Solution of the Phase Problem in the Theory of Structure Determination of Crystals from X-Ray Diffraction Experiments

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We present a solution to a long-standing basic problem encountered in the theory of structure determination of crystalline media from x-ray diffraction experiments; namely, the problem of determining phases of the diffracted beams.

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In a well-known paper published almost 100 years ago, Laue laid the foundation for a method for determining the structure of crystalline media from x-ray diffraction experiment [1]. Since then the method has become of basic importance in solid state physics (see, for example, [2,3]) and in other fields, sometimes using neutrons or electrons rather than x rays. However, as is well known, the method suffers from a serious limitation due to the inability to measure phases of the diffracted beams.

In this Letter we show how the phases may be determined. Before doing so we point out that ''the phase problem,'' as usually formulated, has no solution and is, in fact, rather meaningless. We will reformulate it and show that the reformulated problem has a solution which allows unambiguous determination of the crystal structure to be made [4].

We begin with the following observation: In usual treatments, the incident x-ray beam is assumed to be monochromatic. That is an idealization, because monochromatic beams are not realizable. Any beam which can be produced in a laboratory is, at best, quasimonochromatic; i.e., its spectral width $\Delta\omega$ is much smaller than its mean frequency $\bar{\omega}$. Both the amplitudes and the phases of the field oscillations are random variables and, hence, even if they could be measured, they would not provide the required information

The measurable and physically meaningful quantities are the (averaged) intensities and, more generally, certain correlation functions, well known in coherence theory of light ([5], Sec. 10.3; [6], Secs 3.1 and 4.1). In this Letter we show that the measurable correlation functions of an x-ray beam contain information about both the amplitudes and the phases which are needed to determine the crystalline structure, provided that the beams are spatially coherent—a concept which is not equivalent to monochromaticity [7], as is frequently incorrectly assumed. Spatially coherent beams are routinely generated at optical wavelengths and have been produced in recent years in the x-ray region of the electromagnetic spectrum ([8], Chap. 8; [9]).

To obtain the required solution we begin with the so-called mutual coherence function of a fluctuating field $V(\mathbf{r}, t)$ at a point P, specified by position vector $\mathbf{r}$, at time t. It is defined by the expression

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2, \tau) = \langle V^*(\mathbf{r}_1, t)V(\mathbf{r}_2, t+\tau)\rangle, \tag{1}$$

where the angular brackets denote the ensemble average. We assume that the field is statistically stationary, at least in the wide sense ([6], p. 24). The Fourier transform of Γ

$$W(\mathbf{r}_1, \mathbf{r}_2, \omega) = \int_{-\infty}^{\infty} \Gamma(\mathbf{r}_1, \mathbf{r}_2, \tau)e^{i\omega\tau}d\tau \tag{2}$$

is known as the cross-spectral density function of the field. It can be shown that it is also a correlation function. More specifically one can show ([6], Sec. 4.1; [10], Sec. 4.7.2) that there exists an ensemble of frequency-dependent fields $U(\mathbf{r}, \omega)$ such that

$$W(\mathbf{r}_1, \mathbf{r}_2, \omega) = \langle U^*(\mathbf{r}_1, \omega)U(\mathbf{r}_2, \omega)\rangle_\omega, \tag{3}$$

where the angular brackets on the right-hand side, with the subscript ω, indicate that the average is taken over the ensemble $\{U(\mathbf{r}, \omega)\}$. The quantity

$$W(\mathbf{r}, \mathbf{r}, \omega) = I(\mathbf{r}, \omega) \tag{4}$$

represents the averaged intensity at frequency ω of the field, at the point $P(\mathbf{r})$, and

$$\mu(\mathbf{r}_1, \mathbf{r}_2, \omega) = \frac{W(\mathbf{r}_1, \mathbf{r}_2, \omega)}{\sqrt{W(\mathbf{r}_1, \mathbf{r}_1, \omega)W(\mathbf{r}_2, \mathbf{r}_2, \omega)}} \tag{5}$$

is known as the spectral degree of coherence of the field fluctuations at the points $P_1(\mathbf{r}_1)$ and $P_2(\mathbf{r}_2)$. It may be shown that it is bounded by zero and unity in absolute value. The former value, $\mu = 0$, represents complete spatial incoherence; the latter, $|\mu| = 1$, represents complete spatial coherence at frequency ω of the field at the two points. Both the cross-spectral density function and the spectral degree of coherence are measurable quantities, as we will see shortly.

It has been shown ([10], Sec. 4.5.3; [11]) that if the field is spatially completely coherent at frequency ω_0 through-

out a three-dimensional domain D, i.e., if $|\mu(\mathbf{r}_1, \mathbf{r}_2, \omega_0)| = 1$ for all $\mathbf{r}_1 \in D$, $\mathbf{r}_2 \in D$, then the cross-spectral density function of the field at that frequency has necessarily the factorized form

$$W(\mathbf{r}_1, \mathbf{r}_2, \omega_0) = u^*(\mathbf{r}_1, \omega_0)u(\mathbf{r}_2, \omega_0). \quad (6)$$

Moreover, throughout the domain D, $u(\mathbf{r}, \omega_0)$ satisfies the Helmholtz equation

$$(\nabla^2 + k_0^2)u(\mathbf{r}, \omega_0) = 0, \quad (7)$$

where $k_0 = \omega_0/c$, c being the speed of light in vacuum.

If we set

$$u(\mathbf{r}, \omega_0) = |u(\mathbf{r}, \omega_0)|e^{i\phi(\mathbf{r}, \omega_0)}, \quad (8)$$

we readily find from Eqs. (5), (6), and (8) that

$$\mu(\mathbf{r}_1, \mathbf{r}_2, \omega_0) = \exp\{i[\phi(\mathbf{r}_2, \omega_0) - \phi(\mathbf{r}_1, \omega_0)]\}. \quad (9)$$

In view of Eq. (7) the function $u(\mathbf{r}, \omega_0)$ may be identified with the space-dependent part of a monochromatic wave function $v(\mathbf{r}, t) = u(\mathbf{r}, \omega_0)\exp(-i\omega_0 t)$. Thus we have shown that one may associate with any wide-sense statistically stationary field that in some region of space is spatially coherent at frequency ω_0 a monochromatic field $v(\mathbf{r}, t)$ of the same frequency, whose space-dependent part $u(\mathbf{r}, \omega_0)$ yields the (generally complex) cross-spectral density function of the field via Eq. (6). We stress that this monochromatic field is not the actual field (which exhibits random fluctuations), but it is equivalent to it in the sense that both have the same cross-spectral density function $W(\mathbf{r}_1, \mathbf{r}_2, \omega_0)$, whose modulus and phase can be determined by experiment, as we will now show.

Suppose we place an opaque screen A in the path of a beam which is assumed to be quasimonochromatic, with mean frequency ϖ. Suppose further that the opaque screen has small openings at points $Q_1(\mathbf{r}_1)$ and $Q_2(\mathbf{r}_2)$ and we measure the average intensity on a plane B, parallel to A (see Fig. 1); i.e., we perform Young's interference experiment. The average intensity at a point $P(\mathbf{r})$ on the screen B is given by the so-called *spectral intensity law* [[6], p. 65, Eq. (8)], which (in slightly different notation) may be expressed as

$$I(P) = I^{(1)}(P) + I^{(2)}(P) + 2\sqrt{I^{(1)}(P)}\sqrt{I^{(2)}(P)}|\mu(Q_1, Q_2, \varpi)| \times \cos[\beta(Q_1, Q_2, \varpi) - \delta]. \quad (10)$$

Here $I^{(1)}(P)$ denotes the average intensity at the point $P(\mathbf{r})$ of the beam which reaches that point from the pinhole at Q_1 alone (i.e., with the pinhole at Q_2 being closed), $I^{(2)}(P)$ having a similar meaning. Further, $\beta(Q_1, Q_2, \varpi)$ is the phase of the spectral degree of coherence $\mu(Q_1, Q_2, \varpi)$ and $\delta = \bar{k}(R_2 - R_1)$, $(\bar{k} = \varpi/c)$ is the phase difference associated with the distances from the two pinholes to the point $P(\mathbf{r})$ as shown in Fig. 1. As δ varies, the intensity $I(P)$ traces out a sinusoidal interference pattern. The visibility of the interference fringes, which is a measure of their sharpness, can readily be shown to be proportional to $|\mu|$, and the location of the intensity maxima is proportional to $\arg\mu$ ([5], p. 570).

It is clear that from measurement of the average intensities $I(P)$, $I^{(1)}(P)$, and $I^{(2)}(P)$ for several values of δ, one can determine, by the use of Eq. (10), both the amplitude $|\mu|$ and the phase $\beta = \arg\mu$ of the spectral degree of coherence. Measurements of this kind are routinely made with light [12] (see also [13]) and can also be made with x rays, as is evident from the discussions of interference experiments described, for example, in Refs. [8,9].

From the preceding discussion it is clear that a realistic procedure of interpreting results of x-ray diffraction experiments for determining structure of solids is not by means of fictitious monochromatic waves (beams), but rather by means of the space-dependent part $u(\mathbf{r}, \omega_0)$ of the wave function $v(\mathbf{r}, t)$, determined from correlation measurements. It is clear that our analysis introduces a procedure that overcomes the long-standing difficulties relating to measuring phases of diffracted beams in structure determination of crystals.

Finally we mention that the possibility of measuring the phase of the space-dependent part $u(\mathbf{r})$ of the "equivalent" monochromatic wave function of spatially coherent light was discussed not long ago [14] and has been verified experimentally [15].

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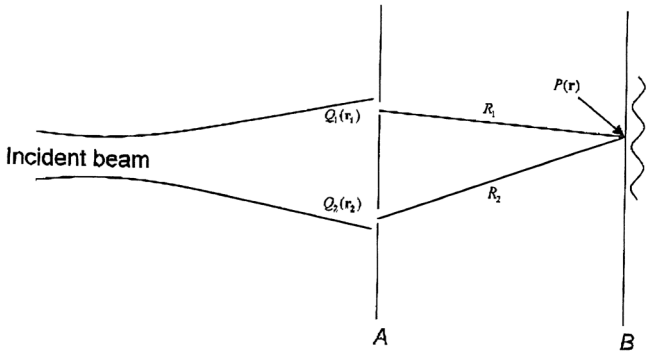

FIG. 1. Illustrating notation relating to Young's interference experiment.

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