

Polarization Waves in Solids

By Tatsumi KUROSAWA*

*The Institute for Solid State Physics,
University of Tokyo, Tokyo, Japan*

(Received January 30, 1961)

A general theory of the polarization waves in crystals is developed in connection with the optical and the dielectric properties of the crystals. The result includes, in more general form, the relations by Szigeti and Fröhlich about the lattice vibrations in ionic crystals and the theory by Heller and Marcus for the exciton. The theory is applied to the analysis of the infra-red data of BaTiO_3 -type crystals.

§ 1. Introduction

Polarization waves in solids are concerned with a wide range of phenomena in solid state physics. The transverse modes of the polarization waves interact with light and determine the optical properties of the solids. The longitudinal modes interact with the electric field caused by charged particles and interchange the energy with them. The polarization waves are also responsible for the dielectric properties of the solids. Thus, it is expected that there may be relations between these phenomena, for they come from the same origin, the polarization waves. In fact, several authors, for instance, Szigeti¹⁾, Fröhlich^{2), 3)} and Mott⁴⁾, derived several important relations between them.

In this paper, the polarization waves in solids are treated from the above-mentioned standpoint. Several phenomenological relations unknown previously are derived, and some known facts are interpreted from a viewpoint different from that used hitherto.

In § 2, a general theory of the lattice waves in ionic crystals is developed; the results include the relations derived by Szigeti and Fröhlich, in more general form. In § 3, the theory of § 2 is applied to alkali halide and BaTiO_3 -type crystals. In the latter cases, the result from the simple ionic model is found to be in large disagreement with the experiment, and a tentative interpretation based upon the ionic model is done in Appendix. In § 4, several problems with respect to the electronic polarization waves are treated similarly as in § 2; for instance, the well-known theory of the exciton by Heller and Marcus is re-interpreted from a different viewpoint.

§ 2. Theory of Lattice Waves in Ionic Crystals

A theory of the lattice vibrations in simple ionic crystals has been developed by Szigeti¹⁾. We shall extend the theory to more complicated crystals, e.g. perovskite type crystals.

Let the number of atoms (ions) in a unit cell be n , and we enumerate them 1, 2, \dots , n . In the first place, we take up a needle-like sample of the crystal. Let us imagine that

* Present address: Faculty of Engineering, Chuo University, 1-1 Koishikawa-cho, Bunkyo-ku, Tokyo.

the ions displace in the direction of the needle. Let the displacements of the ions 1, 2, ..., n be x_1, x_2, \dots, x_n respectively. The polarization is induced as the result. If the displacements are small the induced polarization must be represented by a linear function of them[†];

$$P = N \sum_i e_i^* x_i, \quad (2-1)$$

where N is the number of the unit cells in unit volume. Of course

$$\sum_i e_i^* = 0. \quad (2-2)$$

Generally speaking, e_i^* 's are tensor and the direction of the polarization does not necessarily agree with that of the displacement. However, such a generalization is rather trivial and useless. Hence we assume that e_i^* 's are scalar and the direction of the polarization agrees with that of the needle. Thus, there is no electric field in the crystal.

In the next place, let us consider the case that there exists an electric field E in the crystal. If the ions are held undisplaced at their original positions, the polarization is given by

$$P_0 = \frac{1}{4\pi} (\kappa_0 - 1) E, \quad (2-3)$$

where κ_0 is the high frequency dielectric constant. If the ions displace^{††}, the polarization is given by

$$P = \frac{1}{4\pi} (\kappa_0 - 1) E + N \sum_i e_i^* x_i, \quad (2-4)$$

because there is no cross term. This equation does not depend on the shape of the sample; the effect of the shape is represented by the depolarization field and included in E . The first term is purely electronic and the second term is due to the displacements of the ions.

The static dielectric constant κ is determined as follows: We write the energy increment per unit volume due to the displacements x_1, x_2, \dots, x_n ($E=0$) as

[†] The state of the polarization due to the displacement may be very complicated; the polarization due to the displacement of the i -th ion comes from not only the i -th ion but also the induced polarization on the other ions. If the displacements are small, however, the general form of the polarization is given by Eq. (2-1).

^{††} We regard the displacements as variable irrespective of the electric field.

$$\frac{1}{2} N \sum_{i,j} S_{ij} x_i x_j.$$

When the electric field E exists, the interaction energy between the electric field and the polarization should be added;

$$-(P - P_0)E = -EN \sum_i e_i^* x_i.$$

The equilibrium displacement x_i^0 under the electric field is determined by the condition of minimum energy. Thus x_i^0 's are given by

$$\sum_j S_{ij} x_j^0 = e_i^* E \quad i=1, 2, \dots, n. \quad (2-5)$$

Furthermore, if the electric field oscillates with a frequency ω

$$\sum_j S_{ij} x_j^0(\omega) - M_i \omega^2 x_i^0(\omega) = e_i^* E, \quad (2-6)$$

where M_i is the mass of the i -th ion. $\kappa(\omega)$ is given by

$$\kappa(\omega) = \kappa_0 + (1/E) \cdot 4\pi N \sum_i e_i^* x_i^0(\omega). \quad (2-7)$$

Next, we consider the polar mode lattice waves with sufficiently long wavelength; long compared with the lattice constant but short compared with the size of the sample. In this case, the following relations are well-known²⁾: for the transverse waves^{†††}

$$E = 0, \quad (2-8)$$

and for the longitudinal waves

$$E = -4\pi P, \quad (2-9)$$

where P is the polarization due to the wave. Therefore, writing the displacement of the i -th ion as $x_i \exp(i\Omega_i t)$, we have the equation determining the frequency of the transverse waves;

$$\sum_j S_{ij} x_j - M_i \Omega_i^2 x_i = 0, \quad (2-10)$$

and of the longitudinal waves;

$$\sum_j S_{ij} x_j - M_i \Omega_i^2 x_i = -4\pi e_i^* P, \quad (2-11)$$

where

$$P = N \sum_i e_i^* x_i + \frac{1}{4\pi} (\kappa_0 - 1) (-4\pi P),$$

or

$$P = \frac{N}{\kappa_0} \sum_i e_i^* x_i. \quad (2-12)$$

Therefore, Eq. (2-11) is rewritten as

$$\sum_j S_{ij} x_j + \frac{4\pi N}{\kappa_0} e_i^* \sum_j e_j^* x_j - M_i \Omega_i^2 x_i = 0. \quad (2-13)$$

^{†††} Here we restrict ourselves to such a case that the long polarization waves can be divided into the longitudinal and the transverse waves.

because the electric field $-4\pi P$ acts as a restoring force, the frequency of the longitudinal waves is generally higher than that of the transverse ones and the difference is proportional to e^{*2} .

We write the eigenfrequencies of Eq. (2-10) as $\Omega_{t1}, \Omega_{t2}, \dots, \Omega_{tn-1}$ (we ignore another eigenfrequency $\Omega_t=0$ which corresponds to the acoustical mode) and the eigenvector belonging to $\Omega_{t\nu}$ as $x_{1\nu}, \dots, x_{n\nu}$. The ortho-normal condition is

$$\sum_i M_i x_{i\nu} x_{i\nu'} = A \delta_{\nu\nu'}, \quad (2.14)$$

where A is a constant.

The n -dimensional vector $(x_1^0(\omega), \dots, x_n^0(\omega))$ in Eq. (2-6) can be represented by a linear combination of the eigenvectors $(x_{1\nu}, \dots, x_{n\nu})$'s;

$$x_i^0(\omega) = \sum_\nu a_\nu(\omega) x_{i\nu} \quad \text{for all } i.$$

Inserting this into Eq. (2-6), multiplying $x_{i\nu}$ and summing over i , we find that

$$a_\nu(\omega) = \frac{E}{A(\Omega_{t\nu}^2 - \omega^2)} \sum_i e_i^* x_{i\nu}.$$

By remembering Eq. (2-7), we have the following dispersion relation:

$$\kappa(\omega) = \kappa_0 + 4\pi N \sum_\nu \frac{(\sum_i e_i^* x_{i\nu})^2}{\sum_i M_i x_{i\nu}^2} \cdot \frac{1}{\Omega_{t\nu}^2 - \omega^2}. \quad (2.15)$$

If there are only two ions in a unit cell as alkali halide crystals, this is simplified as follows:

$$\kappa(\omega) = \kappa_0 + \frac{4\pi N e^{*2}}{\mu(\Omega_t^2 - \omega^2)}, \quad (2.16)$$

where μ is the reduced mass of the two ions.

By substituting the expression

$$x_i = \sum_\nu b_\nu x_{i\nu},$$

for x_i of Eq. (2-13), we obtain

$$b_\nu = -\frac{4\pi N}{A(\Omega_{t\nu}^2 - \Omega_t^2)\kappa_0} \sum_j e_j^* x_j \sum_i e_i^* x_{i\nu}.$$

By multiplying $e_i^* x_{i\nu}$ and summing over i and ν , we have the equation giving Ω_t ;

$$\frac{4\pi N}{\kappa_0} \sum_\nu \frac{(\sum_i e_i^* x_{i\nu})^2}{\sum_i M_i x_{i\nu}^2} \cdot \frac{1}{\Omega_{t\nu}^2 - \Omega_t^2} = -1. \quad (2.17)$$

Comparing (2-17) with (2-15), we see that

$$\kappa(\Omega_t) = 0. \quad (2.18)$$

This relation can be derived directly from Eq. (2-9) which states that $D=0$ ³⁾. In general, Eq. (2-17) has $n-1$ roots. We write them as $\Omega_{t1}, \dots, \Omega_{tn-1}$. It is easily found from Eq.

(2-17) that

$$\Omega_{t1} \leq \Omega_{t1} \leq \Omega_{t2} \leq \dots \leq \Omega_{tn-1} \leq \Omega_{tn-1}. \quad (2.19)$$

The equality happens when Ω_t 's degenerate.

Let us note that $\kappa(\omega)$ has the following properties: (1) $\kappa(\omega)$ has the poles at $\Omega_{t1}, \dots, \Omega_{tn-1}$. (2) $\kappa(\omega)$ has the zeros at $\Omega_{t1}, \dots, \Omega_{tn-1}$. (3) $\kappa(\omega)$ tends to κ_0 for large ω . Therefore, if we take the summation of (2-15) over ν in the following form:

$$\kappa(\omega) = \frac{\sum_{k=0}^{n-1} c_k \omega^{2k}}{\prod_\nu (\Omega_{t\nu}^2 - \omega^2)}, \quad (2.20)$$

this must be factorized as follows:

$$\kappa(\omega) = \kappa_0 \prod_\nu \left(\frac{\Omega_{t\nu}^2 - \omega^2}{\Omega_{t\nu}^2} \right). \quad (2.21)$$

Especially, if we put $\omega=0$,

$$\frac{\kappa}{\kappa_0} = \prod_\nu \frac{\Omega_{t\nu}^2}{\Omega_{t\nu}^2}. \quad (2.22)$$

This is a generalization of the well-known similar relation in the diatomic case¹⁾.

By comparing the coefficients of ω^{2n-4} of (2-20) and (2-21), we find a relation;

$$4\pi N \frac{\sum_\nu (\sum_i e_i^* x_{i\nu})^2}{A} = \kappa_0 \sum_\nu (\Omega_{t\nu}^2 - \Omega_{t\nu}^2). \quad (2.23)$$

On the other hand, the vector (e_1^*, \dots, e_n^*) can be expanded by the vectors $(M_1 x_{1\nu}, \dots, M_n x_{n\nu})$'s;

$$e_i^* = \frac{1}{A} \sum_\nu (\sum_j e_j^* x_{j\nu}) M_i x_{i\nu}.$$

By multiplying this by e_i^*/M_i and summing over i , we have

$$\sum_\nu (\sum_i e_i^* x_{i\nu})^2 = A \cdot \sum_i \frac{e_i^{*2}}{M_i}.$$

Thus, Eq. (2-23) becomes

$$4\pi N \sum_i \frac{e_i^{*2}}{M_i} = \kappa_0 \sum_\nu (\Omega_{t\nu}^2 - \Omega_{t\nu}^2). \quad (2.24)$$

Here, we shall comment on the relation between the present e_i^* and the effective charge e_s^* introduced by Szigeti¹⁾. We may define his effective charge by writing the polarization in a spherical sample of a diatomic crystal as $Ne_s^* x$ when the positive and the negative ions displace homogeneously with the relative displacement x . According to the present viewpoint, the polarization of the spherical sample is given by

$$P = \frac{1}{4\pi} (\kappa_0 - 1) \left(-\frac{4\pi}{3} P \right) + N \sum e_i^* x_i,$$

from Eq. (2-4), because the depolarization

field in the spherical sample is $(-4\pi P/3)$. Or,

$$P = \frac{3}{\kappa_0 + 2} N \sum e_i^* x_i. \quad (2-25)$$

In the diatomic case, writing $x_1 - x_2 = x$ and $e_1^* = -e_2^* = e^*$, we have

$$e_s^* = \frac{3}{\kappa_0 + 2} e^*, \quad (2-26)$$

and in general

$$e_{si}^* = \frac{3}{\kappa_0 + 2} e_i^*. \quad (2-27)$$

Combining Eqs. (2-16) and (2-26), we get the relation derived by Szigeti;

$$\kappa = \kappa_0 + \left(\frac{\kappa_0 + 2}{3} \right)^2 \cdot \frac{4\pi N e_s^{*2}}{\mu \Omega_i^2}. \quad (2-28)$$

Similarly, if we write the polarization due to the longitudinal wave as

$$P = N \sum_i e_{li}^* x_i,$$

we obtain

$$e_{li}^* = \frac{e_i^*}{\kappa_0}. \quad (2-29)$$

This agrees with the effective charge introduced by Callen⁵⁾ in the diatomic case.

In some cases, e_s^* is appropriate to discuss the microscopic properties of the polarization. On the other hand, the present e_i^* , which corresponds to the effective charge of the transverse wave, is more directly related to the optical and the dielectric properties of

the crystal as seen from Eq. (2-15).

According to Eq. (2-15), the general features of $\kappa(\omega)$ are schematically as Fig. 1a and the optical properties become as Fig. 1b and 1c; the absorption intensity has peaks at Ω_i 's and the peak height is proportional to $(\sum e_i^* x_i)^2 / \sum M_i x_i^2$, the crystal shows the metallic reflection when $\kappa(\omega) < 0$ and the reflectivity is zero at Ω_r where $\kappa(\Omega_r) = 1$.

§ 3. Application of the Theory

Alkali halide and other simple ionic crystals

For these crystals, the analysis by Szigeti^{1b)} and Fröhlich²⁾ has been known, and we have little to be added to them. We tabulated the values of e^* and e_s^* in Table I for reference. As Szigeti has pointed out, e_s^*/e should be an integer if the simple ionic model were a good approximation†. We have shown that the deviation of e_s^*/e from an integer may be interpreted as brought by the short range

Table I. The values of the effective charge.

	e^*	e_s^*		e^*	e_s^*
LiF	1.12	0.86	RbCl	1.17	0.84
NaF	1.16	0.93	RbBr	1.17	0.81
NaCl	1.06	0.75	CsCl	1.32	0.86
NaBr	1.08	0.70	CsBr	1.29	0.81
NaI	1.16	0.71	AgCl	1.58	0.79
KCl	1.09	0.79	TlCl	2.60	1.10
KBr	1.10	0.76	CuCl	2.04	1.10
KI	1.08	0.69	MgO	2.90	1.76

Table II. Comparisons between the calculated κ from (3-1) and the observed κ .

	λ_t (μ)	λ_r	κ_0	κ	
				cal.	obs.
NaCl	61.1	31	2.25	5.86	5.62
TlCl	117	~45	5.10	28.7	31.9
ZnS	33	24	5.07	8.69	8.3
CdTe	69	58	8.53	11.7	~11

† Through the present paper, we mean by the term "simple ionic model" that the binding is perfectly ionic and the interaction between the polarizations can be expressed only by the Lorentz correction, and by "ionic model" we take into account the short range interaction energies between the polarizations especially the cross terms like $B_{ij}x_i p_j$, where p_j is the electronic polarization of the j -th ion.

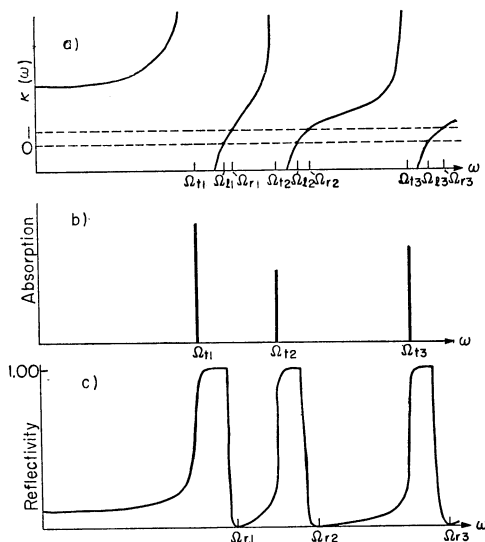


Fig. 1. General features of the dielectric constant, the optical absorption and the reflectivity of crystals.

interaction energy due to the interionic overlapping which causes cross terms between the ionic displacement and the electronic polarization, at least in the case of the alkali halide crystals⁶⁾.

In order to verify the theory of § 2, we compare in Table II the dielectric constant κ obtained experimentally and that calculated from the following relation:

$$\kappa - 1 = (\kappa_0 - 1) \frac{\Omega_r^2}{\Omega_t^2},$$

and from the observed values of κ_0 , Ω_t and Ω_r ,^{7)†} where the above relation is a special case of the more general relation;

$$\kappa(\omega) - 1 = (\kappa_0 - 1) \prod_v \frac{\Omega_{rv}^2 - \omega^2}{\Omega_{tv}^2 - \omega^2}, \quad (3-1)$$

this can be derived similarly as Eq. (2-21).

BaTiO₃ and the related crystals

We take up these crystals, because of the comparatively satisfactory experimental data about them as well as their peculiar dielectric properties.

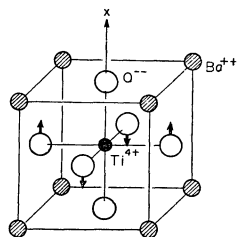


Fig. 2. The crystal structure of BaTiO₃ crystal.

These crystals have five ions in a unit cell and have fifteen independent modes of the lattice waves; three acoustical and twelve optical. However, three optical modes illustrated in Fig. 2 (two oxygen ions oscillate to the opposite direction with the same amount) have no dipole moment and are optically inactive. Thus, there remain three longitudinal modes and 3×2 transverse modes for sufficiently long waves. Last⁸⁾ has observed two absorption peaks (Ω_t) and two reflection minima^{††} (Ω_r) for BaTiO₃, SrTiO₃ and PbTiO₃ crystals. Furthermore, we can guess that the one more Ω_t may be nearly zero from

their quite large κ . The one more Ω_r has not been observed. We tabulated them in Table III. If Ω_{r1} were observed, we could determine $(\sum_i e_i^* x_i)^2 / \sum_i M_i x_i^2$'s of three modes using Eq. (2-15)^{†††}. Furthermore, if a quite precise measurement using the isotopes were performed, it would be possible to determine the e_i^* of each ion separately. Although it is also possible to estimate the $(\sum e_i^* x_i)^2 / \sum M_i x_i^2$ from the absorption intensity, practically the reliable determination is difficult.

Table III. (cm⁻¹).

	SrTiO ₃	BaTiO ₃	PbTiO ₃
Ω_{t1}	~0	~0	~0
Ω_{r1}	?	?	?
Ω_{t2}	395	400	405
Ω_{r2}	490	475	455
Ω_{t3}	610	545	590
Ω_{r3}	890	800	(800)

Table IV. The values of $4\pi N \sum_i e_i^{*2} / M_i (10^6 \text{ cm}^{-2})$.

	From the infra-red data	From the simple ionic model
SrTiO ₃	2.26~2.96	17.4
BaTiO ₃	1.95~2.71	10.6
PbTiO ₃	2.02~3.00	12.3

Nevertheless, we can derive an inequality about the effective charges. In the same way as the derivation of Eq. (2-24), we have

$$4\pi N \sum_i \frac{e_i^{*2}}{M_i} = (\kappa_0 - 1) \sum_v (\Omega_{rv}^2 - \Omega_{tv}^2). \quad (3-2)$$

On the other hand, clearly

$$\Omega_{t2} > \Omega_{r1} > \Omega_{t1} \simeq 0.$$

Thus we have the upper and lower limits of the $\sum e_i^{*2} / M_i$ (Table IV).

† We have used Ω_r , because it can be more easily determined than Ω_t from usually available experimental data.

†† The reflection is not perfectly zero because of the absorption tail at Ω_r .

††† In the case of BaTiO₃ crystal, it may help the understanding to imagine the following process: When the BaTiO₃ crystal is compressed the curie point T_c is lowered because of the increased interionic repulsive forces. If the compression is continued, the T_c will be lowered down to 0°K and the crystal will lose its ferroelectricity. We may expect, however, that rather a small contraction of the lattice constant (about 2~3%) and rather a small increase of the repulsive force is sufficient to remove the ferroelectricity on the one side and causes no appreciable change of the other properties; Ω_t , Ω_l , Ω_r and e_i^* on the other side.

For comparison, we calculate the $\sum e_i^{*2}/M_i$ assuming the simple ionic model, where e_i^{*} 's can be calculated by the following process:

$$e_i^* = Z_i e + \sum_j \epsilon_{ij} \quad (3-3)$$

and

$$p_i = \sum_j \epsilon_{ij} x_j, \quad (3-4)$$

where Z_i , x_i , p_i are the valency (e.g. $Z_{\text{Ti}} = +4$), the displacement and the electronic polarization of the i -ion respectively. p_i is given by

$$p_i = \alpha_i F_i \quad (3-5)$$

and

$$F_i = N \left\{ \sum_j L_{ij} p_j + \sum_j L_{ij} Z_j e (x_j - x_i) \right\}, \quad (3-6)$$

where α_i and F_i are the polarizability and the local field. The coefficients L_{ij} 's are given by many authors⁹⁾, for instance when $i = \text{Ti}^{4+}$ and $j = \text{O}^{2-}$, $L_{ij} = 4\pi \times 2.727$. We calculated $\sum e_i^{*2}/M_i$'s (Table IV), by substituting for α_i the following values: 0.2 (Ti^{4+}), 1.6 (Sr^{++}), 2.5 (Ba^{++}), 3.1 (Pb^{++}) and $2.2 \times 10^{-24} \text{ cm}^3$ (O^{--}).[†] The values of $\sum e_i^{*2}/M_i$ from the infra-red data are only 1/5~1/4 times of those from the simple ionic model, although the above polarizabilities are consistent with κ_0 . On the other hand, in the case of alkali halide crystals, if we assume the simple ionic model as above and take the polarizabilities as consistent with κ_0 , e^* is given by

$$e^* = \left(\frac{\kappa_0 + 2}{3} \right) e.$$

Thus the ratio of the infra-red value to the simple ionic model value of $\sum e_i^{*2}/M_i$ is $(e_s^*/e)^2$, that is about 0.5~0.9. In this case, we have interpreted the difference by the effect of the short range interaction energy between the ionic displacement and the electronic polarization of ions; the displacement works to induce the electronic polarization with the opposite direction through the overlapping between ions. However, the ratios 1/5~1/4 seem too small to be interpreted by the same effect.

The experiments about the spontaneous polarization of BaTiO_3 are also consistent

with the present analysis about the effective charge. The spontaneous polarization is given by

$$P_s = N \sum_i e_i^* x_i^s, \quad (3-7)$$

where x_i^s is the spontaneous displacement of the i -th ion and has been determined from the experiments of the neutron¹¹⁾ or the x-ray diffraction¹²⁾. Although e_i^* of each ion is not known, we have an inequality;

$$P_s^2 = (N \sum_i e_i^* x_i^s)^2 \leq N^2 \sum_i \frac{e_i^{*2}}{M_i} \sum_i M_i x_i^{s2}. \quad (3-8)$$

By substituting for x_i^s 's the values from the neutron diffraction experiment, we have

$$P_s < 31 \text{ microcoulomb/cm}^2.$$

The x_i^s 's from the x-ray diffraction give nearly the same result. The direct experimental value of P_s by Merz¹³⁾ is 26 microcoulomb/cm². The spontaneous displacement x_i^s can be regarded as brought by the instabilized transverse vibration mode with the lowest frequency Ω_{t1} and as again stabilized by unharmonicity. Therefore, if the $(\sum e_i^* x_i)^2 / \sum M_i x_i^2$ of the Ω_{t1} mode were known, the P_s could be estimated more precisely;

$$P_s^2 = N^2 \left[\frac{(\sum_i e_i^* x_i)^2}{\sum_i M_i x_i^2} \right]_{\Omega_{t1} \text{ mode}} \times \sum_i M_i x_i^{s2}. \quad (3-9)$$

Nevertheless, the inequality (3-8) is consistent with the experiment.

There may be two possible standpoints in interpreting the difference between calculated (simple ionic model) values and the observed (infra-red) values of the effective charge; one attributes the disagreement to the homopolar-binding, and another interprets it within the range of the ionic model. Although it is not within the scope of the present analysis to discuss this problem, a trial upon the latter standpoint is done in Appendix.

It may be allowable to interpret a ferroelectric crystal as a crystal of which the polar mode lattice wave of $\vec{k}=0$ is unstable (in the first approximation) and an antiferroelectric crystal as a crystal of which a lattice wave of $\vec{k} \neq 0$ (e.g. at the zone boundary) is unstable, in the case of the ionic crystals. Generally speaking, the \vec{k} -dependence of the frequency of the polar mode lattice wave is rather small and has complicated properties,

[†] The values for Ti^{4+} , Sr^{++} and Ba^{++} are taken from the paper of Tessman, Kahn and Shockley¹⁰⁾, that of O^{--} ion is adjusted to give the optical dielectric constant κ_0 of BaTiO_3 and SrTiO_3 and that of Pb^{++} ion is taken to be consistent with κ_0 of PbTiO_3 .

therefore the theoretical prediction whether a crystal is ferroelectric or antiferroelectric is a delicate problem.

§ 4. The Electronic Polarization Waves

It is possible to apply the viewpoints in § 2 to the case of the electronic polarization waves in some degree.

Notes on the theory of Heller and Marcus

Let us suppose an atom (or an ion or a molecule) under an oscillating electric field F with a frequency ω . The induced dipole moment is

$$m = \alpha(\omega)F, \quad (4.1)$$

where let the polarizability $\alpha(\omega)$ be scalar and given by

$$\alpha(\omega) = \frac{e^2}{m_e} \sum_i \frac{f_i}{\omega_i^2 - \omega^2}. \quad (4.2)$$

The oscillator strength f_i satisfies the sum rule;

$$\sum_i f_i = n, \quad (4.3)$$

where n is the number of the electrons belonging to the atom.

In the next place, let us suppose a crystal consisting of these atoms and the polarization waves propagating in it. The electronic polarization of the i -th atom is given by

$$\vec{m}_i = \vec{m}_0 \cdot \exp(i\vec{k}\vec{R}_i - i\omega t). \quad (4.4)$$

The relations (2-8) and (2-9) for sufficiently long waves are valid also in this case. If we neglect the overlapping between the atoms, the interaction between the polarizations is only the dipole-dipole one. This interaction can easily be taken into account merely by considering the local field acting on each atom due to the dipole moments on the other atoms. For instance, in the case of the polarization waves of $k=0$ in a cubic crystal, the local field F is given by

$$F = E + \frac{4\pi}{3}P. \quad (4.5)$$

Therefore, by combining the Eqs. (2-8), (4-1), (4-2) and (4-5), we find that the frequency Ω_i of the transverse wave in this case must satisfy the following relation:

$$\frac{4\pi}{3}N\alpha(\Omega_i) = \frac{\omega_p^2}{3} \sum_i \frac{f_i}{\omega_i^2 - \Omega_i^2} = 1, \quad (4.6)$$

where

$$\omega_p^2 = \frac{4\pi Ne^2}{m_e}. \quad (4.7)$$

Similarly, the frequency of the longitudinal wave is given by

$$-\frac{2\omega_p^2}{3} \sum_i \frac{f_i}{\omega_i^2 - \Omega_i^2} = 1. \quad (4.8)$$

On the other hand, under the same assumptions the dielectric constant $\kappa(\omega)$ is given by

$$\kappa(\omega) = 1 + \frac{4\pi N\alpha(\omega)}{1 - (4\pi/3)N\alpha(\omega)}. \quad (4.9)$$

Comparing Eqs. (4-6) and (4-8) with (4-9), we can ascertain that Ω_i 's and Ω_i 's correspond to the poles and the zeros of $\kappa(\omega)$ respectively, as in § 2.

Eqs. (4-6) and (4-8) can be transformed as follows: e.g. in the case of $i=1$

$$\Omega_{i1}^2 - \omega_1^2 = -\frac{f_1\omega_p^2}{3} \cdot \frac{\kappa^{(1)}(\Omega_{i1}) + 2}{3} \quad (4.10)$$

and

$$\Omega_{i1}^2 - \omega_1^2 = \frac{2f_1\omega_p^2}{3} \cdot \frac{3\kappa^{(1)}(\Omega_{i1})}{\kappa^{(1)}(\Omega_{i1}) + 2}, \quad (4.11)$$

where $\kappa^{(1)}(\omega)$ is given by

$$\kappa^{(1)}(\omega) = 1 + \frac{4\pi N\alpha^{(1)}(\omega)}{1 - (4\pi/3)N\alpha^{(1)}(\omega)} \quad (4.12)$$

and

$$\alpha^{(1)}(\omega) = \frac{e^2}{m_e} \sum_{i \neq 1} \frac{f_i}{\omega_i^2 - \omega^2},$$

that is, $\kappa^{(1)}(\omega)$ is the dielectric constant due to the oscillators other than the ω_1 -oscillator. Eqs. (4-10) and (4-11) represent the shift of the atomic levels due to the dipole interaction in the crystal.

If we put $\kappa^{(1)}(\omega)=1$ (i.e. neglect the effect of the other levels) and take only the first order term of f_1 , (4-10) and (4-11) can be simplified as

$$\Omega_{i1} = \omega_1 - \frac{f_1\omega_p^2}{6\omega_1}$$

and

$$\Omega_{i1} = \omega_1 + \frac{f_1\omega_p^2}{3\omega_1}. \quad (4.13)$$

These results agree with the energy of the exciton of $k=0$ by Heller and Marcus⁽⁴⁾.

If there are many excited states, however, each mode of the polarization waves should be represented by a mixture of various atomic excitations; the dipole moment due to an atomic excitation induces that corresponding to the other atomic excitations. The latter is

superposed on the former and the resultant dipole moment is $\{\kappa^{(1)}(\Omega_{t1})+2\}/3$ times the original one in the case of the transverse waves. The local field, that is the variation in the restoring force, is proportional to the dipole moment, thus we have the factor $\{\kappa^{(1)}(\Omega_{t1})+2\}/3$ of Eq. (4-10).

The frequency of the polarization wave with an arbitrary \vec{k} is to be easily found, if we perform the dipole sum as Lyddane and Herzfeld¹⁵⁾ have done and calculate the local field at an atom.

If we express the dielectric constant $\kappa(\omega)$ as

$$\kappa(\omega)=1+\frac{4\pi Ne^2}{m_e}\sum_i\frac{F_i}{\Omega_{ti}^2-\omega^2}, \quad (4-14)$$

F_i corresponds to the oscillator strength of the i -th excitation mode in the crystal; it is proportional to the optical absorption intensity and (4-14) has the same form as the expression of $\kappa(\omega)$ neglecting the local field correction;

$$\kappa(\omega)=1+4\pi N\alpha(\omega)=1+\frac{4\pi Ne^2}{m_e}\sum_i\frac{f_i}{\omega_i^2-\omega^2}.$$

Comparing (4-9) and (4-14), we have a relation after simple manipulations;

$$F_i=f_i\left\{\frac{\kappa^{(1)}(\Omega_{t1})+2}{3}\right\}^2/\left\{1+\frac{f_1\omega_p^2}{9}\left[\frac{d\kappa^{(1)}(\omega)}{d(\omega^2)}\right]_{\omega=\Omega_{t1}}\right\}\simeq f_i\left\{\frac{\kappa^{(1)}(\Omega_{t1})+2}{3}\right\}^2. \quad (4-15)$$

This represents the change of the absorption intensity in the crystal. The change is caused by the mixing of the other atomic excitation modes. The relation with a similar property has been derived by Dexter¹⁶⁾. Furthermore, the following relations are readily found:

$$\sum_i F_i = \sum_i f_i = n, \quad (4-16)$$

this is natural,

$$\kappa(\omega)=\prod_i\left(\frac{\omega^2-\Omega_{ti}^2}{\omega^2-\Omega_{ti}^2}\right) \quad (4-17)$$

and

$$\frac{1}{2}\sum_i(\Omega_{ti}^2-\omega_i^2)=\sum_i(\omega_i^2-\Omega_{ti}^2)=\frac{n}{3}\omega_p^2. \quad (4-18)$$

In the above discussions, we adopted a semi-classical approach. However, so far as the interaction between the atoms is the dipole-dipole one and the response of the atom to the electric field is given by (4-1) and (4-2), the above discussions would hold even if the motion of the system were governed by any mechanics; the relations (4-10), (4-11) and (4-15) are to be equivalent to the results calculated quantum mechanically up to the higher order terms of the interaction. The response (4-1), however, holds only for sufficiently weak electric fields except the case of the harmonic oscillator. On the other hand, an atomic transition causes finite electric fields on the neighbouring atoms, namely, the electric field due to the electronic polarization wave fluctuates up to finite values even if it is sufficiently small on an average, such a situation differs from the classical polarization waves. Thus the deviations from the above relations are expected in quantum mechanics. It is not difficult to verify that the above relations agree with the quantum mechanical results up to the terms of f_i 's and $f_i f_j$'s ($i \neq j$) in the power series expansions with respect to f_i 's. It is supposed, however, that both do not agree for higher order terms in general.[†]

On the other hand, the level scheme given by Eqs. (4-10) and (4-15) is equivalent to the expression of $\kappa(\omega)$ given by (4-9), therefore the deviation from the so-called Lorentz correction is expected in quantum mechanics from the order of f^3 even if the interaction is only the dipole-dipole one.^{††}

[†] Although it is difficult to investigate quantum mechanically the higher order terms than f^2 in general, we can verify this supposition for special cases, for instance; (1) Two atom system. (2) A crystal composed of the atoms with three atomic levels; s (ground state), p and d levels. In this case, the exact polarization waves should include d -component as well as s - and p -components at the same time differing from the classical polarization waves. (3) In the case of the extremely strong interaction, Ω_{t1} becomes zero or imaginary (see Eq. (4-10)), but such a behaviour cannot be expected in general.

^{††} The same conclusion has been independently obtained by T. Izuyama (private communication).

The above discussions are more suitably applied to molecular crystals rather than to ionic crystals. In most molecular crystals, however, the crystal structure is complicated and the local field is not simply given by (4-5). In order to apply the above theory to these crystals, it is necessary to perform the complicated dipole sum. It is rather trivial, however, to generalize the theory to these cases unless the practical problems are treated.

Similarly as above, the dipole moment due to the excitation of an impurity atom in a crystal induces the dipole moments of the surrounding atoms, therefore the absorption spectra of the impurity atom change from those of the free atom; the shift of the frequency and the change of the intensity are caused¹⁶⁾.

General electronic polarization waves

The properties of the more general electronic polarization waves have been discussed by many authors^{3), 4), 17)}, therefore we briefly summarize them from the present standpoint.

The frequency of the longitudinal polarization wave of $k=0$ satisfies again the relation;

$$\kappa(\Omega_l) = 0. \quad (4-19)$$

So that, if $\kappa(\omega)$ is represented by the expression like (4-14),

$$\Omega_{l1}^2 - \Omega_{l1}^2 = \left(\frac{4\pi N e^2 F_1}{m_e} \right) / \left\{ 1 + \frac{4\pi N e^2}{m_e} \sum_{i \neq 1} \frac{F_i}{\Omega_{li}^2 - \Omega_{l1}^2} \right\} = \frac{4\pi N e^2 F_1}{m_e \kappa^{(1)}(\Omega_{l1})}. \quad (4-20)$$

Particularly, in the case of $\Omega_{l1}=0$, that is in metals, Ω_{l1} becomes the plasma frequency of the electron system shielded by the dielectric constant $\kappa^{(1)}(\Omega_{l1})$.

In general, however, crystals have continuous absorption spectra, hence the roots of Eq. (4-19) are complex. In this case, it is appropriate to investigate the relation between the response of the system to the electric field $E(t)$ and that to the electric displacement $D(t)$. The electric current in a crystal induced by microscopically homogeneous $E(t)$ and $D(t)$ is generally given by

$$\begin{aligned} J(t) &= \int_{-\infty}^{\infty} \Phi(t-t') E(t') dt' \\ &= \int_{-\infty}^{\infty} \Psi(t-t') D(t') dt'. \end{aligned} \quad (4-21)$$

Clearly, the response functions $\Phi(t)$ and $\Psi(t)$ have the following properties: (1) $\Phi(t) = \Psi(t) = 0$, for $t < 0$. (2) $\Phi(t)$ and $\Psi(t)$ are real. (3) $\Phi(0) = Nne^2/m_e$, where Nn is the total number of the electrons per unit volume, $\Phi(0)$ is the current which is induced instantly by the electric field of $\delta(t)$ type. By noting that

$$D(t) = E(t) + 4\pi \int_{-\infty}^t J(t') dt', \quad (4-22)$$

we have

$$\Psi(t) = \Phi(t) - 4\pi \int_0^t dt' \Phi(t-t') \int_0^{t'} dt'' \Psi(t''). \quad (4-23)$$

If we write

$$\Phi(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \sigma(\omega) e^{i\omega t} d\omega$$

and

$$\Psi(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} s(\omega) e^{i\omega t} d\omega, \quad (4-24)$$

(where $\sigma(\omega) = \sigma^*(-\omega)$ and $s(\omega) = s^*(-\omega)$ because of the reality of $\Phi(t)$ and $\Psi(t)$), we have from Eq. (4-23)

$$s(\omega) = \frac{\sigma(\omega)}{1 - 4\pi i \sigma(\omega)/\omega}. \quad (4-25)$$

From the definitions of $\sigma(\omega)$ and $s(\omega)$, it is clear that their physical meaning is that the current due to the oscillating E and D with the frequency ω is given by

$$J = \sigma(\omega) E = s(\omega) D. \quad (4-26)$$

Moreover, because

$$1 - \frac{4\pi i \sigma(\omega)}{\omega} = \kappa(\omega), \quad (4-27)$$

the relation (4-25) is equivalent to

$$s(\omega) = \frac{\sigma(\omega)}{\kappa(\omega)}. \quad (4-28)$$

This is rather trivial.

On the other hand, if we put $t=0$ in Eq. (4-23), we have

$$\Psi(0) = \Phi(0) = \frac{Nne^2}{m_e}. \quad (4-29)$$

By comparing this with (4-24), we have the sum rules;

$$\int_0^{\infty} \sigma_r(\omega) d\omega = \int_0^{\infty} s_r(\omega) d\omega = \frac{\pi Nne^2}{m_e}, \quad (4-30)$$

where σ_r and s_r are the real parts of σ and s respectively. Furthermore, from Eq. (4-25)

$$s(\omega) - \sigma(\omega) = 4\pi i \frac{\sigma(\omega)s(\omega)}{\omega},$$

therefore

$$\begin{aligned} 0 &= \int_{-\infty}^{\infty} \frac{\sigma(\omega)s(\omega)}{\omega} d\omega \propto \int_{-\infty}^{\infty} \omega \frac{(\kappa-1)^2}{\kappa} d\omega \\ &= \int_0^{\infty} \omega \left(\kappa - \kappa^* + \frac{1}{\kappa} - \frac{1}{\kappa^*} \right) d\omega \\ &\propto \int_0^{\infty} \left\{ \sigma_r(\omega) - \frac{\sigma_r(\omega)}{|\kappa(\omega)|^2} \right\} d\omega \end{aligned}$$

or

$$\int_0^{\infty} \sigma_r(\omega) d\omega = \int_0^{\infty} \frac{\sigma_r(\omega)}{|\kappa(\omega)|^2} d\omega = \frac{\pi N n e^2}{m_e}. \quad (4-31)$$

On the other hand, the rate of the energy loss per unit volume of the crystal, if $E = E_0 \cos \omega t$ and $D = D_0 \cos \omega t$, is given by

$$\text{Loss} = \frac{1}{2} \sigma_r(\omega) E_0^2 = \frac{\sigma_r(\omega)}{2|\kappa(\omega)|^2} D_0^2. \quad (4-32)$$

Thus the relations (4-30) and (4-31) are the sum rules concerning the electric current and the energy loss due to E and D respectively. The conductivity $\sigma_r(\omega)$ determines the intensity of the optical absorption and the $\sigma_r(\omega)/|\kappa(\omega)|^2$ does the energy loss† of a high energy charged particles⁹⁾, for the charged particle acts as a source of D rather than of E .

The oscillator strength of the exciton in alkali halide crystals

As stated in §3, we can determine $(\sum e_i^* x_i)^2 / \sum M_i x_i^2$'s which correspond to the oscillator strength in the electronic case, from Ω_t (absorption peak) and Ω_r (reflection minimum) instead of the absorption intensity. The similar method is applicable to the elec-

tronic case, if the absorption peak is isolated. For instance, in the case of the so-called exciton absorption in alkali halide crystals, $\kappa(\omega)$ is given by

$$\kappa(\omega) = \frac{4\pi N e^2}{m_e} \frac{f}{\Omega_t^2 - \omega^2} + \kappa'(\omega),$$

near the exciton peak, where f is the oscillator strength of the exciton level and N is the number of unit cells per cm^3 , $\kappa'(\omega)$ is the dielectric constant coming from the other levels. The reflection minimum arises when $\kappa(\Omega_r) = 1$. We estimate $\kappa'(\omega)$ from the reflectivity of the region over $(\hbar\Omega_t - 0.2 \text{ eV}) \sim (\hbar\Omega_t - 0.5 \text{ eV})$, since it may be approximately regarded as a constant within the narrow frequency range from $(\hbar\Omega_t - 0.5 \text{ eV})$ to $\hbar\Omega_r$. The results are summarized in Table V. The oscillator strength of the exciton level is rather small, if we remember that there are at least six electrons participating in the exciton level in a unit cell. The contribution to κ_0 from the exciton level is about 0.1. This method may be useful to estimate the oscillator strength when the quantitative data of the absorption intensity are not available, although it is not new in principle.

Table V. The oscillator strength of the exciton.

	κ'	$\hbar\Omega_t$	$\hbar(\Omega_r - \Omega_t)$	f
NaI	3.7	5.6 eV	0.12 eV	0.19
KI	4.1	5.8	0.12	0.27
RbI	3.7	5.7	0.15	0.33

The author wishes to express his gratitude to Prof. J. Yamashita for his helpful discussions.

Appendix. The Effective Charge of BaTiO₃ Crystal

As stated in §3, the ratio;

$$\frac{(\text{the experimental value of } \sum_i e_i^{*2}/M_i \text{ from the infra-red data})}{(\text{the calculated value of } \sum_i e_i^{*2}/M_i \text{ from the simple ionic model})} \quad (A-1)$$

is $1/5 \sim 1/4$ in BaTiO₃ and the related crystals. We investigate here whether such a great difference may be interpreted by the ionic model or not. In the case of alkali halide

† Of course, the weight with respect to the final states of the particle must be multiplied to this.

crystals, the ratio (A-1) is $0.5 \sim 0.9$, and we can interpret⁶⁾ the difference by assuming the short range interaction energy between the polarization due to the ionic displacement and the electronic polarization, although we cannot explain it by the simple ionic model only.

In the case of BaTiO₃ and the related crystals, we attempt to bring the ratio (A-1) from 1/5~1/4 to 0.5 within the range of the simple ionic model and expect that the remaining difference may be interpreted by the similar mechanism as in alkali halide crystals.

The large calculated values of $\sum e_i^{*2}/M_i$ come mainly from the large polarizability of the oxygen ions. However, the polarizabilities assumed in § 3 are not well-founded, although they are consistent with the experimental κ_0 . Therefore we regard them as the adjustable parameters and examine whether the above ratio can be brought to the expected value (≈ 0.5) or not with the reasonable values of them.

It is a way to this purpose to decrease the polarizability of the O²⁻ ions and increase that of the divalent metal ion. The polarizability of Ti⁴⁺ ion is too small to influence the result. It is necessary, however, to compensate the decrease of the polarizability of three O²⁻ ions with the increase of that of only one metal ion to hold the κ_0 unchanged, so that unreasonably large polarizability of the metal ion is necessary to bring the ratio (A-1) to the expected range. For instance, if we put the polarizability of Sr²⁺ ion as 3.4 Å³ instead of 1.6 Å³ in § 3 the above ratio for SrTiO₃ becomes 0.5. This value of the polarizability is inconsistent with κ_0 of SrO crystal, in which the *total* polarizability is to be 3.5 Å³.

Another way is to assume the anisotropic polarizability of the O²⁻ ions. It is well-known that the polarizability of O²⁻ ion fluctuates from compound to compound and generally increases with the volume per O²⁻ ion¹⁰. In the BaTiO₃ type crystals, the ionic configuration is close-packed in the Ti-O direction and loose-packed in the Ba-O direction (Table VI), so that, it is probable that the

polarizability of the O²⁻ ion is small in the Ti-O direction and large in the Ba-O direction. Since the most important contribution to the calculated values of $\sum e_i^{*2}/M_i$ comes from the electronic polarization of the so-called O_a ion, the above assumption is favorable to our purpose. For instance, in the case of BaTiO₃ crystal, the following polarizabilities bring the above ratio to 0.5 and are also consistent with κ_0 : O²⁻ ion (Ti-O direction) 1.7 Å³, (Ba-O direction) 2.5 Å³, Ba²⁺ ion 2.5 Å³ and Ti⁴⁺ ion 0.2 Å³ (the last two values are equal to those in § 3). The circumstances are nearly the same in the other titanates. The polarizability of O²⁻ ion varies considerably from compound to compound, e.g. 1.6 Å³ in MgO and 3.0 Å³ in BaO crystals, so that the anisotropy as above is possible. Of course, the above discussions only suggest a possibility of the ionic model and do not deny the possibility of the homopolar binding.

References

- 1) B. Szigeti: Trans. Faraday Soc. **45** (1949) 155; Proc. Roy. Soc. (London) **A**, **204** (1950) 51.
- 2) H. Fröhlich: *Theory of Dielectrics* (Clarendon Press, 1949) § 18.
- 3) H. Fröhlich and H. Pelzer: Proc. Phys. Soc. **A**, **68** (1955) 525.
- 4) N. F. Mott: Proceedings of the 10th Solvay Congress, Brussels, 1954.
- 5) H. Callen: Phys. Rev. **76** (1949) 1394.
- 6) J. Yamashita and T. Kurosawa: J. Phys. Soc. Japan **10** (1955) 610.
- 7) M. Czerny: Z. Phys. **65** (1930) 600. H. Yoshinaga: Phys. Rev. **100** (1955) 753. A. Mitsuishi et al.: The 15th annual meeting of the Physical Society of Japan (1960).
- 8) J. T. Last: Phys. Rev. **105** (1957) 1740.
- 9) See for instance, J. C. Slater: Phys. Rev. **78** (1950) 748.
- 10) J. R. Tessman, A. H. Kahn and W. Shockley: Phys. Rev. **92** (1953) 890.
- 11) B. C. Frazer, H. R. Danner and R. Pepinsky: Phys. Rev. **100** (1955) 745.
- 12) W. Känzig: Helv. Phys. Acta **24** (1951) 175.
- 13) W. J. Merz: Phys. Rev. **91** (1953) 513.
- 14) W. R. Heller and A. Marcus: Phys. Rev. **84** (1951) 809.
- 15) Lyddane and Herzfeld: Phys. Rev. **54** (1938) 846.
- 16) D. L. Dexter: Phys. Rev. **101** (1956) 48.
- 17) See for instance, D. Pines: Rev. Mod. Phys. **28** (1956) 184.
- 18) E. A. Taft and H. R. Philipp: J. Phys. Chem. Solids **3** (1957) 1.

Table VI.

	I	II	(I-II)	III	IV
CaTiO ₃	2.70	0.99	1.71	1.23	2.40
SrTiO ₃	2.76	1.13	1.63	1.27	2.57
BaTiO ₃	2.83	1.35	1.48	1.32	2.76

I. O²⁻-Me²⁺ distance; II. Ionic radius of Me²⁺ ion; III. (Ti⁴⁺-O²⁻ distance)-(Ionic radius of the Ti⁴⁺ ion); IV. O²⁻-Me²⁺ distance in MeO crystal (10⁻⁸ cm).