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Harmonic reflexions with a camera of the Guinier type. By J. GOODYEAR and W. J. DUFFIN, *Department of Physics, The University, Hull, England*

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In powder cameras of the Guinier type it is common practice to employ a quartz crystal for the focusing monochromator, and for most applications use is made of the $K\alpha$ radiation reflected in the first order from the 10.1 face of the crystal. The chief disadvantage of quartz is that the intensity of the second-order reflexion is relatively large; consequently the reflected radiation contains not only the $K\alpha$ component, of wavelength λ say, but also a harmonic of wavelength $\frac{1}{2}\lambda$, which is selected from the continuous radiation. Thus the powder pattern consists both of λ and $\frac{1}{2}\lambda$ reflexions and the latter, if misinterpreted as being due to $K\alpha$ radiation, correspond to apparent spacings twice those of the lattice planes from which they originate. The strengths of the $\frac{1}{2}\lambda$ lines may be sufficiently great to give misleading results in the interpretation of a powder pattern, particularly if their true nature is unsuspected.

In the camera designed by de Wolff (1948) the transmission method is used, the incident beam making an angle of 60° with the surface of the powder layer. With this kind of camera, employing Co $K\alpha$ radiation with a tube voltage of 45 kV., experimental values of the ratio of the intensity of $\frac{1}{2}\lambda$ reflexions to those of corresponding λ reflexions have been determined for powder specimens of fluorite and quartz. These results are shown in Table 1,

Table 1. *Powder data*

Specimen	$\mu_\lambda t$	Reflexion *hkl*	θ_λ (°)	$(I_{\frac{1}{2}\lambda}/I_\lambda)_{\text{obs.}}$	Rx'
Fluorite	2·43	111	16·5	0·053	0·052
		220	27·7	0·051	0·056
Quartz	0·56	10·1	15·5	0·010	0·009

and they suggest that the intensity of a $\frac{1}{2}\lambda$ reflexion may be diminished by reducing the value of $\mu_\lambda t$ for the specimen, t being the thickness of the specimen and μ_λ its linear absorption coefficient for the $K\alpha$ radiation. The dependence of the intensity ratio on $\mu_\lambda t$ can readily be calculated for the particular geometry of the de Wolff camera.

The recorded integrated intensity of a reflexion for X-rays of wavelength λ is proportional to $I_0\lambda^3 f_1(\theta)A$. Here I_0 is the intensity of the $K\alpha$ component in the incident beam, A is the absorption factor for the powder specimen and

$$f_1(\theta) = (1+\cos^2 2\theta' \cos^2 2\theta)\operatorname{cosec}^2\theta \sec\theta \sec(2\theta-\gamma)\,,$$

θ' being the Bragg angle for the monochromator and γ the angle between the incident beam and the normal to the specimen layer. The absorption factor is given by

$$A = tf_2(\theta, \mu_\lambda t) = t\left[\frac{\sin(2\theta+\alpha)}{\sin\alpha-\sin(2\theta+\alpha)} \times \frac{\exp\{-\mu_\lambda t \operatorname{cosec}\alpha\}-\exp\{-\mu_\lambda t\operatorname{cosec}(2\theta+\alpha)\}}{\mu_\lambda t}\right],$$

where α is the angle between the incident beam and the specimen surface; in the special case when $2\theta = 180°-2\alpha$, $f_2 = \operatorname{cosec}\alpha\exp(-\mu_\lambda t\operatorname{cosec}\alpha)$ (see Brindley, 1955). If x be the ratio of the intensity of the $\frac{1}{2}\lambda$ radiation to that of the $K\alpha$ radiation in the incident beam, then for a particular set of lattice planes the ratio of the recorded integrated intensity of the $\frac{1}{2}\lambda$ reflexion to that of the λ reflexion is given by

$$\frac{I_{\frac{1}{2}\lambda}}{I_\lambda} = \frac{x}{8}\frac{[f_1f_2]_{\frac{1}{2}\lambda}}{[f_1f_2]_\lambda} = Rx, \quad \text{say}\,. \qquad (1)$$

Clearly when $\mu_\lambda t \ll 1$, $(f_2)_\lambda$ and $(f_2)_{\frac{1}{2}\lambda}$ tend to cosec α and $R = \frac{1}{8}(f_1)_{\frac{1}{2}\lambda}/(f_1)_\lambda$.

The variation of $f_2(\theta, \mu t)$ with μt for $\alpha = 60°$ is shown in Fig. 1(*a*). Calculations of R for different values of $\mu_\lambda t$ and θ_λ, the Bragg angle for a λ reflexion, are represented graphically in Fig. 1(*b*); these results are for Co $K\alpha$ radiation and for $(\mu_m)_{\frac{1}{2}\lambda}/(\mu_m)_\lambda = 0{\cdot}14$, μ_m being the mass absorption coefficient of the powder specimen. Since for many minerals the ratio of the mass absorption coefficients is nearly 0·14 for Co $K\alpha$ and Cu $K\alpha$ radiations, the curves shown in Fig. 1(*b*) should apply reasonably well to both, even though a slight difference arises through the θ' term in $f_1(\theta)$.

Before equation (1) can be compared directly with the ratio of the blackenings of corresponding λ and $\frac{1}{2}\lambda$ lines on a powder photograph, two points need to be considered. In the first place the film, in general, will absorb a greater proportion of incident energy of wavelength λ than of wavelength $\frac{1}{2}\lambda$, and consequently, for the range of wavelengths considered here, the measured ratio of the integrated intensities will be less than that predicted by equation (1). The effect can be taken into account by setting $(I_{\frac{1}{2}\lambda}/I_\lambda)_{\text{obs.}} = Rx'$, x' being a proportionality factor which is less than x. Secondly, the λ and $\frac{1}{2}\lambda$ diffracted beams are incident on the film at different angles, in the de Wolff arrangement the angle between a reflected beam and the film being given by $i = 120°-2\theta$, and clearly the greater the obliquity of incidence the greater will be the blackening of the film. For the range of 2θ values 0–60° the work of Cox & Shaw (1930) suggests that the blackening can be reduced to correspond approximately to the case of normal incidence simply by multiplying the measured value by $\sin i$. The observed values of $I_{\frac{1}{2}\lambda}/I_\lambda$ given in Table 1 have been corrected for the obliquity effect, and taking a value for $x' = 0{\cdot}01$ the calculations account for them reasonably well. The agreement is sufficiently good to suggest that the curves of Fig. 1(*b*) may be used to predict the extent to which $\frac{1}{2}\lambda$ reflexions appear.

The $\frac{1}{2}\lambda$ reflexions can be eliminated completely by reducing the voltage on the X-ray tube, but this procedure is not usually recommended since the exposure time is greatly increased. With the usual optimum applied voltage, $\frac{1}{2}\lambda$ reflexions can be minimized by keeping the value of $\mu_\lambda t$ for the specimen as small as possible. It seems that a value of $\mu_\lambda t = 1$ would not be too serious, since in this circumstance only the strongest $\frac{1}{2}\lambda$ reflexions would be

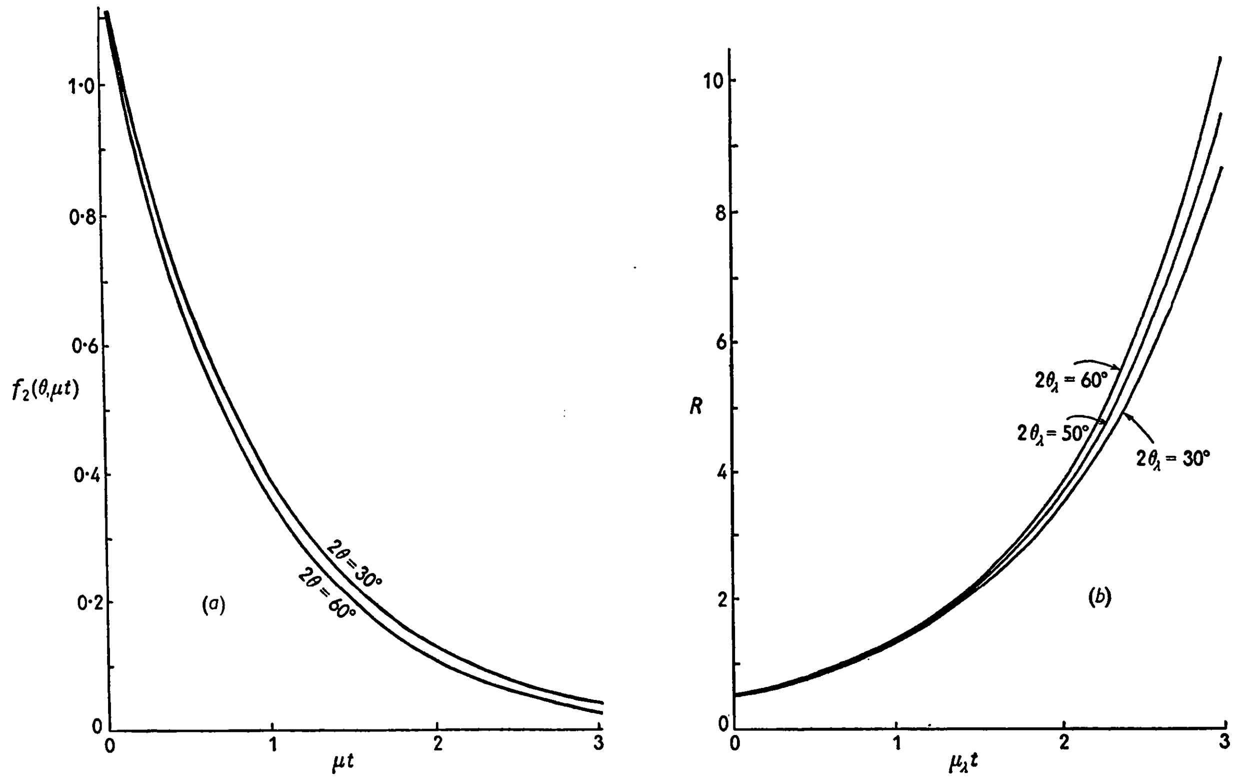

Fig. 1. (a) Variations of $f_2(\theta, \mu t)$ with μt for $\alpha = 60°$. Curves for $2\theta = 10°$, $20°$, $40°$ and $50°$ lie between curves for $2\theta=30°$ and $60°$. (b) Variation of R with $\mu_\lambda t$ for $(\mu_m)_{\frac{1}{2}\lambda}/(\mu_m)_\lambda=0{\cdot}14$. Curves for $2\theta_\lambda=10°$, $20°$ and $40°$ lie close to curve for $2\theta_\lambda=30°$.

recorded. This arrangement is also convenient because it nearly represents the condition for minimum exposure time to record λ reflexions over a range of Bragg angle from 0° to 45°.

Finally, although this investigation has been related to the geometry of the de Wolff camera, no doubt the general conclusions reached will apply to any Guinier-type camera incorporating a quartz-crystal monochromator.

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Neutron magnetic scattering factors in the presence of extinction.

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One of us has recently proposed a scheme for determining a crystal structure factor in the presence of extinction by the use of polarized X-rays (Chandrasekhar, 1956). The ability to obtain polarized neutrons offers similar possibilities in magnetic substances. Consider a crystal in which the extinction is less than 20% being irradiated with monochromatic neutrons. The integrated reflexion can be written as

$$R^\theta = \alpha|F|^2-\beta|F|^4\,,$$

where

$$\alpha = \frac{V\lambda^3 e^{-2W} e^{-N\sigma\bar{t}}}{V_0^2 \sin 2\theta}\,,$$

and β involves certain geometrical factors which determine the amount of extinction present. Here

V = volume of the crystal,
e^{-2W} = Debye–Waller temperature factor,
$e^{-N\sigma\bar{t}}$ = beam attenuation factor due to absorption, etc.,
V_0 = unit cell volume,
F = structure factor.

The structure factor F is the sum of the nuclear and magnetic structure factors F_N and F_P. If the neutrons are polarized, it can be arranged so that F_P is either positive or negative. For the two cases