \quad 30.080/4\pi=2.394=q. \tag{17}$$

Then we have:

$$\begin{aligned} \text{Field on Ti}&=E+(1/\epsilon_0)[\tfrac{1}{3}P_{\mathrm{Ti}}+\tfrac{1}{3}P_{\mathrm{Ba}}\\ &\quad+(q+\tfrac{1}{3})P_{\mathrm{O}a}+(-\tfrac{1}{2}q+\tfrac{1}{3})(P_{\mathrm{O}b1}+P_{\mathrm{O}b2})].\\ \text{Field on Ba}&=E+(1/\epsilon_0)[\tfrac{1}{3}P_{\mathrm{Ti}}+\tfrac{1}{3}P_{\mathrm{Ba}}\\ &\quad+(-p+\tfrac{1}{3})P_{\mathrm{O}a}+(\tfrac{1}{2}p+\tfrac{1}{3})(P_{\mathrm{O}b1}+P_{\mathrm{O}b2})].\\ \text{Field on O}a&=E+(1/\epsilon_0)[(q+\tfrac{1}{3})P_{\mathrm{Ti}}+(-p+\tfrac{1}{3})P_{\mathrm{Ba}}\\ &\quad+\tfrac{1}{3}P_{\mathrm{O}a}+(\tfrac{1}{2}p+\tfrac{1}{3})(P_{\mathrm{O}b1}+P_{\mathrm{O}b2})].\\ \text{Field on O}_{b1}&=E+(1/\epsilon_0)[(-\tfrac{1}{2}q+\tfrac{1}{3})P_{\mathrm{Ti}}\\ &\quad+(\tfrac{1}{2}p+\tfrac{1}{3})P_{\mathrm{Ba}}+(\tfrac{1}{2}p+\tfrac{1}{3})P_{\mathrm{O}a}+\tfrac{1}{3}P_{\mathrm{O}b1}\\ &\quad+(-p+\tfrac{1}{3})P_{\mathrm{O}b2}]. \end{aligned} \tag{18}$$

The equation for the field at O_{b2} is like that at O_{b2}, with subscripts 1 and 2 interchanged. We observe, as we pointed out above, the very large factor $q+\frac{1}{3}$ by which the Ti ions and the type a oxygen ions interact on each other.

We can now set up simultaneous equations, stating that the polarization resulting from each type of ion equals the corresponding polarizability per unit volume,

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[12] L. W. McKeehan, Phys. Rev. **43**, 913 (1933); **72**, 78 (1947).

[13] J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946); **72**, 257 (1947).

multiplied by the appropriate local field.[14] Let the polarizabilities of Ti, Ba, and O be α_{Ti}, α_{Ba}, and α_{O}, respectively; α_{Ti} will be assumed to be the electronic polarizability, and will be specifically augmented by the ionic polarizability when we are dealing with low frequencies. Then we have

$$\begin{aligned} P_{\mathrm{Ti}} &= (\alpha_{\mathrm{Ti}}/v)(\text{field on Ti}),\\ P_{\mathrm{Ba}} &= (\alpha_{\mathrm{Ba}}/v)(\text{field on Ba}),\\ P_{\mathrm{O}a} &= (\alpha_{O}/v)(\text{field on O}a),\\ P_{\mathrm{O}b1} &= (\alpha_{O}/v)(\text{field on O}b_1),\\ P_{\mathrm{O}b2} &= (\alpha_{O}/v)(\text{field on O}b_2), \end{aligned} \tag{19}$$

where the fields are as given in (18). We at once see by inspection that $P_{\mathrm{O}b1}=P_{\mathrm{O}b2}$, so that we have four simultaneous equations for the four unknowns P_{Ti}, P_{Ba}, $P_{\mathrm{O}a}$, $P_{\mathrm{O}b1}$. These equations can be solved by determinants for the polarizations, as functions of E. We can also solve for the dielectric constant, which we get from the sum of all the polarizations, divided by the field. In expressing these quantities, we encounter the combinations $\alpha_{\mathrm{Ti}}/\epsilon_0 v$, and similar expressions for the other polarizabilities. We abbreviate these as X_{Ti}, etc., so that by definition we have $X_{\mathrm{Ti}}=\alpha_{\mathrm{Ti}}/\epsilon_0 v$ (in m.k.s. units), or $4\pi\alpha_{\mathrm{Ti}}/v$ (in Gaussian units), with similar expressions for X_{Ba}, X_{O}. In terms of these quantities, the solutions of (19) prove to be

$$\begin{aligned} P_{\mathrm{Ti}}/(\epsilon_0 E) &= (X_{\mathrm{Ti}}/\Delta)\{1+pX_{\mathrm{O}}\\ &\qquad -(3/2)p(p+q)X_{\mathrm{Ba}}X_{\mathrm{O}}+\tfrac{1}{2}p(3q-p)X_{\mathrm{O}}^2\}\\ P_{\mathrm{Ba}}/(\epsilon_0 E) &= (X_{\mathrm{Ba}}/\Delta)\{1+pX_{\mathrm{O}}\\ &\qquad -(3/2)q(p+q)X_{\mathrm{Ti}}X_{\mathrm{O}}-2p^2X_{\mathrm{O}}^2\}\\ P_{\mathrm{O}a}/(\epsilon_0 E) &= (X_{\mathrm{O}}/\Delta)\{1+2pX_{\mathrm{O}}+qX_{\mathrm{Ti}}-pX_{\mathrm{Ba}}\\ &\qquad -\tfrac{1}{2}q(3q-p)X_{\mathrm{Ti}}X_{\mathrm{O}}-2p^2X_{\mathrm{Ba}}X_{\mathrm{O}}\}\\ P_{\mathrm{O}b1}/(\epsilon_0 E) &= (X_{\mathrm{O}}/\Delta)\{1+\tfrac{1}{2}pX_{\mathrm{O}}-\tfrac{1}{2}qX_{\mathrm{Ti}}+\tfrac{1}{2}pX_{\mathrm{Ba}}\\ &\qquad -\tfrac{1}{2}q(3q-p)X_{\mathrm{Ti}}X_{\mathrm{O}}-2p^2X_{\mathrm{Ba}}X_{\mathrm{O}}\}\\ \kappa-1 &= (1/\Delta)\{X_{\mathrm{Ti}}+X_{\mathrm{Ba}}+3X_{\mathrm{O}}+pX_{\mathrm{Ti}}X_{\mathrm{O}}\\ &\qquad +pX_{\mathrm{Ba}}X_{\mathrm{O}}+3pX_{\mathrm{O}}^2-(3/2)(p+q)^2X_{\mathrm{Ti}}X_{\mathrm{Ba}}X_{\mathrm{O}}\\ &\qquad -\tfrac{1}{2}(3q-p)^2X_{\mathrm{Ti}}X_{\mathrm{O}}^2-8p^2X_{\mathrm{Ba}}X_{\mathrm{O}}^2\}\\ \Delta &= 1-\tfrac{1}{3}(X_{\mathrm{Ti}}+X_{\mathrm{Ba}})+(p-1)X_{\mathrm{O}}\\ &\qquad -(\tfrac{1}{3}p+(3/2)q^2)X_{\mathrm{Ti}}X_{\mathrm{O}}-p(\tfrac{1}{3}+(3/2)p)X_{\mathrm{Ba}}X_{\mathrm{O}}\\ &\qquad -p(1+\tfrac{1}{2}p)X_{\mathrm{O}}^2+\tfrac{1}{6}(3q-p)^2X_{\mathrm{Ti}}X_{\mathrm{O}}^2\\ &\qquad +(8/3)p^2X_{\mathrm{Ba}}X_{\mathrm{O}}^2+\tfrac{1}{2}(p+q)^2X_{\mathrm{Ti}}X_{\mathrm{Ba}}X_{\mathrm{O}}. \end{aligned} \tag{20}$$

In Eqs. (20) we have solved our problem of setting up the correct Lorentz factors for the $BaTiO_3$ structure. Let us now examine some of the implications of these formulas. It can be verified that in spite of their complication they reduce to the exact Lorentz expression in two important cases: first, when X_{Ti} is zero, and X_{Ba} equals X_{O}; second, when X_{O} is zero. The first case is one in which the oxygen and barium ions, assumed identical for that special case, together form a face-centered cubic lattice; the latter that in which the barium and titanium together form a body-centered cubic lattice. Let us now ask what is the situation with the actual numerical values for $BaTiO_3$, in the optical spectrum, so that we disregard the ionic polarizability of the Ti. As values for the electronic polarizabilities of the various ions, we take the following values:

$$\begin{gathered} \alpha_{\mathrm{Ti}}/\epsilon_0(\text{m.k.s.})=4\pi\alpha_{\mathrm{Ti}}\ (\text{Gaussian})=2.34\times10^{-24}\ \text{cc}\\ \alpha_{\mathrm{Ba}}/\epsilon_0=24.42\times10^{-24}\ \text{cc},\quad \alpha_O/\epsilon_0=30.0\times10^{-24}\ \text{cc}. \end{gathered} \tag{21}$$

The values for Ti and Ba were supplied by P. W. Anderson and W. Shockley of the Bell Telephone Laboratories; they come from unpublished work involving an intercomparison of the refractivities of a good many crystals.[15] The value for oxygen is chosen to give the correct value for the optical dielectric constant, which except for a small deviation very close to the Curie point is approximately $(2.40)^2=5.76$. This procedure is in accordance with the findings of the group at the Bell Telephone Laboratories, who find that the oxygen ion appears to show different polarizabilities in compounds of different structure.[16] We take the lattice spacing to be 4.00×10^{-8} cm, a value which is correct at a temperature in the required range (we neglect the thermal expansion at this point), so that v is 64×10^{-24} cc. Then we have

$$X_{\mathrm{Ti}}=0.0365,\quad X_{\mathrm{Ba}}=0.382,\quad X_{\mathrm{O}}=0.470. \tag{22}$$

When we substitute these values, and p and q as given in (17), into Eqs. (20), we find that we get the correct value 5.76 for the dielectric constant. The associated value of $(\kappa-1)/(\kappa+2)$ is 0.613. If the ordinary Lorentz correction were applicable, this would be equal to $\frac{1}{3}(X_{\mathrm{Ti}}+X_{\mathrm{Ba}})+X_{\mathrm{O}}$, which is 0.609. In other words, in this case of the optical refractivities, the ordinary Lorentz formula gives a very good approximation to the truth. The reason for this is undoubtedly that X_{Ti} is small, X_{Ba} is of the same order of magnitude as X_{O}, so that we are not very far from the special case $X_{\mathrm{Ti}}=0$, $X_{\mathrm{Ba}}=X_{\mathrm{O}}$, in which we have pointed out that (20) reduces exactly to the Lorentz case.

It is also interesting to calculate the polarizations of the various types of ions in this high frequency case. When we substitute, we find

$$\begin{aligned} P_{\mathrm{Ti}}/(\epsilon_0 E) &= (X_{\mathrm{Ti}}/\Delta)(1.262)=3.30X_{\mathrm{Ti}},\\ P_{\mathrm{Ba}}/(\epsilon_0 E) &= (X_{\mathrm{Ba}}/\Delta)(0.921)=2.41X_{\mathrm{Ba}},\\ P_{\mathrm{O}a}/(\epsilon_0 E) &= (X_{\mathrm{O}}/\Delta)(1.174)=3.08X_{\mathrm{O}},\\ P_{\mathrm{O}b1}/(\epsilon_0 E) &= (X_{\mathrm{O}}/\Delta)(0.946)=2.47X_{\mathrm{O}}. \end{aligned} \tag{23}$$

If the ordinary Lorentz correction were applicable, we should find these numerical coefficients in each case to be equal to $(\kappa+2)/3=2.59$. We notice that they are of the same order of magnitude; but there is a distinct tendency for the Ti and the type a oxygen ions to be polarized more than this value, and for the others to be polarized somewhat less. We shall find in the low frequency case, where the Ti is polarized much more, that this tendency is greatly enhanced.

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[14] Similar equations have been set up for this case by J. M. Richardson, formerly of the Bell Telephone Laboratories, in unpublished work, but the results were not carried as far as in the present work. See J. M. Richardson and W. Shockley, Phys. Rev. **70**, 105 (1946). See also J. H. van Santen and W. Opechowski, Physica's Grav. **14**, 545 (1948).

[15] W. Shockley, Phys. Rev. **70**, 105(A) (1946).

[16] W. Shockley, Phys. Rev. **73**, 1273 (1948).

Now let us pass on to the problem of the static dielectric constant, where the Ti ions can polarize by ionic displacement. Let us assume that the total polarizability of the titanium is the sum of the value given in (21), and another quantity α_{Ti}', a function of temperature which is given by (12). Let the corresponding value of X be $X_{\mathrm{Ti}}'=\alpha_{\mathrm{Ti}}'/\epsilon_0 v$. We shall then have to use $X_{\mathrm{Ti}}+X_{\mathrm{Ti}}'$ in place of X_{Ti} in Eqs. (20). In that case we see at once from (20) that the dielectric constant can be written in the form

$$\kappa-1=\frac{c_1+c_2X_{\mathrm{Ti}}'}{c_3+c_4X_{\mathrm{Ti}}'}=\frac{c_2}{c_4}+\frac{(c_1/c_3)-(c_2/c_4)}{1+(c_4/c_3)X_{\mathrm{Ti}}'}$$

where

$$\begin{aligned}c_1=X_{\mathrm{Ti}}+X_{\mathrm{Ba}}+3X_{\mathrm{O}}+pX_{\mathrm{Ti}}X_{\mathrm{O}}&\\ +3pX_{\mathrm{O}}^2-(3/2)(p+q)^2X_{\mathrm{Ti}}X_{\mathrm{Ba}}X_{\mathrm{O}}&\\ -\tfrac{1}{2}(3q-p)^2X_{\mathrm{Ti}}X_{\mathrm{O}}^2-8p^2X_{\mathrm{Ba}}X_{\mathrm{O}}^2&\\ c_2=1+pX_{\mathrm{O}}-(3/2)(p+q)^2X_{\mathrm{Ba}}X_{\mathrm{O}}-\tfrac{1}{2}(3q-p)^2X_{\mathrm{O}}^2&\end{aligned}$$

$c_3=\Delta$ from Eq. (20),

including terms in X_{Ti} but not in X_{Ti}'

$$\begin{aligned}c_4=-\tfrac{1}{3}-(\tfrac{1}{3}p+(3/2)q^2)X_{\mathrm{O}}+\tfrac{1}{6}(3q-p)^2X_{\mathrm{O}}^2&\\ +\tfrac{1}{2}(p+q)^2X_{\mathrm{Ba}}X_{\mathrm{O}}.&\quad(24)\end{aligned}$$

In case X_{Ti}, X_{Ba}, X_{O} are all zero, so that the only polarization comes from the ionic displacement, we have $c_1=0$, $c_2=c_3=1$, $c_4=-\frac{1}{3}$, and we have at once the values given in the introductory section,

$$\kappa=1+\frac{X_{\mathrm{Ti}}'}{1-\frac{1}{3}X_{\mathrm{Ti}}'}=-2+\frac{3}{1-\frac{1}{3}X_{\mathrm{Ti}}'}\qquad(25)$$

in our present notation. However, when we put in the values of X_{Ti}, etc., from (22), determined from the optical behavior of the material, the situation is entirely different; we find

$$\begin{aligned}&c_1=1.834,\quad c_2=-5.892,\quad c_3=0.385,\quad c_4=-2.076,\\ &\kappa=3.84+1.93/(1-5.39X_{\mathrm{Ti}}').\end{aligned}\qquad(26)$$

This important result (26) shows that the effect of the polarization of the other ions is greatly to enhance the effect of the ionic displacement of the Ti ions in producing ferroelectricity. Thus from (25) we see that if these other ions were not helping the polarization, we should get ferroelectricity only when $X_{\mathrm{Ti}}'=3$. On the other hand, from (26), we get the same result when $5.39X_{\mathrm{Ti}}'=1$, or when $X_{\mathrm{Ti}}'=0.186$. This indicates enhancement of the effect of the ionic displacement by a factor of approximately 16. Some such enhancement, of course, would arise from the ordinary Lorentz correction. If this correction were applicable in its simple form, we should get ferroelectricity when

$$\tfrac{1}{3}(X_{\mathrm{Ti}}+X_{\mathrm{Ti}}'+X_{\mathrm{Ba}})+X_{\mathrm{O}}=1.$$

We already know that $\frac{1}{3}(X_{\mathrm{Ti}}+X_{\mathrm{Ba}})+X_{\mathrm{O}}=0.609$. Thus we should require that $X_{\mathrm{Ti}}'=3(1-0.609)=1.173$, as compared with the value 0.186 which we find from our more correct theory. The elementary theory of the Lorentz correction thus is so far wrong that the ionic polarizability of the Ti ion needs to be only $0.186/1.173=0.160$ times as great, or about one-sixth as great, as if the elementary theory held. Let us now examine how this very large enhancement of the effect of ionic displacement comes about.

We can understand the situation if we examine the relative polarizations of the various types of ions. We can use (20) to find these, now using $X_{\mathrm{Ti}}+X_{\mathrm{Ti}}'$ instead of X_{Ti} for the Ti ion. In this case, for ferroelectricity, the determinant Δ', obtained by using $X_{\mathrm{Ti}}+X_{\mathrm{Ti}}'$ instead of X_{Ti}, is zero, so that at the Curie point the polarization per unit field is infinite. We can still evaluate the brackets in (20), however, and these will still give the relative magnitudes of the polarizations of the various types of ions. We then find

$$\begin{aligned}P_{\mathrm{Ti}}/(\epsilon_0E)&=[(X_{\mathrm{Ti}}+X_{\mathrm{Ti}}')/\Delta'](1.262),\\ P_{\mathrm{Ba}}/(\epsilon_0E)&=(X_{\mathrm{Ba}}/\Delta')(-0.047),\\ P_{\mathrm{O}a}/(\epsilon_0E)&=(X_{\mathrm{O}}/\Delta')(0.939),\\ P_{\mathrm{O}b1}/(\epsilon_0E)&=(X_{\mathrm{O}}/\Delta')(0.046).\end{aligned}$$

These values are strikingly different from those of (23). Only the relative values now have significance; and we see that the polarization is almost entirely contributed by the Ti ions, and the type *a* oxygen ions. The Ba and type *b* oxygen ions are hardly polarized at all. In fact, when we take account of the polarizabilities, we find that the Ti ions contribute about 37 percent of the total polarization (of which about 31 percent comes from ionic displacement, six percent from electronic polarization), the type *a* oxygen ions about 59 percent, the type *b* oxygen ions about six percent, and the Ba ions about two percent in the reverse direction. We thus see the evidence of the effect which we discussed in the introductory section: the Ti ions, by their polarization, polarize the type *a* oxygen ions; these in turn act back on the Ti ions; and the net result is to build up the polarization of both types of ions, resulting in linear chains of dipoles all pointing in the same direction, the positive end of one to the negative end of the other, and producing spontaneous polarization below the Curie point.

Now that we have found the influence of the polarizability of the other ions on the dielectric constant, we can combine Eq. (26) with an assumption similar to (2), to investigate Curie's law. It is clear that, to make the denominator of (26) vanish at the Curie point, we must assume that

$$5.39X_{\mathrm{Ti}}'=5.39[\alpha_{\mathrm{Ti}}'/(\epsilon_0v)]=1-C(T-T_c).\qquad(27)$$

If we insert this value in (26), we find that

$$\kappa=3.84+1.93/C(T-T_c),\qquad(28)$$

as a substitute for (3). It is interesting to find that, in spite of the large change in the general situation produced by the electronic polarizability, still (28) is not very different from (3), so that the qualitative discussion given in the introductory section regarding the temperature coefficient of the ionic polarizability of the Ti ion is still correct. The constant C, however, is now seen to be about 1.3×10^{-5}, instead of the value 2×10^{-5} given in the introductory section.

We may now compare (27) with (12), the ionic polarizability as determined from our molecular model, and ask whether the constants of (12) have reasonable values. Comparing them, we have approximately

$$5.39q^2/(2a\epsilon_0 v)=1, \quad C=[k(3b_1+2b_2)]/a^2. \tag{29}$$

If we combine these equations, we have

$$(3b_1+2b_2)/a=(5.39Cq^2)/(2\epsilon_0 vk). \tag{30}$$

If we assume that the charge q is n times the electronic charge (where n is 4 if the Ti ion is quadruply charged), and use the value of C given above, and $v=64\times10^{-24}$ cc $=64\times10^{-30}\mathrm{m}^3$, the right side of (30) becomes $1.15\times10^{20}n^2$ (m.k.s. units). We can judge whether this value is reasonable or not, by recalling that our expansion of the energy, which in the case of spherical symmetry can be written $ar^2+br^4+\cdots$, is really the beginning of a power series, which is bound to diverge, or have a singularity, when the Ti ion gets very close to one of the oxygen ions of the octahedron. This divergence will arise because all terms of the series have the same order of magnitude. Thus we should expect that at a distance r where we have a divergence, ar^2 and br^4 should be of the same order of magnitude, or $r^2=a/b$, where for this crude calculation we may set $b_1=b_2=b$. Then $b/a=(1.15/5)\times10^{20}n^2=2.30\times10^{19}n^2$, and $r^2=1/2.30\times10^{-19}/n^2$, $r=(2.1/n)\times10^{-10}\mathrm{m}=2.1/n$ angstroms. This is certainly of the right order of magnitude for interatomic distances, showing that the value of b which we have found necessary to explain the Curie constant is of a reasonable magnitude. Since the actual distance between the Ti ion and its neighboring oxygen ion is just 2A, this crude argument suggests that it might be more likely that n should be approximately unity than 4, which we should have with a quadruply charged ion.

From (29) we can also estimate the value of the constant a. If we assume again that q equals n electronic charges, we find that $a=7.6n^2$ ev/(angstrom)^2. That is to say, the energy of the displaced ion, displaced a distance of 1A from its position of equilibrium, would be $7.6n^2$ volts. This again is of a reasonable order of magnitude, 1A being halfway to the oxygen ion. Here again $n=1$ would be more reasonable than $n=4$, which would lead to an energy of about 120 volts at a distance of 1A. Without more detailed study of the interionic forces, however, it is hardly possible to estimate how great the expected restoring forces should be. It is, of course, not inconsistent with the structure of $BaTiO_3$ to assume a smaller value of n than 4, which would correspond to the strictly ionic compound. Thus if the oxygen ions on the average were singly rather than doubly charged, the Ti ion would have to have a single positive charge. Some evidence as to the charge carried by the Ti ion should eventually become available, when it is known by x-ray measurements exactly how much the Ti ions displace in the spontaneously polarized condition. The magnitude of the spontaneous polarization is known, being equal to about 16×10^{-6} coulomb/cm^2. We have seen that we may expect about 31 percent of this, or 5×10^{-6}, to come from ionic displacement. With a charge of n electronic charges on each Ti ion, this would correspond to a displacement of $0.20/n$ angstroms. There is some x-ray evidence for a displacement of about [17] 0.16A, suggesting $n=1$; but also some evidence for a smaller displacement,[18] suggesting a larger value of n. These questions must await further experimental information.

V. THE LORENTZ CORRECTION AND THE FREE ENERGY

In Section IV we have considered only linear terms in the force acting to polarize the various ions. Now we shall pass to the more general problem, where we include higher power terms as in Section II, but treat the Lorentz correction properly as in Section IV. We shall find it convenient to work backward, starting from the equations for the electric field in terms of the polarization, ending up by integrating these expressions to get a formula for the free energy. First we note that by differentiating (10) with respect to P_x we get the x component of the field polarizing the Ti ion. We have

$$E_x=\frac{2aP_{x\mathrm{Ti}}'}{Nq^2}\left\{1+\frac{kT}{a^2}(3b_1+2b_2)\right\} + \frac{4P_{x\mathrm{Ti}}'}{N^3q^4}\left[b_1P_{x\mathrm{Ti}}'^2+b_2(P_{y\mathrm{Ti}}'^2+P_{z\mathrm{Ti}}'^2)\right] \tag{31}$$

where we have now written the polarization arising from ionic displacement of the Ti ion as P_{Ti}'. The field acting here is of course the local field, not the external field; in Section II we were not taking account of the difference between these two fields. But now, using results of Section IV, we know how to find this local field: it is set up in Eq. (18). In interpreting that set of equations, we must now distinguish between that part of the polarization of the Ti ions arising from electronic polarization, and that from ionic displacement. We shall call the first part of the polarization P_{Ti}, the second part P_{Ti}', so that Eqs. (18) are now to be modified by replacing P_{Ti} where it appears by $P_{\mathrm{Ti}}+P_{\mathrm{Ti}}'$. As before, we let X_{Ti} equal $\alpha_{\mathrm{Ti}}/\epsilon_0 v$, where α_{Ti} is the electronic polarizability of the Ti ion. The corresponding relation giving the ionic polarizability must now be given by (31), where we recall that the E_x appearing in that equation is the local field acting on the Ti ion. We may then rewrite Eqs. (18) and (19), modi-

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[17] Danielson, Matthias, and Richardson, Phys. Rev. **74**, 986 (1948).

[18] Kay, Wellard, and Vousden, Nature **163**, 636 (1949).

fied to take account of (31), in the form

$$\epsilon_0 E_x+\tfrac{1}{3}(P_{x\mathrm{Ti}}+P_{x\mathrm{Ti}}'+P_{x\mathrm{Ba}})+(q+\tfrac{1}{3})P_{x\mathrm{Oa}}+(-\tfrac{1}{2}q+\tfrac{1}{3})(P_{x\mathrm{Ob1}}+P_{x\mathrm{Ob2}})=\frac{2a\epsilon_0 P_{x\mathrm{Ti}}'}{Nq^2}\left[1+\frac{kT}{a^2}(3b_1+2b_2)\right]+\frac{4\epsilon_0 P_{x\mathrm{Ti}}'}{N^3q^4}[b_1P_{x\mathrm{Ti}}'^2+b_2(P_{y\mathrm{Ti}}'^2+P_{z\mathrm{Ti}}'^2)],$$

$$\epsilon_0 E_x+\tfrac{1}{3}(P_{x\mathrm{Ti}}+P_{x\mathrm{Ti}}'+P_{x\mathrm{Ba}})+(q+\tfrac{1}{3})P_{x\mathrm{Oa}}+(-\tfrac{1}{2}q+\tfrac{1}{3})(P_{x\mathrm{Ob1}}+P_{x\mathrm{Ob2}})=P_{x\mathrm{Ti}}/X_{\mathrm{Ti}},$$

$$\epsilon_0 E_x+\tfrac{1}{3}(P_{x\mathrm{Ti}}+P_{x\mathrm{Ti}}'+P_{x\mathrm{Ba}})+(-p+\tfrac{1}{3})P_{x\mathrm{Oa}}+(\tfrac{1}{2}p+\tfrac{1}{3})(P_{x\mathrm{Ob1}}+P_{x\mathrm{Ob2}})=P_{x\mathrm{Ba}}/X_{\mathrm{Ba}},$$

$$\epsilon_0 E_x+(q+\tfrac{1}{3})(P_{x\mathrm{Ti}}+P_{x\mathrm{Ti}}')+(-p+\tfrac{1}{3})P_{x\mathrm{Ba}}+\tfrac{1}{3}P_{x\mathrm{Oa}}+(\tfrac{1}{2}p+\tfrac{1}{3})(P_{x\mathrm{Ob1}}+P_{x\mathrm{Ob2}})=P_{x\mathrm{Oa}}/X_{\mathrm{O}},$$

$$\epsilon_0 E_x+(-\tfrac{1}{2}q+\tfrac{1}{3})(P_{x\mathrm{Ti}}+P_{x\mathrm{Ti}}')+(\tfrac{1}{2}p+\tfrac{1}{3})P_{x\mathrm{Ba}}+(\tfrac{1}{2}p+\tfrac{1}{3})P_{x\mathrm{Oa}}+\tfrac{1}{3}P_{x\mathrm{Ob1}}+(-p+\tfrac{1}{3})P_{x\mathrm{Ob2}}=P_{x\mathrm{Ob1}}/X_{\mathrm{O}}. \quad (32)$$

There is an equation similar to the last one for P_{xOb2}. We can now solve all equations except the first for $P_{x\mathrm{Ti}}$, $P_{x\mathrm{Ba}}$, P_{xOa}, P_{xOb1}, P_{xOb2} in terms of $P_{x\mathrm{Ti}}'$ and E_x. We then substitute these values into the first equation of the set (32), and this becomes an equation relating E_x and P_{Ti}', containing now the higher power terms from that equation. When we carry out these steps, which can be simplified by comparison with the similar problem involved in finding the first equation of (20), the resulting equation is

$$E_x=\frac{c_3}{c_5}\left\{\frac{2aP_{x\mathrm{Ti}}'}{Nq^2}\left[1+\frac{kT}{a^2}(3b_1+2b_2)\right]+\frac{4P_{x\mathrm{Ti}}}{N^3q^4}\times[b_1P_{x\mathrm{Ti}}'^2+b_2(P_{y\mathrm{Ti}}'^2+P_{z\mathrm{Ti}}'^2)]\right\}+\frac{c_4}{c_5}\frac{P_{x\mathrm{Ti}}'}{\epsilon_0}, \quad (33)$$

where

$$c_5=1+pX_{\mathrm{O}}-3/2p(p+q)X_{\mathrm{Ba}}X_{\mathrm{O}}+\tfrac{1}{2}p(3q-p)X_{\mathrm{O}}^2,$$

and c_3 and c_4 are as given in (24).

In case the electronic polarizabilities of all the various ions are zero, we have $c_3=c_5=1$, $c_4=-\frac{1}{3}$, and hence the only effect of the Lorentz correction in (33) is to subtract the term $P_{\mathrm{Ti}}'/3\epsilon_0$ from the right-hand side, or to substitute a local field $E+P/3\epsilon_0$ for the field E, as we should expect, and as we saw in Eq. (11). However, when we take account of the electronic polarizability, there are two changes: the Lorentz correction term $P/3\epsilon_0$ is changed from $-\frac{1}{3}$ to c_4/c_5, and the other term is multiplied by a factor c_3/c_5. When we insert the numerical values which we have been using, we find that $c_3/c_5=0.309$, $c_4/c_5=-1.69$. In other words, the Lorentz correction term is $3\times1.69/0.309=16.4$ times as important as would be given by the simple Lorentz theory. This is the same enhancement factor which we have already met in our discussion of Eq. (26), only now expressed in somewhat different language.

In the process of setting up the solution (33), we have had to solve separately for the various polarizations P_{Ba}, etc. We shall not give the separate formulas for these quantities, but we shall give the formula for the total polarization P, in terms of P_{Ti}'. We find that

$$P_x=\frac{c_1}{c_5}\epsilon_0\left\{\frac{2aP_{x\mathrm{Ti}}'}{Nq^2}\left[1+\frac{kT}{a^2}(3b_1+2b_2)\right]+\frac{4P_{x\mathrm{Ti}}'}{N^3q^4}\times[b_1P_{x\mathrm{Ti}}'^2+b_2(P_{y\mathrm{Ti}}'^2+P_{z\mathrm{Ti}}'^2)]\right\}+\frac{c_2}{c_5}P_{x\mathrm{Ti}}'.$$

We are particularly interested in the relation in the case of spontaneous polarization, when $E=0$, but P and P_{Ti}' are not. In that case, we may combine with (33), and find

$$P_x=P_{x\mathrm{Ti}}'[(c_2c_3-c_1c_4)/c_3c_5].$$

But we can prove, by straightforward algebra, that

$$c_2c_3-c_1c_4=c_5^2.$$

Thus the equation above becomes

$$P_x=(c_5/c_3)P_{x\mathrm{Ti}}', \quad (34)$$

under conditions of spontaneous polarization. When we insert numerical values, we find $P_x=P_{x\mathrm{Ti}}'/0.309=3.24P_{x\mathrm{Ti}}'$, as we have mentioned in earlier paragraphs. We readily verify that above the Curie point, where we are interested in the dielectric constant, this same relation still holds to a first order of accuracy, agreeing with the results of Section IV.

We can then use (34) in connection with (33), to express the field in terms of P, rather than P_{Ti}', and find

$$E_x=\frac{c_3}{c_5}\left\{\frac{2a}{Nq^2}\frac{c_3}{c_5}P_x\left[1+\frac{kT}{a^2}(3b_1+2b_2)\right]+\left(\frac{c_3}{c_5}\right)^2\frac{4P_x}{N^3q^4}\times[b_1P_x^2+b_2(P_y^2+P_z^2)]\right\}+\frac{c_3c_4}{c_5^2}\frac{P_x}{\epsilon_0}. \quad (35)$$

This expression allows us to integrate Eq. (7), taking account of (10), to get the free energy A_P. We have

$$A_P=-NkT\ln[(e/Nh^3)(\pi kT)^3(2m/a)^{\frac{3}{2}}]+[N(kT)^2/a^2]\tfrac{3}{4}(3b_1+2b_2)+\left(\frac{c_3}{c_5}\right)^2\frac{aP^2}{Nq^2}\left[1+\frac{kT}{a^2}(3b_1+2b_2)\right]+\left(\frac{c_3}{c_5}\right)^4\frac{1}{N^3q^4}[b_1(P_x^4+P_y^4+P_z^4)+2b_2(P_y^2P_z^2+P_z^2P_x^2+P_x^2P_y^2)]+\frac{c_3c_4}{c_5^2}\frac{P^2}{2\epsilon_0}. \quad (36)$$

If we use (34), and express this in terms of P_{Ti}', the expression (with the exception of the last term) reduces to the same value (10) which we found earlier (when we remember that the P appearing in (10) is just the ionic polarization of the Ti ions, which we are now calling P_{Ti}'). The last term, however, is not the same as the Lorentz correction function in Section III. That was $-P_{\mathrm{Ti}}'^2/6\epsilon_0$, whereas our term $(c_3c_4/c_5^2)(P^2/2\epsilon_0)$ can be written as $(c_4/c_3)(P_{\mathrm{Ti}}'^2/2\epsilon_0)$. We verify from (24) that this reduces to $-P_{\mathrm{Ti}}'^2/6\epsilon_0$ for the case where the only polarization is that of the Ti ion, thus verifying our result; but for the actual case, it is 16.4 times as great, in agreement with previous statements concerning the effect of the correct treatment of the Lorentz correction.

Expression (36) is the one which we should use for discussing relations between theory and experiment. We may define the Curie point as the point where the term in P^2 goes to zero. That is,

$$-(c_4/c_3)(Nq^2/2\epsilon_0 a)=1+kT_c(3b_1+2b_2)/a^2, \tag{37}$$

to be compared with (14), the formula derived from the simple Lorentz theory, in which c_4/c_3 is replaced by $-\frac{1}{3}$. If we substitute (37) in (36), we can rewrite the term in P^2 in the form

$$(c_3/c_5)^2(aP^2/Nq^2)(k(T-T_c)/a^2)(3b_1+2b_2).$$

We can also use (37) to rewrite the other terms of (36) in alternative forms; we can disregard the terms of (37) involving the b's in terms which are small of the first order. When we do this, we find the alternative formula in place of (36),

$$\begin{aligned}A_P=&-NkT\ln[(e/Nh^3)(\pi kT)^3(2m/a)^{\frac{3}{2}}]\\&+(N(kT)^2/a^2)\tfrac{3}{4}(3b_1+2b_2)\\&+(c_4/\epsilon_0c_5)^2(Nq^2/4a^3)P^2k(T-T_c)(3b_1+2b_2)\\&+(c_4/\epsilon_0c_5)^4(Nq^4/16a^4)[b_1(P_x^4+P_y^4+P_z^4)\\&\qquad+2b_2(P_y^2P_z^2+P_z^2P_x^2+P_x^2P_y^2)].\end{aligned} \tag{38}$$

This form of the expression is chosen to make comparison easy with Devonshire's formulas. We get agreement with the terms linear in the b's, in Devonshire's Eq. (10.13) (correcting for certain obvious misprints in his equation), if we set his β (Lorentz factor) equal to

$$\begin{aligned}\beta=-c_4/(\epsilon_0c_5)=-(4\pi c_4)/c_5(\text{Gaussian units})\\=5.09(4\pi/3).\end{aligned} \tag{39}$$

That is, for these terms, we must use a Lorentz correction 5.09 times as great as given by the elementary theory. On the other hand, in the terms independent of the b's, leading to the value of the Curie temperature, we get agreement with Devonshire's values if we use a value of β equal to

$$\begin{aligned}\beta=-c_4/(\epsilon_0c_3)=-(4\pi c_4)/c_3(\text{Gaussian units})\\=16.4(4\pi/3),\end{aligned} \tag{40}$$

thereby bringing about agreement between our Eq. (36) and Devonshire's (10.17). In other words, no single modified Lorentz factor will take care of the whole correct Lorentz treatment, as we have developed it.

VI. FREE ENERGY AND ELASTIC STRAIN

The free energy as we have computed it disregards the elastic energy; it is calculated on the assumption that the crystal does not deform when it polarizes. As we have pointed out earlier, this does not lead to the correct formula for the polarization below the Curie point. If we set $E_x=0$ in (35), solve for P_x (assuming that $P_y=P_z=0$), and use (37), we have

$$\frac{P_x^2}{\epsilon_0}=-\frac{c_5^2}{c_3c_4}Nk\frac{(3b_1+2b_2)}{b_1}(T_c-T), \tag{41}$$

as compared with (15), where we have the factor 3 in place of $-c_5^2/c_3c_4$. We find $-c_5^2/c_3c_4=1.93$; in other words, the relation between polarization and temperature is not very different on the correct treatment from the value given in the elementary theory, so that the disagreement between this function and experiment is as bad as that discussed in Section III.

We have already mentioned that, as pointed out by Devonshire, this disagreement is removed by supplementing A_P, as given in (38), by additional terms in the elastic strains, and terms involving both strains and polarization components, which therefore are responsible for the piezoelectric effect. The partial derivative of this free energy with respect to one of the strain components then gives the related stress component; if we set the stresses equal to zero we get in this way a set of equations from which we can solve for the various strains under conditions of vanishing stress. We substitute these values in the expression for free energy, and have finally a free energy as a function of polarization components, for the condition of vanishing stress. We find that the resulting correction terms are of the fourth-power in the polarization, hence modifying the fourth-power terms in (38), and changing completely the relation (41), and thus the polarization below the Curie point. Since our argument at this point follows exactly that of Devonshire, we merely refer the reader to his paper, particularly his Eq. (9.1), giving the free energy in terms of strains and polarizations. To facilitate comparison with his results, we give formulas, in our notation, for various coefficients appearing in his paper, his Eqs. (10.14), (10.15), (10.16):

$$\begin{aligned}\chi''&=\left(\frac{c_4}{\epsilon_0c_5}\right)^2\frac{Nq^2}{2a^3}k(T-T_c)(3b_1+2b_2),\\\xi_{11}''&=\left(\frac{c_4}{\epsilon_0c_5}\right)^4\frac{Nq^4}{4a^4}b_1,\\\xi_{12}''&=\left(\frac{c_4}{\epsilon_0c_5}\right)^4\frac{Nq^4}{4a^4}b_2.\end{aligned} \tag{42}$$

Devonshire has made some attempt to compare the numerical predictions of the theory with experiment, and it is obvious that the present paper, making very large changes in some of the coefficients, will invalidate most of that comparison. We shall not attempt at this time, however, to make an alternative comparison with experiment. There are two ways in which this comparison can be made. First, the observed Curie temperature permits an evaluation of q^2/a, and the temperature dependence of the dielectric constant gives us $(3b_1+2b_2)/a^2$. We have already considered the resulting values of these constants, and have shown them to be of reasonable order of magnitude. To check them better we should have to have an elaborate study of the structure of the crystal from the standpoint of atomic theory, in order to be able to compute the interionic forces. Devonshire has given such a theory in a rather elementary way, but the writer believes that a more elaborate treatment would be necessary before the results could have great pretensions to accuracy. On the other hand, the behavior of the polarization below the Curie point gives information about the coefficients of the fourth-power terms (and sixth-power terms, which Devonshire also has to introduce), but modified by the contributions resulting from the elastic strain. If the elastic and piezoelectric constants of single crystals were known accurately enough, we could evaluate these modifications, and then we should be able to find the b's independently from the fourth-order terms, as well as from the second-order terms, and hence have a valuable internal check of the theory. Unfortunately, these elastic and piezoelectric constants are not known sufficiently well. It is to be hoped that future experiments will supply this missing information. In the meantime, it can be said that there does not seem to be anything about the present form of the theory which does not have a good chance of agreeing with experiment, when better experimental data are available.

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Evaporation of Zinc and Zinc Oxide under Electron Bombardment

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By use of a mass spectrographic method, the rate of evaporation of zinc and zinc oxide is measured as a function of temperature both with and without electron bombardment of the surface being evaporated. In the case of zinc metal no increase of evaporation could be detected as resulting from bombardment whereas a definite increase was observed in the evaporation of zinc oxide. The enhancement of the evaporation rate of zinc oxide increases slowly at first and then rapidly with increasing temperature.

1. INTRODUCTION

The experimental investigation of many solid state phenomena would be much simplified if a sensitive method of microanalysis were available for measuring the chemical constitution of solids containing impurities in very small concentration. Especially would this be the case if the method were capable of analyzing the constituents of solid surfaces, for many surface phenomena such as thermionic emission, secondary electron emission, photoelectric emission, etc., are very sensitive to the atomic or molecular constitution of the surface in question. The mass spectrometer is an instrument which would be very well suited to such analysis if means could be found to remove atoms or molecules from the surface and subsequently identify them in the spectrometer.

There is evidence that under electron bombardment atoms or ions may be removed from solids. Baldock[1] found that calcium ions are obtained from calcium metal when it is bombarded with electrons. Jacobs[2] found oxygen compounds to be removed by electron bombardment from anodes coated with thin layers, and Sproule[3] found evidence that electron bombardment of heated triple oxide surfaces removed barium, strontium and calcium atoms. The experiments reported below were undertaken to study this phenomenon in greater detail in order to see whether electrons of themselves can cause dissociation of atoms from a surface or whether this comes about only by virtue of the heating produced by the electrons. A beam of electrons was directed against a target whose temperature could be controlled. The relative number of atoms leaving its surface was detected with a mass spectrometer and compared with the number leaving by thermal evaporation alone.

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