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X-ray powder diffraction data for hexagonal zinc sulphide.*

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1. Introduction

In the volume of X-ray powder diffraction data prepared by Swanson & Fuyat (1953), spacings and intensities were given for thirty inorganic substances, including hexagonal zinc sulphide. These data were recommended for replacement of existing cards in the A.S.T.M. *Index* and, in fact, have been incorporated in the fifth supplement of that *Index* as of 'high reliability'.

The new intensity data for hexagonal zinc sulphide given by Swanson & Fuyat (Table 1) differ from the relative intensities usually observed in powder photographs. Furthermore, the values disagree with those calculated by Blake (1934) and also with previously published experimental data (Aminoff, 1923; Ulrich & Zachariasen, 1925; Fuller, 1929; Hanawalt, Rinn & Frevel, 1938; Frey, 1948), the more recent of which are given in Table 1.

Because of this general lack of agreement, and in view of the recently revived interest in the crystal structure of this substance, we have made measurements on powder photographs of hexagonal zinc sulphide and have recalculated the theoretical intensities.

2. Powder diffraction measurements

The sample of zinc sulphide used had been heat treated at a temperature which yielded only hexagonal crystals. The powder was examined under the polarizing microscope, and the average size of the crystals, all of which were uniformly anisotropic, was found to be in the region of 25μ. The powder was diluted with gum tragacanth to reduce absorption errors to a minimum, and was coated on a thin Lindemann glass fibre.

A 19 cm. diameter Unicam powder camera was used with Cu $K\alpha$ radiation, and microdensitometer traces were obtained for the first nine reflexions. An intensity scale was used to calibrate the microdensitometer, and subtraction of background level was made in the usual way.

A number of photographs were measured and some spread in the relative intensities was obtained; the average intensities are given in Table 1.

3. Calculated intensities

Intensities were calculated for the various reflexions measured experimentally, using not only the usually accepted sulphur parameter $u = 0{\cdot}375$ (Wyckoff, 1951) (Table 1), but values slightly on either side of this (Table 2). Atomic scattering factors for unionized zinc and sulphur were those given by James & Brindley (1931) and Viervoll & Ögrim (1949) respectively. No correction was made for temperature.

4. Discussion

From Table 1, it can be seen that there is good agreement between our calculated and measured intensities. It is to be noted that the calculated values differ from those of Blake (1934), who was found to have used incorrect multiplicity factors; if these are corrected (Table 1), good agreement is obtained between the two sets of results.

Our observed values differ to varying extents from those of the more recent investigators (Swanson & Fuyat, 1953; Frey, 1948; Hanawalt *et al.*, 1938) which are, in any case, not in agreement with one another.

Of earlier authors, Aminoff (1923) has given observed intensities, Fuller (1929) and Ulrich & Zachariasen (1925) have given calculated and observed intensities. These are all quite different from those given in the more recent papers already referred to.

In view of the close agreement between our observed

Table 1. *Powder diffraction data for hexagonal zinc sulphide*

(Intensities are scaled relative to 100 for the $10\bar{1}0$ reflexion)

	Swanson & Fuyat (1953)	Blake (1934); absorption factor omitted		Hanawalt *et al.* (1938)	Frey (1948)	Swanson & Fuyat (1953)	This investigation		
hkil	*d* (Å)	$I_{\text{calc.}}$	$I_{\text{calc.}}$ corrected*	$I_{\text{obs.}}$	$I_{\text{obs.}}$†	$I_{\text{obs.}}$	$I_{\text{calc.}}$	$I_{\text{obs.}}$	$I_{\text{obs.}}$‡
$10\bar{1}0$	3·309	100	100	100	100	100	100	100	95
0002	3·128	31·1	62	47	55	86	64	55	52
$10\bar{1}1$	2·925	102·8	103	100	116	84	109	105	100
$10\bar{1}2$	2·273	34·9	35	47	60	29	37	41	39
$11\bar{2}0$	1·911	76·5	76	83	74	74	73	66	63
$10\bar{1}3$	1·764	77·1	77	100	87	52	73	61	58
$20\bar{2}0$	1·654	11·9	12	—	74	10	11	13	12
$11\bar{2}2$	1·630	25·9	52	67		45	48	48	46
$20\bar{2}1$	1·599	16·7	17	33		12	15	19	18

* After correction of erroneous multiplicity factors.
† Average taken from published graphs.
‡ Scaled to 100 for $10\bar{1}1$—the strongest reflexion.

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Table 2. *Effects of various factors on the intensities relative to* $10\bar{1}0$*

hkil	One-dimensional disorder produced by grinding	Grinding, after Frey (1948)	Presence of cubic ZnS	Change in sulphur parameter on calculated values	
				$u=0{\cdot}36$	$u=0{\cdot}39$
$10\bar{1}0$	—	—	—	100	100
0002	*I*	*I*	*I*	55	73
$10\bar{1}1$	*D*	*D*	—	122	98
$10\bar{1}2$	*D*	*D*	—	32	42
$11\bar{2}0$	*I*	*I*	*I*	73	73
$10\bar{1}3$	*D*	*D*	—	79	65
$20\bar{2}0$	—	*I*	—	11	11
$11\bar{2}2$	*I*		*I*	41	55
$20\bar{2}1$	*D*		—	17	14

* — represents no change, *I* an increase from normal hexagonal ZnS, and *D* a decrease from normal hexagonal ZnS.

and calculated intensities, it appears likely that the observed intensities referred to above are in error. The discrepancies may originate from a number of different factors some of which will now be briefly discussed.

The occurrence of one-dimensional disorder in the hexagonal (wurtzite) structure (Frondel & Palache, 1950; Strock & Brophy, 1955) is observed, for example, in crystals which have been cooled at a rate intermediate between the quenching necessary for the preservation of the hexagonal form and the slow cooling necessary for the formation of the cubic form (Kremheller, 1955). Partial disorder of this type results in changes in the relative intensities.

Any particular sample may also include some material of purely cubic structure, which is the stable form at room temperature and may well be formed in the course of preparation. In addition, it is known that grinding can result in the transformation from hexagonal to cubic (Schleede & Gantzckow, 1923; Frey, 1948). In preparing the data in the second column of Table 2, X-ray powder photographs were taken of hexagonal material submitted to successively severe grinding, and it was observed that the gradual appearance of cubic material appeared to be associated with progressive one-dimensional disordering of the parent wurtzite structure.

The effects on relative intensities of (1) hexagonal zinc sulphide having a disordered structure and (2) the presence of cubic zinc sulphide, are shown in Table 2. Comparison of Tables 1 and 2 shows that the presence both of partially disordered material and of cubic material would explain the discrepancy between Swanson & Fuyat's results and our values.

Relative theoretical intensities depend upon an assumed sulphur parameter, and the effects due to both increase and decrease in this parameter are included in Table 2. It can be seen that an incorrect value would not alone account for the differences between the observed values of, for example, Swanson & Fuyat and the calculated values.

Non-equiaxed crystals can lead to preferred orientation in the specimen used in the X-ray examination, and this would, of course, affect the relative intensities. This factor may be particularly significant in measurements made by counter diffractometer methods. In the photographic method used by the authors, the crystals comprising the powder were approximately uniform in size in all directions and no orientation effects should have been introduced.

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A variation on the σ-phase structure: the crystal structure of the *P* phase, Mo–Ni–Cr.*

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The *P* phase is one of several ternary alloys of transition-group metals discovered by Rideout, Manly, Kamen, Lement & Beck (1951). In the system Mo–Ni–Cr it occupies at 1200° C. a region in the ternary diagram in the neighborhood of atom ratio 42:40:18, between a ternary σ-phase region around 27:28:45 and a binary δ-phase region, Mo–Ni, with atom ratio close to 50:50. The crystal structure of the σ phase in some binary systems has been previously described (Shoemaker & Bergman, 1950; Bergman & Shoemaker, 1954; Dickins, Douglas & Taylor, 1951*a*, *b*; Kasper, Decker & Belanger, 1951), and is closely related to the β-uranium structure (Tucker, 1950; Tucker & Senio, 1953). The crystal structure of the δ phase has not yet been fully solved (Shoemaker, Brink & Fox, work in progress), but, like the *P* phase, it apparently has strong structural relationships to the σ phase.

A specimen of *P* phase of Mo–Ni–Cr of the above

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