

## Resonant Photoemission Studies of Chevrel Phases System: $\text{LaMo}_6\text{Se}_8$ , $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{Mo}_6\text{S}_8$ , $\text{EuMo}_6\text{S}_8$

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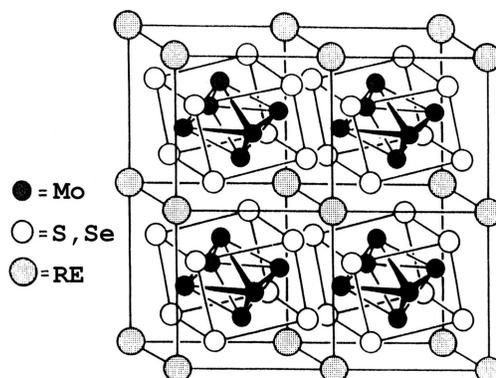
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Electronic structure of  $\text{LaMo}_6\text{Se}_8$ ,  $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{Mo}_6\text{S}_8$ ,  $\text{EuMo}_6\text{S}_8$  compounds known as Chevrel phases were studied by resonant photoemission spectroscopy in the energy range where RE 4f emission is selectively and locally enhanced by intershell 4d-4f transition. The PE spectra show that the intensity of photoemission near  $E_F$  is rather high for all studied compounds that reflect the metallic character of compounds. Resonant photoemission indicates that the density of states (DOS) at the Fermi level has a small S 3p component as well as the dominant Mo 4d character with intercluster Mo 4d-S 3p hybridisation. The valence states of Ce and La in  $\text{REMo}_6\text{S}_8$  are trivalent and bivalent for the Eu compounds. The obtained experimental data were compared with our results of LDA-LCAO band-structure calculations for  $\text{LaMo}_6\text{Se}_8$  and demonstrate good agreement.

### 1. Introduction

In this work we present a preliminary resonant photoemission (PE) study of the family of molybdenum (Mo) cluster compounds with interesting superconducting and magnetic properties, known as Chevrel phases:  $\text{EuMo}_6\text{S}_8$ ,  $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{Mo}_6\text{S}_8$ ,  $\text{LaMo}_6\text{Se}_8$ .

Since the discovery of superconductivity in 1911, the interplay between magnetism and superconductivity has attracted great interest among theorists as

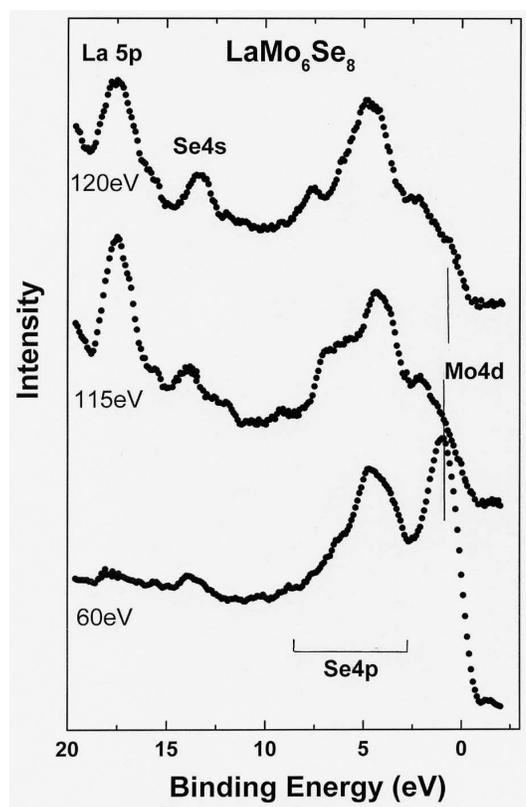


**Figure 1.** Crystallographic structure of Chevrel phases.

well as experimentalists [1]. The one of the main questions is whether magnetic ordering could coexist with superconductivity. For ferromagnets, it was suggested by Jaccarino and Peter, that high exchange field could be compensated by an external field in certain cases. This would allow for ferromagnet to become superconducting in the region of high magnetic fields. Chevrel phases as so called magnetic superconductors can display a variety of such interesting effects.

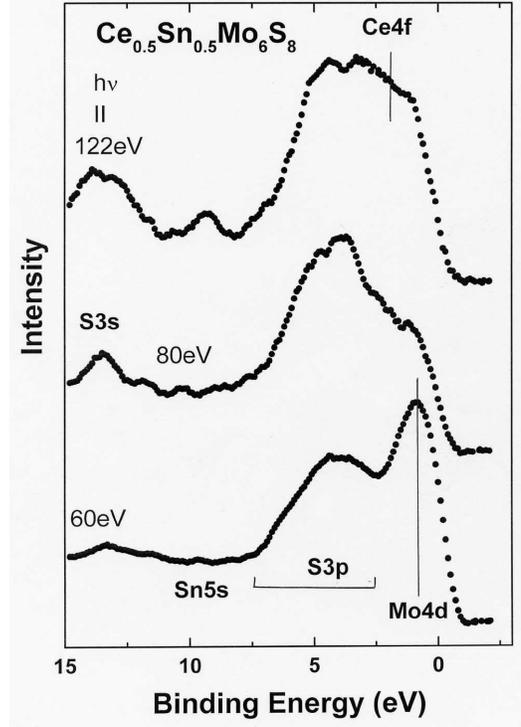
Most of the Chevrel phases crystallize in the rhombohedral space group  $R\bar{3}$  with one formula per unit cell. Figure 1 shows the structure of the ternary Chevrel phases  $MMo_6X_8$  with large M atoms ( $M=Pb, Sn, RE$ ;  $X=S, Se$ ). It is based on a distorted CsCl-type arrangement of individual M atoms and discrete  $Mo_6X_8$  units, each of which consists of a  $Mo_6$  octahedron within tetragonally distorted  $X_8$  cube. The  $Mo_6S_8$  units occupy slightly distorted cubes formed by the ternary element M, sharing a common threefold axis with M-element lattice. The main distortion from cube is a rotation of 15–25 degrees of the  $Mo_6X_8$  units about this axis with respect to the M lattice. The rhombohedral angle is near 90. The crystal structure contains large voids, which may be filled to yield a large variety of ternary compounds.

The stability of the  $Mo_6X_8$  units suggests that these ternaries may be regarded as molecular crystals composed of M atoms bound to quasirigid  $Mo_6X_8$  units. The valence and character (magnetic for RE) of the M atom seem to have little influence [1] on the occurrence of superconductivity. It is believed that the Mo 4d electrons are responsible for superconductivity and that they do not have appreciable overlap onto the M sites. Ternary Chevrel phase possess high critical fields (up to 70 T) and transition temperatures varies between 11



**Figure 2.** Photoemission spectra of  $\text{LaMo}_6\text{Se}_8$  for excitation energy 120 eV (La 4d-4f on-resonance) in comparison to 115 eV (off-resonance), and 60 eV (near Mo 4p-4d resonance) respectively. Position of Mo 4d feature is shown by vertical bar.

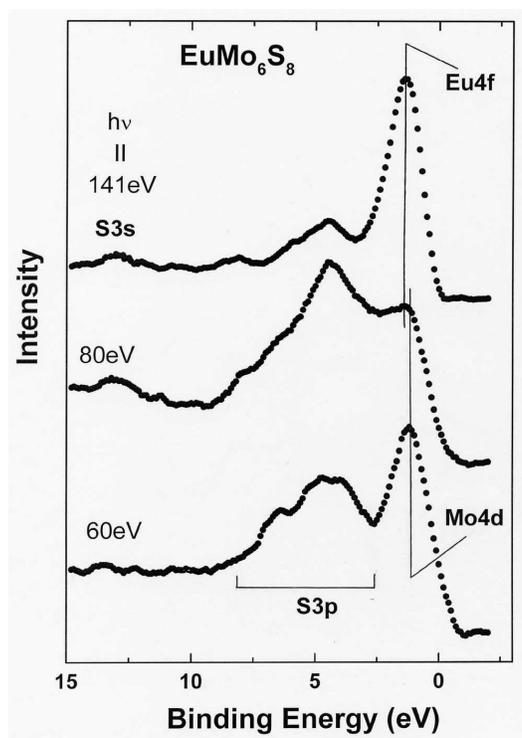
and 15 K and is strongly dependent on the preparation method.  $\text{EuMo}_6\text{S}_8$  is the only rare-earth Chevrel phase that is not superconducting. A structural phase transition in this compound at 110 K from rhombohedral R3 to a low temperature triclinic P1 structure prevents superconductivity. At pressures higher than 13 kbar the structural phase instability is suppressed and superconductivity appears with a transition temperature of about 11 K. The pseudoternary system  $\text{Eu}_{1-x}\text{Sn}_x\text{Mo}_6\text{S}_8$  has attracted great interest because of its anomalous behavior: in the narrow range of concentration (around  $x = 0.2$ )  $T_c$  has the correct value to allow the exotic and exiting phenomenon of magnetic induced superconductivity. This effect has been explained by the Jaccarino-Peter mechanism. The basic idea for such explanation is that if the exchange interaction between the Eu magnetic moment and the conduction electron polarization is negative, the



**Figure 3.** Photoemission spectra of  $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{Mo}_6\text{S}_8$  for excitation energy 122 eV (Ce 4d-4f on-resonance) in comparison to 80 eV (off-resonance), and 60 eV (near Mo 4p-4d resonance) respectively. Position of Mo 4d and Ce 4f features are shown by vertical bars.

latter can be compensated by a high external field. In this case the compound will make a SC-N-SC-N transition in an increasing applied field.

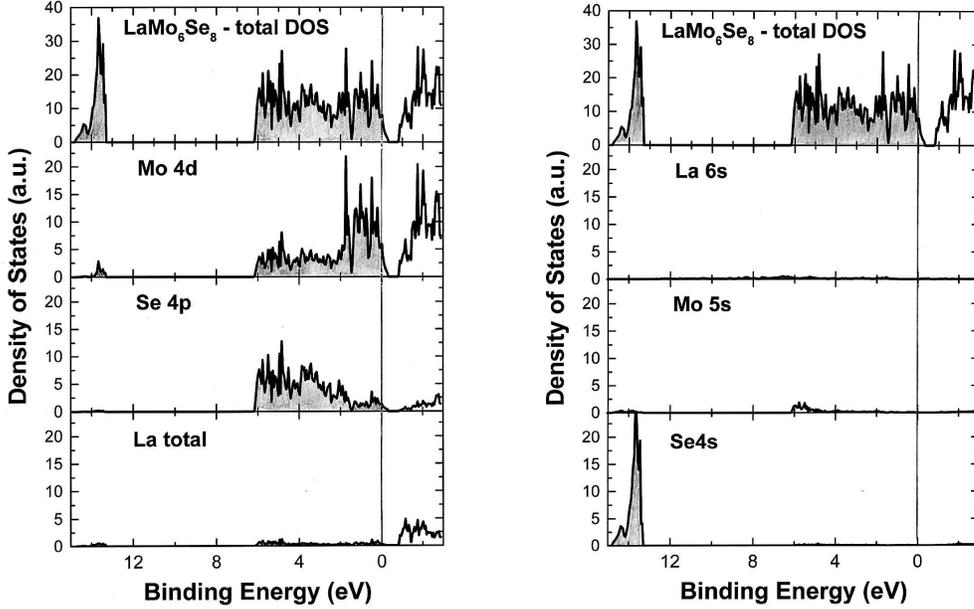
Electronic structure of some Chevrel phases was first investigated in [2] by XPS and it was shown that the quasi-molecular  $\text{Mo}_6\text{X}_8$  clusters remarkably influence the electronic structure of Chevrel phases. Resonant photoemission study of  $\text{Mo}_6\text{Se}_8$  and related compounds [3] clearly demonstrates resonance effect above the Mo 4p threshold ( $4p^64d^4+h\nu \rightarrow 4p^54d^5$ ), revealing the prevalent Mo 4d character of DOS near  $E_F$ . It is also well known that resonant photoemission has been a powerful technique to study electronic structure and correlation effects in rare-earth containing compounds. Thus, with the purposes of further experimental study of details of the electron structure of ternary molybdenum chalcogenides in the present work we have performed the preliminary investigation of rare-earth based Chevrel phases  $\text{EuMo}_6\text{S}_8$ ,  $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{Mo}_6\text{S}_8$ ,  $\text{LaMo}_6\text{Se}_8$ , by resonant photoelectron spectroscopy.



**Figure 4.** Photoemission spectra of  $\text{EuMo}_6\text{S}_8$  for excitation energy 141 eV (Eu 4d-4f on-resonance), 80 eV (off-resonance) and 60 eV (near Mo 4p-4d resonance) respectively. Vertical bars show position of Mo 4d and Eu 4f features.

## 2. Experiment

The polycrystalline samples of Chevrel phases  $\text{EuMo}_6\text{S}_8$ ,  $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{Mo}_6\text{S}_8$ ,  $\text{LaMo}_6\text{Se}_8$  were prepared by direct synthesis from pure components Mo and S and RE and Sn sulfides in sealed quartz tubes in pure helium atmosphere. Starting Mo powder was especially annealed in  $\text{H}_2$  for removing oxygen contamination, RE sulfides were obtained from additionally dried oxides by reaction with  $\text{H}_2\text{S}$ . Components were ground into powder, pressed into disks (4 mm diameter) and annealed at  $1000^\circ\text{C}$  during 24 hours. This procedure repeated several times and resulted in single-phase compounds as it was monitored by X-Ray diffraction data. X-ray diffraction patterns of samples were indexed on the basis of the Chevrel structure with the hexagonal lattice parameters to be  $a = 9.184 \text{ \AA}$ ,  $a = 9.120 \text{ \AA}$  and  $a = 9.456 \text{ \AA}$ , and  $c = 11.534 \text{ \AA}$ ,  $c = 11.430 \text{ \AA}$  and  $c = 11.951 \text{ \AA}$  for  $\text{EuMo}_6\text{S}_8$ ,  $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{Mo}_6\text{S}_8$ ,  $\text{LaMo}_6\text{Se}_8$  respectively.



**Figure 5.** Calculated total and partial density of states for  $\text{LaMo}_6\text{Se}_8$ .

Transitions to the superconducting states were found to occur at 8 K for  $\text{LaMo}_6\text{Se}_8$  and 4.4 K for  $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{Mo}_6\text{S}_8$  respectively.

The samples for photoemission studies were fixed into the sample holder with a conducting silver epoxy. Clean surfaces of the ceramic Chevrel phases  $4 \times 4 \text{ mm}^2$  under study were obtained by in situ scrapping with a diamond file in spectrometer chamber at pressures in the range of  $10^{-10}$  Torr. The surface quality was checked with XPS. The cleaning procedure was repeated until no traces of contaminations could be observed.

Photoemission and resonant PE experiments were performed at the Berliner Speicherring-Gesellschaft für Synchrotronstrahlung (BESSY-I). Monochromatized synchrotron radiation in the range of photon energies from 40 to 200 eV (mainly at 60 eV and in the range 100–145 eV covering both Mo 4p-4d and RE 4d-4f resonances) was obtained from the toroidal grating monochromator (TGM3) beamline. Photoelectrons excited from the Mo 4d, S 3p as well as the RE 4f, 5p and 4d core levels and from the valence states were analyzed by spherical sector electron-energy analyzer AR-65 (Omicron). The overall energy resolution of the experiments (spectrometer and beamline) was approximately 200 meV full width at half maximum. All measurements were performed at the room temperature and near 100 K.

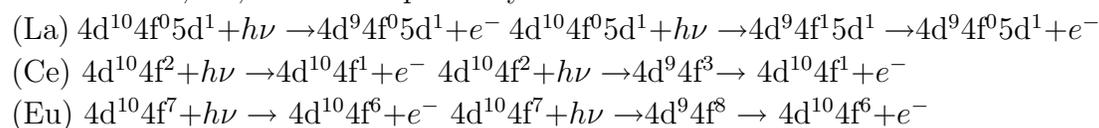
The experimental data were analysed using results of band-structure calcu-

lations for  $\text{LaMo}_6\text{Se}_8$  performed in the present study within the local-density approximation (LDA) employing an optimised methods of linear combination of atomic orbitals (LCAO) in its scalar relativistic version [4]. Results and discussion Details of the valence band spectra of  $\text{LaMo}_6\text{Se}_8$ ,  $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{Mo}_6\text{S}_8$ , and  $\text{EuMo}_6\text{S}_8$  are shown in Fig.2–4 for excitation energy between 60 and 150 eV. In these spectra valence band features of Mo4d, Se4s, Se4p, S3s and 3p and RE 5p and 4f spectra are observed in the binding energy region 0–20 eV. Three main structures are observed in VB at  $E_b = 1.4, 4.5, \text{ and } 13$  eV for all studied RE Chevrel phases. A peak at about 1.4 eV shows a remarkable enhancement at 60 eV. The resonance of this feature is interpreted as a result of excitation of Mo4d states and well agreed with data from [3] on photoemission studies of  $\text{Mo}_6\text{Se}_8$  and related compounds.

Resonant photoemission indicates that the density of states (DOS) at the Fermi level has a small S3p(Se4p) component as well as the dominant Mo 4d character with intercluster Mo 4d-S 3p hybridisation. The PE spectra show that the intensity of photoemission near  $E_F$  is rather high for all investigated compounds that reflect the metallic character of compounds.

A feature with a broad maximum at about 4.5 eV is formed by hybridized S 3p(Se 4p)-Mo4d states with a predominance of np-states of chalcogenes the region 3–8 eV. Peaks at about 13eV in photoemission spectra of  $\text{EuMo}_6\text{S}_8$ ,  $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{Mo}_6\text{S}_8$ , and  $\text{LaMo}_6\text{Se}_8$  are due to photoemission from S3s and Se4s states respectively.

Distribution of Mo4d and S3p(Se4p) states in studied  $\text{REMo}_6\text{S}_8$  compounds are similar and are determined mainly by the same electronic structure of  $\text{Mo}_6\text{S}_8$ -blocks in them. The strong enhancement of the shallow core level photoemission at photon energy close to the 4d–4f photothreshold and resonant behavior of PE spectra from rare earth compounds originates from the process of photoexcitation (near 4d–4f absorption region) with the following decay of the excited configuration via direct and indirect processes. These processes produce the resonant enhancement of photoemission process and can be describe as shown below for La, Ce, and Eu respectively :



Photoemission spectra of  $\text{LaMo}_6\text{Se}_8$  demonstrate (Fig.2) a remarkable resonance of Mo4d states and negligible resonance in the range 3–8eV (except maybe unclear feature at about 7.5eV) and a peak at 17.5 eV due to photoemission from La5p states.

Spectral intensity for Ce compound near 2 eV is enhanced (Fig.3, on-resonance

122eV), an effect which one tends to attribute to emission from Ce4f states. Usually, one observes two main peaks in Ce4f photoemission spectra: one at  $E_F$  and another at about 2 eV. In general, the relative intensity of these peaks is a measure of 4f hybridisation strength, the larger intensity at  $E_F$ , the greater 4f hybridisation and hence the larger the deviation from trivalency. Actually, this characteristic splitting into two peaks is not observed in present data that apparently means the main 4f emission feature at 2eV, weak hybridisation and claim apparently trivalency of Ce. But of course large spectral intensity of Mo4d states and interplay of Mo4d and S3p cross sections with excitation energy could mask Ce4f emission and more careful experiments are needed and planned.

In  $\text{EuMo}_6\text{S}_8$  compounds resonance photoemission at 141 eV clearly demonstrates as shown at Fig.4 the presence of peak at about 1.8 eV which could be interpreted as due to emission from  $\text{Eu}4f^7$  states proves that europium occurs in  $\text{EuMo}_6\text{S}_8$  as  $\text{Eu}^{+2}$  ions.

Thus the valence states of La and apparently Ce in  $\text{REMo}_6\text{S}_8$  and  $\text{RE Mo}_6\text{Se}_8$  is trivalent and bivalent for the Eu compounds.

In order to clarify and to analyse main features in valence band structure of studied RE Chevrel phases we performed the electronic structure calculation for  $\text{LaMo}_6\text{Se}_8$  within local-density approximation (LDA) employing an optimised methods of linear combination of atomic orbitals (LCAO) in its scalar relativistic version. Noted that the band structure calculation for  $\text{SnMo}_6\text{S}_8$ ,  $\text{GdMo}_6\text{S}_8$ , and  $\text{EuMo}_6\text{S}_8$  using LDA approach also were performed by T.Jarlborg and A.Freeman (see for example [1]).

Looking at the results of our band structure calculation one could mentioned that the overall picture of valence band photoemission spectra is qualitatively in a good agreement with our calculations (total and partial density of the most interesting states for  $\text{LaMo}_6\text{Se}_8$  are shown in Fig.5) and agreed with calculation of T.Jarlborg. In our calculations the contribution from La5d and 6s is small, rather featureless and near  $E_F$  negligible. In contrast with La states Mo4d states dominate at  $E_F$  and in the range of binding energy 0–2eV, whereas Se4p states dominate in 2–6 eV regions. The comparison of obtained experimental photoemission data with our results of LDA-LCAO band-structure calculations for  $\text{LaMo}_6\text{Se}_8$  demonstrates rather good agreement in position of main VB features of La, Mo and chalcogene in PE experiments and calculations.

### 3. Conclusions

In summary the resonant photoemission data together with the results of the electronic structure calculations indicate that the density of states at the Fermi

level reveal the dominant Mo4d character for all Chevrel-phase compounds under study. In each case rather high PE intensity at  $E_F$  reflects metallic character of the samples. The S3p and Se4p states dominate in the region of 3 to 8 eV BE's. The Mo4d and S3p (Se4p) DOS in different  $\text{REMo}_6\text{S}_8$  compounds are similar to each other that is mainly determined by the same electronic structure of their  $\text{Mo}_6\text{S}_8$  structural units. The resonantly enhanced peak at 1.8 eV BE in  $\text{EuMo}_6\text{S}_8$  proves a divalent state of the Eu atoms. In contrast to Eu, the Ce and La atoms in the corresponding  $\text{REMo}_6\text{S}_8$  compounds under study are trivalent.

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