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The absorption of X-rays by photographic films. By MICHAEL G. ROSSMANN, *Department of Chemistry, The University, Glasgow W. 2, Scotland*

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Generalized projections have recently been used by the writer to determine the distortion of some aromatic hydrocarbons. The study by Grenville-Wells (1955) of the variation of the film factor (for Cu $K\alpha$ radiation) of Ilford G Industrial X-ray film with the angle of incidence has been most useful in the intensity estimation of non-equatorial layer-line reflexions. The considerable difference between observed and calculated film factors, found by Grenville-Wells, appears to be larger than the likely experimental error. This discrepancy may possibly be due to neglecting the absorption of energy by the photo-chemical effect (Cox & Shaw, 1930).

It is difficult to estimate the loss of intensity from an X-ray beam due to this cause. Let us therefore assume as a very rough first approximation that this loss is proportional to the incident intensity I_0 . Hence the intensity of the X-rays, after passing through a film, is

$$I = I_0(1-C) \exp[-\mu t \sec \nu],$$

where C is the constant of proportionality determined by the nature of the photographic emulsion, μt is the sum of the separate products of the linear absorption coefficients with the thicknesses of black paper, emulsion and film base, and ν is the angle the incident X-rays make with the normal to the film.

Therefore the film factor is given by

$$R = \frac{I_0}{I} = \left(\frac{1}{1-C} \right) \exp[\mu t \sec \nu]$$

(C was assumed equal to zero in Grenville-Wells's analysis).

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On the visual estimation of X-ray reflexion intensities from upper-level Weissenberg photographs. II. Charts for the correction of reflexion spot extension. By D. C. PHILLIPS,* *Division of Pure Physics, National Research Council, Ottawa, Canada*

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The extension and contraction of X-ray reflexion spots recorded on normal-beam and equi-inclination-angle upper-level Weissenberg photographs was discussed in Part I (Phillips, 1954), where it was shown that for a well adjusted instrument and a crystal with length l given by

$$S > l > S\mathfrak{R}_1/(\mathfrak{R}_1 + \mathfrak{R}_2) \quad (28)$$

the fractional increase in area of an extended reflexion spot is given by

$$W = \frac{A + \Delta A}{A} = 1 + \frac{180}{\pi} \cdot \frac{\zeta}{\{4\zeta^2 - (\zeta^2 + \xi^2)\}^{\frac{1}{2}} \{\mathfrak{R}_1/(1 - \zeta^2)^{\frac{3}{2}} + \mathfrak{R}_2\}} \quad (29)$$

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A good straight line was obtained on plotting $\ln R$ against $\sec \nu$, when the experimental results of Grenville-Wells were used. From this graph the constants C and μt were determined. It was thus found that the variation of R with ν could best be represented by

$$R = 1.29 \exp[0.942 \sec \nu].$$

The values of R calculated according to this equation are given in Table 1. The discrepancy between observed

Table 1

ν (°)	sec ν	R (obs.)	G.-W.'s R (calc.) i.e. $C=0$		
			R (calc.) $C=0.225$ $\mu t=0.942$	$\mu t=1.20$	$\mu t=1.15$
0.0	1.000	3.33	3.31	3.20	3.05
6.6	1.007	3.33	3.33	3.35	3.18
13.8	1.030	3.33	3.40	3.44	3.27
20.8	1.070	3.64	3.54	3.61	3.42
28.4	1.137	4.00	3.76	3.92	3.69
35.1	1.222	~4.00	4.08	4.34	4.08
45.8	1.434	5.00	4.98	5.60	5.21
57.0	1.836	7.50	7.28	9.06	8.25

and calculated values is 2.2%, while the two suggested fits to Grenville-Wells's equation give discrepancies of 8.4% ($\mu t = 1.20$) and 6.0% ($\mu t = 1.15$).

References

- COX, E. G. & SHAW, W. F. B. (1930). *Proc. Roy. Soc. A*, **127**, 71.
GRENVILLE-WELLS, H. J. (1955). *Acta Cryst.* **8**, 512.

for photographs taken in the normal-beam setting, and

$$W = \frac{A + \Delta A}{A} = 1 + \frac{180}{4\pi} \cdot \frac{\zeta(\xi_m^2/\xi^2 - 1)^{\frac{1}{2}}}{\{\mathfrak{R}_1/(1 - \zeta^2/4)^{\frac{1}{2}} + \mathfrak{R}_2\}} \quad (30)$$

for photographs taken in the equi-inclination-angle setting. (S is the diameter of the pinholes in a two-pinhole collimating system; \mathfrak{R}_1 and \mathfrak{R}_2 are respectively the camera radius and the first pinhole-to-crystal distance measured in millimetres; A is the spot area of a reflexion recorded without camera translation and ζ , ξ are conventional reciprocal-lattice coordinates. The equation numbers refer to Part I.) The areas of 'contracted' reflexion spots are not so simply expressed since they reach a minimum value when $\Delta A = A$ and then increase again as ΔA increases, an effect which seems to have been ignored in many investigations.

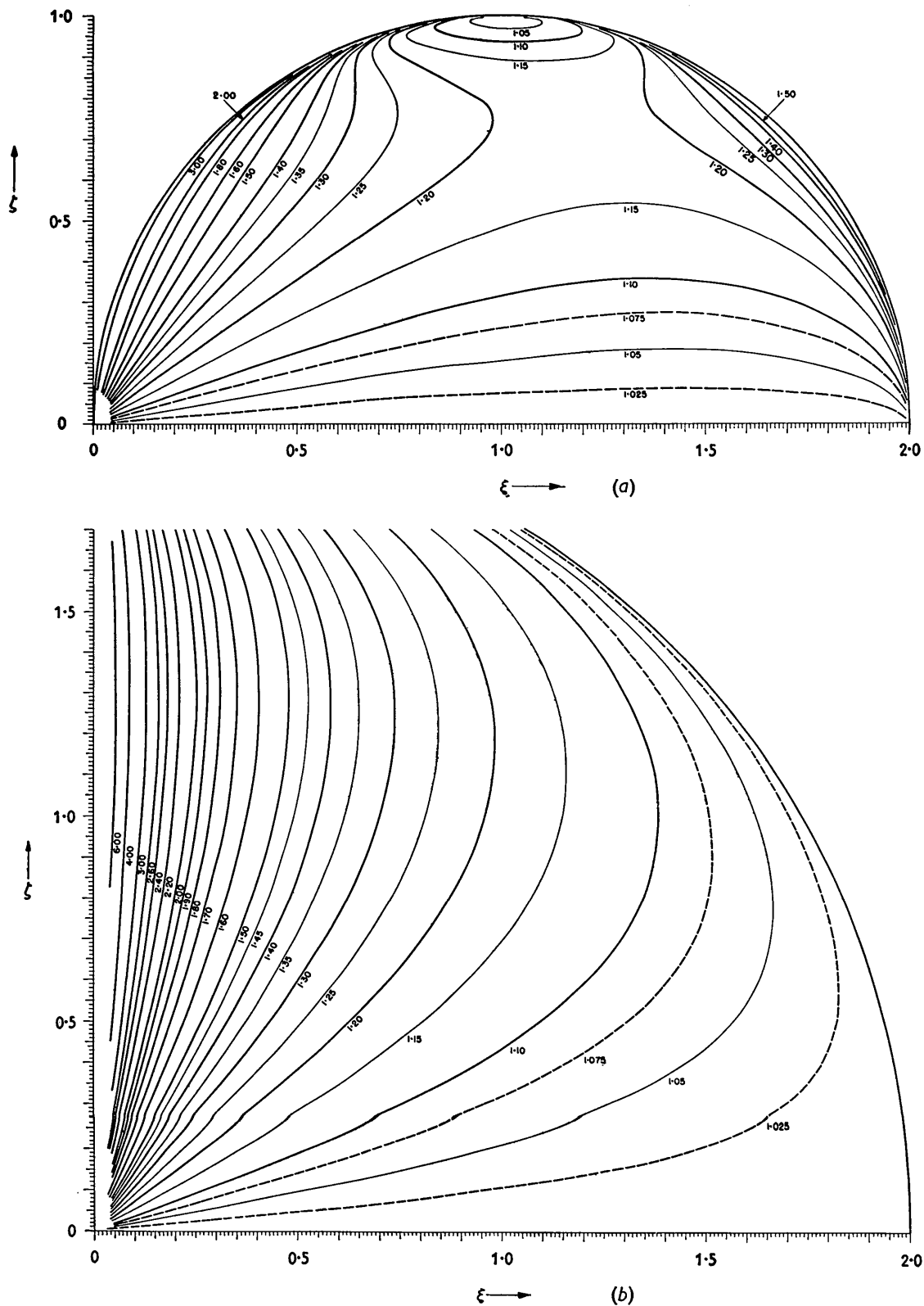


Fig. 1. Curves of constant W in reciprocal space for (a) the normal-beam setting and (b) the equi-inclination-angle setting.

When the distortions are small, $(A + \Delta A)/A$ less than about 1.5, the undistorted intensity can be calculated from the visually estimated intensities of the extended and contracted reflexion spots,

$$I = 2I_E I_C / (I_E + I_C),$$

but when extended and contracted reflexion spots are not both available, as often happens with crystals of low symmetry, and whenever the distortions are severe, it seems best to take into account only the extended spots and to correct the intensities estimated from them by means of the equation

$$I = WI_E,$$

where $W = (A + \Delta A)/A$ is given by (29) or (30).

The charts shown in Fig. 1 give the correcting factors appropriate to all the reflexions which may be recorded in the two crystal settings considered. It is suggested that they can be used in the same way as charts of the Lorentz

and polarization factors (Cochran, 1948; Goldschmidt & Pitt, 1948) in routine correction of visually estimated intensities. The instrumental constants used in their preparation were $\mathfrak{R}_1 = 28.7$ mm. and $\mathfrak{R}_2 = 75.0$ mm., values suitable for use with most commercially available instruments. W in fact does not depend very sensitively on these constants: a simple calculation will show whether the values chosen are nearly enough correct for any particular experimental arrangement.

Copies of the charts, on a scale 10 cm. = 1 r.l.u., can be obtained from the author at the Davy-Faraday Research Laboratory of the Royal Institution, 21 Albermarle Street, London W. 1, England.

References

- COCHRAN, W. (1948). *J. Sci. Instrum.* **25**, 253.
 GOLDSCHMIDT, G. H. & PITT, G. J. (1948). *J. Sci. Instrum.* **25**, 397.
 PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746.

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On the reported inversion of hexagonal to cubic zinc sulphide by grinding. By F. G. SMITH and V. G. HILL, *Department of Geological Sciences, University of Toronto, Toronto, Canada*

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We have been investigating the temperature of stability of zinc sulphide polymorphs, and it became necessary to test whether the hexagonal modifications invert to cubic when crushed, as has been reported by Schleede & Gantzchow (1923), Fuller (1929), Bridgman (1939), Frey (1948), Kullerud (1953), and Stroock (1955).

We found no obvious change in the relative intensities of the first three diffraction spectra of $2H$ zinc sulphide after gentle grinding under alcohol in an agate mortar

from about 40 to about 500 mesh. However, there is a marked change when comminution is carried out by impact in a diamond mortar, using a heavy hammer to drive the piston. After a total of 300 blows, and re-mixing the material after each 10 blows, all of the diffraction spectra became broadened, but the first and third lines decreased nearly to zero, the second increased in intensity, and unresolved spectra appeared at higher angles than the first line. Cubic zinc sulphide treated in a similar way gave a diffraction pattern similar to the above in a qualitative way, as shown in Fig. 1. The change in the diffraction pattern of the cubic material, other than the broadening, is the significant fact.

The diffraction pattern of the two impacted zinc sulphide specimens resemble (except in breadth of spectra) mixtures of complex polytypes which we have made by prolonged sintering of ZnS in NaCl flux at 850–970° C. in evacuated silica glass tubes. Therefore, we consider the impacted material to contain irregular stacking due to glide twinning, analogous to deformation faulting of hexagonal or cubic close-packed metals by cold working. This agrees with data recently reported by Short & Steward (1955).

The hexagonal material cannot be said to invert to cubic during the impact comminution, because cubic material under the same conditions develops some degree of hexagonal packing. Both may be considered to be randomized by the treatment, and if no other energetics were involved, a statistically equal amount of hexagonal and cubic material, over short range, would be developed. However, at room temperature, the free energy of the cubic packing is less than that of the hexagonal packing, and therefore the equilibrium ratio would be expected to be somewhat on the cubic side of equality.

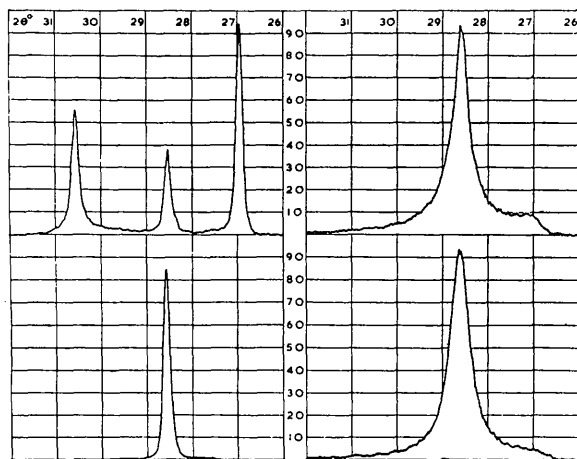


Fig. 1. Tracings of X-ray low-angle diffractograms of zinc sulphide, using Norelco apparatus and Cu K radiation with Ni filter. Top-left is of $2H$ crystalline material and top-right is of the same after hammering. Bottom-left is of $3C$ crystalline material and bottom-right is of the same after hammering.