

On the Quantum Theory of Pyroelectricity

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IT is a modest and almost trivial contribution which I have to offer for the special issue of this journal dedicated to Professor Bohr. The problem is quite out of date but nevertheless it was unsolved until recently. It concerns the dependence on temperature of the pyroelectric moment. An elementary theory of this effect was given by Boguslawski¹ in 1914 with the help of an Einstein model of a crystal, namely, a set of independent linear oscillators. As in the first theories of thermal expansion, these oscillators were assumed to be non-harmonic; then the mean amplitude of vibration is not symmetrical about the equilibrium, and this asymmetry increases with temperature. If the oscillators are charged particles and the crystal lattice of sufficiently low symmetry so that the effects of the asymmetry of the single oscillators do not cancel, an electric moment depending on temperature T is produced. Boguslawski found the same function of T as that representing thermal energy and thermal expansion, hence for low temperatures a T^4 -law. Careful experiments were carried out by Ackermann² in 1915 down to $T=23^\circ\text{K}$. A discussion of his results by Boguslawski showed that although the theoretical curve represents the observations fairly well over a large interval of temperature there are marked deviations for the lowest temperatures. Boguslawski found that a T^2 -law gives much better agreement with the observations than his theoretical T^4 -law.

I took up this problem in several papers and in my book *Atomtheorie des Festen Zustandes*³ from the standpoint of general lattice dynamics; I obtained again the T^4 -law, and I summarized that section of my book with the words: "The contradiction of this theoretical result with Ackermann's measurements remains to be solved."

Falkenhagen, in his article on pyro- and piezoelectricity,⁴ discusses, in connection with this question, a paper of Lindman⁵ which deals with the distinction between "true" and "apparent" pyroelectricity (the latter being the effect of a combination of piezoelectricity and thermal expansion), and he suggests the solution of the problem may consist in the non-existence of true pyroelectricity. This seems to me quite off the point; for as piezoelectricity is little dependent on temperature, the "apparent" pyroelectric moment should behave like the thermal expansion which doubtless follows a T^4 -law.

I have now found the solution of this old problem as part of a general revision of lattice electrodynamics and lattice optics. This work was undertaken in connection with the attacks directed against lattice dynamics by Raman and his collaborators. The Indian physicists have produced many new and accurate observations of electrical, optical and x-ray phenomena. These results led them to deny the validity of the whole theory of lattice dynamics and to propose another theory, the main characteristic of which is the contention that the vibrational spectrum of a lattice is not quasi-continuous, but consists of a small number of sharp lines. This contention is, of course, too absurd to be taken seriously. For in classical mechanics and in quantum mechanics as well, a vibrating system of N particles has $3N-6$ normal modes of vibration (6 being the number of translational and rotational degrees of freedom). Raman would hardly deny that a molecule consisting of 10 atoms has 24 normal modes; perhaps he would also agree that a system of 100 atoms has 294 normal modes—but a system of 1000 atoms which may be already called a micro-crystal would, according to his theory, not have 2994 normal modes but only 48 (if I understand his somewhat vague statements). The attacks of the Indian physicists

¹ J. Boguslawski, *Physik. Zeits.* **15**, 283, 569, 805 (1914).

² W. Ackermann, *Ann. d. Physik* **46**, 197 (1915).

³ M. Born, *Zeits. f. Physik* **7**, 217 (1921); **11**, 327 (1921). "Atomtheorie des Festen Zustandes," *Encycl. d. Math. Wis.* **5**, 529 (see in particular p. 689).

⁴ H. Falkenhagen, *Handbuch der Physik* (1928), Vol. 13, Chap. 8, p. 291 (see in particular pp. 301 and 316).

⁵ K. F. Lindman, *Ann. d. Physik* **62**, 107 (1920).

against lattice dynamics are mainly directed against the use of the cyclic boundary condition; but Ledermann⁶ has given a rigorous proof that the results obtained by this method are asymptotic approximations to the correct solutions. There is no doubt that lattice dynamics as represented in my old book is correct. But the new observations of the Indian scientists are not concerned with *dynamical* but with *thermal*, *electrical* and *optical* phenomena, and I perfectly agree with the Indians that the theory as developed in my book is incapable of accounting for many of these experiments. The reason is that my book was written before the discovery of quantum mechanics; it is based on Bohr's tentative adaptation of classical mechanics and optics to quantum theory, and it misses, therefore, all more refined details. It is strange that during the 20 years which have elapsed since the birth of quantum mechanics nobody has taken up the problem of investigating the optical properties of a crystal from the modern standpoint. The reason is that many of these effects are inconspicuous and of no practical importance while other problems (like the theory of metals and alloys) seemed to be much more urgent. However, now that the skill of the Indian physicists has produced a host of interesting details, it is imperative that they should be explained. Therefore I have worked out the dynamical, electromagnetic, and optical properties of lattices from the standpoint of quantum mechanics, and I have no doubt that all the new observations can be explained in this way. I do not know whether I shall be able to publish these investigations as a whole; but I am pleased to have this opportunity of giving an example which illustrates the method.

From the standpoint of quantum mechanics a crystal, like any molecule, is a system of nuclei and electrons, electrically neutral as a whole, with the special feature that there is only a small number of different kinds of nuclei, say n ; but each kind is represented by N individuals, where N is very large. The method of solving the wave equation for any atomic system has been given

by Oppenheimer and myself.⁷ The result is this: Assume an arbitrary configuration of the nuclei (coordinates X) and solve the wave equation for the electrons (coordinates x). The energy in every electronic state is then a function of the nuclear coordinates X ; let $\Phi(X)$ be this function for the lowest electronic level. The solution of the actual wave equation in which the x and X both are variables can then be expanded in a power series with respect to a parameter $\tau = (m/M)^{1/2}$ where m is the mass of the electron, M that of a nucleus (say the smallest nuclear mass occurring). For $\tau = 0$ one has the solution for fixed nuclei, described above; the eigenfunction can be written

$$\psi(x, X) = \chi(X) \varphi(x, X) \quad (1)$$

where $\chi(X)$ is arbitrary. The condition for the solvability of the next approximation is that the electronic energy $\Phi(X)$ is stationary. If X_0 is a set of solutions of this "equilibrium" condition and $X - X_0 = u$ small deviations, the second approximation provides an equation for the function $\chi(X) = \chi(X_0 + u) = \chi_1(u)$; it is the wave equation for a set of coupled oscillators with nuclear masses and a potential energy which consists in the second-order terms of $\Phi(X + u)$ with respect to the u . Higher approximations describe the rotation of the system, as a whole (which for crystals may be neglected) and of couplings between electronic motion and nuclear vibrations (and rotations).

The total electronic energy in the lowest level $\Phi(X)$ represents, therefore, the potential energy of the nuclei up to terms of the second order in τ . If one writes

$$\Phi(X + u) = \Phi^0 + \sum_{\mu} \Phi_{\mu}^0 u_{\mu} + \frac{1}{2} \sum_{\mu\nu} \Phi_{\mu\nu}^0 u_{\mu} u_{\nu} \quad (2)$$

where Φ^0 , Φ_{μ}^0 , $\Phi_{\mu\nu}^0$ are the values of $\Phi(X)$ and its first and second derivatives for the configuration X_0 , then X_0 is determined by the equations

$$\Phi_{\mu}^0 = 0, \quad (3)$$

where μ indicates all components of all position vectors of the nuclei. Now these Eqs. (3) have the peculiarity that for a crystal, that is, for a system consisting of a small number n of types

⁶ W. Ledermann, Nature **151**, 197 (1943); Proc. Roy. Soc. **182**, 362 (1944).

⁷ M. Born and R. Oppenheimer, Ann. d. Physik **84**, 457 (1927).

of nuclei, each type represented by a large number N of individuals, there exists a solution which approaches more and more a lattice, namely a periodic repetition of n equal groups, the larger N is. Deviations of periodicity occur mainly on the surface. In the limit $N \rightarrow \infty$ one has an exactly periodic lattice; but then the surface has receded into infinity, and the Eqs. (3) are no longer sufficient to determine the configuration completely. One can easily see that they reduce to $3(n-1)$ equations restricting the relative positions of the nuclei in the base, while the shape and size of the cell can be chosen arbitrarily. The latter depends on 6 constants, the scalar products $g_{\alpha\beta} = \mathbf{a}_\alpha \cdot \mathbf{a}_\beta$ of the three base vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. It is clear that these are macroscopic parameters, like the volume of a gas, and have to be determined from statistical mechanics. For this purpose one introduces normal coordinates $\xi(J)$ and their conjugate momenta $p(J)$; here the index J assumes $3Nn$ (more precisely $3Nn-6$) values. By applying cyclic boundary conditions, it is shown that J can be split up into two indices j, \mathbf{q} where $j=1, 2, \dots, 3n$ characterizes different branches of the elastic spectrum and \mathbf{q} , the momentum vector of the elastic waves, is restricted to N lattice points filling the cell of the reciprocal lattice. Now (2) becomes

$$\Phi = \Phi^0 + \frac{1}{2} \sum_J \omega^2(J) \xi^2(J) \quad (4)$$

and the kinetic energy

$$K = \frac{1}{2} \sum_J p^2(J). \quad (5)$$

Here Φ^0 and $\omega^2(J)$ depend still on the arbitrarily chosen parameters of the base, namely the 6 quantities $g_{\alpha\beta} = \mathbf{a}_\alpha \cdot \mathbf{a}_\beta$, and the $3(n-1)$ relative coordinates of the nuclei forming the base. The total energy $\Phi + K$ is now that of an assembly of oscillators and has the energy levels

$$\epsilon_v = \sum_J \hbar \omega(J) \{v(J) + \frac{1}{2}\}, \quad v(J) = 0, 1, 2, \dots \quad (6)$$

The free energy is

$$A = -kT \log \sum_v e^{-\epsilon_v/kT} \\ = \Phi^0 + kT \sum_J \log (1 - e^{-\hbar \omega(J)/kT}). \quad (7)$$

As Φ^0 and $\omega(J)$ depend on the $6+3(n-1) = 3(n+1)$ parameters of the base, the same holds

for A . Small changes of these parameters can be described by

$$6 \text{ components } x_1, x_2, \dots, x_\rho \text{ of the external strain, } 3(n-1) \text{ components } y_\alpha(k), (\alpha=1, 2, 3; k=1, 2, \dots, n-1) \text{ of the internal strain.} \quad (8)$$

The former are the rectangular components of the tensor $\delta g_{\alpha\beta} = \delta(\mathbf{a}_\alpha \cdot \mathbf{a}_\beta)$ ordered in such a way that the indices combinations 11, 22, 33, 23, 31, 12 are now denoted by 1, 2, 3, 4, 5, 6; indices of this kind will be indicated in the following by the letters $\rho, \sigma, 1, 2, \dots, 6$. $y_\alpha(k)$ are the variations of the relative coordinates $x_\alpha(k) - x_\alpha(0)$, ($\alpha=1, 2, 3$) of the base points with respect to one of them ($k=0$).

In the vicinity of an arbitrarily chosen base, A has an expansion in terms of the x_ρ and $y_\alpha(k)$ of the form

$$A = A^0 + \sum_{\rho=1}^6 [\rho] x_\rho + \sum_{k=1}^{n-1} \sum_{\alpha=1}^3 \left[\begin{matrix} k \\ \alpha \end{matrix} \right] y_\alpha(k) \\ + \frac{1}{2} \sum_{\rho, \sigma=1}^6 [\rho\sigma] x_\rho x_\sigma + \sum_{k=1}^{n-1} \sum_{\alpha=1}^3 \sum_{\rho=1}^6 \left[\begin{matrix} k \\ \alpha, \rho \end{matrix} \right] y_\alpha(k) x_\rho \\ + \frac{1}{2} \sum_{k, k'=1}^{n-1} \sum_{\alpha, \beta=1}^3 \left[\begin{matrix} kk' \\ \alpha\beta \end{matrix} \right] y_\alpha(k) y_\beta(k'). \quad (9)$$

Here A^0 and all coefficients (bracket symbols are perfectly defined functions of the arbitrarily chosen base parameters and of temperature. We now define the *primary base* by postulating that the linear terms in A shall vanish for $T=0$:

$$[\rho]_{T=0} = 0, \quad \left[\begin{matrix} k \\ \alpha \end{matrix} \right]_{T=0} = 0, \quad (10)$$

$$\left(\begin{matrix} \alpha = 1, 2, 3; \rho = 1, 2, \dots, 6 \\ k = 1, 2, \dots, n-1 \end{matrix} \right).$$

These are $6+3(n-1)$ equations for the $6+3(n-1)$ parameters of the base. They have also to satisfy the conditions (3); but it is easily seen that these are compatible with (10).

When the base of the lattice for $T=0$ is determined from (10) the quantities $[\rho]$ and $\left[\begin{matrix} k \\ \alpha \end{matrix} \right]$ are functions of T which vanish for $T=0$; they can be interpreted as *thermal stresses*. We intro-

duce the notation

$$\begin{aligned} [\rho] &= -X_\rho(T): \\ &\text{external thermal stress components.} \\ \left[\begin{matrix} k \\ \alpha \end{matrix} \right] &= -Y_\alpha(k; T): \\ &\text{internal thermal stress components.} \end{aligned} \quad (11)$$

If the crystal is free from mechanical surface and volume forces, its shape for the temperature T is determined by

$$\partial A / \partial x_\rho = 0, \quad \partial A / \partial y_\alpha(k) = 0, \quad (12)$$

or explicitly

$$\begin{aligned} \sum_\sigma [\rho\sigma] x_\sigma + \sum_k \sum_\alpha \left[\begin{matrix} k \\ \alpha, \rho \end{matrix} \right] y_\alpha(k) &= X_\rho(T), \\ \sum_\rho \left[\begin{matrix} k \\ \alpha, \rho \end{matrix} \right] x_\rho + \sum_{k'} \sum_\beta \left[\begin{matrix} kk' \\ \alpha\beta \end{matrix} \right] y_\beta(k') &= Y_\alpha(k; T). \end{aligned} \quad (13)$$

The solutions of these equations represent the components of the *thermal strain* relative to the configuration for $T=0$; they have the form

$$\begin{aligned} x_\rho(T) &= \sum_\sigma \{ \rho\sigma \} X_\sigma(T) \\ &\quad + \sum_k \sum_\alpha \left\{ \begin{matrix} k \\ \alpha, \rho \end{matrix} \right\} Y_\alpha(k; T), \\ y_\alpha(k; T) &= \sum_\rho \left\{ \begin{matrix} k \\ \alpha, \rho \end{matrix} \right\} X_\rho(T) \\ &\quad + \sum_{k'} \sum_\beta \left\{ \begin{matrix} kk' \\ \alpha\beta \end{matrix} \right\} Y_\beta(k'; T). \end{aligned} \quad (14)$$

Now if each nucleus carries a resultant charge e_k , defined as the sum of the nuclear charge and that of the electronic cloud of the atom, the internal thermal strain produces an electric moment with the components

$$\begin{aligned} M_\alpha(T) &= \sum_k e_k y_\alpha(k; T) = \sum_k \sum_\rho \left\{ \begin{matrix} k \\ \alpha, \rho \end{matrix} \right\} e_k X_\rho(T) \\ &\quad + \sum_{kk'} \sum_\beta \left\{ \begin{matrix} kk' \\ \alpha\beta \end{matrix} \right\} e_k Y_\beta(k'; T). \end{aligned} \quad (15)$$

It is this expression which in my previous theory (and essentially also in Boguslawski's "monochromatic" theory) was interpreted as pyroelectric moment. In particular, the first term on the right-hand side was identified with the so-called "apparent" pyroelectricity, the second

with the "true" one. The reason for this is the following: If the crystal is subject to a mechanical stress X_ρ and an electrostatic field \mathbf{E} , so that the force on a nucleus is $Y_\alpha(k) = e_k E_\alpha$, the additional mechanical strain satisfies equations of the same form and with the same coefficients as (13) or (14), if the thermal strain and stress components are replaced by the mechanical ones; one has in particular

$$\begin{aligned} x_\rho &= \sum_\sigma s_{\rho\sigma} X_\sigma + \sum_\alpha d_{\alpha, \rho} E_\alpha, \\ M_\alpha &= \sum_\rho d_{\alpha, \rho} X_\rho + \sum_\beta b_{\alpha\beta} E_\beta, \end{aligned}$$

where $s_{\rho\sigma}$ are Voigt's elastic moduli, $b_{\alpha\beta}$ the components of the dielectric tensor, $d_{\alpha, \rho}$ the piezoelectric moduli; one has

$$\begin{aligned} s_{\rho\sigma} &= \{ \rho, \sigma \}, \quad b_{\alpha\beta} = \sum_{kk'} \left\{ \begin{matrix} kk' \\ \alpha\beta \end{matrix} \right\} e_k e_{k'}, \\ d_{\alpha, \rho} &= \sum_k \left\{ \begin{matrix} k \\ \alpha, \rho \end{matrix} \right\} e_k. \end{aligned} \quad (16)$$

This shows that the first term in (15) can be written

$$\sum_\rho d_{\alpha, \rho} X_\rho(T) \quad (17)$$

and represents, therefore, the combined effect of thermal pressure and piezoelectricity, called "apparent" pyroelectricity. Hence the other term in (15) ought to be "true" pyroelectricity; it can be considered as dielectric polarization produced by a "thermal electric field" defined by $e_k E_\alpha(T) = Y_\alpha(k; T)$; for it can be written in the form

$$\sum_{\alpha\beta} b_{\alpha\beta} E_\beta(T). \quad (18)$$

We now see that the dependence of these quantities on temperature is essentially the same as that of the thermal stresses (11), which is obtained from the free energy A ; one has

$$\begin{aligned} X_\rho(T) &= -\frac{\partial A}{\partial x_\rho} \\ &= -\sum_J \hbar \frac{\partial \omega(J)}{\partial x_\rho} \frac{1}{e^{\hbar \omega(J)/kT} - 1}, \\ X_\alpha(k; T) &= -\frac{\partial A}{\partial y_\alpha(k)} \\ &= -\sum_J \hbar \frac{\partial \omega(J)}{\partial y_\alpha(k)} \frac{1}{e^{\hbar \omega(J)/kT} - 1}. \end{aligned} \quad (19)$$

These sums can be evaluated with the help of Debye's approximation; only the three acoustical branches of the spectrum are taken into account, and $\omega(J) = \omega\left(\frac{q}{j}\right)$ is replaced by

$$\omega(J) = c_j q, \tag{20}$$

where c_j is the velocity of sound and q is the length of the wave vector. Hence

$$\frac{d\omega(J)}{dx_\rho} = \frac{\partial c_j}{\partial x_\rho} q = \frac{1}{c_j} \frac{\partial c_j}{\partial x_\rho} \omega,$$

and $\sum_J \dots$ is to be replaced by

$$\int q^2 dq \dots = \frac{1}{c_j^3} \int \omega^2 d\omega \dots$$

Then the expressions (19) are composed of terms of the form

$$\int_0^{\omega_j} \frac{\hbar \omega^3 d\omega}{e^{\omega \hbar / kT} - 1}, \tag{21}$$

where ω_j is Debye's maximum frequency; but (21) is the total thermal energy, and for low temperatures is proportional to T^4 .

This is the result of the older theories which is not confirmed by experiment. But where is a flaw in the reasoning?

It is the assumption that the electric moment \mathbf{M} is obtained by multiplying the internal strain components with some effective charges and summing over the base. This would only be correct if each atom or ion were a rigid structure so that its resultant charge could be considered as being concentrated on the nucleus. That is certainly not the case. But pre-quantum-mechanical theory had no means of dealing adequately with the deformation of the electronic cloud surrounding the nuclei.

Let us consider first an arbitrary atomic system (not necessarily a crystal), the nuclei of which are distinguished by the letter $k = 1, 2, \dots$. Let Z_k be the atomic number of the nucleus, $X_\alpha(k)$ ($\alpha = 1, 2, 3$) its coordinates; let Z_k' be the number of electrons belonging to this nucleus, $x_\alpha(k, s)$, ($s = 1, 2, \dots, Z_k'$) their coordinates. If e is the electronic charge the difference,

$$e(Z_k - Z_k') = e_k \tag{22}$$

is the effective charge of the particle k ($e_k = 0$ for

a neutral atom). The total electric moment is

$$M_\alpha = e \sum_k \left\{ Z_k X_\alpha(k) - \sum_{s=1}^{Z_k'} x_\alpha(k, s) \right\}. \tag{23}$$

It has to be considered as a (multiplication) operator acting on the wave function (1), and one has to form its matrix elements. This can be done in two steps: The first step consists in building the matrix elements with respect to the electronic wave function; these matrix elements are functions of the nuclear coordinates X . The second step consists in forming the matrix elements between the different vibrational states. As we have here to deal only with the electronic ground state with the wave function $\varphi(x, X)$, we get the intermediate diagonal element

$$M_\alpha(X) = \int \varphi^*(x, X) M_\alpha \varphi(x, X) dx. \tag{24}$$

These functions can be calculated only if the electronic problem is explicitly solved. From the standpoint of the present theory they have to be accepted as some definite (though unknown) functions of the nuclear coordinates. However, it can be shown that M_α is a linear function of the X , if the ions are practically rigid structures. This means that the wave function $\varphi(x, X)$ depends only on the relative coordinates

$$x_\alpha'(k, s) = x_\alpha(k, s) - X_\alpha(k). \tag{25}$$

Introducing these in (23) and using (22) we get

$$M_\alpha = \sum_k \left\{ e_k X_\alpha(k) - e \sum_{s=1}^{Z_k'} x_\alpha'(k, s) \right\}. \tag{26}$$

The matrix element (24) written in the variables x' is

$$M_\alpha(X) = \int \varphi^*(x') M_\alpha \varphi(x') dx',$$

or with (26)

$$M_\alpha(X) = \sum_k e_k X_\alpha(k) - m_\alpha^0, \tag{27}$$

where the electronic contribution

$$m_\alpha^0 = e \sum_{s=1}^{Z_k'} \sum_k \int \varphi^*(x') x_\alpha'(k, s) \varphi(x') dx' \tag{28}$$

is independent of the X . The formula (27) is that used in previous theories, and it leads for a homogeneous deformation at once to the expression (15).

But it is clear that the hypothesis of rigid ions is a very poor approximation even in the case of ionic crystals.

In actual fact $M_\alpha(X)$ is not, as in (27), a linear function of the X . In any case $M_\alpha(X^0+u)$ can be expanded in a power series of the u ; combining, as in (2), the indices k, α into a single one μ one has

$$M_\alpha(X^0+u) = M_\alpha^0 + \sum_\mu M_{\alpha,\mu}^0 u_\mu + \sum_{\mu\nu} M_{\alpha,\mu\nu}^0 u_\mu u_\nu + \dots \quad (29)$$

In the case of a crystal the displacements u are of two kinds: a homogeneous deformation or strain superposed by thermal vibrations, symbolically: $u = u_{\text{hom}} + u_{\text{therm}}$. Introducing this into (29) it is sufficient to take only linear terms in u_{hom} into account while higher terms of u_{therm} must be considered. The u_{therm} can be replaced by the normal coordinates ξ . Thus, one can write

$$M_\alpha = M_\alpha(\xi) + \sum_\rho M_{\alpha,\rho} x_\rho + \sum_k \sum_\beta M_{\alpha,\beta}(k; \xi) y_\beta(k), \quad (30)$$

where $x_\rho, y_\alpha(k)$ are the strain components (8). For the special case of rigid ions where M_α is represented by (27), $M_\alpha(\xi)$ becomes a constant, the second term vanishes, as can easily be seen, and the last term reduces to $\sum_k e_k y_\beta(k)$, in agreement with (15). In this case the whole temperature dependence of the electric moment is caused by that of the internal strain components, and this leads, as we have seen, to the wrong T^4 -law for low temperatures.

The correct interpretation of the formula (30) is this: One has to consider all the terms linear in the strain, those with x_ρ and with $y_\alpha(k)$ as well, as "apparent" pyroelectricity and the first term $M_\alpha(\xi)$ (which did not appear in the older theories) as "true" pyroelectricity.

It can now be easily shown that it gives the correct dependence on temperature. For this purpose one has to expand

$$M_\alpha(\xi) = M_\alpha(0) + \sum_J M_\alpha(J) \xi(J) + \sum_{JJ'} M_\alpha(JJ') \xi(J) \xi(J') + \dots \quad (31)$$

and take the thermal average, i.e. the average of the diagonal elements with respect to the vibrations weighted according to the Boltzmann factors of the states. Then $\langle \xi(J) \rangle_{\text{av}} = 0$ while

$$\langle \xi(J) \xi(J') \rangle_{\text{av}} = \delta_{JJ'} \langle \xi^2(J) \rangle_{\text{av}}. \quad (32)$$

As only the change of the pyroelectric moment with temperature is observable one can omit the constant term $M_\alpha(0)$ and also the contribution of zero-point vibration for $\langle \xi^2 \rangle_{\text{av}}$. Hence

$$\langle M_\alpha(\xi) \rangle_{\text{av}} = \sum_J M_\alpha(JJ) \langle \xi^2(J) \rangle_{\text{av}}. \quad (33)$$

The true pyroelectric moment is composed of terms which are not proportional to the mean energy $\epsilon(J)$ of the oscillators, but to the mean square of the amplitude, i.e. to

$$\langle \xi^2(J) \rangle_{\text{av}} = \epsilon(J) / \omega^2(J). \quad (34)$$

If one now uses the Debye approximation one has to replace $M_\alpha(JJ)$ by some constant average; the sum then reduces to

$$\int_0^{\omega_i} \frac{\hbar \omega d\omega}{e^{\hbar \omega / kT} - 1}, \quad (35)$$

which differs from (21) and behaves, for $T \rightarrow 0$, like T^2 . The mean square of the amplitude appears also in Debye's theory⁸ of the influence of temperature on x-ray scattering. He introduced the function

$$\Phi(x) = \frac{1}{x} \int_0^x \frac{\xi d\xi}{e^\xi - 1} \quad (36)$$

and tabulated it with the help of its expansions for small and large x . The pyroelectric moment (33) can be expressed in terms of Φ ; one obtains approximately

$$\langle M_\alpha \rangle_{\text{av}} = C \frac{T}{\Theta} \Phi\left(\frac{\Theta}{T}\right) \quad (37)$$

where Θ is the characteristic temperature used in Debye's theory of specific heat. For large x one has

$$\Phi(x) = \frac{\pi^2}{6} \frac{1}{x} - e^{-x} \left(1 + \frac{1}{x}\right) - \dots, \quad (38)$$

hence for small T , the pyroelectric moment (37) is proportional to T^2 in agreement with Ackermann's observations.

In a similar way one can tackle many other electromagnetic and optical properties of a crystal and obtain results which differ considerably from the quasi-classical older theory. I wish to mention a few examples. The simple theory

⁸ P. Debye, Ann. d. Physik **43**, 49 (1914).

of residual rays (Reststrahlen) is not satisfactory since a fine structure has been observed⁹ consisting of weak maxima of absorption and reflection. Blackman and I¹⁰ have attempted to explain these as the effect of anharmonic terms in the potential energy. I think now that this effect is of secondary importance, and that harmonic vibrations are quite sufficient; the proper explanation can be given on the same lines as those used here, by an application of quantum mechanics to the electric moment induced by the incident light wave. It is easily shown that the ordinary theory of residual rays is then only a first approximation, and that a secondary spectrum exists which depends on a second approximation. Closely connected with this refined theory of infra-red dispersion and

⁹ B. Barnes, *Zeits. f. Physik* **75**, 723 (1932); K. Korth, *Nachr. d. Ges. d. Wiss., Göttingen, Math.-Phys. Kl.* p. 576 (1932); C. H. Cartwright and M. Czerny, *Zeits. f. Physik* **85**, 269 (1933); **90**, 457 (1934).

¹⁰ M. Born and M. Blackman, *Zeits. f. Physik* **82**, 551 (1933); M. Blackman, *Zeits. f. Physik* **86**, 421 (1933).

absorption is the Raman effect in crystals. What the Indian scientists have observed are just the lines of the secondary spectrum. Fermi and Rasetti,¹¹ in their excellent paper on the Raman effect of rocksalt, have indicated the correct theory, but did not work it out because it appeared to them too complicated. The observations show a continuous background with rather sharp lines on top of it. Krishnan¹² contends that these lines prove the fallacy of lattice dynamics which should give only a continuous spectrum. In fact the correct theory explains the background and the lines as well; they are due to the same property of the vibrational spectrum which produces the fine structure of the residual rays, namely the existence of maxima of density in the frequency distribution of the lattice vibrations. I hope to give an account of this investigation, carried out in collaboration with Miss Bradburn, in the near future.

¹¹ E. Fermi and F. Rasetti, *Zeits. f. Physik* **71**, 689 (1931).

¹² R. S. Krishnan, *Proc. Ind. Acad. Sci.* **18**, 298 (1943).