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The Determination of X-Ray Line Shapes by a Double Crystal Spectrometer

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As a result of a new mathematical analysis of the action of the double crystal spectrometer, a method of using the instrument has been found which makes it possible to determine the spectral energy distribution of an x-ray line and to calibrate the instrument without any previous knowledge of the diffraction patterns of the crystals.

INTRODUCTION

Of late, it has become increasingly important to determine precisely the spectral energy distribution of x-ray lines and of absorption limits. It was hoped that such determinations could be made by means of the double crystal spectrometer but this hope has not as yet been satisfactorily realized. The fundamental difficulty lies in the fact that it has been impossible to calibrate a particular spectrometer, which amounts to saying that the effect of the spectrometer on a strictly monochromatic incident beam of x-rays is not completely known for any spectrometer. Since no source of strictly monochromatic x-rays exists, it is of course impossible to carry out a direct calibration. In lieu of this, a number of investigations have been carried out for the purpose of determining the effect of the component parts of the spectrometer on the incident radiation, in particular, the alteration in the radiation produced by the crystals. Unfortunately an impasse was encountered in this regard also, when it was shown by von Laue[1] that the relevant characteristics or diffraction patterns of two identical crystals cannot be determined in general from the experimentally determined rocking curve in the (1, −1) orders. Lacking such characteristics, investigators have made use of theoretical characteristics developed by Darwin,[2] Ewald,[3, 4] Waller[5] and Prins[6] and certain hypothetical characteristics[7, 8, 9] with the hope that some one of these would give results in agreement with experiment for a given pair of crystals and a suitably restricted wave-length region. The procedure has then been to use the adopted characteristics to compute quantities such as rocking curves, coefficients of reflection, etc., which may be compared with the corresponding experimentally measured quantities. The work of S. K. Allison[10] and L. G. Parratt[11] furnishes an excellent example of how such comparisons have been made. In this connection, it should be noted that in making comparisons it is customary to compare quantities like the widths (at half maximum) of the theoretical and experimental rocking curves or the area under such curves, etc. These are not particularly

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[1] M. von Laue, Zeits. f. Physik **72**, 472 (1931).

[2] C. G. Darwin, Phil. Mag. **27**, 325 and 675 (1914).

[3] P. P. Ewald, Ann. d. Physik **54**, 519 (1917).

[4] P. P. Ewald, Phys. Zeits. **26**, 29 (1925).

[5] I. Waller, Upsala Universitets Arsskrift 1925, 11.

[6] Prins, Zeits. f. Physik **63**, 477 (1930).

[7] Ehrenberg and Mark, Zeits. f. Physik **42**, 807 (1927).

[8] Schwarzschild, Phys. Rev. **32**, 162 (1928).

[9] S. K. Allison, Phys. Rev. **38**, 203 (1931).

[10] S. K. Allison, Phys. Rev. **41**, 1 (1932).

[11] L. G. Parratt, Phys. Rev. **41**, 561 (1932).

sensitive to variations in the form of the crystal characteristics and consequently even if they agree with those found experimentally, this does not constitute an adequate test of the correctness of the theoretical crystal characteristic used. Even when the theoretical rocking curves in the $(1, -1)$ orders agree closely with the corresponding curve measured experimentally, it cannot be inferred that the crystal characteristic adopted is the correct one. This fact was realized and mentioned by Allison[10] when he found very close agreement in the $(1, -1)$ rocking curves when the crystal characteristic suggested by Prins[6] was used as the basis for the theoretical curve. The reason for this lack of uniqueness will come out in the subsequent analysis. It is therefore necessary to determine the crystal characteristics experimentally to an extent sufficient for the solution of the problem of determining line shapes. It is the main purpose of this paper to show that there exists a method for doing this which leads to a unique determination of the spectral energy distribution incident on the first crystal of a double crystal spectrometer.

Theoretical and Hypothetical Crystal Characteristics

In order to carry out the subsequent analysis with sufficient generality, the reflected intensity characteristic of a crystal will be defined by means of a function $f(\Phi, \psi, \lambda)$, where Φ denotes the acute angle of incidence of the x-ray beam measured from the crystal surface and ψ is the acute angle between the crystal surface and the direction in which intensity of the reflected radiation is to be measured. It is assumed for the present that the incident and reflected rays lie in a plane perpendicular to the crystal planes. Physically, $f(\Phi, \psi, \lambda)$ is the intensity reflected from a crystal in the angular region between ψ and $\psi+d\psi$ when a beam of radiation of unit intensity whose wave-length lies between λ and $\lambda+d\lambda$ is incident in the angular region between Φ and $\Phi+d\Phi$. It will be noted from this definition that it is contemplated that there will be radiation reflected from an actual crystal at other angles than the angle of incidence; a possibility which has not been taken into account in previous theories of the double crystal spectrometer. As explicitly indicated $f(\Phi, \psi, \lambda)$ is expected to vary with the wave-length of the radiation. In addition to this f will depend on such quantities as the degree of polarization of the radiation, the crystal temperature, etc. In order to justify an assumption with regard to the wave-length variation of the function $f(\Phi, \psi, \lambda)$ which will be made later, it will be necessary to consider briefly the salient features of certain crystal characteristics which have been derived on purely theoretical grounds.

Theoretical derivations of the $f(\Phi, \psi, \lambda)$ have been carried out for certain ideal and special crystals by Darwin,[2] Ewald[3, 4] and Waller.[5] In these derivations it was assumed that an infinitely wide plane parallel monochromatic beam of radiation is incident on a semi-infinite perfect crystal at a glancing angle Φ. It will only be necessary to consider the case where the reflecting planes are parallel to the surface of the crystal and the incident and reflected beams determine a plane perpendicular to the crystal

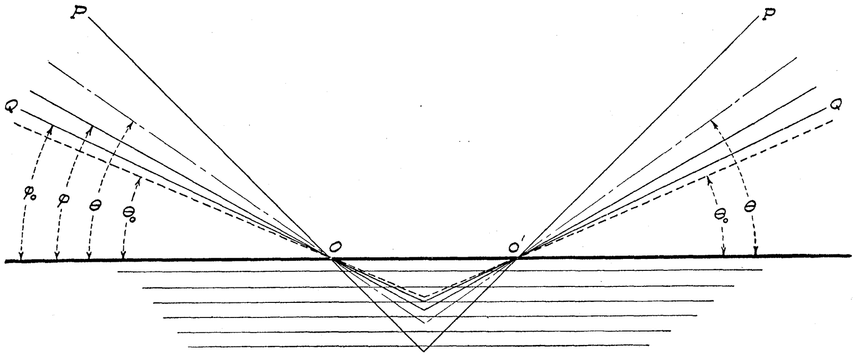

FIG. 1. Diagram showing the tolerance angle of a perfect crystal.

face and finally where the radiation is polarized at right angles to this plane. For this case the above investigations show that there exists an angular region (see Fig. 1) *POQ* in which the incident beam would be totally reflected in contradistinction to the single direction θ_0 given by the Bragg law, $n\lambda = 2d \sin \theta_0$. The angle θ between the bisector of the angle *POQ* and the crystal surface is the Bragg angle corrected for refraction, i.e., $\theta = \theta_0 + 2\delta/\sin 2\theta_0$ where δ is the deviation of the index of refraction from unity. In general the half-width of *POQ* is less than $\theta - \theta_0$. For this ideal arrangement the reflected beam is infinitely wide but accurately plane parallel, making the same glancing angle with the crystal as the initial beam. In terms of the characteristic function this means that $f(\Phi, \psi, \lambda)$ will be zero for all values of ψ except $\psi = \Phi$ and we have a function of one angle only, namely, $f(\Phi, \Phi, \lambda)$. For values of Φ in *POQ*, $f(\Phi, \Phi, \lambda)$ is unity for this ideal case. The actual form of f as computed by Waller for a cubic crystal with identical diffracting centers when Φ is outside of the angle *POQ*, is

$$f_w(\Phi, \Phi, \lambda) = \frac{|\theta - \Phi_0|^2 \sin^2 2\theta_0}{[(\theta - \Phi) \sin 2\theta_0 \pm \{(\theta - \Phi)^2 \sin^2 2\theta_0 - |\theta - \Phi_0|^2 \sin^2 2\theta_0\}^{\frac{1}{2}}]^2}, \tag{1}$$

the plus sign to be taken when $(\theta - \Phi) \sin 2\theta_0 > 0$ and the minus sign when $(\theta - \Phi) \sin 2\theta_0 < 0$. The wave-length dependence is contained in θ and θ_0. $(\theta - \Phi_0)$ depends on a number of factors such as the crystal structure and crystal temperature. The effect of the temperature vibration of the diffracting centers is to make the range $(\theta - \Phi_0)$ smaller.

Darwin's expression for the characteristic function is practically identical with the one given above. In these functions absorption due to quantum processes has not been taken into account. Prins[6] attempted to take such processes into account and arrived at a modified form of Darwin's function, namely

$$f_p(\Phi, \Phi, \lambda) = \left| \frac{a + ib}{\frac{1}{2}(\Phi - \theta) \sin 2\theta_0 - i\beta \pm \{[\frac{1}{2}(\Phi - \theta) \sin 2\theta_0 - i\beta]^2 - (a + ib)^2\}^{\frac{1}{2}}} \right|^2. \tag{2}$$

The additional factors b and β which take into account absorption destroy the symmetry of f about the point $\Phi = \theta$. This function has been plotted by Allison.[10] Another extremely important difference between f_p and f_w is the way in which they depend on the wave-length of the incident beam. As the wave-length is changed the principal alteration of f_w is simply that of displacement along the Φ-axis, while the function f_p is materially changed as can be seen from Fig. 2 in Allison's paper.[10]

Since in the actual crystals used there are surface imperfections as well as lattice structures for which the above functions no longer apply and the incident beam is restricted and not infinite in extent, etc., some investigators have thought that one could come about as near to the correct function by assuming a reasonable type as by trying to use the more complicated ones derived for such ideal conditions. Ehrenburg and Mark[7] and Schwarzschild[8] have assumed that the characteristic function was a Gaussian error function, i.e.,

$$f(\Phi, \Phi, \lambda) = Ae^{-k(\Phi - \theta)^2}. \tag{3}$$

Barnes and Palmer[12] have assumed that the characteristic function was of the same form as that used by Hoyt[13] for representing the shape of an x-ray line, namely,

$$f(\Phi, \Phi, \lambda) = a[1 + (\Phi - \theta)^2/b^2]^{-1}. \tag{4}$$

The above characteristic functions are convenient because in a two crystal spectrometer with identical crystals the rocking curve in the $(1, -1)$ position calculated from them would again be a function of the same form. While rocking curves have been found for certain pairs

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[12] S. W. Barnes and L. D. Palmer, Phys. Rev. **43**, 1050 (1933).

[13] A. Hoyt, Phys. Rev. **40**, 477 (1932).

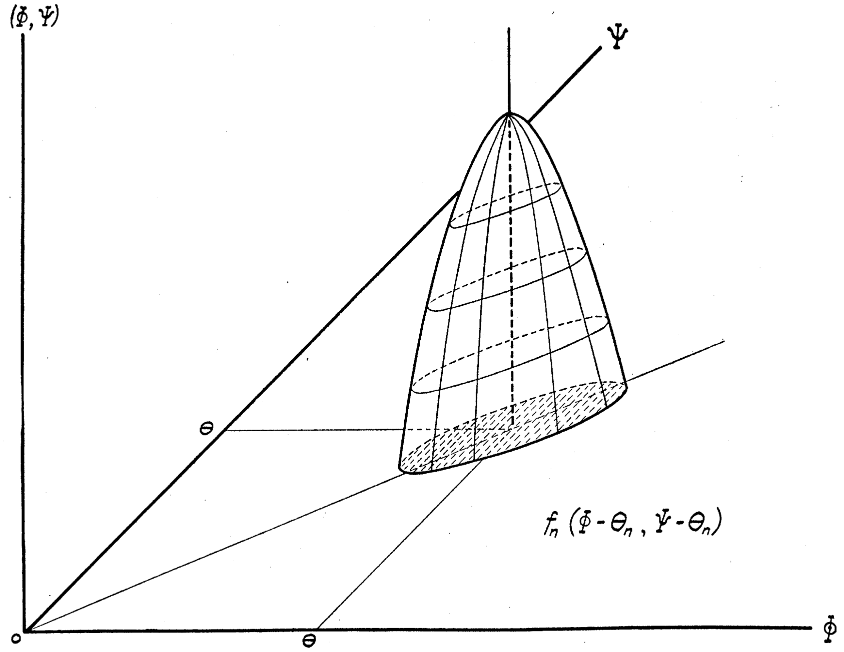

FIG. 2. A schematic representation of the crystal characteristic $f(\Phi, \psi, \lambda)$.

of crystals which agree approximately with one or the other of the functions (3) or (4), this is not universally the case and even if it were it can be shown that there exist asymmetrical crystal characteristics which would yield symmetrical rocking curves of the form (3) or (4).

It should be noted that the form of all of the above characteristic functions precludes the possibility of any radiation being reflected at an angle not equal to the incident angle. In terms of $f(\Phi, \psi, \lambda)$, this means that f is different from zero only when $\psi-\Phi$. This restriction is doubtless justified for the ideal circumstances assumed in the derivation of expressions (1) and (2) but for an actual crystal used in a spectrometer there is considerable departure from the ideal conditions assumed above and it is not *a priori* obvious that ψ should be identically equal to Φ. In fact, evidence is accumulating which makes it unlikely that all the reflected energy leaves the crystal at any one angle. Logically, therefore, it would seem that we should generalize one step further and treat the angles Φ, and ψ as solid angles, which would mean that radiation incident on the crystal at a given angle would be reflected to some extent in all directions in a certain cone. Very likely this is precisely what does occur but, due to the fact that all motions of a properly adjusted double crystal spectrometer are confined to a plane, it will be found that the subsequent analysis can be generalized so as to take account of solid angles. Since this later generalization is possible, it will be much simpler to carry out the analysis treating Φ and ψ as plane angles.

Analysis of the Double Crystal Spectrometer

Before proceeding with the analysis it will be necessary to justify an assumption to be made concerning the wave-length dependence of the characteristic function. Geometrically, the function $f(\Phi, \psi, \lambda)$ represents a surface when λ is held fixed. From our general knowledge of the reflecting properties of a crystal this must be a dome-shaped surface having a maximum in the neighborhood where Φ and ψ equal the corrected Bragg angle. This is roughly shown in Fig. 2. In line with the characteristic functions considered above, it is convenient to measure both of the angle variables from the corrected Bragg angle θ. This can be explicitly indicated by writing $f(\Phi-\theta, \psi-\theta, \lambda)$. From experiment, it is known that $f(\Phi-\theta, \psi-\theta, \lambda)$ is appreciably

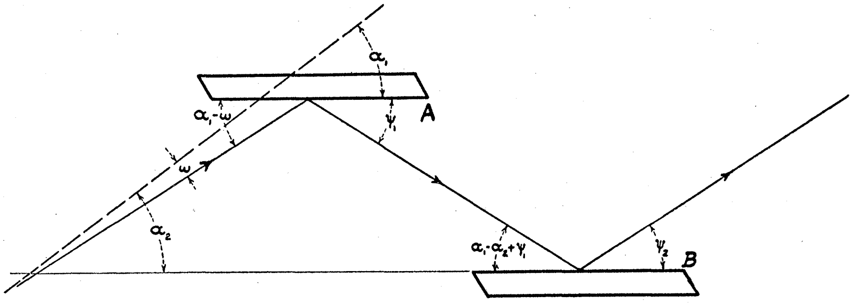

FIG. 3. Crystal arrangement for rocking curves in $(n, -n)$ orders.

different from zero only in a region of the Φ, ψ plane in the vicinity of the point $\Phi=\theta$, $\psi=\theta$. If we were dealing with a function of the Darwin type Eq. (1) then the wave-length dependence would enter in f principally in the angle θ and we would have $f(\Phi-\theta, \psi-\theta)$. For this case a change in the wave-length would merely displace the dome-shaped surface along a 45 degree line in the Φ, ψ plane. It is definitely known, however, that this simple type of wave-length dependence is untenable in general, which is in accord with f_p of Eq. (2). If the change in the actual surface f, with wave-length, aside from the displacement along the line $\Phi=\psi$, is anything like that of f_p, then f will be a sufficiently slowly varying function of λ so that the change in the shape of the surface over a small wave-length interval may be neglected. This certainly obtains for wave-length intervals covered by a spectral line and for certain crystals f does not change appreciably over intervals many times this size, as is indicated by rocking curves taken in the (1, −1) positions for nearby wave-lengths. Therefore, when the incident radiation is line radiation there will be no loss of generality in assuming that a change in wave-length simply displaces the surface f along the line $\Phi=\psi$. So that we may write

$$f_n(\Phi-\theta_n, \psi-\theta_n),$$

where θ_n denotes the corrected Bragg angle in the nth order. The subscript n attached to f indicates that the surface f will, in general, be different for different orders.

It will be sufficient to compute the intensity of radiation reflected from two crystals when the incident and reflected beams from each all lie in the same plane, since it has been shown by Allison[14] that effects due to crystal alignment and vertical divergence of the incident beam can be made negligibly small. Let the geometrical center of the initial beam (dotted line in Fig. 3) be chosen as the reference line for the angular positions of the two crystals and let the surfaces of A and B make angles α_1 and α_2 with it. Suppose also that a beam of radiation of unit intensity having a wave-length between λ and $\lambda+d\lambda$ falls on crystal A in the angular interval between ω and $\omega+d\omega$ measured with respect to the same reference line. The total intensity reflected from the second crystal will be

$$d\lambda\int_{\Delta\psi_1} d\psi_1\int_{\Delta\psi_2} f_{n_1}(\alpha_1-\omega-\theta_{n_1}, \psi_1-\theta_{n_1}) \times f_{n_2}\{\pm(\alpha_1-\alpha_2+\psi_1)-\theta_{n_2}, \psi_2-\theta_{n_2}\}d\psi_2,$$

where the + sign is to be used for the orders $(n_1, -n_2)$ and the − sign for the orders $(n_1, +n_2)$ and $\Delta\psi_1$ and $\Delta\psi_2$ denote the angular intervals over which the function f_{n_1} and f_{n_2} are different from zero. Since f_{n_1} and f_{n_2} are zero outside of these intervals, the intervals can be extended from $-\infty$ to $+\infty$. If the intensity of the incident radiation is not unity but $l(\lambda-\lambda_0)k(\omega)$ where $k(\omega)$ is the distribution in intensity with angle and $l(\lambda-\lambda_0)$ is the distribution of intensity with wave-length measured from the wave-length λ_0 of maximum intensity, then the total reflected intensity from crystal B is

$$\int_{-\infty}^{+\infty} l(\lambda-\lambda_0)d\lambda\int_{-\infty}^{+\infty} d\psi_1\int_{-\infty}^{+\infty} k(\omega) \times f_{n_1}\{\alpha_1-\omega-\theta_{n_1}, \psi_1-\theta_{n_1}\}d\omega\int_{-\infty}^{+\infty} \times f_{n_2}\{\pm(\alpha_1-\alpha_2+\psi_1)-\theta_{n_2}, \psi_2-\theta_{n_2}\}d\psi_2, \quad (5)$$

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[14] S. K. Allison, Phys. Rev. **44**, 63 (1933).

where the ranges of integration of λ and ω have been extended for the same reasons as mentioned above.

To compute rocking curves in the $(n_1, -n_2)$ orders with crystal A fixed, it is only necessary to let $\alpha_1 = \theta_{n_1}{}^0$ and $\alpha_2 = \theta_{n_2}{}^0 + \epsilon_2$ where $\theta_{n_1}{}^0$ and $\theta_{n_2}{}^0$ denote the corrected Bragg angles for the wave-length λ_0 and indicated orders, while ϵ_2 then gives the angle of deviation of crystal B from the corrected Bragg angle. Denoting such a rocking curve by $r_{n_1,\,-n_2}(\epsilon_2)$ then

$$r_{n_1,\,-n_2}(-\epsilon_2) = \int_{-\infty}^{+\infty} l(\lambda-\lambda_0)d\lambda \int_{-\infty}^{+\infty} d\psi_1 \int_{-\infty}^{+\infty} \times k(\omega) f_{n_1}\{\theta_{n_1}{}^0 - \omega - \theta_{n_1},\ \psi_1 - \theta_{n_1}\} d\omega \int_{-\infty}^{+\infty} \times f_{n_2}\{\theta_{n_1}{}^0 - \theta_{n_2}{}^0 - \epsilon_2 + \psi_1 - \theta_{n_2},\ \psi_2 - \theta_{n_2}\} d\psi_2. \quad (6)$$

If the angular range over which $k(\omega)$ is appreciably different from zero is large compared with the region for which f_{n_1} is different from zero and $k(\omega)$ is a slowly varying function of ω over the latter range, then to a sufficient approximation we may write

$$\int_{-\infty}^{+\infty} k(\omega) f_{n_1}\{\theta_{n_1}{}^0 - \omega - \theta_{n_1},\ \psi_1 - \theta_{n_1}\} d\omega$$

$$= k(\theta_{n_1}{}^0) \int_{-\infty}^{+\infty} f_{n_1}\{\xi,\ \psi_1 - \theta_{n_1}\} d\xi = g_{n_1}(\psi_1 - \theta_{n_1}), \quad (7)$$

where $\xi = \theta_{n_1}{}^0 - \omega - \theta_{n_1}$.

The conditions leading to this relation are usually fulfilled in practice. Letting

$$h_{n_2}(\psi_1 - \epsilon - \theta_{n_2} - \theta_{n_2}{}^0 + \theta_{n_1}{}^0)$$

$$= \int_{-\infty}^{+\infty} f_{n_2}\{\psi_1 - \epsilon - \theta_{n_2} - \theta_{n_2}{}^0 + \theta_{n_1}{}^0,\ \psi_2 - \theta_{n_2}\} d\psi_2 \quad (8)$$

Eq. (6) becomes

$$r_{n_1,\,-n_2}(-\epsilon_2) = \int_{-\infty}^{+\infty} l(\lambda-\lambda_0)d\lambda \int_{-\infty}^{+\infty} g_{n_1}(\psi_1 - \theta_{n_1}) \times h_{n_2}(\psi_1 - \epsilon_2 - \theta_{n_2} - \theta_{n_2}{}^0 + \theta_{n_1}{}^0) d\psi_1. \quad (9)$$

This result is very similar to that obtained when the characteristic functions are of the form $f(\Phi, \Phi, \lambda)$ but the functions appearing in the integrand have wholly different meanings.

Rocking curves in the $(n_1, +n_2)$ orders can be obtained in a similar way by letting $\alpha_1 = \theta_{n_1}{}^0$ and $\alpha_2 = \theta_{n_2}{}^0 + 2\theta_{n_1}{}^0 + \epsilon_2$ and taking the − sign in Eq. (5), thus

$$r_{n_1,\,+n_2}(\epsilon_2) = \int_{-\infty}^{+\infty} l(\lambda-\lambda_0)d\lambda \int_{-\infty}^{+\infty} g_{n_1}(\psi_1 - \theta_{n_1}) \times h_{n_2}(\theta_{n_1}{}^\circ + \theta_{n_2}{}^\circ + \epsilon_2 - \psi_1 - \theta_{n_2}) d\psi_1. \quad (10)$$

Henceforth the subscripts on the variable of integration ψ_1 and ϵ_2 will be dropped.

The analysis would have proceeded in the same manner as the above even when Φ and ψ were considered as solid angles. The only difference in the results would have been in the definition of the functions g and h above. Eqs. (7) and (8) would involve double integrations instead of single and the meaning of g and h would be different but, since they are to be determined from experiment anyway, the subsequent analysis holds for the more general case.

It is worth while to notice several important characteristics of Eqs. (9) and (10). First, the right-hand integral of (9) will be a maximum for a given wave-length when ϵ_2 is adjusted to give maximum overlapping of g_{n_1} and h_{n_2}, i.e., to make the common area under the curves g_{n_1} and h_{n_2} a maximum. If $n_1 = n_2$ then the amount of overlapping remains constant for all wave-lengths and the form of $r_{n_1,\,-n_1}(\epsilon_2)$ is independent of the form of $l(\lambda-\lambda_0)$ and hence of the shape of the incident line and depends only on the total intensity. On the other hand, if n_1 is not equal to n_2 then the amount of overlapping decreases as λ increases and the origins of g_{n_1} and h_{n_2} are translated in the same direction but by a different amount. g_{n_1} and h_{n_2} therefore separate by an amount measured by $|\theta_{n_2} - \theta_{n_1}|$ so that all curves $r_{n_1,\,-n_2}(\epsilon_2)$ when $n_2 \neq n_1$, depend on the line shape. Somewhat similar remarks hold in the case of Eq. (10) except that the amount of overlapping never remains constant as the wave-length changes and consequently all $r_{n_1,\,n_2}(\epsilon_2)$ depend on the form of $l(\lambda-\lambda_0)$. The separation of the origins of the functions g_{n_1} and h_{n^2} is measured by $|\theta_{n_2} + \theta_{n_1}|$ as λ increases. These considerations are important in making use of Eqs. (9) and (10) to determine the line shape $l(\lambda-\lambda_0)$.

DETERMINATION OF THE LINE SHAPE

The possibility of determining the spectral energy distribution of an x-ray line from measurements with an uncalibrated double crystal spectrometer rests on the existence of a unique solution of a set of simultaneous integral equations of the form (9) and (10) and a method for finding it. A method of finding such a solution will now be given.

In order to invert the integral equations it will be convenient to make use of the theory of Fourier transforms. With suitable restrictions (fulfilled for the functions under consideration) a function $f(x)$ can be represented by the Fourier integral

$$f(x)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{+\infty}F(t)e^{-itx}dt, \tag{15}$$

where $F(t)$ is the Fourier transform of $f(x)$ defined by the equation

$$F(t)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{+\infty}f(x)e^{ixt}dx. \tag{16}$$

Throughout the remainder of this paper capital letters will be used to denote the Fourier transforms of the functions denoted by small letters, with the exception of the capital letter L. It should be noted that $F(t)$ is a complex function unless $f(x)$ is an even function in which case $F(t)$ is real. Of the functions to be considered there is a one to one correspondence between the function and its Fourier transform, so that if the transform is known, the function to which it corresponds can be found by Eq. (15).

In addition to the inversion formulae (15) and (16) we shall need to invert a relation of the type

$$\chi(t)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{+\infty}f(x)e^{itu(x)}dx, \tag{17}$$

where $u(x)$ is an odd function of x. Let $s=u(x)$ and the unique inverse be $x=v(s)$; then

$$\chi(t)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{+\infty}f[v(s)]e^{its}v'(s)ds.$$

Using (15) and (16) we have

$$f[v(s)]v'(s)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{+\infty}\chi(t)e^{-its}dt$$

or since

$$dv/ds=1/(du/dx)$$

$$f(x)=(2\pi)^{-\frac{1}{2}}u'(x)\int_{-\infty}^{+\infty}\chi(t)e^{-itu(x)}dt. \tag{18}$$

Eqs. (17) and (18) furnish somewhat more general inversion formulae.

Eq. (9) may be converted into a relation between the Fourier transforms of the functions involved by multiplying through by $e^{-it\epsilon}$ and integrating with respect to ϵ from $-\infty$ to $+\infty$. On inverting the order of integration on the right, the equation becomes

$$\int_{-\infty}^{+\infty}r_{n_1,\,-n_2}r(-\epsilon)e^{-it\epsilon}d\epsilon=\int_{-\infty}^{+\infty}l(\lambda-\lambda_0)\exp\left[it(\theta_{n_2}+\theta_{n_2}{}^0-\theta_{n_1}-\theta_{n_1}{}^0)\right]d\lambda\int_{-\infty}^{+\infty}g_{n_1}(\psi)e^{-it\psi}d\psi$$
$$\times\int_{-\infty}^{+\infty}h_{n_2}(\psi-\epsilon-\theta_{n_2}+\theta_{n_1}-\theta_{n_2}{}^0+\theta_{n_1}{}^0)\exp\left[it(\psi-\epsilon-\theta_{n_2}+\theta_{n_1}-\theta_{n_2}{}^0+\theta_{n_1}{}^0)\right]d\epsilon.$$

Making use of Eqs. (16) and (17) this may be written as

$$R_{n_1,\,-n_2}(t)=2\pi L_{n_1,\,-n_2}(t)G_{n_1}{}^*(t)H_{n_2}(t), \tag{19}$$

where the asterisk denotes the complex conjugate and

$$L_{n_1,\,-n_2}(t)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{+\infty}l(\lambda-\lambda_0)$$
$$\times\exp\left[it(\theta_{n_2}-\theta_{n_1}+\theta_{n_2}{}^0-\theta_{n_1}{}^0)\right]d\lambda. \tag{20}$$

Eq. (10) may be converted to a form similar to (19) by multiplying through by $e^{it\epsilon}$ and integrating as before. The desired relation is

$$R_{n_1,\,n_2}(t)=2\pi L_{n_1,\,n_2}(t)G_{n_1}(t)H_{n_2}(t), \tag{21}$$

where

$$L_{n_1,\,n_2}(t)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{+\infty}l(\lambda-\lambda_0)$$
$$\times\exp\left[it(\theta_{n_2}-\theta_{n_2}{}^0+\theta_{n_1}-\theta_{n_1}{}^0)\right]d\lambda. \tag{22}$$

Of all of the possible relations (19) and (21), six will be required. In order to make the following analysis clear and to save space, the special equations to be used are written below:

$$\left.\begin{aligned}R_{1,\,-1}(t)&=2\pi IG_1{}^*(t)H_1(t), &&\text{(a)}\\ R_{2,\,-2}(t)&=2\pi IG_2{}^*(t)H_2(t), &&\text{(b)}\end{aligned}\right\} \tag{23}$$

$$\left.\begin{aligned} R_{1,+1}(t)&=2\pi L_{1,+1}(t)G_1(t)H_1(t), && \text{(a)}\\ R_{2,+2}(t)&=2\pi L_{2,+2}(t)G_2(t)H_2(t), && \text{(b)}\\ R_{1,+2}(t)&=2\pi L_{1,+2}(t)G_1(t)H_2(t), && \text{(c)}\\ R_{2,+1}(t)&=2\pi L_{1,+2}(t)G_2(t)H_1(t), && \text{(d)} \end{aligned}\right\} \quad (24)$$

where the relations

$$L_{1,-1}(t)=L_{2,-2}(t)=I$$
$$=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{+\infty} l(\lambda-\lambda_0)d\lambda=\text{a constant},$$
$$L_{1,+2}(t)=L_{2,+1}(t)$$

have been used.

The immediate problem is to determine one of the functions $L(t)$ in the above equations. In general $L(t)$ is a complex function of the real variable t so that it may be written

$$L_{n_1,n_2}(t)=|L_{n_1,n_2}(t)|\exp[i\Phi_{n_1,n_2}(t)]. \quad (25)$$

$L_{n_1,n_2}(t)$ is real only when the line shape is symmetrical, i.e., $l(\lambda-\lambda_0)$ is an even function of $(\lambda-\lambda_0)$. It is easy to obtain $|L_{n_1,n_2}(t)|$. Multiplying (24a) by its complex conjugate we have

$$|R_{1,+1}(t)|^2=4\pi^2|L_{1,+1}(t)|^2G_1(t)H_1^*(t)G_1^*(t)H_1(t).$$

Making use of Eq. (23a) this becomes

$$|R_{1,+1}(t)|^2/|R_{1,-1}(t)|^2=|L_{1,+1}(t)|^2/I^2$$

or

$$|L_{1,+1}(t)|=I|R_{1,+1}(t)|/|R_{1,-1}(t)|. \quad (26)$$

Similarly

$$|L_{2,+2}(t)|=I|R_{2,+2}(t)|/|R_{2,-2}(t)| \quad (27)$$

and

$$|L_{1,+2}(t)|=I\left[\frac{R_{1,+2}(t)\cdot R^*_{2,+1}(t)}{R^*_{1,-1}(t)\cdot R_{2,-2}(t)}\right]^{\frac{1}{2}}. \quad (28)$$

Eqs. (26) or (27) would constitute a formal solution to our problem if it were known that the initial line shape were symmetrical. Since this is not known it will be necessary to determine the argument of the functions $L_{n_1,n_2}(t)$. To do this, Eqs. (24a) and (24b) are multiplied together and the result divided by the product of (24c) and (24d), so that

$$\frac{L_{1,+1}(t)L_{1,+2}(t)}{L^2_{1,+2}(t)}=\frac{R_{1,+1}(t)R_{2,+2}(t)}{R_{1,+2}(t)R_{2,+1}(t)}$$
$$=S(t)=|S(t)|e^{i\chi(t)}. \quad (29)$$

Taking logarithms of both sides we have

$$\log L_{1,+1}(t)+\log L_{2,+2}(t)-2\log L_{1,+2}(t)$$
$$=\log S(t). \quad (30)$$

In this equation the principal value of the logarithm is meant so that

$$\log L_{1,+1}(t)=\log|L_{1,+1}(t)|+i\Phi_{1,+1}(t). \quad (31)$$

Eq. (30) involving three unknown functions can be reduced to a functional equation involving only one unknown function. To do this, we expand the angles $\theta_{n_2}+\theta_{n_1}$ occurring in Eq. (22) as Taylor's series in the wave-length λ about the point λ_0, thus

$$\theta_{n_2}+\theta_{n_1}=\theta_{n_2}{}^0+\theta_{n_1}{}^0+\{d(\theta_{n_2}+\theta_{n_1})/d\lambda\}_{\lambda=\lambda_0}$$
$$\times(\lambda-\lambda_0)+\cdots.$$

Use is now made of the fortunate circumstance that for values of $\lambda-\lambda_0$ over which the function $l(\lambda-\lambda_0)$ is appreciably different from zero, only the first two terms of the above expansion are required to give a good approximation for $\theta_{n_2}+\theta_{n_1}$. Examination shows that this approximation holds for x-ray lines over quite a large wave-length region. We may therefore write

$$\theta_{n_2}+\theta_{n_1}-\theta_{n_2}{}^0-\theta_{n_1}{}^0=D_{n_1n_2}(\lambda-\lambda_0)$$

where $D_{n_1n_2}=(d/d\lambda)(\theta_{n_2}+\theta_{n_1})_{\lambda=\lambda_0}$.

Substituting the above expression in Eq. (22) we have

$$L_{n_1,+n_2}(t)=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{+\infty} l(\lambda-\lambda_0)$$
$$\times\exp[itD_{n_1n_2}(\lambda-\lambda_0)]d\lambda$$

or

$$L_{n_1,+n_2}(t/D_{n_1n_2})=(2\pi)^{-\frac{1}{2}}\int_{-\infty}^{+\infty} l(\lambda-\lambda_0)e^{it(\lambda-\lambda_0)}d\lambda.$$

The required relation between $L_{1,+1}(t)$, $L_{2,+2}(t)$ and $L_{1,+2}(t)$ is obtained from this equation, namely,

$$L_{2,+2}(t/D_{22})=L_{1,+2}(t/D_{12})=L_{1,+1}(t/D_{11})$$

or

$$L_{2,+2}(t)=L_{1,+1}(D_{22}t/D_{11})$$

and

$$L_{1,+2}(t)=L_{1,+1}(D_{12}t/D_{11}).$$

Making use of these relations, Eq. (30) reduces to the functional equation

$$\log L_{1,\,+1}(t)+\log L_{1,\,+1}(D_{22}t/D_{11}) \\ -2\log L_{1,\,+1}(D_{12}t/D_{11})=\log S(t). \quad (32)$$

By equating the real and imaginary parts of this equation in accordance with the relation (31) we have

$$\log|L_{1,\,+1}(t)|+\log|L_{1,\,+1}(D_{22}t/D_{11})| \\ -2\log|L_{1,\,+1}(D_{12}t/D_{11})|=\log|S(t)|, \quad (33a)$$

$$\Phi_{1,\,+1}(t)+\Phi_{1,\,+1}(D_{22}t/D_{11}) \\ -2\Phi_{1,\,+1}(D_{12}t/D_{11})=\chi(t). \quad (33b)$$

The unknown argument of $L_{1,\,+1}(t)$ can be found from the second of the above equations and the Fourier transform of the function $l(\lambda-\lambda_0)$ has been completely determined and consequently the original line shape also.

It does not seem worth while, at the present time, to discuss the solution of Eq. (33b) since the method of procedure will depend on the behavior of the function $\chi(t)$. If, in particular, $\chi(t)$ is an analytic function, an expansion of $\chi(t)$ and $\Phi(t)$ in a power series suggests itself since Eq. (33b) will determine the coefficients in the power series for $\Phi(t)$ uniquely. It should be noticed that if $\chi(t)$ is identically equal to zero, then so is $\Phi_{1,\,+1}(t)$ since $\Phi_{1,\,+1}(0)$ is known to be zero and the intensity of the original x-ray line is symmetrical about the point $\lambda=\lambda_0$.

Suggested Procedure in Actual Computations

Since the writer has not as yet carried out the requisite numerical computations to determine the line shape, it cannot be said that the method to be suggested is the best but certain circumstances indicate that it would be a good one to try. In order to carry through the formal mathematical work, it is convenient to have an analytical representation of the various rocking curves. On account of their general form it would appear that they could be represented by a relatively small number of terms in a series of the orthogonal Hermitian functions $\psi_n(x)$ whose generating function is

$$e^{-x^2/2}e^{-(x-t)^2}=\sum_{n=0}^{\infty}(n!)^{-1}\psi_n(x)t^n.$$

Another important reason for employing the functions $\psi_n(x)$ is that they possess the property of being their own Fourier transform except for a possible constant. This should materially facilitate the determination of the Fourier transforms of the rocking curves.

With the function $l(\lambda-\lambda_0)$ thus determined, the functions $G_1(t)$, $H_1(t)$, $G_2(t)$ and $H_2(t)$ can be found from Eqs. (23a), (23b), (24a) and (24b) in an obvious manner. Since these functions depend only on the crystal characteristics the spectrometer can be considered as calibrated for wave-lengths in the neighborhood of λ_0 as soon as they have been determined. It must be remembered, however, that the functions g_1, h_1, etc., whose Fourier transforms are G_1, H_1, etc., are not the diffraction patterns of the crystals as normally defined. It is obvious that it is not possible to determine $f(\Phi,\psi)$ in terms of the functions g, h, etc., but this is not required either to calibrate the spectrometer or to obtain the line shape.

The general problem of determining the spectral energy distribution of an x-ray line and of calibrating the double crystal spectrometer experimentally without appealing to the theoretical diffraction pattern or characteristic function for the crystal has been solved. In conclusion the writer wishes to acknowledge the very considerable help received from very stimulating discussions of this subject with Professor C. C. Murdock.