

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

<i>hkl</i>	One-dimensional disorder produced by grinding	Grinding, after Frey (1948)	Presence of cubic ZnS	Change in sulphur parameter on calculated values	
				$u=0.36$	$u=0.39$
10 $\bar{1}0$	—	—	—	100	100
0002	<i>I</i>	<i>I</i>	<i>I</i>	55	73
10 $\bar{1}1$	<i>D</i>	<i>D</i>	—	122	98
10 $\bar{1}2$	<i>D</i>	<i>D</i>	—	32	42
11 $\bar{2}0$	<i>I</i>	<i>I</i>	<i>I</i>	73	73
10 $\bar{1}3$	<i>D</i>	<i>D</i>	—	79	65
20 $\bar{2}0$	—	—	—	11	11
11 $\bar{2}2$	<i>I</i>	<i>I</i>	<i>I</i>	41	55
20 $\bar{2}1$	<i>D</i>	—	—	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 (Fronde! & Palache, 1950; Strook & 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.

References

- AMINOFF, G. (1923). *Z. Kristallogr.* **58**, 203.
 BLAKE, F. C. (1934). *J. Chem. Phys.* **2**, 320.
 FREY, F. (1948). *Ann. Phys., Lpz.* **2**, 147.
 FRONDE!, C. & PALACHE, C. (1950). *Amer. Min.* **35**, 29.
 FULLER, M. L. (1929). *Phil. Mag.* (7), **8**, 658.
 HANAWALT, J. D., RINN, H. W. & FREVEL, L. K. (1938). *Industr. Engng. Chem. Anal. Ed.* **10**, 457.
 JAMES, R. W. & BRINDLEY, G. W. (1931). *Z. Kristallogr.* **2**, 277.
 KREMHELLER, A. (1955). *Sylvania Tech.* **8**, 11.
 SCHLEEDE, A. & GANTZCKOW, H. (1923). *Z. phys. Chem.* **106**, 37.
 STROCK, L. & BROPHY, V. A. (1955). *Amer. Min.* **40**, 94.
 SWANSON, H. E. & FUYAT, R. K. (1953). *Circ. Nat. Bur. Stand.* No. 539, **2**, 14.
 ULRICH, F. & ZACHARIASEN, W. (1925). *Z. Kristallogr.* **62**, 260.
 VIERVOLL, H. & ÖGRIM, O. (1949). *Acta Cryst.* **2**, 277.
 WYCKOFF, R. W. S. (1951). *Crystal Structures*, vol. 1. London: Interscience Publishers.

Acta Cryst. (1955). **8**, 734

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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composition was kindly furnished by Prof. Paul A. Beck of the University of Illinois. By trial and error with Laue photography a single crystal about 50 microns in size was isolated from the crushed material and oriented, and shown to have D_{2h} Laue symmetry. By Weissenberg photography with Ni-filtered Cu $K\alpha$ radiation, and precession photography with Zr-filtered Mo $K\alpha$ radiation, the following lattice constants were obtained:

$$a_0 = 9.07 \pm 0.05, \quad b_0 = 17.01 \pm 0.10, \quad c_0 = 4.74 \pm 0.05 \text{ \AA}.$$

Spacings calculated from these lattice constants check satisfactorily with powder lines over the low-angle region investigated. From a density value of 9.06 g.cm.⁻³ the number of atoms in the unit cell is calculated to be approximately 54.6. Reflections ($0kl$) with k odd and reflections ($h0l$) with ($h+l$) odd are absent, leading to $D_{2h}^{12} - Pbnm$ or $C_{2v}^2 - Pbn2_1$ as the space group.

The unit cell resembles a σ -phase cell with a nearly doubled b axis and nearly doubled number of atoms. As in the σ phase, the intensity distribution in the reciprocal lattice is, aside from normal decline, essentially invariant to translations $\Delta l = 4n$, showing that the atoms are closely confined to layers $\frac{1}{2}c_0$ apart and suggesting strongly that the first space group given (having a mirror plane) is the correct one. The intensities of ($hk0$) reflections correspond roughly to those in the σ phase, with k values that are twice, or at high values a little less than twice, those in the σ phase. Similar correspondence, not as strong, exists in ($hk1$) and ($hk2$) intensities. Evidently the structure is very closely related to that of the σ phase, which contains two pseudo-hexagonal layers per cell with axial orientations differing by 90° , but the presence of the b glide in the P -phase structure requires that both orientations be present in every main layer. These considerations have led to the trial structure shown in projection in Fig. 1, with atomic positions and parameters given in Table 1. The unit cell contains 56 atoms.

Agreement between calculated and observed structure

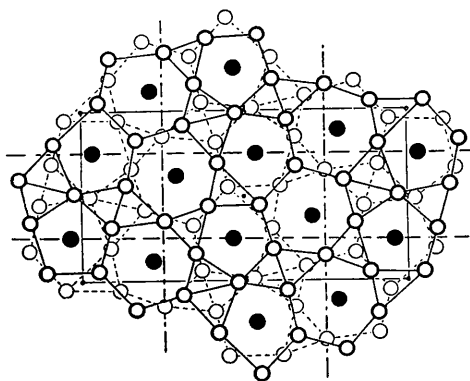


Fig. 1. Projection of P -phase structure on (001). Light open circles indicate atoms at $z = \frac{1}{2}$, heavy open circles indicate atoms at $z = \frac{1}{2}$, lying in both cases on mirror planes. Filled circles indicate atoms at approximately 0.00 and also atoms at approximately 0.50 (coinciding in projection).

Table 1. Approximate atomic parameters in P -phase structure

Atom	Positions	x	y	z	Analogue in σ phase*	Coordination
I	4(c)	0.063	0.118	$\frac{1}{2}$	A	12†
II	4(c)	0.150	0.248	$\frac{1}{2}$	D	12†
III	4(c)	0.340	0.158	$\frac{1}{2}$	D	12†
IV	4(c)	0.590	0.190	$\frac{1}{2}$	C	14
V	4(c)	0.673	0.337	$\frac{1}{2}$	B	15
VI	4(c)	0.443	0.447	$\frac{1}{2}$	(B)	16
VII	4(c)	0.190	0.412	$\frac{1}{2}$	C	14
VIII	4(c)	0.807	0.082	$\frac{1}{2}$	D	12†
IX	4(c)	0.943	0.368	$\frac{1}{2}$	C	14
X	4(c)	0.513	0.027	$\frac{1}{2}$	(C) (D)	15
XI	8(d)	0.250	0.535	0.00	(E)	12†
XII	8(d)	0.380	0.288	0.00	E	14

* Bergman & Shoemaker (1954).

† Distorted regular icosahedron.

factors for ($hk0$), ($hk1$) and ($hk2$) is rough but reasonably satisfactory for a trial structure, especially considering the fact that differences in atomic scattering factor are necessarily ignored at this stage. Refinement operations are in progress.

While no main layer constitutes an infinite continuous pseudo-hexagonal net with a single orientation, such nets, somewhat imperfect, may be said to exist if they may be thought of as 'stepping' from layer to layer. Within any given main layer it will be noted that half of the hexagonal holes present in the σ phase have become distorted pentagons in the P phase. This results in the reduction of the coordination numbers of half of the atoms in the subsidiary layers from 14 to 12. An interesting difference between this structure and the σ -phase structure is the fact that in this structure a larger proportion ($\frac{2}{3}$ as compared to $\frac{1}{3}$) of the atoms have the 12-fold coordination represented by a regular icosahedron, somewhat distorted.

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References

- BERGMAN, G. & SHOEMAKER, D. P. (1954). *Acta Cryst.* **7**, 857.
 DICKINS, G. J., DOUGLAS, A. M. B. & TAYLOR, W. H. (1951a). *Nature, Lond.* **167**, 192.
 DICKINS, G. J., DOUGLAS, A. M. B. & TAYLOR, W. H. (1951b). *J. Iron Steel Inst.* **167**, 27.
 KASPER, J. S., DECKER, B. F. & BELANGER, J. R. (1951). *J. Appl. Phys.* **22**, 361.
 RIDEOUT, S., MANLY, W. D., KAMEN, E. L., LEMENT, B. S. & BECK, P. A. (1951). *Trans. Amer. Inst. Min. (Metall.) Engrs.* **191**, 872.
 SHOEMAKER, D. P. & BERGMAN, B. G. (1950). *J. Amer. Chem. Soc.* **72**, 5793.
 TUCKER, C. W. (1950). *Science*, **112**, 448.
 TUCKER, C. W. & SENIO, P. (1953). *Acta Cryst.* **6**, 753.