

New Type-Structure of Chevrel Phase: Unusual Location of the 3d Chromium Ions in the Mo_6Se_8 Host Lattice

Abdellatif Mançour-Billah,^a Patrick Gougeon,^a Jean Yves Pivan^b,
Marcel Sergent,^a and Roger Chevrel^{a(*)}

^aLaboratoire de Chimie du Solide et Inorganique Moléculaire, URA CNRS 1495, Université de Rennes I, Avenue du Général Leclerc – 35042 Rennes Cédex (France)

^bENSCR, Campus de Beaulieu, Avenue du Général Leclerc – Rennes

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The triclinic structure of CrMo_6Se_8 ternary compound has been solved on single crystals at RT. The triclinic unit-cell is: $a = 6.738(2) \text{ \AA}$, $b = 6.710(2) \text{ \AA}$, $c = 6.783(3) \text{ \AA}$, $\alpha = 98.03(3)^\circ$, $\beta = 91.63(3)^\circ$, $\gamma = 94.65(3)^\circ$, $V = 302.5 \text{ \AA}^3$, $Z = 1$, $D_x = 6.913$, space group $P\bar{1}$, 1771 reflections, 71 refined parameters, $R = 0.023$.

The network framework is built up of distorted Mo_6Se_8 cluster units. The originality of this structure is the new occupancy of chromium atoms. Chromium trivalent ions occupy a particular position just in the inversion centre in $1/2\ 0\ 0$ and are surrounded by six selenium atoms forming a distorted octahedral site (site 2 of the channels). It corresponds to a translation of $1/2\ a$ along the a rhombohedral axis of the Pb ions of the PbMo_6Se_8 structure corresponding to a change of symmetry $R\bar{3}$ to $P\bar{1}$.

INTRODUCTION

Many $\text{M}_x\text{Mo}_6\text{X}_8$ ($X = \text{S}, \text{Se}, \text{Te}$) Chevrel phases have been investigated intensively for structural resolution on single crystals.¹ Most of these phases crystallize in space group $R\bar{3}$ at room temperature, but some of them exhibit a rhombohedral-triclinic transition *versus* temperature or stoichiometry. For instance, the non-stoichiometric $\text{Cu}_x\text{Mo}_6\text{S}_8$ compounds have a trigonal sym-

* Author to whom correspondence should be addressed.

metry at room temperature and show a large triclinic low temperature distortion.² Moreover, the $\text{Fe}_x\text{Mo}_6\text{S}_8$ compound shows a triclinic-rhombohedral transition at room temperature versus the M element content. A sample of composition $\text{Fe}_2\text{Mo}_6\text{S}_8$ has a triclinic structure with parameters very close to those found in the trigonal $\text{Fe}_{1.33}\text{Mo}_6\text{S}_8$ phase.³ On the other hand, the $\text{Cr}_x\text{Mo}_6\text{S}_8$ compound is completely triclinic at room temperature whatever the x content may be.⁴ Generally, this triclinic distortion results from a "freezing" of M^{n+} ions in the tridimensional channels of the structure.

In the rhombohedral compound, the M^{n+} ions occupy two different sites: each one is distributed onto sixfold equivalent positions and in the triclinic structure, (at room temperature or below transition temperature, for instance) they occupy one lattice site which represents two equivalent positions ($\bar{1}$) forming a dumb-bell. There exists another triclinic distorted structure, $\text{Ni}_{0.66}\text{Mo}_6\text{Se}_8$, where the Ni^{2+} ions are still more delocalized and form a dumb-bell in the second site,⁶ like in the $\text{Ni}_{0.84}\text{Mo}_6\text{Te}_8$.⁷

Let it be noted that the Ca, Sr, Ba alkaline earth, europium and even lead Chevrel phases undergo a slight triclinic distortion at low temperature.^{8,9} We report, in this paper, a new triclinic structural type of Chevrel phase, CrMo_6Se_8 .

EXPERIMENTAL AND STRUCTURAL RESULTS

Syntheses of $\text{M}_x\text{Mo}_6\text{Se}_8$ (Cr, Sc, Zr) ternary compounds have been carried out from elements (Cr, Sc, Zr, Mo, Se) or binary selenides such as MoSe_2 , Mo_6Se_8 , Cr_2Se_3 .¹⁰ Reactions take place in vacuum sealed silica tubes with a molybdenum crucible to avoid contamination due to the electropositive character of the metal element (Sc, Zr) under reduced argon pressure. After several steps before the first heat treatment at 1000 °C, 12 hours, the mixture is ground in order to homogenize, pelletized and heat treated anew up to a pure ternary phase. The scandium ternary selenide is stable up to 1150 °C and, then, decomposes in binary alloys (ScMo alloy and Mo_6Se_8).

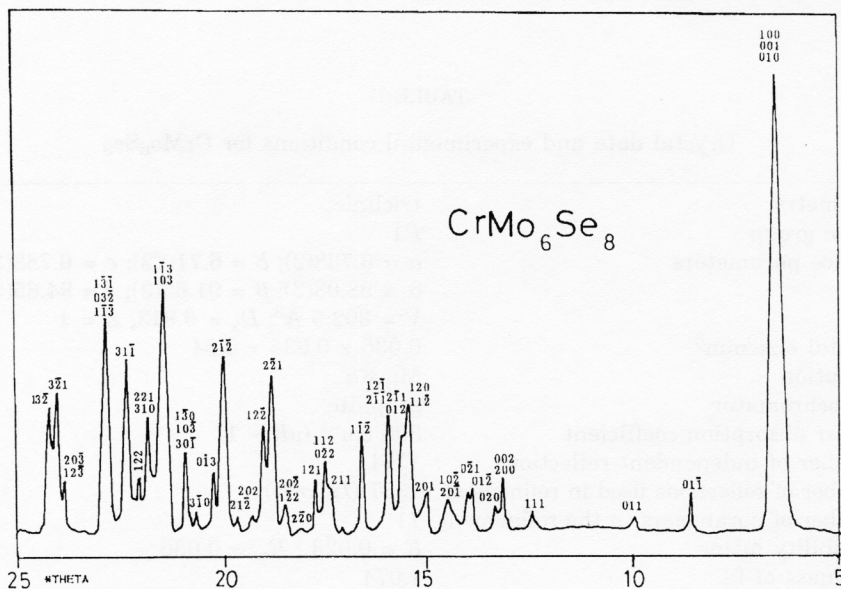
The three phases produce a very close complex X-ray powder diagram. The crystallographic analysis on a single crystal of the CrMo_6Se_8 compound with precession and Weissenberg cameras has enabled us to determine a triclinic unit-cell (P $\bar{1}$). The unit-cell parameters are refined by least-square calculations from 13 measured Bragg angles by indexing in a univocal manner some hkl reflections of the X-ray powder pattern, with silicium as internal standard recorded with an INEL CPS 120 diffractometer, fitted with a localization detector (Cu $K\alpha_1$ radiation) and then, adding new other hkl reflections to refine definitively the unit-cell parameters.

The triclinic unit-cell parameters of ScMo_6Se_8 and $\text{Zr}_{0.75}\text{Mo}_6\text{Se}_8$ compounds are determined by comparison and then refined. The parameters of

TABLE I

Triclinic unit-cell parameters

	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	<i>α</i> /°	<i>β</i> /°	<i>γ</i> /°
CrMo ₆ Se ₈	6.738	6.710	6.783	98.03	91.63	94.65
ScMo ₆ Se ₈	6.78	6.73	6.86	97.80	91.40	95.20
Zr _{0.75} Mo ₆ Se ₈	6.78	6.74	6.84	97.90	91.20	95.00

Figure 1. X-ray diffraction pattern for CrMo₆Se₈ compound (λ Cu K α_1)

these three compounds are given in Table I. The X-ray diffraction pattern of the CrMo₆Se₈ compound and the *hkl* triclinic indexations of the diffraction peaks are shown in Figure 1.

Crystal Growth

Crystal growth can be operated at high temperatures in a graphite resistor furnace with thermoregulation coupled to a dilatation pyrometer PC.CGL. This furnace can reach temperatures up to 2400 °C under vacuum or inert gas pressure. The powder mixture (M, Mo, MoSe₂ or MMo₆Se₈) is introduced in a molybdenum crucible. The thermal cycle consists of a quick

rise up to the melting point, then, a step of 5–10 minutes and a slow cooling by about 100 °C/hour. We have established the phase diagram (an isotherm at 1100 °C) by different attempts and shown the non congruent character of the CrMo_6Se_8 phase. After determination of the primary crystallization zone, we got large single crystals up to few mm^3 at a temperature around 1680 °C.

After selection of the best single crystals, the single crystal of the CrMo_6Se_8 compound was examined on an automated four-circles CAD4 Nonius diffractometer and the intensities of 1771 independent reflections were recorded at room temperature. The experimental conditions for data collection are summarized in Table II.

TABLE II
Crystal data and experimental conditions for CrMo_6Se_8

Symmetry	triclinic
Space group	$P\bar{1}$
Lattice parameters	$a = 6.738(2)$; $b = 6.710(2)$; $c = 6.783(3)$ Å $\alpha = 98.03(3)$; $\beta = 91.63(3)$; $\gamma = 94.65(3)^\circ$ $V = 302.5$ Å ³ ; $D_x = 6.913$; $Z = 1$
Crystal size/ mm^3	$0.035 \times 0.035 \times 0.04$
Radiation	Mo $K\alpha$
Monochromator	graphite
Linear absorption coefficient	305 cm^{-1} ($\mu R \sim 1$)
Number of independent reflections	1771
Number of reflections used in refinement	1327 ($I > 2\sigma(I)$)
Number of parameters in the refinement	71
Reliability factor	$R = 0.023$; $R_w = 0.036$
Goodness of fit	1.074

DISCUSSION

As it can be seen from the atomic coordinates (Table III) and the projection of the structure (Figure 2), the framework of the CrMo_6Se_8 compound essentially represents a triclinic distortion of the Mo_6Se_8 cluster units.

The most striking difference between the rhombohedral structure ($\text{Cu}_x\text{Mo}_6\text{Se}_8$) and the triclinic structure is the new location of the M^{n+} cations in the channels of the structure. All the distances of the distorted Mo_6Se_8 building blocks are reported in Table IV. The structure is built up of quasi molecular cubic Mo_6Se_8 cluster units, which contain triclinic distorted octahedral Mo_6 clusters ($2.652(2)$ Å $\leq d_{\text{intra}}(\text{Mo-Mo}) \leq 2.721(1)$ Å). The average intracluster Mo-Mo length (2.682 Å) is smaller than one in the binary molybdenum selenide (2.76 Å),¹¹ suggesting large electronic transfer from the

TABLE III

Fractional atomic coordinates ($\times 10^5$), thermal parameters, occupancy factors and e.s.d.s in parentheses for the CrMo₆Se₈ compound

Atom	Position	x	y	z	$B_{eq}^*/\text{\AA}^2$	Occupancy
Mo1	2i	23318(8)	41951(8)	54442(8)	0.447(8)	1
Mo2	2i	54678(8)	22989(8)	41101(8)	0.464(8)	1
Mo3	2i	41961(8)	53411(8)	23269(8)	0.463(8)	1
Se1	2i	35005(9)	13251(9)	71176(9)	0.62(1)	1
Se2	2i	73141(9)	35311(10)	10814(9)	0.67(1)	1
Se3	2i	13085(9)	72134(10)	37820(9)	0.62(1)	1
Se4	2i	21802(9)	18866(10)	19543(10)	0.75(1)	1
Cr	1d	$\frac{1}{2}$	0	0	1.26(3)	1

$$* B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i a_j$$

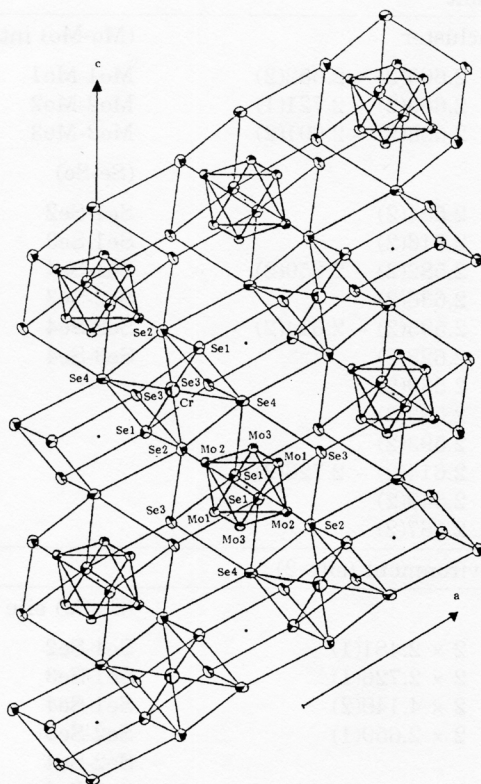


Figure 2. View along the pseudo-hexagonal c axis and the a triclinic axis. The displacement ellipsoids enclose 90% probability.

chromium atoms. The Mo-Mo intercluster distance is 3.468 Å, 3.484 Å and 3.349 Å, the average distance is 3.434 Å and is bigger than 3.266 Å found in the Mo₆Se₈ binary.

The originality of the structure results from the occupancy by the chromium atoms of one of three sites 2: at 1/2 0 0, just in the inversion centre ($\bar{1}$). Site 2 is constituted of eight selenium atoms belonging to four Mo₆Se₈ cluster units. Let it be noted that the Mⁿ⁺ ions of the Chevrel phase structure have been displaced from the origin of site 1 (000, site 1) (for instance, Pb ions in PbMo₆Se₈) along one *a* axis to the origin of site 2 (in 1/2 0 0, site 2). Of course, this translation leads to a change of symmetry (*R* $\bar{3}$ rhombohedral

TABLE IV
Interatomic distances/Å and their e.s.d.s for CrMo₆Se₈

The Mo ₆ Se ₈ unit			
(Mo-Mo) intracluster		(Mo-Mo) intercluster	
Mo1-Mo2	2.669(2) – 2.652(2)	Mo1-Mo1	3.468(2)
Mo1-Mo3	2.663(2) – 2.721(1)	Mo2-Mo2	3.484(2)
Mo2-Mo3	2.698(2) – 2.691(2)	Mo3-Mo3	3.349(2)
(Mo-Se)		(Se-Se)	
Mo1-Se1	2.534(2)	Se1-Se2	3.588(1)
Mo1-Se2	2.616(2)	Se1-Se3	3.647(2)
Mo1-Se3	2.582(2) – 2.650(2)	Se1-Se4	3.667(2)
Mo1-Se4	2.636(2)	Se2-Se3	3.692(2)
Mo2-Se1	2.595(2) – 2.614(2)	Se2-Se4	3.635(2)
Mo2-Se2	2.628(2)	Se3-Se4	3.715(3)
Mo2-Se3	2.539(2)		
Mo2-Se4	2.593(2)		
Mo3-Se1	2.593(2)		
Mo3-Se2	2.614(2) – 2.726(2)		
Mo3-Se3	2.549(2)		
Mo3-Se4	2.567(2)		
The cation environment (site 2)			
(Cr-Se)		(Se-Se) site 2	
Cr-Se1	2 × 2.481(1)	Se1-Se2	3.643(2)
Cr-Se2	2 × 2.726(1)	Se1-Se3	3.644(2)
Cr-Se3	2 × 4.149(2)	Se1-Se4	3.402(2)
Cr-Se4	2 × 2.659(1)	Se2-Se3	3.433(2)
(Cr-Mo)		Se2-Se4	3.635(2)
Cr-Mo2	2.987(2)	Se3-Se4	3.542(2)
Cr-Mo3	3.703(2) – 3.796(2)		

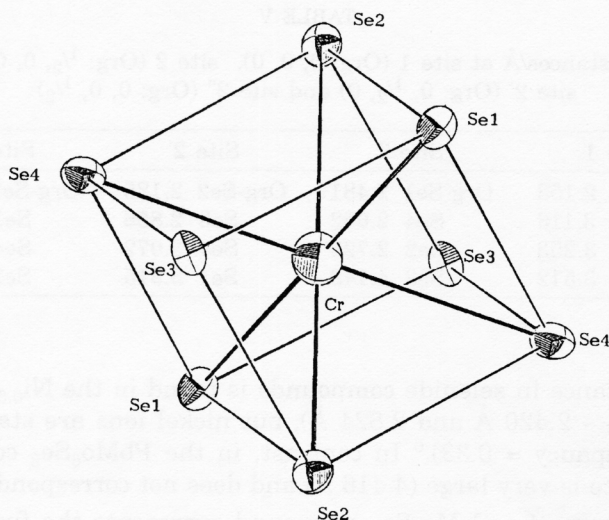


Figure 3. The chromium environment (site 2). The displacement ellipsoids enclose 90% probability.

phase to $P\bar{1}$ triclinic phase) through loss of the 3 fold axis. Chromium atoms occupy the centre of the distorted pseudo-cubic chalcogen network (site 2) and each Cr atom is surrounded by six chalcogen atoms forming a distorted octahedral site (Figure 3). The Cr-Se distances repeat two times (2.481 Å, 2.652 Å, 2.726 Å). The strong charge transfer onto the octahedral Mo_6 cluster (short Mo-Mo intracluster distances) seems to exhibit the presence of trivalent chromium ions, as already proved by magnetic properties.¹⁰ We can recall here the divalent nature of chromium atoms in the chromium sulphide Chevrel phase.⁴

The full occupancy of this site 2 (fixed position) leads to a definite compound CrMo_6Se_8 . This exceptional position of chromium ions in the channels arises from triclinic distortions of site 1 and the two other corresponding sites 2 (in the middle of the b and c axes). In fact, the Cr-Se shortest distance (2.481 Å) at site 2 ($1/2\ 0\ 0$) proves the impossibility to put the Cr^{3+} ions in octahedral interstices of site 1 (Org-Se = 2.153 Å; Org = origin of the considered site) and the two other sites 2 (Org($0\ 1/2\ 0$)-Se = 2.185 Å and Org($0\ 0\ 1/2$)-Se = 2.198 Å) (Table V).

The other important structural parameters, with respect to the electronic structure, are the Mo-Mo distances between the clusters and the Cr-Mo interactions. The particular situation of Cr ions in the network of chalcogen atoms at the midpoint of the a axis corresponding to site 2 allows some real periodic M-Mo interactions ($d_{\text{Cr-Mo}} = 2.987\ \text{Å}$). Of course, the short-

TABLE V

Distances/Å at site 1 (Org: 0, 0, 0), site 2 (Org: $1/2$, 0, 0), site 2' (Org: 0, $1/2$, 0) and site 2'' (Org: 0, 0, $1/2$)

	Site 1	Site 2	Site 2'	Site 2''			
Org-Se4	2.153	Org-Se1	2.481	Org-Se2	2.185	Org-Se3	2.198
Se2	3.116	Se4	2.652	Se3	2.856	Se1	2.744
Se1	3.253	Se2	2.726	Se4	3.072	Se4	2.938
Se3	3.512	Se3	4.149	Se1	3.915	Se2	4.259

est M-Mo distance in selenide compounds is found in the $\text{Ni}_{0.66}\text{Mo}_6\text{Se}_8$ compound (Ni-Mo \sim 2.420 Å and 2.824 Å), but nickel ions are statistically distributed (occupancy = 0.33).⁶ In contrast, in the PbMo_6Se_8 compound, the Pb-Mo distance is very large (4.416 Å) and does not correspond to any bond.

The structure of a CrMo_6Se_8 compound represents the first member of a new family of selenium Chevrel phases¹² where the M^{n+} cations occupy only the second site in the channels of the structure.

Supplementary Materials. – Crystallographic data (excluding structure factors which are available from the authors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-109/68-891. Copies of the data can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: 44 (0) 1223-336033; E-mail: teched@chemcryst.cam.ac.uk).

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SAŽETAK

Novi oblik strukture Chevrelovih faza: neuobičajen položaj iona kroma 3d u rešetki Mo₆Se₈

Abdellatif Mançour-Billah, Patrick Gougeon, Jean Yves Pivan, Marcel Sergent i Roger Chevrel

Određena je struktura ternarnoga triklinskog spoja CrMo₆Se₈. Parametri jedinične ćelije su slijedeći: $a = 6.738(2) \text{ \AA}$, $b = 6.710(2) \text{ \AA}$, $c = 6.783(3) \text{ \AA}$, $\alpha = 98.03(3)^\circ$, $\beta = 91.63(3)^\circ$, $\gamma = 94.65(3)^\circ$, $V = 302.5 \text{ \AA}^3$, $Z = 1$, $D_x = 6.913$, prostorna grupa $P\bar{1}$, 1771 refleks, 71 parametar, $R = 0.023$. Struktura se sastoji iz deformiranih klusterskih jedinica Mo₆Se₈. Posebnost strukture jest u novom razmješčaju kromovih atoma. Ioni trovalentnog kroma zauzimaju posebne položaje upravo u centru inverzije $1/2\ 0\ 0$ i okruženi su sa 6 selenijevih atoma koji čine dislocirano oktaedarsko mjesto (mjesto 2 u kanalu). To je u skladu s translacijom od $1/2$ uzduž romboedarske osi a olovnih iona u strukturi PbMo₆Se₈, što odgovara promjeni simetrije iz $R\bar{3}$ u $P\bar{1}$.