# CCCLXXII.—*The Crystal Structure of Silver Subfluoride.*

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The peculiar valency relationships existing in sub-compounds make it desirable to establish conclusively the existence of these substances as definite chemical individuals, and for this purpose *X*-ray methods appear to yield the most promising results (compare Levi, *Gazzetta*, 1924, **54**, 598). Silver subfluoride, $Ag_2F$, one of the most interesting and well-defined of these compounds, was chosen for investigation in this manner, but a specimen of the substance prepared by Wöhler's method (*Z. anorg. Chem.*, 1912, **78**, 242) yielded unsatisfactory *X*-ray photographs in which the presence of silver lines indicated the heterogeneity of the sample. However, since the commencement of this work, Hettich (*ibid.*, 1927, **167**, 70) has prepared large crystals of silver subfluoride electrolytically and demonstrated its chemical entity by an *X*-ray comparison of his product with silver and with the normal fluoride. Hettich's method of preparation was therefore adopted by us, and our main object was then confined to the elucidation of the crystal structure of silver subfluoride as revealed by its *X*-ray diffraction pattern.

Silver subfluoride crystals, prepared by electrolysing a concentrated solution of silver fluoride at 60° with a low current density, were washed with alcohol and ether and dried in a vacuum (Found : total Ag, 91·5; soluble Ag, 45·1; F, 8·0. Calc. : total Ag, 91·9; soluble Ag, 45·95; F, 8·1%).

A comparison photograph of silver subfluoride and sodium chloride was obtained by the powder method of Debye–Scherrer and Hull, a Shearer tube fitted with a copper anticathode being used as a source of *X*-radiation. The results of measurements made upon this photograph are given in Table I, the calculated values of $d_{hkil}/n$ being based on a hexagonal lattice of side 2·989 Å.U. and height 5·710 Å.U., which was deduced from the observed values of the interplanar spacings by means of Hull's plots (*Physical Rev.*, 1921, **17**, 549). One molecule of $Ag_2F$ in a cell of these dimensions requires a density of 8·78, whereas the experimentally determined value is 8·64 (Hettich gives 8·57).

In Table II are recorded measurements made upon a plain silver subfluoride photograph, and the strong lines have been employed for calibration purposes, data from Table I being used. In this way it has been possible to identify the weak lines and thus obtain useful information for intensity considerations.

## TABLE I.

| Sodium chloride. | | | Silver subfluoride. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $d_{hkil}$ of standard lines. | Distance between corresponding lines. | Calculated value of camera radius. | Distance between corresponding lines. | Estimated value of camera radius. | Angle of reflexion, $\theta$. | Cosec $\theta$. | $d_{hkil}/n$ obs. | $d_{hkil}/n$ calc. | Indices, *hkil.* |
| | | | 15·575 | 3·001 | 15° 38′ | 3·711 | 2·857 | 2·855 | 0002 |
| 2·814 | 15·525 | 3·001 | | | | | | | |
| | | | 14·850 | 3·000 | 19 5 | 3·059 | 2·355 | 2·358 | 1011 |
| 1·990 | 14·075 | 2·999 | | | | | | | |
| | | | 13·850 | 2·999 | 23 41 | 2·490 | 1·917 | 1·918 | 1012 |
| | | | | | | | | 1·903 | 0003 |
| 1·625 | 12·925 | 3·000 | | | | | | | |
| | | | 12·550 | 2·999 | 29 46 | 2·014 | 1·551 | 1·533 | 1013 |
| | | | 12·350 | 2·998 | 30 59 | 1·943 | 1·496 | 1·495 | 1120 |
| 1·407 | 11·887 | 2·997 | | | | | | | |
| 1·258 | 10·975 | 3·010 | which coincides with | | | | | 1·250 | 1014 |
| | | | 10·275 | 3·007 | 41 2 | 1·523 | 1·173 | 1·179 | 2022 |
| | | | | | | | | 1·175 | 1123 |
| 1·149 | 10·050 | 3·005 | | | | | | | |
| | | | 8·875 | 3·009 | 46 54 | 1·370 | 1·054 | 1·045 | 1015 |
| | | | | | | | | 1·032 | 1124 |
| 0·938 | 7·325 | 3·013 | | | | | | | |
| | | | 6·725 | 3·011 | 58 1 | 1·179 | 0·908 | 0·908 | 1125 |
| 0·890 | 6·325 | 3·010 | which coincides with | | | | | 0·893 | 1016 |
| | | | | | | | | 0·885 | 2132 |

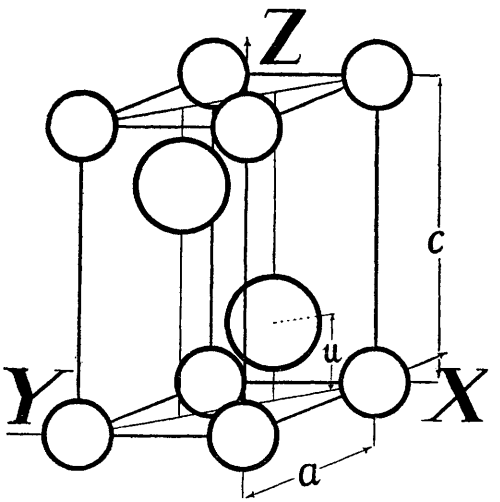
## TABLE II.

| $d_{hkil}$ of standard lines. | Distance between corresponding lines. | Calculated value of camera radius. | Distance between corresponding lines. | Estimated value of camera radius. | Angle of reflexion, $\theta$. | Cosec $\theta$. | $d_{hkil}/n$ obs. | $d_{hkil}/n$ calc. | Indices, *hkil.* |
|---|---|---|---|---|---|---|---|---|---|
| 2·855 | 15·540 | 2·994 | | | | | | | 0002 |
| | | | 15·220 | 2·993 | 17° 16′ | 3·369 | 2·594 | 2·590 | 1010 |
| 2·358 | 14·820 | 2·992 | | | | | | | 1011 |
| | | | 13·850 | 2·991 | 23 40 | 2·491 | 1·918 | 1·918 | 1012 |
| 1·903 | 13·810 | 2·991 | | | | | | | 0003 |
| | | | 12·470 | 2·987 | 30 11 | 1·989 | 1·531 | 1·533 | 1013 |
| | | | 12·350 | 2·986 | 30 45 | 1·956 | 1·505 | 1·495 | 1120 |
| | | | 11·377 | 2·985 | 35 24 | 1·726 | 1·329 | 1·325 | 1122 |
| | | | 10·955 | 2·984 | 37 25 | 1·646 | 1·267 | 1·262 | 2021 |
| 1·250 | 10·830 | 2·984 | | | | | | | 1014 |
| 1·175 | 10·270 | 2·989 | | | | | | | 1123 |
| | | | | | | | | | 2022 |
| | | | 9·912 | 2·989 | 42 30 | 1·480 | 1·140 | 1·144 | 0005 |
| | | | 8·625 | 2·989 | 48 40 | 1·332 | 1·025 | 1·045 | 1015 |
| | | | | | | | | 1·032 | 1124 |
| | | | 7·775 | 2·990 | 52 45 | 1·256 | 0·967 | 0·978 | 2130 |
| | | | | | | | | 0·964 | 2131 |
| 0·908 | 6·675 | 2·990 | | | | | | | 1125 |
| | | | 6·305 | 2·990 | 59 47 | 1·157 | 0·891 | 0·893 | 1016 |
| | | | | | | | | 0·885 | 2132 |

Silver subfluoride is a hard, metallic-looking substance, not easily reduced to powder in a mortar. It seems probable, therefore, that the atoms of silver and fluorine are closely packed, and the compound would appear to have a " cadmium iodide " structure.

This is shown in Fig. 1, in which the large circles denote silver atoms and the small circles fluorine atoms. Fluorine occupies the position (0, 0, 0) and silver the positions ($\frac{1}{3}$, $\frac{2}{3}$, $\mu$) and ($\frac{2}{3}$, $\frac{1}{3}$, $\bar{\mu}$). The value of the parameter $\mu$, the distance between successive planes of silver and fluorine atoms, may be deduced from intensity considerations, and for this purpose the relations between the intensities of the various orders of reflexion from the 0001 plane are valuable. It has been possible to obtain crystals with well-developed faces parallel to the 0001 plane and also to the 1011 plane, and to record the various orders of reflexion from them. The observed intensities of the first-, second-, and third-order reflexions from the 0001 plane do not exhibit a normal decline : the second order is stronger than the first, and the third order is stronger than the first but weaker than the second. A weak fifth-order reflexion also occurs. In the case of the 1011 plane only a first-order reflexion is obtained. In Table III an estimated value of the intensity of reflexion is given for each line observed, and intensities calculated for several values of $\mu$ are also given for comparison. The lines have been divided into groups in which each is derived from the same type of plane. Some of the lines are unresolved doublets, and in these cases it has been impossible to assign any definite observed intensity values to the components. The indices of co-operating planes have therefore been inserted after the observed intensity value.

FIG. 1.




The expression $I = NS^2/\sin^2\theta$, where $N$ is the number of co-operating planes and $S = 10 + 46[e^{i2\pi n(h/3 + 2k/3 + \mu l)} + e^{i2\pi n(2h/3 + k/3 + \bar{\mu} l)}]$, has been used in the above calculations.

The most satisfactory agreement between observed and calculated values occurs when $\mu = 0{\cdot}3$. There is, however, an obvious discrepancy in the case of the 1120 plane, but this could not be eliminated by a change of $\mu$. Apart from this inconsistency, the general similarity of observed and calculated intensities in each

TABLE III.

| Indices of plane *hkil.* | Observed intensity. | Intensity calculated for different values of $\mu$. 0·1. | 0·2. | 0·3. | 0·4. | 0·5. |
|---|---|---|---|---|---|---|
| 0001 | 7 | 385 | 77 | 17 | 217 | 356 |
| 0002 | 10 | 20 | 56 | 56 | 20 | 143 |
| 0003 | 9 | 5 | 25 | 43 | 9 | 41 |
| 0004 | — | 14 | 5 | 5 | 14 | 35 |
| 0005 | 2 (1124) | 15 | 22 | 15 | 22 | 15 |
| 0006 | — | 6 | 2 | 2 | 6 | 16 |
| 1010 | 2 | 110 | 110 | 110 | 110 | 110 |
| 2020 | — | 11 | 11 | 11 | 11 | 11 |
| 1011 | 9 | 300 | 360 | 216 | 0 | 222 |
| 1012 | 8 | 240 | 0 | 321 | 198 | 43 |
| 1013 | 3 | 66 | 172 | 11 | 150 | 68 |
| 1014 | 7 | 0 | 84 | 102 | 138 | 18 |
| 1015 | 1 | 32 | 12 | 32 | 12 | 32 |
| 1016 | 7 (2132) | 68 | 50 | 43 | 12 | 10 |
| 1120 | 1 | 240 | 240 | 240 | 240 | 240 |
| 1121 | — | 137 | 28 | 6 | 78 | 131 |
| 1122 | 2 | 25 | 73 | 73 | 24 | 187 |
| 1123 | 5 (2022) | 4 | 58 | 99 | 14 | 95 |
| 1124 | 2 (0005) | 43 | 15 | 15 | 43 | 110 |
| 1125 | 7 | 56 | 87 | 56 | 87 | 56 |
| 2021 | 1 | 154 | 81 | 218 | 218 | 53 |
| 2022 | 5 (1123) | 71 | 124 | 0 | 90 | 19 |
| 2130 | 2 (2131) | 30 | 30 | 30 | 30 | 30 |
| 2131 | 2 (2130) | 51 | 34 | 25 | 0 | 13 |
| 2132 | 7 (1016) | 51 | 0 | 71 | 42 | 9 |

group is good, and it is suggested that a " cadmium iodide " structure, with $\mu$ = app. 0·3, is fairly representative of silver subfluoride.

When $\mu = 0{\cdot}3$, the atomic diameter of silver with respect to silver is about 2·8 Å.U. and with respect to fluorine about 3·6 Å.U., and it is significant that these values are equal to the atomic diameters of silver in the metallic state and in normal combination, respectively. This seems to indicate that the relation between adjacent silver atoms resembles that existing in the metallic state, and that the relation between adjacent silver and fluorine atoms is similar to that in normal silver fluoride. Perhaps in the formation of a molecule of subfluoride two silver atoms partly share their uncompleted rings of electrons, leaving between them in reserve an electron to complete the electron ring of a fluorine atom. If this be the case, previous hypotheses postulating the existence of " sub-ions " would appear to have some justification, and the metallic properties of silver subfluoride (*e.g.*, electrical conductivity of the order of that of graphite) would find a ready explanation.

*Summary.*

Silver subfluoride has been examined by the powder method, and found to possess a hexagonal unit cell of dimensions $a = 2{\cdot}989$ Å.U. and $c = 5{\cdot}710$ Å.U. The density corresponds to one molecule in the unit cell. Intensity considerations appear to agree with a

" cadmium iodide " structure with the parameter $\mu$ equal to about 0·3.

In conclusion, one of us (H. D.) wishes to express his grateful thanks to the Salters' Institute for a grant which has enabled him to take part in this research.

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