

Contribution from Ames Laboratory,[†] U.S. Department of Energy,
and the Department of Chemistry, Iowa State University, Ames, Iowa 50011-3020

Hexagonal LiMoO₂: A Close-Packed Layered Structure with Infinite Mo-Mo-Bonded Sheets

Lorraine E. Aleandri and Robert E. McCarley*

Received June 10, 1987

A new compound, LiMoO₂, with hexagonal layered structure has been prepared by reaction of Li₂MoO₄ with Mo metal at 900 °C for 21 days. Neutron powder diffraction Rietveld analysis shows that LiMoO₂ is isomorphous with α-NaFeO₂; space group *R*3̄*m*, *a* = 2.8663 (1) Å, *c* = 15.4743 (5) Å, *Z* = 3. The structure consists of cubic close-packed oxide layers with Mo and Li atoms occupying octahedral sites between alternate layers. Each Mo atom is thus bonded to six other Mo atoms in a hexagonal sheet with *d*(Mo-Mo) = 2.8663 (1) Å. The Mo-O and Li-O distances are 2.0520 (9) and 2.146 (1) Å, respectively. DOS and COOP curves from extended Hückel band calculations indicate that all Mo-Mo bonding states are filled within the O-Mo-O slabs.

Introduction

Among the various classes of host structures suitable for use as cathodes in batteries, layered dichalcogenides have been the most investigated. Layered oxide systems also may be potential hosts. In this laboratory, a series of layered Na-Mo oxides have been prepared and characterized, viz. Na_{0.45}MoO₂, Na_{0.51}MoO₂, and Na_{0.66}MoO₂.¹⁻⁵ The structures of these compounds feature the presence of extended chains consisting of fused molybdenum rhomboidal clusters. The chains are sandwiched between close-packed layers of oxygen atoms to form three-layer O-Mo-O slabs. These O-Mo-O sheets are then separated by layers of sodium ions. Lithium ions, due to their smaller size and potentially greater mobility, may be more promising with respect to application of such compounds as battery cathodes. Thus, the high-temperature syntheses of Li-Mo oxides were explored, yielding the analogous compound Li_{0.74}MoO₂.^{2,3} Tarascon^{6,7} has studied the electrochemical intercalation of both the sodium and lithium M_xMoO₂ systems, and the work reveals that the Li_xMoO₂ system is indeed a promising cathode material for secondary lithium cells.

An important structural feature of the Na-Mo oxides and Li_{0.74}MoO₂ is the extensive molybdenum bonding in the form of chains of condensed rhomboidal clusters. This mode of Mo-Mo bonding may be compared to the discrete Mo rhombuses observed in the less electron-rich systems of Ba_{1.14}Mo₈O₁₆⁸ and K₂Mo₈O₁₆.⁹ Interestingly, studies of more electron-rich systems with related layer structures, such as CoMo₂S₄¹⁰ and ReSe₂,¹¹ reveal the occurrence of chains consisting of distorted rhomboidal units interlinked in one dimension. Thus, beginning with a layer of close-packed metal atoms, a range of clustering is possible, from discrete units to chains of linked units, to condensed ribbons, and to a hexagonal sheet. In this paper, we report the synthesis and structural characterization of the end member of this series, LiMoO₂, revealing for Mo-Mo-bonded compounds the unprecedented arrangement of an infinite hexagonal sheet.

Experimental Section

Materials. Lithium molybdate (Alfa Products, purity 98.5%) was recrystallized from water, dried at 150 °C under vacuum for 12 h, and stored in a drybox. In synthetic efforts, handling of the hygroscopic lithium molybdate was confined solely to the inert atmosphere of the drybox. Molybdenum tubing was obtained from Thermo-Electron Corp. (purity 99.97%), molybdenum powder from Aldrich (99.99%), and copper tubing from laboratory stock.

Synthesis. The title compound was first observed in the multiphase product obtained in an exploratory reaction between Li₂MoO₄ and Mo (1:1 molar ratio). The reaction mixture was ground in a mortar and sealed by electron beam welding into an evacuated Mo reaction vessel, which was then loaded into a high-vacuum furnace and fired at 1500 °C for 2 days. The product revealed unreacted lithium molybdate, black polycrystalline powder, and a few chunky hexagonal prisms. The lithium molybdate was removed by washing with water. After drying, a Guinier

Table I. Observed and Calculated X-ray Powder Diffraction Data for LiMoO₂

<i>d</i> spacing, Å ^a	intens ^b	<i>hkl</i>	<i>d</i> spacing, Å ^c	intens ^c
5.168 (6)	s	003	5.156	100.0
2.579 (1)	w	006	2.578	7.1
2.450 (1)	ms	101	2.451	36.9
3.363 (1)	m	012	2.363	16.5
2.0893 (9)	ms	104	2.0891	42.5
1.9371 (7)	w	015	1.9362	17.0
		009	1.7187	3.7
1.6509 (5)	mw	107	1.6506	14.2
1.5265 (4)	mw	018	1.5254	16.6
1.4343 (4)	mw	110	1.4333	14.1
1.3826 (3)	mw	113	1.3809	16.7
		1,0,10	1.3128	5.3
		0,0,12	1.2890	3.6
1.2525 (2)	vw	116	1.2527	9.1
1.2359 (2)	w	021	1.2373	6.3
1.2231 (2)	w	0,1,11	1.2236	7.5

^a Values observed from Guinier X-ray powder pattern indexed to give hexagonal cell: *R*3̄*m*, *a* = *b* = 2.8666 (8) Å, *c* = 15.469 (8) Å.

^b Relative intensities: s, strong; m, medium; w, weak; vw, very weak.

^c Values based on calculated powder pattern with hexagonal cell: *R*3̄*m*, *a* = *b* = 2.8666 Å, *c* = 15.469 Å, Li at 0, 0, 1/2, Mo at 0, 0, 0, and O at 0, 0, 0.257.

powder pattern was taken of the product. The pattern indicated the presence of a new lithium molybdenum oxide that could be indexed on the basis of the pattern observed for α-NaFeO₂.¹² This X-ray powder pattern also showed the lines of unreacted Mo metal.

Subsequent work showed that X-ray-pure hexagonal layered material could be prepared by oxidizing Mo metal in the presence of an excess of lithium molybdate. The reactants were thoroughly ground in a mortar, sealed in an evacuated copper vessel, and held at 900 °C for 21 days. The polycrystalline product was powdered in a mortar and washed several times with deionized water to remove unreacted Li₂MoO₄; the solid was then dried under vacuum at 120 °C.

X-ray Powder Diffraction Data. The Enraf-Nonius Delft triple-focusing Guinier camera was used with Cu Kα₁ radiation (λ = 1.54056

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[†] Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Office of Basic Energy Sciences.

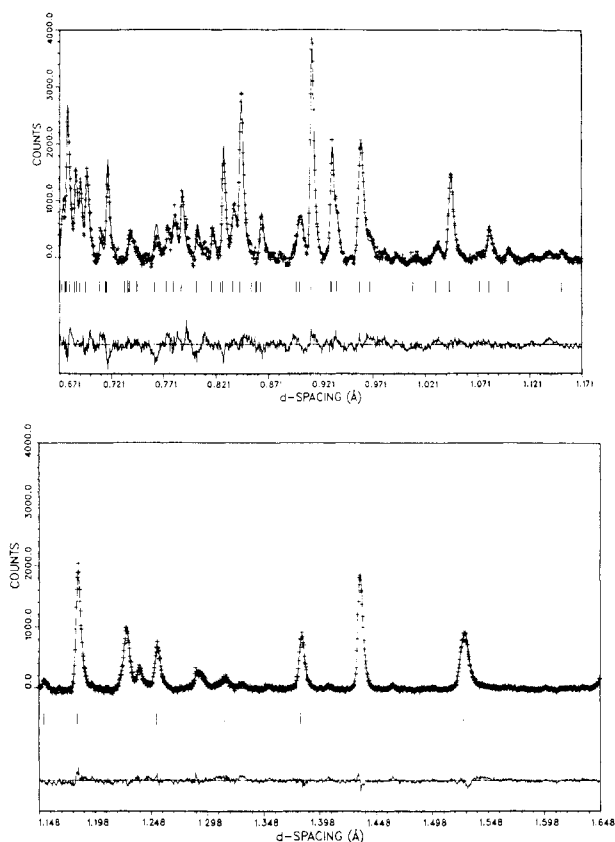


Figure 1. Profile refinement of the low d space portion of the 150° bank neutron diffraction data with d spacings ranging (a, top) from 0.671 to 1.171 Å and (b, bottom) from 1.148 to 1.648 Å. Observed data are indicated by crosses and calculated data by a solid line. Marks directly beneath the pattern indicate positions of reflections. A difference curve appears at the bottom.

Å) to obtain the powder diffraction and unit cell data. The diffraction lines of LiMoO_2 (Table I) were indexed on the basis of the reported pattern of $\alpha\text{-NaFeO}_2$ yielding the hexagonal cell ($R\bar{3}m$ No. 166): $a = b = 2.8666$ (8) Å, $c = 15.469$ (8) Å, and $V = 110.09$ (9) Å³. From these cell constants and the atomic positions (Li on the 3b site; Mo on the 3a site; O on the 6c site with $Z = 0.257$) was generated a calculated powder pattern of LiMoO_2 . There was a good correlation between the observed and calculated intensities, indicating that the model was correct. Subsequently, the structure was refined by using neutron powder data as detailed below.

Neutron Powder Diffraction Data. Neutron powder diffraction data were collected on the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. IPNS uses a proton accelerator and synchrotron to produce high-energy neutrons by bombardment of a spallation target (uranium). These neutrons are then moderated to lower energies before they are used for diffraction. The GPPD is equipped with time-of-flight detectors, of which there are two sets each at 30, 45, 60, 75, 90, and 150° . Time-of-flight data were collected on a 5-g sample loaded in a vanadium cell at 300 K with an exposure time of 12 h. The high-resolution data obtained from the 150° detector bank were used in the Rietveld refinement. The diffractometer and the Rietveld refinement software are discussed in ref 13–18.

Table II. Crystallographic Data for LiMoO_2 ^a

cryst system: trigonal	no. of data points: 4013
space group: $R\bar{3}m$	no. of reflns: 95
$a = 2.8663$ (1) Å	d space region: $0.657 \text{ \AA} < d < 2.57 \text{ \AA}$
$c = 15.4743$ (5) Å	no. of parameters refined: 22
$V = 110.097$ (3) Å ³	expected $R^b = 3.64\%$
$Z = 3$	profile $R^c = 3.45\%$
$d(\text{calcd}) = 6.10 \text{ g/cm}^3$	weighted $R^d = 5.10\%$
diffractometer: GPPD	intensity $R^e = 8.76\%$

^a For details on Rietveld refinement of the neutron diffraction data, see the text. ^b $R_c = [N(\text{degrees of freedom})]^{1/2} / \sum w Y_o^2$; $w = 1/\sigma^2(Y_o)$. ^c $R = \sum |Y_o - (Y_c \times \text{scale})| / \sum |Y_o|$. ^d $R_w = [\sum [w(Y_o - (Y_c \times \text{scale}))^2] / \sum w(Y_o^2)]^{1/2}$. ^e $R_i = \sum |I_o - (I_c \times \text{scale})| / \sum |I_o|$.

Table III. Positional Parameters for LiMoO_2

atom	sym position	x	y	z	$B, \text{ \AA}^2$ ^a
Li	3b ($\bar{3}m$)	0	0	$1/2$	3.22 (3)
Mo	3a ($\bar{3}m$)	0	0	0	1.916 (4)
O	6c ($3m$)	0	0	0.25481 (9)	1.013 (3)

^a The isotropic equivalent thermal parameter is defined as $B = 4/3[2a^2\beta_{11} + c^2\beta_{33} + 2a^2(\cos 120^\circ)\beta_{12}]$.

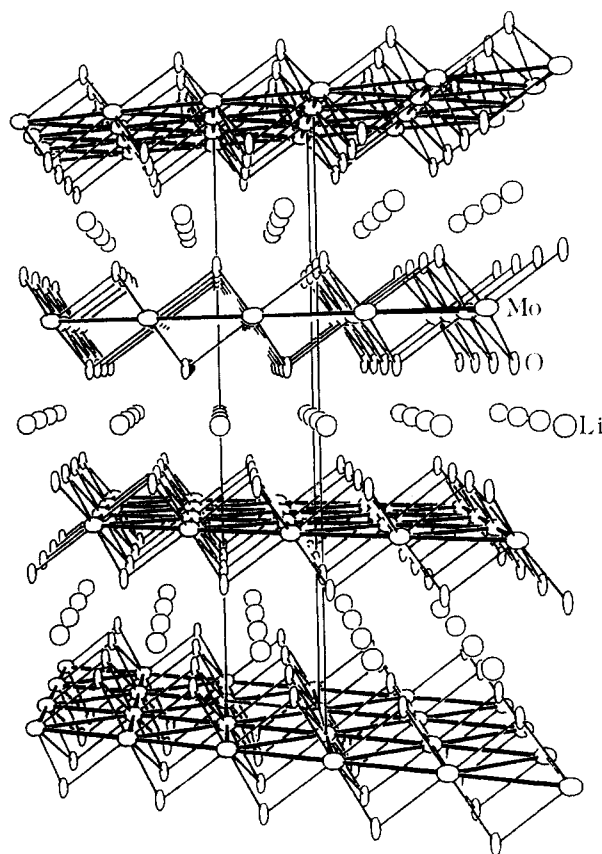


Figure 2. Three-dimensional view of the unit cell of the LiMoO_2 structure as seen along the a axis. The framework consists of Mo sheets [$d(\text{Mo-Mo}) = 2.8663$ (1) Å] bridged by oxygen atoms [$d(\text{Mo-O}) = 2.0520$ (9) Å] to form O-Mo-O slabs separated by layers of Li ions [$d(\text{Li-O}) = 2.146$ (1) Å].

The structure of LiMoO_2 was refined by using the atomic positions determined in the model discussed above. The refinement involved 4013 data points, 95 Bragg reflections in the d space region of 0.657–2.579 Å, and 22 parameters. The refined parameters included five background parameters, a scale factor, extinction, absorption, anisotropic peak broadening, lattice constants, positional and anisotropic thermal parameters on each atom, and the occupancy of lithium. Table II lists the final cell parameters (which correspond well with those calculated from the X-ray powder pattern) along with the residual factors, while Table III gives the positional parameters for each atom.

The spectrum showed broadening of certain peaks, [00 l] type, with respect to the others, which could be caused by stacking defects along the c axis. This effect was taken into account by including anisotropic

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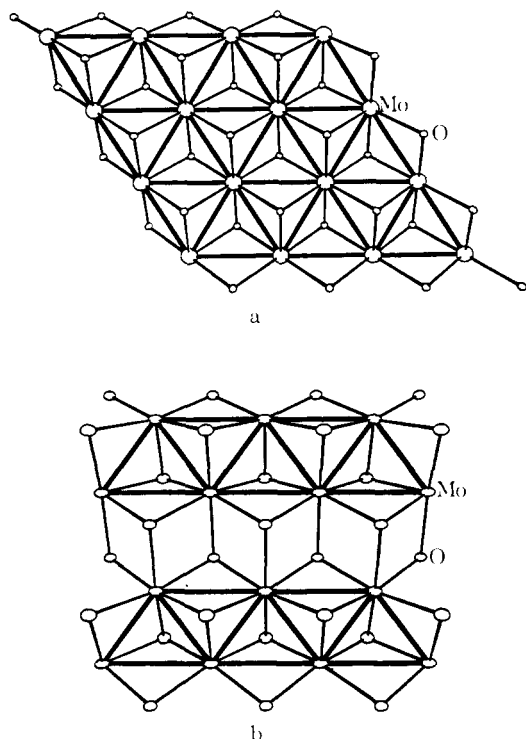


Figure 3. (a) View down the *c* axis of LiMoO₂ illustrating a single O-Mo-O slab with Mo bonding in heavy lines and the Mo-O interactions in lighter lines. The Mo atoms form an infinite hexagonal sheet with bonding distances of 2.8663 (1) Å. (b) View down the *a* axis of Li_{0.74}MoO₂ showing an O-Mo-O slab. The Mo atoms distort from a hexagonal array to generate metal ribbons with Mo-Mo distances of 2.881 (1) Å along the chain and of 2.549 (2) Å diagonally, forming zigzag bonds.

peak broadening along the *c* (stacking) axis.^{15b}

Figure 1 illustrates the low *d* space region of the Rietveld refinement. A close examination of the difference between the calculated and experimental profiles revealed extra reflections such as those found between 1.10 and 1.15 Å. These lines and other extra peaks correspond to the diffraction pattern of lithium molybdate. Due to the low concentration

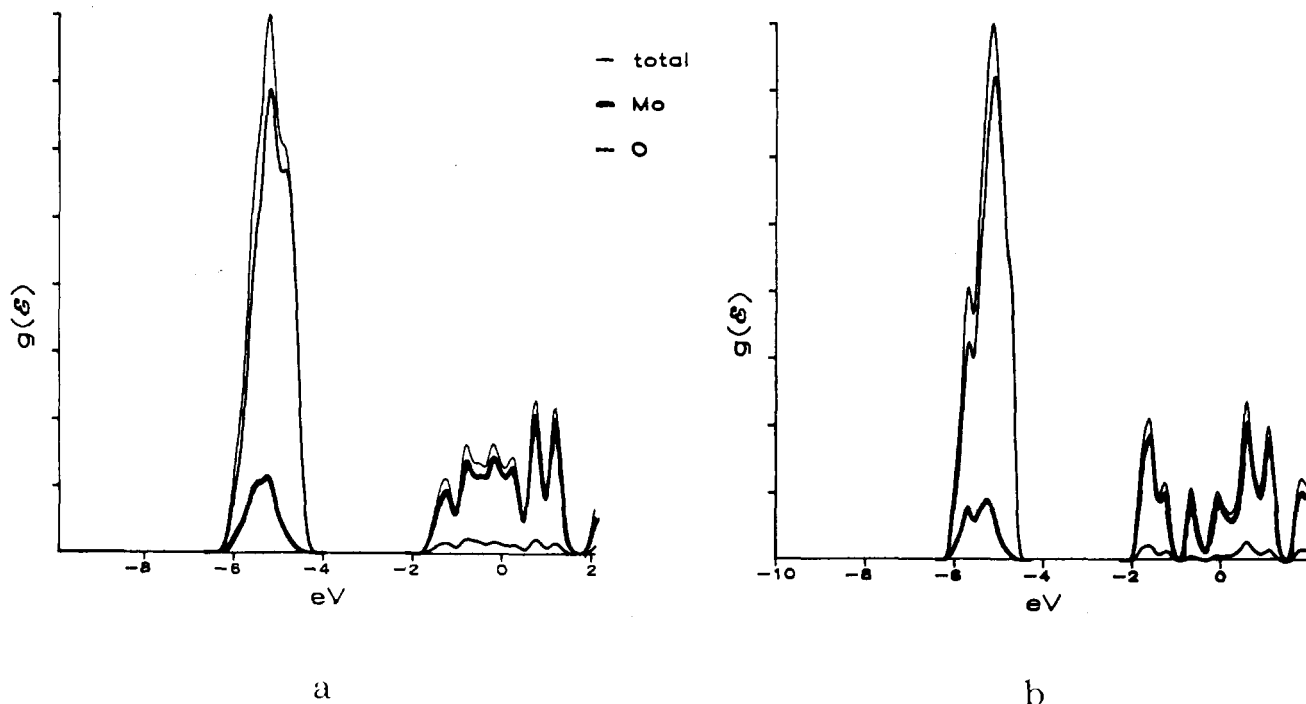


Figure 4. Density of states (DOS) curve for the structural modifications of LiMoO₂ (*d*³ systems): (a) hexagonal structure with a Mo-bonded sheet; (b) monoclinic framework with chains comprised of condensed rhomboidal units. The heavy curve indicates Mo states, and the lighter curve indicates the O contribution.

and the complex diffraction pattern of lithium molybdate, the structure could not be satisfactorily refined via multiphase refinements. Since this second compound was not taken into account, the background fitting led to a slight oscillatory function in the single-phase refinement's difference plot that was not observed in the multiphase experiments. To achieve the best fit of the data, and to subsequently refine the Li occupancy, the oscillatory function based on all scattering data was fitted and removed from the background.¹⁶ The Li occupancy converged to a value of 1.02 (5) per MoO₂ unit.

Quantitative Analysis. A precipitation method was employed for the determination of percent molybdenum. Samples were decomposed in a basic solution and neutralized to methyl red with an acetic acid/sodium acetate buffer. Quantitative precipitation of MoO₂(ONC₅H₆)₂ was effected by addition of a solution of 8-hydroxyquinoline. The precipitate was filtered into previously tared, fritted crucibles and dried at 140 °C overnight. The oxidation state of the molybdenum was determined via a cerium titration. Samples were oxidized by a known excess of standardized Ce(IV), and the solution was back-titrated to an Fe(1,10-phenanthroline)₃²⁺ end point with a freshly standardized Fe(II) solution. From these data, the electron to Mo ratio was calculated. The percent lithium was determined by atomic absorption techniques. Anal. Found: Li, 5.66%; Mo, 64.96%; e/Mo, 2.48.

Since the samples were contaminated with lithium molybdate, the following relationship was used to determine the Li content of the layered material and the amount of lithium molybdate in the mixture:

$$(1-x)\text{Li}_2\text{MoO}_4 + x\text{Li}_y\text{MoO}_2 = 1$$

where *x* equals the mole fraction of Li_{*y*}MoO₂ and (1 - *x*) equals the mole fraction of Li₂MoO₄. This relationship yields the equations

$$\text{Li/Mo} = 1.205 = 2(1-x) + xy$$

$$e/\text{Mo} = 2.48 = (1-x)0 + x(2+y)$$

which can be solved to give

$$x = 0.82 \quad y = 1.03$$

Thus, the sample consists of

$$0.18\text{Li}_2\text{MoO}_4 + 0.82\text{Li}_{1.03}\text{MoO}_2$$

and the formula for the hexagonal compound may be taken as LiMoO₂.

Discussion

The layered structure of LiMoO₂ can be viewed in Figure 2. As discussed above, the material is isostructural with α-NaFeO₂ with an oxygen packing sequence of ABCABC with Mo and Li

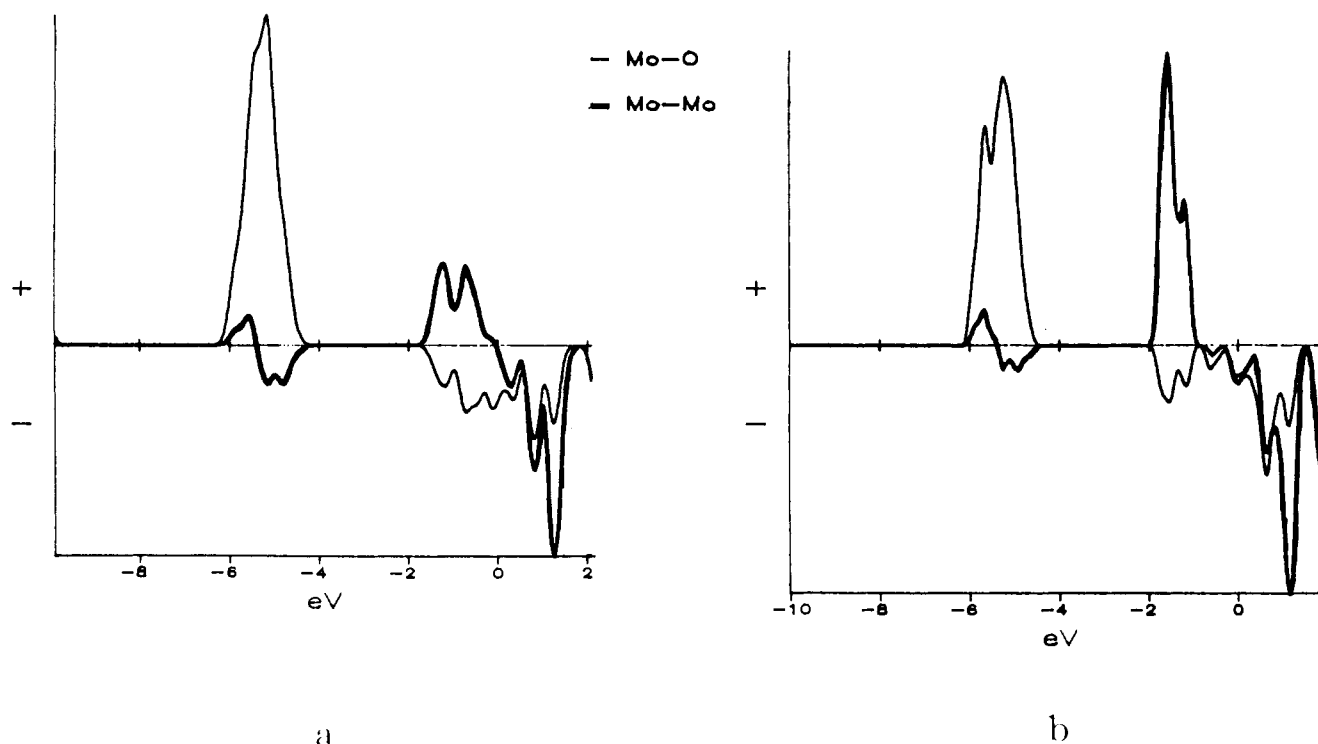


Figure 5. Comparative orbital overlap population (COOP) curves for the structural modifications of LiMoO_2 (d^3 systems): (a) hexagonal structure with a Mo-bonded sheet; (b) monoclinic framework with chains composed of condensed rhomboidal units. The heavy curve represents the Mo-Mo states while the light curve corresponds to Mo-O levels.

occupying octahedral coordination sites between alternate layers. During the structural determination, the Li multiplier was refined to a value of 1.02 (5) per MoO_2 unit, indicating that every octahedral site between the O-Mo-O slabs is occupied by a lithium cation.

The change in layering from the monoclinic compound, $\text{Li}_{0.74}\text{MoO}_2$ [$C2/m$, $a = 10.647$ (6) Å, $b = 2.881$ (1) Å, $c = 4.953$ (2) Å, $\beta = 99.64$ (5)°], to that observed in LiMoO_2 is the result of the slippage of the MoO_2 slabs via a small decrease in the monoclinic β angle. The corresponding cell dimensions for LiMoO_2 in the monoclinic setting are $a = 10.448$ Å, $b = 2.8663$ Å, $c = 4.9645$ Å, and $\beta = 99.10$ °.

Structurally, the most important feature of the title compound is the mode of Mo-Mo bonding. As shown in Figure 3a, the Mo atoms are found in a hexagonal close-packed layer with Mo-Mo bond distances of 2.8663 (1) Å. In contrast, as shown in Figure 3b, the metal ions in $\text{Li}_{0.74}\text{MoO}_2$ are distorted from an ideal hexagonal array toward neighboring Mo atoms to form infinite chains having two parallel rows of Mo atoms with bond distances of 2.881 (1) Å between adjacent Mo atoms of the same row and of 2.549 (2) Å between Mo atoms of adjoining rows, generating the zigzag bonds within the chains.

Extended Hückel calculations performed in this laboratory and those reported by Burdett and Hughbanks¹⁹ indicate that the distorted monoclinic form is energetically slightly more stable than the ideal hexagonal arrangement. Computations were done on an O-Mo-O slab by utilizing the observed atomic positions from the Rietveld refinement for the hexagonal structure and the single-crystal refinement of $\text{Li}_{0.74}\text{MoO}_2$ for the chain structure, with the Mo and O functions taken from ref 20. The energy difference between the monoclinic and hexagonal frameworks, each with d^3 -electron population on Mo, is only 0.08 eV. Because the extended Hückel calculations are not adequate to account for all important interactions, this small energy difference in favor of the monoclinic structure, with infinite chain formation, could be

incorrect. The long reaction time, 21 days, at 900 °C for preparation of the hexagonal structure, indeed indicates that the latter structure is the more stable for LiMoO_2 with the d^3 -electron population. No evidence such as supercell reflections was found in neutron diffraction data that would signal long-range clustering of Mo atoms in LiMoO_2 . However, the oscillatory function noted in the background of the single-phase refinement may be indicative of diffuse scattering resulting from short-range ordering of molybdenum atoms.

The density of states (DOS) curve (Figure 4a) obtained via extended Hückel calculations clearly shows a high density of states at the Fermi level, suggesting that LiMoO_2 should be a metallic conductor. The resistivity of this material has not yet been measured due to the lack of success in obtaining single crystals.

In reviewing the comparative orbital overlap population (COOP) curves (Figures 5), one notes that for a d^3 system, Mo-Mo-antibonding states are occupied in the distorted monoclinic structure whereas in the hexagonal structure the metal-bonding states are totally full and the antibonding levels empty. This contrast in the occupancy of the metal-antibonding states may be the reason that the hexagonal structure is observed. The COOP curve raises the question of what would happen to the metal-metal bonding as the lithium content is lowered. It is expected that as the bonding levels are emptied, the Mo sheet would rearrange to form Mo ribbons or some other type of clustering favored by the lower electron to Mo ratio. At present, more detailed work is being carried out with respect to the structural changes of the hexagonal phase upon delithiation and ion exchange. The results of this investigation will be forthcoming.

Acknowledgment. We thank J. Faber, Jr., J. Richardson, Jr., and R. Hitterman of Argonne National Laboratory for providing valuable assistance and advice during collection and Rietveld refinement of the neutron data.

Registry No. Li_2MoO_4 , 13568-40-6; LiMoO_2 , 69550-44-3; Mo, 7439-98-7.

Supplementary Material Available: A table of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

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