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A THEORETICAL STUDY OF THE DIELECTRIC CONSTANT
OF PEROVSKITE TYPE CRYSTALS

by

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Chapter I

INTRODUCTORY IDEAS

The dielectric properties of perovskite type crystals are of interest because some of the compounds having this crystal structure are ferroelectric. The word ferroelectric is derived by analogy with the word ferromagnetic; it means that the material has a spontaneous electric polarization just as a magnet has a spontaneous magnetic polarization. While in this country the term ferroelectric is universally used, in Europe the term seignettoelectric is often used instead. This usage stems from the fact that the first ferroelectric discovered was Seignette salt or Rochelle salt.

Ferroelectric materials are of interest because they are piezoelectric, they have high dielectric constants, and their dielectric constants are strongly temperature dependent. These properties lead to many applications. A study of the theory of ferroelectrics should be useful in utilizing their properties and in discovering new ferroelectrics.

Perovskite is the common name given to CaTiO$_3$. Since this was the first compound of this type to be studied, the crystal structure has come to bear its name. However, it happens that CaTiO$_3$ is not a ferroelectric and is of little interest.
The perovskite type of crystal structure is illustrated in fig. 1 by the unit cell of BaTiO₃. This structure

![Diagram of BaTiO₃ unit cell]

- ○ -- Ba ion
- ◊ -- Ti ion
- ◊ -- O ion

Figure 1: Unit cell of BaTiO₃.

is the simplest in which ferroelectricity has so far been found. It is a combination of body-centered and face-centered cubic types. The Ba ions are at the corners of the cube, the Ti ions at the body centers, and the O ions at the face centers. The Ba ions need only be replaced by Ca or Sr ions to obtain the corresponding titanates. However, these latter two compounds are not ferroelectric, although mixtures of barium and strontium titanates are ferroelectric until they approach pure SrTiO₃.

Other ferroelectrics of this class are NaTaO₃, KTaO₃, NaNbO₃, and KNbO₃. In these compounds the Na or K ions take the places of Ba ions, and the Ta or Nb ions take the places of the Ti ions.

A comprehensive review of the experimental facts obtained on BaTiO₃ has been given by von Hippel. The
behavior of the dielectric constant and of the crystal structure are here illustrated in fig. 2. The values for the dielectric constant are those obtained by Merz(2) for single crystals. The values of the lattice parameters are those obtained by Kay and Vousden,(3) also for single crystals. One can see from fig. 2 that BaTiO$_3$ undergoes three transitions. The transitions in the neighborhoods of 0° C and -90° C are generally agreed to be first order phase transitions. However, there is considerable dispute in the literature concerning whether the transition in the neighborhood of 120° C is of first or second order. Recent evidence(4) indicates that it too is a first order transition.

The changes that BaTiO$_3$ undergoes in going from high to low temperatures may be described as follows.(3) In the region of fig. 2 above 120° C there is no spontaneous polarization, the dielectric constant $\mathbf{K}$ follows a Curie-Weiss law $\mathbf{K} = K_0 + \mathbf{M} / (\mathbf{T} - \mathbf{T}_0)$, and the crystal structure is exactly the perovskite type. The three dimensions of the unit cell are equal.

After going down through the 120° C transition, a spontaneous polarization appears along one of the cubic axes—say the $\mathbf{z}$-axis. The dielectric constant along the $\mathbf{z}$ direction is now different from the value along the $\mathbf{x}$ and $\mathbf{y}$ directions. Also the unit cell departs slightly from the cubic form to become tetragonal. In this and lower regions the crystal structure is pseudoperovskite.
a: Dielectric constant of BaTiO₃ along x and z axes.

b: Dimensions dₓ, dᵧ, and d𝕫 along x, y, and z axes of BaTiO₃ unit cell.

Figure 2
On going from the tetragonal region down through the 0° C transition, the spontaneous polarization shifts to a position midway between the z-axis and another axis—say the y-axis. The unit cell is slightly sheared in the yz-plane, and the structure is orthorhombic.

Below the transition at -90° C, the spontaneous polarization shifts to a position symmetrically located between all three axes. All faces of the unit cell are equally sheared, and the structure is rhombohedral. The fact that the dielectric constant is not once again isotropic is attributed by Merz(2) to domain effects.

The dielectric constant illustrated in fig. 2 is the low frequency dielectric constant. The optical dielectric constant,(2) which is the square of the index of refraction, varies somewhat with temperature but is within a few percent of 5.3 over the range 20--140° C.

Due to the difficulty of growing single crystals, measurements were first made on ceramic specimens. A ceramic is made up of a large number of randomly oriented microcrystals. The results obtained for ceramics are similar to those for single crystals but are smeared out.

The dielectric constants of two other perovskite type crystals are shown in figs. 3 and 4. In fig. 3 is shown Youngblood's(5) data for a ceramic specimen of SrTiO₃. Fig. 4 shows the results of Hulm, Matthias, and Long(6) for two single crystals of KTaO₃.
\[ K = \frac{M}{\frac{T_1}{2} \coth \frac{T_1}{2T} - T_0} \]

\[ M = 7.180 \times 10^4 \ \text{cm}^{-1} \]

\[ T_1 = 98.00^{\circ} \text{K} \]

\[ T_0 = 37.89^{\circ} \text{K} \]

Figure 3: Dielectric Constant of SrTiO$_3$
Curves according to

\[ K = \frac{M}{\frac{T_1}{2} \coth \frac{T_1}{2T} - T_0} \]

For sample 1:
- \( M = 5.900 \times 10^4 \ \text{O}^{\text{K}}^{-1} \)
- \( T_1 = 74.46^\circ \text{K} \)
- \( T_0 = 23.18^\circ \text{K} \)

For sample 2:
- \( M = 7.000 \times 10^4 \ \text{O}^{\text{K}}^{-1} \)
- \( T_1 = 89.92^\circ \text{K} \)
- \( T_0 = 32.69^\circ \text{K} \)

Figure 4: Dielectric Constant of KTaO₃
Chapter II
GENERAL THEORY OF DIELECTRICS

1. **Introduction.** In the present chapter—and throughout the whole work—discussion will be limited to materials not in the ferroelectric state. Reasons for this will appear as the work progresses. This restriction to the non-ferroelectric state will mean that ferroelectrics such as BaTiO₃ can be considered only above their Curie point or uppermost transition temperature.

While this restriction will necessarily preclude a study of the actual ferroelectric properties of the materials, it will center attention on the question of why the materials become ferroelectric. In this case in which ferroelectrics are most like ordinary dielectrics, the fundamental differences stand out most clearly. Also of interest will be the studies of materials, such as SrTiO₃, which almost become ferroelectric.

2. **The Lorentz Correction.** In order to understand the dielectric behavior of crystals, one must take into account the Lorentz correction to the electric field. Several authors\(^{(7,8,9,10)}\) have recently emphasized the effect this factor may have on ferroelectricity.

To get to an understanding of it, first consider an ion in an electric field but isolated from all other matter. We shall suppose that the dipole moment \(p\) is proportional to the electric field \(E\). Then we may write
\( p = \alpha \mathbf{E} \) where \( \alpha \) will be called the polarizability of the ion.

Next consider, as Lorentz\(^{(1)}\) did originally, a simple cubic lattice composed of identical ions and placed in a uniform electric field \( \mathbf{E} \). The dipole moment of an ion will no longer by given by \( p = \alpha \mathbf{E} \) because of the interactions between the dipoles. The relationship can best be given in terms of the dipole moment per unit volume \( P = p/v \) where \( v \) is the volume of the unit cell. Lorentz showed that \( P = (\alpha/v)\mathbf{E}_{\text{loc}} \) where the local field \( \mathbf{E}_{\text{loc}} = \mathbf{E} + P/3\varepsilon_0 \). In more complicated cases the coefficient \( 1/3 \) of \( P/\varepsilon_0 \) must be replaced by a tensor.

The dielectric constant of this material may now be obtained as follows:\(^{(7)}\)

\[
P = (\alpha/v)(\mathbf{E} + P/3\varepsilon_0) \tag{1}
\]

\[
P = \frac{(\alpha/v)\mathbf{E}}{1 - \alpha/3\varepsilon_0 v} \tag{2}
\]

\[
\chi = \frac{P}{\varepsilon_0 \mathbf{E}} = \frac{\alpha/\varepsilon_0 v}{1 - \alpha/3\varepsilon_0 v} \tag{3}
\]

\[
K = 1 + \chi = 1 + \frac{\alpha/\varepsilon_0 v}{1 - \alpha/3\varepsilon_0 v} = -2 + \frac{3}{1 - \alpha/3\varepsilon_0 v} \tag{4}
\]

From eqn. (4) it can be seen that \( \alpha \) need not be infinite to give an infinite \( K \); it is only necessary that \( \alpha/\varepsilon_0 v = 3 \). When this condition is fulfilled, a polarization with zero electric field—or spontaneous polarization—may exist.

Furthermore if

\[
(\alpha/\varepsilon_0 v) = 3 - 3(T - T_0)/C \tag{5}
\]

then

\[
K = -2 + \frac{C}{T - T_0} \tag{6}
\]
and the material will follow a Curie-Weiss law above $T_0$.

Slater\(^{(7)}\) has considered, in the special case of BaTiO$_3$, the more involved Lorentz correction that is necessary for perovskite type crystals. His notation will be followed as closely as possible. He considered the Lorentz correction for the optical case and for the low frequency case. In the optical case the result is little different from what would be obtained by using the simple Lorentz correction outlined above. In the low frequency case the result is quite different.

For low frequency fields the polarizability of an ion can be separated into electronic and ionic parts. The electronic polarizability is due to the deformation of the electron cloud of an ion in a field. The optical polarizability is just the electronic polarizability.

The ionic polarizability is due to the displacement of an ion as a whole in a field. An ion as a whole cannot follow the rapidly varying field of a light wave because of the large mass of the ion.

To compute the Lorentz correction for the low frequency case Slater used the same values of the electronic polarizabilities that he used for the optical case. In addition he assumed that there would be an ionic polarizability for the Ti ions but not for the others. The basis of this last assumption lies in considerations of the ionic radii involved. These radii seem to indicate that the Ti ions have more space in the lattice than they actually need.
The Ti ions should be loosely bound in this case. If the binding is loose enough, the ionic polarizabilities of the other ions may be neglected. Also, for loose binding, each Ti ion can be treated as an individual oscillator rather than using a normal coordinate treatment.

Since the index of refraction is virtually temperature independent, the electronic polarizabilities must be temperature independent. Then the low frequency dielectric constant can depend on temperature only through $\alpha_{Ti}'$ the ionic polarizability of the titanium ion and through $\gamma$. It is convenient to combine these two quantities into the single quantity $x_{Ti}' = \alpha_{Ti}'/\varepsilon_0\gamma$.

Slater has given a very detailed numerical treatment for BaTiO$_3$. However, the general form of his result can readily be seen from his eqns. (18) and (19) relating the polarization to the field. Due to the linearity of these equations, one can write

$$K = K_0 + \frac{A}{1 - Bx_{Ti}'}$$

(7)

Slater's eqn. (26) is a particular example of this relation for BaTiO$_3$. The constants $K_0$, $A$, and $B$ will depend on the electronic polarizabilities of the ions and on the geometry of the lattice.

3. **Temperature and Pressure Effects.** Now consider the temperature and pressure variations that may enter into $K$ through $x_{Ti}'$. Three separate effects can be distinguished: density effect, relaxation effect, and pure
temperature effect. The first two of these effects will cause both temperature and pressure variations of $K$, while the last one will cause only temperature variation.

The density effect is merely the variation of $K$ due to the factor $v$ in $\lambda_{T_1}'$. The relaxation effect is a bit harder to see. It occurs because the elastic forces between ions are only approximately Hooke’s law forces. If the distance between ions changes slightly, the constant in Hooke’s law must be changed slightly to keep the best approximation to the true force law. This results in a slight change in the ionic polarizability.

The pure temperature effect also comes out of the departure from Hooke’s law forces. As the temperature changes, the amplitudes of vibration of the ions in the lattice will change. This will cause a slight change in the frequency of vibration and effective force constant, causing in turn a change in the polarizability of the ion.

The total temperature effect may be treated as follows. Let $K' = K - K_0$. The three effects noted above may be expressed in the relations $\lambda = \lambda(v,T)$ and $v = v(T,P)$, resulting in $K' = K'(T,P)$. For the present denote $\lambda_{T_1}'$ by just $\lambda$.

$$\frac{1}{K'} = \frac{1}{A} - B \lambda_{T_1}' = \frac{1}{A} - B \frac{\lambda}{\varepsilon_0 v}$$

$$(8)$$

$$\frac{\partial(1/K')}{\partial T} = -\frac{B}{A} \left[ \frac{\lambda}{\varepsilon_0} \frac{\partial(1/v)}{\partial v} \frac{\partial v}{\partial T} + \frac{1}{\varepsilon_0 v} \frac{\partial \lambda}{\partial v} \frac{\partial v}{\partial T} + \frac{1}{\varepsilon_0 v} \frac{\partial \lambda}{\partial T} \right]$$

$$(9)$$

Letting $v = d^3$ and $\beta = \text{linear coefficient of expansion}$,
\[
\frac{\partial (1/v)}{\partial v} \frac{\partial v}{\partial T} = -\frac{3\beta}{v} \tag{10}
\]

\[
\frac{\partial \alpha}{\partial v} \frac{\partial v}{\partial T} = \alpha \frac{d}{\partial \alpha} \frac{\partial \alpha}{\partial \alpha} \beta \tag{11}
\]

and

\[
\frac{\partial (1/K')}{\partial T} = \frac{B}{A} \frac{\alpha}{\varepsilon_0 v} \left[ (3 - \frac{d}{\alpha} \frac{\partial \alpha}{\partial d}) \beta - \frac{1}{\alpha} \frac{\partial \alpha}{\partial T} \right] \tag{12}
\]

Near the Curie point \( B\alpha/\varepsilon_0 v \) is approximately 1.

\[
\frac{\partial (1/K')}{\partial T} = \frac{1}{A} \left[ (3 - \frac{d}{\alpha} \frac{\partial \alpha}{\partial d}) \beta - \frac{1}{\alpha} \frac{\partial \alpha}{\partial T} \right] \tag{13}
\]

The pressure variation is very similar except that \( \partial \alpha/\partial P = 0 \).

\[
\frac{\partial (1/K')}{\partial P} = -\frac{B}{A} \left[ \frac{\alpha}{\varepsilon_0} \frac{\partial (1/v)}{\partial v} \frac{\partial v}{\partial P} + \frac{1}{\varepsilon_0 v} \frac{\partial \alpha}{\partial v} \frac{\partial v}{\partial P} \right] \tag{14}
\]

Letting \( \gamma = \kappa/3 \) where \( \kappa \) is the volume compressibility,

\[
\frac{\partial (1/v)}{\partial v} \frac{\partial v}{\partial P} = \frac{3\gamma}{v} \tag{15}
\]

\[
\frac{\partial \alpha}{\partial v} \frac{\partial v}{\partial P} = -\alpha \frac{d}{\alpha} \frac{\partial \alpha}{\partial d} \gamma \tag{16}
\]

\[
\frac{\partial (1/K')}{\partial P} = -\frac{1}{A} (3 - \frac{d}{\alpha} \frac{\partial \alpha}{\partial d}) \gamma \tag{17}
\]

The relative importance of the various causes of temperature variation of \( K' \) in BaTiO₃ can now be estimated. Using Mason's\(^{(12)}\) data for ceramics, Merz\(^{(13)}\) calculates \( \kappa = 12.2 \times 10^{-3} \) cm.\(^2\)/dyne \( \approx 12.0 \times 10^{-7} \) cm.\(^2\)/kg. This will give \( \gamma = 4.0 \times 10^{-7} \) cm.\(^2\)/kg. Shirane and Sato\(^{(14)}\) measured \( \partial (1/K')/\partial P \) for several samples of barium-strontium titanate mixtures. They found the value 7.3 \( \times 10^{-8} \) cm.\(^2\)/kg. for all of the samples. This would then be expected to be the value for pure BaTiO₃. Slater\(^{(7)}\) has computed \( A \) to be 1.93 and gives 1.5 \( \times 10^5 \) °C for the Curie constant of BaTiO₃. This latter value gives 6.7 \( \times 10^{-6} \) °C\(^{-1} \) for
\( \alpha(1/K')/\alpha T \). Finally, Kay and Vousden's measurements\(^3\) give \( \beta = 1.3 \times 10^{-5} \, \text{C}^{-1} \).

Using these values,

\[
\frac{1}{A}(3 - \frac{d}{x} \frac{dx}{df}) = \frac{1}{r} \frac{\alpha(1/K')}{\alpha T} = -.18
\]  
(18)

\[
\frac{1}{A}(3 - \frac{d}{x} \frac{dx}{df}) \beta = -2.4 \times 10^{-5} \, \text{C}^{-1}
\]  
(19)

\[
-\frac{1}{A} \frac{1}{x} \frac{dx}{dT} = \frac{\alpha(1/K')}{\alpha T} - \frac{1}{A}(3 - \frac{d}{x} \frac{dx}{df}) = 9.1 \times 10^{-6} \, \text{C}^{-1}
\]  
(20)

From eqn. (18) it is seen that the density and relaxation effects almost cancel each other out. Comparison of eqns. (19) and (20) shows that the pure temperature effect is about 4 times the sum of the other two effects. Therefore, it would be expected that the dielectric constant of BaTiO\(_3\)--and probably all other perovskite type crystals--will be determined above the Curie point by the pure temperature effect or constant volume effect.
Chapter III
QUANTUM MECHANICAL TREATMENT OF SLATER'S MODEL

1. Introduction. Having observed that the dielectric behavior of BaTiO₃ above the Curie point must be primarily a pure temperature effect, Slater(7) has proposed a theory of such an effect. His model treats the crystal as though the Ba and O ions were fixed in position and as though each Ti ion acted like an independent harmonic oscillator with small additional anharmonic forces. The Ti ion is supposed to be very loosely bound, and the only interaction between these oscillators is through the electric field. The system was then treated by statistical mechanics in a completely classical fashion. It has seemed desirable to find also the results of a quantum mechanical treatment, particularly at low temperatures.

2. Derivation of the Quantum Mechanical Formula. Following Slater, let the potential energy of the Ti ion with charge q in an electric field be given by

$$\phi = a(x^2 + y^2 + z^2) + b_1(x^4 + y^4 + z^4) + 2b_2(x^2y^2 + x^2z^2 + y^2z^2) - q(\mathbf{E}_x + \mathbf{E}_y + \mathbf{E}_z)$$

(21)

Let the part of $\phi$ independent of the $b$'s be called $\phi_1$ and the part containing the $b$'s be called $\phi_2$. Treat $\phi_2$ as a perturbation on $\phi_1$. Let

$$x' = x - \frac{q\mathbf{E}_x}{2a}, \quad y' = y - \frac{q\mathbf{E}_y}{2a}, \quad z' = z - \frac{q\mathbf{E}_z}{2a}$$

(22)
Then
\[ \phi_1 = a(x'^2 + y'^2 + z'^2) - \frac{qE^2}{4a} \]  \hspace{1cm} (23)

Schroedinger's equation is
\[ \mathcal{H} \psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + \phi_1 \right) \psi = \varepsilon \psi \]  \hspace{1cm} (24)

The characteristic energies and characteristic solutions will be
\[ W_{rst} = (r + s + t + 3/2)\hbar \nu - \frac{qE^2}{4a} \]  \hspace{1cm} (25)

\[ \psi_{rst} = F_r(\sqrt{\theta} \ x') \ F_s(\sqrt{\theta} \ y') \ F_t(\sqrt{\theta} \ z') \]  \hspace{1cm} (26)

where
\[ \beta = \frac{2a}{\hbar \nu}, \quad \nu = \frac{1}{2 \pi \sqrt{m}} \]  \hspace{1cm} (27)

and the \( F_r(\sqrt{\theta} \ x') \) are the Hermite normalized orthogonal functions of \( x' \). This unperturbed problem is just that of a simple harmonic oscillator in an electric field.

The zero order energy levels above are degenerate so that the first order perturbations \( W_{rst}^1 \) must be obtained by solving a series of determinants. Assuming that the energy perturbations are small compared to \( kT \), one can use the approximation
\[ e^{-\frac{W_{rst}^1}{kT}} = 1 - \frac{W_{rst}^1}{kT} \]  \hspace{1cm} (28)

The justification of this approximation will be considered in sec. 4 of this chapter. For any group of levels having the same unperturbed energy, the sum of the energy perturbations is equal to the sum of the diagonal matrix elements. Then using an approximation similar to eqn. (28) with the diagonal matrix elements in place of the energy perturbations, it can be seen that the diagonal matrix elements
may be used in place of the true first order energy perturbations to compute the partition function.

In order to compute the matrix elements, it will be necessary to use the following integrals:

\[
\int_{-\infty}^{\infty} x'^m \left| F_r(\sqrt{\beta} x') \right|^2 \, dx' = \begin{cases} 
1 & \text{if } m = 0 \\
\frac{2r+1}{2} & \text{if } m = 2 \\
\frac{3(2r^2+2r+1)}{4} & \text{if } m = 4 \\
0 & \text{if } m = 1 \text{ or } 3 
\end{cases} 
\] (29)

Substituting in \( \phi_2 \) for \( x, y, \) and \( z \) in terms of \( x', y', \) and \( z' \) by means of eqns. (22) and using eqn. (29), the diagonal matrix elements \( \langle \text{rst} | \phi_2 | \text{rst} \rangle \) are given by

\[
\langle \text{rst} | \phi_2 | \text{rst} \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \phi_2(x',y',z') \left| \psi_{\text{rst}}(x',y',z') \right|^2 \, dx' \, dy' \, dz' 
\]

\[
= b_1 \left\{ \frac{3a^2}{\sqrt{\beta}} \left[ (2r^2+2r+1)+(2s^2+2s+1)+(2t^2+2t+1) \right] + \frac{3a^2}{4a}\left[ (2r+1)E_x^2+(2s+1)E_y^2+(2t+1)E_z^2 \right] + \frac{a^4}{16a} \left[ E_x^4+E_y^4+E_z^4 \right] \right\} 
\]

\[
+ 2b_2 \left\{ \frac{1}{\sqrt{\beta}} \left[ (2r+1)(2s+1)+(2r+1)(2t+1)+(2s+1)(2t+1) \right] + \frac{a^2}{8a^2} \left[ (2r+1)(E_x^2+E_z^2)+(2s+1)(E_x^2+E_z^2)+(2t+1)(E_x^2+E_z^2) \right] + \frac{a^4}{16a^4} \left[ E_x^2E_y^2+E_x^2E_z^2+E_y^2E_z^2 \right] \right\} 
\] (30)
Let $z$ be the partition function of an individual oscillator and $Z$ be the partition function for $N$ oscillators contained in unit volume.

$$z = \sum_{r,s,t=0}^{\infty} \sum \frac{W_{rst}^0(rst | \varphi_2 | rst)}{kT}$$

$$Z = z^N_{N!} \quad (31)$$

In evaluating $z$ use will be made of the following expressions:

$$\sum_{m=0}^{\infty} m e^{-mx} = \frac{1}{1 - e^{-x}} \quad (33)$$

$$\sum_{m=0}^{\infty} m e^{-mx} = \sum_{m=0}^{\infty} \frac{d}{dx}(e^{-mx}) = - \frac{d}{dx} \left( \frac{1}{1 - e^{-x}} \right)$$

$$\sum_{m=0}^{\infty} m^2 e^{-x} = \sum_{m=0}^{\infty} \frac{d^2}{dx^2}(e^{-mx}) = \frac{d^2}{dx^2} \left( \frac{1}{1 - e^{-x}} \right)$$

Now

$$z = e^{\frac{-3h\nu}{2kT}} \cdot \frac{-W_0}{kT} \left(1 - \frac{h\nu}{kT} \right)^{-3}$$

$$\cdot \left\{ 1 - \frac{(3b_1 + 2b_2)}{kT} \left[ \frac{3(h\nu)^2}{16a^2} \coth^2 \frac{h\nu}{2kT} + \frac{q^2E_2^2h\nu}{8a^3} \coth \frac{h\nu}{2kT} \right] \right\}$$

where

$$W_0 = -\frac{q^2E_2^2}{4a} + \frac{q^4}{16a^4} \left[ b_1(E_x^4 + E_y^4 + E_z^4) + 2b_2(E_x^2E_y^2 + E_x^2E_z^2 + E_y^2E_z^2) \right]$$

From $Z$ can be obtained the Helmholtz potential $A_E$ by

$$A_E = -kT \ln Z. \quad \text{The subscript } E \text{ serves to denote that}$$
the electric field is an independent variable. Using Stirling's approximation for $N!$ and the approximation $\ln(1+x) \approx x$ for the factor enclosed in braces in eqn. (34),

$$A_E = \frac{3}{2}N\hbar \nu + NkT \ln \left[ \frac{N_e}{N} \left( 1 - e^{-\frac{\hbar \nu}{kT}} \right)^3 \right]$$

$$+ \frac{3N(3b_1+2b_2)}{16a^2} (\hbar \nu)^2 \coth^2 \frac{\hbar \nu}{2kT}$$

$$- \frac{NqE^2}{4a} \left[ 1 - \frac{(3b_1+2b_2)\hbar \nu}{2a^2} \coth \frac{\hbar \nu}{2kT} \right]$$

$$+ \frac{Nq^4}{16a^4} \left[ b_1(E^4_x + E^4_y + E^4_z) + 2b_2(E^2_x E^2_y + E^2_x E^2_z + E^2_y E^2_z) \right]$$

(35)

The polarization can be obtained from $A_E$ by

$$P_x = -\frac{\partial A_E}{\partial E_x} = \frac{Nq^2E_x}{2a^2} \left[ 1 - \frac{(3b_1+2b_2)\hbar \nu}{2a^2} \coth \frac{\hbar \nu}{2kT} \right]$$

(36)

neglecting higher powers of $E$. Neglecting the higher powers of $E$ restricts the rest of the discussion to the case in which there is no spontaneous polarization.

The ionic polarizability of the Ti ions can now be obtained,

$$P_x = \frac{\alpha_{Ti}'}{\nu} E_x = N \alpha_{Ti} ' E_x$$

so that

$$\alpha_{Ti} ' = \frac{q^2}{2a^2} \left[ 1 - \frac{(3b_1+2b_2)\hbar \nu}{2a^2} \coth \frac{\hbar \nu}{2kT} \right]$$

(37)

This formula will be good in the absence of spontaneous polarization and for sufficiently weak fields.
The following two relations will hold at high and low temperatures.

\[ \coth \frac{\hbar \nu}{2kT} \approx \frac{2kT}{\hbar \nu} \quad \text{as } T \to \infty \]  \hspace{1cm} (38)

\[ \coth \frac{\hbar \nu}{2kT} \to 1 \quad \text{as } T \to 0 \]  \hspace{1cm} (39)

Using eqn. (38), it can be shown that the quantum mechanical discussion above reduces to Slater's classical discussion\(^{(7)}\) for \(kT \gg \hbar \nu\).

3. **Applicability of the Quantum Mechanical Formula.**

Combining eqns. (37) and (7) and assuming \(K_0\) is negligible gives

\[ K = \frac{M}{\frac{T_1}{2} \coth \frac{T_1}{2T} - T_0} \]  \hspace{1cm} (40)

where

\[ T_1 = \frac{\hbar \nu}{k} \]  \hspace{1cm} (41)

\[ M = \frac{2a^3 \varepsilon_0 \nu A}{q^2 (3b_1 + 2b_2) k_B} \]  \hspace{1cm} (42)

\[ T_0 = \frac{2a^3 \varepsilon_0 \nu}{q^2 (3b_1 + 2b_2) k_B} \left( \frac{Bq^2}{2a^3 \varepsilon_0 \nu} - 1 \right) \]  \hspace{1cm} (43)

The behavior of eqn. (40) as applied to SrTiO\(_3\) and KTaO\(_3\) is shown in figs. (3) and (4). In each case \(M, T_1,\) and \(T_0\) are adjusted to give the best fit to the experimental data. The dashed portion of the curve for sample 2 in fig. 4 indicates the predicted behavior of \(K\) if the material did not become ferroelectric. The constants \(M, T_1,\) and \(T_0\) are
not known to the precision indicated by the significant figures. However, when any two are specified, the other must be specified to the indicated accuracy in order to get the best possible fit.

For $T \gg T_1$, $\frac{4T_1}{\alpha} \coth(T_1/2T)$ asymptotically approaches $T$ and (40) becomes a Curie-Weiss law. As $T$ approaches $0^\circ K$, $K$ will approach $M/(4T_1 - T_0)$. Roughly it may be said that $T_1$ is the dividing point between the low temperature region where quantum effects are important and $K$ deviates from a Curie-Weiss law and the high temperature region where a classical approximation and a Curie-Weiss law are good. If a material undergoes a transition to the ferroelectric state at a temperature above $T_1$, the quantum effect will be unnoticed.

How well this theory may be applied to BaTiO$_3$ may be seen as follows. Using Slater's value of $a = 7.8 \ \text{n}^2 \ \text{ev./A}^2 = 1.2 \times 10^2 \ \text{n}^2 \ \text{joules/m.}^2$ and $m$ as the mass of the titanium atom gives $T_1 = 410 \ ^\circ \text{n}$ degrees absolute where $n$ is the number of electronic charges on the Ti ion. Since the Curie-Weiss law holds in BaTiO$_3$ down to the transition temperature at about $390^\circ K$, $n$ cannot be much above 1.

Consider the values of the constants in eqn. (40) in the case of BaTiO$_3$. Experimentally $M = 1.5 \times 10^5$, $T_0 = 390^\circ K$ and Slater has computed $A = 1.93$. This gives

$$\frac{2a^3e^2v}{q^2(3b_1+2b_2)kB} \sim 10^5$$ (44)
\[
\left( \frac{Bq^2}{2\epsilon_0 V} - 1 \right) \sim 4 \times 10^{-3}
\]  

Eqn. (45) may be said to be zero so that

\[ a = \frac{Bq^2}{2\epsilon_0 V} \]  

as Slater has given in his eqn. (29) with \( \overline{\beta} = 5.39 \).

Now it seems reasonable that the quantities involved in eqn. (40), excepting \( T_0 \), will be of the same order of magnitude for other compounds of the same structure as BaTiO_3. The \( T_0 \) can vary quite drastically because it is determined by the difference of two very nearly equal quantities. Nevertheless it will still be expected that the order of magnitude indicated in eqn. (45) will still hold and that eqn. (46) will still apply.

It also seems of some interest that the behavior of LiTlC_4H_4O_6H_2O, reported recently by Matthias and Hulm\(^{15}\), above its transition to the ferroelectric state follows something of the nature of eqn. (40). Of course the theory given here could not be expected to fit this case because of the entirely different crystal structure. However, any model having discrete energy levels will cause \( k \) to level off near absolute zero because the system settles into the ground state and thereby loses its temperature dependence.

4. **Justification of the Approximation to the Exponential.**

In sec. 2 of this chapter the approximation in eqn. (28) and a similar one, involving the diagonal matrix elements
in place of the energy perturbations, were used. The validity of these must be examined after the values of certain constants are determined. Since the energy perturbations and diagonal matrix elements are of the same order of magnitude, the two approximations will both be good or both be bad. The one involving the matrix elements will be examined.

Assuming $b_1 = b_2 = b$ and using eqns. (42) and (46),

$$\frac{b}{a^2} = \frac{A}{5Mk} \tag{47}$$

It can be seen from eqn. (30) that the validity of the approximation in question depends on

$$\frac{b}{a^2kT} \ll 1 \tag{48}$$

Using eqns. (27) and (41),

$$\frac{b}{a^2kT} = \frac{AT_1}{20M} \frac{T_1}{T} \tag{49}$$

The quantities $T_1$ and $M$ can be determined experimentally, but $A$ cannot. Slater finds $A = 3$ for the simple Lorentz correction and $A = 1.93$ for his more involved theory. Since $A$ varies but little for these two quite different situations, it seems safe to assume an upper limit of 10 in general.

Now for SrTiO$_3$ at $T = 100^\circ$ K, $b/a^2kT = 7 \times 10^{-4}$. At $T = 50^\circ$ K, $b/a^2kT = 1.4 \times 10^{-2}$. Somewhat below $50^\circ$ K the
expansion will fail even for the ground state. However, note that at $5^\circ$, $\exp(-\frac{\hbar \nu}{kT}) = \exp(-20) = 2 \times 10^{-9}$. Then at $5^\circ$ K the system will be practically in its ground state and $\mathcal{z}$ will consist of only one term

$$
- \frac{w_{A00}^0 \exp(000 | 0, 2 | 000)}{kT}
$$

This will mean that $A_2$ and hence $X_{Ti}'$ and $k$ will be temperature independent. But at $5^\circ$ K the formula (40) given for $k$ is already virtually temperature independent since

$$
\frac{dk}{dT} = -5 \times 10^{-4} \quad \Omega_k^{-1}
$$

(50)

$$
\frac{1}{k} \frac{dk}{dT} = -8 \times 10^{-8} \quad \Omega_k^{-1}
$$

(51)

Some consideration should also be given to the validity of using the approximation to the exponential at high temperatures. At any given temperature the expansion will fail for sufficiently large $r$, $s$, and $t$. It is necessary to depend on the rapid decrease of $\exp[-(r+s+t)\hbar \nu/kT]$ as $r$, $s$, and $t$ increase in order to make the failure of the approximation unimportant. As $T$ increases, $\hbar \nu/kT$ will decrease to a point where the exponential factor will no longer decrease rapidly enough with $r$, $s$, and $t$ to make failure of the approximation for large quantum numbers unimportant. In order to estimate at what temperature this effect becomes important, a quadratic term was added to the approximation to the exponential and its effect on
\( \alpha_{Ti} \)' was computed. For BaTiO\( _3 \) at 500\(^\circ\) K the contribution of the quadratic term was about one per cent of that from the linear term. As the temperature increases, the ratio of the quadratic contribution to the linear contribution will be proportional to the temperature. Hence it is felt that the formula for \( \alpha_{Ti} \)' is good at all temperatures at which the dielectric constant can be measured.

5. Discussion of a Discrepancy. We may expect the quantities involved in the theory—excepting \( T_0 \)—to be roughly the same value for other perovskite type crystals as for BaTiO\( _3 \). This should be particularly true among the titanates. But there is very poor agreement between the value of \( T_1 = 98^\circ \) K obtained for SrTiO\( _3 \) by fitting the above theory to the experimental data and the value of \( T_1 = 410 \) \( ^\circ \) degrees absolute obtained for BaTiO\( _3 \) by using the value of \( \alpha \) obtained by Slater's theory. Let us examine the factors which influence \( T_1 \) as calculated for BaTiO\( _3 \).

The mass \( m \) to be used in calculating \( \nu \) might be larger than that of the Ti due to a coupling of the Ti ion to the other ions of the lattice in a normal coordinate vibration. But even using the sum of the masses of all the ions in a unit cell only reduces the value of \( T_1 \) by a factor of slightly more than 2. Normal vibrations of BaTiO\( _3 \) are considered in some detail in the following chapter.

A small value of \( n \) cannot be used to secure agreement because, as Slater has pointed out, experimental data on spontaneous polarization and X-ray data on the ionic
displacements rule against a value of \( n < 1 \). The value of \( a \) cannot be expected to change enough between the two compounds to account for the difference between the values of \( T_1 \). If the value of \( B \) were more nearly the Lorentz value of \( 1/3 \), rather than the value of 5.39 computed by Slater, the \( a \) for BaTiO\(_3\) would be small enough to reduce \( T_1 \) by a factor of 4. However, such a change does not seem possible unless rather large changes are made in the electronic polarizabilities and other quantities used in Slater’s work.

In this connection it is interesting to note that the vibration of the Ti ions corresponds to a reststrahlen frequency. Since the binding is supposed to be very loose, the frequency should be unusually low. However, a frequency \( \nu \) which gives \( h\nu/k \) of the order of 400° K is not at all low. It seems that the large Lorentz correction which Slater has computed has made ferroelectricity possible with bindings ordinarily found in crystals. Measurement of the reststrahlen frequencies would provide another means of determining the two values of \( T_1 \). Without such measurements there seems to be no explanation of the difference in \( T_1 \) between BaTiO\(_3\) and SrTiO\(_3\).

6. **Electrocaloric Effect.** From the similarity between the behavior of ferroelectric materials and paramagnetic effects at low temperatures, it might be supposed that reversible temperature changes could be caused in ferroelectrics by the adiabatic application and removal of
electric fields. This has been tried by Schmitt\(^{(16)}\) at liquid helium temperatures with BaTiO\(_3\). The result was roughly equal heatings on application and removal of the field. This would appear to be due to the hysteresis effects which are known to be present in BaTiO\(_3\) in the ferroelectric state. It seemed that there would be a better chance of success if a material were used which was still above the Curie point at low temperatures. Accordingly, Swim\(^{(17)}\) looked for the electrocaloric effect in SrTiO\(_3\). The result in this case was also roughly equal heatings on application and removal of the field.

Schmitt concluded that the heatings in BaTiO\(_3\) were due to irreversible effects and that the apparent temperature gradient of \(K\) at low temperatures was due to the increase of the coercive field at low temperatures. In order to discuss the heatings in SrTiO\(_3\) a little must be said about the theory of the electrocaloric effect.

If it is assumed that pressure-volume changes are negligible but that electric field changes are not,

\[
dU = T \, dS + E \, dD \tag{52}
\]

where the symbols have their usual thermodynamic and electrical significance. The Helmholtz potential will be

\[
A = U - ED - TS \tag{53}
\]

Then

\[
dA = - S \, dT - D \, dE \tag{54}
\]
and
\[ (\frac{\partial D}{\partial T})_E = (\frac{\partial S}{\partial E})_T \] (55)

During an isothermal process
\[ dQ = T \, dS = T (\frac{\partial S}{\partial E})_T \, dE = T (\frac{\partial D}{\partial T})_E \, dE = \epsilon_e \, E T (\frac{\partial K}{\partial T})_E \, dE \]
\[ dQ = \frac{\epsilon_e \, T (\frac{\partial K}{\partial T})_E}{2} \, d(E^2) \] (56)

If it is assumed that the temperature change is small and that \( K \) is independent of \( E \), then for an adiabatic process,
\[ dT = -\frac{dQ}{C_v} = -\frac{\epsilon_e \, T (\frac{\partial K}{\partial T})_E}{2C_v (\frac{\partial K}{\partial T})_E} \, d(E^2) \] (57)

At the low temperatures involved \( C_v \) may be assumed to follow a Debye \( T^3 \) law. Using eqn. (40) for \( K \), one can predict the temperature at which the maximum temperature change occurs. For \( SrTiO_3 \) this is found to be \( 21^\circ \, K \). To calculate the actual temperature change a value of the Debye theta must be assumed. The estimated temperature change will be conservative if a low value of \( 150^\circ \, K \) is assumed. Now, at the optimum temperature of \( 21^\circ \, K \), the estimated temperature change is \( 0.07^\circ \, K \) for a change in \( E \) of \( 0 \) to \( 10^4 \) volts/cm.

At \( 21^\circ \, K \), \( \frac{\partial K}{\partial T} = 100 \, ^\circ K^{-1} \). It is interesting to compare this value with that given in eqn. (50). This indicates that the temperature change at \( 5^\circ \, K \) would be about \( 10^{-4} \) of the change at \( 21^\circ \, K \). In view of this it is not at all surprising that Swim observed only irreversible effects.
The exact nature of these irreversible effects can perhaps be understood by considering the measurements shown in fig. (3) and for sample 2 in fig. (4) and the methods used to obtain them. The two substances are different chemical compounds, SrTiO$_3$ and KTaO$_3$, and are prepared by different methods, one being a ceramic and the other a single crystal. However, in view of the overall similarities between the two curves, it seems a bit strange that one becomes ferroelectric while the other one does not.

The means used by Youngblood$^5$ to obtain the measurements on SrTiO$_3$ was a capacitance bridge. The field applied to the sample in this method was a few volts/cm. The means used by Hulm, Matthias, and Long$^6$ to obtain the measurements on KTaO$_3$ was the observation with an oscilloscope of hysteresis loops. The field applied to the sample in this method was a few thousand volts/cm.

It seems plausible, if not probable, that the transition to the ferroelectric state in the case of KTaO$_3$ is induced by the strong electric fields used in the measurements. Caspari and Merz$^{18}$ have reported a similar occurrence for BaTiO$_3$. They observed that the application of strong electric fields immediately above the Curie temperature caused the appearance of domains or a transition to the ferroelectric state.

This supposition of a strong electric field causing a transition to the ferroelectric state in SrTiO$_3$ and KTaO$_3$
at low temperatures can easily be and should be checked experimentally before being accepted. If it proves true, it should explain Swim's observations on SrTiO$_3$. 
Chapter IV
NORMAL VIBRATIONS OF BaTiO₃

1. Relationship to Dielectric Properties. In the previous chapter Slater’s model of BaTiO₃ was discussed. This model treated the Ti ions as independent oscillators rather than using normal vibrations. Now the task will be to formulate a normal vibration treatment. The discussion will be confined to the temperature range above 120° C where the crystal is cubic.

Fortunately—for BaTiO₃ will be seen to have very complicated normal vibrations—not all the modes of motion need be studied. The only modes which can have a resultant macroscopic polarization are the ones having very long or infinite wave length. These then are the only ones which need to be considered for the present purposes. Some discussion relative to this point has been given by Szigeti.\(^{(19)}\)

2. Equations of Motion. For a general treatment of the theory of normal vibrations, the reader is referred to Seitz.\(^{(20)}\) Although his method of approach will be used in the following, his notation will not be followed.

In order to establish the necessary terminology, reference will be made back to fig. 1. The ions making up the unit cell will be denoted as follows. The O ion lying along the \(x\)-axis from the Ti ion will be denoted by the subscript 1, that along the \(y\)-axis by 2, and that
along the $z$-axis by 3. The Ti ion will be denoted by a subscript 4, and the Ba ion by a subscript 5. The mass of the O ion will be denoted by $m_0$, the mass of the Ti ion by $m_{Ti}$, and the mass of the Ba ion by $m_{Ba}$.

Suppose that the crystal of $BaTiO_3$ being considered is a rectangular parallelepiped with $A$ unit cells in the $x$-direction, $B$ unit cells in the $y$-direction, and $C$ unit cells in the $z$-direction. Specify the locations of the various cells by the set of numbers $(a, b, c)$ where $a = 1, 2, \ldots, A$; $b = 1, 2, \ldots, B$; $c = 1, 2, \ldots, C$. Let the edge of the unit cube be $2d$. Arrange the origin of the coordinate system so that the various types of ions are located at the following sets of points:

- Ti -- [2ad, 2bd, 2cd]
- Ba -- [(2a+1)d, (2b+1)d, (2c+1)d]
- O$_1$ -- [(2a+1)d, 2bd, 2cd]
- O$_2$ -- [2ad, (2b+1)d, 2cd]
- O$_3$ -- [2ad, 2bd, (2c+1)d]

Displacements of the various ions from their equilibrium positions will be denoted by $x$, $y$, and $z$ components with the appropriate subscripts in terms of $a$, $b$, and $c$.

The forces to be treated here will be central forces of a Hooke's law type. The electrical forces involved have been discussed by many authors such as Kellerman$^{(21)}$ and Broch.$^{(22)}$ However, the electrical forces will not be considered since they will be included in the Lorentz
factor. The present interest is in the elastic forces.
It will be assumed that the forces to be considered are
those for which the Hooke's constant is given in Table I.

<table>
<thead>
<tr>
<th>Force Constant</th>
<th>Between Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>Ti--6 nearest O, O--2 nearest Ti</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>Ti--3 nearest Ba, Ba--8 nearest Ti</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>Ba--12 nearest O, O--4 nearest Ba</td>
</tr>
<tr>
<td>( k_4 )</td>
<td>Ba--6 nearest Ba</td>
</tr>
<tr>
<td>( k_5 )</td>
<td>O--8 nearest O</td>
</tr>
<tr>
<td>( k_6 )</td>
<td>O--4 next-nearest O</td>
</tr>
</tbody>
</table>

Because of the symmetry of the crystal, it will only
be necessary to write down four of the fifteen basic
equations of motion. The other eleven may be obtained
from these four by suitable permutations of the coordinate
axes. The four necessary are eqns. (58) through (61).
Eqn. (58) is for the motion of an \( O_1 \) ion in the \( \mathbf{x} \)-direction,
(59) is for the motion of an \( O_1 \) ion in the \( \mathbf{y} \)-direction,
(60) is for the motion of a Ti ion in the \( \mathbf{x} \)-direction,
and (61) is for the motion of a Ba ion in the \( \mathbf{x} \)-direction.

The boundary conditions will be assumed to be the
Born-von Karman cyclic conditions.
\[ m_0 \frac{d^2x_{2a+1,2b,2c}}{dt^2} = -k_1 \left[ (x_{2a+1,2b,2c} - x_{2a+2,2b,2c}) \right. \\
\left. - (x_{2a,2b,2c} - x_{2a+1,2b,2c}) \right] \\
-k_5 \left\{ \frac{1}{2} \left[ (x_{2a+1,2b,2c} - x_{2a+2,2b+1,2c}) \right. \\
\left. - (x_{2a,2b-1,2c} - x_{2a+1,2b,2c}) \right. \\
\left. + (y_{2a+1,2b,2c} - y_{2a+2,2b+1,2c}) \right. \\
\left. - (y_{2a,2b-1,2c} - y_{2a+1,2b,2c}) \right] \right\}^{(1/2)} \left[ (x_{2a+1,2b,2c} - x_{2a+2,2b-1,2c}) \right. \\
\left. - (x_{2a,2b+1,2c} - x_{2a+1,2b,2c}) \right. \\
\left. - (y_{2a+1,2b,2c} - y_{2a+2,2b-1,2c}) \right. \\
\left. + (y_{2a,2b+1,2c} - y_{2a+1,2b,2c}) \right] \right\} \tag{58} \\
\left\{ \frac{1}{2} \left[ (x_{2a+1,2b,2c} - x_{2a+2,2b,2c+1}) \right. \\
\left. - (x_{2a,2b,2c-1} - x_{2a+1,2b,2c}) \right. \\
\left. + (z_{2a+1,2b,2c} - z_{2a+2,2b,2c+1}) \right. \\
\left. - (z_{2a,2b,2c-1} - z_{2a+1,2b,2c}) \right] \right\}^{(1/2)} \left[ (x_{2a+1,2b,2c} - x_{2a+2,2b,2c-1}) \right. \\
\left. - (x_{2a,2b,2c+1} - x_{2a+1,2b,2c}) \right. \\
\left. - (z_{2a+1,2b,2c} - z_{2a+2,2b,2c-1}) \right. \\
\left. + (z_{2a,2b,2c+1} - z_{2a+1,2b,2c}) \right] \right\} \]
\[
\frac{d^2 y_{2a+1,2b,2c}}{dt^2} = \\
\begin{align*}
-k_6 \left[ (y_{2a+1,2b,2c} - y_{2a+1,2b+2,2c}) \\
- (y_{2a+1,2b-2,2c} - y_{2a+1,2b,2c}) \right] \\
-k_5 \{(1/2)\left[ (y_{2a+1,2b,2c} - y_{2a+2,2b+1,2c}) \\
- (y_{2a,2b-1,2c} - y_{2a+1,2b,2c}) \\
+ (x_{2a+1,2b,2c} - x_{2a+2,2b+1,2c}) \\
- (x_{2a,2b-1,2c} - x_{2a+1,2b,2c}) \right] \\
+ (1/2)\left[ (y_{2a+1,2b,2c} - y_{2a,2b+1,2c}) \\
- (y_{2a+2,2b-1,2c} - y_{2a+1,2b,2c}) \\
- (x_{2a+1,2b,2c} - x_{2a+2,2b+1,2c}) \\
+ (x_{2a+2,2b-1,2c} - x_{2a+1,2b,2c}) \right] \right]\] \\
-k_3 \{(1/2)\left[ (y_{2a+1,2b,2c} - y_{2a+1,2b+1,2c+1}) \\
- (y_{2a+1,2b-1,2c-1} - y_{2a+1,2b,2c}) \\
+ (z_{2a+1,2b,2c} - z_{2a+1,2b+1,2c+1}) \\
- (z_{2a+1,2b-1,2c-1} - z_{2a+1,2b,2c}) \right] \\
+ (1/2)\left[ (y_{2a+1,2b,2c} - y_{2a+1,2b+1,2c-1}) \\
- (y_{2a+1,2b-1,2c+1} - y_{2a+1,2b,2c}) \\
- (z_{2a+1,2b,2c} - z_{2a+1,2b+1,2c-1}) \\
+ (z_{2a+1,2b-1,2c+1} - z_{2a+1,2b,2c}) \right] \right]\)
\]
\[
\frac{d^2 x_2a,2b,2c}{dt^2} =
- k_1 \left[ \begin{pmatrix} x_2a,2b,2c - x_2a+1,2b,2c \\ - (x_2a-1,2b,2c - x_2a,2b,2c) \end{pmatrix} \right]
- k_2 \left\{ \frac{1}{3} \left[ \begin{pmatrix} x_2a,2b,2c - x_2a+1,2b+1,2c+1 \\ - (x_2a-1,2b-1,2c-1 - x_2a,2b,2c) \\ + \left( y_2a,2b,2c - y_2a+1,2b+1,2c+1 \right) \\ - \left( y_2a-1,2b-1,2c-1 - y_2a,2b,2c \right) \\ + \left( z_2a,2b,2c - z_2a+1,2b+1,2c+1 \right) \\ - \left( z_2a-1,2b-1,2c-1 - z_2a,2b,2c \right) \right] \right\}
+ \frac{1}{3} \left[ \begin{pmatrix} x_2a,2b,2c - x_2a+1,2b+1,2c-1 \\ - (x_2a-1,2b-1,2c+1 - x_2a,2b,2c) \\ + \left( y_2a,2b,2c - y_2a+1,2b+1,2c-1 \right) \\ - \left( y_2a-1,2b-1,2c+1 - y_2a,2b,2c \right) \\ + \left( z_2a,2b,2c - z_2a+1,2b+1,2c-1 \right) \\ - \left( z_2a-1,2b-1,2c+1 - z_2a,2b,2c \right) \right] \right\}
+ \frac{1}{3} \left[ \begin{pmatrix} x_2a,2b,2c - x_2a+1,2b-1,2c+1 \\ - (x_2a-1,2b+1,2c-1 - x_2a,2b,2c) \\ - \left( y_2a,2b,2c - y_2a+1,2b-1,2c+1 \right) \\ + \left( y_2a-1,2b+1,2c-1 - y_2a,2b,2c \right) \\ + \left( z_2a,2b,2c - z_2a+1,2b-1,2c+1 \right) \\ - \left( z_2a-1,2b+1,2c-1 - z_2a,2b,2c \right) \right] \right\}
+ \frac{1}{3} \left[ \begin{pmatrix} x_2a,2b,2c - x_2a+1,2b-1,2c-1 \\ - (x_2a-1,2b+1,2c+1 - x_2a,2b,2c) \\ - \left( y_2a,2b,2c - y_2a+1,2b-1,2c-1 \right) \\ + \left( y_2a-1,2b+1,2c+1 - y_2a,2b,2c \right) \\ - \left( z_2a,2b,2c - z_2a+1,2b-1,2c-1 \right) \\ + \left( z_2a-1,2b+1,2c+1 - z_2a,2b,2c \right) \right] \right\}
\]

\[
\frac{d^2x_{2a+1,2b+1,2c+1}}{dt^2} = m_{Ba} \left[ -k_4 \left[ (x_{2a+1,2b+1,2c+1} - x_{2a+3,2b+1,2c+1}) ight.ight. \\
- (x_{2a-1,2b+1,2c+1} - x_{2a+1,2b+1,2c+1}) \left. \right] \\
-k_3 \left\{ (1/2) \left[ (x_{2a+1,2b+1,2c+1} - x_{2a+2,2b+2,2c+1}) ight. \right. \\
- (x_{2a+2,2b+2,2c+1} - x_{2a+1,2b+1,2c+1}) \left. \right. \\
+ (y_{2a+1,2b+1,2c+1} - y_{2a+2,2b+2,2c+1}) \left. \right. \\
- (y_{2a+2,2b+2,2c+1} - y_{2a+1,2b+1,2c+1}) \left. \right] \left. \right] \\
+ (1/2) \left[ (x_{2a+1,2b+1,2c+1} - x_{2a+2,2b+2,2c+1}) ight. \right. \\
- (x_{2a+2,2b+2,2c+1} - x_{2a+1,2b+1,2c+1}) \left. \right. \\
- (y_{2a+1,2b+1,2c+1} - y_{2a+2,2b+2,2c+1}) \left. \right. \\
+ (y_{2a+2,2b+2,2c+1} - y_{2a+1,2b+1,2c+1}) \left] \right. (61) \right. \\
+ (1/2) \left[ (x_{2a+1,2b+1,2c+1} - x_{2a+2,2b+2,2c+1}) ight. \right. \\
- (x_{2a+2,2b+2,2c+1} - x_{2a+1,2b+1,2c+1}) \left. \right. \\
+ (z_{2a+1,2b+1,2c+1} - z_{2a+2,2b+1,2c+2}) \left. \right. \\
- (z_{2a+2,2b+1,2c+2} - z_{2a+1,2b+1,2c+1}) \left. \right] \right. \\
+ (1/2) \left[ (x_{2a+1,2b+1,2c+1} - x_{2a+2,2b+2,2c}) ight. \right. \\
- (x_{2a+2,2b+2,2c} - x_{2a+1,2b+1,2c+1}) \left. \right. \\
- (z_{2a+1,2b+1,2c+1} - z_{2a+2,2b+1,2c}) \left. \right. \\
+ (z_{2a+2,2b+1,2c} - z_{2a+1,2b+1,2c+1}) \right. \right] \right. \\
(continued on next page)
(continuing eqn. 61 from preceding page)

\[-k_2\left\{(1/3) \left[ (x_{2a+1,2b+1,2c+1} - x_{2a+2,2b+2,2c+2})
- (x_{2a,2b,2c} - x_{2a+1,2b+1,2c+1})
+ (y_{2a+1,2b+1,2c+1} - y_{2a+2,2b+2,2c+2})
- (y_{2a,2b,2c} - y_{2a+1,2b+1,2c+1})
+ (z_{2a+1,2b+1,2c+1} - z_{2a+2,2b+2,2c+2})
- (z_{2a,2b,2c} - z_{2a+1,2b+1,2c+1}) \right] \right\} \]

\[+ (1/3) \left[ (x_{2a+1,2b+1,2c+1} - x_{2a+2,2b+2,2c+2})
- (x_{2a,2b,2c+2} - x_{2a+1,2b+1,2c+1})
+ (y_{2a+1,2b+1,2c+1} - y_{2a+2,2b+2,2c+2})
- (y_{2a,2b,2c+2} - y_{2a+1,2b+1,2c+1})
+ (z_{2a+1,2b+1,2c+1} - z_{2a+2,2b+2,2c+2})
- (z_{2a,2b,2c+2} - z_{2a+1,2b+1,2c+1}) \right] \]

\[+ (1/3) \left[ (x_{2a+1,2b+1,2c+1} - x_{2a+2,2b+2,2c+2})
- (x_{2a,2b+2,2c} - x_{2a+1,2b+1,2c+1})
+ (y_{2a+1,2b+1,2c+1} - y_{2a+2,2b+2,2c+2})
- (y_{2a,2b+2,2c} - y_{2a+1,2b+1,2c+1})
+ (z_{2a+1,2b+1,2c+1} - z_{2a+2,2b+2,2c+2})
- (z_{2a,2b+2,2c} - z_{2a+1,2b+1,2c+1}) \right] \]
3. Solution of Equations of Motion. The following set of eqns. (62) can be shown to be a solution of the problem with the proper choice of constants involved. Let

\[ x_{2a,2b,2c} = U_{4x} \cos \left[ 2\pi \left( \frac{x(2a) + \rho(2b) + \Gamma(2c)}{2A} \right) - \omega t + \phi \right] \]

\[ x_{2a+1,2b+1,2c+1} = U_{5x} \cos \left[ 2\pi \left( \frac{x(2a+1) + \rho(2b+1) + \Gamma(2c+1)}{2A} \right) - \omega t + \phi \right] \]

\[ x_{2a+1,2b,2c} = U_{1x} \cos \left[ 2\pi \left( \frac{x(2a+1) + \rho(2b) + \Gamma(2c)}{2A} \right) - \omega t + \phi \right] \]

\[ x_{2a,2b+1,2c} = U_{2x} \cos \left[ 2\pi \left( \frac{x(2a) + \rho(2b+1) + \Gamma(2c)}{2A} \right) - \omega t + \phi \right] \]

\[ x_{2a,2b,2c+1} = U_{3x} \cos \left[ 2\pi \left( \frac{x(2a) + \rho(2b) + \Gamma(2c+1)}{2A} \right) - \omega t + \phi \right] \]

and similar equations for the \( y \)'s and \( z \)'s.

where \( x = 1, 2, \ldots, A; \ \beta = 1, 2, \ldots, B; \) and \( \Gamma = 1, 2, \ldots, C \).

The expressions for the \( y \) and \( z \) displacements can be obtained from those for the \( x \) displacements by replacing the \( U_{1x} \)'s by \( U_{1y} \)'s and \( U_{1z} \)'s.

There will be 15 \( ABC \) values of \( \omega \) and corresponding sets of \( U \)'s. For each solution all ions in the crystal will vibrate with the same frequency \( \omega \). The sets of numbers \((x, \beta, \Gamma)\) specify the wave vectors for the various normal vibrations. But as stated before, we shall be
interested only in the case of infinite wave length or 
\( \alpha = \beta = r = 0 \).

Substituting the displacements given in eqns. (62) into eqn. (58) and using trigonometric identities for the sum and difference of two angles, one can make the cosine factor containing the time to be the same in each term of the equation. Then this time dependent factor may be divided out of the equation. The result will be an equation placing a condition on \( \omega \) and the set of \( U \)'s. A similar result can be obtained for eqns. (59), (60), and (61). In order these eqns. are

\[
\begin{align*}
\left[ \left((2\kappa_1+4\kappa_5)-m_3\omega^2\right)U_{1x} - 2k_5\cos\frac{\pi x}{A}\cos\frac{\pi \theta}{B} U_{2x} \\
-2k_5\cos\frac{\pi x}{A}\cos\frac{\pi \theta}{C} U_{3x} - 2k_1\cos\frac{\pi x}{A} U_{4x} \\
+2k_5\sin\frac{\pi x}{A}\sin\frac{\pi \theta}{B} U_{2y} + 2k_5\sin\frac{\pi x}{A}\sin\frac{\pi \theta}{C} U_{3z} = 0
\end{align*}
\]

\[
\begin{align*}
2k_5\sin\frac{\pi x}{A}\sin\frac{\pi \theta}{B} U_{2x} + \left[2(k_5+k_3)+2k_6(1-\cos\frac{\pi \theta}{B})-m_0\omega^2\right]U_{1y} \\
-4k_5\cos\frac{\pi x}{A}\cos\frac{\pi \theta}{B} U_{2y} - 2k_5\cos\frac{\pi \theta}{B}\cos\frac{\pi \theta}{C} U_{5y} \\
2k_3\sin\frac{\pi \theta}{B}\sin\frac{\pi \theta}{C} U_{5z} = 0
\end{align*}
\]

\[
\begin{align*}
-2k_1\cos\frac{\pi x}{A} U_{1x} + (2k_1+\frac{8k_2}{3}-m_1\omega^2)U_{4x} \\
-\frac{8k_2}{3}\cos\frac{\pi x}{A}\cos\frac{\pi \theta}{B}\cos\frac{\pi \theta}{C} U_{5x} + \frac{8k_2}{3}\sin\frac{\pi x}{A}\sin\frac{\pi \theta}{B}\cos\frac{\pi \theta}{C} U_{5y} \\
+\frac{8k_2}{3}\sin\frac{\pi x}{A}\cos\frac{\pi \theta}{B}\sin\frac{\pi \theta}{C} U_{5z} = 0
\end{align*}
\]
\[-2k_3 \cos \frac{\pi x}{A} \cos \frac{\pi r}{C} U_{2x} - 2k_3 \cos \frac{\pi x}{A} \cos \frac{\pi r}{B} U_{3x} \]
\[-\frac{8}{3} k_2 \cos \frac{\pi x}{A} \cos \frac{\pi r}{B} \cos \frac{\pi r}{C} U_{4x} + [4k_3 + 8k_3 + 2k_4 (1 - \cos^2 \frac{\pi \alpha}{A}) - m_B \omega^2] U_{5x} \]
\[+ 2k_3 \sin \frac{\pi x}{A} \sin \frac{\pi r}{B} U_{3y} + \frac{8}{3} k_2 \sin \frac{\pi x}{A} \sin \frac{\pi r}{B} \cos \frac{\pi r}{C} U_{4y} \]
\[+ 2k_3 \sin \frac{\pi x}{A} \sin \frac{\pi r}{B} U_{3z} + \frac{8}{3} k_2 \sin \frac{\pi x}{A} \sin \frac{\pi r}{B} \sin \frac{\pi r}{C} U_{4z} = 0 \]

By interchanging the roles of the y and z coordinates in eqn. (64), the equation resulting from the motion of an \( O_1 \) ion in the z-direction can be obtained. It is

\[2k_5 \cos \frac{\pi x}{A} \cos \frac{\pi r}{C} U_{3x} + 2k_3 \cos \frac{\pi x}{B} \cos \frac{\pi r}{C} U_{5x} + [2(k_5 + k_3) + 2k_4 (1 - \cos^2 \frac{\pi r}{C}) - m_B \omega^2] U_{1z} \]
\[-2k_3 \cos \frac{\pi x}{A} \cos \frac{\pi r}{C} U_{3z} - 2k_3 \cos \frac{\pi x}{B} \cos \frac{\pi r}{C} U_{5z} = 0 \]

By successive permutations of the coordinate axes, eqns. (63), (64), (64'), (65), and (66) will yield ten similar eqns., each placing a condition on \( \omega \) and the set of \( U \)'s. The matrix of the coefficients of the \( U \)'s in the fifteen equations is shown on p. 42. The symbols composed of the braces represent products of sines and cosines. A letter \( \alpha \) contained in the upper row of the symbol represents a factor \( \sin (\pi \alpha / A) \), while an \( \alpha \) in the lower row represents a factor \( \cos (\pi \alpha / A) \). Hence

\[\{ \alpha \beta \} = \sin \frac{\pi \alpha}{A} \sin \frac{\pi \beta}{B} \cos \frac{\pi r}{C} \]

\[\{ \alpha \beta \} = \cos \frac{\pi \alpha}{A} \cos \frac{\pi \beta}{B} \cos \frac{\pi r}{C} \]

\[\{ \alpha \beta \} = \cos \frac{\pi \alpha}{A} \]

etc.
\[
\begin{array}{cccccc}
& U_{1x} & U_{2x} & U_{3x} & U_{4x} & U_{5x} \\
U_{1x} & \frac{2k_1 + 3k_5}{m_0\omega^2} & -2k_5\{\alpha\} & -2k_5\{\alpha\} & -2k_5\{\alpha\} & 0 \\
U_{2x} & -2k_5\{\alpha\} & \frac{2k_5 + 2k_3 - m_0\omega^2}{2k_6(1 - \{\alpha\})} & 0 & 0 & -2k_3\{\alpha\} \\
U_{3x} & -2k_5\{\alpha\} & 0 & \frac{2k_5 + 2k_3 - m_0\omega^2}{2k_6(1 - \{\alpha\})} & 0 & -2k_3\{\alpha\} \\
U_{4x} & -2k_5\{\alpha\} & 0 & 0 & \frac{2k_1 + \frac{3}{5}k_2}{m_{1r}\omega^2} & -\frac{8}{3}k_2\{\alpha_{\parallel}\} \\
U_{5x} & 0 & -2k_3\{\alpha\} & -2k_3\{\alpha\} & -\frac{4}{3}k_2\{\alpha_{\parallel}\} & \frac{4k_5 + \frac{8}{3}k_2 - m_{Ba}\omega^2}{2k_4(1 - \{\alpha\})} \\
U_{1y} & 0 & 2k_5\{\alpha\} & 0 & 0 & 0 \\
U_{2y} & 2k_5\{\alpha\} & 0 & 0 & 0 & 0 \\
U_{3y} & 0 & 0 & 0 & 0 & 0 \\
U_{4y} & 0 & 0 & 0 & \frac{8}{3}k_2\{\alpha_{\parallel}\} & 0 \\
U_{5y} & 0 & 0 & 0 & 0 & -2k_3\{\alpha\} \\
U_{1z} & 0 & 0 & 0 & 0 & 0 \\
U_{2z} & 0 & 0 & 0 & 0 & 2k_3\{\alpha\} \\
U_{3z} & 0 & 0 & 0 & 0 & 0 \\
U_{4z} & 0 & 0 & 0 & \frac{8}{3}k_2\{\alpha_{\parallel}\} & 0 \\
U_{5z} & 0 & 2k_3\{\alpha\} & 0 & 0 & 0 \\
\end{array}
\]
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<th>$U_{2y}$</th>
<th>$U_{3y}$</th>
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Note: The table represents a portion of a larger matrix, with each element expressed in terms of various constants and functions.
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</tbody>
</table>
One of the fifteen equations can be obtained from each row of the matrix. Multiply each element of the row by the \( U \) above its column, form the sum of these products, and equate the sum to zero.

This set of fifteen equations may be regarded as a set of homogeneous linear equations for the \( U \)'s. In order to have any solution other than all \( U \)'s zero, the determinant of the coefficients must be zero. Expanding this determinant will give an equation of fifteenth order in \( \omega^2 \). This equation will have fifteen roots—some of which may coincide—for each set of numbers \( (\alpha, \beta, \gamma) \). Each of these values of \( \omega^2 \) will give a set of \( U \)'s or a normal vibration. Since there are \( \text{ABC} \) sets of numbers \( (\alpha, \beta, \gamma) \), there will be \( 15\text{ABC} \) normal vibrations.

In the particular case of \( \alpha = \beta = \gamma = 0 \), the fifteenth order determinant reduces to the product of three identical fifth order determinants:

\[
\begin{vmatrix}
(2k_1 + 4k_5 & -2k_5 & -2k_5 & -2k_1 & 0 \\
-m_0\omega^2 & (2k_3 + 2k_5 & 0 & 0 & -2k_3 \\
-2k_5 & 0 & (2k_3 + 2k_5 & 0 & -2k_3 \\
-2k_5 & 0 & 0 & (2k_1 + \frac{8}{3}k_2 & -\frac{8}{3}k_2 \\
-2k_1 & 0 & 0 & 0 & \text{m}_{(1}^{\omega^2)} & \text{m}_{(1}^{\omega^2)} \\
0 & -2k_3 & -2k_3 & -\frac{8}{3}k_2 & (4k_3 + \frac{8}{3}k_2 \\
& & & & -\text{m}_{(3}^{\omega^2)} & \text{m}_{(3}^{\omega^2})
\end{vmatrix} = 0 \quad (67)
\]
To simplify the problem a bit let \( r_1 = k_1/k_5 \), \( r_2 = k_2/k_5 \), \( r_3 = k_3/k_5 \), and

\[
\omega^2 = \frac{k_5}{m_0} w
\]  

(68)

Using the mass ratios \( m_{r_1}/m_0 = 2.9938 \) and \( m_{r_3}/m_0 = 8.5914 \), eqn. (67) now becomes

\[
\begin{bmatrix}
2r_1 + 4 - w & -2 & -2 & -2r_1 & 0 \\
-2 & 2r_3 + 2 - w & 0 & 0 & -2r_3 \\
-2 & 0 & 2r_3 + 2 - w & 0 & -2r_3 \\
\frac{-r_1}{1.4969} & 0 & 0 & \frac{r_1 + 4r_2}{1.4969} - w & \frac{-r_2}{1.1227} \\
0 & \frac{-r_3}{4.2957} & \frac{-r_3}{4.2957} & \frac{-r_2}{3.2218} & \frac{r_3 + 2r_2}{2.1479} - w
\end{bmatrix} = 0
\]  

(69)

If the third row is subtracted from the second, and then the second column added to the third, the result is

\[
\begin{bmatrix}
2r_1 + 4 - w & -2 & -4 & -2r_1 & 0 \\
0 & 2r_3 + 2 - w & 0 & 0 & 0 \\
-2 & 0 & 2r_3 + 2 - w & 0 & -2r_3 \\
\frac{-r_1}{1.4969} & 0 & 0 & \frac{r_1 + 4r_2}{1.4969} - w & \frac{-r_2}{1.1227} \\
0 & \frac{-r_3}{4.2957} & \frac{-r_3}{4.2957} & \frac{-r_2}{3.2218} & \frac{r_3 + 2r_2}{2.1479} - w
\end{bmatrix} = 0
\]  

(70)

Then one root is

\[ w = 2r_3 + 2 \]  

(71)

and the reduced determinant is
If the determinant in eqn. (72) is expanded, it will be found that the constant term is zero. This means that \( w = 0 \) is a root. The reduced cubic equation must be solved numerically for the remaining roots. The solution of a cubic equation has been discussed by Dickson\(^{23}\) and many others.

Now that the roots of eqn. (69) have been found, the \( U's \) can be found. Corresponding to the reduction of the fifteenth order determinant to three fifth order determinants, the fifteen equations can be grouped into three groups of five each such that each group contains only \( U_{1x}'s \), \( U_{1y}'s \), or \( U_{1z}'s \). Since the three groups of equations are identical except for the subscript \( x, y, \) or \( z \), only one group need be treated. Let this be the \( x \) group.

The equations for the \( U_{1x}'s \) are

\[
(2r_1+4-w_j)U_{1x} - 2U_{2x} - 2U_{3x} - 2r_1 U_{4x} = 0 \tag{73}
\]
\[
-2U_{1x} + (2r_3+2-w_j)U_{2x} - 2r_3 U_{5x} = 0 \tag{74}
\]
\[
-2U_{1x} + (2r_3+2-w_j)U_{3x} - 2r_3 U_{5x} = 0 \tag{75}
\]
\[
- \frac{r_1}{1.4969} U_{1x} + \left( \frac{r_1+4}{2} \frac{r_2}{1.4969 - w_j} \right) U_{4x} - \frac{r_2}{1.1227} U_{5x} = 0 \tag{76}
\]
\[- \frac{r_3^2}{4.2957 U_2 x} - \frac{r_3}{4.2957 U_3 x} - \frac{r_2}{3.2218 U_4 x} + \left( \frac{r_3 + r_2}{2.1479 - w_j} \right) U_5 x = 0 \]  

(77)

where the \(w_j\) are the roots of (69) with \(j = 1, 2, 3, 4, 5\).

It should be noted that eqns. (73) through (77) can be solved only to the extent that four of the unknowns can be found in terms of the fifth. This is all of the information which can ever be gained when solving such a set of homogeneous linear equations.

For the root given in eqn. (71), the solution of eqns. (73)-(77) is \(U_{3x} = -U_{2x}, U_{1x} = U_{4x} = U_{5x} = 0\). For the root \(w = 0\), the solution is \(U_{1x} = U_{2x} = U_{3x} = U_{4x} = U_{5x}\). These results can readily be verified by substitution in the equations.

If \(2r_3 + 2 - w \neq 0\), it can be seen from eqns. (74) and (75) that \(U_{2x} = U_{3x}\). This fact may be used to reduce the labor in the remaining three cases. Some of the \(w\)'s and \(U\)'s for several combinations of \(r_1, r_2, r_3\) are shown in Table II. Actually the only ones shown are those which arise out of the numerical solution of the reduced cubic equation. Also shown is one calculation for SrTiO\(_3\). In this case \(m_{Ba}/m_0\) was replaced by \(m_{Sr}/m_0 = 5.4769\), which slightly altered various equations. The reduced cubic equations for the various cases are

\[
\text{case 1: } w^3 - 26.83 w^2 + 188 w - 188 = 0
\]  

(78)

\[
\text{case 2: } w^3 - 16.867 w^2 + 72.84 w - 66.2 = 0
\]  

(79)

\[
\text{case 3: } w^3 - 17.485 w^2 + 80.53 w - 82.07 = 0
\]  

(80)

\[
\text{case 4: } w^3 - 12.565 w^2 + 35.705 w - 17.60 = 0
\]  

(81)
Table II

<table>
<thead>
<tr>
<th>Compound</th>
<th>$r_1, r_2, r_3$</th>
<th>$w$</th>
<th>$U_{1x}$</th>
<th>$U_{2x} = U_{3x}$</th>
<th>$U_{4x}$</th>
<th>$U_{5x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>$4.25, 4$</td>
<td>15.47</td>
<td>1</td>
<td>-.482</td>
<td>-.214</td>
<td>.0674</td>
</tr>
<tr>
<td>(case 1)</td>
<td></td>
<td>10.15</td>
<td>1</td>
<td>1.282</td>
<td>-.379</td>
<td>.273</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.21</td>
<td>1</td>
<td>1.222</td>
<td>1.490</td>
<td>.560</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>$2.5, 2$</td>
<td>10.55</td>
<td>1</td>
<td>-.483</td>
<td>-.154</td>
<td>.0497</td>
</tr>
<tr>
<td>(case 2)</td>
<td></td>
<td>5.060</td>
<td>1</td>
<td>1.102</td>
<td>-.367</td>
<td>.242</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.24</td>
<td>1</td>
<td>1.195</td>
<td>1.89</td>
<td>.752</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>$2.5, 2$</td>
<td>10.644</td>
<td>1</td>
<td>-.508</td>
<td>-.152</td>
<td>.0905</td>
</tr>
<tr>
<td>(case 3)</td>
<td></td>
<td>5.420</td>
<td>1</td>
<td>.988</td>
<td>-.323</td>
<td>.359</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.421</td>
<td>1</td>
<td>-.603</td>
<td>2.25</td>
<td>1.19</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>$5.25, 2$</td>
<td>8.689</td>
<td>1</td>
<td>-.912</td>
<td>-.04</td>
<td>.113</td>
</tr>
<tr>
<td>(case 4)</td>
<td></td>
<td>3.253</td>
<td>1</td>
<td>.450</td>
<td>-.093</td>
<td>.197</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.622</td>
<td>.133</td>
<td>-1</td>
<td>4.58</td>
<td>1.412</td>
</tr>
</tbody>
</table>

It should be noted that the values of $w$ only give relative values of the frequencies. Eqn. (58) must be taken into account. In order for case 2 to have the same compressibility as case 1, it would be necessary to increase $k_5$ for case 2 over case 1. This would bring the values of $w$ for case 2 more nearly into line with those for case 1.

The results in Table II are only of a preliminary nature. About the only conclusion that can be drawn is that the overall nature of the various normal coordinates is not greatly affected by moderate changes of the masses or force constants in the lattice. The results would probably be changed a great deal by the proper inclusion of the Lorentz correction. The proper treatment with normal coordinates and the Lorentz correction might resolve the discrepancy discussed in sec. 5 of the preceding chapter.
REFERENCES

5. J. L. Youngblood, private communication.
17. R. T. Swim, private communication.

23. L. E. Dickson, Theory of Equations (John Wiley & Sons, New York), ch. V.