Remarks on the Relation between Microscopic and Macroscopic Crystal Optics

By J. van Laar*, H. J. Endeman† and J. M. Bijvoet‡

Laboratorium voor Kristalchemie der Rijks-Universiteit, Utrecht, The Netherlands

The microscopic equations for the polarization caused by a travelling light wave in an infinite crystal are brought into a form that is analogous to that of macroscopic optics. The role of the 'incident' field term in the elementary theory and that of a magnetic contribution to the optical rotatory power are discussed.

1. Introduction

Calculation of the rotatory power of $NaClO_3$ and $NaBrO_3$ crystals – performed in view of their unexpected relative behaviour – has previously been reported (Beurskens-Kerssen, Kroon, Endeman, van Laar & Bijvoet, 1963). Our calculations were based on Born's classical coupled oscillator model and we used the rapidly converging expressions for the dipole interaction in a crystal obtained by Ewald by means of his θ transformation of lattice sums (Ewald, 1916*a*, 1921).

Its first presentation (Bijvoet, 1960) at the meeting of the I.U.Cr. in Cambridge was given in terms of the elementary scheme (§ 5) which includes an incident field term. The misuse of the latter conception has been thoroughly discussed by Ewald (1916*a,b*) in his monumental studies on the light propagation in an infinite as well as in a 'half' crystal. This misuse was kindly brought to our attention by Prof. Ewald after the section meeting. Ewald's remark induced the present comparison of exact and elementary equations for the crystal polarization; furthermore the microscopic equations for the polarization of the different sublattices [equation (7)] have been shaped into one equation (17), which is analogous to that of macroscopic optics.

Especially to the oldest of the present authors this contribution to the volume dedicated to Prof. Ewald offers the opportunity of expressing his profound admiration for the originality and charm of both Ewald's work and person.

2. General outline of calculations

We shall choose a rectangular coordinate system in the crystal with axis (u_1, u_2, u_3), the origin being situated at the corner of a unit cell. With r_h $[(r_h)_1, (r_h)_2, (r_h)_3]$ we denote the coordinates of an atom in this special unit cell. There are n atoms per unit cell, so $h = 1 \ldots n$. r^l

stands for the vector to a lattice point and r_h^l for the vector to atom number h in the unit cell at r^l, *i.e.* $r_h^l = r^l + r_h$. With a we denote an arbitrary unit-cell dimension and with V the unit cell volume.

Further, the following notation will be used for the quantities of the electromagnetic field: $E(r)$ and $H(r)$ electric and magnetic field strength at point r; $Z(r)$ Herz vector; p_h^l dipole moment of atom r_h^l; k wave vector; n index of refraction; ω circular frequency; λ and λ_0 wavelength in the medium and vacuum wavelength respectively and c the velocity of electromagnetic waves in vacuum. Tensors will be denoted with A letters.

We consider the valence electrons to be quasi-elastically bound to their equilibrium position, thus acting as harmonically oscillating dipoles under the influence of an electromagnetic field. We assume these dipoles to be located at the centres of the atoms.

To eliminate the complications caused by boundary conditions, we follow the method of Ewald (1916*a*) in which an infinite crystal is considered. Consequently there is no incident beam of light.

An electromagnetic wave field will exist in such a crystal if it satisfies the condition that the vibration of each dipole is just maintained by the field that is brought about by all the others. This condition can be fulfilled by a plane travelling electromagnetic wave if for a given angular frequency ω the wavelength λ is chosen properly. The equation of motion for the harmonic vibrations of valence electron (l, h) reads:

$$(- M\omega^2 + i\beta\omega + \alpha_h)u_h^l = e \sum_{l', h'}{}' E_{h'}^{l'}(r_h^l), \qquad (1a)$$

where u_h^l is the deviation of the electron from its equilibrium position, M and e its mass and charge; α_h and β are constants and $E_{h'}^{l'}(r)$ denotes the electric field at r due to dipole (l', h'). The prime in the summation means that dipole (l, h) itself has to be omitted.

If ω is not too close to one of the resonance frequencies $[(\alpha_h)_j/M]^{\frac{1}{2}}$, the damping term with β can be neglected; with $p_h^l = eu_h^l$ one gets:

$$\frac{\alpha_h - M\omega^2}{e^2} p_h^l \equiv \gamma_h p_h^l = \sum_{l', h'}{}' E_{h'}^{l'}(r_h^l). \qquad (1b)$$

$E_{h'}^{l'}(r)$ will be proportional to $p_{h'}^{l'}$ and moreover only dependent on the distance between point r and atom $r_{h'}^{l'}$:

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* Present address: Philips Research Laboratories, Eindhoven, The Netherlands.

† Present address: Clinic of Internal Medicine, University of Utrecht, The Netherlands.

‡ Present address: Meddo D27, Winterswijk, The Netherlands.

$$\mathbf{E}_{h'}^{l''}(\mathbf{r}) = \mathbf{a}(\mathbf{r} - \mathbf{r}_{h'}^{l''})\mathbf{p}_{h'}^{l''} . \tag{2}$$

Substitution of (2) into (1b) yields:

$$\gamma_h \mathbf{p}_h^l = \underset{l'', h'}{\Sigma'} \mathbf{a}(\mathbf{r}_h^l - \mathbf{r}_{h'}^{l''})\mathbf{p}_{h'}^{l''} . \tag{3}$$

This infinite system of homogeneous equations in $\mathbf{p}_h^l$ can be reduced to a system of n equations owing to the periodicity of the crystal. For this purpose we assume a solution for $\mathbf{p}_h^l$ of the form:

$$\mathbf{p}_h^l = {}^0\mathbf{p}_h \exp(-i\omega t + i\mathbf{k} . \mathbf{r}_h^l) . \tag{4}$$

Substitution of (4) into (3) results in:

$$\gamma_h{}^0\mathbf{p}_h = \underset{h'}{\Sigma} {}^0\mathbf{p}_{h'}[\underset{l''}{\Sigma'} \mathbf{a}(\mathbf{r}_h^l - \mathbf{r}_{h'}^{l''}) \exp\{-i\mathbf{k} . (\mathbf{r}_h^l - \mathbf{r}_{h'}^{l''})\}] \tag{5}$$

and in this equation the sum between square brackets is evidently independent of the special cell chosen in (3). Hence we can define:

$$\underset{l''}{\Sigma'} \mathbf{a}(\mathbf{r}_h^l - \mathbf{r}_{h'}^{l''}) \exp\{-i\mathbf{k} . (\mathbf{r}_h^l - \mathbf{r}_{h'}^{l''})\}$$
$$\equiv \mathbf{A}(\mathbf{r}_h - \mathbf{r}_{h'}) \equiv \mathbf{A}_{hh'} \tag{6} .$$

Putting (6) into (5) leads to:

$$\gamma_h{}^0\mathbf{p}_h = \underset{h'}{\Sigma} \mathbf{A}_{hh'}{}^0\mathbf{p}_{h'} \tag{7}$$

independent of l. Therefore a solution of the infinite system (3) can indeed be obtained by combining (4) with the solution of the homogeneous system of n equations (7).

Consequently the problem of determining the possible electromagnetic field is solved, in principle, after the calculation of the interaction coefficients $\mathbf{A}_{hh'}$, and substituting them in the system (7). As will appear in the following, these coefficients $\mathbf{A}_{hh'}$, contain $\mathbf{k}$ and so k (and n) can be found from the condition that the determinant of (7) must be zero and then the solution of (7) yields the vectors ${}^0\mathbf{p}_h$ and hence the electromagnetic field in the crystal.

3. The explicit form of the coefficients $\mathbf{A}_{hh'}$

We need for the subsequent discussion a brief outline of the calculation of the interaction coefficients according to Born's (1933) method.

A linear formula of the form (2) for the contribution of each dipole $\binom{l''}{h'}$ will hold for every field quantity $\mathbf{F}(\mathbf{r})$:

$$\mathbf{F}_{h'}^{l''}(\mathbf{r}) = \mathbf{b}(\mathbf{r} - \mathbf{r}_{h'}^{l''})\mathbf{p}_{h'}^{l''}$$

which yields after substitution of (4) and summation over l'':

$$\mathbf{F}_{h'}(\mathbf{r}) \equiv {}^0\mathbf{F}_{h'}(\mathbf{r}) \exp(-i\omega t + i\mathbf{k} . \mathbf{r}) \equiv \underset{l''}{\Sigma} \mathbf{F}_{h'}^{l''}(\mathbf{r})$$
$$= {}^0\mathbf{p}_{h'} \exp(-i\omega t + i\mathbf{k} . \mathbf{r}) . [\underset{l''}{\Sigma} \mathbf{b}(\mathbf{r} - \mathbf{r}_{h'}^{l''})$$
$$\exp\{-i\mathbf{k} . (\mathbf{r} - \mathbf{r}_{h'}^{l''})\}] . \tag{8}$$

The sum between square brackets has the lattice period.

For the case that $\mathbf{F}$ is the Herz vector, the contribution of the dipole $\binom{l''}{h'}$ is given by

$$\mathbf{Z}_{h'}^{l''}(\mathbf{r}) = \mathbf{p}_{h'}^{l''} \frac{\exp\{i\omega|\mathbf{r} - \mathbf{r}_{h'}^{l''}|/c\}}{|\mathbf{r} - \mathbf{r}_{h'}^{l''}|} ;$$

i.e. $\mathbf{b}$ is a scalar function. Hence formula (8) for the contribution of sublattice h' becomes:

$$\mathbf{Z}_{h'}(\mathbf{r}) = {}^0\mathbf{p}_{h'} \exp[-i\omega t + i\mathbf{k} . \mathbf{r}]s(\mathbf{r}) \tag{9}$$

in which $s(\mathbf{r})$ representing the lattice sum in (8) is a scalar function with the lattice period. Hence it can be expanded in a Fourier series. The result is:

$$s(\mathbf{r}) = \frac{4\pi}{V} \underset{m}{\Sigma} \exp(i\mathbf{q}_m . \mathbf{r})/(|\mathbf{q}_m + \mathbf{k}|^2 - k^2/n^2) , \tag{10}$$

in which $\mathbf{q}_m$ are the lattice points in the reciprocal lattice and $n \equiv k/k_0$ (see *e.g.* Ewald, 1916a,b; Born, 1933).

This formula can be derived by making use of the fact that $\mathbf{Z}_{h'}^{l''}$ and hence $\mathbf{Z}_{h'}$, obeys a wave equation:

$$\Delta\mathbf{Z}_{h'} - \frac{1}{c^2} \frac{\partial^2\mathbf{Z}_{h'}}{\partial t^2} = 0$$

holding for every $\mathbf{r}$ except for the points $\mathbf{r}_{h'}^{l''}$ in which $\mathbf{Z}_{h'}$ is singular.

Except for $m = 0$ the factors $(|\mathbf{q}_m + \mathbf{k}|^2 - k^2/n^2)^{-1}$ can be expanded in a power series of the vector components

$$k_j/|q_m| , \quad \text{as} \quad 2\pi/\lambda = |k| \ll 1/a \leqslant |q_m| .$$

The Fourier series (10) is only conditionally convergent. By means of Ewald's θ transformation it can be converted into the sum of two rapidly converging series, one in reciprocal and one in normal space. [This means the implicit introduction of a special summation sequence in (10)].

The terms in the resulting series can be expanded in a power series of $\mathbf{k} . a$ as was the case in (10). From the series for s $Z_{h'}(\mathbf{r})$ is obtained by substitution into (9) and the electric field $\mathbf{E}_{h'}(\mathbf{r})$ due to sublattice h' is then calculated from the relation

$$\mathbf{E} = \text{rot rot}\mathbf{Z} = \text{graddiv } \mathbf{Z} - \Delta\mathbf{Z}$$

or, with the aid of the wave equation for $\mathbf{Z}_{h'}$:

$$\mathbf{E}_{h'}(\mathbf{r}) = \text{graddiv } \mathbf{Z}_{h'}(\mathbf{r}) + (k^2/n^2)\mathbf{Z}_{h'}(\mathbf{r}) . \tag{11}$$

Now $\mathbf{A}_{hh'}$ is calculated from $\mathbf{E}_{h'}$: equation (8) yields for the case of $\mathbf{E}(\mathbf{r})$:

$$\mathbf{E}_{h'}(\mathbf{r}) = {}^0\mathbf{p}_{h'} \exp(-i\omega t + i\mathbf{k} . \mathbf{r})[\underset{l''}{\Sigma} \mathbf{a}(\mathbf{r} - \mathbf{r}_{h'}^{l''})$$
$$\exp\{-i\mathbf{k} . (\mathbf{r} - \mathbf{r}_{h'}^{l''})\}] .$$

With the aid of definition (6) for $\mathbf{A}_{hh'}$, one gets immediately for $h \neq h'$:

$$\mathbf{E}_{h'}(\mathbf{r}_h) = \mathbf{A}_{hh'}{}^0\mathbf{p}_{h'} \exp(-i\omega t + i\mathbf{k} . \mathbf{r}_h) .$$

For $h = h'$ the term due to dipole $\mathbf{r}_h^0$, which is singular at $\mathbf{r}_h^0$, has to be subtracted.

The result is for $h \neq h'$ up to first order in $\mathbf{k} . a$:

$$\text{Re}(A_{hh'})_{ij} = \frac{4\pi}{V} \left\{ \frac{\delta_{ij} - n^2 S_{ij}}{n^2 - 1} - \underset{m}{\Sigma'} \frac{(q_m)_i(q_m)_j}{|q_m|^2} \right.$$
$$\left. \exp\left(-\frac{|q_m|^2}{4\varepsilon^2}\right) \cos(\mathbf{q}_m . \mathbf{r}_{hh'}^{00}) \right\}$$
$$+ \underset{l''}{\Sigma} \left\{ \frac{3(r_{hh'}^{0l''})_i (r_{hh'}^{0l''})_j - \delta_{ij}|r_{hh'}^{0l''}|^2}{|r_{hh'}^{0l''}|^5} \Gamma(\tfrac{5}{2}, \varepsilon^2|r_{hh'}^{0l''}|^2) \right.$$
$$\left. + \delta_{ij} \frac{4\varepsilon^3}{3\sqrt{\pi}} \exp(-\varepsilon^2|r_{hh'}^{0l''}|^2) \right\} .$$

$$\text{Im}(A_{hh'})_{ij} = \sum_n k_n \left[\frac{4\pi}{V} \sum_m' \left\{ -(q_m)_i \delta_{jn} - (q_m)_j \delta_{in} \right. \right.$$

$$\left. + \left(\frac{1}{2\varepsilon^2} + \frac{2}{|q_m|^2} \right) \frac{(q_m)_i (q_m)_j (q_m)_n}{|q_m|^2} \right\}$$

$$\exp \left(\frac{-|q_m|^2}{4\varepsilon^2} \right) \sin(q_m \cdot r^{00}_{hh'})$$

$$+ \sum_{l'} \left\{ \frac{3(r^{0l'}_{hh'})_i (r^{0l'}_{hh'})_j - \delta_{ij} |r^{0l'}_{hh'}|^2}{|r^{0l'}_{hh'}|^5} \Gamma(\tfrac{5}{2}, \varepsilon^2 |r^{0l'}_{hh'}|^2) \right.$$

$$\left. \left. + \delta_{ij} \frac{4\varepsilon^3}{3\sqrt{\pi}} \exp(-\varepsilon^2 |r^{0l'}_{hh'}|^2) \right\} (r^{0l'}_{hh'})_n \right] , \quad (12)$$

in which $r^{0l'}_{hh'} \equiv r_h - r''_{h'}$, S is a tensor with components $S_{ij} = \dfrac{k_i k_j}{|k|^2}$, ε is an arbitrary positive number and

$$\Gamma(\tfrac{5}{2}, x^2) \equiv \frac{2}{\sqrt{\pi}} \left\{ \int_x^\infty \exp(-y^2 dy) \right\}$$

$$+ \{2|x|/\sqrt{\pi} + 4|x|^3/(3\sqrt{\pi})\} \exp(-x^2)$$

is an incomplete gamma function; the prime in the summation over m denotes that the term $q_m = 0$ has to be omitted.

For $h = h'$ the term $l' = 0$ which becomes infinite has to be omitted from the summation. These explicit formula can also be found in the work of Hermann (1923).

In the following we only need some general properties of $A_{hh'}$. It is seen from (12) that the zero order terms in k are real and the first order ones are imaginary and that the zero order terms contain n and hence k only in the constant $\dfrac{4\pi}{V}(I - n^2 S)/(n^2 - 1)$. Furthermore it is seen from (12) that:

$$A_{hh'} = \tilde{A}_{hh'} \tag{13a}$$

$$A_{hh'} = A^*_{h'h} \tag{13b}$$

$$A_{hh'}(k) = A^*_{hh'}(-k) . \tag{13c}$$

4. Comparison of microscopic and macroscopic equations

The linear relations (7) can easily be interpreted in terms of conventional optics. In order to do this, we introduce in (7) instead of $A_{hh'}$, the tensors $B_{hh'}$, defined by

$$A_{hh'} = B_{hh'} + \gamma_h \delta_{hh'} + (4\pi/V)(I - n^2 S)/(n^2 - 1) . \tag{14}$$

Now the system (7) becomes:

$$\sum_{h'} B_{hh'} {}^0p_{h'} = -\{(4\pi/V)(I - n^2 S)/(n^2 - 1)\} \sum_{h'} {}^0p_{h'} ; \tag{15}$$

on account of one of the general properties of $A_{hh'}$, mentioned above, the tensors $B_{hh'}$ contain k only in the imaginary part of first order in k.

Now we reduce the system (15) to one vector equation in $\sum_{h'} {}^0p_{h'}$. Consider the $n \times n$ matrix consisting of the $B_{hh'}$ tensors as elements. This matrix can also be written as a $3n \times 3n$ matrix $\mathscr{B}$ with elements $\mathscr{B}_{3h+i,3h'+j} \equiv (B_{hh'})_{ij}$. We introduce the inverse matrix $\mathscr{C}$ of $\mathscr{B}$

and form n 3×3 tensors $C_{hh'}$ from $\mathscr{C}$ analogous to $B_{hh'}$. The relation $\mathscr{C}\mathscr{B} = 1$ than reads in 3×3 tensor notation:

$$\sum_h C_{h''h} B_{hh'} = I \delta_{h''h'} . \tag{16}$$

Multiplication of both members of equation (15) by $C_{h''h}$, summation over h'' and h, and application of (16) yields:

$$\sum_{h'} {}^0p_{h'} = -\frac{4\pi}{V} \sum_{h'',h} C_{h''h}(I - n^2 S)$$

$$(n^2 - 1)^{-1} \sum_{h'} {}^0p_{h'} . \tag{17}$$

With the aid of (13a, b) it can easily be shown that the tensor $\sum_{h'',h} C_{h''h}$ is hermitian if considered as a 3×3 matrix in its components (Endeman, 1965).

We conclude that n and $\sum_{h'} {}^0p_{h'}$, can simply be found by solving the 3×3 system (17) instead of the complete $3n \times 3n$ system (15). Furthermore we remark that the average of any field quantity over a unit cell, $[F(r)]_{av}$, is directly proportional to $\sum_{h'} {}^0p_{h'}$. This can be derived immediately from relation (8), as the sum between square brackets in this formula has the lattice period, and so its average over the unit cell is a constant tensor T.

Hence:

$$\sum_{h'} [F_{h'}(r)]_{av} = T(\sum_{h'} {}^0p_{h'}) \exp(-i\omega t + i k \cdot r)$$

if terms of higher than first order in $k \cdot a$ are neglected in $\exp(ik \cdot r)$.

Now we consider a plane travelling electromagnetic wave in a medium characterized by its complex dielectric constant ε. We assume no absorption of light, so ε is a hermitian matrix in its components. The macroscopic Maxwell equations yield after elimination of the magnetic field vectors:

$$D = n^2(I - S)E . \tag{18}$$

We introduce in (18) the polarization per unit volume P instead of D by application of

$$4\pi P = D - E . \tag{19}$$

The result is:

$$4\pi P = \{(n^2 - 1)I - n^2 S\}E$$

or after inversion:

$$E = 4\pi \{I - n^2 S\}(n^2 - 1)^{-1}P \tag{20}$$

(19) yields with $D = \varepsilon E$ and after substitution of (20):

$$P = \{\varepsilon - 1\}\{I - n^2 S\}(n^2 - 1)^{-1}P . \tag{21}$$

The foregoing equations also hold for the amplitudes of the wave vectors, giving e.g. for equation (20)

$${}^0E = 4\pi \{I - n^2 S\}(n^2 - 1)^{-1}({}^0P) . \tag{22}$$

Now we see that (17) is just identical with relation (21) obtained by solving the macroscopic Maxwell equations for a medium with dielectric constant ε, if we make the formal identifications:

$$\frac{1}{V} \left(\sum_{h'} {}^0\mathbf{p}_{h'} \right) = {}^0\mathbf{P}$$

$$-\frac{4\pi}{V} \sum_{h'',h} \mathbf{C}_{h''h} = \varepsilon - 1 . \tag{23}$$

As is well known, the imaginary part of ε in (21) yields optical activity. (For example in a cubic crystal, where ε is a complex scalar, the solution of (21) consists of right and left handed circular polarized waves with different index of refraction.) According to (23) this part of ε corresponds to the imaginary part of $\sum_{h,h''} \mathbf{C}_{h''h}$, which is linear in $\mathbf{k}$ as is the case for the imaginary part of $\mathbf{B}_{hh'}$, owing to the general properties of $\mathbf{A}_{hh'}$ and (14). This linear dependence of the optical activity is always found in phenomenological and elementary microscopic theories*.

As this is useful in further discussions we put the first equation of (23) into the right hand member of (15), which yields after application of (22):

$$\sum_{h'} \mathbf{B}_{hh'} {}^0\mathbf{p}_{h'} = - {}^0\mathbf{E} . \tag{24}$$

By means of (23) the quantities of the microscopic theory are related to the macroscopic field. This relation was based only on formal grounds. A real proof of (23) can only be found in Ewald's extinction theorem (Ewald, 1916b) in which a half-infinite crystal is considered, and it is shown that an electromagnetic wave incident on its surface will penetrate only about one unit cell in the crystal and beyond this distance will give rise to an electromagnetic wavefield of the same form as found for an infinite crystal. So the quantities of this field can indeed be related to the macroscopic field in vacuum.

5. Comparison of exact and elementary theory

In elementary calculations on optical properties one can distinguish two parts:

(a) The macroscopic Maxwell equations are combined with a 'material equation', i.e. in general some phenomenological relation between $\mathbf{E}$ and $\mathbf{D}$ and one between $\mathbf{B}$ and $\mathbf{H}$, and travelling wave type solutions of this system are considered.

As mentioned above an optical active medium is obtained if a relation $\mathbf{D} = \varepsilon \mathbf{E}$ is introduced with complex dielectric constant ε.

(b) The material equations are derived from atomic models of the medium. Hence in theories of this type the field quantities are averaged to eliminate fluctuations on atomic scale before the Maxwell equations are applied. The difference with the method of calculation as treated above can best be demonstrated in the derivation of equation (17) and (21). In the consequent microscopic theory we get directly equation (17), which con-

tains only microscopic quantities. In an elementary treatment equation (21) is first obtained (part (a) of the calculation), and afterwards the microscopic expression for ε [i.e. the second of equations (23)] must be put in to get equation (17).

This elementary method has been frequently used for the case of liquids, but also for crystals (Ramachandran, 1951a,b, 1952), although in this case there is no need for the averaging procedure before application of the Maxwell equations. Although the method is very unsatisfactory from a theoretical point of view, the results are in most cases identical with that of a consequent microscopic theory based on the same model (in the following denoted as 'exact' theory). To demonstrate this we consider briefly the calculation of the refractive index for a crystal according to an elementary treatment based on the coupled oscillator model.

For the calculation of the interaction between the polarizable units only neighbours within a sphere with radius R are individually taken into account; the influence of the remainder of the crystal is represented by a Lorentz correction. This Lorentz correction together with the external field $\mathbf{E}$ yields e.g. in an isotropic medium a contribution $\tilde{\mathbf{e}}$ to the local microscopic field; this contribution amounts to

$$\tilde{\mathbf{e}} = \mathbf{E} + (4\pi/3)\mathbf{P} . \tag{25}$$

The field due to dipole $\mathbf{p}_{h'}^{\prime\prime}$, inside the sphere, at $\mathbf{r}_h^l$ is linear in $\mathbf{p}_{h'}^{\prime\prime}$:

$$\mathbf{E}_{h'}^{\prime\prime}(\mathbf{r}_h^l) = \mathbf{f}(\mathbf{r}_h^l - \mathbf{r}_{h'}^{\prime\prime})\mathbf{p}_{h'}^{\prime\prime} . \tag{26}$$

As long as $R \ll \lambda$ the retardation can be neglected in calculating $\mathbf{f}$. The complete microscopic field at $\mathbf{r}_h^l$ becomes:

$$\mathbf{E}(\mathbf{r}_h^l) = \tilde{\mathbf{e}} + \sum_{h',l'} \mathbf{f}(\mathbf{r}_h^l - \mathbf{r}_{h'}^{\prime\prime})\mathbf{p}_{h'}^{\prime\prime} . \tag{27}$$

In the left hand member of (27) we substitute $\mathbf{E}(\mathbf{r}_h^l) = \gamma_h \mathbf{p}_h^l$, i.e. (1b); in the right hand member $\mathbf{p}_{h'}^{\prime\prime} = {}^0\mathbf{p}_h \exp(-i\omega t + i\mathbf{k} . \mathbf{r}_{h'}^{\prime\prime})$, i.e. (4) and for $\tilde{\mathbf{e}}$ a plane travelling wave:

$$\tilde{\mathbf{e}}(\mathbf{r}) = {}^0\tilde{\mathbf{e}} \exp(-i\omega t + i\mathbf{k} . \mathbf{r}) . \tag{28}$$

This results in:

$$\sum_{h'} [\gamma_{h'}\delta_{hh'} - \mathbf{F}_{hh'}]{}^0\mathbf{p}_{h'} = {}^0\tilde{\mathbf{e}} \tag{29}$$

with the abbreviation:

$$\mathbf{F}_{hh'} = \sum_{l'} \mathbf{f}(\mathbf{r}_h - \mathbf{r}_{h'}^{\prime\prime}) \exp\{-i\mathbf{k} . (\mathbf{r}_h - \mathbf{r}_{h'}^{\prime\prime})\} . \tag{30}$$

The solution of (29), combined with (25) and (28) yields ${}^0\mathbf{p}_h$ and hence $\mathbf{P}$ as a function of $\mathbf{E}$, i.e. a material equation.

An elementary calculation as sketched above is of course open to much criticism. First the vacuum wave does not penetrate into the crystal and hence it is not clear why the external field stands in equation (25). Secondly, the restriction to atoms within radius R in the calculation of the dipole field is not a good approximation in a crystal, as the dipole forces are decreasing very slowly with distance and consequently large fluctuations appear in the dipole field as a func-

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* The relation $\mathbf{D} = \text{Re}(\varepsilon)\mathbf{E} + i\mathbf{gs} \wedge \mathbf{E}$, in which $\mathbf{g}$ is the gyration tensor can also be derived from (17) and (23). The calculations are trivial but lengthy.

tion of R. Hence it seems a better approach to take R and the crystal itself infinite. Of course the Lorentz correction has then to be omitted from (25). Then, however, the 'external field' **E** has no meaning and the retardation can no longer be neglected in the calculation of $\mathbf{F}_{hh'}$. The remarkable fact is found, however, that maintaining the external field and neglecting the retardation in the infinite crystal leads to a result that is in most cases identical with that of the correct microscopic theory.

This can best be shown by considering that the unretarded field $\mathbf{E}_{h'}^{l'}$ of dipole $\mathbf{p}_{h'}^{l'}$ is calculated from a Herz vector

$$\mathbf{Z}_{h'}^{l'}(\mathbf{r}-\mathbf{r}_{h'}^{l'})=\mathbf{p}_{h'}^{l'}/|\mathbf{r}-\mathbf{r}_{h'}^{l'}| \qquad (31)$$

with the relations:

$$\mathbf{E}_{h'}^{l'}(\mathbf{r})=\text{graddiv } \mathbf{Z}_{h'}^{l'}(\mathbf{r}), \qquad (32a)$$

$$\Delta \mathbf{Z}_{h'}^{l'}=0, \qquad (32b)$$

which are the unretarded equivalent of equation (11) and the wave equation respectively. Of course (32) also holds for the field of the whole sublattice h':

$$\mathbf{Z}_{h'} \equiv \sum_{l'} \mathbf{Z}_{h'}^{l'}.$$

After introduction of $^0\mathbf{p}_{h'}$ by means of (4), we derive the equivalent of formula (9):

$$\mathbf{Z}_{h'}(\mathbf{r})=^0\mathbf{p}_{h'} \exp(-i\omega t+i\mathbf{k}.\mathbf{r})s'(\mathbf{r}) \qquad (33)$$

with s' having the lattice period.

Following Born's method, we find for s' the Fourier series

$$s'=\frac{4\pi}{V}\sum_m \exp(i\mathbf{q}_m.\mathbf{r})/|\mathbf{q}_m+\mathbf{k}|^2, \qquad (34)$$

in which only the term $-k^2/n^2$ in the denominator is lacking as compared with the formula (10) for a dipole lattice with retardation. After expansion in a power series of $\mathbf{k}/\mathbf{q}_m$ in first order approximation, this difference only appears in the term $\mathbf{q}_m=0$ which now becomes $(4\pi/V)k^2$ instead of $(4\pi/V)k^2n^2/(n^2-1)$. In the application of the Ewald θ transformation to (34) of course no new differences occur. $\mathbf{E}_{h'}$ is now calculated from

$$\mathbf{E}_{h'}=\text{graddiv } \mathbf{Z}_{h'} \qquad (35)$$

instead of from formula (11):

$$\mathbf{E}_{h'}=\text{graddiv } \mathbf{Z}_{h'}+(k^2/n^2)\mathbf{Z}_{h'}.$$

The difference in the term $\mathbf{q}_m=0$ of the Fourier series leads to a zero order term $-(4\pi/V)\mathbf{S}$ in $\mathbf{F}_{hh'}$ instead of the term $-(4\pi/V)n^2\mathbf{S}(n^2-1)^{-1}$ as found in the interaction coefficient $\mathbf{A}_{hh'}$ for a retarded dipole field.

The term $(k^2/n^2)\mathbf{Z}_{h'}$ in (11) gave rise to the term $(4\pi/V)(n^2-1)^{-1}$ in $\mathbf{A}_{hh'}$. This term is lacking in $\mathbf{F}_{hh'}$ according to equation (35).

Summarizing, we get the relation:

$$\mathbf{F}_{hh'}=\mathbf{A}_{hh'}-(4\pi/V)\{(1-n^2\mathbf{S})(n^2-1)^{-1}\}-(4\pi/V)\mathbf{S}.$$

Substituting this formula in (29) and introducing $\mathbf{B}_{hh'}$ instead of $\mathbf{A}_{hh'}$ (equation 14) yields as a result of the elementary theory:

$$\sum_{h'}\{\mathbf{B}_{hh'}-(4\pi/V)\mathbf{S}\}^0\mathbf{p}_{h'}=-^0\tilde{\mathbf{e}},$$

or with (25), in which the Lorentz correction term $(4\pi/3)\mathbf{P}$ has to be omitted as the dipole summation has been extended over the whole crystal:

$$\sum_{h'}\{\mathbf{B}_{hh'}-(4\pi/V)\mathbf{S}\}^0\mathbf{p}_{h'}=-^0\mathbf{E}, \qquad (36)$$

which is identical with formula (24) except for the term $-(4\pi/V)\mathbf{S}$. If we take $\mathbf{k}$ e.g. in the $\mathbf{u}_3$ direction, the terms with $\mathbf{S}$ in the components along $\mathbf{u}_1$ and $\mathbf{u}_2$ of vector equation (36) are zero. So in this case these become identical with that of (24), and omitting the retardation is just compensated by the 'external field'. The longitudinal component of (36) is not correct and hence the right form of the general macroscopic formula (21) is not found in this elementary theory.

Assuming *a priori* $\sum_{h'}(^0\mathbf{p}_{h'})_3=0$ makes the longitudinal components of (36) and (24) also identical. This assumption always holds for cubic crystals and generally for the principal directions of ε if $\mathbf{k}$ is taken in such a direction. As this is usually made in calculations of the refractive index and rotatory power, the elementary theory gives the correct result for these quantities.

A third difficulty in the elementary theory as sketched above is the problem of the so-called magnetic contribution to the optical rotatory power: an oscillating electric dipole in an electromagnetic wavefield represents a magnetic dipole moment $c^{-1}\mathbf{p}\wedge\mathbf{H}$, which gives rise to a complex magnetic permeability in the coupled oscillator model, and this would result in a contribution to the optical activity of the same order of magnitude as that caused by the complex ε. In the literature the opinion is found that this contribution has actually to be taken into account (*e.g.* Born, 1933, p.414). Of course this problem does not arise in the exact treatment, as no material equations occur at all. Moreover, it appears that in the elementary theory no magnetic contribution must be taken into account in the Born model as its equation(36) – the equivalent of the electrical material equation – is identical with the exact equation (24).

References

BEURSKENS-KERSSEN, G., KROON, J., ENDEMAN, H. J., LAAR, J. VAN & BIJVOET, J. M. (1963). In G. N. Ramachandran, *Crystallography and Crystal Perfection*. London and New York: Academic Press.

BIJVOET, J. M. (1960). *Acta Cryst.* **13**, 1100.

BORN, M. (1933). *Optik*. Berlin: Springer.

ENDEMAN, H. J. (1965). Thesis, State Univ. Utrecht.

EWALD, P. P. (1916a). *Ann. Phys. Lpz.* **49**, 1.

EWALD, P. P. (1916b). *Ann. Phys. Lpz.* **49**, 117.

EWALD, P. P. (1921). *Ann. Phys. Lpz.* **64**, 253.

HERMANN, C. (1923). *Z. Phys.* **16**, 103.

RAMACHANDRAN, G. N. (1951a). *Proc. Indian Acad. Sci.* A, **33**, 217.

RAMACHANDRAN, G. N. (1951b). *Proc. Indian Acad. Sci.* A, **33**, 309.

RAMACHANDRAN, G. N. (1952). *Proc. Indian Acad. Sci.* A, **34**, 127.