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Is the border surface of a crystal indeed the weakest point of the dynamical theory of diffraction?

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In Laue's dynamical theory of diffraction, the boundary conditions claim to introduce a mathematical plane instead of the discrete atomic surface of the crystal. This assumption is analysed from the point of view of Ewald's theory based on the microscopic discrete model of a crystal, where no boundary conditions are needed.

1. The crystal surface as a mathematical problem of Laue's theory

To deal with the problem of the diffraction from crystalline materials in the short-wavelength region, mostly the approach introduced by Bethe (1928) and von Laue (1941) is used. The fundamental equations of Laue's theory are

$$\Delta\mathbf{D} - \frac{1}{c^2}\frac{\partial^2\mathbf{D}}{\partial t^2} = -4\pi \,\mathrm{curl}\,\mathrm{curl}\,\mathbf{P}, \quad \chi\mathbf{P} = \mathbf{D}. \tag{1}$$

The electric susceptibility χ has the periodicity of the crystal. To pass over from an infinite crystal to the diffraction of an external wave on a semi-infinite crystal, von Laue writes (Laue, 1941, p. 264): 'The mathematical solution of the problem raises immediately the question about the nature of the border surfaces. The optics of the visible region considers them by right as mathematical surfaces because molecular roughness is not important as compared with the wavelengths. For much shorter X-rays, this simplification is not valid. The mathematical surface of a given orientation as a boundary of an ideal crystal lattice divides, with a few exceptions, the atoms and is not therefore a reality. But there is no better idea of the surface. Luckily the predominant majority of experiments with X-rays say that the crystal boundary influence is missing; the total reflection at grazing incidence is the unique exception. Therefore as the hypothesis about the nature of the boundary is not important we can make, with the exception of grazing incidence and reflection, the most comfortable assumption: the mathematical surface. Anyway this is the weakest point of the dynamical theory'. A similar assertion can be found in Pinsker (1978, p. 37): 'The scheme using the mathematical crystal–vacuum boundary agrees well with experimental data available'.

The same problem appears in the dynamical diffraction of neutrons. Sears (1989, p. 178) starts with the Schrödinger equation

$$\Delta\psi + v(\mathbf{r})\psi = E\psi, \tag{2}$$

$v(r)$ being a periodical function in the crystal volume V and $v(r) = 0$ outside V, and continues: 'Since $v(\mathbf{r})$ is discontinuous at the surface of V we must find separate solutions of equation (2) inside and outside V and then match these solutions by requiring that $\psi(\mathbf{r})$ and $\nabla\psi(\mathbf{r})$ be continuous at the boundary. One might, perhaps, question whether it is permissible to treat the boundary as a well defined geometrical surface, since the wavelength of thermal neutrons is typically of order of 1 Å and, hence, of the same order of magnitude as the interatomic distance in a crystal. However, the important parameter here is not the wavelength but the extinction length which is typically 50 μm which is very much greater than the interatomic distance. Thus, as long as the scale of any surface roughness is much less than the extinction length, the surface is optically smooth and equation (2) is valid'.

On the other hand, Ewald's conception (1916*a*,*b*, 1917, 1932, 1937, 1965) was different from that of Bethe and von Laue.[1] Ewald considered a crystal as a discrete system of classical electrical vibrating dipoles

$$\mathbf{p}_\mathbf{m}(t) = \mathbf{p}_\mathbf{m}\exp(-i\omega t) \tag{3}$$

fixed at the lattice points. The dipoles are coupled with retarded electromagnetic forces. An external electromagnetic wave excites the mechanical vibrations of this system of coupled dipoles. The electromagnetic waves generated by oscillating dipoles and superposed on the incident wave are registered outside the crystal as the reflected and transmitted waves. Thus the problem of Ewald was in fact the mechanical problem of forced oscillations of a system of electromagnetically coupled oscillators where no boundary conditions appear. Nevertheless, in an excellent Commentary on Ewald's fundamental papers of the dynamical theory of X-ray diffraction by H. J. Juretschke (1992, p. 96), we can read: 'It seems to me that for Ewald a major stumbling block in an elegant theory probably was the question of where to locate

[1] A very good paper on the relations between Ewald's and Laue's theories is that of Wagenfeld (1968).

the boundary. For one atom per cell this boundary can be taken as a mathematical plane, even for arbitrary surface orientations. But with a distributed cell content, such a surface would split cells, surely violating some chemical principles. This question of the true nature of the surface was one of continuing debate between Ewald and von Laue . . . '.

2. The physical and mathematical boundary of a crystal

In this paper, we tackle the problem of the boundary surface using Ewald's approach based on the discrete model of a crystal (Ewald, 1916*a*,*b*).[2] Let us study the diffraction of a scalar plane wave[3]

$$f(\mathbf{r}) = f\exp(i\mathbf{kr}) \tag{4}$$

on a periodic system of scatterers fixed on the lattice points forming a semi-infinite crystal

$$\mathbf{R_m} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a_3}, \quad \mathbf{m} = (m_1, m_{2,}, m_3) \tag{5}$$
$$m_1, m_2 = 0, \pm1, \pm2, ..., \pm\infty; \quad m_3 = 0, 1, 2, \ldots, \infty.$$

The origin of the orthogonal coordinate system lies at the lattice point (0,0,0), the plane *Oxy* coincides with the crystal surface plane ($\mathbf{a}_1\mathbf{a}_2$). The axis *Oz* (the unit vector $\mathbf{e}_3$) and the vector $\mathbf{a}_1 \times \mathbf{a}_2$ point into the crystal. The lattice ($\mathbf{b}_1$,$\mathbf{b}_2$) is reciprocal to the two-dimensional lattice ($\mathbf{a}_1$,$\mathbf{a}_2$).

The crystal surface lowers the three-dimensional translational symmetry of an ideal infinite crystal into a two-dimensional one. Then the wavevectors of the waves reflected by a semi-infinite crystal are

$$\mathbf{K}^-_{pq}(\mathbf{k}) = \mathbf{k}'' + p\mathbf{b}_1 + q\mathbf{b}_2 - \mathbf{e}_3K_{pqz}(\mathbf{k})$$

with

$$K_{pqz}(\mathbf{k}) = +[k^2 - (\mathbf{k}'' + p\mathbf{b}_1 + q\mathbf{b}_2)^2]^{1/2},$$

p, q being zero, negative or positive integers.

Let us write down the Ewald quantum-mechanical equations for the diffraction of scalar waves on Fermi delta potentials (Sears, 1989; Dederichs, 1982). The wavefunction $\Psi(\mathbf{r})$ describing the diffraction of particles (*e.g.* neutrons) on a simple perfect lattice formed by Fermi delta potentials is

$$\Psi(\mathbf{r}) = f\exp(i\mathbf{kr}) - \sum_{\mathbf{n}} Q\frac{\exp(ik|\mathbf{r} - \mathbf{R_n}|)}{|\mathbf{r} - \mathbf{R_n}|}\varphi^{\mathbf{n}}(\mathbf{R_n}), \tag{6}$$

which is the superposition of the incident plane wave (4) and of the spherical waves excited by the point scatterers forming the crystal. The diffraction amplitude of the **n**th atom is $Q\varphi^{\mathbf{n}}(\mathbf{R_a})$, where Q is the diffraction length of the scatterer and the effective field $\varphi^{\mathbf{n}}(\mathbf{R_n})$ incident on the **n**th atom must satisfy equations

$$\varphi^{\mathbf{n}}(\mathbf{R_n}) = f\exp(i\mathbf{kR_n}) - \sum_{\mathbf{m}\neq\mathbf{n}} Q\frac{\exp(ik|\mathbf{R_m} - \mathbf{R_n}|)}{|\mathbf{R_m} - \mathbf{R_n}|}\varphi^{\mathbf{m}}(\mathbf{R_m}). \tag{7}$$

The method of the solution of (6) and (7) is described by Litzman & Rózsa (1977), Litzman (1978, 1986), Litzman & Dub (1990), Litzman *et al.* (1996) in detail. Here we only summarize the results obtained. Evaluating $\varphi^{\mathbf{n}}(\mathbf{R_n})$ from (7) and inserting the results into (6), we get for the wavefunction $\Psi^r(\mathbf{r})$ of the reflected particles[4]

$$\Psi^r(\mathbf{r}) = \sum_{pq}\Psi^r_{pq}(\mathbf{r}), \tag{8}$$

where, in the standard two-beam approximation,[5]

$$\Psi^r_{pq}(\mathbf{r}) = f\exp[i(\mathbf{K}^-_{pq} - \mathbf{k})\mathbf{a}_3/2](k_z/K_{pqz})^{1/2} \times [Y_{pq} - \mathrm{sign}(Y_{pq})(Y^2_{pq} - 1)^{1/2}]\exp(i\mathbf{K}^-_{pq}\mathbf{r}) \tag{9}$$

with[6]

$$Y_{pq}(\mathbf{k}) = -\tfrac{1}{2}[(k_z/K_{pqz})^{1/2} + (K_{pqz}/k_z)^{1/2}]\cos[\mathbf{a}_3(\mathbf{k} - \mathbf{K}^-_{pq})/2] + h_o a_{3z}(k_zK_{pqz})^{1/2}\sin[\mathbf{a}_3(\mathbf{k} - \mathbf{K}^-_{pq})/2]. \tag{10}$$

The dimensionless parameter h_o renders the interaction between radiation and matter,

$$h_o = \frac{[\mathbf{a}_1 \times \mathbf{a}_2]}{2\pi a_{3z}Q_o}, \quad \text{with} \quad Q_0 = (Q^{-1} - ik)^{-1}.$$

For example, in neutron diffraction h_o is of order 10^5 and $a_{3z}(k_zK_{pqz})^{1/2}$ is of order 10^0.

Formula (8) for the wavefunction of reflected waves has been deduced within the frame of the microscopic discrete model of a bounded crystal by using the algebraic procedure. Thus no crystal boundary plane as used in optics of continuous media has been considered. Nevertheless, we can pose the question whether it is possible to introduce a 'mathematical' boundary plane in such a way that the waves (4) and (9) may be regarded as waves incident and reflected on this plane. Thus, let us rewrite (9) in the form

$$\Psi^r_{pq}(\mathbf{r}) = f\exp(-i\mathbf{ka}_3/2)(k_z/K_{pqz})^{1/2}[Y_{pq} - \mathrm{sign}(Y_{pq}) \times (Y^2_{pq} - 1)^{1/2}]\exp[i\mathbf{K}^-_{pq}(\mathbf{r} + \mathbf{a}_3/2)]. \tag{11}$$

Comparing the exponential terms in (4) and (11), we can see that this 'mathematical' plane should be shifted from the uppermost atomic layer $m_3 = 0$ by the vector $\mathbf{d} = -\mathbf{a}_3/2$. This conclusion is apparently connected by the fact that the shift between two neighbour crystal planes is equal to $\mathbf{a}_3$.

In Litzman & Dub (1990), we compared the results yielded by our treatment with formulae used in Laue's theory and found that the differences are of order $(\Delta\xi)^2$, where $\Delta\xi = \xi - \xi_B$ is the deviation of the incident wave (4) from the Bragg diffraction position. Thus, the assumption of a mathematical boundary plane used in Laue's theory indeed provides good results. Furthermore, considering the crystalline slab formed by $N + 1$ atomic planes (*i.e.* $m_3 = 0, 1, 2, \ldots, N$), we found in Litzman & Rózsa (1990) that its thickness is $(N + 1)a_{3z}$ (and not Na_{3z}), which means that the 'mathematical' upper

[2] The differences between the mathematical treatments of the problem used by Ewald and by us are outlined in Appendix *A*.

[3] The scattering of an electromagnetic wave on a system of coupled point dipoles can be handled in an analogous way (Litzman & Rózsa, 1977; Litzman, 1978).

[4] See equations (8)–(10) in Litzman & Dub (1990).

[5] In equation (9) of the paper by Litzman & Dub (1990), we put $R_2 = 1$ [*cf.* equation (18) in Litzman & Dub (1990)] and express R_1 by means of equation (2.27) in Litzman *et al.* (1996).

[6] In equation (2.28) in Litzman *et al.* (1996), we put $F^{(1)}_{00,pq} = 1$ (see discussion on p. 4717 in this paper).

(bottom) boundary plane is to be shifted from the atomic plane $m_3 = 0$ ($m_3 = N$) by the vector $\mathbf{d} = -\mathbf{a}_{3z}/2$ ($\mathbf{d} = \mathbf{a}_{3z}/2$).

It should be mentioned that our formulae (9) and/or (11) are valid (in contradiction to the usual results of Laue's theory) for both coplanar and noncoplanar reflections, near to or far from the Bragg diffraction positions, and can be generalized to the multiwave case (Litzman & Mikulík, 1999). On the other hand, (9) has been derived for the crystal with the cell containing one atom only. As for a lattice with a basis, we found the general solution of the diffraction problem in Litzman (1986) but resulting formulae for reflected waves in such a simple and transparent form as in (9) and (10) have not been obtained yet. Nevertheless, taking into account the structure of general results derived by Litzman (1986), we may expect that also in this case a 'mathematical' boundary plane would lie above the uppermost atomic layer, the shift vector **d** being of course dependent on the content of the cell.

3. Conclusions

Summarizing, we may assert that the approach to the boundary problem used in the Laue dynamical diffraction theory has been justified by the results we obtained within the framework of Ewald's theory, which being based on the microscopic discrete model of a crystal does not claim to set up any boundary conditions.

This result may be supported by more physical arguments. The differential equation (1) provides, according to the Lorentz theory, a macroscopic description of microscopic interactions in the crystal. If the crystal is sufficiently large, the diffraction becomes a bulk effect being only slightly influenced by the surface. A concluding note is that the problem of the boundary in Laue's theory is similar to that of cyclic boundary conditions (see *e.g.* Born & Huang, 1954; Ledermann, 1944; Litzman, 1975).

APPENDIX *A*

Here, we mention the differences between the mathematical treatment used by Ewald and by us.

Equation (7) is analogous to that for forced vibrations of a system of electromagnetically coupled oscillators in Ewald's papers. As to his method of the solution of (7), let us recall Ewald's own words (Ewald, 1916*b*): '*Es erscheine wenig aussichtsreich, wollte man versuchen, metodisch das System von Bewegunsgleichungen für alle Dipole, anfangend mit denen des Randes, aufzustellen und zu lösen. Denn die auf der rechten Seite dieser Gleichung erscheinenden Kräfte hängen selbst von sämtlichen Dipolschwingungen ab, und zwar in verwickelter Art, so dass die Berechnung der Kräfte ohne vorherige Kenntnis der Dipolschwingungen gar nicht möglich ist. Eine andere Methode der Lösung besteht in einem geschickten Ansatz der Dipolschwingungen. Wir können dann die elektrischen Kräfte summieren und uns überzeugen, ob die dynamischen Bedingungen für die Schwingunsweize des Ansatzes erfüllt sind.*'

Thus, Ewald started by finding the field inside an unbounded crystal. Next, using formal manipulations he showed that a half-crystal produces (i) the same interior field as in the unbounded crystal, and (ii) two additional sets of fields composed of waves travelling with the velocity of light in vacuum. Waves of one set move away from the crystal and correspond to the reflected field. Waves of the other set propagate into the crystal. These waves and the incident wave penetrating into the crystal are made to cancel throughout the crystal. The vibration of the crystal is then superposition of dynamically possible proper modes with no alien fields destroying the self-consistency. The result is that the amplitudes of the diffracted rays are fully determined in terms of the amplitude of the incident wave.

On the other hand, we solve immediately the system of equations (7). Thus we obtain (i) the dispersion relation for the z components of wavevectors of refracted waves, and (ii) the inhomogeneous system of linear algebraic equations for the amplitudes of the atomic vibrations generated by the incident wave (4) impinging upon the crystal from the vacuum. The reflected field is found straightforwardly by inserting the solution of (7) into (6). Moreover, if we know the solution of the equations of motion (7) the field inside the crystal may also be evaluated (Dub, 1984). Let us emphasize that both reflected and refracted fields as well as the extinction theorem have been derived in Litzman & Rózsa (1977), Litzman (1978, 1986) and Dub (1984) by a purely algebraic way from the basic equations without any further assumptions.

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