

help in selecting and mounting the crystals, and to Dr P. Piret for sending us a preprint of his work. We are also grateful to Professor D. E. Appleman for his suggestions.

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Pb²⁺ Cation Ordering in Pb₃(Mo₄O₆)₄

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Abstract

The commensurately modulated structure of lead molybdenum oxide, Pb₃(Mo₄O₆)₄, has been determined by single-crystal X-ray diffraction. The Pb/Pb repulsion leads to a four-cell superlattice along the *c*-axis direction. Commensurate ordering of Pb²⁺ ions in the supercell was taken into account in the structure refinement. Crystal data are: *M*_r = 2540.6, tetragonal, *P4/mnc* (No. 128), *a* = 9.615 (1), *c* = 11.362 (3) Å, *V* = 1050.4 (3) Å³, *Z* = 2, *D*_x = 8.033 Mg m⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 33.21 mm⁻¹, *F*(000) = 2220, *T* = 297 K, *R* = 0.030, *wR* = 0.032 for 409 unique reflections. Refinement of the occupancy numbers of the Pb²⁺ sites in the supercell leads to the formula Pb₃(Mo₄O₆)₄, which reflects an ordering of Pb²⁺ in three of four sites in the tunnel. Each Pb²⁺ has a coordination environment of eight O atoms in a tetragonal arrangement.

The supercell is characterized by an ordering of the lead ions and vacancies in the tunnel following the sequence ...Pb—Pb—Pb—Δ... The Mo—Mo bond lengths parallel to the tunnel direction are regular.

Introduction

The structure of the reduced ternary molybdenum oxide NaMo₄O₆ (Torardi & McCarley, 1979) is comprised of infinite molybdenum metal cluster chains based on edge-shared Mo₆O₁₂ building blocks with the ternary metal cation in the tunnels formed by four metal cluster chains cross-linked by Mo—O bonds. The tunnels are parallel to the fourfold rotation axis of the tetragonal space group. Several compounds containing different ternary metal cations were found to adopt this structure type. It was noted that the stoichiometry of the cation *A* in A_xMo₄O₆ (*x* ≤ 1) depends upon its valency and size. When *A* is a small univalent cation, there is one

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cation per unit cell such that the repeat distance in the tunnel direction is the distance between neighboring cations. For example, the c -axis lengths are 2.860 (1), 2.8628 (4) and 2.8732 (4) Å in NaMo_4O_6 , InMo_4O_6 (Lii, 1985) and KMo_4O_6 -I (Hoffman & Hoppe, 1990), respectively. When the cation A is divalent, there is less than one cation per formula unit. The stoichiometry of divalent A is determined by its radius. In order to reduce the repulsion between A , the larger the radius of A the smaller the x value. For example, $x = 0.62$ for Ba (Torardi & McCarley, 1981), 0.77 for Pb (Lii, 1985) and 0.90 for Sn (Aufdembrink, 1985). These divalent cation-containing compounds exhibit superstructures due to cation ordering. The Ba^{2+} ion ordering in the tunnel in $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$ was determined in an eight-cell supercell. It was found that there was remarkable alternation of Mo—Mo bond distances between adjacent cluster units in $\text{Ba}_5(\text{Mo}_4\text{O}_6)_8$ (Torardi & McCarley, 1986).

The interesting features of these structures pertaining to the positions and occupancies of the cations have aroused our attention. In this paper, we report the supercell structure of $\text{Pb}_{0.75}\text{Mo}_4\text{O}_6$, in which the Pb^{2+} cation ordering in the tunnel was determined. In contrast to the barium compound the Mo—Mo bond lengths in $\text{Pb}_3(\text{Mo}_4\text{O}_6)_4$ parallel to the tunnel direction are regular.

Experimental

The sample was prepared by reacting PbMoO_4 , MoO_3 and Mo in a 3:2:7 mole ratio at 1215 K for 10 days (Lii, 1985). The stoichiometry of $\text{Pb}_3(\text{Mo}_4\text{O}_6)_4$ was determined from single-crystal X-ray diffraction data. A black needle-like single crystal of dimensions $0.02 \times 0.02 \times 0.10$ mm was selected for X-ray analysis. Indexing and data collection were performed on a four-circle Nicolet $R3m/V$ diffractometer equipped with graphite monochromator (Mo $K\alpha$ radiation, 0.7107 Å). A tetragonal cell with $a \approx 9.62$, $c \approx 2.84$ Å was obtained by indexing 14 reflections from a rotational photograph. A subsequent axial oscillation showed a couple of satellites at $0.75c^*$. Scans along $(00l)$, $(10l)$ and $(20l)$ showed that the modulation propagation vector q^* had a commensurate value of $0.25c^*$. Scans along $(h00)$ did not show any superlattice reflections. A long-exposure rotation photograph along the c axis and Weissenberg photographs also showed that there were only sharp superlattice reflection points along the c^* direction. Thus, a four-cell supercell along c was established ($c_{\text{super}} = 4c_{\text{sub}}$). The lattice parameters were refined from 21 reflections with 2θ in the range $14 \leq 2\theta \leq 29^\circ$. The following measurement conditions were used: $\theta/2\theta$ scan, scan speed $2.09\text{--}14.65^\circ \text{ min}^{-1}$, scan width 1.08° plus $K\alpha$ separation, background measuring time

equal to half of the scan time, three standard reflections checked every 50 reflections. 2357 reflections up to $(\sin\theta)/\lambda = 0.756 \text{ \AA}^{-1}$ were collected ($0 \leq h \leq 14$, $0 \leq k \leq 14$, $0 \leq l \leq 17$). L_p and empirical absorption corrections were applied. Corrections for absorption were based on φ scans of a few suitable reflections with χ values close to 90° (Alcock, 1974). Both subcell and supercell structures were solved by direct methods and successive Fourier syntheses, and refined by full-matrix least-squares methods based on F values. All calculations were performed on a DEC MicroVAX II computer system using *SHELXTL-Plus* programs (Sheldrick, 1990). Neutral-atom scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Subcell analysis

Among the 2357 reflections collected, 807 were sublattice reflections which resulted in 235 observed [$I \geq 3\sigma(I)$] independent reflections. The intensity data set showed $4/mmm$ Laue symmetry and the systematic absences: $0kl$, $k = 2n + 1$; $h00$, $h = 2n + 1$. Therefore, the space group $P4/mbm$ (No. 127) was selected for the subcell. Direct methods successfully yielded a phase solution from which the positions of one Pb and two Mo atoms were obtained. Two O atoms were located on a subsequent difference Fourier map. After all atoms were refined anisotropically, the occupancy of the Pb site was allowed to vary. At convergence, $R = 0.0314$ and $wR = 0.0314$ [$w^{-1} = \sigma^2(F) + 0.00056F^2$]. The occupancy number, 0.387 (2), which corresponded to 0.77 Pb atoms per formula unit, indicated that there were probably three Pb^{2+} ions in the tunnel in every four units.

Supercell analysis

Examination of the complete data set showed the extinction conditions: $0kl$, $k + l = 2n + 1$; hhl , $l = 2n + 1$; $h00$, $h = 2n + 1$. Based on these systematic absences, E statistics gave $|E^2 - 1| = 1.029$, and successful structure refinement, the space group of the four-cell supercell was determined as $P4/mnc$ (No. 128). After averaging equivalent reflections ($R_{\text{int}} = 0.0093$), 409 reflections were considered observed [$I \geq 3\sigma(I)$] and used in the structure determination and refinement. The phase solution gave an E map on which two Pb and three Mo atoms were located. Four O atoms were subsequently found on a difference Fourier map. Least-squares refinements with isotropic temperature factors for this model yielded an agreement factor $R = 0.15$. At this stage, the difference Fourier map showed two peaks corresponding to 28.8 and 27.8 $e \text{ \AA}^{-3}$ at $(0,0,z)$, $z = 0.45$ and 0.24, respectively. Thus another two Pb atoms,

Pb3 and Pb4 were placed at these 4(*e*) positions. The occupancies of all four independent lead sites were allowed to vary. At convergence, the least-squares refinement with anisotropic temperature factors for all of the Pb and Mo atoms gave an agreement factor $R = 0.0295$. The result indicated that the Pb2 site was fully populated. The Pb1 site was nearly 75% occupied and the Pb3 and Pb4 sites were almost at equal occupancy of 12.5%. Finally, a refinement with each lead site assigned a fixed value was conducted. For 409 reflections and 46 variables, the refinement converged at $R = 0.0296$, $wR = 0.0332$ [$w^{-1} = \sigma^2(F) + 0.0026F^2$] ($R = 0.044$ for 174 superlattice reflections only). The final difference map was essentially featureless with $\rho_{\max} = 3.9$, $\rho_{\min} = -3.1 \text{ e } \text{Å}^{-3}$, which were near ($\sim 0.6 \text{ Å}$) Pb3. $\Delta/\sigma_{\max} = 0.02$. The total occupancy number of Pb atoms corresponded to the formula Pb₃(Mo₄O₆)₄.

Results and discussion

Structure description and discussion of the Pb_{0.75}Mo₄O₆ subcell

The final positional and thermal parameters are given in Table 1(*a*). Selected bond distances and angles are given in Table 2(*a*). The atom labels in this table correspond to those in Fig. 1(*a*). The framework of Pb_{0.75}Mo₄O₆ is essentially the same as that of NaMo₄O₆. Fig. 1(*a*) shows a repeat unit of an Mo₆O₁₂ cluster chain in this subcell. Both Mo1 and Mo2 are eleven-coordinate; the equatorial Mo atoms, Mo1, are bonded to seven Mo and four O atoms, and the apical Mo atoms, Mo2, are bonded to six Mo and five O atoms. According to the subcell refinement, the lead ions in Pb_{0.75}Mo₄O₆ are displaced to (0,0,0.1568), resulting in Pb—O distances of 2.522 (6) ($\times 4$) and 2.982 (6) Å ($\times 4$). The displacement of the cations from the center of the tunnel was also seen in the indium and barium compounds. In the former case, the indium ions are disordered at two sites related by a mirror plane. The distance between indium ions in the tunnel is the same as the repeat distance in the tunnel direction. In the latter case, there are also two barium sites. But these sites are only partially occupied. In the tunnel, there are 0.62 barium ions per Mo₄O₆ unit. Thus, there should be a distribution of the Ba—Ba distances. A similar situation was also found in the lead compound except that the lead site was a little more densely populated.

Structure description and discussion of the Pb₃(Mo₄O₆)₄ supercell

The final positional and thermal parameters are given in Table 1(*b*). Selected bond distances and

Table 1. *Positional and thermal parameters*

	Posi- tion	Occu- pancy	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{Å}^2)^*$
<i>(a) Subcell [Pb_{0.75}Mo₄O₆]</i>						
Pb1	4(<i>e</i>)	0.387 (2)	0	0	0.1568 (9)	0.0358 (7)
Mo1	4(<i>h</i>)	1.0	0.60194 (9)	0.10194 (9)	0.5	0.004 (2)
Mo2	4(<i>g</i>)	1.0	0.14360 (9)	0.64360 (9)	0	0.008 (3)
O1	8(<i>f</i>)	1.0	0.0423 (8)	0.7618 (7)	0.5	0.008 (2)
O2	4(<i>g</i>)	1.0	-0.2072 (8)	0.7072 (7)	0	0.007 (2)
<i>(b) Supercell [Pb₃(Mo₄O₆)₄]</i>						
Pb1	4(<i>e</i>)	0.75†	0	0	0.3009 (2)	0.0097 (3)
Pb2	2(<i>a</i>)	1.0	0	0	0	0.0474 (9)
Pb3	4(<i>e</i>)	0.125	0	0	0.4458 (10)	0.0295 (36)
Pb4	4(<i>e</i>)	0.125	0	0	0.2474 (10)	0.0134 (23)
Mo1	8(<i>g</i>)	1.0	0.1435 (2)	0.6435 (2)	0.25	0.0076 (6)
Mo2	8(<i>h</i>)	1.0	0.1445 (3)	0.6434 (2)	0	0.0091 (8)
Mo3	16(<i>i</i>)	1.0	0.6024 (1)	0.1015 (1)	0.1250 (1)	0.0043 (3)
O1	8(<i>g</i>)	1.0	-0.2067 (12)	0.7067 (12)	0.75	0.008 (3)
O2	16(<i>i</i>)	1.0	0.0415 (11)	0.7627 (11)	0.1237 (9)	0.005 (2)
O3	16(<i>i</i>)	1.0	0.0413 (12)	0.7597 (12)	0.3750 (9)	0.010 (2)
O4	8(<i>h</i>)	1.0	-0.2098 (19)	0.7043 (19)	0.5	0.010 (3)

* Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

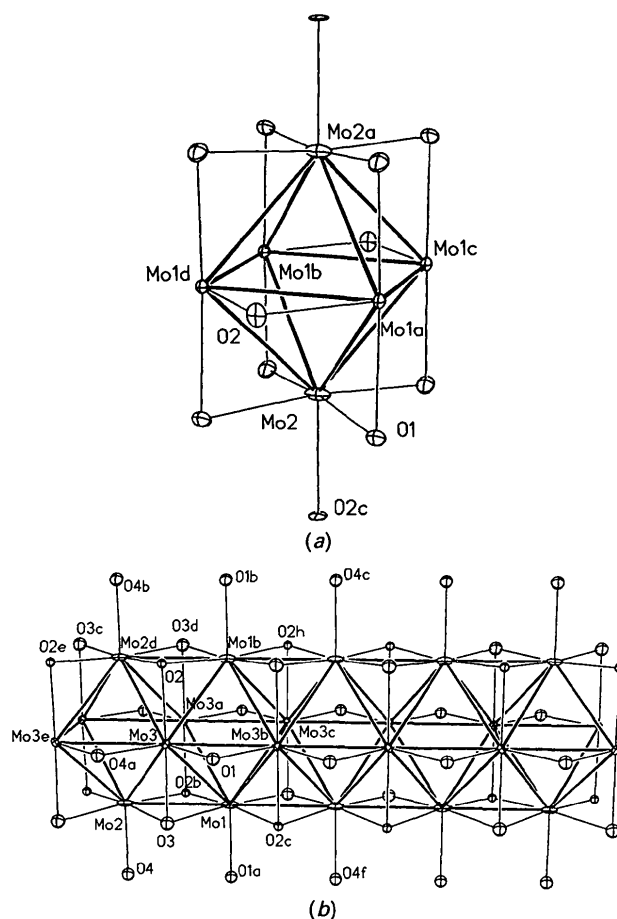
† When the occupancies were allowed to vary, they were 0.751 (5), 1.010 (8), 0.122 (5) and 0.129 (4) for Pb1, Pb2, Pb3 and Pb4, respectively.

angles are given in Table 2(*b*).* The atom labels in this table correspond to those in Fig. 1(*b*), in which a section of one molybdenum oxide cluster chain with four subcell units extended along the *c* axis is shown. The structure of Pb₃(Mo₄O₆)₄ as viewed down the *c* axis showing the cross-linking of cluster chains and the lead sites along the tunnel is depicted in Fig. 2. Mo1 and O1 lie on a twofold axis of rotation running parallel to the *ab* diagonal, Mo2 and O4 lie in mirror planes perpendicular to the *c* axis at $z = 0$ and $\frac{1}{2}$ respectively, and all the other atoms occupy general positions in the space group $P4/mnc$. Although the symmetry of the molybdenum oxide cluster chain in the supercell is not exactly the same as that in the subcell, the architecture of the chains and the connectivity within and between cluster chains are basically the same as described above for the Pb_{0.75}Mo₄O₆ subcell. The differences in the Mo—Mo and Mo—O bond lengths are within 1 to 2σ between the subcell and the supercell; thus, the unit of a Mo₆O₁₂ cluster in the supercell is actually equivalent to that in the subcell. This equivalence also can be deduced from the correlation between the positions of Mo atoms in the two cells. Mo1_{sub} (Mo1 in the subcell) corresponds to Mo3_{super} (Mo3 in the supercell); Mo2_{sub} corresponds to Mo1_{super} and Mo2_{super}. The situation is rather different in the barium compound. The tetragonal cell was distorted to an orthorhombic one for the larger barium ion and the infinite edge-shared molybdenum oxide cluster chains were distorted in Ba₅(Mo₄O₆)₈ such that there was a remarkable alter-

* Lists of structure factors and structure variances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53981 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

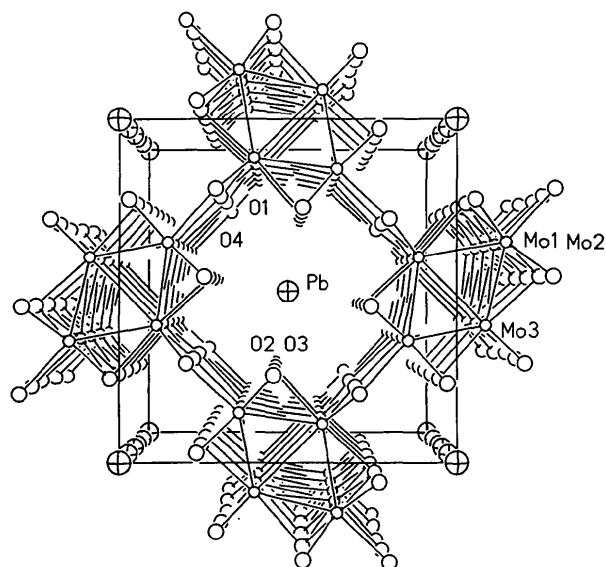
Table 2. Selected bond distances (Å) and angles (°)

(a) Subcell ($Pb_{0.75}Mo_4O_6$)			
Mo1a—Mo2	2.784(1) (× 4)	Mo2—Mo1a	2.784(1) (× 4)
Mo1a—Mo1c	2.772(3) (× 1)	Mo2—Mo2	2.841(1) (× 2)
Mo1a—Mo1d	2.841(1) (× 2)	Mo2—O1	2.064(5) (× 4)
Mo1a—O1	2.070(7) (× 2)	Mo2—O2c	2.029(1) (× 1)
Mo1a—O2	2.017(1) (× 2)	Pb1—O1	2.982(6) (× 4)
O1—Mo1a	2.070(7) (× 1)	Pb1—O1	2.522(6) (× 4)
O1—Mo2	2.064(5) (× 2)	O2—Mo1a	2.017(1) (× 2)
		O2—Mo2d	2.029(1) (× 1)
Mo1c—Mo1a—Mo1d	90.0(1)	Mo1a—Mo2—Mo1d	61.4(1)
Mo2—Mo1a—Mo1d	59.3(1)	Mo1c—Mo2—Mo1d	90.9(1)
Mo2—Mo1a—Mo2a	89.1(1)	Mo1d—Mo2—Mo1b	59.7(1)
Mo2—Mo1a—Mo1c	60.1(1)	Mo1a—O1—Mo2	84.7(2)
Mo1a—O2—Mo1d	89.6(2)		
(b) Supercell [$Pb_3(Mo_4O_6)_4$]			
Mo1—Mo2	2.841(1) (× 2)	Mo2—Mo1	2.841(1) (× 2)
Mo1—Mo3	2.787(2) (× 2)	Mo2—Mo3	2.787(3) (× 4)
Mo1—Mo3a	2.779(2) (× 2)	Mo2—O2b	2.068(10) (× 2)
Mo1—O1a	2.037(16) (× 1)	Mo2—O3	2.051(11) (× 2)
Mo1—O2c	2.082(10) (× 2)	Mo2—O4	2.027(19) (× 1)
Mo1—O3	2.056(11) (× 2)	O1—Mo3	2.012(11) (× 2)
Mo3—Mo1	2.787(2) (× 2)	O1—Mo1	2.037(16) (× 1)
Mo3—Mo1b	2.779(2) (× 2)	O2—Mo1b	2.082(10) (× 1)
Mo3—Mo2	2.787(2) (× 2)	O2—Mo2d	2.068(10) (× 1)
Mo3—Mo3a	2.771(3) (× 1)	O2—Mo3	2.066(10) (× 1)
Mo3—O1	2.012(12) (× 1)	O3—Mo1	2.056(11) (× 1)
Mo3—O2	2.066(11) (× 1)	O3—Mo2	2.051(11) (× 1)
Mo3—O3	2.055(10) (× 1)	O3—Mo3	2.055(12) (× 1)
Mo3—O4a	2.015(10) (× 1)	O4—Mo2	2.027(19) (× 2)
Pb1—Pb2	3.419(2)	O4—Mo3	2.015(13) (× 1)
Pb1—Pb3	1.646(13)	Pb2—Pb4	2.811(11)
Pb1—Pb4	0.608(11)	Pb3—Pb4	2.253(17)
Pb1—O2	3.069(10) (× 4)	Pb2—O2	2.709(10) (× 8)
Pb1—O3	2.491(11) (× 4)	Pb3—O3	2.479(12) (× 4)
Pb4—O2	2.709(12) (× 4)	Pb3—O3	3.106(14) (× 4)
Pb4—O3	2.756(13) (× 4)		
Mo3e—Mo3—Mo3a	90.0(1)	Mo3—Mo2—Mo3e	61.3(1)
Mo3—Mo3b—Mo3c	90.0(1)	Mo3b—Mo1—Mo3	61.4(1)
Mo2—Mo3—Mo3e	59.2(1)	Mo3a—Mo2—Mo3e	90.8(1)
Mo1—Mo3b—Mo3	59.4(1)	Mo3c—Mo1—Mo3	90.8(1)
Mo2—Mo3—Mo2d	89.2(1)	Mo2—Mo3—Mo3a	60.2(1)
Mo1—Mo3b—Mo1b	89.0(1)	Mo1—Mo3b—Mo3c	60.3(1)
Mo2—O3—Mo3	85.5(4)	Mo3—O4a—Mo3e	89.6(7)
Mo1—O2c—Mo3b	84.1(4)	Mo3b—O1—Mo3	89.8(7)

Fig. 1. A repeat unit of an Mo_4O_6 cluster chain in (a) $Pb_{0.75}Mo_4O_6$ (b) $Pb_3(Mo_4O_6)_4$.

nation of Mo—Mo bond distances in the pattern large, small, large, ..., between cluster units.

The supercell and space group change in $Pb_3(Mo_4O_6)_4$ is solely due to the distribution of the lead ions in the tunnel. The arrangement of these lead ions along one tunnel of the unit cell is shown in Fig. 3. Each lead ion is surrounded by eight intrachain O atoms, O2 and O3, forming a tetragonal box ($3.275 \times 3.275 \times 2.812$ Å) around Pb2 or a slightly distorted tetragonal box ($3.316 \times 3.316 \times 2.855$ Å and angles in the range 89.5 – 90°) for Pb1. On average, three of the four boxes stacking along the c axis of the unit cell are occupied by lead ions. Pb2 lies on an inversion center at $(0,0,0)$. The Pb2—O distance is 2.709 Å. The two Pb1 ions are related through the mirror plane at $z = \frac{1}{2}$. From the occupancy of Pb1, Pb3 and Pb4, it is apparent that the lead ions are disordered among these three sites with a distribution ratio of 6:1:1. Thus, on average three of the four tunnels have lead ions in the sequence $\dots(Pb1-Pb2-Pb1-\Delta)-Pb1\dots$ ($\Delta =$ vacancy) (Fig. 3a) with Pb—Pb distances 3.42, 3.42 and 4.52 Å, respectively. The fourth possesses lead ions in both the sequence

Fig. 2. The structure of $Pb_3(Mo_4O_6)_4$ as viewed down the c axis showing the cross-linking of cluster chains, and lead ion positions along the tunnel (unconnected ellipsoids).

...Pb3—Δ—Pb2—Pb4—Pb3... (Fig. 3*b*) and the sequence ...Pb4—Pb2—Δ—Pb3—Pb4... (Fig. 3*c*) with Pb—Pb distances [case 3(*b*)] 5.07, 2.81 and 3.49 Å, respectively. To avoid charge repulsion between lead ions, the Pb1 ions shift away from position (0,0, $\frac{1}{4}$) by 0.051*c* towards a neighboring vacancy as shown in Fig. 3(*a*). Also note that the two lead sites, Pb3 and Pb4, which are only 2.25 Å apart, are too close to be occupied simultaneously. Therefore, unlike the barium compound the central lead ion, Pb2, cannot possess two adjacent empty sites. Pb2 has only one quarter of the opportunity to possess an adjacent vacancy in Pb₃(Mo₄O₆)₄. Nonetheless, the lead distribution in the tunnels can be regarded as corresponding to the sequence ...Pb—Pb—Pb—Δ—...

A larger unit cell is necessary to account for the partial occupancies of Pb1, Pb3 and Pb4. However, film work on the data crystal did not reveal any superlattice reflections for an even larger supercell. In the tunnels, the shortest distance between lead ions is 2.81 (1) Å [*d*_{Pb2—Pb4} in Figs. 3(*b*) and 3(*c*)]. Since the ionic radius for Pb²⁺ is 1.43 Å (Shannon, 1976), the distance 2.81 Å, which is thought possible, is not favorable. Thus, Pb2 would tend to shift away, either to a neighboring empty site in the *c*-axis direction, or in the *ab* plane to avoid such a close distance. This tendency is indicated by its rather large thermal parameters as shown in Table 3.

Concluding remarks

The crystal structure of Pb₃(Mo₄O₆)₄ may be regarded as consisting of two sublattices. The molybdenum oxide framework forms a sublattice of which the repeat distance in the *c* direction is 2.841 Å. A unit cell four times larger has to be used

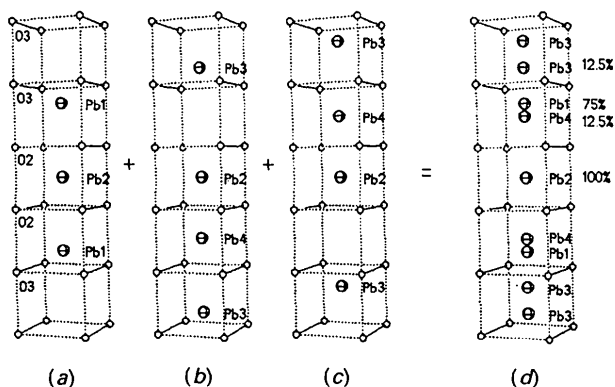


Fig. 3. The arrangement of lead ions along one tunnel of the unit cell in Pb₃(Mo₄O₆)₄. The probability for the sequence (a) is 75% in the crystal. The probability for the sequence (b) and (c) is 25%.

Table 3. Anisotropic displacement coefficients (Å²) for Pb₃(Mo₄O₆)₄

The anisotropic displacement exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})$.

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Pb1	0.0122 (5)	0.0122 (5)	0.0047 (7)	0	0	0
Pb2	0.0372 (13)	0.0372 (13)	0.0678 (22)	0	0	0
Pb3	0.0122 (38)	0.0122 (38)	0.0642 (97)	0	0	0
Pb4	0.0195 (43)	0.0195 (43)	0.0010 (35)	0	0	0
Mo1	0.0023 (11)	0.0023 (11)	0.0183 (10)	0.0015 (12)	-0.0032 (64)	-0.0032 (64)
Mo2	0.0047 (15)	0.0055 (15)	0.0171 (10)	-0.0027 (11)	0	0
Mo3	0.0049 (6)	0.0045 (6)	0.0035 (4)	-0.0001 (3)	0.0001 (5)	-0.0012 (5)

to describe the other sublattice formed by the lead ions. The supercell contains four sites, but there is on average one vacancy per supercell.

This study has shown the ordering pattern of lead ions in the tunnel within a supercell. The type of ...Pb—Pb—Pb—Δ... ordering allows a relaxation of the strong electrostatic repulsion between lead ions. The ordering of lead ions can be considered as primarily three dimensional in the crystal because the superlattice reflections are very sharp. The study has also shown that the ordering of Pb²⁺ cations in the tunnel does not affect the structure of the framework. In contrast to the barium compound, the Mo—Mo bonds in Pb₃(Mo₄O₆)₄ parallel to the tunnel direction are regular. It then appears that the state of the order in the tunnels in the structure of A₃Mo₄O₆ is critically dependent upon the valency and radius of the ternary metal cation. Similar to the hollandite-type compounds, the symmetry of the structure is to some extent related to the size of the cation (Vicat, Fanchon, Strobel & Qui, 1986). Distortion to orthorhombic symmetry was observed in the crystals of KM_{0.4}O₆-I and Ba_{0.62}Mo₄O₆ because of the large K⁺ and Ba²⁺ cations. Although Pb₃(Mo₄O₆)₄ has a metal cluster electron count of 13.5 electrons, it does not exhibit the distortion observed in Ba₅(Mo₄O₆)₈.

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Crystalline Phases Related to the Icosahedral Al–Li–Cu Phase: a Single-Crystal X-ray Diffraction Study of the Hexagonal Z-Al₅₉Cu₅Li₂₆Mg₁₀ Phase

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Abstract

Z phase, Al_{0.59}Cu_{0.05}Li_{0.26}Mg_{0.10}, $M_r = 23.35$, hexagonal, $P6_3/mmc$, $a = 14.116$ (3), $c = 28.235$ (6) Å, $V = 4873$ (3) Å³, $Z = 272$, $D_x = 2.164$, D_m (by flotation) = 2.14 Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.25$ mm⁻¹, $F(000) = 3013$, $T =$ room temperature, $R = 0.042$ for 1794 reflections. The hexagonal Z phase belongs to a family of intermetallics Al–Li–(Cu–Zn–Mg) which have relationships with the icosahedral Al–Cu–Li phase. By using a description proposed by Samson [*Structural Chemistry and Molecular Biology* (1968), edited by Rich & Davidson, pp. 687–717. San Francisco: Freeman], a basic structural unit can be defined in the Z structure as an arrangement of ten Friauf polyhedra which forms a half-Samson polyhedron. This polyhedron is directly related to the complete Samson polyhedron determined in the b.c.c. structure of $R\text{-Al}_5\text{CuLi}_3$. Such a result suggests that the Friauf polyhedron could be the only structural unit common to quasicrystalline and related crystalline Al–Li–(Cu–Zn–Mg) phases.

Introduction

Research concerning the atomic structure of quasicrystals has been carried out by different methods. The exact structural features of this state of matter are not yet fully understood and each approach to the atomic structure is in fact based on various assumptions.

One empirical method consists of performing a direct atomic decoration of the two basic cells of the icosahedral quasilattice, *i.e.* the prolate and oblate

rhombohedra (Henley & Elser, 1986; Elswijk, de Hosson, van Smaalen & de Boer, 1988; Audier & Guyot, 1988*a*). In that case, it is assumed that such an icosahedral quasilattice, resulting from an irrational cut and projection operation from a six-dimensional periodic space (Elser, 1985; Duneau & Katz, 1985) constitutes the equivalent of a Bravais lattice for the quasicrystal. However, the main difficulty, which has not been resolved, is to reconcile the complicated matching rules (Katz, 1988) and inflation rules (Elser, 1985; Audier & Guyot, 1988*b*) of the icosahedral quasilattice rules with a unique decoration of each type of rhombohedron. Such an atomic decoration, respecting density and chemical composition, has been attempted for the icosahedral Al–Li–Cu phase (Guyot, Audier & de Boissieu, 1989), by considering an aggregation of atomic clusters, derived from those defined in the related cubic $R\text{-Al}_5\text{CuLi}_3$ phase (Cherkashin, Kripyakevich & Oleksiv, 1964; Audier, Pannetier, Leblanc, Janot, Lang & Dubost, 1988). Comparisons between calculated X-ray and neutron spectra and experimental crystal diffraction data (G. Heger & J. Pannetier, private communication; Janot, Pannetier, Sainfort, Dubost, Audier & Bouvaist, 1987) are only partially satisfactory: expressed in terms of a reliability factor ($R = \sum |F_{\text{obs}} - F_{\text{calc}}| / \sum |F_{\text{obs}}|$), values of 0.16 and 0.13 have been obtained for 56 X-ray reflections and 40 neutron reflections respectively. Better results have been obtained by using a method equivalent to the so-called direct methods of crystallography, where it is assumed that periodic schemes are recovered in six-dimensional space (de Boissieu, Janot, Dubois, Pannetier, Audier & Dubost, 1991). In that case, the