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LETTER TO THE EDITOR

Study of Chevrel phases for thermoelectric applications: band structure calculations on $M_xMo_6Se_8$ compounds (M = metal)

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Abstract. Chevrel phases, $M_xMo_6Se_8$, present large voids in their lattice, where cations can be inserted. These cations are weakly bound and constitute good scattering centres for phonons. The lattice thermal conductivity of these compounds must be very low, and these phases are then good candidates for thermoelectric application. But most of them are metallic and superconducting. Some band structure calculations have been performed in order to find a semiconducting one. $SnMo_6Se_8$ and $Cu_2Mo_6Se_8$ are found to be metallic and $Zn_2Mo_6Se_8$ semiconducting.

New thermoelectric materials are investigated in order to increase the figure of merit $Z = \alpha^2/\rho\lambda$ (where α = thermopower, λ = thermal conductivity, ρ = electrical resistivity).

Slack [1] proposed a model for the ideal thermoelectric material with high figure of merit. He called this material a 'phonon-glass and an electron-crystal' (PGEC) which conducts heat like a glass and electricity like a metal. These materials must have low electronegativity difference between the atoms which constitute the compound, the band gap must be about $10kT$, for example 0.25 eV at room temperature (above this limit the thermal conductivity increases, and below this limit the thermopower decreases). The lattice thermal conductivity of such a compound is minimal. The idea is then to find materials which have a value of lattice thermal conductivity close to the minimum. This can be achieved by increasing the scattering of the phonons. Compounds with an open lattice with large unit cells are then good candidates. Skutterudites [2–5] have been studied because atoms can be inserted in their lattice. This atoms are weakly bound and are therefore good scattering centres for phonons. Other good candidates are the so-called Chevrel phases and Slack [1] proposed the compound Mo_6Te_8, which is a Chevrel phase, as a good candidate. They have been studied especially for their superconducting properties. We will describe here the crystal structure of these compounds and present results of some band structure calculations on ternary molybdenum selenides $M_xMo_6Se_8$ (M = Sn, Cu, Zn).

The arrangement of host structure is the same for all compounds. It consists of a stacking of Mo_6X_8 building blocks [6, 7] (where X is a chalcogen S, Se or Te). Each building block (figure 1) represents a unit cell of Cu_3Au structure type, i.e. a cube formed by eight chalcogens atoms which contains an octahedron of tightly packed molybdenum atoms. These atoms are slightly outside the middle of the faces of the X atom cube. The isolated Mo_6X_8 unit then has almost cubic symmetry. In the crystal, the corners of each Mo_6X_8 cube lie directly opposite to the face centres of adjacent cubes. That means that there are close contacts between Mo atoms of one isolated unit and the chalcogen atoms

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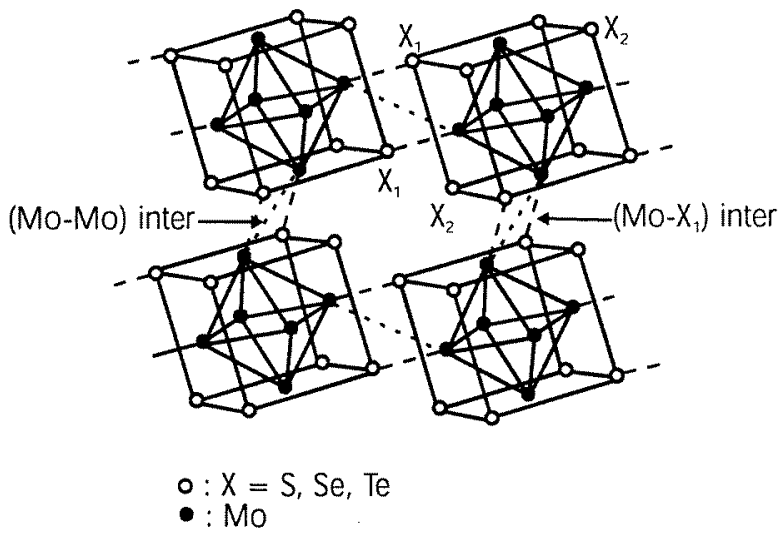

Figure 1. Building block arrangement. (Mo–Mo) intercluster liaisons and (Mo–X1) intercluster liaisons are represented by dashed lines.

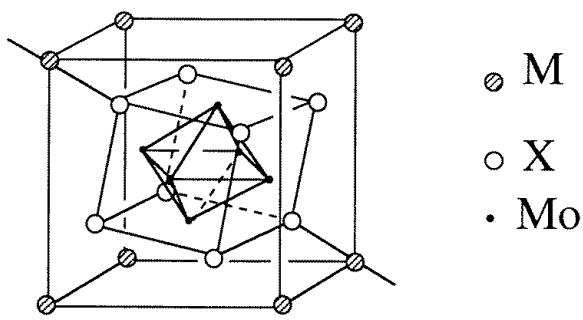

Figure 2. Elementary cell of rhombohedral structure. Inserted cations are located in position (0, 0, 0), the unit block Mo_6X_8 is turned by an angle of about 27° around the ternary axis.

of the other units (figure 1). The unit cell is constructed as shown in figure 2. The cation (inserted in a cavity described below) is in position (0, 0, 0) on the ternary axis. The other inserted cations are distributed on the corners of the rhombohedral cell which has an angle close to 90°. But the symmetry is not cubic, even if $\alpha = 90°$, because the Mo_6X_8 building blocks are not parallel to the unit cell vectors but are turned by an angle ϕ of about 27° around the ternary axis.

The arrangement of these building blocks leaves, as said before, a certain number of cavities in the chalcogen atom network [6–8]. There are three types of cavity in the lattice (figure 3). The largest one (site 1) is approximately cube shaped and is formed by eight chalcogen atoms belonging to eight different Mo_6X_8 units. Smaller cavities (site 2) are formed by eight chalcogen atoms belonging to four different building blocks, and have a more irregular shape. The last type of cavity (site 3) is formed by eight chalcogen atoms belonging to two building blocks.

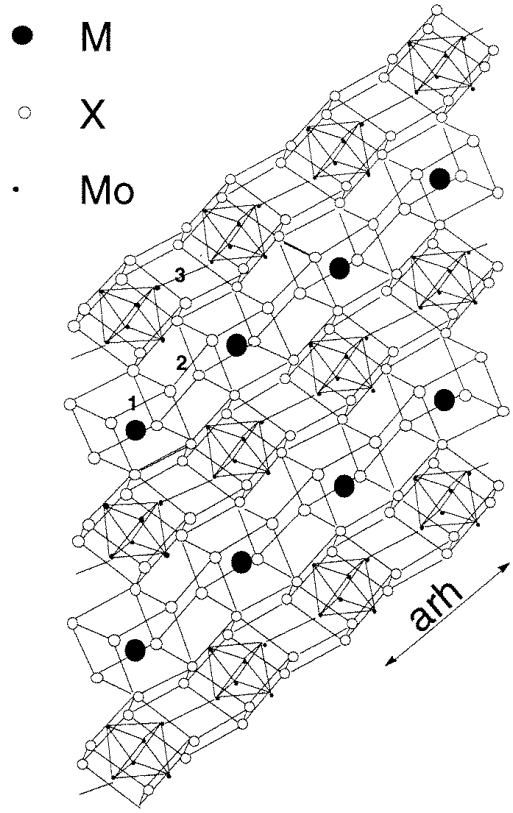

Figure 3. Projection on the hexagonal $(11\bar{2}0)$ plane. The three types of cavity are represented. Large cations M are located in site 1.

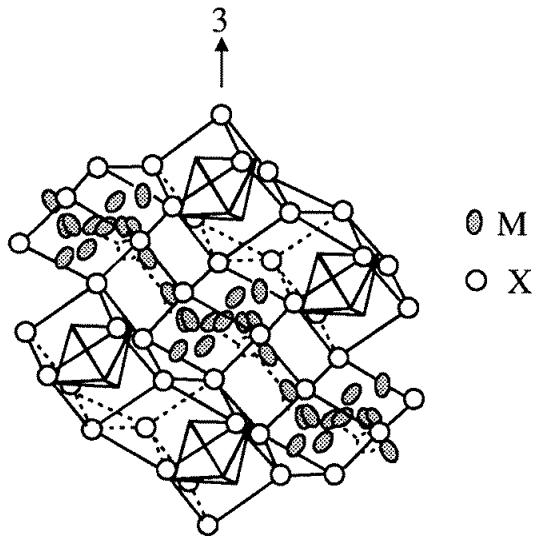

Figure 4. Distribution of small cations in the lattice.

All these cavities are empty in the binary compounds Mo_6X_8 and are filled with cations in the ternary compounds $M_xMo_6X_8$ (M = metal). The type of cavity filled depends mainly on the size of the cation. Large atoms (Pb, Sn, . . .) occupy site 1 (figure 3), and lead to a

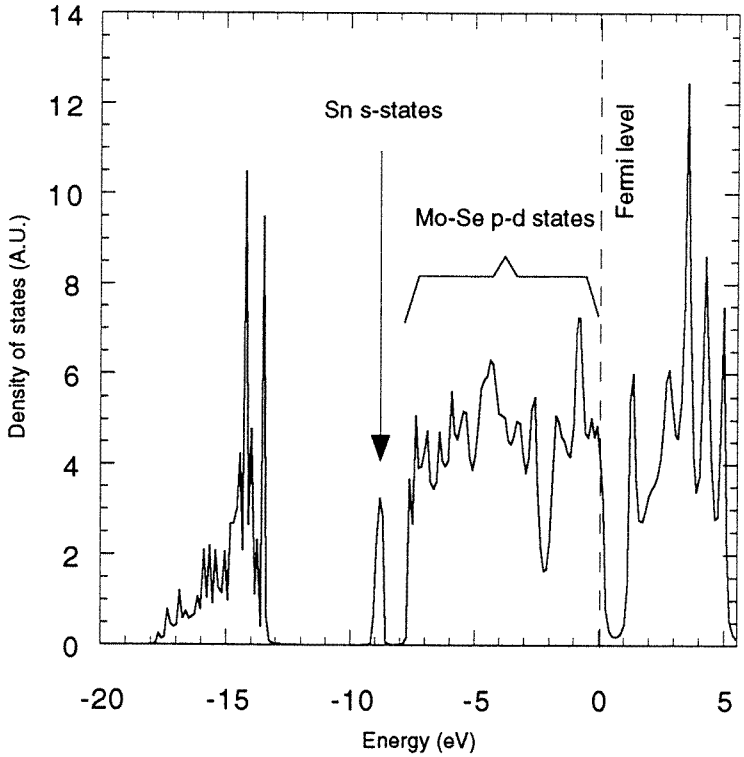

Figure 5. Density of states of $SnMo_6Se_8$. The x-axis is in eV, the y-axis is in arbitrary units; the Fermi level is taken as an energy reference.

stoichiometric compound ($x \approx 1$). Small atoms (Cu, Zn, Ni, . . .) are statistically distributed between sites 1 and 2 (figure 4), and lead to a non-stoichiometric compound ($x > 1$).

The size and shape of the cavities depends on the nature of the inserted cation. It modifies the distances between Mo atoms. For some compounds a lattice transformation leading to a triclinic structure is observed [6, 9]. The limit concentration of the cation M^{n+} is not determined by geometric but electronic factors. Indeed as one adds M atoms, the number of valence electrons increases due to charge transfer from the M atoms to the Mo atoms. The Mo_6 octahedron then contracts and becomes more regular. The number of valence electrons per Mo atom is therefore a parameter of interest. Yvon and Paoli [10] proposed calling this quantity the 'cluster valence electron concentration' (cluster VEC). It is calculated by adding the number of valence electrons of the M atoms to the number of valence electrons of the Mo atoms and by subtracting the number of electrons required to fill the octet of the chalcogen atoms. This is true for sulphur, but the formal charge of selenium and tellurium is lower than that of sulphur because of an increase in covalence (distances between atoms are smaller in the compound than purely ionic distances). Yvon supposes that each Mo atom forms a liaison with Mo atoms of neighbouring clusters. The X1–X2 liaisons (figure 1) are supposed to be completely saturated, four electrons are then needed to saturate the Mo–Mo liaisons. When the Mo–Mo liaisons are saturated, the VEC equals 24 and we can expect the compound to be a semiconductor.

First thermoelectric measurements have been made by Caillat and Fleurial [11] on a

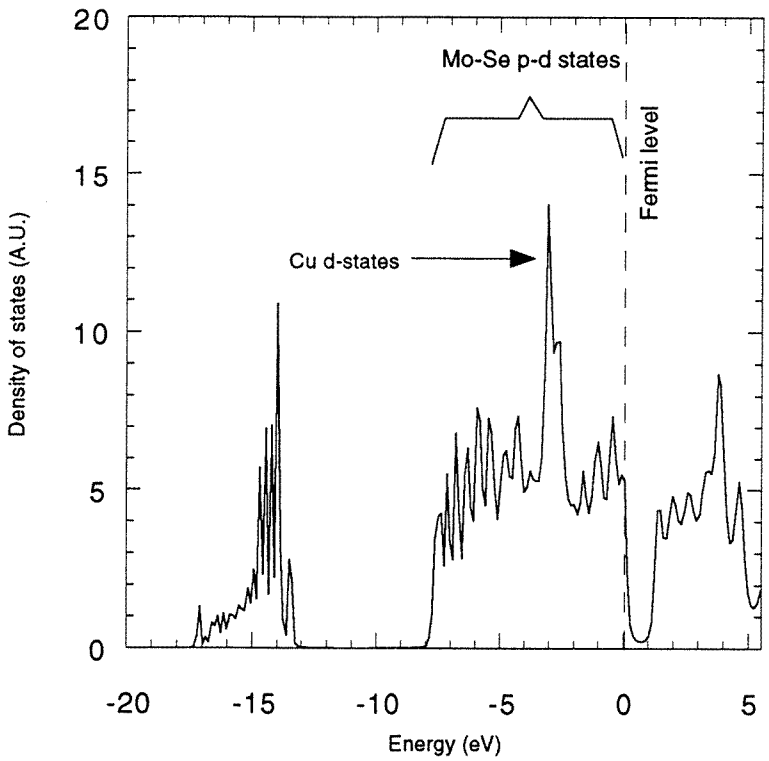

Figure 6. Density of states of $Cu_2Mo_6Se_8$. The x-axis is in eV, the y-axis is in arbitrary units; the Fermi level is taken as an energy reference.

substitution compound $Mo_2Re_4Se_8$. We want to study compounds with inserted cations and in order to find a semiconducting phase we have made some preliminary band structure calculations.

The calculations were made on selenide compounds. We used the LMTO–TB (linear muffin tin orbitals–tight binding) method in the ASA (atomic sphere approximation). The density of states was calculated in direct space using the recursion method to obtain the Green function for each orbital of the unequivalent atoms [12]. We use the simple square root termination for the continuous fraction so that we obtain a very deep minimum of the density of states instead of a real gap.

Calculations for $SnMo_6Se_8$ and $PbMo_6Se_8$ have been performed using other methods by Freeman and Jarlborg [13] and Nohl *et al* [14] respectively. They both found metallic superconducting compounds. No calculations have been published for small cations, as far as we know.

We performed calculations for $Cu_2Mo_6Se_8$ and $Zn_2Mo_6Se_8$. To obtain a periodic system, we have chosen a given Cu1 and a given Cu2 site (respectively Zn) as occupied, the other being empty. The six Mo atoms and the eight Se atoms become inequivalent and we have to treat a 16 inequivalent atom unit cell. Following Nohl *et al* [14] we used the metallic sphere radius for Mo ($r = 1.55$ Å) and atomic radius for Se ($r = 1.40$ Å) and Sn ($r = 1.62$ Å, atomic radius). For copper and zinc, we chose the radius so that the overlap with the nearest Se neighbours is smaller than 20% ($r_{Cu} = 1.39$ Å, metallic radius and $r_{Zn} = 1.39$ Å,

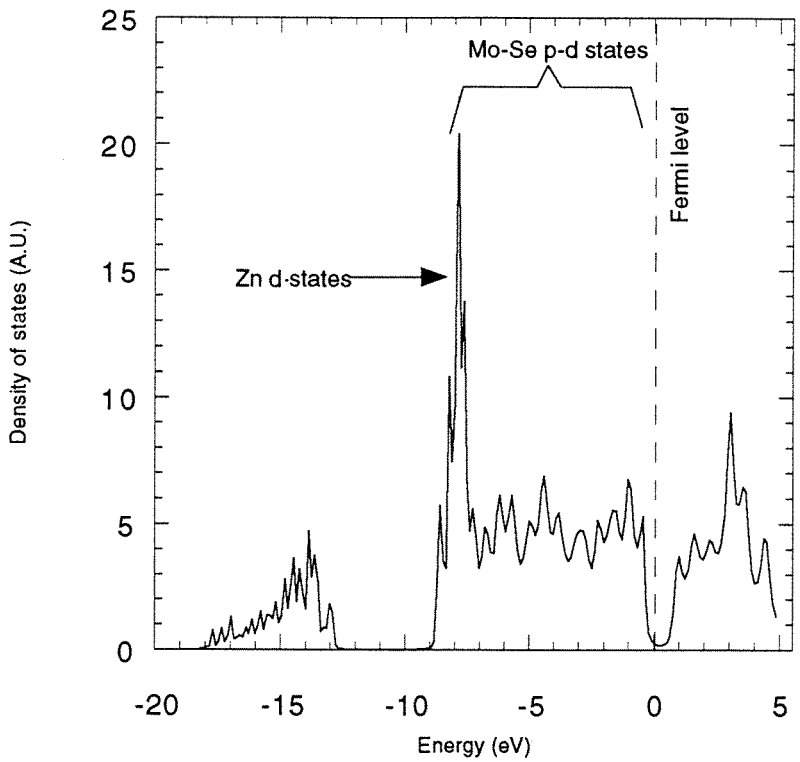

Figure 7. Density of states of $Zn_2Mo_6Se_8$. The x-axis is in eV, the y-axis is in arbitrary units; the Fermi level is taken as an energy reference.

atomic radius). Since no information on the position of Zn in $Zn_2Mo_6Se_8$ exist, we used the positions we found for Cu in $Cu_2Mo_6Se_8$, because the lattice parameter and the angle of rhombohedral structure of both compounds are very similar.

A test calculation for $SnMo_6Se_8$ gives results very similar to those obtained by Freeman and Jarlborg [13] (who use a complete self-consistent calculation but on a simplified structure). In particular we obtain below the main p–d band (between d orbitals of Mo and p orbitals of Se) a narrow Sn s band (figure 5). This is filled by two electrons, so that the Sn compound is metallic and superconducting (with two holes in the p–d band). In contrast one calculation for $Cu_2Mo_6Se_8$ (figure 6) and $Zn_2Mo_6Se_8$ (figure 7) shows no distinct s band for Cu and Zn. We only found a narrow Cu (or Zn) d band, which falls within the p–d (Mo–Se) band (at 3.2 and 7.8 eV below the Fermi level for Cu and Zn respectively). Since these d states are filled anyway, the two valence electrons of the two Cu ions are in the p–d band and the compound is always conducting. The four valence electrons of the two Zn ions are also in the p–d band so that $Zn_2Mo_6Se_8$ is a semiconductor.

The calculation thus predicts that stoichiometric $Zn_2Mo_6Se_8$ is a semiconductor while slightly sub-stoichiometric $Zn_xMo_6Se_8$ (with $x < 2$) should be a p doped semiconductor.

Band structure calculations made with our method confirm the results obtained on $SnMo_6Se_8$ and $Cu_2Mo_6Se_8$ (Chevrel phases). These two compounds have a metallic behaviour. But $Zn_2Mo_6Se_8$ has a semiconducting behaviour and appears to be a good candidate for thermoelectric applications.

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