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,

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

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 $\mathfrak{R}_1 = 28{\cdot}7$ mm. and $\mathfrak{R}_2 = 75{\cdot}0$ 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 Albemarle 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.

Acta Cryst. (1956). **9**, 821

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*

(*Received* 3 *May* 1956 *and in revised form* 14 *June* 1956)

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 Strock (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 remixing 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.

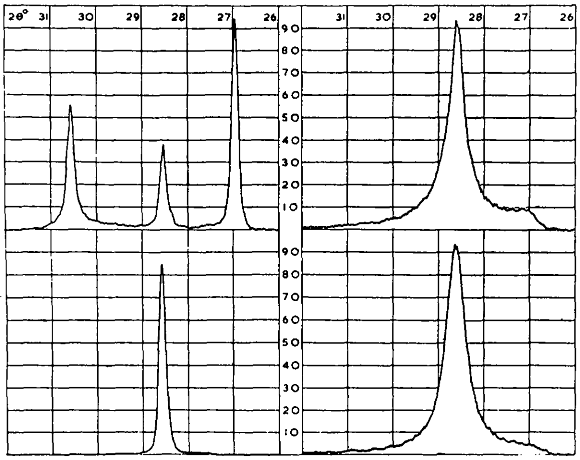

Fig. 1. Tracings of X-ray low-angle diffractograms of zinc sulphide, using Norelco apparatus and Cu K radiation with Ni filter. Top-left is of $2H$ crystalline material and top-right is of the same after hammering. Bottom-left is of $3C$ crystalline material and bottom-right is of the same after hammering.

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.

The ratio of hexagonal to cubic packing in complex polytypes or mixtures may be measured approximately by intergrating all of the specular and diffuse diffraction intensity from, and including, the first line, 10.0, up to, but not including the second, $00.1+10.\frac{1}{3}$ (unit layer indices), and taking the ratio of this to the integrated intensity of the second line (Smith, 1955). The change of this ratio with change in the ratio of packing is assumed to be the same as for mechanical mixtures of hexagonal ($2H$) and cubic ($3C$) material. Using this method, the weight percentage of cubic packing in the two starting materials and the two impacted materials were calculated. The results are:

	Weight % cubic packing (approximate)
Hexagonal phase	0
Same after hammering	61
Cubic phase	93
Same after hammering	76

Paterson (1952) calculated that deformation faulting of a cubic close-packed structure should cause broadening of the diffraction spectra, and certain shifts of peak angles. The simplest shifts are of the 200 reflection to smaller Bragg angle, and of 400 to larger angle. A measurement of the cubic starting material and the same after hammering showed that the 200 reflection was broadened 0·44° (2θ) and shifted 0·1° (2θ) to lower angle. Similarly, the 400 reflection was broadened 1·0° (2θ) and shifted 0·1° (2θ) to higher angle. Therefore the sense of the shifts of diffraction angle are in accord with deformation faulting deduced from the qualitative change in the diffraction pattern itself. However, the large amount of broadening suggests that in part this may be due to small size of the crystals in the hammered material.

Assuming tentatively that all of the broadening of the second diffraction spectrum ($00.1+10.\frac{1}{3}$) is due to the size effect, and using an approximate method of calculation given by Klug and Alexander (1954), the mean size of particles is 240 Å in the material originally cubic, and 330 Å in the material originally hexagonal.

The grain size is too small for optical resolution, but examination of electron photomicrographs of the two hammered specimens indicated that the mean sizes are at least five times the above calculated values. Evidently much of the broadening of the diffraction spectra is due to the size effect, but some is due to deformation faulting (glide twinning).

We conclude that impact grinding of zinc sulphide randomizes the structure by deformation faulting and, independent of the starting material (cubic or hexagonal), a similar product is obtained.

References

BRIDGMAN, P. W. (1939). *Amer. J. Sci.* **237**, 7.

FREY, F. (1948). *Ann. Phys., Lpz.* **2**, 147.

FULLER, M. L. (1929). *Phil. Mag.* (7), **8**, 658.

KLUG, H. P. & ALEXANDER, L. E. (1954). *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, chap. 9. London: Chapman and Hall.

KULLERUD, G. (1953). *Norsk geol. Tidsskr.* **32**, 61.

PATERSON, M. S. (1952). *J. Appl. Phys.* **23**, 805.

SCHLEEDE, A. & GANTZCHOW, H. (1923). *Z. phys. Chem.* **106**, 37.

SHORT, M. A. & STEWARD, E. G. (1955). *Acta Cryst.* **8**, 733.

SMITH, F. G. (1955). *Amer. Min.* **40**, 658.

STROCK, L. W. (1955). *Sylvania Techn.* **8**, 71.

Acta Cryst. (1956). **9**, 822

Crystal data for two new coordination compounds.

By MORTIMER I. KAY and LEWIS KATZ, *Department of Chemistry, University of Connecticut, Storrs, Connecticut, U.S.A.*

(*Received* 25 *June* 1956)

Murmann (1956) has recently prepared two new coordination compounds: bis-(3-amino-3-methyl-2-butanone oxime)nickel(II) perchlorate and the corresponding palladium compound. The similarity of oscillation, Weissenberg, and precession photographs for crystals of the two compounds indicates they are isomorphous. The space group is $P2_1/c$. For the nickel compound

$$a = 13{\cdot}0\pm0{\cdot}1,\ b = 12{\cdot}75\pm0{\cdot}1,\ c = 20{\cdot}9\pm0{\cdot}1\ \text{Å},\quad \beta = 105^\circ\ 59'\pm30'\ .$$

For the palladium compound

$$a = 13{\cdot}0\pm0{\cdot}1,\ b = 12{\cdot}85\pm0{\cdot}1,\ c = 21{\cdot}2\pm0{\cdot}1\ \text{Å},\quad \beta = 105^\circ\ 52'\pm30'\ .$$

Each unit cell contains eight formula weights (calculated from density measurements: 7·95).

Crystals grown from water solution are elongated in the a direction. All of the crystals examined were twinned. The twinning does not become obvious in the form of 'spot splitting' on Weissenberg photographs about a until the second level. The first-level photographs appear normal since $10l$ spots from one individual lie very nearly half way between $10l$ spots from the other, and remaining $1kl$ spots are nearly coincident in pairs; the zero-level appears altogether normal. One twinned individual can be isolated fairly well by cutting with a razor blade.

Although several interesting questions could be answered by complete structure determinations of these compounds, the apparent necessity for three-dimensional methods from the outset has decided us against making the attempt.

We are grateful to Research Corporation for a grant-in-aid.

Reference

MURMANN, R. K. (1956). *J. Amer. Chem. Soc.* To be published.