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A new increasing delocalization of $M = 3d$-elements (Ti, Fe, Co) in the channels network of the ternary $M_yMo_6Se_8$ Chevrel phases

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Abstract

A structural investigation on single crystals of $M_yMo_6Se_8$ Chevrel phases ($M = 3d$: Ti, Fe, and Co) has been carried out. These latter compounds as well as others with Cr, Mn, and Ni atoms make part of a new original family of Chevrel phases. The M ions occupy new interstices in the tridimensional channels network never observed in the other classical Chevrel phases as Li_y, Cu_y Mo_6X_8. They occupy only cavity 2 centered on $(\frac{1}{2}00)$ and $\hookleftarrow$ with a progressive delocalization of the M cation versus the nature of the cation from the center of the cavity to the outside . The position in cavity 2 is different from the position of the Cu (2) atoms, the second position of the copper atoms in the channels of the $Cu_yMo_6X_8$ compounds. This new position reinforces the interaction with the Mo_6 cluster, and may be able to involve new remarkable physical properties as thermoelectric properties.

Keywords: Single crystals; Structural investigation; Selenide Chevrel phase; Tridimensional channels; Cluster compounds

1. Introduction

The ternary molybdenum chalcogenides the so-called Chevrel phases of $M_yMo_6X_8$ formula (M = Cu, Ni,..., Pb, Sn, RE; $X = S$, Se, Te) have attracted great interest because of their very high-field superconducting properties [1]. Their crystalline structure is generally very well understood. The framework of these compounds consists of a stacking of Mo_6X_8 cluster units which leaves between the clusters with a system of quasi-orthogonal interconnected three-dimensional channels formed by chalcogen atoms. These channels are made up of two kinds of eight-chalcogen pseudo-cubic cavities; first, a cavity 1 with eight chalcogens belonging to eight different Mo_6X_8 pseudo-molecular units, is located on a three-fold axis at the origin of the rhombohedral unit-cell: (000), and a second cavity the so-called cavity 2 with eight chalcogens belonging to only four different Mo_6X_8 cluster units (one edge of each Mo_6X_8 unit shared with cavity 2).The center of these cavities 2 is located at the middle of the rhombohedral axes (or triclinic axes) with an inversion center in $(\frac{1}{2}00)$, $(0\frac{1}{2}0)$, and $(00\frac{1}{2})$.

Generally, these cavities are occupied, either by a large cation ($\geqslant 1$ Å) Pb, Sn, RE at the center of cavity 1 (origin (000) of the rhombohedral unit-cell) leading to a stoichiometry: $M_1Mo_6X_8$ or, by a small cation-like Li, Cu, Ni, etc. leading to an off-stoichiometry $M_yMo_6X_8$ compound. In the later case, the cations are disordered over 12 potential lattice positions around the unit-cell origin: the first occupied position is a 6f-position constituting a first six-hexagonal or puckered ring inside cavity 1 the so-called "inner sites" and then, the second occupancy is a second 6f-position outside to cavity 1 in six different cavities 2 the so-called "outer sites", both positions are statistically occupied and have very distorted "tetrahedral" environments. The occupancies of these positions allow to change the content of the M element in these compounds and explain their off-stoichiometry. Let us remark that a third cavity with eight chalcogen atoms is described in literature but cannot be occupied because of strong Mo–chalcogen interunit bonds.

In the previous literature, we said: "in ternary molybdenum selenides, $M_yMo_6Se_8$, type III (M = Fe,

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Mn, Cr, V, and Ti), these triclinic phases exist for $y \sim 1.2$" [2,3]. These results were only obtained on powder data. These selenide materials have recently been investigated and presented a very low lattice thermal conductivity exhibiting a large potential for thermoelectric applications [4] and, after that, band structure calculations have been carried out [5]. So, the structural determination by X-rays on single crystals will allow to give a stoichiometric or off-stoichiometric composition in these compounds and proving the originality of these materials.

Up to now, in Chevrel phases, only two kinds of structural phase transitions, trigonal–triclinic transitions, were well understood. A structural phase transition, Triclinic $P\bar{1} \leftrightarrow$ Trigonal $R\bar{3}$, is observed versus temperature and can be schematized by a freeze of the cations at lower temperature from six positions (ring) to only two positions (dumb-bell) in cavity 1. Transition can take place above or below room temperature and is a function of the nature of small cations and the content [6]. Another type of triclinic–trigonal transition can be observed on these compounds with large divalent cations (Ca, Sr, Ba, and Eu) at low temperatures [7,8]. The origin of such a transition is purely electronic.

So, what is the nature of structural transition in the 3*d*-metal molybdenum selenides? The phases with a 3*d*-metal: Cr, Mn, Ti, and Fe are triclinic at room temperature while the phases with M = Co and Ni are trigonal. The phases with Cr or Mn ions have an original triclinic structure: the M ions are located at the center of one of the three cavities 2 [9]. Note that, in the $Ni_yMo_6Se_8$ system, a selenide phase with a low nickel content equal to 0.66 presents a triclinic symmetry [10] and more recently, an equivalent telluride phase was also found to be triclinic [11]. Furthermore, a selenide with a high nickel content, equal to 1.25, exhibits a trigonal symmetry [12].

The present contribution deals with the new distribution of 3*d* cations (Ti, Fe, and Co) inside Mo_6Se_8 network.

2. Crystal growth

The ternary phase diagrams have been investigated. In the Ti–Mo–Se system, the melting point of the ternary compound is around 1700°C but the melting is not congruent and at 1680°C, there is already a slight decomposition. The primary zone of crystallization is just situated below the line $TiMo_6Se_8$–$TiSe_2$ and the starting material is enriched with Ti and Se elements; the nominal composition being $Ti_{1.5}Mo_6Se_{8.5}$. The two other compounds, $FeMo_6Se_8$ and $CoMo_6Se_8$, have congruent melting points at 1680°C, 1690°C, respectively. So, the starting material has a stoichiometric composition. The metal content of each compound has been determined on single crystals by X-ray structural analysis and confirmed by EDS microprobe analysis.

The product is put inside a Mo crucible, protected by an alumina crucible, sealed under low argon pressure and heated in a graphite resistor furnace [9]. The step at melting point is 10 mn, followed by a slow cooling at the rate 50°C/h down to 1500°C and 100°C/h down to 1100°C. The single crystals of the titanium and cobalt molybdenum selenides are some tenth mm^3, but the $FeMo_6Se_8$ single crystals present a very good size (0.5 to 1 mm^3).

3. Structural investigations

Single crystals of these three series of compounds have been examined with an automated four-circles CAD4 Nonius Diffractometer and the intensities have been collected and reported in Table 1 (graphite monochromatized MoKα radiation).

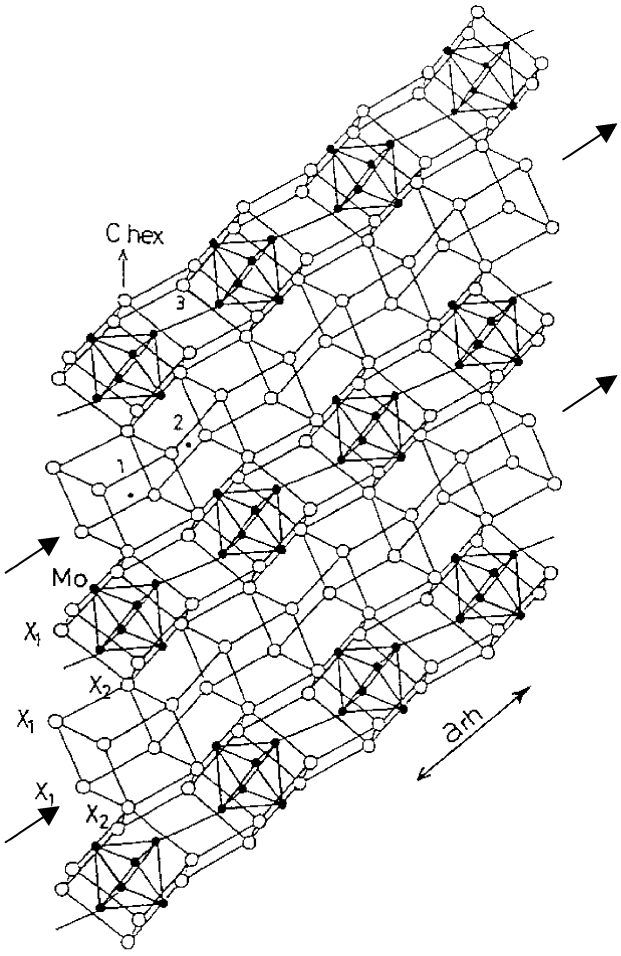

Fig. 1. Projection of the Mo_6Se_8 host network on hexagonal plane. One of the views of the tridimensional channels with the unoccupied cavities 1 and 2.

The structure is solved by placing the molybdenum and the selenium atoms as the coordinates of these atoms in the Ni $_{0.66}Mo_6Se_8$ structure [10] and is then refined. The position of the M cations was derived from difference Fourier maps.

The atomic coordinates, the equivalent isotropic thermal parameters and the occupancy factor of the M^{n+} cation are given in Table 2.

These ternary molybdenum selenides are built up from the more or less distorted pseudo-molecular Mo_6Se_8 cubic cluster units (Fig. 1). Even, in trigonal symmetry, the octahedron is distorted; there is a lengthening along a trigonal axis with two different Mo–Mo distances: one short distance is the so-called Mo–Mo intratriangle distance approximatively along the three-fold axis and one long distance is the so-called

Table 1
Crystal data and experimental parameters for the intensity data collection of $Ti_{0.88}Mo_6Se_8$, $Fe\sim_1Mo_6Se_8$ and $Co_{0.54}Mo_6Se_8$

Formula $M_yMo_6Se_8$	$M=Ti_{0.88}$	Fe_1	$Co_{0.54}$
Space group	$P\bar{1}$	$P\bar{1}$	$R\bar{3}$
Parameters (Å and °)	$a=6.745(4)$ $b=6.668(4)$ $c=6.794(3)$ $\alpha=98.25(3)$ $\beta=91.18(4)$ $\gamma=94.72(3)$	$a=6.717(2)$ $b=6.750(3)$ $c=6.767(3)$ $\alpha=95.96(3)$ $\beta=90.57(3)$ $\gamma=94.47(2)$	$a_R=6.704(1)$ $\alpha_R=92.23(1)$ $a_H=9.664(1)$ $c_H=11.151(1)$
V(Å^3)	$301.2(3)Z=1$	$304.1(2)Z=1$	$V_R=300.6(1)Z=1$ $V_H=901.8(1)Z=3$
d_{th} (g/cm^3)	6.89	6.89	6.84
Number of measured reflections	1456	1245	700
Validity of refinement (GOF)	1.5	1.03	1.63
Unweighted agreement factor R	0.036	0.026	0.038
Weighted agreement factor R_W	0.059	0.036	0.048

Table 2
Occupancy factors: positional and thermal parameters of $Ti_{0.88}Mo_6Se_8$ ($P\bar{1}$). $Fe_1Mo_6Se_8$ ($P\bar{1}$) and $Co_{0.54}Mo_6Se_8$ ($R\bar{3}$)

Atom	Site	x	y	z	τ occup.	B_{eq}[a](Å^2)
$Ti_{0.88}Mo_6Se_8$						
Mo_1	2i	0.23143(9)	0.41862(9)	0.54428(9)	1	0.31(1)
Mo_2	2i	0.54738(9)	0.22962(9)	0.40828(9)	1	0.32(1)
Mo_3	2i	0.41990(9)	0.53288(9)	0.22832(9)	1	0.34(1)
Se_1	2i	0.3510(1)	0.1349(1)	0.7145(1)	1	0.64(1)
Se_2	2i	0.7390(1)	0.3557(1)	0.1101(1)	1	0.57(1)
Se_3	2i	0.1330(1)	0.7236(1)	0.3778(1)	1	0.47(1)
Se_4	2i	0.2148(1)	0.1864(1)	0.2007(1)	1	0.68(1)
Ti	2i	0.5046(5)	−0.0506(4)	−0.0116(5)	0.44	0.85(6)
$Fe_1Mo_6Se_8$						
Mo_1	2i	0.23284(9)	0.41729(9)	0.54575(9)	1	0.51(1)
Mo_2	2i	0.54875(9)	0.23097(9)	0.40900(9)	1	0.54(1)
Mo_3	2i	0.42040(9)	0.53802(9)	0.22881(9)	1	0.51(1)
Se_1	2i	0.3547(1)	0.1297(1)	0.7190(1)	1	0.76(1)
Se_2	2i	0.7449(1)	0.3708(1)	0.1135(1)	1	0.78(1)
Se_3	2i	0.1341(1)	0.7281(1)	0.3803(1)	1	0.66(1)
Se_4	2i	0.2166(1)	0.1997(1)	0.2059(1)	1	0.82(1)
Fe	2i	0.5123(4)	0.0819(5)	0.0207(4)	0.5	2.12(5)
$Co_{0.54}Mo_6Se_8$						
Mo	6f	0.22705(7)	0.41598(8)	0.54650(7)	1	0.434(7)
Se_1	6f	0.37539(9)	0.12612(9)	0.74085(9)	1	0.637(9)
Se_2	2c	0.21382(9)	0.21382(9)	0.21382(9)	1	0.726(4)
Co	6f	0.507(2)	0.142(2)	0.050(1)	0.089(3)	0.9(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq}=4/3\sum_i\sum_j B_{ij}a_ia_j$.

Table 3
Interatomic distances (Å) of $Ti_{0.88}Mo_6Se_8$, $FeMo_6Se_8$, $Co_{0.54}Mo_6Se_8$ and $Ni_{1.25}Mo_6Se_8$ (12)

Distances (Å)		$Ti_{0.88}Mo_6Se_8$	$FeMo_6Se_8$	Distances (Å)	$Co_{0.54}Mo_6Se_8$	$Ni_{1.25}Mo_6Se_8$
Mo_6X_8 cluster unit						
Intra-triangle						
$(Mo–Mo)_A$	$Mo_1–Mo_2$	2.649 (1)	2.675(1)	$(Mo–Mo)_A$	2.688 (1)	2.686 (1)
	$Mo_1–Mo_3$	2.688 (1)	2.666 (1)			
	$Mo_2–Mo_3$	2.697 (1)	2.704 (1)			
Inter-triangle						
$Mo_A–Mo_A$	$Mo_1–Mo_2$	2.678(1)	2.680 (1)	$Mo_A–Mo_A$	2.781 (1)	2.760
	$Mo_1–Mo_3$	2.757(1)	2.751 (1)			
	$Mo_2–Mo_3$	2.729(1)	2.762 (1)			
Inter-cluster						
Mo–Mo	$Mo_1–Mo_1$	3.457 (1)	3.473 (1)	Mo–Mo	3.332 (1)	3.355
	$Mo_2–Mo_2$	3.485 (1)	3.488 (1)			
	$Mo_3–Mo_3$	3.288 (1)	3.289 (1)			
Mo–Se						
	$Mo_1–Se_1$	2.531 (1)	2.552 (1)	$Mo–Se_2$	2.559 (1)	2.571
	$Mo_1–Se_2$	2.595 (1)	2.581 (1)	$Mo–Se_1$	2.554 (1)	2.562
	$Mo_1–Se_3$	2.590 (1)	2.605 (1)	$Mo–Se_1$	2.590 (1)	2.608
	$Mo_1–Se_4$	2.604 (1)	2.593 (1)	$Mo–Se_1$	2.601 (1)	2.623
	$Mo_1–Se_3$ Inter-unit	2.652 (1)	2.653 (1)	$Mo–Se_1$ Inter-unit	2.633(1)	2.655
	$Mo_2–Se_1$	2.605(1)	2.604 (1)			
	$Mo_2–Se_2$	2.627(1)	2.622 (1)			
	$Mo_2–Se_3$	2.547(1)	2.532 (1)			
	$Mo_2–Se_4$	2.598(1)	2.592 (1)			
	$Mo_2–Se_1$ Inter-unit	2.614(1)	2.630 (1)			
	$Mo_3–Se_1$	2.571 (1)	2.595 (1)			
	$Mo_3–Se_2$	2.625 (1)	2.621 (1)			
	$Mo_3–Se_3$	2.551 (1)	2.558 (1)			
	$Mo_3–Se_4$	2.574 (1)	2.559 (1)			
	$Mo_3–Se_2$ Inter-unit	2.740(1)	2.707 (1)			
Se–Se						
	$Se_1–Se_2$	3.540 (1)	3.560 (1)	$Se_1–Se_1$	3.549 (1)	3.576
	$Se_1–Se_3$	3.621 (1)	3.582 (1)	$Se_1–Se_2$	3.729 (1)	3.747
	$Se_1–Se_4$	3.662 (1)	3.672 (1)			
	$Se_2–Se_3$	3.689 (1)	3.653 (1)			
	$Se_2–Se_4$	3.713 (1)	3.725 (1)			
	$Se_3–Se_4$	3.701 (1)	3.724 (1)			
Cavity 2 $(\frac{1}{2}00)$						
M cation surroundings						
	$M–Se_1$	2.382 (4)	2.354 (3)	$M–Se_1$	2.218 (8)	2.243
	$M–Se_1$	2.619 (4)	2.575 (3)	$M–Se_1$	2.457 (8)	2.517
	$M–Se_2$	2.510 (3)	2.427 (3)	$M–Se_1$	2.208 (8)	2.188
	$M–Se_2$	3.020 (3)	3.423 (3)	$M–Se_1$	3.897 (8)	3.788
	$M–Se_3$	4.043 (4)	3.876 (3)	$M–Se_1$	3.907 (8)	3.979
	$M–Se_3$	4.225 (4)	4.297 (3)	$M–Se_1$	3.920 (8)	4.049
	$M–Se_4$	2.470 (4)	2.497 (3)	$M–Se_2$	2.345 (9)	2.258
	$M–Se_4$	2.893 (4)	3.045 (4)	$M–Se_2$	3.550 (9)	3.698

Table 3 (*continued*)

Distances (Å)		$Ti_{0.88}Mo_6Se_8$	$FeMo_6Se_8$	Distances (Å)	$Co_{0.54}Mo_6Se_8$	$Ni_{1.25}Mo_6Se_8$
Se–Se distances						
	Se_4–Se_1	3.424 (1)	3.427 (1)	Se_2–Se_1	2×3.428 (1)	3.443
	Se_4–Se_2	3.713 (1)	3.725 (1)	Se_2–Se_1	1×3.729 (1)	3.747
	Se_4–Se_3	3.477 (1)	3.515 (1)			
	Se_3–Se_1	3.622 (1)	3.582 (1)	Se_1–Se_1	1×3.549 (1)	3.576
	Se_3–Se_2	3.421 (1)	3.456 (1)	Se_1–Se_1	2×3.576 (1)	3.587
	Se_2–Se_1	3.649 (1)	3.690 (1)			
Distances *M*–Mo and *M*–*M*						
(*M*–*M*)		0.679 (4)	1.111 (6)		1.991 (6)	2.253
(*M*–Mo)	*M*–Mo_2	2.789 (3)	2.716 (3)		2.499 (8)	2.481
	M–Mo_2	3.172 (3)	3.413 (3)		2.893 (8)	2.848
	M–Mo_3	3.422 (3)	3.221 (3)		3.012 (8)	2.904
	M–Mo_3	3.431 (3)	3.255 (3)		3.905 (8)	4.068

Mo–Mo intertriangle distance. The average Mo–Mo intratriangle bond length in the distorted octahedral Mo_6 clusters is 2.678 and 2.682 Å for the titanium and iron triclinic phases respectively and is very close to bond length of cobalt and nickel trigonal phases (2.688 and 2.686 Å) and even to the one in the binary selenide (2.684 Å) (Table 3).

On the contrary, the Mo–Mo intertriangle bond length changes and is generally characteristic of a certain electronic charge transfer from *M* element to the Mo_6 cluster, usually called valency electron concentration on the cluster (VEC). The average Mo–Mo intertriangle distance is 2.721 and 2.731 Å for the titanium and iron selenide compounds and is different in the cobalt and nickel ternary selenides: 2.781 and 2.760 Å, respectively, and 2.836 Å in the binary selenide.

Furthermore, these different values do not fit with the VEC's law reported by Yvon for the classic Chevrel phases [6]. That difference (low electronic transfer) arises from the originality of these new selenides: the *M* cations are located in the channels, but only in cavity 2 and not in cavity 1 as for the 3*d*-elements in the ternary molybdenum sulfides. Already, a trend towards a depopulation of the inner ring (cavity 1) for the benefit of cavity 2 with increasing ternary atom had already been seen in the ternary molybdenum selenides especially with Li element: occupancy of 0.42 Li(1) in cavity 1 against 2.76 Li(2) in cavity 2 in $Li_{3.2}Mo_6Se_8$ [13].

Another feature arises from the progressive delocalization with a new special position of the 3*d*-transition element in the ternary molybdenum selenides inside cavity 2 from the origin of this cavity ($\frac{1}{2}00$) (inversion center: $\bar{1}$) for the chromium or manganese ions [9] to the outside of the cavity for the titanium, iron, or nickel ions (Figs. 2–4). The *M* atoms, occupying interstices of the chalcogen network in cavity 2, are disordered over pairs of inversion-related sites (two equivalent positions via the inversion center $\bar{1}$ located at the center of cavity 2 ($\frac{1}{2}00$). So, the occupancy is partial: 0.44 for the titanium compound, 0.5 for the iron compound but is much lower (0.089) for the cobalt compound and 0.208 for the nickel compound [12] (because of trigonal symmetry and a delocalization in the three cavities 2, the distance between the two positions does not correspond to a true bond; for instance, for titanium and iron atoms).

This position, in cavity 2 is different from the position of Cu(2) found in the copper molybdenum chalcogenides [6,14]. The link vector between the two positions for the copper phases is closely parallel to the direction of the chalcogen channels (close to the direction of the rhombohedral axes). On the other hand, the link between both these new positions is quasi-orthogonal to the direction of the chalcogen channels and the delocalization makes the M ions closer and closer to the molybdenum atoms of the octahedral cluster.

Remark: Cavity 2 is built up from eight selenium atoms belonging to four Mo_6Se_8 cluster units contrary to cavity 1 which is constituted of eight selenium atoms belonging to eight Mo_6Se_8 cluster units. The distorted cubic cavity 1, centered on (000), is then, formed by six equivalent faces(each face consists of four chalcogen atoms) sharing six cavities 2. On the contrary, cavity 2, centered on ($\frac{1}{2}00$) and $\hookleftarrow$, is made up of six faces: two faces sharing two cavities 1 and the four others sharing four cavities 3 (where are the Mo–*X* and Mo–Mo intercluster bondings). Cavity 2 is surrounded by four Mo_6Se_8 cluster units.

This new position of the 3*d*-ion in the 3*d*-ternary molybdenum selenides, in order to differentiate the position of Cu(2) in the copper molybdenum chalcogenides, is called site M(2′) in cavity 2 and besides both

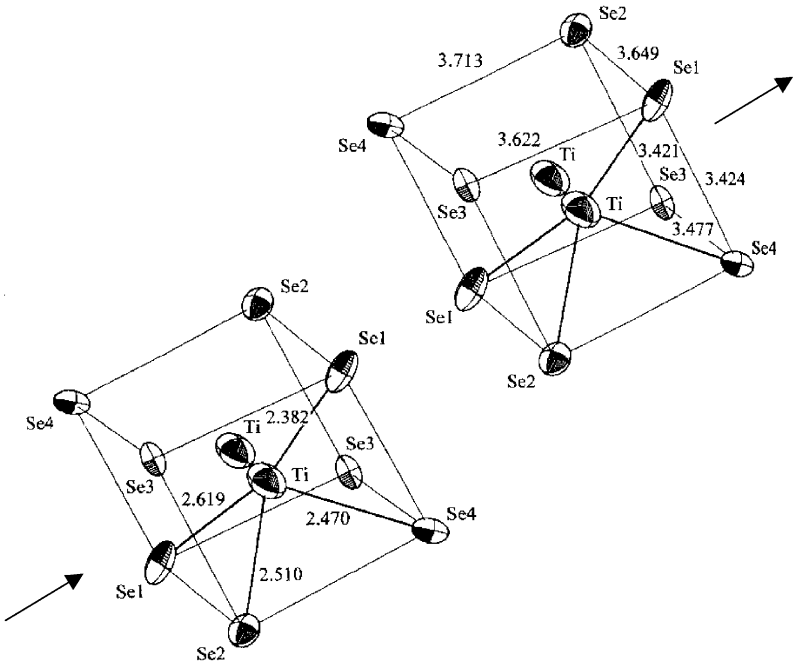

Fig. 2. View only of cavity 2 centered on $\frac{1}{2}00$: the titanium ions are disordered over pairs of inversely related sites 2′ (occupancy = 0.44) in a $Ti_{0.88}Mo_6Se_8$ triclinic compound. The Ti–Se distances (tetrahedral distorted site) are presented in the left bottom figure and the Se–Se distances on the right top figure. The arrows indicate the direction of the channels.

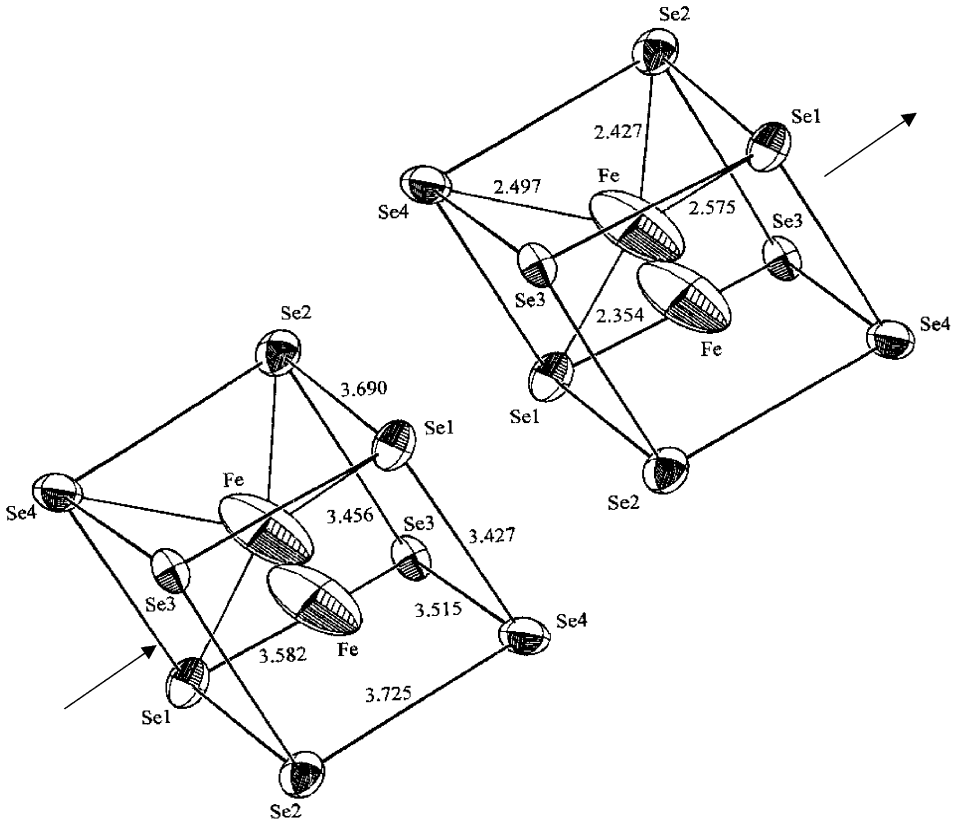

Fig. 3. View only of cavity 2 ($\bar{1}$ at $\frac{1}{2}00$): Delocalization of the iron ions over pairs of sites 2′ in a $Fe_1Mo_6Se_8$ triclinic compound. The Fe–Se distances (tetrahedral distorted site) are presented in the right top figure and the Se–Se distances on the left bottom figure. The arrows indicate the direction of the channels.

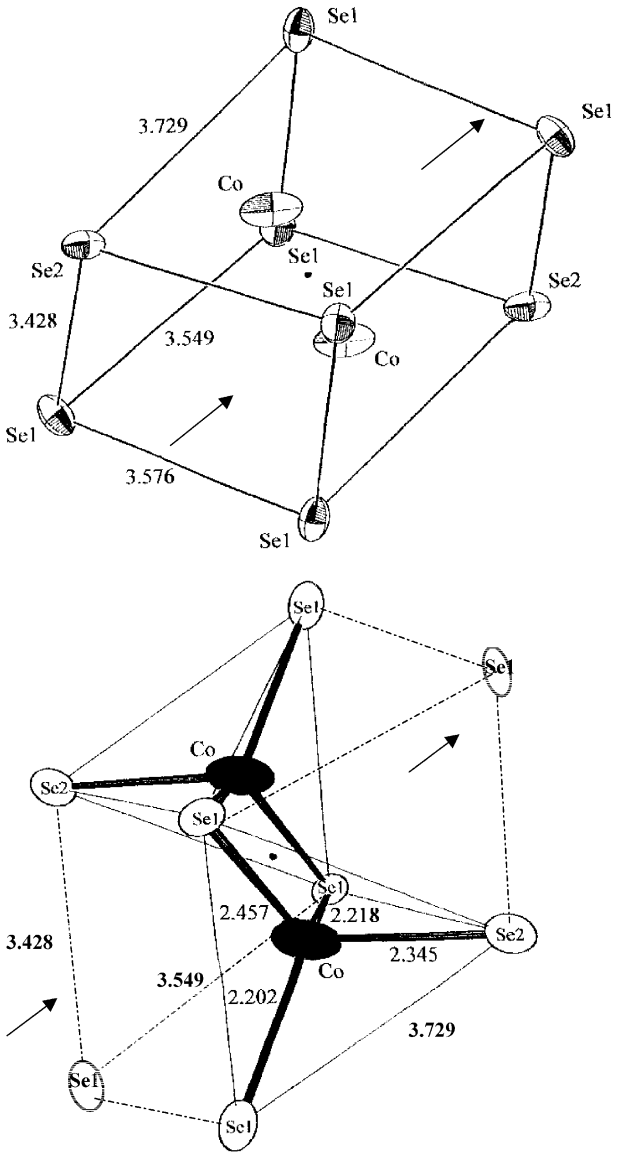

Fig. 4. View only of cavity 2: delocalization of the cobalt ions in a $Co_{0.54}Mo_6Se_8$ trigonal compound. The Co–Se distances (tetrahedral distorted site) are presented in the bottom figure and the Se–Se distances on the top figure. The arrows indicate the direction of the channels.

the positions are visualized in the nickel molybdenum sulfo-selenide [12].

The M-M distance varies from 0.679 Å (Ti), 1.111 (Fe), 1.991 (Co) and 2.253 (Ni) and can be considered only as a bond for the nickel compound (Table 3). The M ion is more and more far away from the center of cavity 2 and is closer and closer to the molybdenum atoms. The M–Mo distance is 2.789, 2.716, 2.499, and 2.481 Å for the titanium, iron, cobalt, and nickel compounds, respectively, and forms a stronger and stronger bonding.

The environment of the M cations by selenium atoms is shown in Figs. 2–4. While the chromium or manganese atoms, located at the origin of cavity 2 have six chalcogen neighbors which form a distorted octahedron [9], the titanium, iron or cobalt atoms have four neighboring atoms which form a very distorted tetrahedron. The M–Se distances are presented in Table 3 and Figs. 2–4. Each selenium tetrahedron in cavity 2 has two opposite edges belonging every one to two-opposite Se_4 faces separating one cavity 2 from two cavities 1 in the direction of the channels.

In the copper molybdenum chalcogenides, Cu (2) atoms are in cavity 2 but in another very different distorted tetrahedron .

4. Conclusion

The 3d-metal molybdenum selenides form a new family in Chevrel phases. They have always a framework made up of Mo_6Se_8 cluster units with interconnected tridimensional channels but the occupancy of the channels is completely original. The 3d-ions occupy only cavity 2; they are localized at the center of cavity 2 for the chromium and manganese selenides in a distorted octahedral environment forming a stoichiometric MMo_6Se_8 compound. They are more and more delocalized from the origin of cavity 2 to the outside for the titanium, iron, cobalt and nickel molybdenum selenides on two new equivalent positions the so-called M(2′) which is different from Cu(2) positions in copper molybdenum chalcogenides. Delocalization is carried out in cavity 2 along the direction of the channels for the Cu(2) positions and is quasi-orthogonal to the direction of the channels on site 2′for the 3d transition elements (M = Ti, Fe, Co, Ni). These 3d-ions occupy new tetrahedral interstices in cavity 2 and can constitute off-stoichiometric compounds. This family exhibits original thermoelectric properties which may be due to the progressive delocalization of the M–3d ions, orthogonal to the direction of the channels causing strong M–Mo bonding interactions.

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