Summary

The system, ferric oxide–sulfur trioxide–water, has been studied over the temperature range from 50° to 200°.

The following crystalline phases were encountered: Fe_2O_3; $Fe_2O_3 . H_2O$; $3Fe_2O_3 . 4SO_3 . 9H_2O$; $Fe_2O_3 . 2SO_3 . H_2O$; $Fe_2O_3 . 2SO_3 . 5H_2O$; $2Fe_2O_3 . 5SO_3 .-17H_2O$; $Fe_2O_3 . SO_3$ (2 forms); $Fe_2O_3 . 3SO_3 . 6H_2O$; $Fe_2O_3 . 3SO_3 . 7H_2O$; $Fe_2O_3 . 4SO_3 . 3H_2O$ and $Fe_2O_3 . 4SO_3 . 9H_2O$.

The conditions under which these substances are formed, the ranges of their stabilities, and their relations to one another, also some of their crystallographic and optical properties, were determined. The data obtained are presented by means of tables, and graphically by means of curves and a solid model.

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THE CRYSTAL STRUCTURE OF SILVER MOLYBDATE

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Introduction

Crystals of silver molybdate, Ag_2MoO_4, were obtained by the slow evaporation of ammonia from a solution of silver molybdate in ammonium hydroxide. From the best of these, most of which were flat, rather imperfect octahedral plates, 3 or 4 mm. across, a satisfactory reflection photograph was prepared. The Laue photographs, on the other hand, were made from a perfect appearing octahedron less than 1 mm. in greatest dimension. It is of interest to observe that such a small crystal can furnish satisfactory Laue photographic data. Optical examination showed these crystals to be essentially isotropic; no assignment to a particular class of symmetry on the basis of the ordinary crystallographic information appears ever to have been made.

The Crystal Structure of Silver Molybdate

This determination of structure was made by the generally applicable procedure which has previously been described.[2] Measurements of a comparison reflection photograph against the (111) face of silver molybdate and the (100) face of calcite, combined with an estimation of the density of the salt, showed that either 8 or 64 chemical molecules are to be

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[2] Wyckoff, *Am. J. Sci.*, **50,** 317 (1920). Wyckoff and Posnjak, THIS JOURNAL, **43,** 2292 (1921).

contained within the unit cell. By this same measurement the length of the side of the cube containing eight molecules was found to be 9.26 Å.

Three Laue photographs were prepared with the X-rays making different angles with the normal to the (111) face. Calculating wavelengths upon the basis of the unit containing 8 molecules, no values were found less than 0.24. This wavelength is the shortest which, from a knowledge of the impressed voltage, is present in the X-ray beam. The small unit may consequently be chosen as the correct one.

Taking as a working basis the 8 molybdenum atoms as equivalent to one another and the 16 silver atoms as likewise equivalent, it is necessary to search for space groups having 8, 16 and, if the oxygen atoms are also alike, 32 equivalent positions within the unit cell. Three space groups meet this requirement: $T_h{}^4$, O^4 and $O_h{}^7$. The atomic arrangements arising from all 3 of these space groups are identical and therefore in themselves possess holohedral symmetry. It is a characteristic of these space groups that crystals developed from them will give reflections in the first order region only from planes having all odd indices and no reflections in the second order from planes of the forms $\{0kl\}$, where k and l are one even and the other odd.[3] Examination of the Laue photographic data from silver molybdate shows that these conditions are fulfilled. It is, therefore, probable that the arrangement of the atoms of this crystal is one deducible from these space groups. In this case the problem of the structure of silver molybdate becomes the same as that of the structures of magnetite[4] (Fe_3O_4) and potassium zinc cyanide,[5] ($K_2Zn(CN)_4$) which have already been treated in detail.

Placing the molybdenum atoms in the positions[6] (8f) $000; \frac{1}{2}\frac{1}{2}0 : \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}$; the positions of the oxygen atoms will be defined by

(32b)　$uuu; u + \frac{1}{2}, u + \frac{1}{2}, u; u + \frac{1}{2}, u, u + \frac{1}{2}; u, u + \frac{1}{2}, u + \frac{1}{2};$
　　　$u\bar{u}\bar{u}; u + \frac{1}{2} \frac{1}{2} - u, \bar{u}; u + \frac{1}{2}, \bar{u}, \frac{1}{2} - u; u, \frac{1}{2} - u, \frac{1}{2} - u;$
　　　$\bar{u}u\bar{u}; \frac{1}{2} - u, u + \frac{1}{2}, \bar{u}; \frac{1}{2} - u, u, \frac{1}{2} - u; \bar{u}, u + \frac{1}{2}, \frac{1}{2} - u;$
　　　$\bar{u}\bar{u}u; \frac{1}{2} - u, \frac{1}{2} - u, u; \frac{1}{2} - u, \bar{u}, u + \frac{1}{2}; \bar{u}, \frac{1}{2} - u, u + \frac{1}{2};$
$^1/_4 - u, {}^1/_4 - u, {}^1/_4 - u; \frac{3}{4} - u, \frac{3}{4} - u, {}^1/_4 - u; \frac{3}{4} - u, {}^1/_4 - u, \frac{3}{4} - u; {}^1/_4 - u,$
$\frac{3}{4} - u, \frac{3}{4} - u;$
$\frac{1}{4} - u, u + \frac{1}{4}, u + \frac{1}{4}; \frac{3}{4} - u, u + \frac{3}{4}, u + \frac{1}{4}; \frac{3}{4} - u, u + \frac{1}{4}, u + \frac{3}{4}; \frac{1}{4} - u,$
$u + \frac{3}{4}, u + \frac{3}{4};$
$u + \frac{1}{4}, \frac{1}{4} - u, u + \frac{1}{4}; u + \frac{3}{4}, \frac{3}{4} - u, u + \frac{1}{4}; u + \frac{3}{4}, \frac{1}{4} - u, u + \frac{3}{4}; u + \frac{1}{4},$
$\frac{3}{4} - u, u + \frac{3}{4};$

[3] Wyckoff, *Am. J. Sci.*, 4, 175(1922).

[4] Nishikawa, *Proc. Tokyo Math. Phys. Soc.*, 8, 199 (1915).

[5] Dickinson, THIS JOURNAL, 44, 774 (1922).

[6] These coördinate positions are taken from the writer's book entitled "The Analytical Expression of the Theory of Space Groups," which, as a publication of the Carnegie Institution of Washington, is now in press. All coördinates, except those of Arrangement (32b), are also given by P. Niggli, "Geometrische Krystallographie des Discontinuums," Leipzig, 1919.

$u + \frac{1}{4}, u + \frac{1}{4}, \frac{1}{4} - u; u + \frac{3}{4}, u + \frac{3}{4}, \frac{1}{4} - u; u + \frac{3}{4}, u + \frac{1}{4}, \frac{3}{4} - u; u + \frac{1}{4},$
$$u + \frac{3}{4}, \frac{3}{4} - u.$$

and the positions of the silver atoms either by

(16b) $\frac{1}{8}\frac{1}{8}\frac{1}{8}; \frac{5}{8}\frac{5}{8}\frac{1}{8}; \frac{5}{8}\frac{1}{8}\frac{5}{8}; \frac{1}{8}\frac{5}{8}\frac{5}{8};$
$\frac{1}{8}\frac{7}{8}\frac{7}{8}; \frac{5}{8}\frac{3}{8}\frac{7}{8}; \frac{5}{8}\frac{7}{8}\frac{3}{8}; \frac{1}{8}\frac{3}{8}\frac{3}{8};$
$\frac{7}{8}\frac{1}{8}\frac{7}{8}; \frac{3}{8}\frac{5}{8}\frac{7}{8}; \frac{3}{8}\frac{1}{8}\frac{3}{8}; \frac{7}{8}\frac{5}{8}\frac{3}{8};$
$\frac{7}{8}\frac{7}{8}\frac{1}{8}; \frac{3}{8}\frac{3}{8}\frac{1}{8}; \frac{3}{8}\frac{7}{8}\frac{5}{8}; \frac{7}{8}\frac{3}{8}\frac{5}{8}.$

or by (16c) $\frac{1}{8}\frac{3}{8}\frac{7}{8}; \frac{7}{8}\frac{1}{8}\frac{3}{8}; \frac{3}{8}\frac{7}{8}\frac{1}{8}; \frac{3}{8}\frac{5}{8}\frac{3}{8};$
$\frac{1}{8}\frac{5}{8}\frac{1}{8}; \frac{1}{8}\frac{1}{8}\frac{5}{8}; \frac{5}{8}\frac{1}{8}\frac{1}{8}; \frac{5}{8}\frac{5}{8}\frac{5}{8};$
$\frac{7}{8}\frac{3}{8}\frac{1}{8}; \frac{1}{8}\frac{7}{8}\frac{3}{8}; \frac{3}{8}\frac{1}{8}\frac{7}{8}; \frac{5}{8}\frac{3}{8}\frac{3}{8};$
$\frac{7}{8}\frac{5}{8}\frac{7}{8}; \frac{7}{8}\frac{7}{8}\frac{5}{8}; \frac{5}{8}\frac{7}{8}\frac{7}{8}; \frac{3}{8}\frac{3}{8}\frac{5}{8}.$

Two distinct arrangements are thus possible according to whether the silver atoms have the positions of (16b) or of (16c). A choice between these two possible structures and an estimation of the value of u, the parameter locating the oxygen atoms, can both be made from the observation that no first order reflection was found from the (111) face and that the second and third orders were of about equal intensity. This latter fact can only be true if the amplitude of the third order reflection considerably exceeds that of the second order reflection. The reduced forms of the customary intensity expressions[2] have been given;[5] using these (and similar ones for the second and third order reflections) the amplitudes, $\sqrt{A^2 + B^2}$, can be calculated for both arrangements and for all values of u from 0 to 0.50. Results of such a calculation are shown in Table I. A consideration of the form of the coördinate positions for the oxygen

TABLE I

CALCULATIONS OF (111) AMPLITUDES FOR VARIOUS OXYGEN POSITIONS

Amplitudes, $\sqrt{A^2 + B^2}$

Oxygen parameter u	First order Silver according to		Second order	Third order Silver according to	
	(16b)	(16c)		(16b)	(16c)
0.00	794	42	752	42	795
0.05	775	23	804	198	554
0.10	747	6	972	300	453
0.15	747	6	972	300	453
0.20	775	23	804	198	554
0.25	794	42	752	42	795
0.30	765	13	700	6	747
0.35	673	79	532	11	763
0.40	554	198	532	289	464
0.45	462	289	700	271	480
0.50	433	319	752	320	433

atoms shows that it is sufficient to treat values of u only up to 0.5. From this table it is immediately seen that no matter what positions are assigned to the oxygen atoms, the calculated amplitude for the third order reflection is always much less than that of the second order reflection if the silver atoms have the arrangement (16b). It must, consequently, be concluded

that, if the scattering powers of these atoms are even very roughly in the ratio of their atomic numbers, (16b) is impossible as an arrangement of the silver atoms; moreover, if they have arrangement (16c), the amplitude of the third order reflection is greater than that of the second order reflection only for the values of u between 0.25 and 0.39.

The general correctness of this structure can be tested and a narrowing of this assignment of position to the oxygen atoms can be accomplished through a study (1) of first order reflections from planes having all odd indices and (2) of second order reflections from planes having at least one even index.   It is a property of this structure that the all-odd planes when reflecting in the first order should group themselves into two classes: because of the relatively weak scattering powers of the oxygen atoms, those planes for which the molybdenum and silver atoms are in phase should be intense, and those where they are operating against one another should be either weak or entirely absent.   The planes belonging to the first class[4,5] are those having either only one or all three of their indices equal to $8p \pm 3$ (where p is an integer which may be different for the different indices); those belonging to the second class have either one or all three of their indices equal to $8p \pm 1$.   The only first order reflections found were from planes of the following forms: $\{533\}$, $\{355\}$, $\{137\}$, $\{157\}$, $\{159\}$, $\{377\}$, $\{577\}$, $\{379\}$, $\{3, 3, 11\}$, $\{579\}$, $\{3, 5, 11\}$, $\{1, 7, 11\}$, and $\{3, 3, 13\}$.   All of these belong to the first class.   No marked abnormalities amongst planes of one of these classes, such as might be used to locate the oxygen atoms with greater accuracy, were observed.   By assuming that the scattering powers of the different atoms were more or less roughly proportional to their atomic numbers, it was found possible in those cases where the computations were undertaken to account for the complete absence of such planes of the second class as were in favorable positions to reflect, if the parameter u has a value close to 0.37.   For instance the calculated amplitude of a plane of the form $\{551\}$ which though favorably situated failed to appear, is shown in Table II.

TABLE II

CALCULATED AMPLITUDES FOR THE ABSENT PLANE $\{551\}$ FOR VARIOUS POSITIONS OF OXYGEN

Oxygen parameter (u)	Amplitude	Oxygen parameter (u)	Amplitude
0.33	− 65	0.36	− 22
0.34	− 10	0.37	− 94
0.35	+ 7	0.38	−182

Second order reflections from planes having two even and one odd indices, to which only oxygen atoms contribute, were all apparently absent from the photographs.   This absence is explicable either if the oxygen atoms are situated exactly at $^3/_8$ or if the scattering power of the oxygen

atoms is very small compared with those of the other atoms. At the present time it is scarcely advisable to choose between these two explanations.

Silver and oxygen atoms contribute to second order reflections from planes having two odd and one even indices. Abnormalities amongst such planes, though relatively slight, were of such a character as to indicate that u has a value near to $q/8$, where q is an odd number. Taken in connection with the definite elimination of the region about $1/8$ that arises from a consideration of (111) reflections, this likewise points to a value of u around $3/8$.

If definite information were available about the relative scattering powers of the different atoms involved, the position of the oxygen atoms could be determined with a very considerable accuracy. It can, however, be safely said that u has a value close to 0.37. How far from this position the oxygen may be and still satisfy the observations will depend somewhat on the scattering powers that are chosen; it does not seem probable, though, that u can be less than 0.34 nor greater than 0.40.

The agreements with the structure under consideration are of a nature so varied and are so striking in character that there can be no doubt of its fundamental correctness. The arrangement of the atoms in crystals of silver molybdate can consequently be concluded to be: molybdenum, (8f); silver, (16c); oxygen, (32b), with a value of u close to 0.37. The distance between molybdenum and adjacent oxygen atoms is thus about 2.00 Å.; between silver and the nearest oxygen atoms about 2.31 Å.; and between nearest molybdenum and silver atoms 4.02 Å.

It might appear natural to consider the close association of 4 oxygen atoms with each molybdenum atom as evidence for the existence of molybdate ions (MoO_4^{--}) in the crystalline state. As was pointed out in the case of potassium zinc cyanide,[5] however, the same argument would indicate the existence of highly improbable MgO_4 groups in the magnesium aluminum spinel.

Summary

Using the generally applicable methods based upon the results of the theory of space groups and taking the data from reflection spectra and Laue photographs, it is shown that silver molybdate has the same crystal structure as the spinels and magnetite. The length of the side of the unit cube, which contains 8 molecules, is 9.26 Å.; the parameter defining the position of the oxygen atoms is close to $3/8$.

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