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Accuracy of Intensity Measurements from Large Single Crystals

By Gösta Brogren

Department of Physics, Chalmers University of Technology, Gothenburg S, Sweden

Currently used techniques for studying the perfection of large single crystals often fail to show any evidence of mosaicity when the dislocation density is very small. This mosaicity may be revealed by the use of relatively high-energy γ-sources. In single and also in double crystal spectrometers corrections must be made for the fluorescent radiation: this cannot be eliminated by pulse-height discrimination techniques.

Intensity measurements from large single crystals have been carried out for several years by means of commonly-used methods and detectors. Since these are well known, I do not intend to deal with them, but will refer to a few observations that have given rise to trouble and misinterpretation.

Intensity measurements and crystal perfection studies are carried out either by using an X-ray tube with a small focal spot, or an extended source, in which case gamma sources with short wavelengths are generally used. These two methods often give contradictory results. In both cases, flat crystal spectrometers are used – generally double crystal spectrometers.

The theory of crystal diffraction has been outlined elsewhere (Compton & Allison, 1935; Zachariasen, 1945; James, 1962).

In order to simplify our analysis, let us assume that a monochromatic and perfectly parallel beam is impinging on a thick single crystal adjusted for symmetric Laue diffraction. If the crystal is rotated slowly while the intensity of the diffracted beam is recorded, we can calculate the shape of the diffraction pattern from the dynamical theory. If we simplify our discussion to the case of no absorption, we obtain from Zachariasen (1945)* for the intensity P of the diffracted beam

$$\frac{P}{I_0}=\frac{1}{2}\left[\frac{\sin^2(A\sqrt{1+y_n^2})}{1+y_n^2}+\frac{\sin^2(A\sqrt{1+y_p^2})}{1+y_p^2}\right]$$
$$\simeq\frac{1}{4}\left[\frac{1}{1+y_n^2}+\frac{1}{1+y_p^2}\right],$$

n and p being the normal and parallel polarization respectively. y is the angular coordinate. A is a factor which contains among other terms the thickness and the polarization factor. When A becomes very great its value is no longer sharply defined since the thickness must vary somewhat along the crystal plate. If the uncertainty ΔA is greater than $\pi/2$ the $\sin^2$ can be replaced by its average value of $\frac{1}{2}$. For the following discussion, we also neglect the difference in polarization, putting the polarization factor, $K=|\cos 2\theta_B|=1$. This gives

$$\frac{P}{I_0}=\frac{1}{2(1+y^2)}\,.$$

The semi half-width ω_y on the y scale is 1 which gives the following value ω, in radians:

$$\omega=\frac{e^2\,.\,\lambda^2\,.\,F}{mc^2\quad V}\cdot\frac{1}{\sin 2\theta_B}\simeq k\,.\,\lambda\,,$$

where e=the charge of the electron, m=the mass of the electron, c=the velocity of light, F=the crystal structure factor, V=the volume of the unit cell, λ= the wavelength, and θ_B=the Bragg angle.

The width of the diffraction pattern is thus proportional to the wavelength. Since

$$\int_{-\infty}^{+\infty}\frac{dy}{1+y^2}=\pi$$

the integrated intensity R_y in y-units is easily obtained as

$$R_L^y=\frac{\pi}{2}\,.$$

Hence the integrated intensity on an angular scale is also roughly proportional to the wavelength.

A corresponding analysis of the Bragg case in a non-absorbing crystal leads to a half maximum width $\omega_y=\frac{2}{3}\sqrt{3}\simeq 1{\cdot}15$ on the y scale as compared with the value $\omega_y=1$ in the Laue case. The integrated Bragg reflexion R_B^y turns out to be

$$R_B^y=\pi$$

which is twice the value for the Laue case.

There have always been difficulties in finding completely perfect crystals. It has, however, been proved that crystals with low dislocation densities behave like perfect crystals. No influence of dislocation density upon the diffraction properties of the type discussed here could be found.

Almost every real crystal has a mosaic structure. According to Darwin's original ideas (1914, 1922), the majority of crystals are built from minute blocks 10^{-4} to 10^{-5} cm in linear dimensions, mutually disoriented by angles of the order of seconds of arc or more. Bragg (1940) and Burgers (1940) later introduced the assumption that mosaic blocks may be considered as areas separated by dislocation walls. Gay, Hirsch & Kelly (1953) assumed that one dislocation line corresponds to one mosaic block. How do these assumptions influence the reflexion properties of a crystal?

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* For notation see Zachariasen p. 113 and following.

Let us assume that all mosaic blocks have the same dimension t (equal to the spacing of the dislocations), that the dislocation density is ϱ, the Burgers vector b and the mean mutual deviation angle between two blocks is α. Then

$$\alpha = \frac{b}{t} = b \,.\, \varrho^{1/2}$$

$$t = 1/\sqrt{\varrho}\,.$$

The angular distribution function is a Gaussian error function. As the impinging X-ray beam passes across a crystal, over a length L, the number of blocks passed is L/t. The probable misfit between the first and the last crystal block will be $\alpha(L/t)^{\frac{1}{2}}$. Since the distribution function is Gaussian, the half-width ω_M of the diffraction curve is

$$\omega_M \simeq \tfrac{1}{2}\alpha(L/t)^{1/2} = \tfrac{1}{2}\,.\, b\,.\, L^{1/2}.\, t^{-3/2}$$

$$\omega_M \simeq \frac{b}{2}\cdot L^{1/2}\,.\, \varrho^{3/4}.$$

This rough estimate can now be applied to a silicon or germanium crystal. The stable dislocations generally have a Burgers vector $|b| = \frac{1}{2}a\langle 110\rangle$. If $L = 1$ cm and $\varrho = 10^4$ cm^{-2} the full width $2\omega_M$ is about 4·2 sec of arc according to this rough estimate.

If the integrated intensity (R_θ) is calculated the following expressions are obtained for the perfect crystal and the ideal mosaic crystal respectively.

$$R_\theta(\text{perfect}) = \frac{8}{3\pi}\cdot\frac{e^2}{mc^2}\cdot\frac{|F|}{V}\cdot\frac{1+|\cos 2\theta_B|}{2\cos\theta_B}\cdot d\,.\,\lambda$$

$$R_\theta(\text{mosaic}) = \left(\frac{e^2}{mc^2}\right)^2\cdot\left(\frac{F}{V}\right)^2 \times d\cdot\frac{1+|\cos 2\theta_B|}{2\cos\theta_B}\cdot\lambda^2\,.\,\Delta V,$$

where d=the spacing and ΔV=the reflecting volume.

The integrated intensity is proportional to wavelength in the perfect crystal but proportional to λ^2 in the mosaic.

Generally, the properties of a large single crystal are examined with a characteristic $K\alpha$-line from an X-ray tube with a focal spot width of ~0·1 cm. The reflexion properties are investigated point by point. The intensity from the line used is so high that the white radiation can be neglected. The reflexion properties (including the mosaic spread) are obtained only from the projection of the focal spot onto the crystal through the Bragg angle. Even if a large area is exposed the values obtained are characteristic only for this very small region (size L=0·1 cm). Generally Mo $K\alpha$ or Cu $K\alpha$ lines are used, and sometimes Ag or W $K\alpha$ in transmission. The mosaic spread for L=0·1 cm is of the order of 1″ sec of arc even for a dislocation density as high as 10^4 cm^{-2}. 100 dislocations per cm^2 reduces the spread to the order of 0·1 sec of arc. Such small broadenings cannot be detected.

The qualitative behaviour of a real crystal is shown in Fig. 1, which applies to Laue diffraction. For $\lambda < \lambda_1$ the reflexion P present in a perfect crystal is less than 0·5. If the crystal is not dislocation-free the crystal gives rise to a mosaic spread ω_M. For $\lambda = \lambda_2$, ω_{perfect} becomes equal to ω_M.

Recently some double and single crystal spectrometers with very large crystals have been constructed (Knowles, 1959; Lundquist & Nilsson, 1964; Nilsson, 1968; Nilsson, Falkström & Boreving, 1968). Some of these crystals have sizes up to 70×100×6 mm^3. Investigations of germanium 220 with common X-rays and a small focal spot gave indications of a perfect crystal. However, 122, 244, and 344 keV gamma rays from ^{152}Eu gave integrated intensities indicating an increasing mosaic behaviour. $R_{\text{exp}}/R^{\text{mosaic}}_{\text{theor}}$ is 0·1 for 122 keV and 0·5 for 344 keV indicating this behaviour. The experimental diffraction width was approximately 27 sec of arc, which is in good agreement with the rough estimate of ω_M which gave 35 sec of arc.

These results indicate that even if the counting system is very accurate, it is necessary to study the degree of perfection of the crystal used in a better way than has been done hitherto. Otherwise large errors can be introduced.

Another source of inaccuracy is the fluorescent radiation from the crystal to be investigated. In order to point out its influence I want to report some results from a study of the atomic scattering factor of germanium around the Ge K edge.

A beam from an X-ray tube contains, in addition to the characteristic lines, a continuous spectrum of wavelengths above a minimum wavelength $\lambda_{\min} = \dfrac{12{\cdot}4}{U}$ Å which is determined by the tube voltage U in kV. When $\lambda_{\min}$ is less than the wavelength of a critical absorption

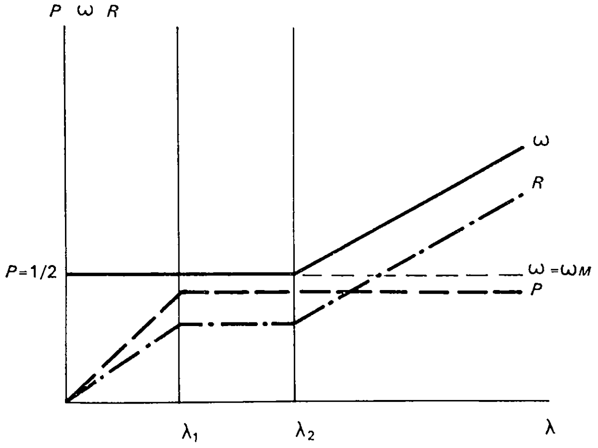

Fig. 1. The qualitative behaviour of P, ω and R as a function of wavelength in the Laue case. For $\lambda > \lambda_1$ the present reflexion P is $\frac{1}{2}$. Above $\lambda = \lambda_2$ the half-width of the diffraction pattern of a perfect crystal is larger than the discussed mosaic half-width ω_M.

edge for the crystal struck by the beam, fluorescent radiation is excited. The Bragg reflected radiation from a single crystal is then superimposed on a background consisting mainly of two contributions: diffusely scattered radiation and characteristic fluorescent radiation. The latter contribution is the most important when investigations are made in the vicinity of an absorption edge. The total intensity and the spectral distribution of the background may vary widely depending on the crystal, the X-ray tube voltage and other experimental conditions.

The unwanted background radiation (scattered and fluorescent) can be reduced by pulse height discrimination. A thorough discussion of this is given for example by Dowling, Hendee, Kohler & Parrish (1956) where the diffraction pattern of iron powder obtained with Cu $K\alpha$ radiation is selected as a rather difficult case. The efficiency of pulse height discrimination in suppressing the unwanted Fe K radiation ($\lambda_{\text{Fe}\ K} = 1{\cdot}74$ Å) when the window is set for Cu $K\alpha$ (1·54 Å) will depend on the energy resolution of the counter. For a symmetrical analyser window setting the ratio of detection efficiencies Cu $K\alpha$/Fe K is 1·6 for a proportional counter and 1·2 for a scintillation counter. For an asymmetrical setting the figures are 25 and 4·1 respectively. Hence a large reduction of the undesired fluorescent radiation is not possible with a scintillation counter.

The present observations of the influence of the fluorescent radiation were made in connexion with the measurement of integrated intensities for thick germanium crystals in the Bragg–Laue case. The intensities are small and therefore the most suitable counter is the scintillation counter because of its high quantum counting efficiency and its almost uniform spectral response in the wavelength region 0·2–2·5 Å. Using this counter it is not, however, possible to eliminate the undesired fluorescent radiation by pulse height discrimination when working close to the K-absorption edge. Far from the absorption edge, using strong emission lines and weak continuous radiation, the background contributions are negligible but the use of emission lines just below the absorption edge will produce strong fluorescence and the contribution from fluorescent radiation will be large. It is thus necessary to determine this contribution in order to correct the experimental results (*e.g.* Brogren, 1962).

The fluorescent radiation can also be used for different experiments. Batterman (1964), for example, measured the fluorescence scattering as well as the diffracted beam as a germanium crystal was rotated through the Bragg reflexion region and obtained direct evidence for the formation of the two types of standing-wave fields formed within the crystal during the diffraction process. Annaka (1967) has made a similar investigation for the Laue reflexion case for perfect germanium crystals.

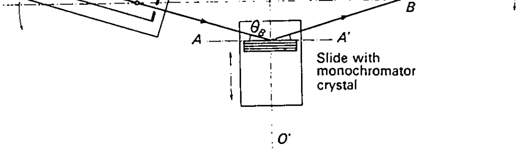

Fig. 2. Schematic drawing of the single-crystal spectrometer.

For our purpose the 220 germanium reflexion and radiation from an X-ray tube with a tungsten target were used. A sketch of the spectrometer is shown in Fig. 2. A description of the equipment has been given previously (Brogren, 1951; Brogren, Efimov, Laussen & Persson, 1968). For the monochromator crystal, a germanium single crystal with the (220) planes parallel to the surface was used. The X-ray tube and the collimator are mounted on a plate that can be revolved around an axis H. By turning the plate, the angle between the direction OO' and the X-ray beam is changed. Consequently, the conditions for Bragg reflexion will be changed. Only radiation of the corresponding wavelength will be reflected. For every wavelength, the position of the crystal on the axis OO' can be calculated so that the X-ray beam will always be incident upon the same spot on the crystal. Wavelengths within the range 0·800–1·700 Å were used.

When $\lambda_{\min}$ is less than the wavelength λ_K of the critical K edge for germanium (1·117 Å), fluorescent radiation is excited, only Ge K radiation being of any importance since the L fluorescent radiation ($\lambda_{L_I} = 8{\cdot}77$ Å) will be completely absorbed by the air. The K fluorescent radiation is emitted in all directions from the part of the crystal struck by the incident beam and is measured together with the Bragg reflected beam by the scintillation counter. From the uniform distribution in space of the fluorescent radiation, it follows that its value will be proportional to the area of the slit S in front of the counter. One way to decrease the contribution from the fluorescent radiation is to decrease this area. In some cases this is impossible because of the nature of the physical problem. Sometimes it is easier to measure the fluorescent radiation than to alter the experimental conditions so that its influence will be negligible.

In the present case the width of the slit was 3·5 mm and the height 10 mm. This choice was made to provide optimal conditions for the measurement of integrated intensities for thick germanium crystals in the Bragg–Laue case.

For the measurement of the fluorescent radiation, the counter was rotated away from the position for the measurement of the Bragg reflected beam. The angle turned had to be larger than $\varphi = \frac{S}{l} = \frac{3{\cdot}5}{190} \simeq 0{\cdot}018\ \text{rad} \simeq 1^\circ$, where S is the slit width and l the distance between the crystal and the counter. In the present case an angle of 3·5° was arbitrarily chosen. Measurements were made on both sides of the Bragg reflected beam. The mean value of these two recordings was taken as the intensity of the fluorescent radiation.

The influence of wavelength, tube voltage, tube current and size of the pulse height analyser window on the relative value of the fluorescent radiation was investigated. For every wavelength the window was set symmetrically around the maximum of the pulse amplitude distribution.

In Fig. 3, the contribution of the fluorescent radiation to the Bragg reflected beam, $\frac{I_f}{I_0-I_f}$, is plotted as a function of the wavelength λ_B. I_f is the intensity of the fluorescent radiation, (I_0-I_f) the intensity of the Bragg reflected beam and λ_B the wavelength that satisfies the Bragg conditions. The tube current, I, was 30 mA and the voltages, U, 30, 24, 20 and 16 kV respectively. The size of the pulse height analyser window was constant. As can be seen in this Figure, the relative value of the fluorescent radiation is strongly dependent on λ_B. The value is large for wavelengths where continuous radiation is used and is small for emission lines. This is to be expected from the non-uniform distribution of energy in the spectrum from the tungsten target.

The function $f=\frac{I_f}{I_0-I_f}=f(I)_{\substack{U=\text{const}\\ \lambda_B=\text{const}}}$ is constant.

In Fig. 4, the absolute values of (I_0-I_f) and I_f are plotted as a function of the wavelength λ_B. The tube current and voltage were kept constant ($I=30$ mA, $U=30$ kV) as well as the size of the window of the pulse height analyzer. It is obvious that the marked change of the value of $\frac{I_f}{I_0-I_f}$ is connected with the distribution of intensity in the tungsten spectrum. The fluorescent radiation is almost constant in the wavelength interval 1·10–1·35 Å.

In Fig. 5, the value of f $\left(\text{defined as } \frac{I_f}{I_0-I_f}\right)$ is plotted as a function of the tube voltage for different wavelengths. Tube current and window size were kept constant. The increase of f with increasing voltage is small for short wavelengths and all emission lines. For wavelengths obtained from the continuous spectrum near the K edge, there is a strong dependence of f on the tube voltage.

The present results show that it is necessary to determine the contribution of fluorescent radiation in single-crystal spectrometer investigations. It is just as important in double-crystal spectrometer experiments, since in this case the reflected beam from the first crystal is incident upon the second crystal. This beam will contain some fluorescent radiation and thus the experimental results (per cent reflexion, integrated intensity, *etc.*) must be corrected for the contribution

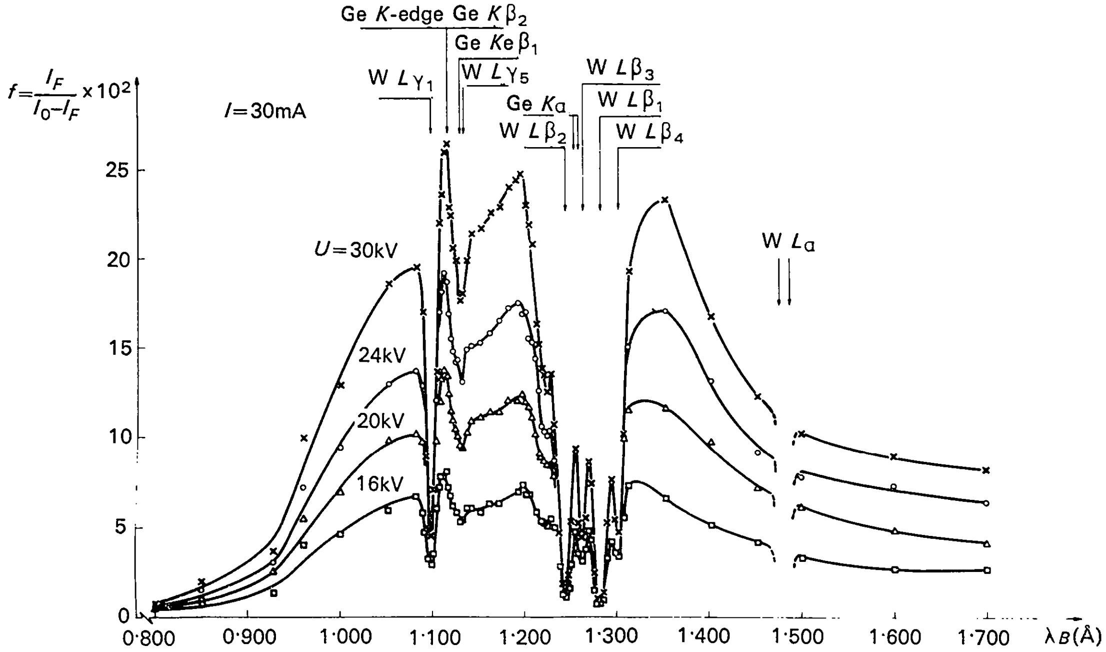

Fig. 3. $\frac{I_f}{I_0-I_f}$ *versus* λ_B for different values of the tube voltage.

from this fluorescent radiation.* Even if the X-ray beam is strongly collimated by various slit systems after the monochromator crystal in order to reduce this contribution, it is necessary to determine its value, since for certain experimental conditions the value can be very large.

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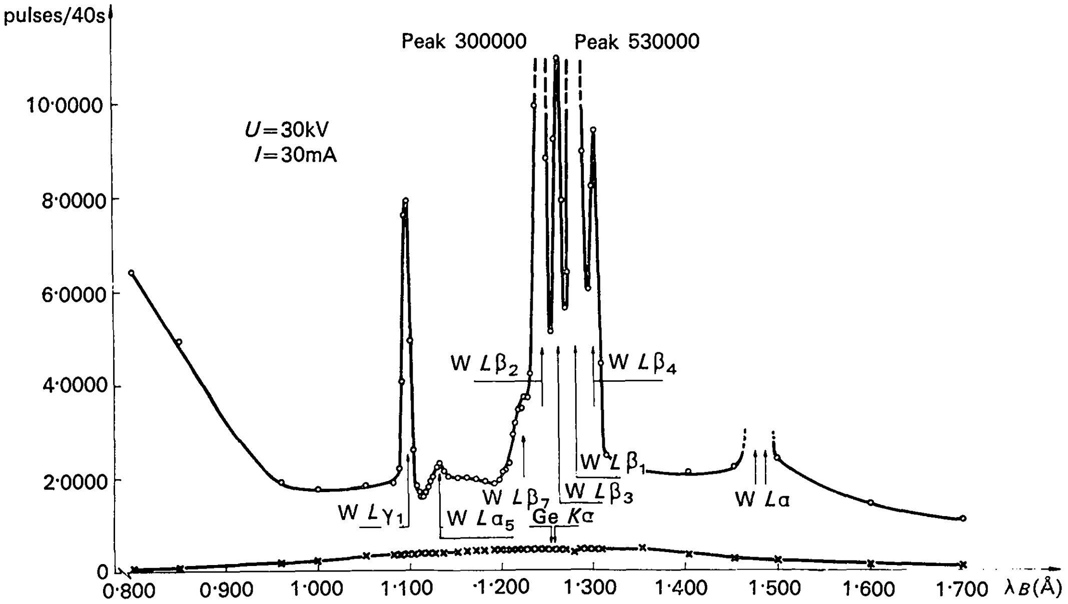

Fig. 4. $(I_0 - I_f)$ (circles) and I_f (crosses) *versus* λ_B.

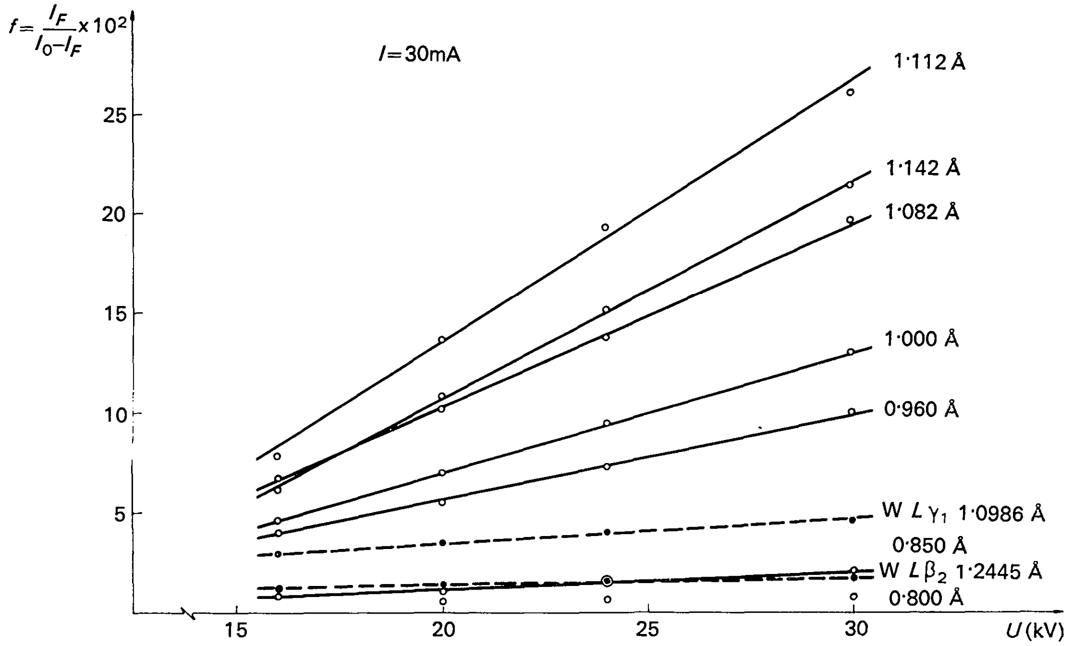

Fig. 5. $\frac{I_f}{I_o - I_f}$ *versus* the tube voltage U for different wavelengths. Continuous lines denote wavelengths from the continuous tungsten spectrum and dashed lines denote emission lines.

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* We do not consider the reflected and excited fluorescent radiation from the second crystal, which in some cases will require additional corrections.

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DISCUSSION

JENNINGS: Have you measured the integrated intensities in Bragg reflexion with a view to obtaining the absolute value of the structure factor?

BROGREN: No. The measurements we are making actually allow a much more sensitive test of various theoretical wave functions than do measurements of the integrated Bragg intensities.

Our measurements were made to determine only the anomalous contribution to the atomic scattering factor. The accuracy demands in our experiments are higher than in experiments where only $|F|$ is sought and where F is not being divided into real and imaginary parts. However, the structure factor values could be derived from our experiments.

JENNINGS: There is at present disagreement to the extent of about 2% as to the integrated Bragg intensity of Ge 111. If you are in a position to make such a measurement easily, it would be most helpful if you could either publish such results or communicate them directly to those who have been active in making such measurements.

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Debye–Waller Factor and Anomalous Absorption (Ge; 293-5°K)

BY J. LUDEWIG

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, Germany

PRESENTED BY G. BORRMANN

Experiments measuring the intensity of three reflexions from a 'very thick' Ge crystal (Laue case) were made, while the temperature of the crystal was lowered from 293 to 5°K. The variation of the intensity agreed with the dynamic theory, when the Debye temperature Θ, used for the evaluation of the Debye–Waller factor, was assumed to be 290°K throughout the temperature range. This result may suffer some slight correction in the future, but there is no variation of Θ at 20°K. Θ = constant contrasts with the specific heat data of Θ but essentially agrees with Batterman & Chipman's prediction.

The absorption of Ewald waves

The intensity of interfering X-rays transmitted through a 'thick' perfect crystal varies very much with the temperature of the crystal. This is mainly due to the imaginary part of the scattering factor, so it is a matter of absorption. All the wave fields produced under the condition of Bragg's law, each of them represented by a point (the tiepoint) on the dispersion surface, exhibit different absorption.* The one whose absorption is the weakest we call the least absorbable Ewald wave. Its two components ('two beam case') have equal intensities, its Poynting vector is parallel to the 'reflecting' lattice plane, and its nodal planes coincide with the reflecting lattice planes (in the case of a simple lattice, and, for instance, in the case of the even-numbered planes of the diamond lattice). At the exit surface of a thick crystal, whose reflecting net plane is perpendicular to the surface, the least absorbed Ewald wave will predominate. It will be decomposed, and one of the two beams or both may be measured. For some purposes it is a good approximation to neglect all the strongly absorbed wave fields. An example is our topic. For the final evaluation the well-known formulae of the integrated intensity in both directions were used.

The probability of the photoeffect, the main contribution to the absorption, would be zero, if all the electrons were concentrated in the nodes of the electric field. The thermal vibrations of the atoms and the finite volume of their electron cloud prevent the absorption from disappearing. The dynamic theory accounts for these two facts by introducing the factors D_h and W_h

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* At the Cambridge Meeting the name Ewald wave was proposed for such a wave field (see Ewald, 1917).