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The Determination of the Interatomic Distances in Silver Molybdate, Ag_2MoO_4

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Silver molybdate was first examined by the X-ray method in 1922 by Wyckoff,[2] who found that crystals of the substance had what is now called the spinel structure. With the methods available at that time, Wyckoff was unable to determine accurately the value of the oxygen parameter; an approximate value of $x = {}^3/_8$ was given by him.

Since a precise value of the parameter would yield accurate values for both the molybdenum–oxygen and the silver–oxygen distance, we have reinvestigated this crystal by the X-ray method. The size of the molybdate group does not appear to have been hitherto determined and the length of the silver–oxygen bond is of interest in connection with the problem of correlating color and bond character.[3-5]

Experimental

Silver molybdate was prepared by adding aqueous silver nitrate to aqueous sodium molybdate. The resulting precipitate was washed with water and dissolved in dilute ammonium hydroxide. Slow evaporation of the solution yielded small bright yellow octahedral crystals.

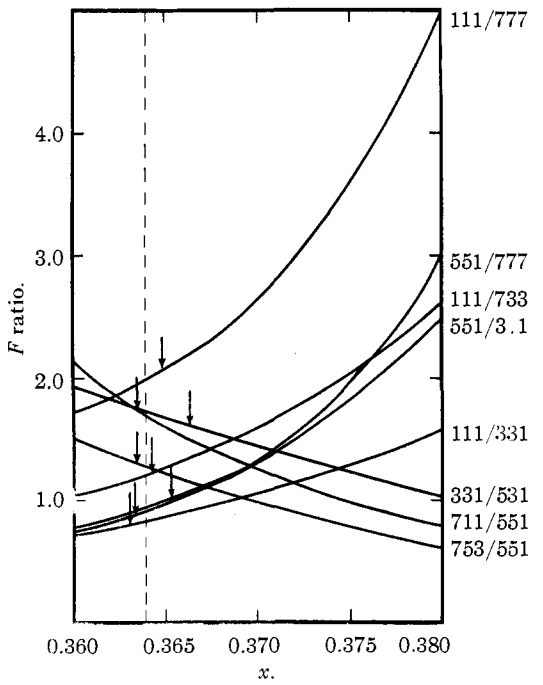

Fig. 1.—Variation in the ratios of F values with the parameter x. Arrows indicate the observed values of the ratios.

A tiny crystal, about 0.1 mm. in its greatest dimension, was chosen for X-ray examination. Measurement and indexing of symmetric and asymmetric Laue photographs taken with the general radiation from a tungsten target, and of a series of oscillation photographs taken with $MoK\alpha$ radiation ($\lambda = 0.711$ Å.) confirmed the size of the unit cell, $a_0 = 9.26$ Å., and the space group, $O_h^7 - Fd3m$, found by Wyckoff.[2] The intensities of the reflections on the oscillation photographs were estimated visually by means of the multiple film technique; the three films used in each set were interleaved by 0.001 inch copper foil in order to decrease the intensity on the successive films sufficiently.

In all calculations of F values the atomic f curves in "Internationale Tabellen zur Bestimmung von Kristallstrukturen" were used; dispersion corrections of 1.5 and 4.0 were subtracted from the values for silver and molybdenum, respectively. The corrected f curves were then multiplied by the temperature factor, $e^{-\beta(\sin\vartheta/\lambda)^2}$; the value $\beta = 1.5$ was determined from the observed F values of the reflections (hkl) for which $h = 4n$, $k = 4n$, $l = 4n$; these F values are not very structure sensitive. The effect of absorption was ignored since it is believed to have been unimportant because of the favorable size and shape of the crystal used.

Determination of the Parameter

Although the scattering power of oxygen is small compared to those of silver and molybdenum, the calculated F values of many of the reflections to which the contributions of the silver atoms and the molybdenum atoms are of opposite sign were found to vary sufficiently with x to allow a precise determination of the parameter.

Preliminary consideration of the ratio $F_{(333)}/F_{(111)}$ fixed the limits $0.36 < x < 0.38$. The F values of the ten available reflections of the type mentioned above were then calculated for values of x between these limits, in intervals of 0.002 in x. These F values were then used to calculate the dependence on x of the ratio of F values of any two reflections, the restriction being made however that all ratios between F values whose plots of F *vs.* x were of nearly the same slope were not calculated. By comparing the ratio curves so obtained with the observed ratios, twenty-one values of x were obtained. Some of these data are illustrated in Fig. 1. These values were weighted by multiplying each by the difference in slope of the two F curves involved. The weighted mean value of the parameter x obtained in this way is 0.3639, the average deviation is 0.0018, and the most probable deviation is 0.0004. On the other hand, if the observed and calculated F values of these ten reflections are treated by the method of least squares,[6] a simple procedure if the calculated F curves are used to evaluate the values of $\partial F_{hkl}/\partial x$, the value $x = 0.3634$ is obtained. We adopt 0.364 ± 0.002 as the best value of x, taking all sources of error into account.

(1) Predoctoral Fellow of the National Research Council.
(2) R. W. G. Wyckoff, THIS JOURNAL, **44**, 1944 (1922).
(3) K. S. Pitzer and J. H. Hildebrand, *ibid.*, **63**, 2472 (1941).
(4) L. Helmholz and R. Levine, *ibid.*, **64**, 354 (1942).
(5) J. Donohue and L. Helmholz, *ibid.*, **66**, 295 (1944).
(6) E. W. Hughes, *ibid.*, **63**, 1737 (1941).

A comparison of calculated and observed F values for some representative reflections is presented in Table I. The agreement between observed and calculated F values of the strongest reflections could probably be improved by correcting for extinction.

TABLE I

VALUES OF F_{hkl}

(hkl)	$F_{obs.}$	$F_{calcd.}$	(hkl)	$F_{obs.}$	$F_{calcd.}$
111*	118	109	862	112	78
220	264	248	951	167	139
311	405	456	10.2.2	179	178
222	306	396	953	<40	34
400	398	447	10.4.2	73	67
331*	145	130	11.3.1*	50	53
333	383	376	882	<40	3
511	282	303	10.6.0	59	54
440	450	659	866	80	67
531*	72	75	10.6.2	156	141
442	<35	2	777*	57	54
620	160	140	10.6.4	92	61
622	249	279	12.4.0	197	215
444	231	339	12.4.2	<40	2
551*	51	50	10.8.2	57	52
711*	89	85	10.6.6	135	114
642	127	127	12.6.2	60	45
731	227	258	10.10.0	60	48
800	376	356	10.8.6	45	34
733*	96	90	11.9.1	76	63
822	99	105	10.10.2	102	94
555	182	181	12.8.2	<40	2
662	226	222	12.6.6	33	33
840	176	197	13.7.1	64	68
911	39	42	14.6.0	59	38
753*	67	64	10.10.6	66	76
842	<40	2	12.10.2	25	28
664	108	83	13.9.1	53	57
931	167	171	16.0.0	145	111
844	304	341	12.10.6	35	24
933	<40	43	12.12.0	86	80
771*	73	73	14.10.2	44	46
10.2.0	97	83			

* These reflections were used in the parameter determination.

Discussion

The $MoO_4^{=}$ group has the configuration of a regular tetrahedron, with Mo–O = 1.83 ± 0.03 Å. Each silver atom is surrounded by a nearly regular octahedron of oxygen atoms, each at 2.42 ± 0.02 Å.

A plausible single bond tetrahedral radius for molybdenum can be derived from the apparent radius of 1.38 Å. for molybdenum in MoS_2[7] and $K_4Mo(CN)_8 \cdot 2H_2O$[8] by applying a correction factor of 0.97 for change in coördination.[9] The value obtained, 1.34 Å., may be slightly large because of the difference expected between the radii of quadrivalent and sexavalent molybdenum.[10]

The observed molybdenum–oxygen distance is thus 0.17 Å. shorter than the sum of the radii. This shortening is of the same order of magnitude as the following shortenings in other tetrahedral XO_4^{n-} ions which have been observed previously: 0.23 Å. in $SiO_4^{=}$,[11] 0.21 Å. in $PO_4^{\equiv}$,[11] 0.10 Å. in $AsO_4^{\equiv}$,[4] 0.22 Å. in $VO_4^{\equiv}$,[12] 0.19 Å. in $SO_4^{=}$,[11] 0.17 Å. in ClO_4^{-},[11] and 0.15 Å. in IO_4^{-}.[13]

The Ag–O distance of 2.42 Å. is somewhat shorter than the ionic radius sum of 2.46 Å.[4] Ag–O distances of 2.51, 2.50 and 2.42 Å. have been found in the colorless salts $AgClO_3$, Ag_2SO_4 and $KAgCO_3$, respectively.[5] In the yellow salts Ag_3PO_4 and Ag_2CO_3 the distances are 2.34 and 2.3 Å., respectively, and in Ag_3AsO_4, which is red, the distance is also 2.34 Å.[5] These distances are in only rough accord with the Pitzer–Hildebrand rule, which states that the color of a salt formed from colorless ions is a measure of the covalent character of the bonds between the ions.[3] Considerable work on the absorption spectra of various compounds is needed before the relation of color to covalence can be fully discussed.

Summary

A redetermination of the parameter in silver molybdate has been carried out using data obtained from oscillation photographs. The value obtained, $x = 0.364 \pm 0.002$, leads to the distances Mo–O = 1.83 ± 0.03 Å. and Ag–O = 2.42 ± 0.02 Å. The significance of these distances is briefly discussed.

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(8) J. L. Hoard and H. H. Nordsieck, *ibid.*, **61**, 2853 (1939).

(9) (a) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 184; (b) Lister and Sutton, *Trans. Faraday Soc.*, **37**, 393 (1941), quote the value 0.943. The reason for the change was not explained.

(10) Ref. 9a, p. 182.

(11) Ref. 9a, *ibid.*, p. 240.

(12) E. Broch, *Z. physik. Chem.*, **20B**, 345 (1933).

(13) E. Hazlewood, *Z. Krist.*, **98**, 439 (1938).