Comments on the Dynamical Theory of X-Ray Diffraction in Crystals

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Von Laue reformulated Ewald's dynamical theory of X-ray diffraction in crystals by solving Maxwell's equations for an electric susceptibility which has the periodicity of the crystals lattice. Absorption was in the original paper not included. Kohler showed that in this case the electric susceptibility is directly proportional to the electron charge density within the crystal.

Von Laue assumed that the divergence of the electric field vector $\boldsymbol{E}$ is equal to the electron charge density which is excited by the electromagnetic field, and this is in accordance with Lorentz' classical electron theory. Under this assumption $\boldsymbol{E}$ is in contrast to $\boldsymbol{D}$ not a transverse wave. This is the reason that von Laue derived the fundamental equations in terms of $\boldsymbol{D}$, and in order to obtain a simple wave equation he used the approximation $4\pi \boldsymbol{P} = \chi \boldsymbol{D}$. Here $\boldsymbol{P}$ is the vector of the electric polarization and χ is 4π times the electric susceptibility. This approximation is well justified, and von Laue's formulation is used in most publication on this subject.

However some authors derived the fundamental equations in terms of $\boldsymbol{E}$ using the correct relation $4\pi \boldsymbol{P} = \chi \boldsymbol{E}$. In most publications they assumed that the longitudinal component of the vector $\boldsymbol{E}$ is small and neglected it. This point and the comparison with von Laue's formulation was discussed by Miyake and Ohtsuki. We show here that the divergence of $\boldsymbol{E}$ can be put zero if inelastic processes are excluded. This follows from Kohler's and Molière's papers on the wave mechanical foundation of the dynamical theory of X-ray diffraction. However if higher perturbation terms are taken into account then the divergence of $\boldsymbol{E}$ differs from zero.

In multiple beam cases the fundamental equations are much simpler if they are expressed in terms of $\boldsymbol{E}$. In the region of anomalous dispersion, and here in particular in the region where the X-ray energy is close and above and crystal absorption edge, the wave equations should be expressed in terms of the electric field vector $\boldsymbol{E}$.

Introduction

Ewald completed his famous doctoral thesis on crystal optics in 1912. Subsequently he published the first of a series of papers on this topic [1]. He had solved a unique many body problem by calculating the total interaction of an electromagnetic field with an infinite three-dimensional array of electric dipoles representing a crystal structure. His early papers dealt with the dispersion theory, the reflection and refraction of light waves in anisotropic crystals. After the discovery of X-ray diffraction by von Laue, Friedrich and Knipping [2], Ewald [3] discussed his original results for shorter wave lengths than light, namely X-rays. He thereby developed his form on the dynamical theory of X-ray diffraction in perfect crystals. He made significant theoretical predictions which were later confirmed experimentally when perfect single crystals became available. In addition Ewald developed theoretical tools which later were applied in the theory of solid state physics. In order to make Ewald's fundamental and important papers accessible to a wider audience, Juretschke [4] edited recently an English translation of Ewald's papers on the foundations of crystal optics.

Von Laue [5] reformulated Ewald's dynamical theory of X-ray diffraction. In this paper von Laue neglected inelastic processes, but adopted otherwise concepts which had been developed in quantum theory. He therefore solved Maxwell's equations for a periodic electric susceptibility which, as Kohler [6] showed by means of a semiclassical quantum mechanical radiation theory, is directly proportional to the electron charge density within the crystal. Therefore the electric susceptibility for X-rays has the periodicity of the crystal lattice. Von Laue used vectorial Bloch waves for the solution of the appropriate electromagnetic wave equation and derived straight forward the fundamental equations of the dynamical theory and subsequently dispersion equations. However he used for the discussion of the dispersion equations the elegant concepts which were already introduced by

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Ewald. Von Laue's presentation of the dynamical theory is relatively easy to follow and therefore used in most publications on dynamical X-ray scattering in crystals. Molière [7] developed the dynamical theory for the region of anomalous dispersion using an appropriate extension of Kohler's calculations.

Formulations of the Dynamical Theory of X-Ray Diffraction

Von Laue formulated the wave equation for the elastic interaction of X-rays in terms of the vector of the electric displacement **D**. He did this because the divergence of the vector **D** is zero and hence **D** is a transverse wave. In order to obtain a simple wave equation in terms of **D** von Laue used the equation

$$4\pi \boldsymbol{P} = \frac{\chi}{1+\chi} \boldsymbol{D} \approx \chi \boldsymbol{D}. \tag{1}$$

Here χ is 4π times the electric susceptibility of the crystal. The correct relation is given by

$$4\pi \boldsymbol{P} = \chi \boldsymbol{E}. \tag{2}$$

However the mean value of χ is for X-rays of the order of -10^{-5} or smaller and therefore the error in Eq. (1) is small*. With the approximation (1) von Laue derived from Maxwell's equations a wave equation which is homogeneous in **D**:

$$\nabla^2 \boldsymbol{D} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\boldsymbol{D} + \nabla \times \nabla \times \chi \boldsymbol{D} = 0. \tag{3}$$

Von Laue expands χ in a Fourier series over the crystal lattice and subsequently **D** in a vectorial Bloch wave and obtains the fundamental equations of the dynamical theory**

$$\frac{K_h^2 - k^2}{K_h^2} \boldsymbol{D}_h - \sum_g \chi_{h-g} \boldsymbol{D}_{g[h]} = 0. \tag{4}$$

Here is K_h^2 the square of the crystal wave number and k^2 the square of the vacuum wave number. $\boldsymbol{D}_h$ and χ_h are coefficients of the Fourier expansions of **D**, and $\boldsymbol{D}_{g[h]}$ is defined by

$$\boldsymbol{D}_{g[h]} = -\frac{1}{k_h^2}(\boldsymbol{K}_h \times \boldsymbol{K}_h \times \boldsymbol{D}_g). \tag{5}$$

Von Laue assumed that

$$\nabla \cdot \boldsymbol{E} = 4\pi \varrho_s, \tag{6}$$

where ϱ_s is a charge density which is excited by the electromagnetic field of the X-rays within the crystal.

Batterman and Cole [14] formulated in a review article on the dynamical theory the wave equation inside the crystal in terms of the electric vector **E**. A comparison between their and von Laue's formulations is due to Miyake and Ohtsuki [15]. They assumed as well that the divergence of the electric field vector **E** is not zero and that therefore the electric field vector is not a transverse wave. However they simplified the fundamental equations by assuming that the longitudinal component of this electric field vector is very small and they therefore neglected it. They then obtained a set of simple fundamental equations ([15] page 104, Eq. (9)):

$$\frac{K_h^2 - k^2}{k^2} \boldsymbol{E}_h - \sum_g \chi_{h-g} \boldsymbol{E}_g = 0. \tag{7}$$

The wave numbers have been written in von Laue's notation, i.e. k is the vacuum wave number and $\boldsymbol{K}_h$ is a wave vector in the crystal. We now shall show that for pure elastic scattering the longitudinal component of **E** is zero.

The Longitudinal Component of the Electric Field Vector

Kohler [6] calculated the electric susceptibility χ by means of a semi-empirical quantum theory and used the following form of Maxwell's equations:

$$\nabla \times \boldsymbol{H} = \frac{1}{c}\dot{\boldsymbol{E}} + \frac{4\pi}{c}\boldsymbol{J}, \tag{8}$$

$$\nabla \times \boldsymbol{E} = -\frac{1}{c}\dot{\boldsymbol{H}}, \tag{9}$$

$$\nabla \cdot (\dot{\boldsymbol{E}} + 4\pi \boldsymbol{J}) = 0. \tag{10}$$

Here **J** is the electron current density which is induced within the crystal by the electromagnetic field of the X-rays within the crystal. Kohler calculated **J** from quantum mechanics and assumed $\nabla \cdot \boldsymbol{A} \neq 0$, as did von Laue. This statement is in accordance with electrodynamics but not with quantum mechanics if we assume that there are no inelastic interactions of the X-rays within the crystal, i.e. the crystal remains in the ground state. This will be shown now. The stationary

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* For a detailed discussion we refer to von Laue's textbooks [8], [9], and detailed monographs by other authors for instance [10] to [13] who all use basically the same approach as given by von Laue.

** See for instance von Laue [9] Eqs. (26.32), page 310.

solutions of the unperturbed Schrödinger equation are

$$\Phi_n(\boldsymbol{r},t)=\varphi_n(\boldsymbol{r})\exp\left\{i\frac{E_n t}{\hbar}\right\}. \tag{11}$$

We include the electromagnetic field into the Schrödinger equation by means of the vector $\boldsymbol{A}$. The Schrödinger equation then becomes time dependent:

$$\frac{1}{2m}\left(\frac{\hbar}{i}\boldsymbol{V}+\frac{e}{c}\boldsymbol{A}\right)^2+V\psi=-\frac{\hbar}{i}\frac{\partial}{\partial t}\psi. \tag{12}$$

If one multiplies this equation from the left hand side with ψ^* and the conjugate complex equation with ψ and subtracts the two equations, then one obtains

$$\boldsymbol{V}\cdot\left[-\frac{e^2}{mc}\boldsymbol{A}\,\psi^*\psi+\frac{e\hbar}{2mi}(\psi^*\boldsymbol{V}\psi-\psi\boldsymbol{V}\psi^*)\right]=-\frac{\partial}{\partial t}\psi^*\psi. \tag{13}$$

Here

$$-e\psi^*\psi=\varrho_{\mathrm{e}} \tag{14}$$

is the electron charge density. A comparison with the classical continuity equation for electrodynamics

$$\boldsymbol{V}\cdot\boldsymbol{J}=\frac{\partial}{\partial t}\varrho_{\mathrm{e}} \tag{15}$$

leads to the following equation for the electron current density:

$$\boldsymbol{J}=-\frac{e^2}{mc}\boldsymbol{A}\,\psi^*\psi+\frac{e\hbar}{2mi}(\psi^*\boldsymbol{V}\psi-\psi\boldsymbol{V}\psi^*). \tag{16}$$

Kohler derives by means of Dirac's time dependent perturbation theory the following solution for (12):

$$\psi_n(\boldsymbol{r},t)=\Phi_n+\frac{e\hbar}{\varrho\pi m\nu}\cdot\sum_{n'}\left[\frac{\exp\left\{i\frac{(E_n+2\pi h\nu)t}{\hbar}\right\}-\exp\left\{i\frac{E_{n'}t}{\hbar}\right\}}{E_n-E_{n'}+h\nu}B_{n'n}-\frac{\exp\left\{i\frac{(E_n-2\pi h\nu)t}{\hbar}\right\}-\exp\left\{i\frac{E_{n'}t}{\hbar}\right\}}{E_n-E_{n'}+h\nu}B^*_{nn'}\right]\Phi_n \tag{17}$$

with

$$B_{n'n}=\sum_s\int\varphi^*_{n'}(\boldsymbol{r}')\boldsymbol{V}_{\mathrm{s}}\hat{\boldsymbol{A}}_{\mathrm{s}}\varphi_n(\boldsymbol{r})\,\mathrm{d}\tau'. \tag{18}$$

The summation is carried out over all electrons. $\hat{\boldsymbol{A}}_{\mathrm{s}}$ is a unit vector in the direction of $\boldsymbol{A}$ which is parallel to the electric field vector. If we now ignore, as von Laue did in his early paper [5], all inelastic processes, then (16) for the electron current density contains only the first term, and if we assume further that the electrons within the crystal are and remain in the ground state, then one can disregard in (17) the second term. The equation for the current density takes now the form *

$$\boldsymbol{J}=-\frac{e^2}{mc}\boldsymbol{A}\,\Phi_0^*\Phi_0=-\frac{e^2}{mc}\boldsymbol{A}\,\varphi_0^*\varphi_0. \tag{19}$$

Here

$$-e\varphi_0^*\varphi_0=\varrho \tag{20}$$

is the electron charge density of the crystal for the ground state which is time independent. A comparison with the continuity Eq. (15) leads therefore to the result

$$\boldsymbol{V}\cdot\boldsymbol{J}=0. \tag{21}$$

Since $\boldsymbol{J}=2\pi\nu\boldsymbol{P}$, it follows that the divergence of $\boldsymbol{P}$ is zero, and because the divergence of $\boldsymbol{D}$ is zero it follows from the equation $\boldsymbol{D}=\boldsymbol{E}+4\pi\boldsymbol{P}$ that the divergence of $\boldsymbol{E}$ becomes zero too. This point has been apparently overlooked. However this holds correctly only for pure elastic scattering. We conclude that it is convenient to express the fundamental equations of the dynamical theory of X-ray diffraction in terms of the electric field vector $\boldsymbol{E}$. The Eq. (8) are in this case correct.

The fundamental equations by von Laue (see for instance [9]) are only approximately valid if the approximation in (1) is applied. This, however, does not effect the calculations for the two beam case. Miyake and Ohtsuki [15] pointed out correctly that in the two-beam case Batterman and Cole's equations and the equations by von Laue lead to the same result. This is due to the fact that von Laue replaces in the denominator of the resonance terms (equations (4)) the square of the crystal wave numbers by the square of the vacuum wave number k.

Many Beam Cases

Cases where more then one reflection is excited by the X-rays within a crystal are more cumbersome to

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* This equation is already discussed by G. Molière [7] (see page 276). It assumes here that the second term in (17) can be neglected, and that is exactly what Kohler [6] does in his publication.

handle in the dynamical theory of X-ray diffraction, relatively to electron or neutron diffraction. This is due to fact that one deals in the last two cases with scalar wave equations, whereas in X-ray diffraction one deals with vector waves. A general discussion of many beam cases in Laue's theory was carried out at a very early stage by Lamla [16]. Since then many papers on multiple beam reflection have been published in particular in recent years. In many cases von Laue's notations have been applied. The fundamental equations are then somewhat cumbersome. We only want to indicate this for the case where two reflections are excited simultaneously (three-beam case). Let us assume the two reflections have the reciprocal lattice points g and h. The fundamental equations are then in von Laue's notation

$$\begin{aligned}
&[K_0^2(1-\chi_0)-k^2]\boldsymbol{D}_0-\chi_{-g}[K_0^2\boldsymbol{D}_g-(\boldsymbol{K}_0\cdot\boldsymbol{D}_g)\boldsymbol{K}_0]\\
&\quad-\chi_{-h}[K_0^2\boldsymbol{D}_h-(\boldsymbol{K}_0\cdot\boldsymbol{D}_h)\boldsymbol{K}_0]=0,\\
&-\chi_g[K_g^2\boldsymbol{D}_0-(\boldsymbol{K}_g\cdot\boldsymbol{D}_0)\boldsymbol{K}_g]+[K_g^2(1-\chi_0)-k^2]\boldsymbol{D}_g\\
&\quad-\chi_{g-h}[K_g^2\boldsymbol{D}_h-(\boldsymbol{K}_g\cdot\boldsymbol{D}_h)\boldsymbol{K}_g]=0,\\
&-\chi_h[K_h^2\boldsymbol{D}_0-(\boldsymbol{K}_h\cdot\boldsymbol{D}_0)\boldsymbol{K}_h]-\chi_{h-g}[K_h^2\boldsymbol{D}_g\\
&\quad-(\boldsymbol{K}_h\cdot\boldsymbol{D}_g)\boldsymbol{K}_h]+[K_h^2(1-\chi_0)-k^2]\boldsymbol{D}_h=0.
\end{aligned}\tag{22}$$

The corresponding equations in terms of $\boldsymbol{E}$ are (see (8))

$$\begin{aligned}
&[K_0^2-k^2(1+\chi_0)]\boldsymbol{E}_0-k^2\chi_{-g}\boldsymbol{E}_g-k^2\chi_{-h}\boldsymbol{E}_h=0,\\
&-k^2\chi_g\boldsymbol{E}_0+[K_g^2-k^2(1+\chi_0)]\boldsymbol{E}_g-k^2\chi_{g-h}\boldsymbol{E}_h=0,\\
&-k^2\chi_h\boldsymbol{E}_0-k^2\chi_{h-g}\boldsymbol{E}_g+[K_h^2-k^2(1+\chi_0)]\boldsymbol{E}_h=0.
\end{aligned}\tag{23}$$

As already pointed out, these equations are correct for pure elastic scattering. However if the region of anomalous dispersion (e.g. absorption) is included, then the electric field vectors $\boldsymbol{E}$ have an longitudinal component and the fundamental equations take the following form [17]

$$\begin{aligned}
&[K_0^2-k^2(1+\chi_0)]\boldsymbol{E}_0-\boldsymbol{K}_0(\boldsymbol{K}_0\cdot\boldsymbol{E}_0)-k^2\chi_{-g}\boldsymbol{E}_g\\
&\quad-k^2\chi_{-h}\boldsymbol{E}_h=0,\\
&-k^2\chi_g\boldsymbol{E}_0+[K_g^2-k^2(1+\chi_0)]\boldsymbol{E}_g-\boldsymbol{K}_g(\boldsymbol{K}_g\cdot\boldsymbol{E}_g)\\
&\quad-k^2\chi_{g-h}\boldsymbol{E}_h=0,\\
&-k^2\chi_h\boldsymbol{E}_0-k^2\chi_{h-g}\boldsymbol{E}_g+[K_h^2-k^2(1+\chi_0)]\boldsymbol{E}_h\\
&\quad-\boldsymbol{K}_h(\boldsymbol{K}_h\cdot\boldsymbol{E}_h)=0.
\end{aligned}\tag{24}$$

The notation in (24) assumes that the Fourier coefficients χ_g can be written in the form of scalar complex quantities [18].

Molière [7] discussed the dynamical theory for the region of strong anomalous coefficients of the electric susceptibility become tensors of second rank. Molière [7] replaces in his paper in equation (2.98) the Fourier components of $\boldsymbol{E}$ by the Fourier components of the field vector $\boldsymbol{D}$ (2.10). The reason for this approximation is that the divergence of $\boldsymbol{D}$ is zero. However this leads in our opinion to inconsistencies which will be discussed in a separate paper. Molière discusses in his publication the formal structure of the theory without any detailed calculations. Ohtsuki discussed the temperature dependence of the X-ray absorption [19]. He however expresses correctly the fundamental equations in terms of the electric field vector $\boldsymbol{E}$, and this agrees with a quantum field theoretical discussion of the dynamical theory by Ohtsuki and Yanagawa [20]. We conclude that in our opinion a formulation of the fundamental equations of the dynamical theory of X-ray diffraction in terms of the electric field vector can be justified and simplifies the theory.

The discussion in this paper could be useful in a scalar formulation of the N-beam X-ray scattering [21].

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