

vibrational levels formed in (2b) would increase the inequality. This result is in agreement with that reached in Sec. III.A.

* This work was supported by grants received from the National Research Council of Canada, The Defence Research Board of Canada, and U.S. Army Research Office—Durham, N.C.

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THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 55, NUMBER 3

1 AUGUST 1971

Crystal Structure Refinement of SrMoO₄, SrWO₄, CaMoO₄, and BaWO₄ by Neutron Diffraction*

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(Received 10 March 1971)

The crystal structures of CaMoO₄, SrMoO₄, SrWO₄, and BaWO₄ have been refined from neutron diffraction data taken in the (*h*0*l*) and (*h**h**l*) zones. Oxygen position refinement is started from the parameters proposed by Sill n and Nylander and results in an improvement of over an order of magnitude in the oxygen coordinates. A comparison of coordinates for the different compounds shows several systematic differences.

In 1943, Sill n and Nylander¹ carefully reviewed the evidence for the oxygen positions in a series of scheelite crystals such as CaWO₄. They were led to propose oxygen coordinates which were nearly constant fractions of the *a*, *b*, and *c* unit-cell dimensions, but with necessarily large limits of uncertainty,

CaMoO₄, CaWO₄:

$$x = 0.25 \pm 0.02, y = 0.15 \pm 0.02, z = 0.075 \pm 0.015,$$

SrMoO₄, SrWO₄:

$$x = 0.25 \pm 0.02, y = 0.14 \pm 0.02, z = 0.075 \pm 0.015,$$

PbMoO₄, PbWO₄:

$$x = 0.25 \pm 0.02, y = 0.13 \pm 0.02, z = 0.075 \pm 0.015,$$

BaMoO₄, BaWO₄:

$$x = 0.25 \pm 0.02, y = 0.11 \pm 0.02, z = 0.075 \pm 0.015.$$

Recently two refinement studies were simultaneously reported for CaWO₄, one from x-ray diffraction data by Zalkin and Templeton² and the other from neutron diffraction data by Kay, Frazer, and Almodovar.³ The results from the two are in remarkably good agreement. A neutron-diffraction refinement has also been reported by Leciejewicz⁴ for PbMoO₄. We have attempted to duplicate the treatment of Kay *et al.* on four additional scheelites to allow a closer comparison among the compounds than has thus far been possible. The diffraction

measurements were made at the 2.0-MW University of Michigan Ford Nuclear Reactor.

The scheelite structures are represented by the generic form AXO₄, where A is Ca, Sr, or Ba and X is Mo or W. These crystals all belong to the space group *C*_{4h}⁶(*I*₄/*a*), space group No. 88.⁵ For the cell origin at $\bar{4}$, the coordinates of all atom positions are

$$(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) +$$

$$4 \text{ A in } 4b \text{ at } (0, 0, \frac{1}{2}); (0, \frac{1}{2}, \frac{3}{4})$$

$$4 \text{ X in } 4a \text{ at } (0, 0, 0); (0, \frac{1}{2}, \frac{1}{4})$$

$$16 \text{ O in } 16f \text{ at } (x, y, z); (\bar{x}, \bar{y}, z); (x, \frac{1}{2} + y, \frac{1}{4} - z);$$

$$(\bar{x}, \frac{1}{2} - y, \frac{1}{4} - z); (\bar{y}, x, \bar{z}); (y, \bar{x}, \bar{z});$$

$$(\bar{y}, \frac{1}{2} + x, \frac{1}{4} + z); (y, \frac{1}{2} - x, \frac{1}{4} + z).$$

Figure 1 shows a *b*-axis projection of the unit cell, where the notation is that of Sill n and Nylander and the numbers on each atom are the fractional *y* coordinates (for CaMoO₄). The unit-cell parameters deduced from powder diffraction data⁶ were used. These are, in Angstrom units,

$$\text{CaMoO}_4: \quad a = 5.226, \quad c = 11.43,$$

$$\text{SrMoO}_4: \quad a = 5.3944, \quad c = 12.02,$$

$$\text{SrWO}_4: \quad a = 5.4168, \quad c = 11.951,$$

$$\text{BaWO}_4: \quad a = 5.6134, \quad c = 12.72.$$

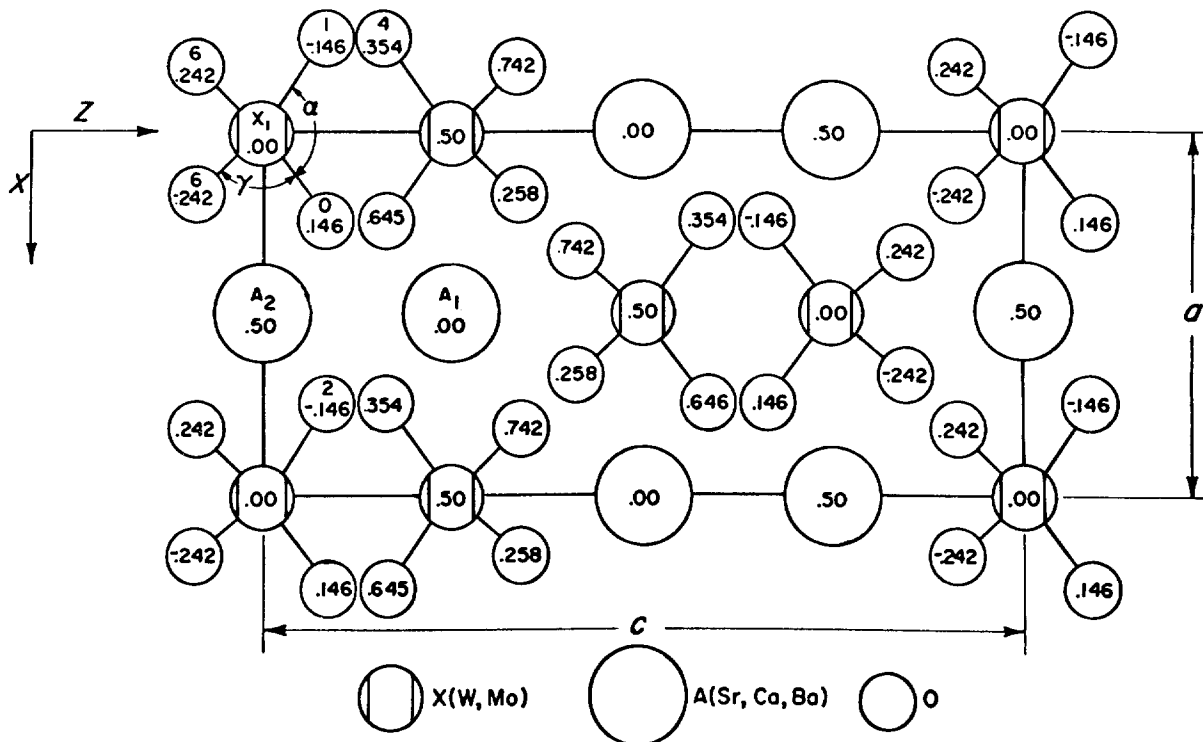


FIG. 1. The b -axis projection of a unit cell. The numbers for each atom are the y coordinates in fractions of the cell dimension. The approximate numbers for CaMoO_4 are shown.

All samples were synthetically grown (we are indebted to R. T. Farrar of the Harry Diamond Laboratories for providing these crystals) and were approximately 0.3 cm in diameter by 1.2–1.6 cm in length. Samples with the cylindrical axis along the $[010]$ direction and along the $[110]$ direction were used to measure all available Bragg events in the $(h0l)$ and (hhl) zones, respectively. Spot checks of the measurements on CaWO_4 by Kay *et al.* were made initially to verify reproducibility; the values obtained for the structure factors were in good agreement with those of Kay *et al.* except for a few very weak reflections. These we have attributed to multiple scattering.

The least squares refinement program of Busing, Levy, and Martin,⁷ with necessary modifications, was used to reduce the neutron data. The neutron scattering lengths used were as follows⁸:

$$b_{\text{O}} = 0.577 \times 10^{-12} \text{ cm},$$

$$b_{\text{Ba}} = 0.52,$$

$$b_{\text{Ca}} = 0.49,$$

$$b_{\text{Mo}} = 0.661,$$

$$b_{\text{Sr}} = 0.683,$$

$$b_{\text{W}} = 0.466.$$

Data from the strongly reflecting planes (0012) ,

(204) , (208) , and (402) consistently showed significant extinction and were not included in the refinement. However, they were used to provide small ($< 10\%$) extinction corrections to all other recorded events; an average approximate exponential coefficient was obtained by comparing the measured intensities of these strong events with computed intensities required by the uncorrected refinement parameters. The refinement was then repeated. The extinction effect on the final coordinates was small, well below the final error limits, although they improved the residues somewhat. No thermal diffuse scattering correction and no anisotropic temperature refinement were felt to be justified for these data. The effect of these omissions is negligible in the coordinate determinations, but does introduce error in the temperature factors. This was demonstrated by a number of computer test runs on all the data.

Many computer trials also demonstrated that it was possible for the least squares refinement to converge on false minima for different starting coordinates. These invariably showed worse residues. This pitfall, also encountered in lattice dynamics, was overcome by trial and error and the physical consistency of all the results. It was thus not true in all cases that the starting parameters were exactly those of Sillén and Nylander.

The observed and calculated structure factors are listed in Table I together with the residual factors. Table II gives the resulting parameters and their standard deviations and those of Refs. 2–4 for CaWO_4 and

TABLE I. Observed and calculated structure factors and residues.

<i>(hkl)</i>	CaMoO ₄		SrMoO ₄		SrWO ₄		BaWO ₄	
	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>F</i> _{obs}	<i>F</i> _{calc}
004							0.66	0.42
008	0.53	0.11	0.46	0.07	0.36	0.38	2.08	2.04
103	2.48	2.44	1.87	1.74	1.28	1.19	1.94	1.92
105	2.22	2.28	2.77	2.77	3.38	3.37	3.03	3.09
107	2.05	2.15	2.69	2.63	3.20	3.27	2.76	2.80
109	2.47	2.17	1.36	1.24	0.85	0.80	0.87	0.80
1011	1.56	1.25	0.67	0.47				
1013	1.18	1.43	1.39	1.25	0.61	0.57	1.71	1.64
200	1.44	1.22	0.40	0.21	0.72	0.69	0.36	0.35
202	2.90	2.97	2.86	2.99	2.91	2.99	3.42	3.45
206	0.47	0.08	0.51	0.32			0.88	0.77
2010	2.62	2.66	3.10	3.00	2.87	2.87	3.58	3.46
2014					2.22	2.27	1.71	1.65
301	1.15	1.19	1.87	1.89	2.58	2.64	2.02	2.09
303	2.01	2.06	1.90	1.89	2.46	2.53	1.29	1.40
305	4.65	4.67	3.38	3.36	3.20	3.15	2.69	2.57
307	4.61	4.51	3.19	3.28	3.02	3.06	2.54	2.62
309	2.16	1.64	1.50	1.24	2.25	2.04	0.44	0.24
3011							1.03	0.86
3013							2.13	2.06
400	5.19	5.10	4.78	4.63	4.38	4.31	3.03	3.04
404			4.62	4.66	4.36	4.24	3.48	3.42
406					0.57	0.42	1.38	1.32
408	3.90	4.03	4.62	4.54	4.01	4.15	3.35	3.33
4010							5.87	5.90
501	1.49	1.31			0.61	0.63	0.82	0.81
503			2.25	2.22	2.68	2.65	3.07	3.16
505	0.59	0.75	1.16	1.25			2.13	2.24
507	0.83	0.71					1.49	1.28
600	3.58	3.27	2.92	2.64	2.79	2.82	0.27	0.21
602	5.05	5.53	3.79	3.88	4.34	4.39	1.77	1.87
604					4.70	4.67	3.87	3.98
606					0.49	0.28		
116	4.13	4.39	4.27	4.36	3.75	3.82		
1110	4.56	4.48	4.89	4.74	4.47	4.34		
1112	0.43	0.31	0.90	1.01	0.57	0.64		
1114			4.30	4.59				
222	0.84	0.68	1.20	1.08	1.34	1.22		
224	3.22	3.44	4.05	4.27	3.72	3.57		
226	0.27	0.02			0.37	0.08		
228	3.54	3.23	4.12	4.00	3.57	3.38		
2210			0.99	1.08	1.03	1.17		
2212			5.12	5.33				
332	4.84	4.99	5.26	5.44	4.83	5.11		
334	2.67	2.68	3.62	3.67	3.23	3.29		
336	3.47	3.32	3.18	3.09	2.35	2.41		
338	2.55	2.43	3.30	3.13	2.97	2.93		
3310			5.10	4.89				
440	2.52	2.34	2.16	2.20	2.48	2.47		
442					1.07	0.77		
446			0.85	0.05				
Residue	0.073		0.054		0.038		0.039	

TABLE II. Fractional oxygen coordinates and temperature factors. The isotropic factors B have dimensions of square angstroms and are related to the isotropic β_{ij} factors by $\beta_{ij} = \delta_{ij} \frac{1}{2} a_i^2 B$, $i=1, 2, 3$. Thus for oxygen in CaMoO_4 the B_0 would give $\beta_{11} = \beta_{22} = 0.0068$, $\beta_{33} = 0.0014$.

	CaMoO_4	SrMoO_4	SrWO_4	BaWO_4	$\text{CaWO}_4(3)$	$\text{CaWO}_4(2)$	$\text{PbMoO}_4(4)$
Oxygen							
x	0.2428 ± 0.0010	0.2374 ± 0.0009	0.2362 ± 0.0005	0.2332 ± 0.0006	0.2413 ± 0.0005	0.2415 ± 0.0014	0.2352 ± 0.00068
y	0.1465 ± 0.0010	0.1357 ± 0.0008	0.1395 ± 0.0005	0.1227 ± 0.0005	0.1511 ± 0.0006	0.1504 ± 0.0013	0.1366 ± 0.00073
z	0.0826 ± 0.0003	0.0809 ± 0.0003	0.0818 ± 0.0002	0.0781 ± 0.0002	0.0861 ± 0.0001	0.0861 ± 0.0006	0.08110 ± 0.00024
B_0	0.747 ± 0.178	0.531 ± 0.141	0.595 ± 0.094	1.116 ± 0.093			1.317 ± 0.0507
β_{11}					0.0073 ± 0.0014	0.0115 ± 0.0016	
β_{22}					0.0057 ± 0.0012	0.0100 ± 0.0016	
β_{33}					0.0016 ± 0.0003	0.0016 ± 0.0003	
β_{12}					-0.0014 ± 0.0007	-0.0016 ± 0.0013	
β_{13}					-0.0005 ± 0.0002	-0.0008 ± 0.0006	
β_{23}					0.0004 ± 0.0002	0.0004 ± 0.0006	
A(Ca, Sr, Ba, Pb)							
B_A	0.606 ± 0.280	0.336 ± 0.176	0.180 ± 0.120	0.787 ± 0.129			1.079 ± 0.0502
β_{11}					0.0051 ± 0.0022	0.0071 ± 0.0004	
β_{33}					0.0019 ± 0.0006	0.0011 ± 0.0001	
X(W, Mo)							
B_X	0.364 ± 0.205	0.345 ± 0.171	0.345 ± 0.142	0.649 ± 0.131			0.678 ± 0.0641
β_{11}					0.0038 ± 0.0022	0.0036 ± 0.0001	
β_{33}					0.00038 ± 0.0005	0.00095 ± 0.00003	

TABLE III. Bond lengths and near-neighbor distances.

	CaMoO ₄	SrMoO ₄	SrWO ₄	BaWO ₄	CaWO ₄		PbMoO ₄ Ref. 4
					Ref. 3	Ref. 2	
O ₀ -X ₁	1.757±0.005	1.766±0.005	1.779±0.003	1.781±0.003	1.788±0.003	1.78	1.772
O ₀ -A ₁	2.459	2.591	2.579	2.738	2.438	2.44	2.61
O ₀ -A ₂	2.471	2.617	2.610	2.777	2.479	2.48	2.63
O ₀ -O ₁	2.964	2.950	2.972	2.958	2.984	2.98	2.955
O ₀ -O ₂	3.093	3.191	3.233	3.296	3.142	3.14	
O ₀ -O ₄	2.924	3.033	3.045	3.212			
O ₀ -O ₆	2.820	2.851	2.870	2.884	2.879	2.88	2.865
α	115°0'	113°14'	113°15'	112°17'	113°27'		112°50'
γ	106°46'	107°36'	107°32'	108°06'	107°56'		107°40'
X ₁ -O ₄	2.945	3.103	3.079	3.313		2.91	3.15
A ₁ -X ₁	3.871	4.037	4.032	4.241	3.867		
A ₂ -X ₂	3.695	3.814	3.830	3.969	3.707		
(O ₀ -A) _{Av}	2.465	2.604	2.594	2.758	2.458		
(O-A) _{oxide}	2.405	2.580	2.580	2.761	2.405		

PbMoO₄. Interatomic dimensions and some resulting angles are given in Table III.

Our data appear to be somewhat inferior to the data for CaWO₄. As expected, there is little consistency in the temperature factors for the A- and X-atom species. Nevertheless, we believe the results are sufficiently accurate to permit the following comparative observations:

(a) The tetrahedral bond length, X-O, is independent of the A species for a given X, within the experimental precision.⁹

(b) The setting angle of the oxygen tetrahedron in the *ab* plane (angle between the *xy* projection of O₀-X₁ and the X axis) diminishes systematically with increasing A, changing from 31 to 25.7° for the molybdates and from 32 to 27.8° for the tungstates.

(c) The presence of two slightly different bond lengths connecting the A ion with its eight oxygen neighbors (O₀-A₁, O₀-A₂) is evident in all cases, the magnitudes in the present data being somewhat less consistent than shown in Refs. 2 and 3.

(d) If the average of the two A-O distances for each scheelite is compared with the empirical interionic radii given by Pauling,¹⁰ the agreement is very close. The percentage differences between the average scheelite separations and those given by Pauling for Ca-O, Sr-O, and Ba-O, respectively, are 2.9%, 2.5%, and 0.3%. The agreement is essentially the same when the Goldschmidt numbers are used.¹¹ If these averages are

compared to measured CaO, SrO, and BaO separations,¹² the percentage differences are 2.3%, 0.7%, and 0.1%, respectively.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Mr. David Wehe for his support in the computer studies.

* Work supported by the National Science Foundation under Grant Number GK-1943.

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