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MEASUREMENT OF DISORDER IN ZINC AND CADMIUM SULPHIDES

M. A. SHORT,* AND E. G. STEWARD, *Research Laboratories of the General Electric Company Limited, Wembley, England.*

It is well known that the effect of mechanical work, such as grinding or the application of pressure, is progressively to convert zinc sulphide of initially hexagonal structure towards the cubic structure. In the course of an investigation (1) into the effect of grinding on the structure and luminescence of zinc and zinc-cadmium sulphides, it became necessary to measure the relative amounts of cubic and hexagonal stacking after various times of grinding.

Smith (2) and Wecker (3) have both suggested the use of relative intensities of certain *x*-ray powder reflections for evaluating the hexagonal:cubic stacking ratio. We have used the principle of the method suggested by Smith, but we have found it necessary to make two important modifications to the method as described by him.

METHOD

Smith's method is based upon consideration of the *x*-ray powder reflections that should be obtained from a number of different zinc sulphide polytypes. In the hexagonal-cubic transformation through the intermediate polytype structures, reflections from the (10.0) planes tend to extinguish, and a number of 10.*l* reflections appear between the 10.0 and 00.2 reflections (Fig. 1). Smith showed, by approximate calculation, that the value of the intensity of the 10.0 reflection plus the intensity of the polytype reflections *between* 10.0 and 00.2 decrease linearly from 2.04 at the hexagonal limit to zero at the cubic limit relative to the intensity of the combined 00.2 and overlapping polytype reflections, which increases nearly linearly from 1 at the hexagonal limit to 4 at the cubic limit (Fig. 1). Consequently Smith suggested using the ratio I(10.0+10.0 to 00.2):I(00.2) as a measure of the hexagonal:cubic stacking ratio. Furthermore, he claimed that his procedure could be applied without modification to mixtures of cubic and hexagonal stacking whether on an atomic or a macroscopic scale, that is, for both random and "ordered" disorder. When the disorder is random, however, as in the case of hexagonal zinc sulphide that has been ground, diffraction patterns of the type Smith suggested to be typical of polytypes or mixtures of polytypes are not obtained. *X*-ray diffraction photographs of hexagonal zinc sulphide after grinding show the following features:

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* Now at the Department of Fuel Technology, Pennsylvania State University, Pa.

(a) slight broadening of all reflections due to the introduction of lattice strain and reduced crystal size.

(b) diffuseness of reflections with $h+2k \neq 3n$, $(l=0)$, due to the introduction of random stacking disorder.

(c) appearance of reflections due to the specific formation of the cubic stacking sequence. These reflections are very diffuse because the stacking is of very short range, and the effective crystal size is therefore very small.

A microdensitometer trace of hexagonal zinc sulphide after grinding for two hours is shown in Fig. 1*d*. As expected, the 10.0 reflection shows only slight broadening due to grinding, and therefore any reflection between the 10.0 and 00.2 lines and between the 00.2 and 10.1 lines is due essentially to a broad cubic 111 reflection. It follows that in any ground

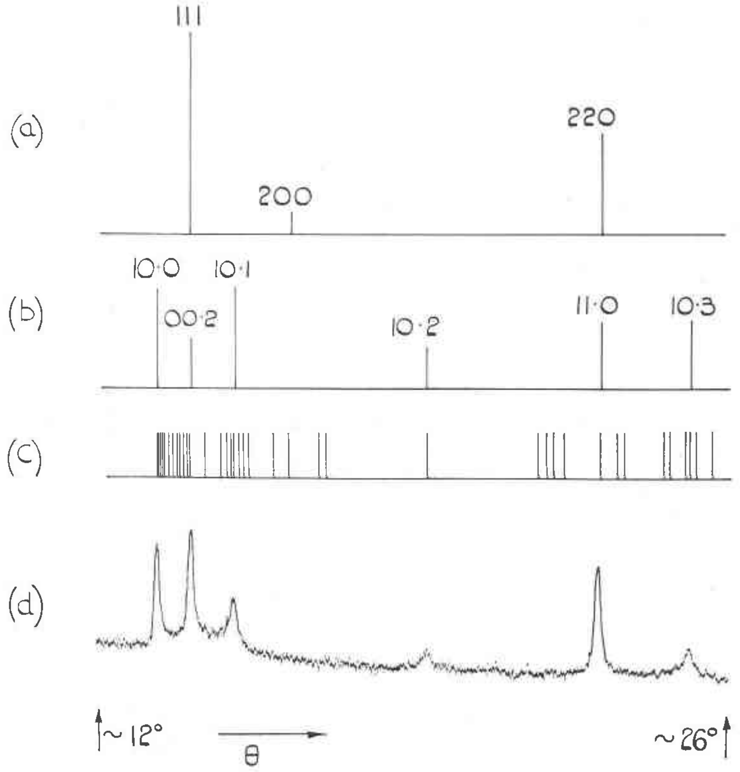

FIG. 1. (a) Positions and intensities for low-angle reflections from cubic ZnS.
(c) The same for hexagonal ZnS.
(c) Positions given by Smith for reflections from various ZnS polytypes.
(d) Microdensitometer trace for hexagonal ZnS after grinding for 2 hours.
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material the proportion of the hexagonal stacking present can be deduced from the ratio of the integrated intensity of the 10.0 reflection to the integrated intensity in the θ range $\theta_{10.0} < \theta < \theta_{10.1}$. Between $\theta_{00.2}$ and $\theta_{10.1}$ there will also be some disorder broadening of the 10.1 reflection, but this can be allowed for by measurement of the intensity distribution on the high θ side of the 10.1 reflection.

INTENSITY VALUES

The various relative intensities for the purely hexagonal and purely cubic structures can be denoted as follows:

	I(00.2+111)	I(10.0)
Hexagonal	1	α
Cubic	β	0

where α and β can be found.

If, in a given material, there is a fraction H of the hexagonal stacking sequence and, therefore, $(1-H)$ of the cubic stacking sequence, we can write:

$$\frac{I(10.0)}{I(00.2+111)} = \frac{H\alpha}{\beta - H(\beta - 1)}$$

The ratio I(10.0):I(00.2) for purely hexagonal zinc sulphide is also used by Smith in the method he has described. He obtained a ratio of 2.04 theoretically and for this he considered the crystals as "$\frac{2}{3}$ perfect." He preferred this theoretical figure owing to the wide variation in observed intensities reported by earlier workers. For x-ray *powder* work, however, the crystals constituting the powder should have been considered as "ideally imperfect," and calculation has shown (4) that the theoretical ratio of I(10.0):I(00.2) is, in fact, 1.56.

Our calculations confirmed Smith's statement that as the hexagonal stacking in zinc sulphide changes to cubic stacking, the value of the relative theoretical intensity of the 00.2 (111) reflection increases from 1 to 4. We also found that the 00.2 reflection intensity for cadmium sulphide increased from 1 to 4.

As it was proposed to apply the method of measuring the hexagonal:cubic stacking ratio to ground zinc-cadmium sulphides, it was important that the reference intensity ratios for both zinc and cadmium sulphides should be known accurately. For a solid solution of zinc-cadmium sulphide the appropriate values of α and β are determined from a linear combination of the values for the end-members.

It had previously been found (4) that the "highly reliable" intensity values obtained by the National Bureau of Standards for zinc sulphide (5) were in error due to the presence of disorder in their sample. A cursory

TABLE 1

hkl	ZnS			CdS		
	obs.	calc.	NBS (5)	obs.	calc.	NBS (6)
10.0	96	92	119	57	59	75
00.2	54	59	102	43	43	59
α	1.78	1.56		1.33	1.37	
10.1	100	100	100	100	100	100
11.0	64	67	88	50	49	57
10.3	64	67	62	50	50	42

examination of their figures for cadmium sulphide (6) suggested that here also their specimen may have contained some disorder. The whole question of the intensities of the x-ray reflections due to both cubic and to hexagonal zinc and cadmium sulphides has therefore been re-examined. With a refined microdensitometer technique, the observed intensities have been evaluated, using 19 cm. powder photographs as previously reported (4), for both zinc and cadmium sulphides. These intensity data and, for comparison, the N.B.S. data, are listed in Table 1.

The agreement obtained between our observed and calculated values confirms that our materials were essentially free from disorder.

Using the *experimental* values for α and putting $\beta=4$, the fraction (H) of hexagonal stacking in a sample of disordered sulphide is given by the expression:

$$\frac{\mathrm{I}(10.0)}{\mathrm{I}(00.2+111)}=\left(\frac{1.78\mathrm{H}}{4-3\mathrm{H}}\right)_{\mathrm{ZnS}}$$
$$=\left(\frac{1.33\mathrm{H}}{4-3\mathrm{H}}\right)_{\mathrm{CdS}}$$

In a similar way, H can also be determined by using the 11.0 and 10.3 reflections: The following expressions apply:

$$\frac{\mathrm{I}(10.3)}{\mathrm{I}(11.0+220)}=\left(\frac{\mathrm{H}}{1.69-0.69\mathrm{H}}\right)_{\mathrm{ZnS}}$$
$$=\left(\frac{\mathrm{H}}{1.96-0.96\mathrm{H}}\right)_{\mathrm{CdS}}$$

It is found that these ratios are particularly sensitive to the presence of small amounts of cubic stacking.

REFERENCES

(1) SHORT, M. A. AND STEWARD, E. G. (1957), The effect of grinding on the structure and luminescence of zinc and zinc-cadmium sulphides: *Z. phys. Chem.* (*Frankfurt*), **13,** 298.

(2) SMITH, F. G. (1955), Structure of zinc sulphide minerals: *Am. Mineral.*, **40,** 658.

(3) WECKER, F. (1942/3), Röntgenographische Strukturuntersuchung an Zinksulfid-Kupfer-Phosphoren nach der Pulvermethode. *Ann. Physik.*, **42,** 561.

(4) Short, M. A. and Steward, E. G. (1955), *X*-ray powder diffraction data for hexagonal zinc sulphide: *Acta Cryst.*, **8**, 733.
(5) Swanson, H. E. and Fuyat, R. K. (1953), Standard *x*-ray diffraction powder patterns, *NBS Circular 539*, **2**, 14.
(6) Swanson, H. E., Fuyat, R. K. and Ugrinic, G. M. (1955), *ibid.*, **4**, 15.

Note added in proof: in a recent paper, V. G. Hill (*Can. Mineral.*, 1958, **6**, 234) has found α for ZnS to have the very high values of 2.17 (fine crystals) and 2.37 (ground crystals). This is probably due to his use of a diffractometric technique, which we have found to be unsatisfactory for the study of ZnS, and also, in the case of the ground crystals, to pulverisation.

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THE DISPERSION AND THE TEMPERATURE COEFFICIENT OF THE BIREFRINGENCE OF SELENITE*

Myron A. Jeppesen and Richard E. Payne,
Bowdoin College, Brunswick, Maine.

Values of the indices of refraction of selenite ($CaSO_4 \cdot 2H_2O$) precise to five significant figures have been published by Tutton (1). For his measurements he used prisms with the crystal axes oriented so that the method of minimum deviation could be used. The birefringence obtained by taking differences between the indices of refraction so determined has a rather large uncertainty in the second significant figure and shows no consistent change with wavelength.

Using multiple-wave plates cleaved from natural crystals we have made direct measurements of the birefringence ($n_\gamma - n_\alpha$). A diagram of the experimental arrangement is shown in Fig. 1. The crystal is mounted normal to a collimated beam of light in a temperature controlled enclosure. The α and γ axes of the indicatrix are oriented at an angle of 45° to the transmission axes of a pair of Glan-Thompson prisms. An image of the crystal is formed on the slit of the spectrograph.

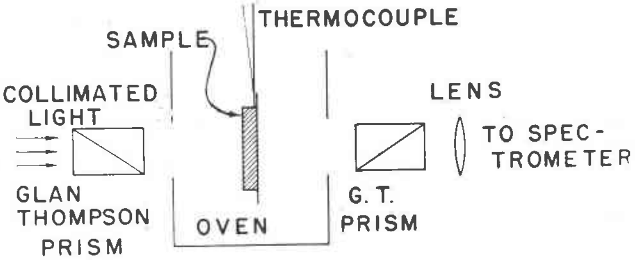

Fig. 1. Diagram of the apparatus for birefringence measurements.

The crystal introduces a phase difference between the light vibration components parallel to the fast and to the slow axes. For those wave-

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