

## The Crystal Structure of Aluminum Molybdate, $\text{Al}_2(\text{MoO}_4)_3$ , Determined by Time-of-Flight Powder Neutron Diffraction

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The room temperature crystal structure of aluminum molybdate,  $\text{Al}_2(\text{MoO}_4)_3$ , was refined using time-of-flight powder neutron diffraction data. It is monoclinic, with  $a = 15.3803(9)$  Å,  $b = 9.0443(1)$  Å,  $c = 17.888(1)$  Å, and  $\beta = 125.382(3)^\circ$ , space group  $P2_1/a$ . It is isostructural with  $\text{Fe}_2(\text{MoO}_4)_3$  and  $\text{Cr}_2(\text{MoO}_4)_3$ . The application of the Rietveld method to complex structures is discussed. © 1988 Academic Press, Inc.

### Introduction

Several well-defined structural types of stoichiometry  $M_2(\text{XO}_4)_3$  ( $M$  = trivalent cation;  $X$  = Mo, W) have been discovered (1). Our own work has focused on phases containing smaller  $M^{3+}$  cations which may be considered to be related to the  $A_3M_2(\text{XO}_4)_3$  garnet framework (2). With the removal of all the  $A$  cations, there remains a flexible, open network of  $\text{MO}_6$  octahedra and  $\text{XO}_4$  tetrahedra sharing only vertices. Each  $\text{MO}_6$  unit is connected to six different  $\text{XO}_4$  units and each  $\text{XO}_4$  unit is connected to four different  $\text{MO}_6$  units, resulting in an infinite three-dimensional network. All the oxide ions are 2-coordinated by an  $M^{3+}$  and an  $X^{6+}$  ion. The first structures of this type to be determined were those of orthorhombic  $\text{Sc}_2(\text{MoO}_4)_3$  (3) in space group  $Pnca$  and

$\text{Fe}_2(\text{MoO}_4)_3$ , which adopts a monoclinic structure, space group  $P2_1/a$  (4). Aluminum tungstate,  $\text{Al}_2(\text{WO}_4)_3$  (5), is isomorphous with the former, but chromium molybdate,  $\text{Cr}_2(\text{MoO}_4)_3$  (6), and aluminum molybdate,  $\text{Al}_2(\text{MoO}_4)_3$  (7), are reported to be isostructural with ferric molybdate. Sleight and Brixner (8) showed that the two structural types ( $\text{Sc}_2(\text{MoO}_4)_3$  and  $\text{Fe}_2(\text{MoO}_4)_3$ ) are related by a facile displacive ferroelastic phase transition and that a number of other molybdates and tungstates show similar behavior.

Our own work on  $M_2(\text{XO}_4)_3$  systems has included studies of ferric molybdate (9) and the related ferric sulfate (10), which were shown to be L-type ferrimagnets due to the crystallographically different cation sites exhibiting slightly different magnetizations at low temperatures. Chromium molyb-

date,  $\text{Cr}_2(\text{MoO}_4)_3$ , was found to be chemically and magnetically isostructural with ferric molybdate but with a substantially higher Néel temperature (11). We recently prepared ferric tungstate,  $\text{Fe}_2(\text{WO}_4)_3$ , for the first time (12). This phase also adopts the ferric molybdate structure and its catalytic behavior toward methanol oxidation has been compared to that of  $\text{Fe}_2(\text{MoO}_4)_3$  (12). We prepared mixed  $M_{2-x}M'_x(\text{MoO}_4)_3$  phases (13) and showed that iron, chromium, and aluminum form a complete series of solid solutions for all compositions. The catalytic behavior of these mixed molybdates has also been investigated (14).

In addition to their magnetic and catalytic interest, monoclinic  $M_2(\text{XO}_4)_3$ -type phases present a challenging problem in powder neutron data analysis. Over 100 structural and profile parameters may be varied, which approaches the limit of complexity that may be studied using current techniques. The magnetism of ferric molybdate (9) was studied on a constant wavelength neutron diffractometer using fixed atomic coordinates, but the structure of chromium molybdate was refined using time-of-flight neutron data (11), yielding atomic parameters with rather poor precision. This was somewhat surprising, since time-of-flight powder neutron diffractometers operating in the backscattering mode offer, in principle, enhanced resolution compared with constant wavelength machines over a wide wavelength range (15). However, the  $\text{Cr}_2(\text{MoO}_4)_3$  powder diffraction data were considerably line broadened due to particle size effects, emphasizing the importance of sample quality in obtaining the best results at high resolution. In this study, we analyzed time-of-flight powder neutron diffraction data for the isomorphous aluminum molybdate,  $\text{Al}_2(\text{MoO}_4)_3$ , to determine what precision can be attained in a structural refinement of such a complex phase, when the sample quality is good.

## Experimental

Polycrystalline aluminum molybdate was prepared as follows. Appropriate quantities of  $\text{Al}_2\text{O}_3$  and  $\text{MoO}_3$ , both of Johnson–Matthey Specpure grade, were intimately mixed and fired in air in a platinum crucible at  $700^\circ\text{C}$  for about 2 weeks, with several intermediate regrindings. The product was finally cooled to room temperature over 4 hr, the resultant phase being a white powder. Analytical electron microscopy (16), carried out on a JEOL 100CX Temscan instrument using the “ratio method,” indicated that the product was pure and homogeneous. The X-ray powder pattern, recorded using a graphite monochromated  $\text{CuK}\alpha$  Philips automated diffractometer, corresponded closely to those of ferric molybdate and chromic molybdate and could be indexed and refined on a monoclinic cell of dimensions  $a = 15.36(4)$  Å,  $b = 9.03(1)$  Å,  $c = 17.86(5)$  Å,  $\beta = 125.36(6)^\circ$ . This is consistent with Sleight and Brixner’s DTA study (8), which indicated that  $\text{Al}_2(\text{MoO}_4)_3$  should be monoclinic at room temperature. Visual inspection of the X-ray powder patterns for  $\text{Al}_2(\text{MoO}_4)_3$  and  $\text{Cr}_2(\text{MoO}_4)_3$  confirmed that the lines for the former phase were substantially sharper than those of the chromium salt, suggesting that the crystallinity of the aluminum phase is higher than that of the chromium phase. This may well be due to the solution-based preparation method used for chromium molybdate (11).

Room temperature neutron powder diffraction data were recorded on the General Purpose Powder Diffractometer, GPPD, at the Intense Pulsed Neutron Source, IPNS, at Argonne National Laboratory (17). The sample was mounted in a cylindrical vanadium can, data collection taking place in the standard manner. At the  $150^\circ$  bank, data extending from very short  $d$ -spacings to ca.  $3$  Å were collected using a constant time channel width of  $5$   $\mu\text{sec}$ , thus optimizing the balance between resolution and count-

ing statistics. The data collection time was 12 hr.

## Results

The powder neutron data were analyzed by the Rietveld method, with appropriate modifications for treating time-of-flight data (18). All refinements were carried out on a VAX 11-780 computer. The starting model was that of  $\text{Fe}_2(\text{MoO}_4)_3$ , as determined by Chen (19) from single-crystal X-ray data. This complex structure contains 34 atoms in the asymmetric unit, consisting of 4 irons, 6 molybdenums, and 24 oxygens on general  $x, y, z$  positions in the monoclinic cell, space group  $P2_1/a$ . Typical profile parameters describing the peak shape and neutron background coefficients from previous runs were used as starting values. Coherent neutron scattering factors,  $b(\text{Al}) = 3.449$  fm,  $b(\text{Mo}) = 6.950$  fm,  $b(\text{O}) = 5.805$  fm were taken from Ref. (20).

The final cycle of full-matrix least-squares refinement consisted of 114 adjustable parameters, including 102 general positional parameters, 3 atom-type isotropic temperature factors, appropriate profile

TABLE I

FINAL CELL PARAMETERS AND AGREEMENT FACTORS FOR  $\text{Al}_2(\text{MoO}_4)_3$

Unit cell constants	
Space group = $P2_1/a$ (No. 14)	
$a = 15.3803(9)$ Å	
$b = 9.0442(1)$ Å	
$c = 17.888(1)$ Å	
$\beta = 125.382(3)^\circ$	
$V = 2028.7(3)$ Å <sup>3</sup>	
$Z = 8$ formula units per unit cell	
Agreement factors	
$R_{\text{nuc}} = 3.08\%$ , $R_{\text{pr}} = 3.40\%$ , $R_{\text{wpr}} = 5.18\%$ , $R_{\text{exp}} = 3.98\%$ , $\chi^2 = 1.69$	

TABLE II  
FINAL ATOMIC PARAMETERS FOR  $\text{Al}_2(\text{MoO}_4)_3$

Atom	$x/a$	$y/b$	$z/c$
Al(1)	0.381(1)	0.974(2)	0.313(1)
Al(2)	0.373(1)	0.454(2)	0.050(1)
Al(3)	0.117(1)	0.471(2)	0.179(1)
Al(4)	0.109(1)	0.979(2)	0.420(1)
Mo(1)	-0.0035(8)	0.247(1)	0.4888(6)
Mo(2)	0.3580(7)	0.122(1)	0.1318(6)
Mo(3)	0.1433(7)	0.111(1)	0.2563(6)
Mo(4)	0.1470(8)	0.618(1)	0.3805(6)
Mo(5)	0.3531(8)	0.626(1)	0.2194(6)
Mo(6)	0.0026(8)	0.745(1)	0.0180(8)
O(1)	0.5802(8)	0.392(1)	-0.0095(7)
O(2)	0.9897(9)	0.417(1)	0.1676(8)
O(3)	0.831(1)	0.190(1)	0.0958(7)
O(4)	0.7655(9)	0.501(1)	0.0460(8)
O(5)	0.5200(8)	0.431(1)	0.1482(7)
O(6)	0.7358(9)	0.515(1)	0.2727(7)
O(7)	0.4176(8)	0.115(1)	0.4036(7)
O(8)	0.1798(9)	0.292(1)	0.2506(7)
O(9)	0.5554(9)	0.361(1)	0.4471(7)
O(10)	0.3909(9)	0.320(1)	0.9845(7)
O(11)	0.0715(8)	0.372(1)	0.0737(7)
O(12)	0.4116(9)	0.358(1)	0.5020(8)
O(13)	0.8607(9)	0.395(1)	0.2314(7)
O(14)	0.2500(9)	0.020(1)	0.5183(7)
O(15)	0.127(1)	0.098(1)	0.3445(7)
O(16)	0.525(1)	0.937(1)	0.3562(7)
O(17)	0.745(1)	0.972(1)	0.2013(7)
O(18)	0.662(1)	0.930(1)	0.2946(8)
O(19)	0.973(1)	0.943(1)	0.3225(8)
O(20)	0.0974(9)	0.327(1)	0.5927(7)
O(21)	0.1607(9)	0.803(1)	0.3970(8)
O(22)	0.053(1)	0.646(1)	0.1197(8)
O(23)	0.3620(9)	0.599(1)	0.1236(7)
O(24)	0.3415(8)	0.817(1)	0.2307(7)

Note. All atoms on Wyckoff positions of type 4e. Atom type isotropic temperature factors: Al =  $0.85(14)$  Å<sup>2</sup>, Mo =  $1.31(5)$  Å<sup>2</sup>, O =  $1.44(4)$  Å<sup>2</sup>.

parameters, and an overall scale factor. Cell parameters and agreement factors are listed in Table I, with final atomic coordinates in Table II. Figure 1 shows the final observed, calculated, and difference profiles: 2006 reflections covering a  $d$ -spacing range of 2.86 to 1.00 Å were included in the 2500 contributing data points, leading to a

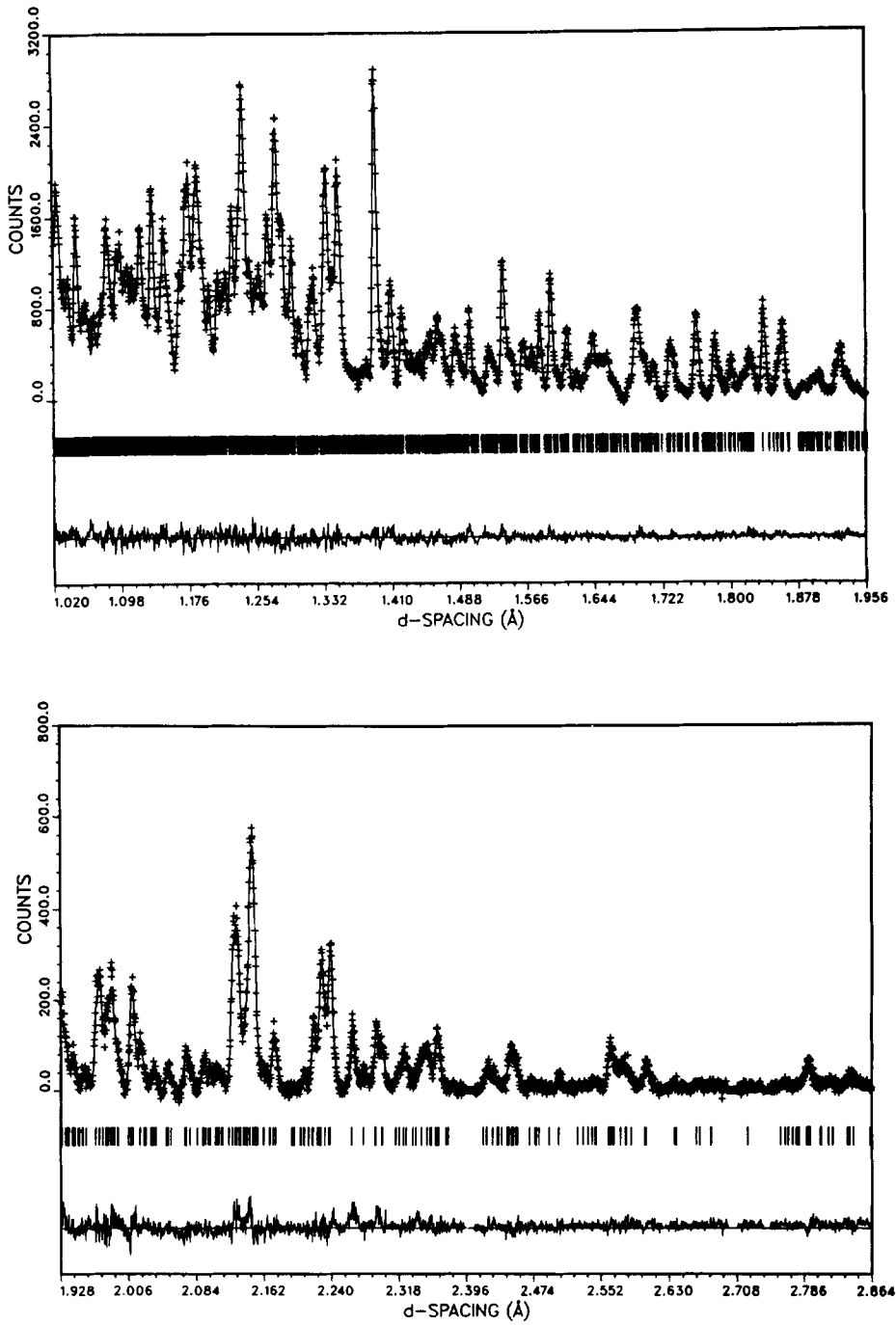


FIG. 1. Final observed (points), calculated (line), and difference profiles for  $\text{Al}_2(\text{MoO}_4)_3$  plotted as a function of  $d$ -spacing. Reflection positions are indicated by tick marks.

TABLE III  
FINAL BOND DISTANCES FOR  $Al_2(MoO_4)_3$

Bond	Distance (Å)	Bond	Distance (Å)
Al(1)-O(6)	1.904(20)	Al(3)-O(2)	1.917(19)
-O(7)	1.874(22)	-O(8)	1.941(21)
-O(13)	1.763(22)	-O(11)	1.815(20)
-O(16)	1.906(21)	-O(17)	1.832(22)
-O(20)	2.022(21)	-O(18)	1.982(22)
-O(24)	1.872(24)	-O(22)	1.833(24)
Average =	1.890	Average =	1.887
Al(2)-O(1)	1.897(21)	Al(4)-O(9)	1.855(21)
-O(3)	1.842(21)	-O(12)	1.938(22)
-O(4)	1.844(20)	-O(14)	1.878(21)
-O(5)	1.911(19)	-O(15)	1.871(19)
-O(10)	1.814(20)	-O(19)	1.816(21)
-O(23)	1.934(20)	-O(21)	1.929(22)
Average =	1.874	Average =	1.881
Mo(1)-O(7)	1.794(16)	Mo(4)-O(14)	1.803(14)
-O(9)	1.765(15)	-O(16)	1.741(16)
-O(12)	1.736(15)	-O(18)	1.730(15)
-O(20)	1.750(15)	-O(21)	1.698(16)
Average =	1.760	Average =	1.743
Mo(2)-O(2)	1.769(15)	Mo(5)-O(17)	1.744(16)
-O(3)	1.782(15)	-O(19)	1.800(15)
-O(4)	1.760(15)	-O(23)	1.812(15)
-O(13)	1.764(14)	-O(24)	1.767(16)
Average =	1.769	Average =	1.781
Mo(3)-O(5)	1.798(13)	Mo(6)-O(1)	1.786(16)
-O(6)	1.716(15)	-O(10)	1.797(15)
-O(8)	1.754(15)	-O(11)	1.717(15)
-O(15)	1.739(14)	-O(22)	1.756(15)
Average =	1.751	Average =	1.764
Mo-O bond distances (Å) in $Cr_2(MoO_4)_3$			
Mo(1)-O(7)	1.82(2)	Mo(4)-O(14)	1.79(2)
-O(9)	1.69(4)	-O(16)	1.80(4)
-O(12)	1.83(4)	-O(18)	1.73(5)
-O(20)	1.60(2)	-O(21)	1.73(3)
Mo(2)-O(2)	1.73(4)	Mo(5)-O(17)	1.64(4)
-O(3)	1.72(3)	-O(19)	1.78(2)
-O(4)	1.87(3)	-O(23)	1.84(3)
-O(13)	1.72(3)	-O(24)	1.72(3)
Mo(3)-O(5)	1.75(2)	-O(1)	1.84(4)
-O(6)	1.73(3)	-O(10)	1.86(4)
-O(8)	1.78(3)	-O(11)	1.69(2)
-O(15)	1.73(4)	-O(22)	1.67(4)

final  $\chi^2$  residual of 1.69. Attempts to refine individual isotropic or anisotropic thermal factors were unsuccessful, leading to physically unreasonable final values or divergence of the least-squares process. No correction was made for extinction or absorption. The  $\alpha$  and  $\beta$  parameters describing the two abutted exponentials which may be attributed to the moderator contribution to the peak shape (18) were not refined. The Gaussian  $\sigma$  parameter,

which may be equated with geometrical and sample contributions to the peak width, indicated that the reflections for  $Al_2(MoO_4)_3$  were much sharper than for  $Cr_2(MoO_4)_3$ . The other profile parameters refined to physically reasonable values.

Attempts to refine the structure in an orthorhombic setting using the starting coordinates of  $Al_2(WO_4)_3$  (4) resulted in a substantially poorer final fit.

## Discussion

This study confirms that the room temperature crystal structure of aluminum molybdate is of the monoclinic ferric molybdate type. The final bond distances (Table III) show that a considerable improvement in precision has been gained compared to our earlier study of chromic molybdate (11). The aluminum-oxygen distances have an average value of 1.88 Å, compared to the ionic radii sum (21) for 6-coordinate  $Al^{3+}$  and 2-coordinate  $O^{2-}$  of 1.88 Å. The molybdenum-oxygen distances, which are expected to be quite constant average 1.76 Å with a range from 1.698 to 1.812 Å; the expected sum of the ionic radii is 1.77 Å. The Mo-O bond distances in  $Cr_2(MoO_4)_3$  had a spread from 1.60 to 1.87 Å, leading to some chemically unreasonable contacts (see Table III). However, Chen's high quality single-crystal results for ferric molybdate (19) giving an average Fe-O distance of 1.990(5) Å and an average Mo-O distance of 1.754 Å, with a spread from 1.740(4) to 1.766(3) Å, are an order to magnitude better than those for the present study. Our results confirm, therefore, that with a good sample it is feasible to obtain a chemically sensible refinement of a structure of this complexity by using time-of-flight powder neutron methods, but the precision remains inferior to that of a good single crystal X-ray study. Only limited information concerning thermal parameters may be extracted from

powder diffraction data for complex structures such as this.

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