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1940 Proc. Phys. Soc. 52 167

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X-RAY DIFFRACTION BY FINITE AND IMPERFECT CRYSTAL LATTICES

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ABSTRACT. The Fourier transform of a crystal is a representation which, if fully known, would be equivalent to, and give the same information as, the usual description of a crystal. At the same time the Fourier transform is very closely related to the diffraction properties and it offers the best survey of the diffraction data obtained, and of those missing, for a discussion of crystal shape and of crystal imperfection. The desirability of an exact quantitative x-ray study of the perfection of an individual metal single crystal before and during plastic deformation is urged.

§ 1. FOURIER TRANSFORM AND DIFFRACTED AMPLITUDE

FOR discussing x-ray diffraction the reciprocal lattice has found general application, but it is not generally realized that the reciprocal lattice is only an incomplete representation of the Fourier transform of the crystal and that much clearness of discussion can be gained by making full use of the conception of the Fourier transform.

If the diffracting body is characterized by the density-distribution of scattering matter $\rho(\mathbf{x})$, the Fourier transform of ρ is the function $F(\mathbf{b})$ in the Fourier integral representation

$$\rho(\mathbf{x}) = \int F(\mathbf{b}) e^{2\pi i(\mathbf{b}\mathbf{x})} dv_b; \quad F(\mathbf{b}) = \int \rho(\mathbf{x}) e^{-2\pi i(\mathbf{b}\mathbf{x})} dv_x. \quad \dots(1)$$

Here \mathbf{b} is the coordinate vector in Fourier space and dv_b its element of volume. $(\mathbf{b}\mathbf{x})$ is the scalar product of the two vectors and since this must be a pure number, in order to make sense in the exponent, \mathbf{b} must have the dimension of the reciprocal of a length, since \mathbf{x} is a length in physical space. Both integrals are to be extended over the whole of their space.

To connect $F(\mathbf{b})$ with diffraction by the crystal, imagine that a plane monochromatic x-ray wave of wave vector \mathbf{k}_1 ($|\mathbf{k}_1| = 1/\lambda$) falls on an element dv_x of the body situated at \mathbf{x} . Suppose that we observe at great distance the wave scattered classically in an arbitrary direction, thus of wave vector \mathbf{k} , where $|\mathbf{k}| = |\mathbf{k}_1|$. Omitting the factor E/r , where E is the amplitude of the incident wave and r the distance of the observer from the crystal, the diffracted wave will have the amplitude $\rho(\mathbf{x}) dv_x e^{2\pi i(\mathbf{k}_1 - \mathbf{k}, \mathbf{x})}$. Putting $\mathbf{k} - \mathbf{k}_1 = \mathbf{b}$ (the dimension of \mathbf{b} is $1/\lambda$), the total amplitude obtained from the body is

$$F(\mathbf{b}) = \int \rho(\mathbf{x}) e^{-2\pi i(\mathbf{b}\mathbf{x})} dv_x. \quad \dots(2)$$

For a given direction of incidence \mathbf{k}_1 , the vector \mathbf{b} connects the origin O of the Fourier space with any point on the sphere of reflection drawn through O with A

as centre, where $OA = -\mathbf{k}_1$. If we intercept all diffracted waves \mathbf{k} proceeding from a given point of propagation A , we obtain a spherical section of the Fourier transform. By observing the effects of a monochromatic wave at all directions of incidence and of diffraction, we can at best explore the region of the Fourier transform of $\rho(\mathbf{x})$ that is included in a sphere of radius $2/\lambda$ surrounding the origin. This is a re-statement of the fact that the resolving power of a radiation of wave-length λ is finite. The more details we wish to obtain concerning $\rho(\mathbf{x})$, the shorter must be the wave-length employed for diffraction. The non-classical Compton scattering, however, sets a limit to the applicability of short wave-length diffraction.

From the quite general formulae (1) we see that the Fourier transform is an equivalent way of representing the crystal, and that it has the advantage of giving nearly all properties of the crystal in a form ready for physical application.† The symmetry of equation (1) with regard to $\rho(\mathbf{x})$ and $F(\mathbf{b})$ furthermore shows that for every result obtained by interpreting $\rho(\mathbf{x})$ as the density in crystal space and $F(\mathbf{b})$ as the diffracted amplitude, a corresponding result may be obtained by interchanging the interpretation of the two spaces and functions.

§ 2. THE PEAK FUNCTIONS AND THE OPERATION OF FOLDING

In order to establish the correspondence for a number of examples, it is convenient to introduce two conceptions. The first is that of a *peak function* of content m , i.e. a function which is zero everywhere except at one point $\mathbf{x} = \mathbf{p}$, where it is infinite to such an order that its integrated value is m . We write this function $Z_p^m(\mathbf{x})$; it may be obtained⁽¹⁾ from a Gaussian distribution

$$G_p^m(\mathbf{x}) = \frac{m}{(\pi\alpha^2)^{\frac{3}{2}}} e^{-(\mathbf{x}-\mathbf{p})^2/\alpha^2}, \quad \dots\dots(3)$$

by passing to the limit $\alpha \rightarrow 0$, or from other suitable functions by a similar process. If we introduce a peak function at every lattice point \mathbf{x}_i , we obtain a lattice peak function \mathbf{z}^m . This will be the distribution $\rho(\mathbf{x})$ for a simple lattice of point-like atoms of mass m .

The second convenient conception is that of *folding two functions*, e.g. $\rho(\mathbf{x})$ and $\sigma(\mathbf{x})$. Designating by $\widehat{\rho\sigma}$ (*rho fold sigma*) the result of folding the *fold*, we define

$$\widehat{\rho\sigma}(\mathbf{y}) = \int \rho(\mathbf{x}) \sigma(\mathbf{y} - \mathbf{x}) d\mathbf{x}, \quad \dots\dots(4)$$

the integration to extend over all space.

From the theory of Fourier transforms it is known that multiplying and folding are corresponding operations in the two spaces, i.e. folding ρ and σ in crystal space leads to a transform obtained by multiplying the transforms of ρ and σ in Fourier space and vice versa⁽²⁾.

† No discussion will be given in this paper of the difficulties arising from the fact that, by observing intensities, the absolute values $|F(\mathbf{b})|$ only can be obtained. These difficulties are present also in the study of lattices without imperfections; the Patterson diagram is the direct unamplified presentation of the experimental results (cf. W. L. Bragg, *Nature*, **143**, 73, (1939)). In this paper we shall only deal with ordinary Fourier transforms based on $F(\mathbf{b})$, not on $|F(\mathbf{b})|$.

Let us fold a function $\rho(\mathbf{x})$ into a lattice peak function $\sigma = Z^1$. Since $Z^1(\mathbf{y} - \mathbf{x})$ is zero unless $\mathbf{y} - \mathbf{x} = \mathbf{x}_i$ is a lattice vector, the fold thus reduces to

$$\widehat{\rho Z^1}(\mathbf{y}) = \sum_i \rho(\mathbf{y} - \mathbf{x}_i); \quad \dots\dots(5)$$

that is, by folding with a lattice peak function, $\rho(\mathbf{x})$ is repeated from each lattice point \mathbf{x}_i , and, as far as overlapping occurs, the sum is to be taken.

§ 3. STRUCTURE FACTORS

Let us take ρ to be the density due to a single atom or a molecule. The transform of ρ then is the *atomic* or *molecular structure factor* $f(\mathbf{b})$. The transform of a crystal lattice peak function $Z^1(\mathbf{x})$ is the ordinary reciprocal lattice, i.e. a lattice peak function $Z^{1/v_a}(\mathbf{b})$ in Fourier space, giving peaks of content $1/v_a$ at the lattice points \mathbf{b}_n . By folding the molecular density distribution into $Z^1(\mathbf{x})$, we obtain the *crystal with extended basis*. On the other hand, the transform will be found by multiplying $Z^{1/v_a}(\mathbf{b})$ into $f(\mathbf{b})$, i.e. the transform is a peak function having peaks of content $\frac{1}{v_a} f(\mathbf{b}_n)$ at the lattice points \mathbf{b}_n .

For the study of molecular constitution it is really the molecular structure factor or Fourier transform of the molecule that one tries to extract from x-ray† or electron-diffraction⁽⁴⁾ measurements, i.e. one tries to obtain the whole function $f(\mathbf{b})$ from the evidence concerning the values $f(\mathbf{b}_n)$ at the lattice points.

§ 4. THE UNBOUNDED AND THE BOUNDED CRYSTAL

(1) Any perfectly periodic distribution $\rho(\mathbf{x})$ has a lattice peak function as Fourier transform. The fact that $F(\mathbf{b})$ is zero except for the values $\mathbf{b} = \mathbf{b}_n$ implies infinitely high resolving power. A diffracted beam exists only when the sphere of reflection actually passes through a point of the reciprocal lattice. A perfectly periodic distribution is, of course, infinite and unbounded.

(2) Let us call a *regular crystal* a finite part of the perfectly periodic crystal cut out by a closed boundary, without allowing any re-arrangement of the atoms to take place. Mathematically, the density-distribution $\rho_s(\mathbf{x})$ of the finite crystal is obtained by multiplying the distribution $\rho_\infty(\mathbf{x})$ of the perfectly periodic crystal into a *shape function* $s(\mathbf{x})$, which is defined as having value 1 inside and 0 outside the boundary of the finite crystal:

$$\rho_s(\mathbf{x}) = \rho_\infty(\mathbf{x}) s(\mathbf{x}).$$

The Fourier transform $S(\mathbf{b})$ of the shape function can be interpreted as the diffraction effect of a continuum, of scattering density 1, having the same shape as the crystal. For a prismatic shape function (depending on two coordinates only) the transform will be a two-dimensional function similar to the familiar amplitude-curve of diffraction produced by a light wave behind a diaphragm having the form of the cross-section of the prism.

† The idea of using the structure factor or transform of a single molecule seems to have been first formulated by A. Hettich⁽³⁾.

The transform of ρ_s is obtained by folding the shape transform into the lattice peak function, representing the transform of ρ_∞ . The result will be a function consisting of a repetition of the shape transform round each lattice point \mathbf{b}_n . If the regular crystal contains a great number of atoms in all directions, the diffraction effect of the shape will extend only over a small angular range, i.e. it will be narrow as compared to the angular separation of the diffracted beams of different orders, owing to the atomic distances in the crystal. The shape transform does not therefore extend far into the cell of the reciprocal lattice, and practically no overlapping of the shape transforms occurs in consequence of the folding operation (figure 1).

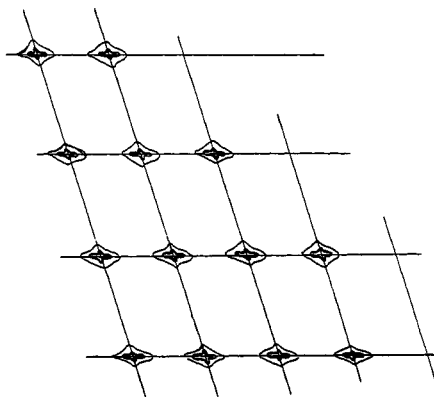


Figure 1. Schematic drawing of Fourier space with the reciprocal lattice of the perfectly periodic crystal and the shape transform surrounding each lattice point.

The shape transform may be regarded as a representation of the resolving power of the crystal due to its finite size and particular shape. If the sphere of reflection passes through sufficiently large values of the shape transform, a diffraction effect will be observed even if the conditions of reflection are not fulfilled for the unlimited lattice.

§ 5. EXAMPLES OF SHAPE TRANSFORMS

Special cases of shape transform are: (a) *The crystal flake*. Along the normal to the flake the distribution of the shape transform is the same as that of the diffracted amplitude behind a slit of the same width as the flake, i.e. it is of the form $x^{-1} \sin x$. As a rough approximation the transform can be represented by a little rod normal to the flake, of length $1/Nd$, where N is the number of net planes of spacing d which the flake contains. The length of the rod is thus $1/N$ of the spacing of the points of the reciprocal lattice in the direction normal to the flake. A closer representation should take account of the varying value of the shape transform along the axis of the rod, and of the fact that, for flakes only a few atomic layers thick, the secondary maxima of the shape transforms overlap midway between the nodal points of the reciprocal lattice, so that the transform may reach appreciable values there.

The need for replacing the points of the reciprocal lattice by little rods was first encountered by Kirchner⁽⁵⁾ in his discussion of electron diffraction. In metals the x-ray work of Preston⁽⁶⁾ on AlCu and of Bradley⁽⁷⁾ on FeNiCu has led to the same construction. Guinier⁽⁸⁾, in a recent thesis remarkable for the experimental method which it discloses, has investigated the shape factor of the segregated particles in the AlCu system by studying the diffraction in the neighbourhood of the primary monochromatized ray. If the schematic reciprocal lattice shown in figure 1 were correct, there would be no advantage in studying the surroundings of (000) rather than those of any (*hkl*). It should not, however, be overlooked that the atomic structure factor has to be multiplied by the distribution shown in figure 1, and that the intensity of the effect is very much greater near (000) than near any other point.

(b) If the crystal is *rod-shaped or needle-shaped*, the shape transform is flat and flake-like. In the plane normal to the axis of the needle the central maximum will be surrounded by secondary maxima of decreasing intensity.

(c) The shape transforms of a *sphere* and of a *cylinder* are expressible by Bessel functions, as is well known from diffraction optics. If the particles are very small, the secondary maxima belonging to adjacent lattice points of the reciprocal lattice can overlap midway between the points, and this means that for some directions the regular inner structure enhances the effect due to the smallness of the spherical particle.

If we interchange the meaning of the two spaces, we see that an abrupt falling off of intensities of higher order is to be expected in crystals the molecules of which have a density-distribution falling off in an oscillating manner after the pattern of a Bessel function. Such a distribution may be approximated to by a spherical-shell structure, and this might give an explanation of the sudden decline of intensities with increasing order which has been claimed for some protein molecules.

(d) Laue⁽⁹⁾ has shown that the shape transform can be easily worked out for *any shape bounded by planes*. A general feature of the transform is that it shows intensity spikes normal to the boundary planes and thus is of a star-like appearance. The familiar diffraction pattern obtained from a rectangular or triangular opening is an example of a shape-star in two dimensions. Laue and Riewe⁽¹⁰⁾ worked out the transform of an octahedron and gave a beautiful interpretation of the electron-diffraction effects observed by Cochran⁽¹¹⁾ and by Brück⁽¹²⁾ on submicroscopic silver crystals. A similar technique would doubtless make it possible to find the form of minute precipitates at the initial stage of segregation in some alloys.

If there are a great many diffracting crystallites, the definiteness with which the shape transform is manifested depends on the equality of shape, size, and orientation of these crystallites. Homogeneity in both respects should be expected in the case of alloys carefully heat-treated. The homogeneity was remarkable in Cochran's case of silver films electrolytically deposited on a rock-salt base.

(e) As a last example of a Fourier transform, let us consider a lattice formed of Gaussian atoms, i.e. atoms with a distribution of scattering-density according to a

Gaussian function⁽³⁾. The transform⁽¹⁾ of a Gaussian of width α is again a Gaussian of width $1/\pi\alpha$:

$$\rho(\mathbf{x}) = \frac{m}{(\pi\alpha^2)^{\frac{3}{2}}} e^{-\mathbf{x}^2/\alpha^2} \rightarrow \text{Trsf } f(\mathbf{b}) = m e^{-\pi^2\alpha^2\mathbf{b}^2}.$$

It follows that if we build up a lattice of Gaussian atoms by folding ρ into a lattice peak function, the transform is given by the coefficients

$$F_n = \frac{1}{v_a} f(b_n) = \frac{m}{v_a} e^{-\pi^2\alpha^2 b_n^2}.$$

This transformation shows the easiest way of taking into account the influence of temperature movement on the diffraction, by replacing the actual instantaneous position of the atoms by an averaged Gaussian distribution of scattering mass. The transform F_n is then the Debye temperature factor. An anisotropy of the atomic temperature oscillations can easily be taken into account by substituting $(x/\alpha)^2 + (y/\beta)^2 + (z/\gamma)^2$ for \mathbf{x}^2/α^2 in $\rho(\mathbf{x})$, i.e. by substituting an ellipsoidal Gaussian for the spherical Gaussian. The transform $f(\mathbf{b})$ is then a reciprocal ellipsoidal Gaussian. In the case of magnesium, cadmium and similar hexagonal metals, this has been Brindley's⁽¹³⁾ procedure to account for the abnormally quick or slow falling away of the intensities of the reflections on the basal plane as compared to the other reflections.

Waller's exact treatment of the influence of heat motion on the diffraction has been discussed in a simplified way by the author⁽¹⁵⁾ by means of the reciprocal lattice, and recently Mauguin and Laval⁽¹⁶⁾ have resumed this study of the Fourier transform from both the theoretical and the experimental sides.

Returning to the simple transform of Gaussians and reversing the significance of the spaces, we obtain a physical interpretation of *Laue's method of discussing the relation between line-width and particle-size*. For this discussion, Laue⁽¹⁷⁾ replaces the true pattern surrounding each lattice point of the reciprocal lattice, i.e. the true shape transform, by a mathematically simple smooth function having the same maximum value and the same width or integral value. The line-width is then obtained by discussing the intersection of these substituted functions with the sphere of reflection. Laue uses two simple functions for the substitution, one being an ellipsoidal Gaussian and the other one an algebraic function:

$$\sigma_1(\mathbf{b}) = e^{-\omega^2(m_1^2 b_1^2 + m_2^2 b_2^2 + m_3^2 b_3^2)}; \quad \sigma_2(\mathbf{b}) = \frac{\text{const.}}{\{1 + \omega^2(m_1^2 b_1^2 + m_2^2 b_2^2 + m_3^2 b_3^2)\}^2}.$$

Both shape transforms do not extend far from the lattice points \mathbf{b}_n . The shape of the crystal corresponding to $\sigma_1(\mathbf{b})$ is an ellipsoidal Gaussian again, with half-width covering a great many cells. The smoothing out of the true shape transform in Laue's discussion is thus equivalent to substituting for the true, sharply bounded, particle an average one in which the masses fall off exponentially with the square of the distance from the centre. The function $\sigma_2(\mathbf{b})$ is the shape transform for a crystal of similar mass distribution, differing only in that the decay of the masses is exponentially proportional to the first power of the distance from the centre.

It is easy to understand that in either way an expression can be given to the average size and shape of the particles but also that these will cease to be appropriate if we have to deal with a distribution around a standard uniform size rather than with one ranging down to zero size.

(f) The shape transform $S(\mathbf{b})$ is always centro-symmetrical in the sense that $S(-\mathbf{b}) = S^*(\mathbf{b})$, where the $*$ denotes the complex conjugate value. This follows from equations (1) for every real function of \mathbf{x} . By the folding operation of $S(\mathbf{b})$ into the lattice peak function, the resulting Fourier transform of the finite regular crystal will be centrosymmetrical about each lattice point. If, therefore, acentric distributions are found experimentally, these cannot be explained by particle-size or crystal-shape. Such is the case in Mr Preston's⁽⁶⁾ beautiful work on aluminium-copper alloys where monochromatic streaks were obtained streaming out from normal reflection spots on one side only. This could be interpreted in the reciprocal lattice by making the lattice points the corner points of little cube-edges directed away from the origin. Any shape effect could only result in replacing the point by a centrosymmetrical set of lines.

§ 6. SOME REMARKS ON THE EXPERIMENTAL STUDY OF SHAPE TRANSFORMS

There are two points I would like to emphasize regarding the study of shape transforms. The first is that the shape transform can be studied equally in any order of diffraction, since it is the same round each point of the reciprocal lattice. In order to obtain a complete survey one has to produce reflections of the same order under varying incidence, so as to obtain a variety of intersections of the shape transform with the sphere of reflection. Evidently data obtained on different orders can also be combined into one picture provided it has been established that the diffuseness of the reciprocal lattice is due to a shape factor. The surroundings of the primary beam (000) have the special advantage of higher intensity due to the atomic factor. It is necessary to use monochromatized rays in order to obtain a clear background near the primary beam. Guinier⁽⁸⁾ has done this without sacrifice of intensity, by using a focusing bent-crystal monochromatizer. The aperture of this must, however, be kept small compared to the angular width of the shape transform for the wave-length employed.

The second point is the desirability of studying the shape transform in single-crystal photographs, after the manner of Preston, Guinier, and others. X-ray micro methods, such as those developed by Kratky⁽¹⁸⁾ to obtain diagrams from regions of a crystal 1/100 mm. wide, should prove of great value in preventing the blurring which is bound to occur as a result of the superposition of shape transforms from crystallites varying in size and orientation.

It would lead us too far to discuss the representation of deformed lattices by the Fourier transform. The methods discussed above allow one, for example, to obtain directly the essential properties of the curves given recently by Kochendörfer⁽¹⁹⁾ for the diffraction on a lattice with a sinusoidal displacement of the

reflecting planes. But I would like to stress the importance of making a close x-ray study of the reflecting power of a single metal crystal before and after plastic deformation, in order to ascertain the size and perfection of the coherent domains in the crystal. The reflecting power of a crystal of the mosaic type is many times that of a perfect crystal, and it has been shown by Renninger⁽²⁰⁾ that in a crystal such as rock salt both types of curves can be realized to within about 5 per cent, on the same material, according to treatment. The measurement of the integrated reflection allows one to determine the size of the coherent domains, while the study of the angular distribution of the reflected radiation shows the angular spread of the orientation of these domains. If a small proportion of a metal single crystal was picked out as being approximately perfect with regard to its x-ray diffraction, this would give a much more definite starting point for an x-ray study of the initial stages of plastic deformation than the unspecified material which has been used for this purpose up to the present. Although an investigation of the type of those carried out by Allison⁽²¹⁾ and by Parratt⁽²²⁾ on calcite and by Renninger on rock salt is laborious, it should be worth while performing it on a metal crystal in view of the importance of obtaining as accurate data as possible on the fundamental process of gliding.

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Note added in proof. The latest issue of the *Physical Review* contains two papers by A. L. Patterson⁽²³⁾ which cover partly the same ground as this paper. The shape transforms for several regular shapes, not dealt with before, can be found there