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X-ray Diffraction in the Case of Three Strong Rays. I. Crystal Composed of Non-Absorbing Point Atoms

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The conditions of propagation of a three-ray X-optical field in a crystal built of non-absorbing point atoms are discussed. The discussion follows the outline published in 1937 by one of the authors and is held as general as possible, so as to be applicable to cases not yet studied experimentally. A point of special interest is the closest approach of the Surface of Dispersion to the Laue point, *i.e.* the point in reciprocal space which represents the three-ray field according to the primitive kinematical theory. This approach determines the extent to which absorption is reduced in the corresponding wave field and has therefore a direct bearing on the Borrmann effect. It is shown that for some cases of two simultaneous reflections the surface of dispersion gets much closer to the Laue point than for the reflections occurring singly or in pairs; this explains the 'double Borrmann effect' and is discussed numerically for the simultaneous reflections (111/1$\bar{1}$1) in germanium.

1. Introduction

The present paper can be regarded as the continuation of a series of papers by the senior author (Ewald, 1912, 1916, 1917, 1932, 1937) on the theme: *Foundations of Crystal Optics*. The first three papers are based on the simplest model of a crystal which expresses its internal periodicity and the mode of interaction between light and matter, namely a lattice arrangement of identical, isotropic, point resonators or dipoles. In the 1937 paper this model was extended to a lattice repetition of a base formed by an unspecified number and arrangement of dipoles. This implied the introduction of the structure amplitude, and allowed the transition to be made to a continuous distribution of the scattering power within the cell, thereby getting rid of the assumption of point atoms; by a limiting process it also led to the same assumption as that used by M. von Laue in his reformulation of the dynamical theory, namely that of a continuous dielectric medium (Laue, 1931, 1960). In those papers which dealt with X-rays the general case was discussed of an X-optical field consisting of n coupled plane waves being propagated in the crystal. The details of these waves, *i.e.* the exact lengths and directions of their wave vectors $\mathbf{K}_h$, and the relative amplitudes of their electric and magnetic field vectors are determined by a single point in Fourier space, the *Tiepoint* T, and the condition of self-consistency requires that T lie on a surface in Fourier space, the *Surface of Dispersion* (SurfDisp) $D=0$; only then will the wave field created by the emission of spherical wavelets by each dipole sustain the dipole oscillations. D itself can be shown to be a surface of $2n$ sheets.

With the determination of D the problem of the propagation of an X-optical field in the interior of an unbounded crystal is solved in principle. Moreover, in the case of a half-crystal, *i.e.* one limited to the lower half space $z \geq 0$, the SurfDisp also provides a direct method for relating the field inside the crystal with that outside, which latter includes the incident plane wave. This leads to relations, generalized Fresnel reflection and refraction formulae, which lend themselves to experimental corroboration.

Although the theory has been in existence for a long time, a strong stimulation for a detailed discussion of simultaneous reflections on several sets of planes has arisen only recently through the experiments on nearly perfect crystals, in particular by the discovery of the enhanced Borrmann effect (Borrmann & Hartwig, 1965). The case of a single reflection, *i.e.* the co-existence of only two rays in the crystal, was easy to derive for the crystal with base, and the result, as far as it affected the reflected intensity, was used in an early paper (Ewald, 1925). This theory also applies to the simple Borrmann effect. However, for an optical field of three strong rays, a geometrical hurdle has to be overcome first, and next the difficulty of discussing the equation for the SurfDisp, which is of the sixth order.

In part I (the present paper) the geometry is dealt with satisfactorily, and the equation $D=0$ is discussed in general terms as far as we succeeded. After that, the discussion is restricted towards finding the nearest approach of D to the Laue point *La* (defined in § 4). Finally this discussion is even further specialized to the case of Si and Ge crystals with their simple structure amplitudes obtained by assuming non-absorbing point

atoms. Emphasis has been laid on keeping the discussion as general as possible within each of the restrictions, so that guidance might be gained for cases of interest to the experimentalist.

In part II (the paper immediately following this one), two modifications are introduced in the crystal model, both necessary for a quantitative comparison of theory and experiment: the non-absorbing point resonators are replaced by absorbing atoms of finite size. This implies introduction of an atomic scattering factor which is complex and whose real and imaginary parts are both functions of the scattering angle or order. The dynamical theory has been carried through for absorbing media in general already by Waller (1925) and discussed for the two-ray case by Prins (1930) and by many later authors (*e.g.* Zachariasen, 1945; Hirsch, 1952; Schwarz & Rogosa, 1954; Laue, 1960 book § 33). Most of these authors have been using the dynamical theory in its continuum form introduced by Laue (1931). We shall here follow the original idea of diffraction by discrete atoms which perhaps keeps the treatment in closer contact with crystal structure, though differing from the Laue form only in the stage when Fourier development sets in.

While this publication was being prepared, several papers on the three-ray case appeared (Hildebrandt, 1966; Penning, 1967; Saccocio & Zajac, 1965). In these papers a greater readiness is shown to resort to computer calculation of special cases for which experimental results are available. With the ease of computer calculation, once the programming has been done, it is possible to explore the possibilities of constructing interesting conditions by experimental mathematics. Still, we hope that the survey contained in a theoretical treatment, even if limited, may be found useful.

Finally, as predecessors of this paper, the theoretical discussions of the three-ray SurfDisp by Lamla (1939), Fues (1938, 1939) and Kambe (1957) should be mentioned. The SurfDisp for three co-planar rays was discussed and illustrated by Mayer (1928) for the simple dipole lattice. Saccocio & Zajac restricted their discussion to some fully symmetrical cases in germanium and silicon crystals.

2. Plan of this paper

For the general relation between the SurfDisp and the Borrmann effect the reader is referred to the papers by Ewald (1958, 1965); in these it is shown that the closer the tiepoint T of an X-optical field approaches the Laue point La (defined in § 4), the more efficient the crystal becomes in converting dipole amplitude into field amplitude. Therefore the smaller the distance between these points is, the less dipole amplitude is required for producing field values in the interior of the crystal which balance the impressed field of the incident wave. The absorption, being proportional to the dipole amplitude, therefore diminishes for such fields against its normal value, and these fields are, in a thick crystal, the surviving ones. Those fields which are represented by tiepoints on the sheets of the SurfDisp at greater distance from La, are absorbed more strongly than normal because a large amount of dipole amplitude is needed to create them.

A first difficulty in discussing the three-ray case is the purely geometrical one of finding one's bearings in this essentially three-dimensional problem. The reader will find the next four sections devoted to the vector algebra required for establishing suitable reference systems and for relating them. Once this is done, the application of the theory as outlined in the 1937 paper is straightforward up to the point of writing down the equation of the surface of dispersion. Since, for three rays, this is of the sixth degree, a general discussion presents difficulties. The asymptotic properties can easily be found, but the exploration of the branching of the sheets of the surface near its centre has not been carried through. The papers by Fues and by Kambe, mentioned earlier, give a partial answer to what is happening.

The discussion has therefore been cut down to a discussion of the three-ray case in germanium crystals. This presents a simplification because (i) the crystal is cubic and the geometry depends only on a single parameter $\beta=\lambda/a$, so that results are obtained for any wavelength; and (ii) the structure factor in Ge is limited to three values, and the few combinations that can occur in the three-ray case can easily be discussed separately.

3. Nomenclature and orders of magnitude

The crystal is described by axes $\mathbf{a}_i$, and atoms of sorts s with polarizabilities α_s at positions $\mathbf{x}^s$ in each cell. The reciprocal axes to the $\mathbf{a}_i$ are $\mathbf{b}_i$; both systems are assumed, for convenience, to be right-handed ones. The volume of the crystal cell is v_a, and the mean polarizability is $A=(\sum_s \alpha_s)/v_a$. If we consider the electrons as free, $\alpha_s=-N_s(e^2/m)/\omega^2$, and the optical density of the medium is, according to the Drude–Lorentz optical theory of the refractive index,

$$\mu^2-1=-\frac{4\pi}{v_a}\sum N_s(e^2/m)/\omega^2 = -\frac{1}{\pi}\frac{N}{v_a}(e^2/mc^2)\lambda_0^2=A. \qquad (1)$$

$e^2/mc^2=2{\cdot}818\times10^{-13}$ cm is the classical radius of the electron and $N=\sum N_s$ the total number of electrons in the cell. The minus sign implies that the X-ray cyclic frequency $\omega=2\pi\nu=2\pi(c/\lambda_0)$ lies beyond all proper frequencies of the atoms. If this is not fulfilled for some of the K- or L-shell electrons, it can easily be corrected for; in general, however, the crystal is the optically rarer medium compared with vacuum and the wavelength λ in the crystal is greater than λ_0, the wavelength in empty space. A is a dimensionless number, which for the ordinarily used near-perfect crystals (like calcite, diamond, germanium) and X-rays (like Cu or Mo $K\alpha$)

is of the order of 10^{-5}–10^{-6}. Since the coupling of the simultaneously existing rays produces deformations of the surfaces of dispersion of this same magnitude, these will be measured in multiples of A.

4. Definition of Lorentz and Laue Points

Let the three coexisting waves be represented in Fourier space by their wave-vectors $\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3$ which issue from the tiepoint T to the origin O of the reciprocal lattice and to its lattice points $\mathbf{h}_2$ and $\mathbf{h}_3$, respectively*. The lengths of these vectors must closely approach $|\mathbf{K}| = \mu k_0$, where $k_0 = 1/\lambda_0$, is the wave number for propagation in empty space at frequency ν. We define as the *Lorentz point Lo* the point in Fourier space which is at the *exact* distance $|\mathbf{K}|$ from the three points O, $\mathbf{h}_2$ and $\mathbf{h}_3$. It would be the only tiepoint for which the three rays could coexist without the relaxing influence of their mutual coupling and it is, for this reason, the central point for the splitting up of the surface of dispersion. We shall use the Lorentz point *Lo* as the origin of a coordinate system in which to describe this surface and use the vectors $\mathbf{K}_i$ issuing from *Lo* as the axial system for this description.

We also shall have to use the *Laue point La* which lies at distance k_0 from the three lattice points O, $\mathbf{h}_2$ and $\mathbf{h}_3$; that is, since $k_0 > K$, *La* lies beyond *Lo* on the normal to the plane supported by the vectors $\mathbf{h}_2$ and $\mathbf{h}_3$.

We begin the geometrical orientation by expressing *Lo* and *La* in terms of the vectors $\mathbf{h}_2$ and $\mathbf{h}_3$ and the wave constants K ($\equiv |\mathbf{K}|$) and k_0.

5. Expressions for the Lorentz and Laue points

For handling the multiple vector products, the bracket notation – ( ) for the scalar, [ ] for the vector product – is more convenient than the dot and × notations, and will be adopted. The Lorentz point is the centre of the sphere of radius K which passes through O, $\mathbf{h}_2$ and $\mathbf{h}_3$. It lies on the intersection of the two planes which have equal distance from O and $\mathbf{h}_2$, and O and $\mathbf{h}_3$, respectively, and whose equations are, therefore

$$(\mathbf{x}\mathbf{h}_2) = \tfrac{1}{2}h_2^2 \quad \text{and} \quad (\mathbf{x}\mathbf{h}_3) = \tfrac{1}{2}h_3^2 .$$

We first seek a point $\mathbf{x}'$ in the $\mathbf{h}_2, \mathbf{h}_3$ plane satisfying these conditions, (*i.e.* the centre of the circle circumscribed about the triangle $O, \mathbf{h}_2, \mathbf{h}_3$), by putting $\mathbf{x} = \mathbf{x}' = \alpha\mathbf{h}_2 + \beta\mathbf{h}_3$, and we easily find

$$\mathbf{x}' = \frac{1}{2[h_2h_3]^2}\{h_3^2\{h_2^2 - (h_2h_3)\}\mathbf{h}_2 + h_2^2\{h_3^2 - (h_2h_3)\}\mathbf{h}_3\} . \quad (2)$$

Next we add to this a vector of suitable length along the normal to the plane Oh_2h_3, *i.e.* we put for the Lorentz point

$$\mathbf{x} = \mathbf{x}' - \nu[\mathbf{h}_2\mathbf{h}_3] ,$$

where ν is determined by the condition $\mathbf{x}^2 = K^2$. Since the two parts of $\mathbf{x}$ are at right angles, $\mathbf{x}^2$ is the sum of their squares. It is easily found that

$$\mathbf{x}'^2 = h_2^2h_3^2(\mathbf{h}_2 - \mathbf{h}_3)^2/4[\mathbf{h}_2\mathbf{h}_3]^2$$

and therefore

$$\nu^2 = \{4[\mathbf{h}_2\mathbf{h}_3]^2K^2 - h_2^2h_3^2(\mathbf{h}_2 - \mathbf{h}_3)^2\}/4[\mathbf{h}_2\mathbf{h}_3]^4 .$$

Thus, the *position of the Lorentz point* is at

$$\mathbf{Lo} = \frac{1}{2[h_2h_3]^2}\{h_3^2\{h_2^2 - (h_2h_3)\}\mathbf{h}_2 + h_2^2\{h_3^2 - (h_3h_2)\}\mathbf{h}_3 - \sqrt{4[h_2h_3]^2K^2 - h_2^2h_3^2(h_2 - h_3)^2}\ [\mathbf{h}_2\mathbf{h}_3]\} . \quad (3)$$

The position of the Laue point *La* is obtained by substituting the vacuum wave constant k_0 for K. Its distance from *Lo* is obtained by differentiating *Lo* with respect to K^2 and multiplying with

$$\Delta K^2 \equiv k_0^2 - K^2 = K^2\left(\frac{1}{\mu^2} - 1\right) = -K^2(\mu^2 - 1)/\mu^2 = -Ak_0^2 .$$

Since

$$\frac{d\,Lo}{dK^2} = -\frac{[\mathbf{h}_2\mathbf{h}_3]}{\sqrt{4[\mathbf{h}_2\mathbf{h}_3]^2K^2 - \mathbf{h}_2^2\mathbf{h}_3^2(\mathbf{h}_2 - \mathbf{h}_3)^2}} ,$$

we obtain

$$\overleftarrow{\mathbf{La}} - \mathbf{Lo} = \frac{Ak_0^2}{\sqrt{4[\mathbf{h}_2\mathbf{h}_3]^2K^2 - \mathbf{h}_2^2\mathbf{h}_3^2(\mathbf{h}_2 - \mathbf{h}_3)^2}}[\mathbf{h}_2\mathbf{h}_3] . \quad (4)$$

This expression is a length in Fourier space of order A; since A is negative, *La* lies farther away from the $O\mathbf{h}_2\mathbf{h}_3$) plane than *Lo*.

6. The reference systems attached to the Lorentz point

The vectors $-\mathbf{Lo}$, $-\mathbf{Lo}+\mathbf{h}_2$, $-\mathbf{Lo}+\mathbf{h}_3$, each of length K, would be *the* wave vectors of the coexisting waves if no coupling between the waves took place. We use

* In order to avoid irritating minus signs, $\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3$ should form a right-handed system.

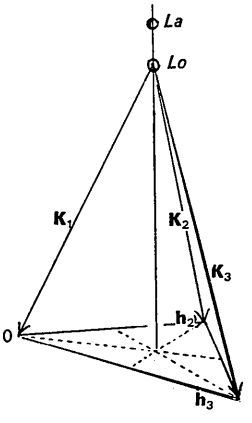

Fig. 1. Fourier space. Reciprocal lattice points 0, $\mathbf{h}_2$, $\mathbf{h}_3$; wave-vectors $\mathbf{K}_1$, $\mathbf{K}_2$, $\mathbf{K}_3$; Lorentz and Laue points. In the drawing, the tiepoint coincides with *Lo*.

unit vectors $\mathbf{s}_1,\mathbf{s}_2,\mathbf{s}_3$ in their directions as the axes of a reference system with origin at *Lo* in order to describe the surface of dispersion. We also need the reciprocal system $\mathbf{t}_1,\mathbf{t}_2,\mathbf{t}_3$ (see Fig. 2).

Using the abbreviation w for the square root in *Lo* we have

$$w=\sqrt{4K^2[\mathbf{h}_2\mathbf{h}_3]^2-\mathbf{h}_2^2\mathbf{h}_3^2(\mathbf{h}_2-\mathbf{h}_3)^2} \tag{5}$$

$$\mathbf{Lo}=\frac{1}{2[\mathbf{h}_2\mathbf{h}_3]^2}\{\mathbf{h}_3^2\{\mathbf{h}_2^2-(\mathbf{h}_2\mathbf{h}_3)\}\mathbf{h}_2+\mathbf{h}_2^2\{\mathbf{h}_3^2-(\mathbf{h}_2\mathbf{h}_3)\}\mathbf{h}_3-w[\mathbf{h}_2\mathbf{h}_3]\} \tag{5'}$$

$$\mathbf{s}_1=\frac{-\mathbf{Lo}}{K},\quad \mathbf{s}_2=\frac{-\mathbf{Lo}+\mathbf{h}_2}{K},\quad \mathbf{s}_3=\frac{-\mathbf{Lo}+\mathbf{h}_3}{K}. \tag{6}$$

The volume supported by the s-axes is

$$v_s=(\mathbf{s}_1[\mathbf{s}_2\mathbf{s}_3])=K^{-3}(-\mathbf{Lo}[-\mathbf{Lo}+\mathbf{h}_2,-\mathbf{Lo}+\mathbf{h}_3])$$
$$=K^{-3}(-\mathbf{Lo}[\mathbf{h}_2\mathbf{h}_3])=K^{-3}\frac{w}{2[\mathbf{h}_2\mathbf{h}_3]^2}[\mathbf{h}_2\mathbf{h}_3]^2=w/2K^3. \tag{7}$$

Since $\mathbf{h}_2$, $\mathbf{h}_3$ and $\mathbf{K}$ are of the same order of magnitude, it is often convenient to introduce the dimensionless

$$\boldsymbol{\eta}_2=\mathbf{h}_2/K\quad \boldsymbol{\eta}_3=\mathbf{h}_3/K \tag{8}$$

which according to Bragg's law may be interpreted as $2\sin\theta_2$ and $2\sin\theta_3$ respectively, where θ_2 and θ_3 are the Bragg angles belonging to the diffraction of orders h_2 and h_3 (including refraction). We have then

$$w=K^3\sqrt{4[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]^2-\eta_2^2\eta_3^2(\boldsymbol{\eta}_2-\boldsymbol{\eta}_3)^2} \tag{9}$$

and

$$v_s=\tfrac{1}{2}\sqrt{4[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]^2-\eta_2^2\eta_3^2(\boldsymbol{\eta}_2-\boldsymbol{\eta}_3)^2}. \tag{9'}$$

For the reciprocal system we find

$$\left.\begin{aligned}\mathbf{t}_3&=[\mathbf{s}_1\mathbf{s}_2]/v_s=\ [-\mathbf{Lo},\mathbf{h}_2]/K^2v_s\\ \mathbf{t}_2&=[\mathbf{s}_3\mathbf{s}_1]/v_s=\ [\mathbf{Lo},\mathbf{h}_3]/K^2v_s\\ \mathbf{t}_1&=[\mathbf{s}_2\mathbf{s}_3]/v_s=\{[-\mathbf{Lo},\mathbf{h}_3-\mathbf{h}_2]+[\mathbf{h}_2\mathbf{h}_3]\}/K^2v_s\\ &=-\mathbf{t}_2-\mathbf{t}_3+[\mathbf{h}_2\mathbf{h}_3]/K^2v_s.\end{aligned}\right\} \tag{10}$$

From the last equation we see that the vector

$$\mathbf{t}_1+\mathbf{t}_2+\mathbf{t}_3=[\mathbf{h}_2\mathbf{h}_3]/K^2v_s=\frac{1}{v_s}[\boldsymbol{\eta}_2\boldsymbol{\eta}_3] \tag{11}$$

is directed along the normal to the plane of h_2 and h_3, *i.e.* lies in the direction $La\rightarrow Lo$.

The explicit expressions for the **t**-vectors are obtained by simple algebra as

$$\left.\begin{aligned}\mathbf{t}_1&=\frac{1}{2v_s[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]^2}\{[\boldsymbol{\eta}_2\boldsymbol{\eta}_3](\eta_2\eta_3)(\boldsymbol{\eta}_2-\boldsymbol{\eta}_3)^2-2v_s[[\boldsymbol{\eta}_2\boldsymbol{\eta}_3](\boldsymbol{\eta}_2-\boldsymbol{\eta}_3)]\}\\ \mathbf{t}_2&=\frac{1}{2v_s[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]^2}\{[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]\{\eta_2^2\eta_3-\eta_3^2(\eta_2\eta_3)\}-2v_s[[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]\boldsymbol{\eta}_3]\}\\ \mathbf{t}_3&=\frac{1}{2v_s[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]^2}\{[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]\{\eta_2^2\eta_3-\eta_2^2(\eta_2\eta_3)\}+2v_s[[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]\boldsymbol{\eta}_2]\}.\end{aligned}\right\} \tag{12}$$

The relation between the reference systems is shown in Fig. 2.

The Laue point, as seen in the t-system, lies at

$$\overleftarrow{\mathbf{La}-\mathbf{Lo}}=\frac{Ak_0^2}{\sqrt{4[h_2h_3]^2K^2-h_2^2h_3^2(h_2-h_3)^2}}[\mathbf{h}_2\mathbf{h}_3]$$
$$=\tfrac{1}{2}KA(1/\mu^2)(\mathbf{t}_1+\mathbf{t}_2+\mathbf{t}_3); \tag{13}$$

here μ can be replaced by 1, and it is to be remembered that A is negative. We call the direction $Lo\rightarrow La$ the *Principal Axis* of the three-ray case and define its positive sense as $-[\mathbf{h}_2\mathbf{h}_3]$.

As seen from O, the position of a tiepoint **T** can be described as

$$\mathbf{T}=\mathbf{Lo}+\tfrac{1}{2}KA\mathbf{v}; \tag{14}$$

here **v** is a dimensionless vector of unit order of magnitude indicating the displacement of T as seen from *Lo*. The Laue point is given by

$$\mathbf{v}_{La}=\mathbf{t}_1+\mathbf{t}_2+\mathbf{t}_3. \tag{15}$$

We are interested in expressing how a displacement **v** affects the *resonance numbers*

$$r_i=\frac{K^2-k_0^2}{K_i^2-k_0^2}=\frac{\mu^2-1}{(K_i/k_o)^2-1}=\frac{A}{(K_i/k_o)^2-1} \tag{16}$$

and their reciprocals

$$1/r_i=(1/A)\{(K_i/k_o)^2-1\}.$$

Putting

$$\mathbf{K}_i=K(\mathbf{s}_i-\tfrac{1}{2}A\mathbf{v}), \tag{17}$$

we have, neglecting terms in $(Av)^2$,

$$1-1/r_i=\mu^2(\mathbf{s}_i\mathbf{v}). \tag{18}$$

If we decompose **v** into components along the **t**-axes, *i.e.*

$$\mathbf{v}=\tau_i\mathbf{t}_i=(\mathbf{s}_i\mathbf{v})\mathbf{t}_i$$

we can write, replacing μ^2 by 1,

$$1-1/r_i=\tau_i, \tag{19}$$

and this will be a convenient expression in the next section.

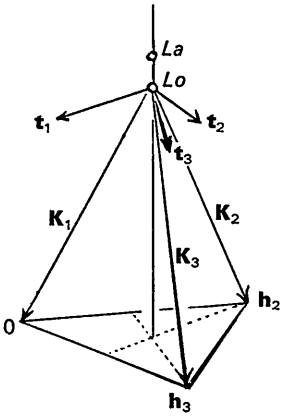

Fig. 2. Same as Fig. 1, but also showing the reference system $\mathbf{t}_1$, $\mathbf{t}_2$, $\mathbf{t}_3$ reciprocal to the unit vectors along the three rays.

7. The dynamical equations

The assumption is made that the dipole moments of the various sorts (s) of atoms correspond to the propagation of a plane wave of wave-vector $\mathbf{K}_1$:

$$\mathbf{p}_l^s = \mathbf{p}^s \,.\, \exp\{j(\mathbf{K}_1\mathbf{X}_l^s)\} \,.\, \exp\{-jvt\} \,. \tag{20}$$

Here $\mathbf{X}_l^s = \mathbf{x}_l + \mathbf{x}^s$ is the position of the atom of sort **s** in the lth (l_1, l_2, l_3) cell, and

$$j = 2\pi i = 2\pi\sqrt{-1} \,.$$

Leaving out the time factor, common to all moments and fields, there follows the Hertz potential of the optical field in the unbounded crystal

$$\mathbf{Z}(\mathbf{x}) = \sum_s \sum_l \mathbf{p}^s \exp\{j(\mathbf{K}_1\mathbf{x}^s)\} \exp\{j(\mathbf{K}_1\mathbf{x}_l)\} \frac{\exp\{jk_o|\mathbf{x}-\mathbf{X}_l^s|\}}{4\pi|\mathbf{x}-\mathbf{X}_l^s|} \tag{21}$$

$$= \frac{1}{v_a} \sum_h \mathbf{S}_h \frac{\exp\{j(\mathbf{K}_h\mathbf{x})\}}{4\pi^2(K_h^2 - k_0^2)} \,. \tag{22}$$

The second of these expressions is the Fourier transform of the first; in it, v_a is the volume of the crystal cell,

$$\mathbf{K}_h = \mathbf{K}_1 + \mathbf{h} = \text{wave-vector of the } h\text{th } (=h_1, h_2, h_3) \text{ wave component} \tag{22'}$$

and

$$\mathbf{S}_h = \sum_s \mathbf{p}^s \exp\{-j(\mathbf{h}\mathbf{x}^s)\} = \textit{Structure Amplitude} \,. \tag{22''}$$

In (22) the summation goes formally over all points **h** of the reciprocal lattice, but is, for the three-ray case, restricted to the three exceedingly large terms 1,2,3 with $h=0$, $h=h_2$ and $h=h_3$, respectively. The derivation of this Fourier transformation has been given previously (Ewald, 1932) as well as the field expression obtained by differentiation:

$$\mathbf{D}(\mathbf{x}) = \frac{1}{v_a} \sum_h \frac{[\mathbf{K}_h[\mathbf{S}_h\mathbf{K}_h]]}{K_h^2 - k_0^2} \exp\{j(\mathbf{K}_h\mathbf{x})\} \,. \tag{23}$$

The double vector product in the numerator is equal to K_h^2 times that part of $\mathbf{S}_h$ which is transverse to $\mathbf{K}_h$, for which we write $\mathbf{S}_{h\perp K_h}$. In the numerator of the three large terms to which the sum is restricted, we replace K_h^2 by k_0^2. The vector so obtained we consider to be the electric vector acting on the dipoles:*

$$\mathbf{E}(\mathbf{x}) = \frac{1}{v_a} \sum \mathbf{S}_{h\perp K_h} \frac{k_0^2}{K_h^2 - k_0^2} \exp\{j(\mathbf{K}_h\mathbf{x})\} \,. \tag{23'}$$

By introducing the polarizability, we next obtain the relation between dipole moment and field at the site of any dipole:

$$\mathbf{p}_l^s = \mathbf{p}^s \exp\{j(\mathbf{K}_1\mathbf{X}_l^s)\} = \frac{\alpha^s}{v_a} \sum_h \mathbf{S}_{h\perp K_h} \frac{k_0^2}{K_h^2 - k_0^2} \exp\{j(\mathbf{K}_h\mathbf{X}_l^s)\} \,. \tag{24}$$

By multiplying both sides by $\exp\{-j(\mathbf{h}'\mathbf{x}^s)\}$ and summing over s, the structure amplitude, $\mathbf{S}_h$, is formed on the left-hand side, whereas on the right the Fourier coefficient of the polarizability distribution in the cell appears:

$$A_{h'-h} = \sum_s \frac{\alpha^s}{v_a} \exp\{-j(\mathbf{h}'-\mathbf{h},\mathbf{x}^s)\} \,; \tag{25}$$

we thus obtain

$$\mathbf{S}_{h'} = \sum_h A_{h'-h}\mathbf{S}_{h\perp K_h} \frac{k_0^2}{K_h^2 - k_0^2} \,. \tag{26}$$

This system of linear homogeneous equations for the structure amplitudes has to be fulfilled (in the case of n rays) if n rays are to coexist. It *can* be fulfilled by adjusting the resonance factors

$$k_0^2/(K_h^2 - k_0^2)$$

by suitable choice of the tiepoint T, since the position of T determines the difference of length of each wave vector $\mathbf{K}_h$ of the wave field and the wave constant in free space. The permissible points T form the surface of dispersion.

As the equations for **S** stand, the small coefficients $A_{h'-h}$ (of order 10^{-6}) have to be compensated by the smallness of the resonance denominators. It is convenient to measure $A_{h'-h}$ against the optical density A, so that both the first and the last factors on the right hand side of (26) are of unit order of magnitude. We introduce the *coupling numbers*,

$$\alpha_{h'-h} = \frac{A_{h'-h}}{A} = \frac{\sum_s \alpha^s \exp\{-j(\mathbf{h}'-\mathbf{h},\mathbf{x}^s)\}}{\sum_s \alpha^s} \,; \quad \alpha_{hh} = 1 \tag{27}$$

and the *resonance numbers*

$$r_h = \frac{Ak_0^2}{K_h^2 - k_0^2} = \frac{(\mu^2-1)k_0^2}{K_h^2 - k_0^2} = \frac{K^2 - k_0^2}{K_h^2 - k_0^2} \tag{28}$$

and write the dynamical equations in their final form:

$$\mathbf{S}_{h'} = \sum_h \alpha_{h'-h} r_h \mathbf{S}_{h\perp K_h} \,. \tag{29}$$

On the right-hand side only the components of $\mathbf{S}_h$ normal to $\mathbf{K}_h$ occur, which are the ones producing the amplitude of the hth wave of the wave-field; the left-hand side, however, leaves the existence of a longitudinal component of the structure amplitudes open. Calling $\mathbf{T}_h$ the transverse components, we write, with undetermined factors λ,

$$\mathbf{S}_h = \mathbf{T}_h + \lambda_h \mathbf{s}_h \tag{30}$$

by substituting in sufficient approximation $\mathbf{s}_h$ for the actual direction of the wave-vector $\mathbf{K}_h$.

The dynamical equations then become

$$\sum_h (\alpha_{h'-h} r_h - \delta_{h'h})\mathbf{T}_h = \lambda_{h'}\mathbf{s}_{h'} \tag{31}$$

* The reason for the change of name of the field vector and for the replacement of K_h by k_0 is this: the coefficients in the infinite sum(23) are asymptotically of order 1. $\mathbf{D}(x)$ therefore has the character of a delta function, or a sum of such, whereas the sum in (23′) converges smoothly. Actually, the latter sum is equal to $\mathbf{D}(x)$ diminished by the electrostatic field of the instantaneous dipole distribution. This comes close to the true field of excitation. *cf.* Lorentz $E = D - P$.)

or, explicitly, in the case of three rays 1, 2, and 3:

$$\left.\begin{aligned}(r_1-1)\mathbf{T}_1+\ \alpha_{12}r_2\mathbf{T}_2+\ \alpha_{13}r_3\mathbf{T}_3&=\lambda_1\mathbf{s}_1\\ \alpha_{21}r_1\mathbf{T}_1+(r_2-1)\mathbf{T}_2+\ \alpha_{23}r_3\mathbf{T}_3&=\lambda_2\mathbf{s}_2\\ \alpha_{31}r_1\mathbf{T}_1+\ \alpha_{32}r_2\mathbf{T}_2+(r_3-1)\mathbf{T}_3&=\lambda_3\mathbf{s}_3\,.\end{aligned}\right\}\quad(31')$$

8. Conditions of solution of the dynamical equations

Two cases have to be distinguished in solving the above equations: *either* a solution is possible with all $\lambda_i\mathbf{s}_i$ equal to zero, *or* not.

(1) In the first case we can take $\mathbf{T}_3$ from one equation and insert the value in the other two equations; these then become homogeneous linear equations between $\mathbf{T}_1$ and $\mathbf{T}_2$, showing that $\mathbf{T}_1$ and $\mathbf{T}_2$ are parallel; then $\mathbf{T}_3$, being a linear combination of $\mathbf{T}_1$ and $\mathbf{T}_2$, is of the same direction. But since each of the vectors is normal to the corresponding direction of the ray, there must exist a common transverse direction of the three rays, *i.e. the rays must be coplanar*. The equations thus reduce to scalar equations for the magnitudes of $\mathbf{T}_1,\mathbf{T}_2,\mathbf{T}_3$, and the vanishing of the determinant

$$\Delta=\begin{vmatrix}(r_1-1) & \alpha_{12}r_2 & \alpha_{13}r_3\\ \alpha_{21}r_1 & (r_2-1) & \alpha_{23}r_3\\ \alpha_{31}r_1 & \alpha_{32}r_2 & (r_3-1)\end{vmatrix}\quad(32)$$

formed from the coefficients of the $\mathbf{T}_i$ gives the condition of compatibility of the homogeneous equations, or, geometrically, the surface of dispersion for the coplanar case. Since this case was thoroughly discussed by Georg Mayer in 1927 we may here only refer to his paper, all the more so as in the recent experiments the three rays are not coplanar.

(2) If the determinant Δ and at least one of the right hand sides in (31') do *not* vanish, the equations can be solved for $\mathbf{T}_1,\mathbf{T}_2,\mathbf{T}_3$ yielding

$$\begin{aligned}\Delta\,.\,\mathbf{T}_1&=\begin{vmatrix}\lambda_1\mathbf{s}_1 & \alpha_{12}r_2 & \alpha_{13}r_3\\ \lambda_2\mathbf{s}_2 & r_2-1 & \alpha_{23}r_3\\ \lambda_3\mathbf{s}_3 & \alpha_{32}r_2 & r_3-1\end{vmatrix}\\ \Delta\,.\mathbf{T}_2&=\begin{vmatrix}r_1-1 & \lambda_1\mathbf{s}_1 & \alpha_{13}r_3\\ \alpha_{21}r_1 & \lambda_2\mathbf{s}_2 & \alpha_{23}r_3\\ \alpha_{31}r_1 & \lambda_3\mathbf{s}_3 & r_3-1\end{vmatrix}\\ \Delta\,.\,\mathbf{T}_3&=\begin{vmatrix}r_1-1 & \alpha_{12}r_2 & \lambda_1\mathbf{s}_1\\ \alpha_{21}r_1 & r_2-1 & \lambda_2\mathbf{s}_2\\ \alpha_{31}r_1 & \alpha_{32}r_2 & \lambda_3\mathbf{s}_3\end{vmatrix}\end{aligned}\quad(33)$$

From these expressions we obtain a determination of the unknowns λ_i, *i.e.* the longitudinal components of the structure amplitudes, by forming the scalar products $(\mathbf{T}_i\mathbf{s}_i)$ which are zero; using the abbreviations $(\mathbf{s}_i\mathbf{s}_k)=s_{ik}$, $s_{ii}=1$, we have

$$\begin{aligned}&\begin{vmatrix}\lambda_1 & \alpha_{12}r_2 & \alpha_{13}r_3\\ \lambda_2s_{21} & r_2-1 & \alpha_{23}r_3\\ \lambda_3s_{31} & \alpha_{32}r_2 & r_3-1\end{vmatrix}=0;\\ &\begin{vmatrix}r_1-1 & \lambda_1s_{12} & \alpha_{13}r_3\\ \alpha_{21}r_1 & \lambda_2 & \alpha_{23}r_3\\ \alpha_{31}r_1 & \lambda_3s_{32} & r_3-1\end{vmatrix}=0;\\ &\begin{vmatrix}r_1-1 & \alpha_{12}r_2 & \lambda_1s_{13}\\ \alpha_{21}r_1 & r_2-1 & \lambda_2s_{23}\\ \alpha_{31}r_1 & \alpha_{32}r_2 & \lambda_3\end{vmatrix}=0\,.\end{aligned}\quad(34)$$

These three linear homogeneous equations for $\lambda_1,\lambda_2,\lambda_3$ have a solution provided the determinant of the coefficients of λ_i vanishes, *i.e.*

$$\begin{vmatrix}\begin{vmatrix}r_2-1 & \alpha_{23}r_3\\ \alpha_{32}r_2 & r_3-1\end{vmatrix} & -s_{21}\begin{vmatrix}\alpha_{12}r_2 & \alpha_{13}r_3\\ \alpha_{32}r_2 & r_3-1\end{vmatrix} & s_{31}\begin{vmatrix}\alpha_{12}r_2 & \alpha_{13}r_3\\ r_2-1 & \alpha_{23}r_3\end{vmatrix}\\ -s_{12}\begin{vmatrix}\alpha_{21}r_1 & \alpha_{23}r_3\\ \alpha_{31}r_1 & r_3-1\end{vmatrix} & \begin{vmatrix}r_1-1 & \alpha_{13}r_3\\ \alpha_{31}r_1 & r_3-1\end{vmatrix} & -s_{32}\begin{vmatrix}r_1-1 & \alpha_{13}r_3\\ \alpha_{21}r_1 & \alpha_{23}r_3\end{vmatrix}\\ s_{13}\begin{vmatrix}\alpha_{21}r_2 & r_1-1\\ \alpha_{31}r_1 & \alpha_{32}r_2\end{vmatrix} & -s_{23}\begin{vmatrix}r_1-1 & \alpha_{12}r_2\\ \alpha_{31}r_1 & \alpha_{32}r_2\end{vmatrix} & \begin{vmatrix}r_1-1 & \alpha_{12}r_2\\ \alpha_{21}r_1 & r_2-1\end{vmatrix}\end{vmatrix}=0\,.\quad(35)$$

Since, by their definition, none of the r_i can vanish except at infinite distance from the Lorentz point, a factor $(r_1r_2r_3)^2$ may be taken out, and, using (19) the equation of the SurfDisp may be written in terms of the components τ_i of the displacement $\mathfrak{v}$ as

$$D=\begin{vmatrix}\begin{vmatrix}\tau_2 & \alpha_{23}\\ \alpha_{32} & \tau_3\end{vmatrix} & -s_{21}\begin{vmatrix}\alpha_{12} & \alpha_{13}\\ \alpha_{32} & \tau_3\end{vmatrix} & s_{31}\begin{vmatrix}\alpha_{12} & \alpha_{13}\\ \tau_2 & \alpha_{23}\end{vmatrix}\\ -s_{12}\begin{vmatrix}\alpha_{21} & \alpha_{23}\\ \alpha_{31} & \tau_3\end{vmatrix} & \begin{vmatrix}\tau_1 & \alpha_{13}\\ \alpha_{31} & \tau_3\end{vmatrix} & -s_{23}\begin{vmatrix}\tau_1 & \alpha_{13}\\ \alpha_{21} & \alpha_{23}\end{vmatrix}\\ s_{13}\begin{vmatrix}\alpha_{21} & \tau_2\\ \alpha_{31} & \alpha_{32}\end{vmatrix} & -s_{23}\begin{vmatrix}\tau_1 & \alpha_{12}\\ \alpha_{31} & \alpha_{32}\end{vmatrix} & \begin{vmatrix}\tau_1 & \alpha_{12}\\ \alpha_{21} & \tau_2\end{vmatrix}\end{vmatrix}=0\quad(36)$$

or, expanded:

$$\begin{aligned}D=&(\tau_{12}-|\alpha_{12}|^2)(\tau_{23}-|\alpha_{23}|^2)(\tau_{31}-|\alpha_{31}|^2)\\ &-s_{123}\{(\alpha_{32}\tau_1-\alpha_{3112})(\alpha_{13}\tau_2-\alpha_{1223})(\alpha_{21}\tau_3-\alpha_{2331})\\ &+*\}-[s_{12}^2\{(\tau_{12}-|\alpha_{12}|^2)(\tau_3\alpha_{12}-\alpha_{1332})\\ &(\tau_3\alpha_{21}-\alpha_{2331})\}+\circlearrowright+\circlearrowright]=0\,.\end{aligned}\quad(37)$$

Here $\circlearrowright$ indicates cyclic replacement of the indices, and $*$ reversal of the order of indices. If the scattering coefficients of the atoms are real, the operation $*$ amounts to adding the conjugate complex to the previous product. In this and the following the abbreviations are used:

$$s_{ik}=(\mathbf{s}_i\mathbf{s}_k) \qquad s_{123}=(\mathbf{s}_1\mathbf{s}_2)(\mathbf{s}_2\mathbf{s}_3)(\mathbf{s}_3\mathbf{s}_1)$$
$$\tau_{12}=\tau_1\,.\,\tau_2 \qquad \tau_{123}=\tau_1\tau_2\tau_3$$
$$\alpha_{1223}=\alpha_{12}\alpha_{23} \qquad \alpha_{123}=\alpha_{12}\alpha_{23}\alpha_{31}$$
$$\alpha_{123}+\alpha_{321}=2C \tag{38}$$

While coefficients such as α_{12} are the direct coupling coefficients of rays 1 and 2, a product such as α_{1223} can be interpreted as causing a *detour coupling* of rays 1 and 3 *via* ray 2; and α_{123} represents a self-coupling of ray 1 *via* its coupling to 2, that of 2 to 3, and finally that of 3 to 1, like a kind of self-inductance of the ray. C is the real part of this self-coupling.

It is often convenient to express D according to decreasing orders of the τ products. This gives the equation of the SurfDisp in the form

$$\begin{aligned}D=&\tau_{123}^2-\tau_{123}\{[\tau_1|\alpha_{23}|^2(1+s_{23}^2)+\circlearrowright+\circlearrowright]\}\\&-\tau_{123}2C(s_{123}-\Sigma\, s_{ik}^2)\\&+2s_{123}\{[\tau_{12}|\alpha_{1332}|^2+\circlearrowright+\circlearrowright]\}+[\tau_{12}|\alpha_{1332}|^2(1-s_{12}^2)\\&+\circlearrowright+\circlearrowright]+[\tau_1^2|\alpha_{23}|^4s_{23}^2+\circlearrowright+\circlearrowright]\\&-2C[\tau_1|\alpha_{23}|^2(s_{123}+s_{23}^2)+\circlearrowright+\circlearrowright]\\&+4C^2s_{123}-|\alpha_{123}|^2v_s^2=0\,,\end{aligned} \tag{39}$$

where

$$v_s^2=1+2s_{123}-s_{12}^2-s_{23}^2-s_{31}^2\,; \tag{40}$$

v_s is the volume supported by the three unit vectors in the directions of the rays, $\mathbf{s}_i$.

9. Properties of the surface of dispersion

(9.1) *Asymptotic form of the surface*

Let one of the τ_i, for instance τ_3, be very much larger than the other two. The terms containing the highest power in τ_3, namely τ_3^2, are, from (39)

$$\tau_3^2\{(\tau_1\tau_2)^2-\tau_1\tau_2|\alpha_{12}|^2(1+s_{12}^2)+s_{12}^2|\alpha_{12}|^4\}\,. \tag{41}$$

The vanishing of the curly bracket yields a quadratic equation for $\tau_1\tau_2$ whose solutions are

$$\tau_1\tau_2=\begin{cases}|\alpha_{12}|^2\\|\alpha_{12}|^2s_{12}^2\,.\end{cases} \tag{41'}$$

This represents, for the two cases of polarization, the two hyperbolic cylinders (along $\mathbf{t}_3$) which form the four sheets of the SurfDisp when only rays 1 and 2 survive, which is obviously the case if we recede far enough from the Lorentz point in the direction $\mathbf{t}_3$, *i.e.* normal to the plane of $\mathbf{s}_1$ and $\mathbf{s}_2$.

(9.2) *Permutational properties*

The SurfDisp is, as is to be expected, invariant against a cyclic permutation of the assignment of the indices 1,2,3 to the three rays. This is seen in (39) from the fact that the single parts are formed by cyclic permutation and that the coefficients occurring singly, like $|\alpha_{123}|^2$, $2C$, s_{123} and v_s^2, remain unchanged by this operation. In a non-cyclic permutation the sense of the positive direction along the principal axis is reversed; the construction of the SurfDisp would take place on the other side of the plane of the vectors $\mathbf{h}_1$ and $\mathbf{h}_2$, but otherwise the surface is not changed.

(9.3) *Phase relations*

From (39) we see that the phases of the complex coupling coefficients $\alpha_{ik}=|\alpha_{ik}|\exp(i\varphi_{ik})$ appear in the expression of D only through the terms with factor

$$2C=\alpha_{123}+\alpha_{321}=|\alpha_{123}|\,.\,2\cos\varphi\,,$$

where

$$\varphi=\varphi_{12}+\varphi_{23}+\varphi_{31}$$

is the *sum* of the phases of α_{12}, α_{23} and α_{31}. Thus the phases do not modify the SurfDisp individually. In other words, provided the phases of two coupling coefficients (structure amplitudes) are known, that of a third may be determined from the geometry of the SurfDisp at simultaneous reflection.

(9.4) *Centrosymmetry*

The terms in odd powers of τ_i are both multiplied by $2C$. Therefore the SurfDisp is centrosymmetric about the Lorentz point if, and only if, $C=0$; this is the case if (i) one or two $\alpha_{ik}=0$; or (ii) $\varphi=\pm\pi/2$.

(9.5) *Consequences of* $\alpha_{123}=0$

If at least one of the coupling coefficients vanishes, then the constant terms in (39) are zero and the lowest order in τ-products is the second. Therefore the Lorentz point, where all $\tau_i=0$, is at least a double point of the SurfDisp, *i.e.* at least two of the six sheets pass through it. By (9.4) the Lorentz point is also a centre of symmetry of the SurfDisp.

(9.6) *Principal points when* $\alpha_{123}=0$

Let us call the intersections of the principal direction with the Surf Disp the *principal points*. Then, whenever one of the coupling coefficients vanishes, say $\alpha_{23}=0$, all six principal points are real. By putting $\tau_1=\tau_2=\tau_3=\tau$ in (39), this equation reduces to

$$D=\tau^2[\tau^4-\tau^2\{\mathrm{I}\}+\{\mathrm{II}\}]=0\,, \tag{42}$$

with

$$\{\mathrm{I}\}=\{|\alpha_{12}|^2(1+s_{12}^2)+|\alpha_{13}|^2(1+s_{13}^2)\}$$
$$\{\mathrm{II}\}=\{|\alpha_{3112}|^2(1+2s_{123}-s_{23}^2)+|\alpha_{12}|^4s_{12}^2+|\alpha_{13}|^4s_{13}^2\}\,.$$

Equating the biquadratic expression in the square bracket of the first line to zero gives two real values of τ^2 because the discriminant is positive:

$$\begin{aligned}\{\mathrm{I}\}^2-4\{\mathrm{II}\}=&[|\alpha_{12}|^2(1-s_{12}^2)-|\alpha_{13}|^2(1-s_{13}^2)]^2\\&+4|\alpha_{2113}|^2[s_{23}-s_{21}s_{13}]^2>0\,.\end{aligned} \tag{43}$$

The principal points are given by the positive and negative roots of the solutions of (42), which are

$$\begin{aligned}&\tau^2=0\,;\ \tau_\pm^2=\tfrac{1}{2}\{|\alpha_{12}|^2(1+s_{12}^2)+|\alpha_{13}|^2(1+s_{13}^2)\}\\&\pm\tfrac{1}{2}\sqrt{[|\alpha_{12}|^2(1-s_{12}^2)-|\alpha_{13}|^2(1-s_{13}^2)]^2+4|\alpha_{2113}|^2[s_{23}-s_{21}s_{13}]^2}\end{aligned} \tag{44}$$

(9.7) *Sections of the SurfDisp in the case* $\alpha_{23}=0$

(*A*) *Section with the* (t_2,t_3)*-plane*

With $\tau_1=0$ there remains

$$D=\tau_2\tau_3|\alpha_{2113}|^2\{2s_{123}+1-s_{23}^2\}+\tau_2^2|\alpha_{13}|^4s_{13}^2+\tau_3^2|\alpha_{12}|^4s_{12}^2 =0 \quad (45)$$

This is a homogeneous equation of the second order. We put

$$\frac{\tau_3|\alpha_{12}|^2s_{12}}{\tau_2|\alpha_{13}|^2s_{13}}=u \quad (46)$$

and obtain for u

$$u=\frac{1}{2s_{12}s_{13}}\{-(2s_{123}+1-s_{23}^2) \pm\sqrt{(1-s_{23}^2)[1-(s_{23}-2s_{12}s_{13})^2]}\}\,. \quad (47)$$

This section is always real and consists of a pair of straight lines passing through Lo; for it is easily seen that the square bracket under the root is positive. Indeed, the expression whose square is to be taken is written with unit vectors as

$$s_{23}-2s_{12}s_{13}=(\mathbf{s}_3\,.\,(\mathbf{s}_2-2\mathbf{s}_1s_{12}))=(\mathbf{s}_3\,.\,\mathbf{s}')\,,$$

and, as $\mathbf{s}'$ is also a unit vector, this expression is the cosine of an angle and its square <1.

(*B*) *Section in the* (t_1,t_3)*-plane*

With $\tau_2=0$

$$D=\tau_3^2|\alpha_{12}|^4s_{12}^2=0\,. \quad (48)$$

The intersection is $\tau_2=\tau_3=0$, *i.e.* the $\mathbf{t}_1$ axis.

(*C*) *Section in the plane* $(\mathbf{t}_1,\mathbf{T})$, *where* $\mathbf{T}=\mathbf{t}_3-\mathbf{t}_2$

The vector $\mathbf{T}$ is normal to $\mathbf{t}_1$ only if $\mathbf{s}_2$ and $\mathbf{s}_3$ are related by a symmetry plane containing $\mathbf{s}_1$. In order to remain in the plane $(\mathbf{t}_1,\mathbf{T})$, we have to put $\tau_2=-\tau_3$ in $D=0$. This gives the equation

$$D=\tau_3^2\{(-\tau_1\tau_3+\tfrac{1}{2}[|\alpha_{13}|^2(1+s_{13}^2) -|\alpha_{12}|^2(1+s_{12}^2)])^2-d^2\}=0 \quad (49)$$

where

$$d^2=\tfrac{1}{4}\{|\alpha_{13}|^2(1-s_{13}^2)-|\alpha_{12}|^2(1-s_{12}^2)\}^2+|\alpha_{1213}|^2v_s^2 \quad (49')$$

is positive.

The section consists of the T axis, counting double, and of two pairs of hyperbolic curves. The condition of the vanishing of the curly bracket in (49) can be written

$$(-\tau_1\tau_3+a+d)(-\tau_1\tau_3+a-d)=0\,, \quad (50)$$

where $a=\frac{1}{2}[\text{---}]$ in (49) and can be positive or negative, and greater or smaller in absolute value than d. Depending on the specific values, the intersections of $D=0$ with the (t_1,T) plane lie as shown schematically in Fig. 3; the hyperbolae represented by the second factor in (50) are shown dotted.

(9.8) *Collapsed base*

If all the basis vectors are put equal to zero, the total scattering power of the base is concentrated at the corners of the cells and the diffraction is as by a lattice of dipoles. The SurfDisp for the case of n strong rays has already been derived for this case in the 1917 paper, and a shorter derivation, using the present nomenclature, was given in 1937. The equation in this case is

$$D=\frac{1}{3!}\sum_{ikl}r_ir_kr_l(\mathbf{s}_i[\mathbf{s}_k\mathbf{s}_l])^2+\frac{1}{2!}(1-R)\sum_{ik}r_ir_k[\mathbf{s}_i\mathbf{s}_k]^2 +(1-R)^2=0 \quad (51)$$

with

$$R=\sum_i r_i\,.$$

The factorials can be omitted by using the convention $i<k<l$; the triple product of the $\mathbf{s}_i$ in the first term is the volume supported by any three unit vectors of ray direction. In the case of three strong rays the first sum reduces to a single term.

Our general expression (35) should reduce to the above equation on collapsing the base. This makes all $\alpha_{ik}=1$ and reduces (35) to

$$D=\begin{vmatrix}1-R+r_1 & s_{12}r_2 & s_{13}r_3\\ s_{21}r_1 & 1-R+r_2 & s_{23}r_3\\ s_{31}r_1 & s_{32}r_2 & 1-R+r_3\end{vmatrix}=0 \quad (52)$$

which is easily seen to lead to the result (51).

(9.9) *Condition for the Laue point to lie on the SurfDisp*

If La satisfies equation (39), then, by putting all $\tau_i=1$, we obtain

$$1-[|\alpha_{23}|^2(1+s_{23}^2)+\circlearrowright\circlearrowright]-2C(s_{123}-\Sigma\, s_{ik}^2) +[|\alpha_{1332}|^2(2s_{123}+1-s_{12}^2)+\circlearrowright\circlearrowright]+[|\alpha_{23}|^4s_{23}^2+\circlearrowright\circlearrowright] -2C[|\alpha_{23}|^2(s_{123}+s_{23}^2)+\circlearrowright\circlearrowright]+4C^2s_{123} -|\alpha_{123}|^2v_s^2=0\,. \quad (53)$$

In the case of a collapsed base, all $\alpha_{ik}=1$ and $C=1$. The condition then becomes, writing Σ for $\Sigma\, s_{ik}^2$,

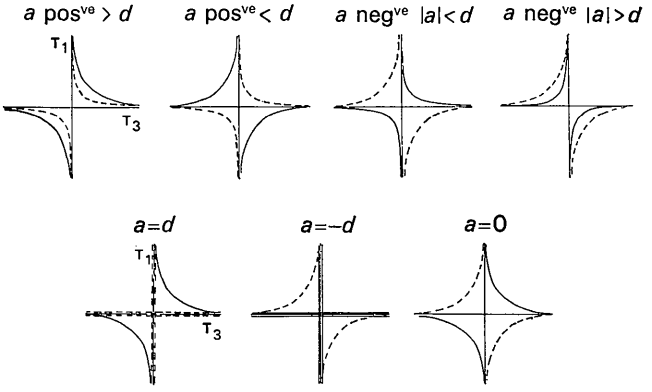

Fig. 3. Schematic diagrams of sections of $(\mathbf{t}_1,\mathbf{T})$ plane and SurfDisp for various combinations of a and d values [equations (49) and (49′)].

$$1-(3+\Sigma)-2(s_{123}-\Sigma)+(6s_{123}+3-\Sigma)$$
$$+\Sigma-2(3s_{123}+\Sigma)+4s_{123}-v^2=0\,,$$

or simply

$$1+2s_{123}-\Sigma-v_s^2=0\,. \qquad (54)$$

This condition is fulfilled [see (40)]; thus, for a collapsed base, the SurfDisp for three rays *always* contains the Laue point.

(9.10) *Three orthogonal rays*

This case can best be discussed for the general (non-collapsed) crystal by noting that if all $s_{ik}=0$, only the first product term of D [equation (37)] survives:

$$D(s_{ik}=0)$$
$$=(\tau_{12}-|\alpha_{12}|^2)(\tau_{23}-|\alpha_{23}|^2)(\tau_{13}-|\alpha_{13}|^2)=0\,. \qquad (55)$$

The surface then consists of the three interpenetrating but undeformed hyperbolic cylinders for the three pairs of rays, 12, 23, 31. For each of these cylinders the electric moment is normal to the plane of the two rays, *i.e.* in the direction of the third. Therefore this moment produces no wave travelling in the third direction, and that ray is uncoupled. If the base is collapsed, the Laue-point is a triple point of the entire surface. If the crystal consists of smooth equidistant sheets of planar molecules, and rays 1 and 2 are at 45° on either side of these planes, then $|\alpha_{12}|$ will be very nearly 1, and one of the (1–2) sheets of the SurfDisp will get very close to *La.* This would, however, happen also without the presence of the third ray for properly polarized X-rays, and no enhancement of the simple Borrmann effect will take place on rotating the crystal about the normal of the molecular plane until ray 3 appears.

10. Silicon and germanium crystals

As it seems unprofitable to continue with the discussion of the general case, we now specialize to the case of silicon or germanium crystals, since these are the most readily available crystals approaching perfection, and the coupling coefficients are sufficiently restricted by the structure to lead to important simplifications if we neglect atomic factors and absorption.

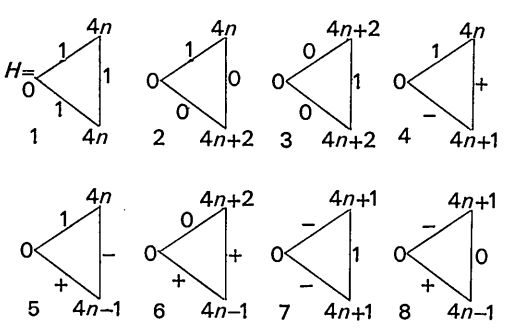

Fig. 4. Possible combinations of H-values and coupling coefficients for germanium structure with point atoms.

(10.1) *Structure factors and combinations of coupling coefficients*

Both crystals are of the diamond type structure and have only four values of the relative structure amplitudes or coupling coefficients. These depend only on $H=h_1+h_2+h_3$ and are

$$\left.\begin{array}{lll} \text{if } H=4n & \alpha=1 & \text{denoted as } 1 \\ =4n+2 & 0 & 0 \\ =4n+1 & \exp(-i\pi/4)/\sqrt{2} & - \\ =4n-1 & \exp(i\pi/4)/\sqrt{2} & + \end{array}\right\}\ ; \qquad (56)$$

n can be any integer. It should also be noted that, since the structure consists of two interpenetrating face-centered cubic lattices, only indices h_1, h_2, h_3 of uniform parity occur.

Ray 1, or (000), is of the form $H=4n$ and therefore the coupling coefficients α_{12} and α_{13} belong to the same class as α_2 and α_3. The remainder (modulo 4) of α_{23} is the difference of the remainders of H_2 and H_3. On account of the permutation properties of the rays, the diagrams (Fig. 4) give a complete survey of the possible combinations of H-values (written at the corners of the diagrams which correspond to the points **O**, $\mathbf{h}_2$ and $\mathbf{h}_3$ of reciprocal space) and of α_{ik} values (written along the sides of the triangles). Of these diagrams, 2 and 3 are of no interest here because they show one of the rays uncoupled from the other two; it is an isolated ray in the sense discussed previously (Ewald, 1937, p. 13), and the SurfDisp is that of the two coupled rays. Cases 4 and 5 have the same coupling coefficients, only in different sequence, and need not both be discussed. Case 6 with $H\equiv(0,2,-1)$ leads to the same SurfDisp as the one with $H\equiv(0,2,+1)$; in considering ray 1 to be the 'primary' ray, this is the case of true 'Umweganregung', whereas on the same assumption case 8 represents an Umweganregung only in the sense that the two secondary rays are not coupled directly but only through the primary ray.

There remain therefore to be distinguished only three cases of interest, characterized (i) by three maximum coupling coefficients (*e.g.* 220/2$\bar{2}$0/040), (ii) two equal and one vanishing coefficient as in case 8 (*e.g.* 111/1$\bar{1}$1/020) and (iii) two conjugate complex and one maximum coupling coefficient, as in case 7 (*e.g.* 111/$\bar{1}$11/220).

For cubic crystals the angles between the rays depend only on the *ratio* of the order vectors to $|\mathbf{K}|$; introducing dimensionless reduced reciprocal axes

$$\boldsymbol{\beta}_i=\mathbf{b}_i/|K|(=\lambda/a_i)\,, \qquad (57)$$

we put

$$\mathbf{h}_i=\sum_k h_{ik}\mathbf{b}_k=K\boldsymbol{\eta}_i \quad \text{with} \quad \boldsymbol{\eta}_i=\sum_k h_{ik}\boldsymbol{\beta}_k\,. \qquad (57')$$

According to (5), the position of the Lorentz point is, in these units,

$$\mathbf{Lo}=K\frac{1}{2[\eta_2\eta_3]^2}\left\{\{\eta_3^2(\eta_2^2-(\eta_2\eta_3)\}\boldsymbol{\eta}_2+\eta_2^2\{\eta_3^2-(\eta_3\eta_2)\}\boldsymbol{\eta}_3 - \sqrt{4[\eta_2\eta_3]^2-\eta_2^2\eta_3^2(\eta_2-\eta_3)^2}[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]\right\} \quad (58)$$

and the distance *La–Lo* according to (13)

$$\mathbf{La}\leftarrow\mathbf{Lo}=K\frac{\mu^2-1}{\mu^2}[\boldsymbol{\eta}_2\boldsymbol{\eta}_3]/\sqrt{4[\eta_2\eta_3]^2-\eta_2^2\eta_3^2(\eta_2-\eta_3)^2}. \quad (59)$$

In terms of $\boldsymbol{\eta}_i$ we easily obtain, formally or by inspection,

$$(\mathbf{s}_1\mathbf{s}_2)\equiv s_{12}=(1-\tfrac{1}{2}\boldsymbol{\eta}_2^2) \qquad (\mathbf{s}_2\mathbf{s}_3)\equiv s_{23}=(1-\tfrac{1}{2}(\boldsymbol{\eta}_2-\boldsymbol{\eta}_3)^2). \quad (60)$$
$$(\mathbf{s}_1\mathbf{s}_3)\equiv s_{13}=(1-\tfrac{1}{2}\boldsymbol{\eta}_3^2)$$

The volume v_s is given by (9). All geometrical factors in the equation for the SurfDisp can now be expressed by the indices of the three reflections, and thereby remain valid for all wave-lengths.

(10.2) *Case of maximum coupling between the rays*: $\alpha_{ik}=1$, *case* 1 *of Fig.* 4

Going back to (39), setting all $\alpha_{ik}=1$, as for a collapsed base, and all $\tau_i=\tau$, we easily factorize the equation for the principal points into

$$D=(\tau-1)^3\{(\tau+1)^3-(\tau+1)\Sigma\, s_{ik}^2-2s_{123}\}=0\,. \quad (61)$$

$\tau=1$, the Laue point, is a threefold root, irrespective of the angles between the rays. It is easily seen that the third order equation for $(\tau+1)$ cannot have a root $\tau>1$; therefore no sheet of the surface intersects *above* the Lauepoint.

(10.3) *Case of direct 'Umweganregung'*

This occurs as case 6 in Fig. 4. Ray 2 is a 'forbidden' reflection with no direct coupling to ray 1. But an indirect coupling, *via* ray 3, exists between the first two rays. We put $\alpha_{12}=0$, and, for simplicity, make $\alpha_{13}=\alpha_{23}=\alpha$. The principal points are then given by

$$D=\tau^2\{\tau^4-\tau^2|\alpha|^2(2+s_{13}^2+s_{23}^2) +|\alpha|^4(2s_{123}+1-s_{12}^2+s_{13}^2+s_{23}^2)\}=0\,. \quad (62)$$

Lo is a double point and centre of symmetry, and the other principal points are at $\pm\tau$, where

$$\tau^2=|\alpha|^2\{1+\tfrac{1}{2}(s_{13}^2+s_{23}^2) \pm\tfrac{1}{2}\sqrt{(s_{13}^2+s_{23}^2)^2+4s_{12}^2-8s_{123}}\}\,. \quad (63)$$

There is a simplification if rays 1 and 2 are at right angles to one another, namely $\tau^2=1$ or $1+s_{13}^2+s_{23}^2$; this requires a special ratio of (a/λ).

(10.4) *Case of indirect 'Umweganregung'*

This is case 8 of the list. Ray 1 is coupled directly to 2 and 3, but the latter are only detour-coupled *via* 1. It is the case on which the double Borrmann effect was first studied (Borrmann & Hartwig, 1965) with

1=000, 2=111, 3=1$\bar{1}$1, 2–3=020 ('forbidden').

The equation for the SurfDisp reduces to

$$D=\tau_{123}^2-\tau_{123}\tfrac{1}{2}(\tau_2(1+s_{13}^2)+\tau_3(1+s_{12}^2)) +\tfrac{1}{4}\tau_2\tau_3(1+2s_{123}-s_{23}^2)+\tfrac{1}{4}(\tau_2^2s_{13}^2+\tau_3^2s_{12}^2)=0\,. \quad (64)$$

All attempts to factorize D have been unsuccessful. The principal points are determined by

$$\tau^2\{\tau^4-\tfrac{1}{2}\tau^2(2+s_{12}^2+s_{13}^2) +\tfrac{1}{4}(1+2s_{123}+s_{12}^2+s_{13}^2-s_{23}^2)\}=0\,. \quad (65)$$

The first factor shows that *Lo* counts double; the other roots follow from

$$\tau^2=\tfrac{1}{4}\{2+s_{12}^2+s_{13}^2 \pm\sqrt{(2+s_{12}^2+s_{13}^2)^2-4(1+2s_{123}+s_{12}^2+s_{13}^2-s_{23}^2)}\}\,. \quad (66)$$

If there is symmetry, as in the case specified above, namely $s_{12}=s_{13}=s$, $s_{23}=s'$, then four of the principal points follow from

$$\tau_\pm^2=\tfrac{1}{2}\left\{\begin{array}{l}1+2s^2-s'\\1+s'\end{array}\right\} \quad (67)$$

and the equation for the intersection of the SurfDisp with the symmetry plane can be factorized:

$$\tau^2\{\tau_1\tau-\tfrac{1}{2}(1+2s^2-s')\}\{\tau_1\tau-\tfrac{1}{2}(1+s')\}=0\,, \quad (68)$$

where $\tau=\tau_2=\tau_3$. The intersection consists of the $\mathbf{t}_1$ axis ($\tau=0$) counting double, and two hyperbolae, both of which lie in those quadrants of the symmetry plane in which τ and τ_1 have the same sign [$\frac{1}{2}(1+2s^2-s')$ is always positive]. Which of the values (60) gives the intersection closest to *La*, *i.e.* $\tau_i=1$, depends on the angles $s_1s_2=s_1s_3$ and s_2s_3. The latter angle can vary from near zero to a maximum of $2s_1s_2$ .Therefore $s'=\cos(s_2s_3)\geq 2s^2-1$, or $s'=2s^2-1+p$, where p is positive and $<2(1-s^2)$. The roots are then

$$\tau^2=1-\tfrac{1}{2}p \quad\text{and}\quad \tau^2=s^2+\tfrac{1}{2}p,$$

and either may be the closer one to 1 .

Fig. 5 illustrates the topmost sheet of the SurfDisp in the symmetrical three-ray case. In the lower part of this drawing in reciprocal space the directions of the three rays are shown as they would be if there was no coupling ($\mathbf{s}_1,\mathbf{s}_2,\mathbf{s}_3$ are directed from the Lorentz point *Lo*). The ellipse represents a plane reference circle through *Lo* normal to the principal axis, and the curvilinear-bounded planes above it are parts of the tangential planes of the intersecting spheres of radius K about the points O, $\mathbf{h}_2$, and $\mathbf{h}_3$. These planes intersect in the edges $\mathbf{t}_1,\mathbf{t}_2,\mathbf{t}_3$. A tiepoint T far from the edges represents a single, nearly uncoupled ray and it must therefore lie on the appropriate tangent plane to one of the spheres. As T approaches one of the edges, two of the rays are coupled, and the SurfDisp leaves the tangent planes, so that the top sheet is lifted towards the parallels to the t-lines going through the Laue point *La*. For the symmetrical case the intersection of the SurfDisp with the symmetry plane (hatched) is drawn. Here the top sheet gets much closer to the Lauepoint than in the peripheral regions. This accounts for the enhancement of the Borrmann effect by the presence of the third ray.

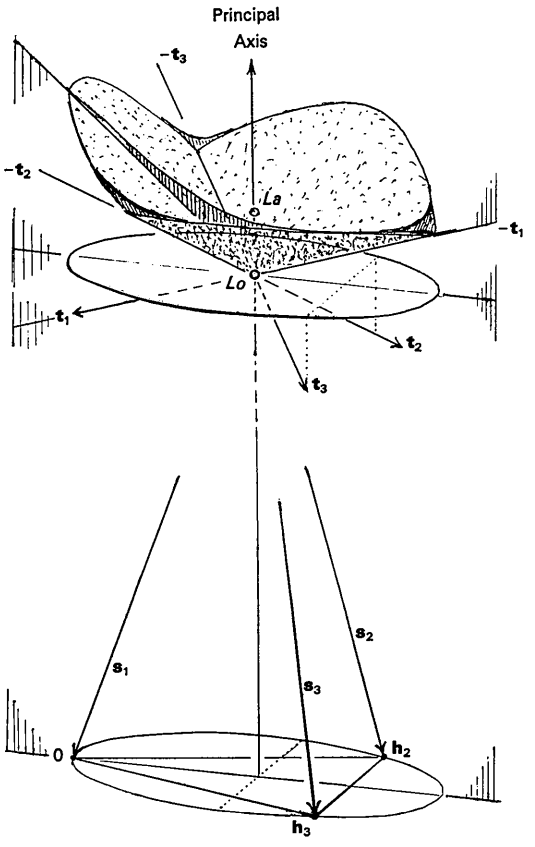

Fig. 5. The top sheet of the SurfDisp for rays 1, 2, 3 in germanium if rays 2 and 3 are related by a symmetry plane containing ray 1. The symmetry plane is indicated on the border of the Figure. The stippled planes, sustained each by two of the -**t**-vectors, are part of the tangent planes to the spheres through *Lo* with **O**, $\mathbf{h}_1$, and $\mathbf{h}_3$ as centres; they form the SurfDisp when only one ray is strong. Two strong rays exist near the -**t** axes, and here the top sheet of the SurfDisp is lifted out of the angle formed by the tangent planes, so as to form one branch of the well-known SurfDisp for two rays, namely a hyperbolic cylinder which descends parallel to the *t* axis towards the Lorentz point, provided the coupling to the third ray is neglected. This coupling, in turn, acts like a tension on the surface along the three *t* axes, pulling the sheet away from *Lo*, so that its section with the symmetry plane – shown with vertical hatching – brings the surface much closer to *La* than it would be without the coupling. This is the origin of the enhanced Borrmann effect.

(10.5) *A numerical estimate*

In the case of *germanium*, $111/1\bar{1}1/020$, and *Cu K radiation* we have [using the same data as Hildebrandt (1966)]

$$a=5{\cdot}6575\text{ Å},\ \lambda=1{\cdot}5390\text{ Å}\ [=(2\lambda_{\alpha_1}+\lambda_{\alpha_2})/3] \quad (69)$$
$$\beta=\lambda/a=0{\cdot}27203;\ \beta^2=0{\cdot}07400\,,$$

and by (51)

$$\left.\begin{aligned} s &= s_{12}=s_{13}=0{\cdot}889;\ s^2=0{\cdot}7903 \\ s' &= s_{23}=0{\cdot}852;\qquad s'^2=0{\cdot}7259 \end{aligned}\right\}. \quad (70)$$

The intersection of the SurfDisp with the symmetry plane is then

$$\tau^2(\tau_1\tau-0{\cdot}926)(\tau_1\tau-0{\cdot}864)=0\,. \quad (71)$$

The two intersections closest to *La* are at

$$\tau_1=\tau=\sqrt{0{\cdot}926}=0{\cdot}9623 \text{ and } \sqrt{0{\cdot}8643}=0{\cdot}9297\,. \quad (72)$$

For an isolated ray the distance of its tiepoint, the Lorentz point, from *La* would be expressed as $\tau_1=\tau=1$; for rays 1 and 2 (without 3) the SurfDisp is given in (9.1), and the closest approach to the Laue point is given by

$$\tau_1=\tau_2=|\alpha_{12}|=1/\sqrt{2}=0{\cdot}7071\,.$$

Thus, without taking account of absorption, the nearest approaches to *La* are in the one-, two-, three-ray cases as

$$1:0{\cdot}2929:0{\cdot}0377=26{\cdot}5:7{\cdot}76:1\,. \quad (73)$$

At the optimum, the dipole amplitude in the three-ray case is thus only 1/26th of that of an isolated ray, and about 1/8th that of the smallest value in the two-ray case. The effective absorption coefficient for amplitude would be expected to be reduced in the same ratios. This gives a pronounced 'double Borrmann effect'. Taking absorption into account pushes the top sheet of the SurfDisp away from *La*, towards *Lo*, and this diminishes the effect; but, especially near the Laue point, absorption remains a secondary effect.

When all structure or coupling factors are unity, as in case 1 of the enumeration (Fig 4), no double Borrmann effect occurs; for then, even in the two-ray case, maximum efficiency is reached because the wavelets scattered by all atoms are in full phase-cooperation.

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