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## On the Calculation of Intensity Factors for the Powder Method of X-Ray Crystal Analysis

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In the July issue of *Reviews of Modern Physics* the writer has surveyed the literature as to intensity factors for the several methods of x-ray analysis. In this survey it was shown that both the atomic form factor  $F$  and the temperature factor  $e^{-M}$  properly enter into the so-called structure factor. Using the terminology of this survey one can distinguish then between the "regular" structure factor  $S$ , given by Eq. (51) of the survey, and what is here called the "reduced" structure factor  $S_0$ , given by  $SFe^{-M}$ . It is highly important both to the pure physicist and to the industrial physicist to be able properly to get

$S_0$  out of  $S$ . How this is done is illustrated in this paper both for wurtzite or  $\alpha$ -ZnS and for sphalerite or  $\beta$ -ZnS. It was shown in the survey that the reason why it is necessary to operate with the reduced structure factor is on account of the phase differences between the waves diffracted by the several electrons of the *same* atom, reduced further by the levelling effect of temperature. How these levelling effects are carried out is here shown. On account of the good observational material available for wurtzite the calculations for this are shown first.

### I. CALCULATION OF REGULAR STRUCTURE FACTOR

WURTZITE is known<sup>1</sup> to be a hexagonal crystal having  $a = 3.84\text{\AA}$  with axial ratio  $2(\frac{2}{3})^{\frac{1}{2}}$ , giving  $c = 6.28\text{\AA}$ . Its space group is  $C_{6v}^4$ . Ewald and Hermann<sup>2</sup> give the literature published on wurtzite. I have taken the results of Fuller<sup>3</sup> as among the best, and the comparison between theory and experiment is made with his results alone. I illustrate first the calculation of the regular structure factor and later that of the reduced factor. Such calculations are much more easily made by operating with the revolving vector than by dealing with sines and cosines. On the other hand, the method of revolving vectors has no advantages for those crystals where symmetry considerations make either the sines or the cosines drop out everywhere. All basal pinacoids except those of even index are of zero intensity hence the first line on a powder photograph for wurtzite is due to face  $10\bar{1}0$ . Wurtzite has two molecules of ZnS per unit cell, the atoms of zinc being located at the positions  $\frac{1}{3}\frac{1}{3}0$ ,  $\frac{2}{3}\frac{2}{3}\frac{1}{2}$  and of sulphur at positions  $\frac{1}{3}\frac{1}{3}\frac{1}{6}$ ,  $\frac{2}{3}\frac{2}{3}\frac{5}{6}$ .

<sup>1</sup> Goldschmidt, *Geochemische Verteilungsgesetze der Elemente*, VIII; see reference 2.

<sup>2</sup> Ewald and Hermann, *Strukturbericht*, p. 128, 1913-1928.

<sup>3</sup> M. L. Fuller, *Phil. Mag.* **8**, 658 (1929).

In the Survey,<sup>4</sup> page 186, the regular structure factor is shown to be

$$S = \sum_r Z_r e^{2\pi i(x_r h + y_r k + z_r l)}, \quad (1)$$

where  $x_r, y_r, z_r$  are the coordinates of the  $r$ th atom and  $hkl$  are the indices, here Bravais-Miller. In considering the face  $10\bar{1}0$  (usually written  $10\cdot0$ , where  $h+k+i=0$ ) one can write in a sort of shorthand  $S = 30[\frac{1}{3}, \frac{2}{3}] + 16[\frac{1}{3}, \frac{2}{3}] = -46$ . Draw two concentric circles, one of radius 16, the atomic number of sulphur, the other of radius 30, the atomic number of zinc. Thinking in terms of the revolving vector we draw two vectors for zinc at positions  $120^\circ$  and  $240^\circ$  away from the positive  $X$ -axis. Similarly, we draw two vectors in exactly the same angular positions for sulphur. The resultant of the two zinc vectors is a single vector of magnitude 30 lying along the negative  $X$ -axis and that of the two sulphur vectors is a single vector of magnitude 16 lying in the same position as the zinc resultant. Hence the regular structure factor is  $S = -30 - 16 = -46$  and  $|S|^2 = 2116$ . Because of the influences of the atomic form factor and the temperature factor in reducing the structure factor and different amounts for different atoms I have found it con-

<sup>4</sup> F. C. Blake, *Rev. Mod. Phys.* **5**, 169 (1933). This article will be referred to as "Survey" throughout paper.

venient in Tables I and II to indicate the regular structure factor  $S$  as the sum of two separate quantities rather than as a single quantity. Of course, when the resultant vectors due to the zinc atoms and to the sulphur atoms separately do not lie along the same direction it is necessary to indicate  $S$  as a complex number.

Again consider face 0002 (00·2) due to the basal pinacoids. Here Eq. (1) gives  $S=60-32i$  at once, for the two zinc vectors lie along the positive  $X$ -axis and the two sulphur vectors along the negative  $Y$ -axis. In Fig. 1 it is convenient in finding the resultant vector for the several faces there shown to draw two concentric circles, one of radius 30, the other of radius 16, or integral multiples of these numbers, hence in the figure corresponding circles look alike but may have different radii.

Face 10 $\bar{1}$ 1 (10·1) is typical of the more complicated patterns of revolving vectors. In my shorthand notation I write

$$S = 30\left[\frac{1}{3}, \frac{1}{6}\right] + 16\left[\frac{7}{24}, \frac{11}{24}\right]. \quad (2)$$

The reader can understand this in the following

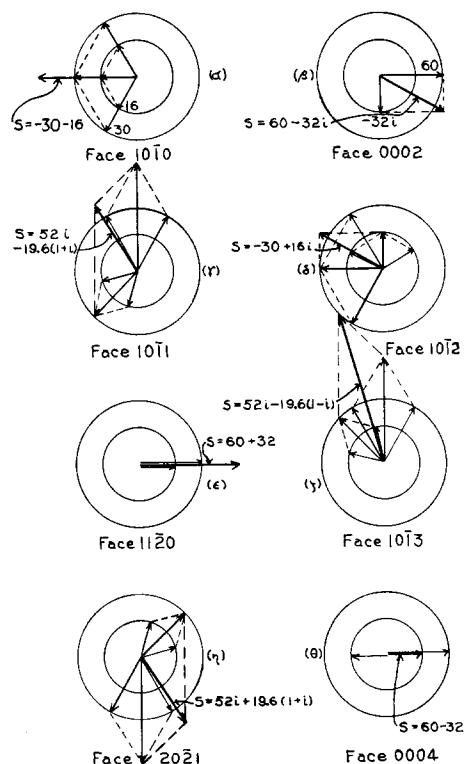


FIG. 1. Wurtzite,  $\alpha$ -ZnS.

way. Eq. (1) gives

$$\begin{aligned} S &= 30[e^{2\pi i(1/3 \cdot 1 + \bar{1}/3 \cdot 0 + 0 \cdot 1)} \\ &\quad + e^{2\pi i(\bar{1}/3 \cdot 1 + 1/3 \cdot 0 + 1/2 \cdot 1)}] \\ &\quad + 16[e^{2\pi i(1/3 \cdot 1 + \bar{1}/3 \cdot 0 + 3/8 \cdot 1)} \\ &\quad + e^{2\pi i(\bar{1}/3 \cdot 1 + 1/3 \cdot 0 + \bar{1}/8 \cdot 1)}] \\ &= 30[e^{2\pi i(1/3)} + e^{2\pi i(1/6)}] \\ &\quad + 16[e^{2\pi i(17/24)} + e^{2\pi i(11/24)}] \end{aligned} \quad (3)$$

which may be shortened to the form given by (2) for the reason that the coefficient of  $2\pi i$  in the exponents of the Napierian base indicates the direction of the amplitude vector. Thus in (2) the figures  $\frac{1}{3}$  and  $\frac{1}{6}$  state that the two zinc vectors lie along directions  $120^\circ$  and  $60^\circ$  away from the positive  $X$ -axis, these figures being in each case  $\frac{1}{3}$  and  $\frac{1}{6}$  of a complete rotation ( $360^\circ$ ). For the two sulphur vectors, on the other hand, we have rotations  $\frac{1}{24}$  ( $= \frac{7}{24}$ ) and  $\frac{11}{24}$ , that is, directions  $-105^\circ$  and  $-165^\circ$ . Drawing the vectors indicated in the third figure of Fig. 1, the resultant of the two zinc vectors gives a vector 51.96 ( $=52$ ) along the positive  $Y$ -axis. The resultant of the two sulphur vectors gives a vector 27.7 along the direction  $-135^\circ$ . This has the two components  $-19.6$  and  $-19.6i$ . The final resultant, indicated in the figure, may accordingly be written  $S = 52i - 19.6(1+i)$ . There is nothing gained by writing this  $32.4i - 19.6$  except for getting  $|S|^2$  in column 6 of Table I, written  $S^2$ . For in getting the reduced structure factor  $S_0$  one must take the resultant amplitude 52 for the zinc atoms and multiply it by  $Fe^{-M}$  for zinc; again the resultant sulphur amplitude 27.7 must be multiplied by  $Fe^{-M}$  for sulphur and this function  $Fe^{-M}$  is a function of the atomic number, directly in  $F$  and indirectly through the atomic weight in  $M$ . The reader should now be able to check for himself the resultant amplitude vectors in the other figures of Fig. 1.

Going now to sphalerite or  $\beta$ -ZnS, it is known<sup>5</sup> to be face-centered cubic of the diamond type containing four molecules,  $a$  being 5.43Å. Its space group is  $T_d^2$ . The zinc atoms are at positions  $000$ ,  $\frac{1}{2}\frac{1}{2}0$ ,  $\frac{1}{2}0\frac{1}{2}$ ,  $0\frac{1}{2}\frac{1}{2}$ , and the sulphur atoms at positions  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ,  $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ ,  $\frac{1}{4}\frac{3}{4}\frac{1}{4}$ ,  $\frac{1}{4}\frac{3}{4}\frac{3}{4}$ , or *vice versa*. For all faces whose regular structure factor

<sup>5</sup> Reference 2, pp. 77 and 127; also reference 1, p. 28.

TABLE I. *Wurtzite,  $\alpha$ -ZnS.*

Face	$\theta$	$\sin \theta$	$S$	$S_0$	$S^2$	$S_0^2$	$S_0^2/S^2$	$n$	$\Phi$	$A$	$I$ (A omitted)	$I$ (A included)	$I$ (obs.) (Fuller)	$I$ (calc.) (Fuller)
10·0	6-7.7	0.1068	-30-16	-36.2	2116	1310	62.0	12	87.1	1.00	97.3	95.6	80	85.5
00·2	6-30.1	.1132	60-32i	47.3-23.5i	4624	2793	60.3	2	76.3	1.01	30.3	30.0	32	52
10·1	6-56.3	.1208	52.0i-19.6(1+i)	26.0i-14.0	1434	872	60.8	24	67.2	1.02	100.0	100.0	76	71.3
10·2	8-57.1	.1556	-30+16i	-21.0+10.0i	1156	541	46.8	24	37.5	1.07	34.0	36.4	20	36.7
11·0	10-39.3	.1849	60+32	56.5	8464	3192	37.8	12	27.8	1.13	74.4	84.1	96	93.2
10·3	11-34.3	.2006	52.0i-19.6(1-i)	42.5i-10.3	5511	1912	34.7	24	23.4	1.16	75.0	87.0	100	100.0
20·0	12-19.7	.2135	-30-16	26.1	2116	681	32.2	12	20.3	1.18	11.6	13.7	(?)	16.5
11·2	12-31.3	.2168	60-32i	35.4-16.0i	4624	1508	32.6	12	19.9	1.19	25.2	29.9	34	70.6
20·1	12-45.6	.2209	-52.0i+19.6(1+i)	-20.3i+9.8	2165	508	23.5	24	19.1	1.20	16.2	19.5	6	17.3
00·4	13-5.3	.2265	60-32	18.6	784	346	44.2	2	18.0	1.21	.87	1.05		
20·2	13-59.1	.2417	-30+16i	-16+3.6i	1156	269	23.3	24	16.0	1.23	7.22	9.77	(?)	12.9
10·4	14-29.9	.2504	-30+16	8.91	196	79	40.3	24	14.3	1.25	1.98	2.48		
20·3	15-49.9	.2728	-52.0i-19.6(1-i)	-34.3i+8.1	5511	1242	22.5	24	11.9	1.31	24.8	32.5	22	48.4
12·0	16-24.4	.2824	-30-16	-21.1	2116	446	21.0	12	11.1	1.34	4.15	5.56	4	36.3
12·1	16-44.5	.2881	-52.0i+19.6(1+i)	-17.6i+7.6	1434	368	25.6	24	10.6	1.35	6.54	8.83	4	18.5
11·4	16-59.9	.2924	60-32	16.5	784	272	34.8	12	10.3	1.36	2.35	3.20		
10·5	17-36.6	.3025	52.0i+19.6(1+i)	31.3i+7.2	5511	1033	18.8	24	9.5	1.39	16.4	22.9	16	57.7
12·2	17-42.6	.3043	-30+16i	-13.8+5.9i	1156	225	19.5	24	9.4	1.40	3.55	4.97		
20·4	18-8.0	.3112	-30+16	-8.0	196	64	32.6	24	9.0	1.41	.97	1.36		
30·0	18-40.7	.3203	60+32	37.8	8464	1429	16.8	12	8.4	1.44	10.07	14.5	8	25.8
12·3	19-14.6	.3296	-52.0i+19.6(1-i)	-29.2i+6.6	5511	895	16.2	24	7.9	1.46	11.8	17.3	27	62.1
00·6	19-51.4	.3397	60±32i	25.3±10.5i	4624	750	16.2	24	7.3	1.50	9.9	14.9	(?)	4.0
20·5	20-46.3	.3546	-52.0i-19.6(1-i)	-15.0i-6.0	1434	261	18.2	24	6.6	1.54	2.90	4.47	4	33.8
10·6	20-51.5	.3561	-30-16i	-12.1-4.9i	1156	170	14.6	24	6.5	1.55	1.85	2.87		
12·4	21-13.4	.3620	-30+16	-7.1	196	50	25.5	24	6.3	1.56	0.53	0.82		
22·0	21-42.2	.3698	60+32	32.7	8464	1070	12.6	12	6.0	1.59	5.38	8.56	2	16.1
13·0	22-38.2	.3849	-30-16	-15.6	2116	243	11.5	12	5.5	1.65	1.12	1.85		
11·6	22-45.1	.3867	60-32i	22.3-8.7i	4624	573	12.4	12	5.4	1.66	5.18	8.61	8	16.9
22·2	22-53.7	.3890	52.0i-19.6(1+i)	13.9i-5.3	1434	221	15.4	24	5.3	1.67	1.96	3.28		
30·8	33-41.4	.5547	60+32	18.9	8464	357	4.2	12	2.3	2.39	2.10	4.94		
60·0	39-49.7	.6405	60+32	14.5	8464	210	2.5	12	1.7	2.87	0.30	0.84		
36·0	57-55.1	.8473	60+32	7.5	8464	56	0.66	12	1.5	4.36	0.07	0.30		
00·16	64-56.0	.9058	60+32	6.4	8464	41	0.48	2	2.0	4.93	0.01	0.05		
36·8	73-53.8	.9608	60+32	5.1	8464	26	0.31	12	3.4	5.55	0.38	2.07		
80·8	75-10.0	.9667	60+32	4.9	8464	24	0.28	24	3.6	5.62	0.14	0.81		
33·14	75-20.0	.9674	60±32i	4.3±0.7i	4624	19	0.41	12	3.7	5.63	0.18	1.00		
90·2	78-4.0	.9784	60+32	4.7	8464	22	0.26	12	4.6	5.77	0.09	0.50		
28·2	80-2.0	.9849	60±32i	4.0±0.6i	4624	16	0.35	24	5.6	5.86	0.31	1.78		

is other than zero there are only four possibilities,  $120 \pm 64$  or  $120 \pm 64i$ . Consider the first face to give a reflection on the powder photograph, *viz.*, 111. Draw two concentric circles of radii  $120 (= 4 \times 30)$  and  $64 (= 4 \times 16)$ . (See Fig. 2.) Eq. (1) gives

$$\begin{aligned}
 S = & 30[e^{2\pi i(0 \cdot 1 + 0 \cdot 1 + 0 \cdot 1)} + e^{2\pi i(\frac{1}{2} \cdot 1 + \frac{1}{2} \cdot 1 + 0 \cdot 1)} \\
 & + e^{2\pi i(\frac{1}{2} \cdot 1 + 0 \cdot 1 + \frac{1}{2} \cdot 1)} + e^{2\pi i(0 \cdot 1 + \frac{1}{2} \cdot 1 + \frac{1}{2} \cdot 1)}] \\
 & + 16[e^{2\pi i(\frac{1}{4} \cdot 1 + \frac{1}{4} \cdot 1 + \frac{1}{4} \cdot 1)} + e^{2\pi i(\frac{1}{4} \cdot 1 + \frac{1}{4} \cdot 1 + \frac{1}{4} \cdot 1)} \\
 & + e^{2\pi i(\frac{1}{4} \cdot 1 + \frac{1}{4} \cdot 1 + \frac{1}{4} \cdot 1)} + e^{2\pi i(\frac{1}{4} \cdot 1 + \frac{1}{4} \cdot 1 + \frac{1}{4} \cdot 1)}], \quad (4)
 \end{aligned}$$

which in my abbreviated notation may be written

$$30[0, 0, 0, 0] + 16[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4}]. \quad (5)$$

Eq. (5) shows that the four zinc atoms give amplitude vectors that superpose along the positive  $X$ -axis and the four sulphur atoms give amplitude vectors that superpose along the

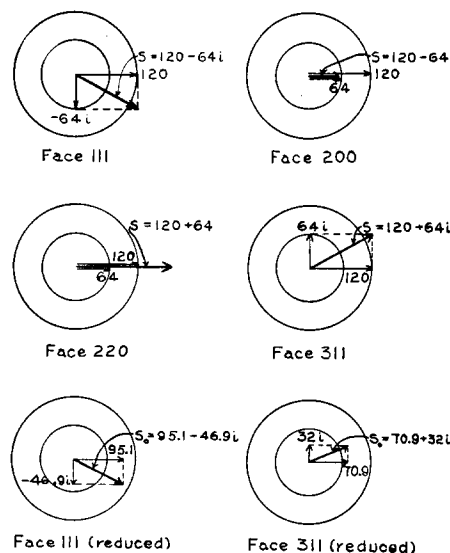
FIG. 2. Sphalerite,  $\beta$ -ZnS.

TABLE II. *Sphalerite,  $\beta$ -ZnS.*

Face	$\theta$	$\sin \theta$	$S$	$S_0$	$S^2$	$S_0^2$	$S_0^2/S^2$	$n$	$\Phi$	$A$	$I$ (calc.) ( $A$ omitted)	$I$ (calc.) ( $A$ incl.)	$I$ (obs.)
111	6-31.0	0.1135	120-64 <i>i</i>	95.1-46.9 <i>i</i>	18496	11240	60.8	8	76.3	1.00	100.0	100.0	100
200	7-30.8	.1308	120-64	48.6	3136	2360	75.2	6	57.0	1.02	11.8	12.0	—
220	10-39.4	.1849	120+64	106.9	33856	11425	33.8	12	27.8	1.13	56.3	65.7	52.8
311	12-31.4	.2169	120+64 <i>i</i>	70.9+32 <i>i</i>	18496	6051	32.7	24	19.9	1.19	42.1	50.1	48.4
222	13-5.4	.2265	120-64	36.4	3136	1325	42.3	8	18.0	1.21	2.72	3.29	—
400	15-9.6	.2615	120+64	90.3	33856	8154	24.0	6	13.0	1.27	9.27	11.8	5.3
331	16-33.5	.2850	120-64 <i>i</i>	58.9-25.1 <i>i</i>	18496	4100	22.2	24	10.9	1.34	15.6	21.0	16.3
420	17-0.0	.2924	120-64	32.3	3136	1044	33.3	24	10.3	1.36	3.76	5.12	—
422	18-40.8	.3203	120+64	75.9	33856	5761	17.0	24	8.4	1.44	17.0	24.4	18.5
511	19-51.6	.3397	120±64 <i>i</i>	50.8±20.6 <i>i</i>	18496	3004	16.2	24	7.3	1.50	10.2	15.3	8.8
333								8					
440	21-42.3	.3698	120+64	65.6	33856	4290	12.7	12	6.0	1.59	4.50	7.16	5.3
531	22-45.4	.3868	120+64 <i>i</i>	44.5-17.5 <i>i</i>	18496	2286	12.4	48	5.4	1.66	8.64	14.3	4.4
620	24-25.4	.4133	120+64	57.4	33856	3300	9.7	24	4.6	1.74	5.31	9.25	3.2
533	25-22.1	.4287	120-64 <i>i</i>	41.0-15.6 <i>i</i>	18496	1924	10.4	24	4.2	1.80	2.83	5.09	—
444	26-56.0	.4530	120+64	51.0	33856	2601	7.7	8	3.70	1.90	1.12	2.13	—
551	27-50.0	.4669	120±64 <i>i</i>	36.5±12.9 <i>i</i>	18496	1498	8.1	24	3.40	1.95	3.57	6.96	—
711								24					
642	29-17.5	.4892	120+64	46.7	33856	2181	6.4	48	3.0	2.02	4.58	9.25	—
553	30-8.7	.5022	120±64 <i>i</i>	32.9±11.3 <i>i</i>	18496	1310	7.1	24	2.83	2.12	3.89	8.25	—
731								48					
800	31-32.1	.5230	120+64	41.8	33856	1750	5.2	6	2.68	2.20	0.41	0.90	—
822	32-49.7	.5421	120+64	38.6	33856	1490	4.4	24	2.40	2.32	1.88	4.36	—
660								12					
840	35-47.2	.5848	120+64	34.5	33856	1190	3.5	24	2.00	2.54	0.83	2.11	—
664	37-49.7	.6133	120+64	31.5	33856	993	2.9	24	1.80	2.72	0.63	1.71	—
844	39-50.1	.6406	120+64	29.6	33856	874	2.6	24	1.63	2.87	0.50	1.43	—
862	41-45.4	.6660	120+64	27.0	33856	729	2.2	48	1.50	2.97	1.15	3.41	—
1020								24					
1042	45-44.4	.7162	120+64	23.1	33856	534	1.6	48	1.41	3.37	0.53	1.79	—
880	47-42.1	.7397	120+64	21.5	33856	463	1.4	12	1.38	3.52	0.11	0.39	—
866	49-41.7	.7624	120+64	19.7	33856	388	1.1	24	1.37	3.70	0.37	1.37	—
1060								24					
884	51-40.6	.7845	120+64	18.6	33856	346	1.02	24	1.38	3.85	0.21	0.81	—
1200								6					
1240	55-47.3	.8270	120+64	16.1	33856	259	0.76	24	1.46	4.19	0.13	0.55	—
888	64-57.7	.9059	120+64	12.2	33856	149	0.44	8	1.98	4.93	0.03	0.17	—
1086	67-36.2	.9246	120+64	11.4	33856	130	0.38	48	2.31	5.14	0.32	1.62	—
1420								24					
1280	70-32.5	.9429	120+64	10.8	33856	117	0.35	24	2.62	5.38	0.11	0.59	—
997	71-44.6	.9497	120-64 <i>i</i>	8.98-1.51 <i>i</i>	18496	83	0.45	24	2.85	5.43	0.25	1.36	—
1193								48					
1266	73-55.0	.9609	120+64	10.1	33856	102	0.30	24	3.32	5.55	0.48	2.67	—
10104								48					
1442	75-21.0	.9675	120 + 64 <i>i</i>	8.49+1.38 <i>i</i>	18496	74	0.40	24	3.70	5.63	0.38	2.14	—
1355								48					
1371	78-6.0	.9785	120+64	9.5	33856	90	0.27	48	4.59	5.77	0.29	1.67	—
1284								48					
1195	80-4.5	.9850	120 + 64 <i>i</i>	7.98+1.25 <i>i</i>	18496	66	0.36	48	5.58	5.86	0.64	3.77	—
1373								48					
1511	80-49.0	.9872	120+64	9.2	33856	84	0.25	24	6.20	5.88	0.18	1.06	—
1088								24					
1460	84-45.5	.9958	120+64	8.9	33856	80	0.24	24	11.00	6.01	0.31	1.86	—

negative  $Y$ -axis, hence the resultant vector is  $S=120-64i$  and  $|S|^2$ , designated as  $S^2$  in column 6 of Table II, becomes  $120^2+64^2=18496$ . The reader can readily check the vector diagrams for the other figures of Fig. 2, face 200 giving  $S=30[0, 0, 0, 0]+16[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}]=120-64i$ , face 220 giving  $S=30[0, 0, 0, 0]+16[0, 0, 0, 0]=120+64i$ , and face 311 giving  $S=30[0, 0, 0, 0]+16[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4}]=120+64i$ . Thus all possibilities are covered in these first four faces.

## II. CALCULATION OF REDUCED STRUCTURE FACTOR

In the Survey, page 189, Fig. 26, there is shown plotted the atomic form factor for all the atoms for which the Thomas-Fermi distribution

of electrons is justifiable. It is there (page 190) stated that probably this distribution holds for all atoms of atomic number greater than 23. Since for compounds the diffraction effects due to heavy atoms outweigh by far those due to light atoms, with zinc having atomic number 30 and sulphur 16 one is safe in saying that for zinc sulphide the Thomas-Fermi distribution holds, hence Fig. 26 of the Survey applies. That figure is here reproduced as Fig. 2a.

Consider now face 10 $\bar{1}0$  for wurtzite. Using  $\lambda$  for molybdenum  $K\alpha$ -rays as 0.710Å we get  $\sin \theta/\lambda$  for this face to be 0.1504 where the factor  $10^8$  is balanced out in Fig. 2a as it is in the Survey, Fig. 26, on account of its reciprocal being implied in the value of  $a$ . Now the "ground-length"  $a$  (Survey, page 189) for zinc is

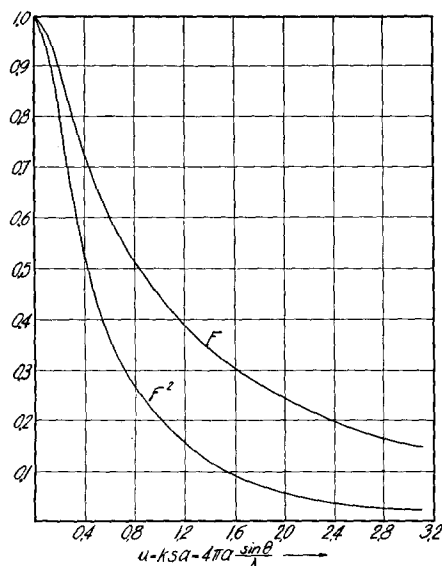


FIG. 2a.

$a = 0.466/30^{\frac{1}{3}} = 0.1499\text{\AA}$  while that for sulphur is  $a = 0.466/16^{\frac{1}{3}} = 0.1850\text{\AA}$ . Hence the value of the abscissa  $u$  in Fig. 2a is

$$\left. \begin{aligned} u_{\text{Zn}} &= 4\pi \sin \theta / \lambda \cdot a_{\text{Zn}} = 2.653 \sin \theta \\ \text{while } u_{\text{S}} &= 4\pi \sin \theta / \lambda \cdot a_{\text{S}} = 3.274 \sin \theta \end{aligned} \right\} \quad (6)$$

Eq. (6) gives for face  $10\bar{1}0$   $u_{\text{Zn}} = 0.2835$  and  $u_{\text{S}} = 0.3498$ . Reading off from Fig. 2a we get  $F_{\text{Zn}} = 0.815$  while  $F_{\text{S}} = 0.770$ . Thus if there were no effect due to temperature the atomic form factor would reduce our value of  $S$  from  $-30 - 16$  to  $-30 \cdot 0.815 - 16 \cdot 0.770 = -36.8$ .

Using Debye's formula for the temperature effect (Survey Eq. (22)) we get

$$M = 6h^2/mk\Theta \cdot \sin^2 \theta / \lambda^2 \left\{ \phi(x) / x + \frac{1}{4} \right\}. \quad (7)$$

As stated by Professor Debye, this formula holds for atoms of a single kind only. However, I have used it as if it held for compounds, such as zinc sulphide. In Eq. (7) the fact that the mass of the atom appears in the denominator means that  $M$  is larger for sulphur than for zinc, and this means that the influence of temperature on the diffraction due to the sulphur atoms is more dissipant than on that due to the zinc atoms, a thing which surely must be in keeping with the physics of the situation, at least in large part. But this would take us back rather to the point of view of Debye's earlier papers, previous to the

improvement made by Born and Karman (Survey, page 175). Hence it is discussed again after the comparison is made between calculation and observation in the case of wurtzite (see below).

I have taken  $\Theta$  for zinc sulphide to be  $325^\circ$  absolute and  $T$  (room temperature) to be  $22^\circ\text{C} = 295^\circ$  absolute, giving  $x$  in Eq. (7) to be 1.102. Thus  $M$  for zinc is evaluated as

$$M_{\text{Zn}} = \frac{6 \cdot (6.55 \times 10^{-27})^2}{65.38 \cdot 1.649 \times 10^{-24} \cdot 1.371 \times 10^{-16}} \times \left\{ \frac{0.758}{1.102} + \frac{1}{4} \right\} \frac{\sin^2 \theta}{\lambda^2}, \quad (8)$$

which for molybdenum  $K\alpha$ -rays becomes  $M_{\text{Zn}} = 0.998 \sin^2 \theta$ . Substituting the atomic weight (32.06) for sulphur for that of zinc we get  $M_{\text{S}} = 2.030 \sin^2 \theta$ . In Eq. (8) the factor 0.758 is  $\phi(x)$  for  $x = 1.102$ , interpolated from Survey, Table I. Thus for face  $10\bar{1}0$   $e^{-M}$  for zinc is 0.989 while that for sulphur is 0.977. Thus  $(Fe^{-M})_{\text{Zn}} = 0.806$  and  $(Fe^{-M})_{\text{S}} = 0.752$ , giving  $S_0 = SFe^{-M} = -30 \cdot 0.806 - 16 \cdot 0.752 = -36.2$  instead of  $-36.8$ , obtained when the temperature effect is ignored, showing, as is well known, that the diffusion or dissipation of the lines on a powder photograph due to temperature is small for  $\sin \theta$  small. Further illustration of temperature calculations is unnecessary; one simply takes

$$M_{\text{Zn}} = 0.998 \sin^2 \theta, \quad M_{\text{S}} = 2.030 \sin^2 \theta, \quad (9)$$

looks up  $e^{-M}$  in a table and makes the calculations as above.

However, I deem it worth while to illustrate for face  $10\bar{1}1$  how the factor  $Fe^{-M}$  reduces  $S$  from the value  $52.0i - 19.6(1+i)$  to  $26.0i - 14.0$ . We find for this face  $M_{\text{Zn}} = 0.01457$  while  $M_{\text{S}} = 0.02965$ , giving  $e^{-M}$  for zinc to be 0.986 and  $e^{-M}$  for sulphur to be 0.970. But  $u$  for zinc is found from (6) to be 0.3208 and for sulphur to be 0.3958, giving  $F_{\text{Zn}} = 0.780$  and  $F_{\text{S}} = 0.735$ . Now it is obvious from Fig. 1 ( $\gamma$ ) that it makes no difference whether I reduce each zinc component by multiplying it by  $0.780 \cdot 0.986 (= 0.769)$  and each sulphur component by  $0.735 \cdot 0.970 (= 0.713)$  and then take resultants or whether I apply these figures respectively to the resultants

already taken. Hence we get  $S_0$  for face  $10\bar{1}1$  to be

$$52i \cdot 0.769 - 19.6(1+i) \cdot 0.713 \\ = 40.0i - 14.0(1+i) = 26.0i - 14.0.$$

The reader now sees how the reduced structure factor is obtained from the regular structure factor and can readily check for himself the values of  $S$  and  $S_0$  in Table I for wurtzite. The method is identical for sphalerite. I happen to have made the calculations in a somewhat different way than for wurtzite. Using the Bragg law,  $n\lambda = 2d \sin \theta$  and remembering that  $d = a/(\hbar^2 + k^2 + l^2)^{1/2} = a/r$ , say, we get  $u_1 = 4\pi a_1 \sin \theta / \lambda = 4\pi a_1 r / 2a$ , where  $a_1$  is the ground length for zinc and  $a$  is the edge of the cubic lattice. Calling  $u_2$  the corresponding  $u$  for sulphur we get  $u_2 = 4\pi a_2 r / 2a$ . One can calculate  $2\pi a_1/a$  and  $2\pi a_2/a$  once for all, which give the  $u$ 's for each face when multiplied by its corresponding  $r$ . I have ignored for the time being the possibility that the elastic spectrum for hexagonal crystals

may not necessarily be the same as for cubic crystals and have used (9) both for wurtzite and sphalerite. We get then for face 111 of sphalerite  $u_1 = 0.3004$  and  $u_2 = 0.3708$ , giving  $F_1 = 0.803$  and  $F_2 = 0.754$ . Now  $M_1 = 0.01286$  and  $M_2 = 0.02615$ , giving  $e^{-M_1} = 0.987$  and  $e^{-M_2} = 0.973$ . Thus  $F_1 e^{-M_1} = 0.792$  and  $F_2 e^{-M_2} = 0.733$ . Whence

$$S_0 = 120 \cdot 0.792 - 64i \cdot 0.733 = 95.1 - 46.9i.$$

The reduced structure factor for the other faces follow equally easily. I have collected into tables, Tables III and IV, the quantities that are useful in getting the reduced structure factor after the regular structure has been obtained, both for wurtzite and sphalerite.

I have also inserted in Tables I and II not only  $S$  and  $S_0$  but also  $S^2$  and  $S_0^2$ , written without the absolute value signs and then  $S_0^2/S^2$ . It is interesting to see how this fraction bobs up and down both for wurtzite and for sphalerite when plotted against  $\sin \theta$ , as shown in Figs. 3 and 4. It should be stated that in Tables I and III no lines are omitted through face  $13 \cdot 1$ , but beyond

TABLE III. Wurtzite.

Face	Sin $\theta$	$U_1$	$F_1$	$U_2$	$F_2$	$M_1$	$e^{-M_1}$	$M_2$	$e^{-M_2}$	$F_1 e^{-M_1}$	$F_2 e^{-M_2}$
10-0	0.1068	0.284	0.815	0.350	0.770	0.0114	0.989	0.0232	0.977	0.806	0.752
00-2	.1132	.300	.803	.371	.754	.0128	.987	.0261	.974	.792	.735
10-1	.1208	.321	.780	.396	.735	.0146	.986	.0300	.970	.768	.713
10-2	.1556	.413	.720	.509	.657	.0242	.975	.0491	.951	.702	.625
11-0	.1849	.491	.669	.605	.595	.0341	.966	.0694	.933	.646	.555
10-3	.2006	.536	.646	.662	.570	.0408	.960	.0831	.920	.620	.524
20-0	.2135	.566	.626	.699	.555	.0455	.956	.0925	.912	.598	.506
11-2	.2168	.575	.619	.710	.550	.0469	.954	.0955	.909	.590	.500
20-1	.2209	.586	.609	.723	.539	.0487	.952	.0991	.906	.579	.488
00-4	.2265	.601	.599	.741	.536	.0512	.950	.1040	.904	.569	.485
20-2	.2417	.655	.573	.810	.505	.0611	.940	.1242	.883	.535	.445
10-4	.2504	.664	.569	.819	.503	.0626	.939	.1274	.880	.534	.444
20-3	.2728	.724	.544	.893	.477	.0741	.929	.1507	.860	.505	.410
12-0	.2824	.751	.533	.926	.463	.0796	.924	.1619	.851	.493	.394
12-1	.2881	.765	.526	.943	.458	.0828	.921	.1685	.845	.484	.387
11-4	.2924	.776	.521	.957	.454	.0853	.918	.1736	.841	.478	.382
10-5	.3025	.803	.508	.991	.442	.0913	.913	.1857	.830	.464	.367
12-2	.3043	.808	.505	.997	.439	.0924	.912	.1880	.829	.460	.364
20-4	.3112	.830	.500	1.024	.431	.0976	.907	.1983	.820	.454	.353
30-0	.3203	.851	.493	1.049	.426	.1024	.903	.2080	.812	.445	.346
12-3	.3296	.875	.485	1.080	.416	.1081	.897	.2193	.803	.435	.334
00-6	.3397	.901	.474	1.112	.406	.1152	.891	.2340	.791	.422	.321
30-2	.3546	.941	.459	1.162	.397	.1255	.882	.2551	.775	.405	.307
20-5	.3561	.945	.457	1.167	.395	.1266	.881	.2573	.773	.402	.306
10-6	.3620	.960	.452	1.185	.391	.1309	.877	.2660	.766	.396	.299
12-4	.3698	.980	.447	1.210	.384	.1364	.873	.2778	.758	.390	.291
22-0	.3849	1.021	.433	1.260	.373	.1479	.863	.3003	.741	.374	.276
11-6	.3867	1.026	.431	1.265	.370	.1493	.861	.3020	.738	.371	.273
22-2	.3890	1.033	.429	1.274	.369	.1510	.860	.3070	.736	.369	.271
13-1	.5547	1.470	.325	1.815	.267	.3071	.736	.6250	.535	.239	.143
30-8	.6405	1.696	.285	2.094	.230	.4085	.665	.8320	.435	.189	.100
33-0	.8473	2.248	.213	2.774	.167	.7165	.489	1.458	.233	.104	.039
60-0	.9058	2.400	.198	2.967	.155	.8184	.441	1.667	.189	.087	.029
36-8	.9608	2.548	.182	3.143	.145	.9212	.398	1.873	.154	.073	.022
90-0	.9667	2.563	.180	3.165	.144	.933	.394	1.897	.150	.071	.022
30-16	.9674	2.566	.180	3.167	.144	.934	.393	1.900	.150	.071	.022
80-8	.9784	2.590	.178	3.200	.142	.955	.385	1.988	.137	.069	.020
90-2	.9849	2.62	.175	3.22	.141	.968	.379	2.00	.135	.066	.019
33-14											
28-0											
28-2											
17-10											

TABLE IV. *Sphalerite*.

Face	$\sin \theta$	$U_1$	$F_1$	$U_2$	$F_2$	$M_1$	$e-M_1$	$M_2$	$e-M_2$	$F_1e-M_1$	$F_2e-M_2$
111	0.1135	0.300	0.803	0.371	0.754	0.0129	0.987	0.0262	0.973	0.792	0.735
200	.1308	.339	.785	.428	.712	.0171	.982	.0347	.965	.771	.687
220	.1849	.491	.670	.606	.598	.0341	.965	.0694	.933	.643	.558
311	.2169	.575	.620	.710	.550	.0469	.953	.0955	.909	.591	.500
222	.2265	.601	.600	.742	.535	.0512	.950	.1043	.901	.570	.486
400	.2615	.694	.557	.856	.494	.0683	.934	.1390	.879	.521	.434
331	.2850	.756	.533	.933	.462	.0810	.922	.1647	.848	.491	.392
420	.2924	.776	.526	.957	.456	.0853	.918	.1736	.840	.483	.383
422	.3203	.850	.496	1.049	.426	.1014	.903	.2065	.813	.448	.346
511	.3397	.901	.475	1.112	.407	.1152	.892	.2343	.793	.423	.322
333											
440											
531	.3698	.981	.447	1.211	.385	.1366	.873	.2780	.758	.390	.292
620	.3868	1.026	.432	1.266	.371	.1493	.860	.3037	.739	.371	.274
533	.4135	1.097	.412	1.354	.350	.1707	.843	.3460	.707	.347	.247
444	.4187	1.111	.407	1.371	.345	.1748	.839	.3550	.701	.342	.243
551	.4530	1.202	.386	1.483	.323	.2048	.814	.417	.660	.314	.207
711	.4669	1.239	.378	1.529	.313	.2176	.804	.443	.643	.304	.201
642											
553											
731	.4892	1.298	.362	1.602	.301	.2390	.803	.486	.615	.291	.185
800	.5022	1.332	.353	1.644	.293	.2515	.777	.512	.599	.274	.176
822	.5230	1.388	.343	1.713	.284	.2730	.761	.555	.573	.261	.163
660	.5421	1.472	.325	1.816	.268	.2933	.747	.596	.550	.243	.147
840	.5848	1.551	.309	1.915	.256	.341	.710	.694	.499	.219	.128
664	.6133	1.627	.296	2.008	.241	.376	.686	.763	.466	.203	.112
844	.6406	1.661	.290	2.097	.230	.410	.664	.833	.435	.193	.100
862	.6660	1.767	.275	2.181	.221	.443	.643	.900	.407	.177	.090
1020											
1042											
880	.7162	1.900	.258	2.345	.204	.512	.599	1.040	.353	.154	.072
866	.7397	1.962	.250	2.422	.196	.546	.580	1.110	.330	.145	.065
1060	.7624	2.023	.240	2.496	.186	.580	.560	1.180	.307	.134	.057
884	.7845	2.081	.233	2.569	.180	.614	.546	1.249	.287	.127	.052
1200											
1240											
888	.8270	2.194	.220	2.708	.170	.683	.505	1.388	.249	.111	.0424
1086	.9059	2.403	.195	2.966	.155	.819	.441	1.665	.189	.0860	.0293
1420	.9246	2.453	.190	3.027	.151	.853	.426	1.733	.177	.0810	.0267
1280	.9429	2.502	.185	3.087	.149	.881	.414	1.805	.164	.0767	.0244
997	.9497	2.520	.184	3.110	.147	.901	.406	1.830	.160	.0747	.0236
1193											
1266											
10104	.9609	2.549	.181	3.146	.145	.921	.398	1.875	.155	.0720	.0225
1442	.9675	2.567	.180	3.168	.144	.934	.392	1.900	.150	.0707	.0216
1177											
1355											
1371	.9785	2.596	.177	3.204	.142	.956	.384	1.941	.144	.0680	.0205
1284	.9850	2.613	.175	3.225	.141	.968	.380	1.970	.139	.0665	.0196
1195											
1373											
1511	.9872	2.619	.175	3.232	.141	.973	.379	1.978	.138	.0663	.0194
1088	.9958	2.642	.173	3.261	.140	.990	.372	2.010	.134	.0644	.0188
1460											

that only certain lines are inserted to see how matters go for large angles. Similarly in Tables II and IV there are no lines omitted as far as face 800, but beyond that only certain lines are recorded, for the reason just given. Perhaps the most interesting feature of Figs. 3 and 4 is the sharp variations of  $S_0^2/S^2$  for faces having  $\theta$  small: Up to the value of  $\sin \theta$  where omissions occur, *viz.*, 0.3890 for wurtzite and 0.5230 for sphalerite, in these figures successive points are joined by short straight lines. The peaked character shown in Fig. 3 for those faces having  $L=4$  stands out very prominently, but unfortunately in Mr. Fuller's paper reflections from those faces are not recorded, presumably because they were too weak to observe as shown by the intensity calculations recorded in columns 12 and 13 of Table I. For sphalerite we find similar

peaks for faces 200, 222 and 420, and again columns 12 and 13 show them to be relatively weak in intensity. Conversely in Fig. 3 negative peaks might be said to be present for faces 20·1 and 20·2, and again they appear weak, for Fuller has observed intensity only about one-third that (correctly) calculated for 20·1, and 20·2 was not recorded. Omitting the peaks in both figures one can draw approximately smooth curves through the other points which clearly reveal the way both intra-atomic phase differences and diffusion or scattering due to temperature pull the reflection intensities down for increasing  $\theta$ .

It could, of course, be successfully argued that the reason these peaks occur in Figs. 3 and 4 is that the temperature factor as applied in this paper, known to be based upon a theory built



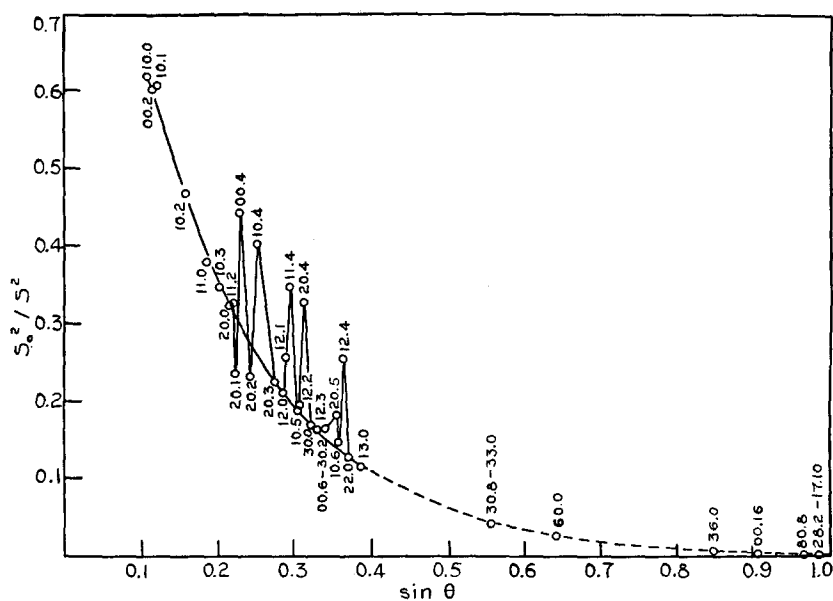


FIG. 3. Plot of [Reduced Structure Factor/Original Structure Factor]<sup>2</sup> versus  $\sin \theta$  for wurtzite or  $\alpha$ -ZnS. ( $\lambda=0.710\text{\AA}$ .)

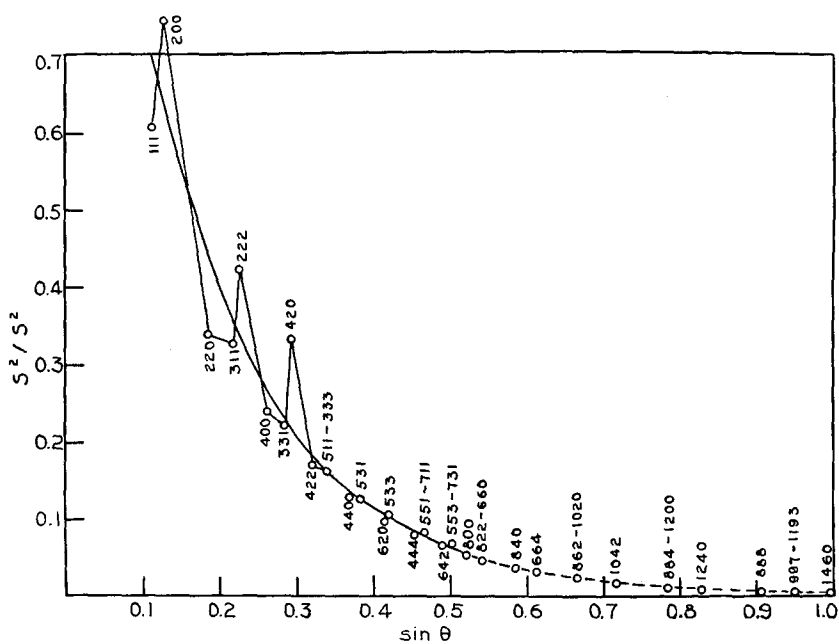


FIG. 4. Plot of [Reduced Structure Factor/Original Structure Factor]<sup>2</sup> versus  $\sin \theta$  for sphalerite or  $\beta$ -ZnS. ( $\lambda=0.710\text{\AA}$ .)

upon one kind of atom only, is wrong and this in the long run may turn out to be the case. I have not had time, as yet, to try Waller's theory (Survey, page 176) of the temperature effect for crystals containing atoms of different kinds, but I mean to do this. It should be expected that the elastic constants of wurtzite and sphalerite are quite different. If the elastic data for these crystals are accurately known it will be interesting to see whether Waller's theory will make smooth curves out of Figs. 3 and 4.

Also recorded in Tables I and II are the values of the other factors occurring in the intensity formula (Survey, Eq. (73) or (74));  $n$  is the form or multiplicity factor,  $\Phi$  the combined Thomson-Lorentz factor, and  $A$  the absorption factor.

### III. COMPARISON WITH EXPERIMENT

I have searched the literature for observations on sphalerite but have found nothing quantitative, Lehmann's<sup>6</sup> results, taken with copper rays, being qualitative. Accordingly I have run a powder sample of it, the crystal being kindly furnished me by Professor W. J. McCaughey. The results are shown in Table II. The last column shows the observed results, run on the photoelectric densitometer. Both a short exposure and a long exposure were made and allowance thereby made for overblackening of the first few lines, by the method given in the Survey (page 192). Just as was there (page 194) found, Table II shows about as good agreement with the calculated value, treating the absorption factor as constant, as with this value when allowance is made for absorption.

There is, of course, the possibility that the difference between theory and experiment, both in Table II and in the monograph, is due to inability properly to correct for extinction, especially primary extinction. Before this can be determined a special investigation must be made, and this is now under way.

There is good agreement found also for wurtzite where I have chosen Fuller's observations rather than those of Ulrich and Zachariasen,<sup>7</sup> for Fuller shows that they had as working

material a mixture of wurtzite and sphalerite while he took special care to have no sphalerite in his sample. Column 14 of Table I gives Fuller's results for two samples which I have weighted equally. Column 15 gives his calculated results based on Wyckoff's formula. In column 12 of both Tables I and II the intensity is calculated on the assumption that the absorption factor is constant, while column 13 is calculated for both tables assuming the radius of the sample to be 0.2 mm and  $\Theta$ , the characteristic temperature of zinc sulphide, to be 325°. This makes  $\mu r = 3$  and the corresponding curve of Fig. 10, Survey, applies. The reader will readily admit the improvement of either column 12 or 13 over column 15 when compared with Fuller's observations, column 14. It should be stated that Fuller's observational material was obtained by visual inspection only. The writer desires to emphasize that the present status of our knowledge of the absorption factor as one important factor in the intensity formula can only be advanced by quantitative rather than qualitative measurements and recommends that more experimenters employ densitometers in their work. As shown by Tables I and II, the total effect on the absorption factor as  $\theta$  is changed from 6° to 90° is 600 percent, and it would have been even more had I chosen the radius of the sample larger so as to use a curve of Fig. 10, Survey, below that used. Nevertheless it is difficult in Table I to say whether column 12 or column 13 is in better agreement with column 14. Certain remarks are in order. Any visual inspection method will underestimate the intensities of lines close in as compared with those farther away because of the greater general blackening close in. Hence it is *unproved* that line 10.3 is the strongest line on the powder photograph as Fuller gives it. The total range of  $\theta$  in Fuller's observations was only 21° and in this range the change in  $A$  was only 66 percent, hence either column 12 or 13 appears almost equally good, when compared with column 14, though considering the qualitative character of the latter it certainly cannot be said that 12 is better than 13. We must await further experimental work.

It should be remarked, also, that, for zinc sulphide at least, when molybdenum rays are used even the  $A$  factor does not pull the intensity

<sup>6</sup> W. M. Lehmann, Zeits. f. Krist. **60**, 379 (1924); see also reference 1, p. 127.

<sup>7</sup> F. Ulrich and W. Zachariasen, Zeits. f. Krist. **62**, 260 (1925).

up sufficiently for values of  $\theta$  near  $90^\circ$  to be able to observe such lines on a powder photograph. The matter could be helped by having a sample tube of larger radius. The case would be far different were copper rays used as shown by the Survey, page 195.

#### IV. DISCUSSION

Certain readers will surely question the methods followed in this paper for getting the reduced structure factor when they recall that Debye's formula, Eq. (7), was worked out on the basis that the crystal lattice contained only one kind of atom. I have not attempted to insert a column in Tables I and II on the basis that I took an atom that would have an atomic number which is the mean between sulphur and zinc. Possibly an arithmetic mean, certainly a sort of center of gravity mean (preponderance of weighting in favor of the heavier atom), would give results very similar to columns 12 and 13. To do this would be rather futile until the observational material for compounds becomes quantitative. If and when it does, and if the other factors of the intensity formula are clinched experimentally as satisfactory, one could then throw light on the correct theory of the influence of temperature on the scattering power of different atoms. Certainly it seems reasonable that increasing temperature will cause lighter atoms to throw more of their energy, relatively, into the general blackening than heavier atoms will, leaving less in the Bragg reflection position—the calculations in this paper were made from this point of view.

The industrial x-ray analyst, desirous of improving his methods, is apt to balk at the labor involved in order to get the correct relative intensities on his powder photographs. Should he use the Debye-Scherrer-Hull method he will have to interpolate from Survey, Fig. 10, to get the correct  $A$  factor, depending upon his values of  $\mu$  and  $r$ . Probably he will not be seriously in error, provided he is using  $\lambda = 0.710\text{\AA}$ , after he has calculated the first few lines on his photograph, to plot them and get the average value of  $S_0^2/S^2$  (similar to Figs. 3 and 4) and extrapolate this value to larger values of  $\theta$ . This paper lends support to the view that in general the

scattering power of an atom, at least for atoms that do not interpenetrate, is independent of its physical state, for the scattering power of atoms obtained from gases seems to hold for crystals also.

In a recent paper Claassen and Burgers<sup>8</sup> have shown by means of x-rays the presence of a new intermetallic compound of zirconium and tungsten, *viz.*  $\text{ZrW}_2$ . It is interesting that the absorption factor covers a range of 4700 percent between the first, or 111, face and the last, or 844, face. They state that they chose the temperature factor such that there was agreement between theory and experiment at the beginning and end of the film, thereby obtaining a value of the coefficient  $B$  for the temperature factor  $e^{-B} \sin^2 \theta$ , that is twice as great for the zirconium tungstide as for the value calculated for metallic tungsten, a result that is plausible considering the fact that  $\text{ZrW}_2$  is lighter than  $W$ . This, of course, in no way precludes another factor or correction such as the extinction factor or the background factor being present, but is considered as absorbed into the temperature factor. Attempts are now being made to see whether the background factor (Survey, page 199) is confused in some way with the extinction correction factor, if present, in our experiments.

Coster, Knol and Prins<sup>9</sup> have shown for zinc blende both theoretically and experimentally that the structure factor for the octahedral (111) faces changes across the  $K$ -absorption limit for zinc. The  $K$ -absorption limit for zinc being at  $1.281\text{\AA}$ , they show that for gold  $L_{\alpha_2}(\lambda = 1.285\text{\AA})$  the Zn and S scatter in phase with each other, while for gold  $L_{\alpha_1}(\lambda = 1.273\text{\AA})$  there is a phase difference of  $10\frac{1}{2}$  degrees for the scattering from the zinc and sulphur atoms. Since we have used for zinc-blende x-rays from a molybdenum target, there can not be appreciable phase changes. Coster and Knol<sup>10</sup> have shown that the phase changes for reflections from iron and aluminum are not over  $4\frac{1}{2}$  degrees, for  $\lambda = 0.710\text{\AA}$  for changes of  $\sin \theta / \lambda$  from 0 to 1. Since the ratio of atomic numbers for iron and aluminum

<sup>8</sup> Claassen and Burgers, *Zeits. f. Krist.* **A86**, 100 (1933).

<sup>9</sup> Coster, Knol and Prins, *Zeits. f. Physik* **63**, 345 (1930). See also J. A. Prins, *Zeits. f. Physik* **47**, 479 (1928).

<sup>10</sup> Coster and Knol, *Proc. Roy. Soc.* **A139**, 459 (1933). See also Coster and Knol, *Zeits. f. Physik* **75**, 340 (1932).

is 2 to 1 and that for zinc and sulphur is somewhat less than this, we are safe in ignoring such possible phase differences for sphalerite.

#### V. ADDENDA

1. It is interesting to note that the density of wurtzite and of sphalerite is the same, *viz.* 4.01. For the volume of unit cell for wurtzite is  $3.84^2 \cdot \sin 60^\circ \cdot 6.28 \text{ \AA}^3 = 80.20 \text{ \AA}^3$ , while the corresponding mass is  $2(65.38 + 32.06)1.649 \times 10^{-24} = 321.36 \times 10^{-24}$  g per unit cell. The volume of unit cell for sphalerite is  $(5.43 \text{ \AA})^3 = 160.1 \text{ \AA}^3$  while its mass is 642.72. Evidently if  $a$  for wurtzite is accurately 3.84 \AA and  $2(\frac{2}{3})^{\frac{1}{2}}$  is the correct axial ratio, the edge of the cube for sphalerite should be  $(160.40)^{\frac{1}{3}} = 5.433 \text{ \AA}$ . Fuller gives for the dimensions of the unit cell of

wurtzite  $a = 3.811 \pm 0.004 \text{ \AA}$ ,  $c = 6.234 \pm 0.006 \text{ \AA}$ ,  $c/a = 1.636$  instead of 1.6328 (= 1.633) \AA. From these figures the volume per unit cell is  $78.40 \text{ \AA}^3$ .

2. To get  $\mu r = 3$  for ZnS we have  $(N\lambda)_{\text{zn}} = 30 \cdot 0.710 = 21.3$ ,  $(N\lambda)_{\text{s}} = 16 \cdot 0.710 = 11.4$ , giving  $(\mu_e L)_k$  for zinc 119 and  $(\mu_e L)_k$  for sulphur 19.9. Thus

$$\left(\frac{\mu}{\rho}\right)_{\text{zn}} = \frac{30 \cdot 119}{65.38} = 54.7 \text{ and } \left(\frac{\mu}{\rho}\right)_{\text{s}} = \frac{16 \cdot 19.9}{32.06} = 9.94.$$

$$\text{Therefore } \left(\frac{\mu}{\rho}\right)_{\text{znS}} = \frac{65.38 \cdot 54.7 + 32.06 \cdot 9.94}{65.38 + 32.06} = 38.0, \text{ giving } \mu = 152.$$

Now  $r$  was taken as 0.2 mm, hence  $\mu r = 3$ .

<sup>11</sup> For notation see Jönsson, Uppsala Dissertation, 1928.