



HAL
open science

Chevrel Phases: Genesis and Developments

André Perrin, Christiane Perrin, Roger Chevrel

► **To cite this version:**

André Perrin, Christiane Perrin, Roger Chevrel. Chevrel Phases: Genesis and Developments. Jean-François Halet. Ligated Transition Metal Clusters in Solid-state Chemistry, 180, Springer, pp.1-30, 2019, Structure and Bonding, 10.1007/430_2019_35 . hal-02284188

HAL Id: hal-02284188

<https://univ-rennes.hal.science/hal-02284188>

Submitted on 12 Sep 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Chevrel-Phases: Genesis and Developments

André Perrin, Christiane Perrin and Roger Chevrel
Institut des Sciences Chimiques de Rennes, UMR CNRS 6226
Université de Rennes 1, Campus de Beaulieu, 35042 Rennes-cedex (France)

Abstract

This chapter summarizes the important role played by Marcel Sergent in the discovery in the Rennes Laboratory of the Chevrel-Phases, which stimulated considerable interest in the international solid state chemistry community, because of their remarkable superconducting properties. After a brief general introduction to this topic the seminal discoveries associated with these phases between 1970 and 1990 are described. After their initial synthesis and structural determination was discovered, it was necessary to establish their critical superconducting transition temperature, the critical magnetic field and the critical current density in wires, single crystals, and thin films. More recently their applications as battery materials, in catalysis and their thermo-electric properties have been studied and are briefly described. These phases opened up the way not only to a rich solid state chemistry, but also to a rich solution chemistry, which complemented the classical field of transition metal carbonyl clusters. The basic cluster units of the Chevrel-Phases continue to be studied in the Rennes laboratory by the heirs of Marcel Sergent and more widely in the international community.

Keywords: Marcel Sergent, Chevrel-Phases, ternary molybdenum sulfide, molybdenum clusters, rhenium clusters, superconductivity, secondary batteries, hydrodesulfuration, thermoelectricity,

Contents

Introduction

1. The early beginnings
2. The discovery of Chevrel-Phases
 - 2.1. *Syntheses of the first thio compounds*
 - 2.2. *Syntheses of the first seleno and telluro compounds*
 - 2.3. *Subsequent syntheses*
3. The crystal structure of Chevrel-Phases
4. The electronic structure of Chevrel-Phases
5. The golden age of Chevrel-Phases
 - 5.1. *Superconductivity*
 - 5.1.1. Critical temperature
 - 5.1.2. Critical magnetic field
 - 5.1.3. Coexistence magnetism-superconductivity
 - 5.1.4. Processing Chevrel-Phases
 - 5.2. *Other properties and potentialities*
 - 5.2.1. Electrodes for secondary batteries
 - 5.2.2. Catalysis
 - 5.2.3. Thermo-electricity

6. The legacy of Chevrel-Phases
 - 6.1. Condensed clusters
 - 6.2. Mo_6 and Re_6 cluster compounds derived from Chevrel-Phases
 - 6.2.1. Mo_6 cluster chalcogenides
 - 6.2.2. Re_6 cluster chalcogenides and chalcogenides
 - 6.3. The beginning of solution chemistry of octahedral clusters
- Conclusion

Introduction

The aim of this chapter dedicated to the memory of Dr. Marcel Sergent is to relate his outstanding contribution to the discovery of the so-called Chevrel-Phases, their developments and the way they have paved the way to a large and important area of cluster chemistry. Although many people consider now that very old papers are obsolete, we have chosen to systematically refer here to original papers in order to get a memory of them, because they are often forgotten by the computer-assisted bibliographic tools and their users: "*if nobody remembers something, it did not ever exist*" [1]. This chapter does not provide an up-to-date and comprehensive review of this area, but a historical account of the scientific contribution of Marcel Sergent to this area and its subsequent development. Consequently, the bibliography concentrates on the literature from 1970 to 1990, for which many details are covered in reference [2], and a more comprehensive review of this area is to be found in a recent paper by O. Peña [3].

1. The early beginnings

The Thesis Dissertation [4] of Marcel Sergent, defended in 1969, was devoted to the synthesis of new "*Alkaline thiomolybdates, thiotungstites and thiochromites*". This topic was chosen because the head of the Laboratory, Prof. J. Prigent, was a specialist of uranium chemistry and decided to extend the study of uranates and thiouranates to molybdenum and tungsten analogues. The experimental solid state route for these syntheses was the sulfuration of the metallate by CS_2 transported by N_2 at around 300-400 °C (Figure 1). The resulting thiometallates, were subsequently reduced under H_2 in the range 500-700 °C. This approach was chosen because the alkaline metals are too reducing and the handling of alkaline sulfides was problematic.

The study of molybdenum and tungsten led to a number of new compounds of general formula $MMeS_2$ (M = alkaline metal, Me = Mo or W) where the Me metal has the formal oxidation state of +3 [5]. Conductivity measurements showed that they were semiconducting and the magnetic measurements suggested the presence of metal-metal bonds. A further reduction under H_2 of the thiotungstites produces metallic W at temperature as low as 850 °C.

In contrast, thiomolybdates are reduced near 900 °C to the new compounds of divalent molybdenum: $M_2Mo_5S_6$ ($M = K, Rb, Cs$) and $M_2Mo_2S_3$ ($M = Li, Na$) [4]. The XRD patterns of the later were very similar to the one reported just previously by Espelund for "SnMo₆S₇", the pattern of which was tentatively indexed with a pseudocubic unit-cell with $a = 6.53 \text{ \AA}$ [6]. Remembering that SnMo₆S₈ was later shown to have a trigonal R-3 unit-cell with $a = 6.52 \text{ \AA}$ and $\alpha = 89.73^\circ$, it becomes clear now that these compounds were in fact the first examples of the Chevrel-Phases (hereafter abbreviated as CPs).

It is noteworthy to mention the Conclusions of the Thesis of Marcel Sergent, relative to these thio-compounds of Mo(II) : *"[they] form a very original series, owing to their electrical and magnetic properties, very different from the ones of chromium and other transition elements. These compounds are actually characteristic of the low valency chemistry of molybdenum, tungsten, niobium, and rhenium, based on Me-Me chains or polymers"*. We can guess that the last word in this sentence would refer in his mind to "MoCl₂" derivatives that were already known since the 1940s to have structures based on octahedral Mo₆ units with strong Mo-Mo bonds [7, 8].

2. The discovery of Chevrel-Phases

As he developed an independent research programme Marcel Sergent decided to pursue this interesting emerging chemistry of ternary molybdenum(II) sulfides. Indeed, Marcel Sergent and his student Roger Chevrel intuitively felt that it may be possible to reduce MoS₂ by Mo and a third metallic element, using high-temperature direct solid-state syntheses in evacuated sealed silica tubes (as was done by Espelund), a method that was not well-developed at that time in the solid-state community. They implemented it in the laboratory, enabling syntheses up to about 1200 °C. Indeed, this approach was very fruitful, and gave opportunity to develop in Rennes the transition element cluster chemistry of the early transition metals. It remains, 50 years on, very commonly used in solid state laboratories worldwide for high temperature solid-state syntheses.

2.1. Syntheses of the first thio compounds

The first attempts were carried out within the framework of the M.Sc. Diploma (unpublished) of his student Roger Chevrel, which described the exploration of the Fe-Mo-S system. Two new phases were detected: FeMo(II)₃S₄ which was later identified and assigned to the so-called Chevrel-Phases (CPs) and also FeMo(III)₂S₄. These synthetic procedures were extended to a number of ternary sulfides and reported in the Thesis of R. Chevrel [9]. The

overall approach was to explore the range of compositions $M_2(I)S-Mo(II)S$ and $M(II)S-Mo(II)S$, targeting formulas $M_2(I)Mo_nS_{n+1}$ and $M(II)Mo_nS_{n+1}$. Following several oral communications in scientific meetings in the 1968-70, the results were first published (in French, see Figure 2) in 1971 in the seminal paper titled "*On New Molybdenum Ternary Sulfides Phases*" [10] and summarized in Table 1.

Stoichiometric compounds were obtained when M was a large cation, namely Ag, Sn, Pb, Sr and Ba. From Weissenberg and Buerger X-ray photographs it was shown that they crystallize in the trigonal system, R3 or R-3 space groups (SG). The unit-cell constants, refined from X-ray diffraction powder data are all close to $a = 6.5 \text{ \AA}$ and $\alpha = 90^\circ$: for instance, in the example of the Pb compound, they are $a = 6.54 \text{ \AA}$, $\alpha = 89^\circ 28'$.

Solid solutions, with a large variability in cation concentration, were obtained with smaller cations, Ni, Co, Fe and Mn. They also crystallize in the R3 or R-3 S.G., with similar unit-cell constants, but α is now slightly larger than 90° . The Cr solid solution in contrast showed a triclinic distortion although the unit-cell remains very close to the trigonal parent, while Mg, Zn and Cd solid solutions undergo a trigonal to triclinic transition for high concentrations of the cations. A special mention concerns the copper compounds as they were apparently characterized by a double non-stoichiometry. In fact, it was found later that the solid solution $Cu_xMo_6S_8$ extended from $x=1.6$ to $x=4$.

Finally, the paper mentioned some alkaline thiomolybdates that present a trigonal unit-cell similar to the above-mentioned ones (for Li, Na), while $M_2Mo_5S_6$ ($M = K, Rb, Cs$) are quadratic.

An important conclusion of this paper, drawn from both the chemical properties and magnetic measurements, was that the molybdenum had a formal oxidation state of +2, and the d^4 configuration was capable of establishing Mo-Mo bonds, and the authors restated a visionary hypothesis of the formation of "metal clusters" (defined by Cotton as "*a finite group of metal atoms held together mainly or at least to a significant extent, by bonds directly between the metal atoms, even though some non-metal atoms may also be intimately associated with the cluster*" [11]) in such compounds, similar to that reported for $MoCl_2$ [7,8].

2.2. Syntheses of the first seleno and telluro compounds

For the synthesis of such compounds, a valuable advantage of the sealed tubes method is the use of elemental Se (Te), avoiding the need to handle the very harmful H_2Se (H_2Te). Consequently, many ternary molybdenum(II) selenides were published in the next few years. O. Bars *et al.* reported in a short paper the synthesis and unit-cells of Mo_3Se_4 and the solid

solutions $M_x\text{Mo}_3\text{Se}_4$ ($M = \text{Fe}, \text{Co}, \text{Ni}$) as early as 1970 [12]. As all these compounds appeared to be isostructural, it was suggested that the binary product would act as a host-structure for counter-cations, leading to the ternary chalcogenides. Some time later, R. Chevrel and M. Sergent extended and completed this work [13]. It is noteworthy that in the meantime the crystal structure of Mo_3Se_4 was solved (see below, section 3), giving unambiguous structural evidence for Mo_6 octahedral clusters-based Mo_6Se_8 units. In their second full paper, Chevrel and Sergent used the notation " $M_x\text{Mo}_3\text{Se}_4$ ", but finally, after structural determinations, it became evident that the use the $M_x\text{Mo}_6\text{Q}_8$ ($\text{Q} = \text{chalcogen}$) formula was more accurate and established that the common basic unit was the rigid Mo_6Q_8 entity, for all the CPs (see section 3).

As previously, large cations led to definite compounds $M_x\text{Mo}_3\text{Se}_4$ where M was Zn, Ag, Cd, Sn and Pb with x close to 0.6. They crystallize as above in the trigonal R3 or R-3 S.G., the unit-cell volume increasing monotonically with the radius of M . For $M = \text{Fe}, \text{Mn}, \text{Cr}, \text{V}$ and Ti a triclinic solid solution is observed ($0.5 < x < 0.7$). For Cu and Co the trigonal solid solution extends from $x = 0$ (*i.e.* Mo_3Se_4) to $x = 1.4$ and 0.7 , respectively. In the example of $\text{Ni}_x\text{Mo}_3\text{Se}_4$ the trigonal solid solution extends in the ranges $0 < x < 0.3$ and $0.6 < x < 0.8$ while in-between is observed a triclinic distortion.

2.3. Subsequent synthetic studies

This pioneering work resulted in an incredible blooming of new compounds during the 1970s. Besides the main group and transition elements, they included rare-earth [14] and actinide counter cations [15,16]. For example, in the late 1970s, more than 80 CP compounds were identified and characterized [2,17]. Also it should be mentioned that the substitution of some of the chalcogens by halogens could be achieved and some of the molybdenum atoms could be replaced by Re or Ru. This opened up the way to very important series of new cluster-based chalcogenides, as discussed in more detail in Section 6.

3. The crystal structures of Chevrel-Phases

The first pertinent work related to CPs was the structure determination in 1973 of the binary Mo_6Se_8 by O. Bars et al. [18]. Indeed, this compound was synthesized some years before by decomposition at 1180°C of MoSe_2 under a vacuum [19], but only the full solid state approach afforded single-crystals easily obtained and suitable for a X-ray diffraction analysis. This pioneering structural work established the presence of slightly distorted octahedral Mo_6 groups, based on octahedral metal "clusters", and M. Sergent realized that

they were similar to those present in MoCl_2 (see Figure 3). Within the cluster, the Mo-Mo distances are 2.68 and 2.83 Å, consistent with the presence of strong metal-metal bonds. In molybdenum metal, the Mo-Mo distance is 2.73 Å [20]. The Mo_6 clusters are inscribed in a Se_8 pseudo-cube, leading to the Mo_6Se_8 units, which are the structural basis of all of the CPs. In addition, there are six longer intercluster Mo-Mo contacts of 3.26 Å. Of special interest in this paper is another illustration of the unit-cells stacking: the small arrows in Figure 3 represent Mo-Se interunit bonds and evidence the fact that a selenium atom lies on each "apical" position of the Mo_6 octahedron (*i.e.* on the pseudo-quaternary axis), exactly like some of the halogen atoms in MoCl_2 . The correct description of the three-dimensional structure is based on the 3-dimensional stacking of $\text{Mo}_6[\text{Se}_2^i\text{Se}_{6/2}^{i-a}]\text{Se}_{6/2}^{a-i}$, where the symbols ^a and ⁱ act as "apical" and "inner" (*i.e.* belonging to the Se_8 pseudo-cube), according to the Schäfer notation [21]. This structure forms some channels and cavities, especially at the origin of the unit-cell, and the assumption was made in the paper that it acted as a host structure in the ternary CPs.

Indeed, this work was followed very soon by the determination of the structures of ternary phases: $\text{Ni}_{0.66}\text{Mo}_6\text{Se}_8$ [22] and $\text{Ni}_2\text{Mo}_6\text{S}_8$ [23] and many others. The structure of PbMo_6S_8 [24,25] was particularly noteworthy, because it is considered as the prototype of CPs with a large cation as well as the structure of the very extended solid solution $\text{Cu}_x\text{Mo}_6\text{S}_8$ ($1.6 < x < 4$) [26]. In the first case, Pb^{2+} counter-cations are located at the origin ("site 1") while in the second one the Cu^+ counter-cations are statistically distributed on a puckered hexagon around this same site 1 and on another one denoted as "site 2". Simultaneously, the structure of the selenide PbMo_6Se_8 was also reported [25].

In the following years, many of these structures were accurately refined, giving evidence for some additional non-stoichiometries: as an example, " PbMo_6S_8 " was actually $\text{PbMo}_{6.35}\text{S}_8$ [15]. However, for reasons of clarity, we will use the simplified formulas hereafter.

4. The electronic structure of Chevrel Phases

Well before the discovery of CPs, the isolated cluster unit $[\text{Mo}_6\text{Cl}_8]^{4+}$ was studied by several authors [27-29] using a simple molecular orbital (MO) approach. Although the precise ordering of the MO levels was uncertain at this stage (it was precisely established some years later as a_{1g} , t_{1u} , t_{2g} , t_{2u} , e_g , from the bottom to top [30]), the important point was the evidence of the formation of 12 metal-metal bonds involving 24 electrons on the metal cluster, a magic

number called valence electron count (VEC) [31]. This corresponds obviously to the establishment of single-bonds with a bond order of 1, as formalized by J.D. Corbett [32].

In the late 70's and early 80's, such calculations were extended to the newly discovered CPs [33-36]. The pedagogic report of T. Hughbanks and R. Hoffmann [37] was particularly noteworthy since their calculations emphasized the crucial role of apical S^{a-i} ligands. This point of view agrees closely with the previous statement of Corbett that "*a maxim of cluster chemistry is that the outer or exo [i.e. 'apical' in the Schäfer notation used here] positions are strongly bonding and are always occupied by some basic group*" [32]. Indeed, this is this feature that imposes a rotation of about 25° (as seen on figure 3) of the cluster-unit inside the counter-cations pseudo-cube, in order to put a sulfur atom of a surrounding cluster-unit in front of each molybdenum of a given (Mo_6S_8) cluster-unit. These additional sulfur atoms lie onto the pseudo quaternary axes of the octahedron. Introducing these apical sulfur ligands in the calculation, instead of restricting to the (Mo_6S_8) cluster-unit, actually opens a gap above the e_g MO, the top-most level of the Mo- d group, as illustrated on figure 4. As the e_g levels are fully occupied for a VEC = 24, this explains why a compound like $Mo_2Re_4Se_8$, strictly isostructural with Mo_6Se_8 , turns out to be a semiconductor, as it accommodates exactly 24 e^- /cluster (see Section 6).

Similar results were reported simultaneously and independently by the team of R. Lissillour [38]. They extended the calculations to a number of $M_6L_8L'_6$ cluster-based compounds ($M = Mo, Re$; L and L' = halogen or chalcogen, see section 6) and formalized their results within their so-called "3-band model", where from the bottom to top lies a band mainly composed of p L ligand orbitals, the second is made of 12 d M metallic orbitals (bonding) and the third, separated by the gap, of 18 d M metallic orbitals (antibonding) [39].

5. The golden age of Chevrel-phases

5.1. Superconductivity

5.1.1. Critical temperature

A very short time after the publication of the paper of R. Chevrel, M. Sergent and J. Prigent on ternary molybdenum sulfides, the group of B.T. Matthias discovered a superconducting behavior in several of them and published in *Science* a short paper entitled: "*High-temperature Superconductors: the First Ternary System*" [40]. For the Cd, Mg, Zn, Cu, Sn and Pb compounds, critical temperatures (T_c) of 2.3, 2.4, 2.7, 10.8, 10.9 and 12.5 K, respectively, were reported. Such a discovery initiated immediately an intense international research on the superconductivity of CPs, promoting in particular a very long-lasting and

fruitful collaboration between the groups of M. Sergent in Rennes and Ø. Fischer in Geneva. As reported in reference [17], the T_c of more than 80 compounds was measured in 1978. Figure 5 illustrates an example of resistive transitions reported early [41].

The effect of doping by a fourth (metal) element suggested that the nature of the counter-cations between the Mo_6S_8 units plays an important role on the value of the critical temperature [42]. However, the subsequent report that $\text{Mo}_6\text{S}_6\text{Br}_2$ exhibits a T_c as high as that in PbMo_6S_8 (see Section 6 below) does not support this assertion. From a study of the effect of the (partial) substitution of S by Se or Te in PbMo_6S_8 and Mo_6S_8 , it was concluded that correlations between T_c and both the rhombohedral angle α and the intercluster Mo-Mo distance [43] existed. Further research showed no direct correlation between the superconductivity and the nature of the ternary element M, suggesting that the $4d$ - electrons of Mo were essentially responsible for the superconducting properties [14]. This was confirmed some years later by theoretical calculations. In contrast, a clear correlation of T_c and the VEC was established [31]. Figure 6 shows a maximum of T_c around a value of 3.7-3.8 electron/Mo, *i.e.* around 22 electrons/ Mo_6 cluster, again in accordance with a maximum of the density of states near this value.

5.1.2. Critical magnetic field

Another striking characteristic of superconducting CPs is their extraordinary high critical magnetic field, which was only exceeded by the so-called HCTS cuprates discovered in 1986. Indeed, the Fischer group reported in 1974 the first measurements, using a pulsed magnetic field limited to 350 kG. For some samples they could not reach the critical magnetic field H_{c2} but deduced from a model values up to about 450 and 550 kG for PbMo_6S_8 and Al-doped SnMo_6S_8 , respectively [44]. The same year, using a new coil delivering up to 510 kG, they obtained at 4 K a critical field estimated to 560 kG (for full destruction of superconductivity), meaning more than 600 kG at 0 K, for a slightly Gd-doped PbMo_6S_8 sample [45]. Finally, the following year, H_{c2} was increased to 580 kG at 4 K and more than 600 kG at 2 K for a sample doped with both Gd and Eu, implying that a magnetic field above 700 kG would be necessary to make it entirely normal [46]. As CPs are not cubic, experiments were carried out on oriented single-crystals. An anisotropy of about 20 % was measured for all three representative PbMo_6S_8 , PbMo_6Se_8 and SnMo_6Se_8 , with the maximum of H_{c2} obtained when H is perpendicular to the ternary axis [47].

5.1.3. Coexistence of magnetism and superconductivity

Finally, it should be mentioned the discovery of the coexistence of magnetism and superconductivity in the (RE)Mo₆S₈ systems. Indeed, it was shown that a partial substitution of Pb or Sn in PbMo₆S₈ or SnMo₆S₈ by magnetic rare-earth ions did not destroy the superconductivity [14,48] (see Figure 7 [14]). A subsequent study, involving all RE ions series, was carried out and most of the (RE)Mo₆S₈ are superconducting above 1.1 K. It was the first time that a system containing a regular lattice of magnetic ions was superconducting. It was concluded that the exchange interaction between the superconducting electrons and the RE-ions was very weak, because the latter are located on the origin site, far away from the Mo₆ cluster [14]. This situation contrasts with the case of small magnetic transition elements of the first group like Fe, where these ions are delocalized around several sites and are then closer to the cluster, fully destroying the superconductivity, as expected. Very unusual behavior was reported for some (RE)Mo₆S₈. For instance, HoMo₆S₈ is superconducting at 1.2 K but becomes normal again below 0.65 K where a magnetic transition occurs [49]; this particular state was called "reentrant superconductivity" [50]. On the other hand, EuHoMo₆S₈ exhibits a phenomenon of magnetic field induced superconductivity : at T < 1 K, superconductivity is destroyed in a low field (about 10 kG), reappears at 80 kG and finally disappears only above 200 kG [51]. Interested readers could find more detail in [3] and the references therein.

5.1.4. Processing Chevrel Phases

Figure 8 illustrates clearly the superiority of PbMo₆S₈ with respect to technical superconductors Nb-Ti, Nb₃Sn and even Nb₃Ge in term of critical field [17]. Indeed, a considerable effort was made to produce wires of CP, because they appear to be excellent candidates to build coils able to sustain higher magnetic fields. For this purpose, they have to be processed in the form of wires, additionally able to support high current density. The main drawback arises from the fact that CPs are very brittle materials (as Nb₃Sn and Nb₃Ge, while in contrast Nb-Ti is a ductile alloy). One of the first attempts was based on the sulfidation of a molybdenum wire, followed by a heat treatment under Pb vapor (see Figure 9) [52]. The current density was quite modest, $2 \cdot 10^7$ A/m² in a field of 40 kG [52]. In the following years the technology of powder metallurgy was developed, implying in most cases the help of specialized factories. Then several consortiums were established, for instance, in France: University of Rennes with CGE Marcoussis, CEN Saclay and Grenoble and SNCI Grenoble;

in Europe: Universities of Rennes, Geneva and Nijmegen with Plansee, Spectrospin and Promogap (European Union Programme Eureka 96). Briefly, the CP (prereacted [53] or its precursors [54]) is compacted in a copper tube ("billet") that is extruded, and then drawn as a long monofilament wire. In further improvements, sections of such wires were assembled in bundles and again extruded and drawn to produce multifilament wires as shown in Figure 10 [50,54]. In order to avoid any contamination of PbMo_6S_8 by Cu, an anti-diffusion barrier (mainly Nb and in some cases Mo) was inserted [50,53-54]. Whatever the route used, the critical current density was in the range $1\text{-}2 \cdot 10^8 \text{ A/m}^2$ at 200 kG and 4.2 K [55]. Values of $5.4 \cdot 10^8$ and $3.1 \cdot 10^8 \text{ A/m}^2$ were further reached at 1.9 K for fields as high as 200 kG and 240 kG, respectively [56]. Figure 11 shows that CP wires over-passed any technical superconductors above 170 kG [57].

Thin-films are the ideal form for some physical measurements, such as critical current density and the development of superconducting junctions. The first attempt used RF sputtering from a composite target to grow CPs with Cu, Ag, Sn and Pb, deposited onto Mo substrates [58]. The films were either grown *in-situ* on heated substrates (750-900 °C) or deposited at room temperature and subsequently annealed in silica tube sealed under vacuum. Critical temperatures close to the one of bulk material were achieved. Such films exhibited J_c as high as 10^9 A/m^2 at zero field [59] and were later used to produce superconducting tunneling junctions based on CPs [60]. In the following years, reactive physical vapor deposition was proposed [61], but other groups used sputtering, with different variants [62,63]. During this period, M. Sergent decided to provide his laboratory with a miniaturized sputtering device and $T_c = 13 \text{ K}$ and $J_c = 3 \cdot 10^7 \text{ A/m}^2$ were achieved for PbMo_6S_8 with this very simple apparatus [64,65]. When pulsed laser deposition became popular, this method was applied to the *in-situ* growth of $\text{Cu}_x\text{Mo}_6\text{S}_8$ and epitaxial thin-films of CPs were obtained for the first time [66]. More recently, films of $\text{Cu}_2\text{Mo}_6\text{S}_8$ were synthesized by chemical solution deposition, based on the use of a polymeric precursor: the coatings were first calcined, then sulfided under a $\text{H}_2/\text{H}_2\text{S}$ flow and finally reduced under H_2 [67]. On the other hand, the preparation of a thick-film (17 μm) of $\text{Cu}_x\text{Mo}_6\text{S}_8$ was done by a chemical transport technique [68], similar to the method used to process wires reported in [52].

Single-crystals are obviously of great importance for many physical measurements. Indeed, crystals suitable for structure determination were in most cases picked from the powders resulting from the synthetic procedures. Chemical transport reactions were carried

out for $\text{Co}_2\text{Mo}_6\text{S}_8$ [9] and PbMo_6S_8 , [69,70], giving isolated well-formed crystals, but the latter were still too small for physical measurements. Crystallization from melt is difficult, because many of CPs undergo incongruent melting. In addition, it is necessary to take into account the sensitivity to oxidation, the high melting temperature and the high chemical reactivity [71]. Then, welded Mo crucibles [72], or high Ar or He counter-pressure [73,74] or liquid-encapsulated melting [75], were proposed, especially in the examples of ternary sulfides with Pb, Sn or Cu. Obviously, much efforts were done for rare earth ternary sulfides, because of their outstanding properties. Sealed Mo crucibles [76], often associated with a Al_2O_3 liner and an excess of RE sulfide [71] were used. A very complete study of the kinetics of the crystal growth of REMo_6S_8 was carried out [77]. It established the possibility of working in open crucibles under argon at atmospheric pressure, as long as the initial charge was sufficiently shifted in composition. A general survey including details about the physical properties measured on REMo_6S_8 crystals is given in [78]. The reader is also referred to the recent review [3]. Finally, the systematic study of the crystal growth of the selenides REMo_6Se_8 was carried out more recently [79].

5.2. Other properties and potentialities

As outlined in the previous section, CPs have been studied in detail for their outstanding superconducting behavior. In addition, this series of compounds exhibits several other striking properties, which are summarized below.

5.2.1. Electrodes for secondary batteries

As mentioned above, the structure of CPs provides an open framework with 3-dimensional channels, where delocalized small counter-cations are accommodated. These metal ions are mobile within these channels. Indeed, Chevrel and Sergent removed the counter-cations from some small-cation CPs (*e.g.* copper and nickel), by leaching them with a dilute inorganic acid, then giving access to the metastable Mo_6S_8 binary compound [80]. The reaction is reversible and ternary representatives can again be obtained using soft conditions. In addition, the process is topotactic in character, and the authors were able to determine and refine the crystal structure of Mo_6S_8 [80]. Soon after, Schöllhorn *et al* succeeded in intercalation-de-intercalation reactions using an electrochemical approach. In their studies both transition-metals CPs were removed with aqueous electrolyte, and alkaline CPs with an organic one [81]. These results opened the way to the study of CPs as cathode materials for rechargeable batteries. Most work was devoted to the Cu, Fe, Ni and Cr-based CPs associated

with lithium and organic electrolyte [82-86]. Thick [87] and thin-films [88,89] were also studied. More recently the group of D. Aurbach highlighted the potential interest of Mg/CP batteries [90] because Mg is eco-friendly, non-toxic, abundant in the earth crust, divalent, and gives fast and reversible intercalation in CP. These CPs have been claimed to be the currently best available model cathode for Mg batteries, as practical energy densities of 60 W h kg^{-1} (about half of the Li-ion battery) with excellent cyclability (> 3000 cycles) were reported [90]. For a recent, complete and critical review, see reference [91]. As a final remark, it is clear that CPs have a limited intrinsic massic capacity, due to their quite high molecular weight. However, they could be very attractive for land based stationary battery systems, in relation to the need for the storage of intermittent renewable energy sources like wind or sun.

5.2.2. Catalysis

In 1984, McCarty and Schröder compared the ability of several CPs as catalysts for hydrodesulfuration of crude oils versus both classical un-promoted and Co-promoted MoS_2 (usually labeled "CoMoS") catalysts [92]. They found that all CPs tested had efficiencies comparable and even better than the standard model catalysts, on the basis of catalyst surface area. In addition, they showed that CPs had a higher selectivity and stability. Their long-term activity was also better than those of classical model catalysts. However, samples were synthesized by the standard high-temperature solid-state route, resulting in low specific surface area, about $1 \text{ m}^2/\text{g}$. Obviously, improved efficiency of the catalytic process depends strongly on the specific area of the material used. Then, M. Sergent and his group launched a program devoted to increasing the surface areas of the CPs. The work drew on a previous result in his Thesis [4] that the hydrogen reduction of alkaline thiomolybdates affords new compounds that turned out to be in fact CPs. The first approach was to reduce mixtures of ammonium thiomolybdates and, for instance, copper salts. The CP $\text{Cu}_x\text{Mo}_6\text{S}_8$ was obtained at temperature as low as $600 \text{ }^\circ\text{C}$, with an intermediate step involving a mixture of MoS_2 and Cu [93]. Subsequently, samples of $\text{Cu}_x\text{Mo}_6\text{S}_8$ supported on alumina were prepared by impregnation with an ammonia solution of ammonium heptamolybdate and copper nitrate, followed by air calcination, sulfuration under a H_2S flow and finally reduction by hydrogen [94]. The crystallites were so small that the CP could not be characterized by X-ray diffraction, only by EXAFS. Also, searching for a pre-industrial route for CP preparation, finely grained $\text{Ni}_x\text{Mo}_6\text{S}_8$ powders ($0.5\text{-}1 \text{ }\mu\text{m}$) were prepared by bubbling H_2S in an aqueous solution of heptamolybdate and Ni nitrate. The co-precipitate was dried and H_2 treated as previously [95]. Finally, an indirect route to prepare supported Ni CP catalyst was to start

from a commercial Ni-Mo catalyst precursor, to sulfide it until the early formed "NiMoS" was fully dissociated in MoS₂ and Ni particles, as mentioned above in the example of copper, and to react and reduce them under hydrogen in order to synthesize the CP [96]. Catalytic activity measurements were used to optimize the reduction treatment. It should be noticed that Cu_xMo₆S₈ was recently evaluated also as a catalyst for the ring-opening of tetrahydrofuran [97] and for hydrogenation, deshydrogenation and hydrogenolysis reactions, similar to those commonly catalysed by platinum group metals [98].

5.2.3. Thermo-electricity

The figure of merit of a thermoelectric material, that is a measure of its efficiency at a temperature T, is given by $ZT = \alpha^2 T / \rho \lambda$, where α is the Seebeck coefficient, ρ the electrical resistivity and λ the thermal conductivity (both electronic and of the lattice). The latter should be minimized and, in this respect, compounds with heavy constituent masses and open structures hosting mobile atoms that act as good scattering centers for phonon are good candidates [99]. This is the case of CPs where the counter-cations have large thermal factors, especially for smaller ones, which are strongly delocalized and are able to "rattle" inside their cage-like site. In addition, partial substitutions are possible both on the chalcogen positions and even on the cluster itself, increasing the local disorder. Finally, the electrical resistivity can be tuned, by varying the VEC. Although first evaluations of Seebeck coefficients of *metallic* CPs were published quite early [100,101], it is only in the late 90's that theoretical calculations were carried out for the search of CP-based thermoelectric materials [102,103]. The same year T. Caillat et al. studied the *semiconducting* mixed-cluster pseudo-binary (see section 6) Mo₂Re₄Se₈ [104], followed by the obtention of a ZT value of 0.6 at 1150 K for Cu_{1.38}Fe_{0.66}Mo₆Se₈ [105]. This value is very encouraging, because it is comparable to that of Si-Ge alloy in the same temperature range and to the state-of-art thermoelectric materials (ZT \approx 1 for most of them) and it was not yet over-passed for any MMo₆Q₈ true CP, in spite of subsequent attempts. In contrast, higher value was recently reported for the condensed cluster (see section 6) compound Ag_{3.8}Mo₉Se₁₁ with ZT \approx 0.7 at 800 K only, about twice the value calculated for Cu_{1.38}Fe_{0.66}Mo₆Se₈ at the same temperature [106]. The thermoelectric properties of this very rich series of condensed clusters materials are still the subject of extensive studies within the framework of a close French collaboration between the Institut des Sciences Chimiques de Rennes and the Institut Jean Lamour in Nancy ([107] and references therein). Interested readers could also refer to the chapter of this volume entitled *Thermoelectric Properties of Ternary and Quaternary Mo₆ and Mo₉ Cluster Selenides*.

6. The legacy of Chevrel-phases

Soon after the discovery of CPs and the realization that they displayed outstanding properties, considerable synthetic works were made in Rennes, under the supervision of Marcel Sergent. These involved changing the conditions for the synthetic procedures and thereby providing opportunities for fine-tuning their properties. These developments are summarized below.

6.1. Condensed clusters

In 1979 M. Sergent and R. Chevrel, working with indium counter-cation, reported the first example of a condensed cluster based on CPs [108]. It was based on the $\text{Mo}_9\text{Se}_{11}$ unit built from two octahedral Mo_6 clusters sharing a common Mo_3 face perpendicular to the ternary axis, as displayed in Figure 12a. This topic was extended with M. Potel and P. Gougeon. Indeed, in the same year the Mo_{12} cluster (Figure 12b) was discovered as well as the infinite chain $(\text{Mo}_{6/2})_\infty$, based on the stacking of Mo_3Q_3 triangular groups staggered along a ternary axis in the structure of $\text{K}_2\text{Mo}_6\text{S}_6$ [109]. Intermediates in this series were discovered when the giant clusters Mo_{18} , Mo_{24} and Mo_{30} [110,111] were synthesized and characterized. All these cluster-units can be written by the general formula $\text{Mo}_{3n}\text{Q}_{3n+2}$ ($n \geq 2$). Note that in many cases the condensed clusters coexist in the structure with the octahedral one: for instance, the compound $\text{K}_2\text{Mo}_{15}\text{S}_{19}$ corresponds to the developed formula $\text{K}_2(\text{Mo}_6\text{S}_8)(\text{Mo}_9\text{S}_{11})$ [109] and, in contrast, $\text{Mo}_9\text{Se}_{11}$ alone was found in the structures of $\text{Ag}_x\text{Mo}_9\text{Se}_{11}$ ($x = 3.6$ and $x \approx 4$) [112]. Many compounds based on such high-nuclearity clusters were synthesized and structurally characterized in the following years. They included the giant cluster $(\text{Mo}_{36}\text{S}_{38})^{10-}$ [113], as well as the $(\text{Mo}_{15}\text{Se}_{17})^{3-}$ [114] and $(\text{Mo}_{21}\text{Se}_{23})^{5-}$ ones [115], the latter having an odd number of molybdenum atoms. A theoretical study of Mo_9Q_{11} , $\text{Mo}_{12}\text{Q}_{14}$ and $(\text{Mo}_3\text{Q}_3)_\infty$ was performed in the early stage [37], followed by a more extensive DFT calculations, which interrelated to the whole series $\text{Mo}_{3n}\text{Q}_{3n+2}$ ($n = 3-8$ and 10) [116]. The filling of all bonding orbitals leads to an optimal VEC of $(13n-2)$ for even n (refer to the value of 24 for CP, with $n=2$) and $(13n-3)$ for odd n . Also, a large HOMO-LUMO gap is maintained in all these compounds [116,117] Then, depending on the filling of the MO, *i.e.* the counter-cation stoichiometry, semi-metallic behavior [112] and semiconductivity [107] were reported. As mentioned above the latter compounds are the subject of intensive research as thermoelectric materials. $\text{InMo}_9\text{Se}_{11}$ and $\text{In}_x\text{Mo}_{15}\text{Se}_{19}$ ($x = 2-3$) were also evaluated for catalysis [118]. Many

of these condensed cluster compounds exhibit superconductivity with T_c in the range 1.7-4 K [110]. In the example of $Tl_2Mo_6Se_6$ ($T_c = 2.2$ K) a very high anisotropy of the critical field was reported [119], as expected from its strongly anisotropic structure. Finally some of these infinite chain compounds $M_xMo_6Q_6$ ($Q=Se,Te$) were dispersed in polar solvents. The pristine material was recovered after evaporation, giving access to highly oriented films by brushing a thin layer of the solution in one direction onto a substrate: the longitudinal conductivity was five times larger than the transverse one [120].

Finally, it is noteworthy that Marcel Sergent also initiated with P. Gougeon the study of another type of condensed clusters, present in low-valence molybdenum oxides, where Mo_6 octahedra share their edges [121]. This family is very rich and its development is still being pursued in Rennes [122].

6.2. Mo_6 and Re_6 cluster compounds derived from Chevrel-Phases

The Mo_6S_8 Chevrel phase with 20 electrons per Mo_6 cluster is not stable and decomposes at $470^\circ C$ [80]. Its stabilization can be obtained by adding up to 24 electrons to the $Mo4d$ band, corresponding to the filling of the energy bands near the Fermi level. This can be achieved by substituting sulfur ligands by halides in Mo_6S_8 or by replacing molybdenum atoms of the Mo_6 cluster by other atoms more rich in valence electrons. M. Sergent developed this topic with C. Perrin and A. Perrin. Fuller details are given in previous review papers [123,124].

6.2.1. Mo_6 cluster chalcogenides

A consequence of the replacement of chalcogen by halide in CPs, performed at high temperature ($1000-1200^\circ C$), resulted in new stable Mo_6 chalcogenides where the VEC values ranged from 20 to 24. The first discovered and structurally characterized of these Mo_6 chalcogenides were $Mo_6Q_{8-x}X_x$ ($X = \text{halogen}$, $Q = \text{chalcogen}$, $0 < x \leq 2$) isostructural to Mo_6Q_8 [125]. In these chalcogenides the cluster units are interconnected in the same way as in CPs by inner-apical chalcogen double bridges (Q^{i-a}/Q^{a-i}) while inner halogens lie on the $2c$ site located on the three-fold axis of the unit. The channels that develop in the three directions of the lattice are empty [126]. When $Q = S$, definite compounds have been obtained with $x = 2$, namely $Mo_6S_6Br_2$ and $Mo_6S_6I_2$. They are superconducting at $T_c \approx 14$ K, exactly like $PbMo_6S_8$, while Mo_6S_8 is superconducting only at a very low temperature. A previous ^{119}Sn Mössbauer study on $SnMo_6S_8$ ($T_c = 11$ K) suggested that the high T_c of CPs could be due in large part to the additional soft lattice mode associated with Sn in $SnMo_6S_8$ [127]. However, the high T_c

reached by $\text{Mo}_6\text{S}_6\text{Br}_2$ and $\text{Mo}_6\text{S}_6\text{I}_2$ without any counter cation in the channels ruled out this assertion. Finally it was assumed that it is essential that the halide ligands occupy the $2c$ sites on the ternary axis in order to maintain the symmetry and then to maintain the two-fold degeneracy of the E_g -band at the Fermi level [125]. In addition, these two chalcogenides have a VEC value of 22 as in PbMo_6S_8 ($T_c = 14$ K), confirming the importance of the VEC for the superconducting properties. As discussed by theoreticians, the 22 VEC value corresponds to a maximum of the density of states near the Fermi level [17].

When $Q = \text{Se}$ or Te , solid solutions $\text{Mo}_6\text{Q}_{8-x}\text{X}_x$ were obtained with $X = \text{Cl}, \text{Br}, \text{I}$ and $0 \leq x \leq 2$. T_c increases correlatively with the VEC value up to 7.0, 7.1 and 7.6 K for $Q = \text{Se}$ and $X = \text{Cl}, \text{Br}$ and I respectively (figure 13). Mo_6Te_8 , not superconducting above 1 K, becomes superconducting after iodine substitution with a maximum $T_c = 2.6$ K for $\text{Mo}_6\text{Te}_6\text{I}_2$ [125].

Note that these compounds constituted the first molybdenum chalcogenides obtained at high temperatures, in contrast to the previous ones synthesized around 500 °C, like MoS_2Cl_2 , MoS_2Cl_3 , $\text{Mo}_2\text{Cl}_5\text{S}_3$ or $\text{Mo}_3\text{S}_7\text{Cl}_4$ [128-130], where molybdenum has a higher oxidation state. These results opened the way to new families of stable, high temperature Mo_6 chalcogenides, in which the 24 VEC Mo_6L_{14} ($L = \text{halogen or chalcogen}$) units are interconnected by shared inner and/or apical ligands as in the following examples:

The three-dimensional $\text{Mo}_6\text{X}_{10}\text{Q}$ ($X = \text{Cl}, \text{Br}$ and $Q = \text{S}, \text{Se}, \text{Te}$; $X = \text{I}$ and $Q = \text{Se}, \text{Te}$), with X^{a-a} interunit connections developing in the three directions of the space [131], are insulating and exhibit dielectric relaxations [132].

The one-dimensional $\text{Mo}_6\text{X}_8\text{Q}_2$ ($X = \text{Br}$ and $Q = \text{S}$; $X = \text{I}$ and $Q = \text{S}, \text{Se}$) develops infinite chains of units via Q^{i-i} and X^{a-a} bridges [133-134]. They are insulating and exhibit as expected a dielectric anisotropy [132].

The semiconducting two-dimensional $\text{Mo}_6\text{Br}_6\text{S}_3$ is built up from chains similar to the ones observed in $\text{Mo}_6\text{X}_8\text{Q}_2$, but here the units are slightly tilted in the chains to establish interchains connections in the second direction of the space via inner-apical ligands (S^{i-a}/S^{a-i}) [135].

6.2.2. Re₆ cluster chalcogenides and chalcogenides

A second way to tune the VEC in CPs was to substitute (at least in part) Mo by a metal more rich in electrons, such as Re [136] or either Ru or Rh [137]. All the compounds synthesized are isostructural with Mo_6Se_8 . As selected examples, the solid solutions $\text{Mo}_2\text{Re}_4\text{S}_{8-x}\text{Se}_x$ ($0 \leq x \leq 8$) and $\text{Mo}_2\text{Re}_4\text{Se}_{8-x}\text{Te}_x$ ($0 \leq x \leq 1.2$) turned out to be a rare example of truly semiconducting CP, owing to the filling of energy band near the Fermi level by 24 valence

electrons (figure 14) [136]. In the case of Te, the synthesis of $\text{Mo}_2\text{Re}_4\text{Te}_8$ failed and in place, the diamagnetic $\text{Mo}_4\text{Re}_2\text{Te}_8$ was obtained. With a VEC of 22 it is a superconductor with $T_c = 3.55$ K (figure 14) and an initial slope of the upper critical field comparable to that of Mo_6Se_8 [136]. $\text{Mo}_4\text{Re}_2\text{Te}_8$ is - with the above mentioned $\text{Mo}_6\text{Te}_6\text{I}_2$ - a rare example of a superconducting telluride Chevrel-Phase. Note that a mixed cluster compound was also obtained with ruthenium: the 24 VEC semiconducting $\text{Mo}_4\text{Ru}_2\text{Se}_8$ [137]. Any attempt to obtain purely Re_6 -based CP structure is of course unattainable because it would imply a VEC value higher than 24, corresponding to the filling of antibonding metal-metal orbitals.

Indeed, these results prompted M. Sargent and A. Perrin to start a systematic search for Re_6 chalcogenides built from Re_6L_{14} (L = halogen/chalcogen) units with various halogen/chalcogen ratios, with a VEC = 24. At the beginning the system Re-Se-Cl was chosen, because it was particularly suitable for x-ray contrast of ligands. The first isolated compound was the lamellar $\text{Re}_6\text{Se}_8\text{Cl}_2$ where adjacent units are connected in a plane by four inner-apical ($\text{Se}^{i-a}/\text{Se}^{a-i}$) double bridges, exactly as in CPs, while in the third direction are terminal Cl^a ligands [138-139]. It is a semiconductor with a resistivity ratio up to 10^2 at room temperature [140] and a band-gap of 1.42 eV [141]. Its discovery was followed by the series of definite compounds $\text{Re}_6\text{Se}_{8-n}\text{Cl}_{2+2n}$ ($n = 1, 2$ and 3) where the cluster-units are linked by Cl^{a-a} halogen bridges extending along 3, 2 and 1 direction, respectively. 0-D compounds were also obtained, namely the neutral $\text{Re}_6\text{Se}_4\text{Cl}_{10}$ (*i.e.* $n=4$) and the ionic compound $\text{KRe}_6\text{Se}_5\text{Cl}_9$ [139]. All these compounds are dielectrics [132], some of them are isostructural with molybdenum analogues while others display original structures.

This work was subsequently extended to brominated compounds, and a number of new structures were reported, for instance $\text{KRe}_6\text{S}_5\text{Br}_9$ [142] or $\text{Cs}_4\text{KRe}_6\text{S}_8\text{Br}_7$ [143], if we restrict ourselves to the first reports. Many original arrangements were subsequently published, the detail of which can be found in review articles [123,124,144,145]. Note that some ionic compounds with large countercations (*viz.* cesium) are readily soluble in various solvents [144] and then could act as starting materials for a solution chemistry (see below).

A review of the photoluminescent properties of Re_6 cluster-based compounds, in relation with theoretical calculations, is reported in the chapter of this volume entitled *Rhenium Hexanuclear Clusters: Bonding, Spectroscopy and Applications of Molecular Chevrel-Phases*.

6.3. The beginning of solution chemistry of octahedral clusters

The CPs are obviously insoluble in any solvent, due to the strong intercluster bridging ligands. This is also the case of most of the cluster-based chalcogenides mentioned above. In contrast, several Mo₆ chalcogenides built from discrete Mo₆L₁₄ units are slightly soluble [146] while the molybdenum halides Cs₂Mo₆X₁₄ (X = Br, I) appear as efficient precursors for solution chemistry [147]. The ionic K₂Re₆Se₅Cl₉ chalcogenide was reported to be slightly soluble in ethanol [148], but not enough to be effective synthetic reagent. Several approaches were proposed to improve the solubility of chalcogenides, in order to have available molecular precursors suitable for developing novel solution chemistry:

- replace the inorganic counter-cation by an organic one, like tetrabutylammonium, *via* a metathesis reaction; this pioneering approach was used for the electro-crystallization of tetrathiafulvalenes derivatives [149,150];

- replace the terminal ligands, either starting from an ionic compound or using an excision reaction; prominent examples include pyridines [151], phosphines [152], cyano [153-155], hydroxo [156,157], or aquo groups [157,158] and dendrimers [159].

The availability of these precursors led to an intensive research programme for making new hybrid compounds. Novel coordination compounds, and self-organized structures resulted (refer for instance to the reviews [123,124,144,155,157]). Further examples can be found in the chapters of this volume entitled *Octahedral Chalcogenide Rhenium clusters: From Solids to Isolated Cluster Complexes* and *Exploring the Breath of Terminal Ligands in [Mo₆X₈]⁴⁺ and [Re₆Q₈]²⁺ Based Cluster Complexes*.

Conclusion

In this chapter we summarized and highlighted the essential role of Marcel Sergent in the discovery and the development of what are now commonly described as the Chevrel Phases and the more general cluster chemistry he and his research group in Rennes developed after this discovery. Marcel Sergent received well deserved and world-wide recognition for his outstanding initiation and participation in this research area. However, we should mention that this topic was only a small part of his scientific activities. For instance, he found another series of ternary molybdenum chalcogenides, namely MMo₂Q₄, characterized by the presence of zigzag chains of molybdenum [160] and series of compounds based on tetrahedral clusters, like Mo₄S₄Br₄ [161] and MMe₄Q₈ (M = Al, Ga; Me = Mo, Nb, Ta, V, Re) [162,163]. The work on Mo₆L₁₄ and Re₆L₁₄ clusters was completed by studies devoted to the Nb₆L₁₈ and

Ta₆L₁₈ ones (see the chapter of this volume entitled *Inorganic Niobium and Tantalum Octahedral Cluster Halide Compounds with Tree-dimensional Frameworks: a Review on their Crystallographic and Electronic Structures*). He started the study of Mo₆ edge-sharing condensed clusters, present in low-valence molybdenum oxides, as mentioned above [121]. He also initiated a research program on ternary phosphides and arsenides with metal chains and diamond-shaped clusters [164]. Last but not least he was strongly involved in the study of high T_c superconducting cuprates, taking advantage from the specific equipment he had previously implemented for the study of Chevrel-phases. The scientific inheritance of Marcel Sergent endures even after several decades. He paved the way for the present research, outside [165-171] and more especially in his laboratory of origin [122,172-178], where his heirs have built new developments from his initial outstanding contributions to Chevrel-Phases and, more generally, to cluster chemistry.

Marcel Sergent was a very effective research advisor, and we consider as a rare privilege to have worked with him during the years. We are confident that all his past students and coworkers, in Rennes and outside, have the same feeling. We will keep in our mind the memory of this exceptional researcher and very kind man. Finally, we would like to associate with this tribute to Marcel Sergent his close coworker and very good friend Ø. Fisher (1942-2013). The emergence of the Chevrel phases was, in a large part, the fruit of their intense and non-lasting collaboration and friendship.

Acknowledgements

The authors are very grateful to Marie-Jeanne Sergent, spouse of Marcel, and to Prof. Odile Sergent, his daughter, for giving them access to helpful documents from their private collection.

References

- 1 - R. Nakamura, *Serial Experiments Lain*, Manga cartoon, Tokyo, 1998
- 2 - Topics in Current Physics, *Superconductivity in Ternary Compounds I*, Ø. Fischer and B. Mapple Ed., Springer-Verlag (1982)
- 3 - O. Penã, *Physica C* 514 (2015) 95
- 4 - M. Sergent, *Sur des Thiomolybdites, des Thiotungstites et des Thiochromites Alcalins*, Thesis Dissertation, University of Rennes (1969), in French
- 5 - M. Sergent and J. Prigent, *C.R. Acad. Sci. Paris* 261 (1965) 5135
- 6 - A.W. Espelund, *Acta Chem. Scand.* 21 (1967) 839
- 7 - C. Brosset, *Arkiv Kemi. Mineral. Geol. A* 20 (1945)
- 8 - H. Schäfer, H.G. von Schnering, J. Tillack, F. Kuhnen, H. Wöhrle, H. Baumann, *Z. Anorg. Allg. Chem.* 353 (1967) 281
- 9 - R. Chevrel, *Nouveaux composés sulfurés ternaires du molybdène de basse valence, présentant des liaisons molybdène-molybdène sous forme de chaînes ou de clusters octaédriques*, Thesis Dissertation, University of Rennes (1974), in French.

- 10 - R. Chevrel, M. Sergent, J. Prigent, *J. Solid State Chem.* 3 (1971) 515
 11 - F.A. Cotton, *Inorg. Chem.* 3 (1964) 1217
 12 - O. Bars, M. Sergent, D. Grandjean, *C.R. Acad. Sc. Paris Ser. C* 270 (1970) 1233
 13 - M. Sergent, R. Chevrel, *J. Solid State Chem.* 6 (1973) 433
 14 - Ø. Fischer, A. Treyvaud, R. Chevrel, M. Sergent, *Sol. State Comm.* 17 (1975) 721
 15 - M. Sergent, R. Chevrel, C. Rossel, Ø. Fischer, *J. Less Common Met.* 58 (1978) 179
 16 - H. Noël, R. Chevrel, M. Sergent, *Actinides 1981*, Los-Angeles CA, 10-15 sept. 1981
 17 - Ø. Fischer, *Appl. Phys.* 16 (1978) 1
 18 - O. Bars, J. Guillevic, D. Grandjean, *J. Solid State Chem.* 6 (1973) 48
 19 - A.A. Opalovskii, V.E. Fedorov, *Izv. Acad. Nauk S.S.S.R. Neorg. Mater.* 2 (1966) 443
 20 - H.E. Swanson, E. Tatge, *Nat. Bur. Standards Circular (U.S.)* 539 (1953) 1-95
 21 - H. Schäfer, H.G.von Schnering, *Angew. Chem.*, 20 (1964) 833
 22 - O. Bars, J. Guillevic, D. Grandjean, *J. Solid State Chem.* 6 (1973) 335
 23 - J. Guillevic, O. Bars, D. Grandjean, *J. Solid State Chem.* 7 (1973) 158
 24 - M. Marezio, P.D. Dernier, J.P. Remeika, E. Corenzwit, B.T. Matthias, *Mat. Res. Bull.* 8 (1973) 657
 25 - J. Guillevic, H. Lestrat, D. Grandjean, *Acta Cryst.* B32 (1976) 1342
 26 - K. Yvon, A. Paoli, R. Flükiger, R. Chevrel, *Acta Cryst.* B33 (1977) 3066
 27 - L.D. Crossman, D.P. Olsen, G.H. Duffey, *J. Chem. Phys.* 38 (1963) 73
 28 - F.A. Cotton, T.E. Hass, *Inorg. Chem.* 3 (1964) 10
 29 - S.F.A. Kettle, *Theor. Chim. Acta* 3 (1965) 211
 30 - L.J. Guggenberger, A.W. Sleight, *Inorg. Chem.* 8 (1969) 2041
 31 - K. Yvon, A. Paoli, *Sol. State Comm.* 24 (1977) 41
 32 - J.D. Corbett, *J. Solid State Chem.* 39 (1981) 56
 33 - O.K. Andersen, W. Klose, H. Nohl, *Phys. Rev.* B17 (1978) 1209
 34 - L.F. Mattheis, C.Y. Fong, *Phys. Rev.* B15 (1977) 1760
 35 - D.W. Bullett, *Phys. Rev. Lett.* 39 (1977) 664
 36 - T. Jarlborg, A.J. Freemann, *Phys. Rev. Lett.* 44 (1980) 178
 37 - T. Hughbanks, R. Hoffmann, *J. Amer. Chem. Soc.* 105 (1983) 1150
 38 - D. Certain, A. Le Beuze, R. Lissillour, *Solid State Comm.* 46 (1983) 7
 39 - D. Certain, R. Lissillour, *Z. Phys.* D 3 (1986) 411
- 40 - B.T. Matthias, M. Marezio, E. Corenzwit, A.S. Cooper, H.E. Barz, *Science* 175 (1972) 1465
 41 - A.C. Lawson, *Mat.Res. Bull.* 7 (1972) 773
 42 - Ø. Fischer, R. Odermatt, G. Bonghi, H. Jones, R. Chevrel, M. Sergent, *Phys. Lett.* 45A (1973) 87
 43 - R. Chevrel, M. Sergent, Ø. Fischer, *Mat. Res. Bull.* 10 (1975) 1169
 44 - R. Odermatt, Ø. Fischer, H. Jones, G. Bonghi, *J. Phys. C* 7 (1974) L13
 45 - Ø. Fischer, H. Jones, G. Bonghi, M. Sergent, R. Chevrel, *J. Phys. C* 7 (1974) L450
 46 - Ø. Fischer, M. Descroux, S. Roth, R. Chevrel, M. Sergent, *J. Phys. C* 8 (1975) L474
 47 - M. Descroux, Ø. Fischer, R. Flükiger, B. Seeber, R. Delesclefs, M. Sergent, *Sol. State Comm.* 25 (1978) 393
 48 - Ø. Fischer, *Proc. Conf. Phys. High Magnetic Fields*, Grenoble, France (September 1974)
 49 - M. Ishikawa, Ø. Fischer, *Sol. State Comm.* 23 (1977) 37
 50 - R. Chevrel, M. Hirrien, M. Sergent, *Polyhedron* 5 (1986) 87
 51 - H.W. Meul, C. Rossel, M. Descroux, Ø. Fischer, G. Remenyi, A. Briggs, *Phys. Rev. Lett.* 53 (1984) 497
 52 - M. Decroux, Ø. Fischer, R. Chevrel, *Cryogenics* 17 (1977) 291
 53 - M. Hirrien, R. Chevrel, M. Sergent, P. Dubots, P. Genevey, *Mater. Lett.* 5 (1987) 173
 54 - R. Chevrel, M. Hirrien, M. Sergent, M. Couach, P. Dubots, P. Genevey, *Mater. Lett.* 7 (1989) 425
 55 - M. Decroux, P. Selvam, J. Cors, B. Seeber, Ø. Fischer, R. Chevrel, P. Rabiller, M. Sergent, *IEEE Trans. Appl. Supercond.* 3 (1993) 1502
 56 - N. Cheggour, M. Decroux, A. Gupta, Ø. Fischer, J.A.A. J. Perenboom, V. Bouquet, M. Sergent, R. Chevrel, *J. Appl. Phys.* 81 (1998) 6277
 57 - R. Chevrel, M. Sergent, L. Le Lay, J. Padiou, O. Peña, P. Dubots, P. Genevey, M. Couach, J.-C. Vallier, *Rev. Phys. Appl.* 23 (1988) 1777
 58 - C.K. Banks, L. Kammerdiner, H.L. Luo, *J. Solid State Chem.* 15 (1975) 271
 59 - S.A. Alterovitz, J.A. Woollam, L. Kammerdiner, H.L. Luo, *Appl. Phys. Lett.* 31 (1977) 233
 60 - R. Ohtaki, B.R. Zao, H.L. Luo, *J. Low Temp. Phys.* 54 (1984) 119
 61 - R.J. Webb, A.M. Goldman, J.H. Kang, J. Maps, M.F. Schmidt, *IEEE Trans. Magn.* 21 (1985) 835
 62 - P. Przyslupski, R. Horyn, J. Szymaszek, B. Gren, *Solid State Comm.* 28 (1978) 869
 63 - G.B. Hertel, T.P. Orlando, J.M. Tarascon, *Physica B* 135 (1985) 168
 64 - Y. Quéré, A. Perrin, J. Padiou, C. Perrin, A. Seignac, R. Horyn, M. Sergent, *Ann. Chim.* 7-8 (1984) 1065

- 65 - Y. Quéré, A. Perrin, R. Horyn, M. Sergent, *Materials Lett.* 3 (1985) 340
- 66 - N. Lemée, M. Guilloux-Viry, J. Padiou, M. Sergent, J. Lesueur, F. Lallu, *Sol. State Comm.* 101 (1997) 909
- 67 - S. Boursicot, V. Bouquet, I. Péron, T. Guizouarn, M. Potel, M. Guilloux-Viry, *Solid State Sci.* 14 (2012) 719
- 68 - H. Hinode, S. Yamamoto, M. Wakihara, M. Taniguchi, *Mater. Res. Bull.* 20 (1985) 611
- 69 - A. Perrin, C. Perrin, R. Chevrel, M. Sergent, R. Brochu, J. Padiou, "*Cristallogénèse Expérimentale*" (Groupe Français de Croissance Cristalline Ed.) 1973, pp.141-148
- 70 - G. Krabbes, H. Oppermann, *Z. anorg. allg. Chem.* 481 (1981) 13
- 71 - R. Horyn, O. Peña, M. Sergent, *J. Less Common Met.* 105 (1985) 55
- 72 - J. Hauck, *Mat. Res. Bull.* 12 (1977) 1015
- 73 - R. Flükiger, M. Devantay, J.L. Jorda, J. Muller, *IEEE Trans. Magn.* MAG-13 (1977) 818
- 74 - H. Takei, T. Takahashi, T. Miura, *Jpn. J. Appl. Phys.* 23 (1984) 420
- 75 - K. Govinda Rajan, N.V. Chandra Shekar, R.N. Viswanath, S. Ramasamy, *J. Phys. D* 22 (1989) 1205
- 76 - F. Holtzberg, S.J. LaPlaca, T.R. McGuire, R.A. Webb, *J. Appl. Phys.* 55 (1984) 2013
- 77 - R. Horyn, O. Peña, C. Geantet, M. Sergent, *Superconduct. Sci. Techn.* 2 (1989) 71
- 78 - O. Peña, M. Sergent, *Proc. Solid St. Chem.* 19 (1989) 165
- 79 - F. Le Berre, C. Hamard, O. Peña, A. Wojakowski, *Inorg. Chem.* 39 (2000) 1100
- 80 - R. Chevrel, M. Sergent, J. Prigent, *Mater. Res. Bull.* 9 (1974) 1487
- 81 - R. Schöllhorn, M. Kümpers, J.O. Besenhard, *Mat. Res. Bull.* 12 (1977) 781
- 82 - Y. Takeda, R. Kanno, M. Noda, O. Yamamoto, *Mat. Res. Bull.* 20 (1985) 71
- 83 - C. Boulanger, J.-M. Lecuire, *Electrochim. Acta* 32 (1987) 345
- 84 - M. Wakihara, T. Uchida, K. Suzuki, M. Taniguchi, *Electrochim. Acta* 34 (1989) 867
- 85 - M. Wakihara, T. Uchida, T. Morishita, H. Wakamatsu, M. Taniguchi, *J. Power Sources* 20 (1987) 199
- 86 - J.M. Tarascon, F.J. Disalvo, D.W. Murphy, G.W. Hull, E.A. Rietman, J. Waszczak, *J. Solid State Chem.* 54 (1984) 204
- 87 - W.R. McKinnon, J.R. Dahn, *Solid State Comm.* 52 (1984) 245
- 88 - N. Lemée, M. Guilloux-Viry, V. Ferré, A. Perrin, M. Sergent, J. Lesueur, F. Lallu, *J. Alloys Compd.* 262-263 (1997) 54
- 89 - Z. Kaidi, C. Boulanger, J.M. Lecuire, N. Lemée, M. Guilloux-Viry, A. Perrin, *Solid State Sci.* 1 (1999) 623
- 90 - D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature* 407 (2000) 724
- 91 - P. Saha, M.K. Datta, O.I. Velikokhatnyi, A. Manivannan, D. Alman, P.N. Kumta, *Progr. Mater. Sci.* 66 (2014) 1
- 92 - K.F. McCarty, G.L. Schröder, *Ind. Eng. Chem. Prod. Res. Dev.* 29 (1984) 519
- 93 - M. Rabiller-Baudry, M. Sergent, R. Chevrel, *Mat. Res. Bull.* 26 (1991) 519
- 94 - M. Rabiller-Baudry, R. Chevrel, M. Sergent, *J. Alloys Compd.* 178 (1992) 441
- 95 - S. Even-Boudjada, L. Burel, R. Chevrel, M. Sergent, *Mat. Res. Bull.* 33 (1998) 419
- 96 - V. Harel-Michaud, G. Pesnel-Leroux, L. Burel, R. Chevrel, C. Geantet, M. Cattenot, M. Vrinat, *J. Alloys Compd.* 317-318 (2001) 195
- 97 - S. Kamiguchi, K. Takeda, R. Kajio, K. Okumura, S. Nagashima, T. Chihara, *J. Clust. Sci.* 24 (2013) 559
- 98 - S. Kamiguchi, K. Arai, K. Okumura, H. Iida, S. Nagashima, T. Chihara, *Appl. Catal. A* 505 (2015) 417
- 99 - G.A. Slack, *CRC Handbook of Thermoelectrics*, D.M. Rowe Ed. (Chemical Rubber, Boca Raton FL, 1995) Chap. 34.
- 100 - A.M. Umarji, G.V. Subba Rao, M.P. Janawadkar, T.S. Radhakrishnan, *J. Phys. Chem. Solids* 41 (1980) 421
- 101 - V. Vasudeva Rao, G. Rangarajan, R. Srinivasan, *J. Phys. F: Met. Phys.* 14 (1984) 973
- 102 - R.W. Nunes, I.I. Mazin, D.J. Singh, *Phys. Rev. B* 59 (1999) 7969
- 103 - C. Roche, R. Chevrel, A. Jenny, P. Pecheur, H. Scherrer, S. Scherrer, *Phys. Rev. B* 60 (1999) 16442
- 104 - T. Caillat, J.-P. Fleurial, *J. Phys. Chem. Solids* 59 (1998) 1139
- 105 - T. Caillat, J.-P. Fleurial, G.J. Snyder, *Solid State Science* 1 (1999) 535
- 106 - T. Zhou, B. Lenoir, C. Candolfi, A. Dauscher, P. Gall, P. Gougeon, M. Potel, E. Guilmeau, *J. Elect. Mater.* 40 (2011) 508
- 107 - P. Masschelein, C. Candolfi, A. Dauscher, C. Gendarme, Al Rahal Al Orabi Rabih, P. Gougeon, M. Potel, P. Gall, R. Gauthier, B. Lenoir, *J. All. Compd.* 739 (2018) 360
- 108 - R. Chevrel, M. Sergent, B. Seeber, Ø. Fischer, A. Grüttner, K. Yvon, *Mat. Res. Bull.* 14 (1979) 567
- 109 - M. Potel, R. Chevrel, M. Sergent, M. Decroux, Ø. Fischer, *C.R. Acad. Sc. Ser. C* 288 (1979) 429
- 110 - P. Gougeon, M. Potel, M. Sergent, P. Monceau, *Physica B* 135 (1985) 386
- 111 - R. Chevrel, P. Gougeon, M. Potel, M. Sergent, *J. Solid State Chem.* 57 (1985) 25
- 112 - P. Gougeon, M. Potel, J. Padiou, M. Sergent, *C.R. Acad. Sc. Ser. II* 296 (1983) 351
- 113 - S. Picard, P. Gougeon, M. Potel, *Angew. Chem., Int. Ed.* 13-14 (1999) 2034

- 114 - P. Gougeon, M. Potel, M. Sergent, *Acta Cryst. C* 45 (1989) 182
- 115 - P. Gougeon, M. Potel, M. Sergent, *Acta Cryst. C* 46 (1990) 2284
- 116 - R. Gautier, P. Gougeon, J.-F. Halet, M. Potel, J.-Y. Saillard, *J. Alloys Compd.* 262-263 (1997) 311
- 117 - R. Ab Rahal Ab Orabi, B. Boucher, B. Fontaine, P. Gall, C. Candolfi, B. Lenoir, P. Gougeon, J.-F. Halet, R. Gautier, *J. Mater. Chem. C* 5 (2017) 12097
- 118 - S.A. Kareem, R. Miranda, *J. Molec. Catal.* 53 (1989) 275
- 119 - J.C. Armici, M. Decroux, Ø. Fischer, M. Potel, R. Chevrel, M. Sergent, *Solid State Comm.* 33 (1980) 607
- 129 - J.M. Tarascon, F.J. Disalvo, C.H. Chen, P.J. Carroll, M. Walsh, L. Rupp, *J. Solid State Chem.* 58 (1985) 290
- 121 - P. Gougeon, M. Potel, M. Sergent, *Acta Cryst. C* 46 (1990) 1188
- 122 - P. Gall, P. Gougeon, *Acta Cryst. E* 72 (2016) 995
- 123 - A. Perrin, C. Perrin, *Europ. J. Inorg. Chem.*, 26 (2011) 3848
- 124 - A. Perrin, C. Perrin, *C. R. Chimie* 15 (2012) 815
- 125 - M. Sergent, Ø. Fischer, M. Decroux, C. Perrin, R. Chevrel, *J. Solid State Chem.* 22 (1977) 87
- 126 - C. Perrin, R. Chevrel, M. Sergent, Ø. Fischer, *Mat. Res. Bull.* 14 (1979) 1505
- 127 - C.W. Kimball, L. Weber, G. Van Landuyt, F.Y. Fradin, B.D. Dunlap, G.K. Shenoy, *Phys. Rev. Lett.* 36 (1976) 412
- 128 - J.-P. Rannou, M. Sergent, *C.R. Acad. Sc. Ser. C*, 265 (1967) 734
- 129 - A.A. Opalowski, V.E. Fedorov, K.A. Khaldoyanidi, *Dokl. Akad. Nauk. SSSR*, 182 (1968) 1095
- 130 - J. Marcoll, A. Rabenau, D. Mootz, H. Wunderlich, *Revue de Chimie Minérale*, 11 (1974) 607
- 131 - C. Perrin, M. Sergent, F. Le Traon, A. Le Traon, *J. Solid State Chem.*, 25 (1978) 197
- 132 - J.C. Pilet, F. Le Traon, A. Le Traon, C. Perrin, A. Perrin, L. Leduc, M. Sergent, *Surf. Sci.* 156 (1985) 359
- 133 - C. Perrin, M. Sergent, *J. Chem. Res. (S)* 2 (1983) 38
- 134 - C. Perrin, M. Sergent, *J. Chem. Res. (M)* (1983) 449
- 135 - C. Perrin, M. Potel, M. Sergent, *Acta Cryst.* 39C (1983) 415
- 136 - A. Perrin, M. Sergent, Ø. Fischer, *Mat. Res. Bull.* 13 (1978) 259
- 137 - A. Perrin, R. Chevrel, M. Sergent, Ø. Fischer, *J. Solid State Chem.* 33 (1980) 43
- 138 - A. Perrin, M. Sergent, *Bull. Soc. Chim. Fr.* 11-12 (1980) 66
- 139 - L. Leduc, A. Perrin, M. Sergent, *C.R. Acad. Sci. Paris Ser. II* 296 (1983) 961
- 140 - L. Leduc, J. Padiou, A. Perrin, M. Sergent, *J. Less-Common Met.* 95 (1983) 73
- 141 - N. Le Nagard, A. Perrin, M. Sergent, C. Levy-Clement, *Mat. Res. Bull.* 20 (1985) 835
- 142 - A. Slougui, A. Perrin, M. Sergent, *Acta Cryst. C* 48 (1992) 1917
- 143 - A. Slougui, S. Ferron, A. Perrin, M. Sergent, *Eur. J. Solid State Inorg. Chem.* 33 (1996) 1001
- 144 - G. Pilet, A. Perrin, *C.R. Chimie* 8 (2005) 1728
- 145 - J.-C.P Gabriel, K. Boubekour, S. Uriel, P. Batail, *Chem. Rev.* 101 (2001) 2037
- 146 - K. Kirakci, S. Cordier, O. Hernandez, T. Roisnel, F. Paul, C. Perrin, *J. Solid State Chem.* 178 (2005) 3117
- 147 - K. Kirakci, S. Cordier, C. Perrin, *Z. Anorg. Chem.* 631 (2005) 411
- 148 - A. Perrin, *New J. Chem.* 14 (1990) 561
- 149 - L. Ouahab, P. Batail, C. Perrin, C. Garrigou-Lagrange, *Mat. Res. Bull.* 21 (1986) 1223
- 150 - P. Batail, L. Ouahab, A. Penicaud, C. Lenoir, A. Perrin, *C.R. Acad. Sci. Ser. II* 304 (1987) 1111
- 151 - S.J. Hilsenbeck, V.G. Young Jr., R.E. McCarley, *Inorg. Chem.* 33 (1994) 1822
- 152 - Z. Zheng, J.R. Long, R.H. Holm, *J. Am. Chem. Soc.* 119 (1997) 2163
- 153 - Y.V. Mironov, A.V. Virovets, V.E. Fedorov, N.Y. Podberezskaya, O.V. Shishkin, Y.T. Struchkov, *Polyhedron* 14 (1995) 3171
- 154 - A. Slougui, Y. Mironov, A. Perrin, V. Fedorov, *Croatica Chemica Acta* 68 (1995) 885
- 155 - S. Cordier, N.G. Naumov, D. Salloum, F. Paul, C. Perrin, *Inorg. Chem.* 43 (2004) 219
- 156 - S.S. Yarovoi, Y.V. Mironov, D.Y. Naumov, Y.V. Gatilov, S.G. Kozlova, S.J. Kim, V.E. Fedorov, *Eur. J. Inorg. Chem.* 2005 (2005) 3945
- 157 - Y. Kim, V.E. Fedorov, S.J. Kim, *J. Mater. Chem.* 19 (2009) 7178
- 158 - V.P. Fedin, A.A. Virovets, A.G. Sykes, *Inorg. Chim. Acta* 271 (1998) 228
- 159 - S. Cordier, K. Kirakci, G. Pilet, D. Méry, D. Astruc, A. Perrin, C. Perrin, *Prog. Solid State Chem.* 33 (2005) 81
- 160 - R. Chevrel, M. Sergent, J. Prigent, *C.R. Acad. Sci.* 267 (1968) 1135
- 161 - C. Perrin, R. Chevrel, M. Sergent, *C.R. Acad. Sci. Ser. C* 281 (1975) 23
- 162 - C. Perrin, R. Chevrel, M. Sergent, *C.R. Acad. Sci. Ser. C* 280 (1975) 949
- 163 - H. Ben Yaich, J.C. Jegaden, M. Potel, M. Sergent, A.K. Rastogi, R. Tournier, *J. Less-Common Met.* 102 (1984) 9

- 164 - R. Guérin, M. Sergent, J. Prigent, C.R. Acad. Sci. 274 (1972) 1278
- 165 - L. Geng, J.P. Scheifers, J. Zhang, K.N. Bozhilov, B.P.T. Fokwa, J. Guo, Chem. Mater. 30 (2018) 8420
- 166 - M.L. Agiorgousis, Y.-Y. Sun, D. West, S. Zhang, ACS Appl. Energy Mater. 1 (2018) 440
- 167 - M. Mao, T. Gao, S. Hou, C. Wang, Chem. Soc. Rev. 47 (2018) 8804
- 168 - K. Ojha, S. Banerjee, M. Sharma, P. Dagar, A.K. Ganguli, Bull. Mater. Sci. 41 (2018) 119
- 169 - J. Richard, A. Benayad, J.-F. Colin, S. Martinet, J. Phys. Chem. C 121 (2017) 17096
- 170 - J. Yue, X. Zhu, F. Han, X. Fan, L. Wang, J. Yang, C. Wang, ACS Mater. Interfaces 10 (2018) 39645
- 171 - X. Zhong, K. Lee, B. Choi, D. Meggiolaro, F. Liu, C. Nuckolls, A. Pasupathy, F. De Angelis, P. Batail, X. Roy, X. Zhu, Nano Lett. 18 (2018) 1483
- 172 - S. Boursicot, V. Bouquet, A. Bombard, M. Langer, C. Boulanger, M. Guilloux-Viry, Electrochem. Acta 257 (2017) 436
- 173 - L. Gannon, L. Boeri, C.A. Howard, P. Gougeon, P. Gall, M. Potel, D. Salloum, A.P. Petrovic, M. Hoesch, Phys. Rev. B 98 (2018) 014104
- 174 - F. Camerel, F. Kinloch, O. Jeannin, M. Robin, S.K. Nayak, E. Jacques, K.A. Brylev, N.G. Naumov, Y. Molard, Dalton Trans. 47 (2018) 10884
- 175 - K. Guy, P. Ehni, S. Paofai, R. Forschner, C. Roiland, M. Amela-Cortes, S. Cordier, S. Laschat, Y. Molard, Angew. Chem. Int. Ed. 57 (2018) 11692
- 176 - P. Pellen-Mussi, S. Tricot-Doleux, C. Neaime, N. Nerambourg, F. Cabello-Hurtado, S. Cordier, F. Grasset, S. Jeanne, J. Nanosci. Nanotech. 18 (2018) 3148
- 177 - A. Gandubert, M. Amela-Cortes, S.K. Nayak, C. Vicent, C. Meriadec, F. Artzner, S. Cordier, Y. Molard, J. Mater. Chem. 6 (2018) 2556
- 178 - J. Barbosa, C. Prestipino, O.J. Hernandez, S. Paofai, C. Dejoie, M. Guilloux-Viry, C. Boulanger, Inorg. Chem. 58 (2019) 2158

Cation	n value or range	Comment
Ag	4	Stoichiometric compounds (Trigonal)
Sn	5	
Pb	6	
Sr	6	
Ba	7	
Ni	3 to 5	Solid solutions (Trigonal)
Co	3 to 5	
Fe	2 to 5	
Mn	2 to 6	
Cr	2 to 3	Triclinic
Cu _x	3 to 4 and x = 1 to 2	Double solid solution
Mg	2 to 6	Trigonal → Triclinic transition depending upon stoichiometry
Zn	3 to 6	
Cd	3 to 5	
Li or Na	2	Trigonal

Table 1 - $M_2(I)Mo_nS_{n+1}$ and $M(II)Mo_nS_{n+1}$ compounds reported in the first paper published by R. Chevrel, M. Sergent and J. Prigent [10].

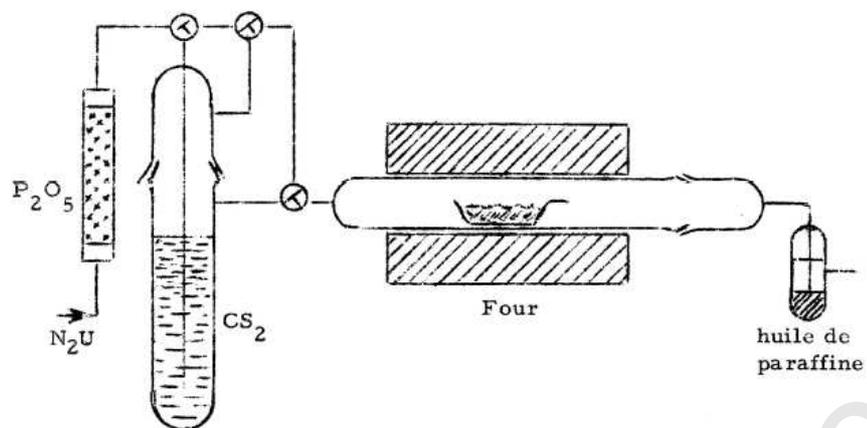


Figure 1 - The setup used by Marcel Sergent in his Thesis for the sulfuration experiments [4].

Sur de Nouvelles Phases Sulfurées Ternaires du Molybdène

ROGER CHEVREL, MARCEL SERGENT, ET JACQUES PRIGENT

*Laboratoire de Chimie Minérale B-Equipe Associée au C.N.R.S.
Faculté des Sciences, Avenue du Général Leclerc-35-Rennes-France*

Received March 1, 1971

The authors describe the preparation of new sulfides of formula $M^II Mo_n S_{n+1}$. If $M = Ag, Sn, Ca, Sr, Pb, Ba$, they are stoichiometric; if $M = Ni, Co, Fe, Cr, Mn, Cu, Mg, Zn, Cd$, solid solutions are observed with $2 \leq n \leq 6$. Another series of formula $M_2 Mo_n S_{n+1}$ was also prepared, where $M =$ alkali metal and $n = 2$ or 5 . The crystallographic properties are investigated: the phases obtained are generally rhomboedral, with an eventual triclinic distortion.

Figure 2 - A partial facsimile of the first report on Chevrel phases [10]
(Reproduced from J. Solid State Chem., with permission)

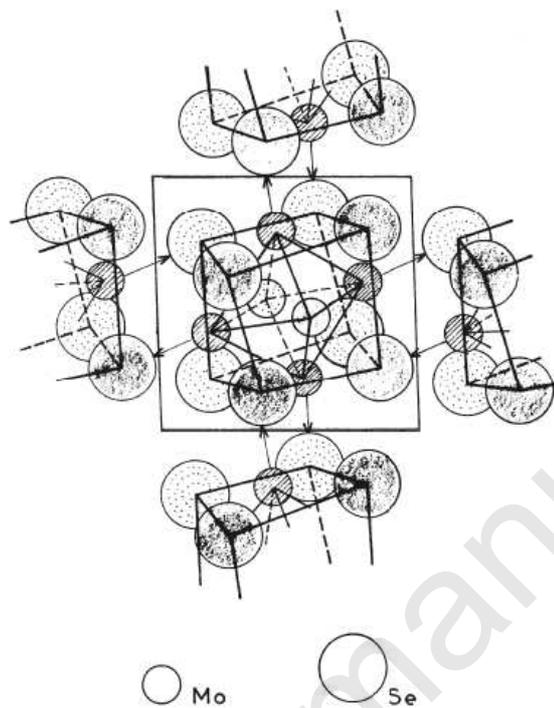


Figure 3 - The first representation of a Chevrel-Phase structure: the empty Mo_6Se_8 binary host [18].

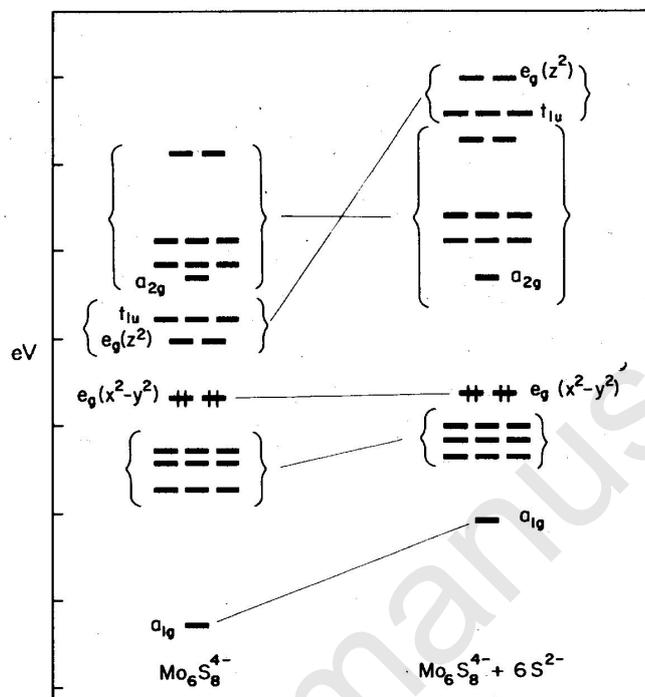


Figure 4 - Molecular orbitals diagram of Chevrel-Phases, illustrating the perturbation of the Mo₆S₈⁴⁻ levels by six apical S²⁻ ions, consequently opening the gap [37].

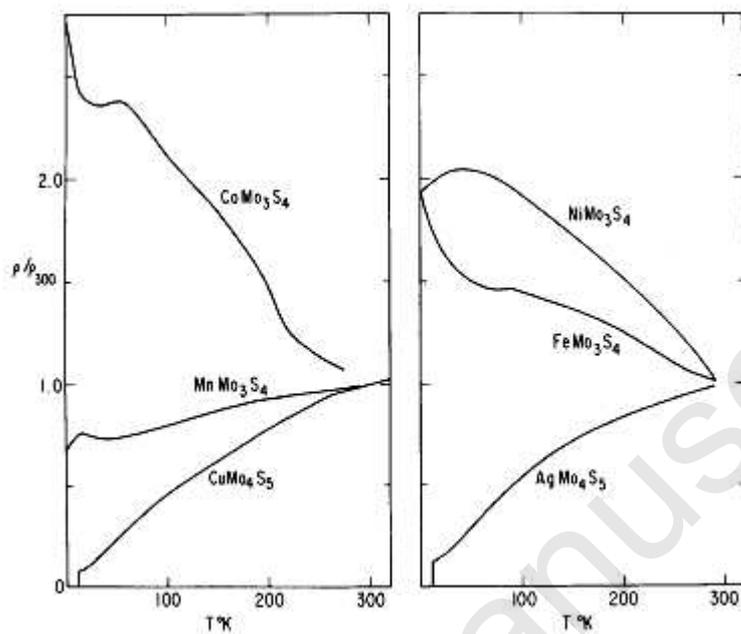


Figure 5 - Early reported resistivity curves of several Chevrel-Phases, illustrating the superconducting transitions for the copper and silver compounds [41].

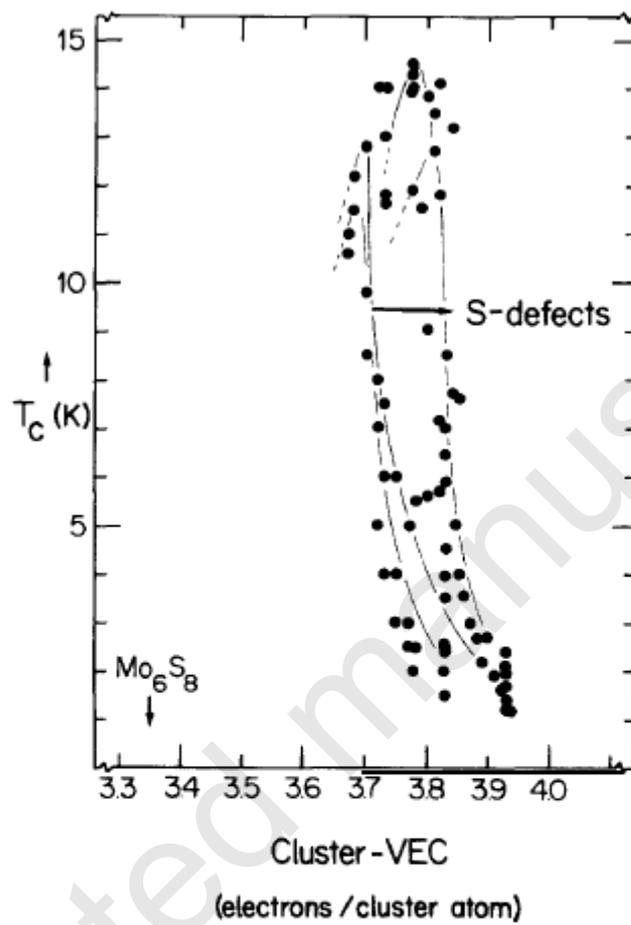


Figure 6 - A correlation between the critical temperature and the VEC (here relative to one molybdenum atom) for a number of superconducting Chevrel-Phases [31].

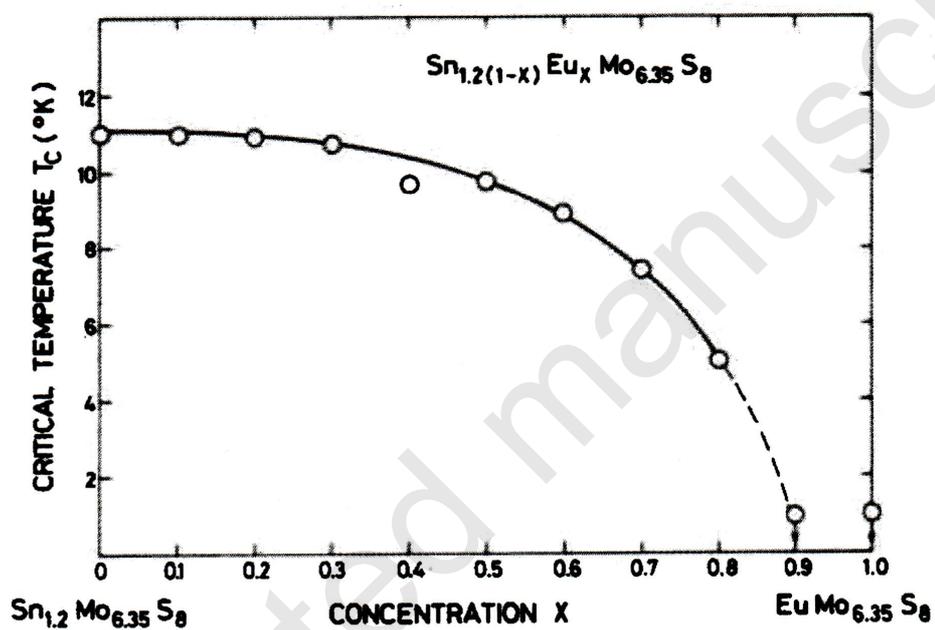


Figure 7 - Critical temperature versus concentration x of europium ions in $\text{Sn}_{1.2(1-x)}\text{Eu}_x\text{Mo}_{6.35}\text{S}_8$ [14].

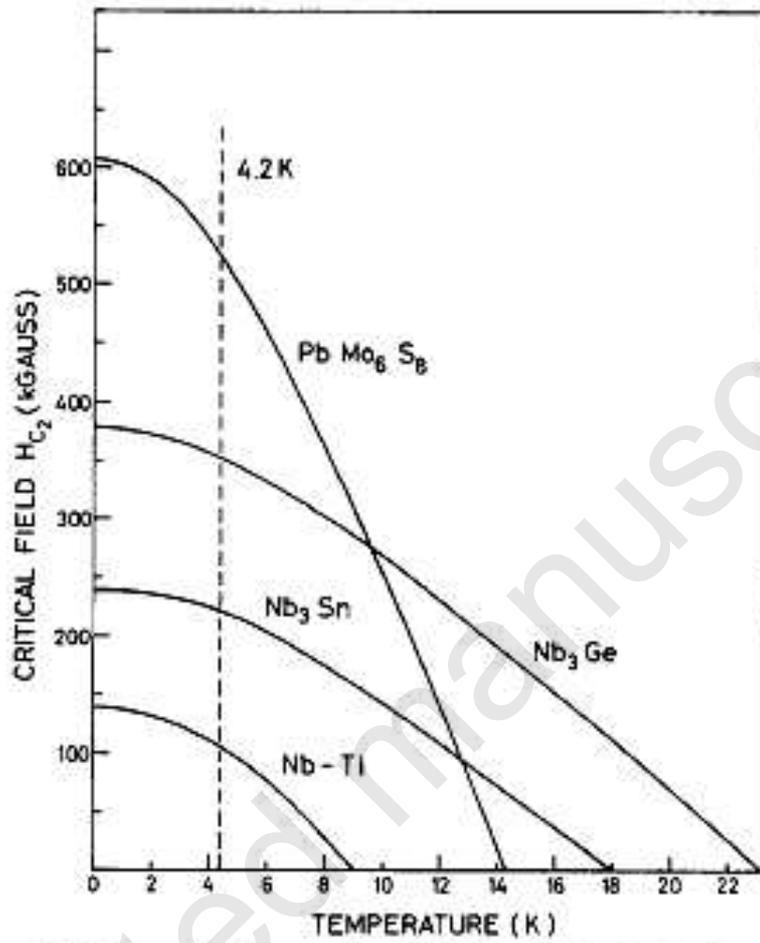


Figure 8 - Comparison between the critical fields of PbMo_6S_8 , Nb_3Ge , Nb_3Sn and the Nb-Ti alloy [17].

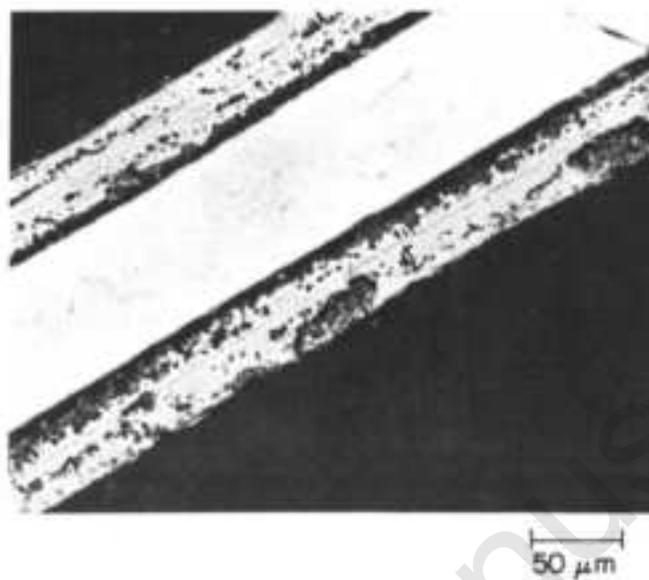


Figure 9 - A cut along the axis of a PbMo_6S_8 wire grown on the surface of a molybdenum wire [52].

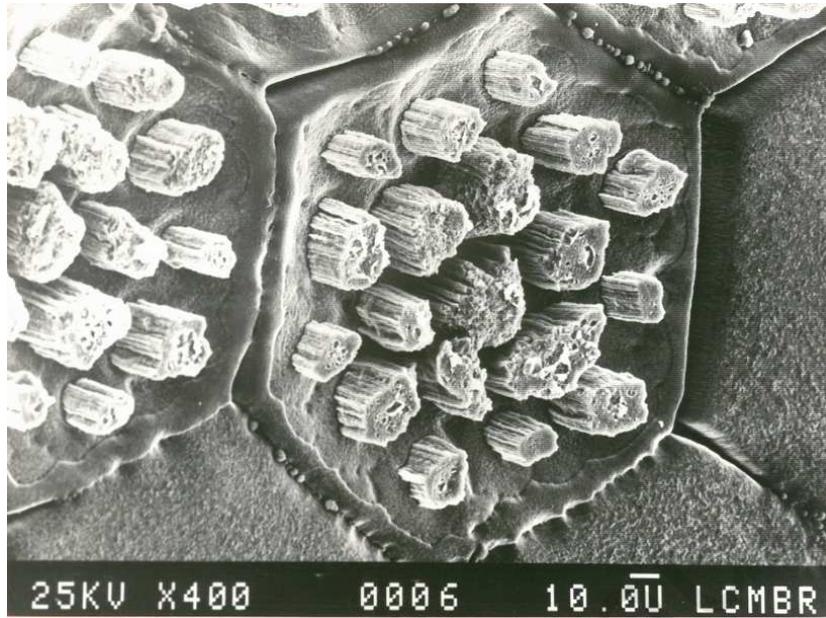


Figure 10 - A scanning electron micrograph of a Chevrel-Phase multifilament wire in copper matrix. © A. Perrin LCMBR

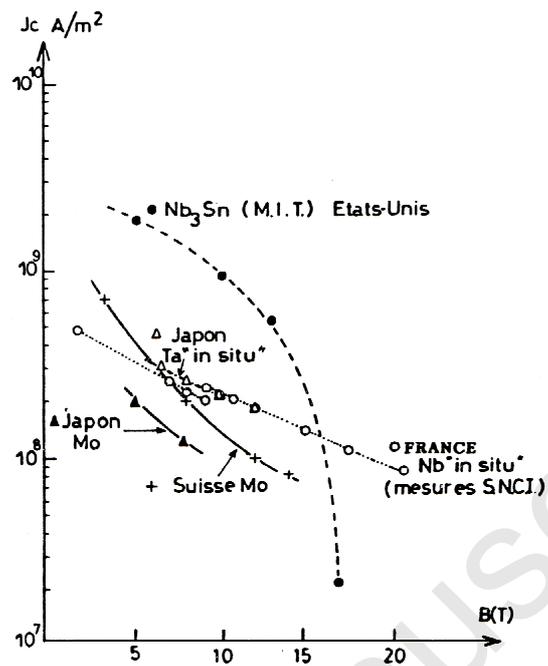


Figure 11 - A graph of the best critical current densities as a function of applied magnetic field for single wire Chevrel-Phases obtained in various laboratories, compared to the classical Nb_3Sn superconductor [57].

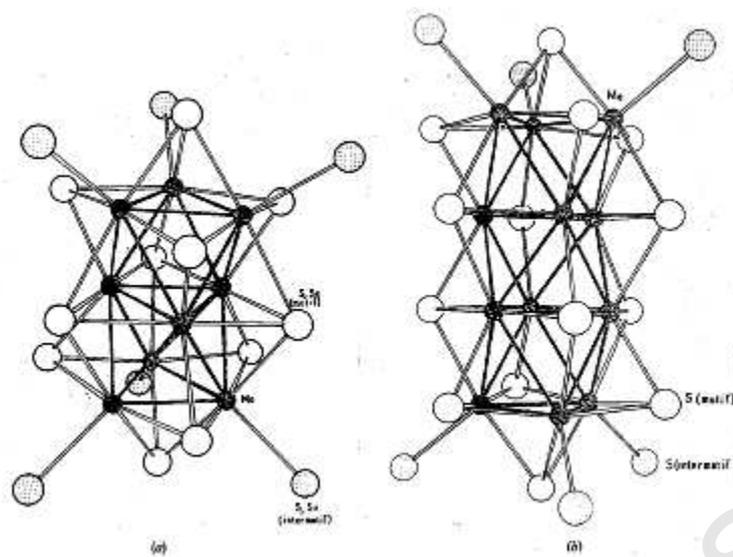


Figure 12 - The Mo_9S_{11} unit in $\text{K}_2\text{Mo}_{15}\text{S}_{19}$ (a) and the $\text{Mo}_{12}\text{S}_{14}$ (b) unit in $\text{K}_2\text{Mo}_9\text{S}_{11}$ [109]

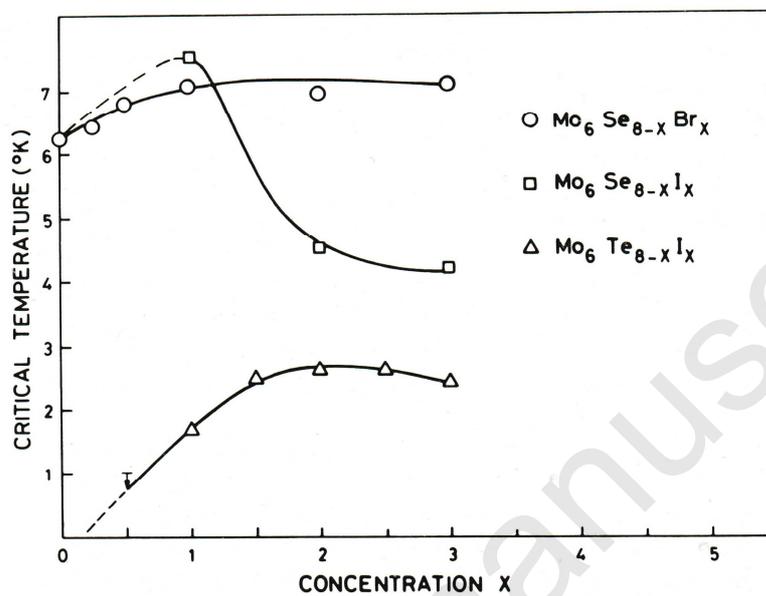


Figure 13 - Critical temperature T_c as a function of halogen concentration x for the solid solutions $\text{Mo}_6\text{Se}_{8-x}\text{Br}_x$, $\text{Mo}_6\text{Se}_{8-x}\text{I}_x$ and $\text{Mo}_6\text{Te}_{8-x}\text{I}_x$ [125]

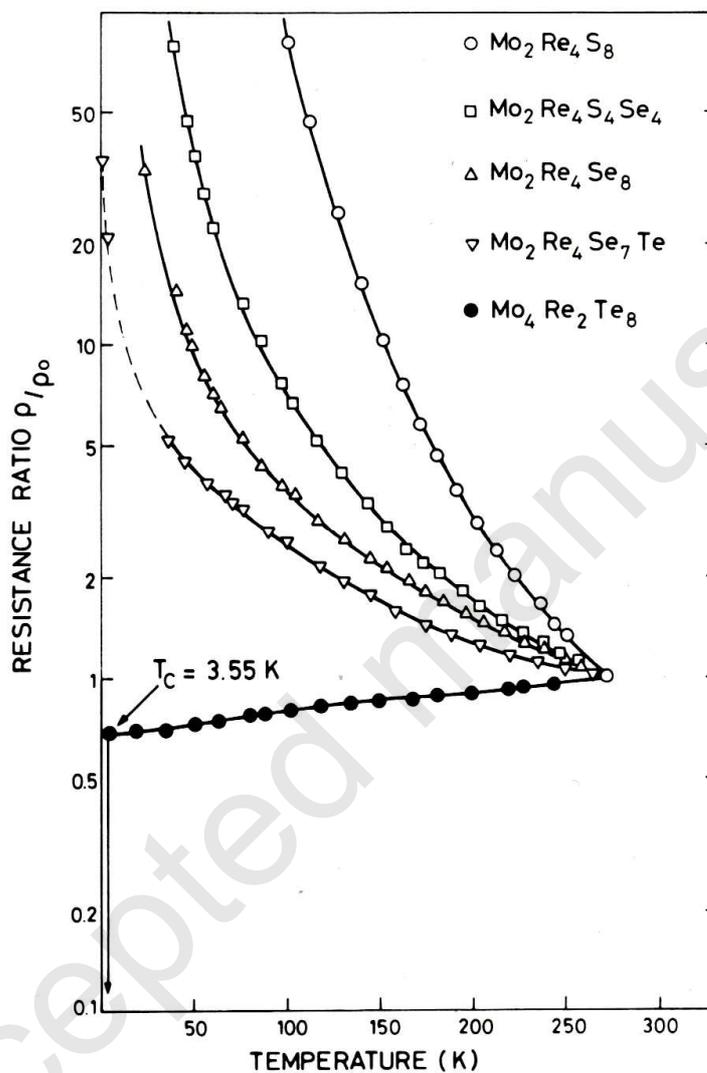


Figure 14 - Temperature dependence of the resistance ratio of the semiconducting $\text{Mo}_2\text{Re}_4\text{S}_8$, $\text{Mo}_2\text{Re}_4\text{S}_4\text{Se}_4$, $\text{Mo}_2\text{Re}_4\text{Se}_8$, $\text{Mo}_2\text{Re}_4\text{Se}_7\text{Te}$, and the superconducting $\text{Mo}_4\text{Re}_2\text{Te}_8$ compounds [136]