Note on the Crystal Structure of Silver Sulphate, Ag_2SO_4.

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In Z. Krist. **80**, 402. 1931 K. Herrmann and W. Ilge published a paper on the crystal structure of silver sulphate. The paper contains statements which cannot go unchallenged.

Herrmann and Ilge give the parameter values for oxygen as $x = 0.025$, $y = 0.22\ (0.28)$, $z = 0.23\ (0.27)$. (For particulars the original paper must be consulted.) A sulphur atom in (000) is surrounded by four oxygen atoms having positions $(\frac{1}{4} - x, \frac{1}{4} - y, \frac{1}{4} - z)$, $(\frac{1}{4} - x, y + \frac{3}{4}, z + \frac{3}{4})$, $(x + \frac{3}{4}, y + \frac{3}{4}, \frac{1}{4} - z)$, $(x + \frac{3}{4}, \frac{1}{4} - y, z + \frac{3}{4})$. These four oxygen atoms form a polyhedron which is far from being a regular tetrahedron. F. ex. the distance between the oxygen atoms in $(\frac{1}{4} - x, \frac{1}{4} - y, \frac{1}{4} - z)$ and $(\frac{1}{4} - x, y + \frac{3}{4}, z + \frac{3}{4})$ is only 0.86 Å. This enormous deformation Herrmann and Ilge attribute to the polarizing influence of the silver atoms. It is hard, however, to believe such a statement. It is naturally not unlikely that the silver atoms really cause some deformation of the SO_4-group; but the present author is of the opinion that it would not be large enough to be detected by photographic methods.

The object of the present note is to show that the observations given by Herrmann and Ilge can be satisfactorily accounted for on the basis of a reasonable structure.

Some months ago Mr. G. E. Ziegler and I submitted to Z. Krist. a paper on the crystal structure of Na_2SO_4. This compound, as it is well known, is reported to be isomorphous with Ag_2SO_4. We based our determination of the parameters on a large number of oberservations and we succeeded in fixing all parameter values with considerable accuracy. The SO_4-group proved to be an almost perfect tetrahedron.

Using parameter values only slightly different from those which I found in Na_2SO_4 it is possible to obtain satisfactory agreement between observed and calculated intensities for Ag_2SO_4, as the following table shows.

Table I.

hkl	Int. obs.	(*F*) calc. Zach.	Int. calc. Herrmann and Ilge	*hkl*	Int. obs.	(*F*) calc. Zach.	Int. calc. Herrmann and Ilge
022	s	250	55	066	s-vs	500	63
040	s	668	167	404	nil	69	0
220	vs	628	299	008	m	343	15
202	s	314	331	0.10.2	w	228	17
004	w	216	4	0.12.0	m	428	25
044	nil	113	0	1.0.88	m	248	11
026	s	441	164	660	ms	351	25
080	ms	429	122	606	ms	321	26
400	s	431	128	0.0.12	ms	332	31
440	s	481	67	0.16.0	ms	368	41

vs = very strong, s = strong, m = medium, w = weak.

The structure amplitudes given in column 3 in the above table were calculated on the basis of the following parameter values:

1) Referred to centre of symmetry as origin

$$u = 0.450 \quad x = 0.022 \quad y = 0.058 \quad z = 0.208,$$

2) Referred to the origin used by Herrmann and Ilge

$$u = 0.325 \quad x = 0.147 \quad y = 0.067 \quad z = -0.083.$$

As F curves for S and O, I used the ones given in the Na_2SO_4 paper while the F-curve for Ag was calculated by Thomas' method. The observations in table I are arranged according to increasing glancing angle. Minor discrepancies may be due to the high absorption. It would have been desirable if Herrmann and Ilge had published the observations also for reflections from planes with general indices. The amount of data which they used hardly justifies the boldness of their statement.

With my parameter values the interatomic distances are:
In SO_4-group: S—O 1.48 Å O—O 2.40, 2.42 and 2.42 Å.
Ag is surrounded by six oxygen atoms at distances 2.76 Å, 2.40 Å and 2.34 Å.

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K. Herrmann: Bemerkung zur Notiz von W. H. Zachariasen.

Der Befund von Herrn Zachariasen, dessen Berechtigung wir nach Nachprüfung nicht bestreiten können, verpflichtet uns, das Silbersulfat einer erneuten Untersuchung zu unterziehen, wobei wir nach Möglichkeit Intensitätsmessungen, nicht Schätzungen verwenden wollen. Wir hoffen, so Klarheit zu gewinnen, ob das SO_4-Tetraeder soweit gehend zerdrückt ist, wie wir es gefunden zu haben glauben, oder nur so wenig, wie es Herr Zachariasen berechnet.

Selbst für den Fall aber, daß sich die von uns angegebenen Parameter der Sauerstoffatome als irrig erweisen sollten, bleiben unsere Überlegungen in der Schlußbemerkung unserer Arbeit bestehen, da ja für diese nur die Raumgruppe und die geometrischen Orte der Ionen von Bedeutung sind. Die Raumgruppe aber, sowie die geometrischen Orte der Ionen und auch der Parameter der Silber-Ionen werden ja von Herrn Zachariasen nicht bezweifelt.