Theoretical search for Chevrel phase based thermoelectric materials

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We investigate the thermoelectric properties of some semiconducting Chevrel phases. Band structure calculations are used to compute thermopowers and to estimate of the effects of alloying and disorder on carrier mobility. Alloying on the Mo site with transition metals like Re, Ru or Tc to reach a semiconducting composition causes large changes in the electronic structure at the Fermi level. Such alloys are expected to have low carrier mobilities. Filling with transition metals was also found to be incompatible with high thermoelectric performance based on the calculated electronic structures. Filling with Zn, Cu, and especially with Li was found to be favorable. The calculated electronic structures of these filled Chevrel phases are consistent with low scattering of carriers by defects associated with the filling. We expect good mobility and high thermopower in materials with the composition close to (Li,Cu)₄Mo₆Se₈, particularly when Li-rich, and recommend this system for experimental investigation.

Widespread use of thermoelectric materials, as an alternative technology for power generation and refrigeration, remains a desirable but elusive goal. The efficiency of devices based on current state-of-the-art materials (such as PbTe, SiGe, and Bi₂Te₃/Sb₂Te₃/Bi₂Se₃ alloys) is low. This largely restricts them to the applications where reliability outweighs efficiency or small device sizes are needed. In recent years, the center of gravity of the search for new thermoelectric materials has moved towards crystallographically more complicated compounds. This is motivated in part by the fact that low values of thermal conductivity, needed for thermoelectric performance, are more likely in such materials, and partly because such structures provide more avenues for chemical optimization. Good examples are high figure of merit (ZT) skutterudite and Zn-Sb thermoelectrics. First principles calculations are proving to be a useful tool in sorting out the mechanisms by which high ZT values can arise in these complex materials and in exploring the effects of various chemical modifications on the thermoelectric properties.

A good thermoelectric material has high thermopower, a low lattice contribution to the thermal conductivity κ and a sizeable electric conductivity σ. The thermoelectric figure of merit is $ZT = \sigma S^2 T / \kappa$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient (thermopower), and $\kappa = \kappa_{el} + \kappa_{latt}$ is the thermal conductivity ($\kappa_{el}$ and $\kappa_{latt}$ are the electronic and lattice contributions, respectively). Current thermoelectric materials have $ZT \approx 1$. Large values of $S$ are typical of doped semiconductors, while $\sigma$ is large in metals. Starting from a material with low $\kappa$, the above expression suggests that enhanced values of $ZT$ can be obtained by searching for compositions which maximize the power factor, $\sigma S^2$, with respect to the carrier concentration $n$. An additional requirement arises from the Wiedemann-Franz law, which sets a rough lower bound on the Lorentz number $L = \kappa / \sigma T$ [$L_{min} = (\pi^2 k_B / 3e)$]. A value $S \geq 160 \mu V/K$ is thus needed for $ZT \geq 1$, even if $\kappa_{latt}$ is negligibly small. Empirical evidence and minimum thermal conductivity theories imply that materials having large numbers of atoms in the unit cell and large atomic masses (soft phonons), are most likely to have the requisite low thermal conductivities. Here we investigate the materials in the family of molybdenum (Mo) cluster compounds known as “Chevrel phases”. These are based on the binaries Mo₆X₈, where X is a chalcogen (S, Se, Te). The crystal structure contains large voids, which may be filled to yield a large variety of ternary compounds with the general formula MₓMo₆X₈, where M can be a simple or transition metal atom, or a rare-earth element. This provides opportunities for obtaining low thermal conductivities, analogous to skutterudites, as well as a chemical knob for modifying the electronic properties. These materials fulfill the requirements for low $\kappa$ outlined above, and experimental evidence indicates that their thermal conductivity is indeed low.

The band structure of the unfilled Mo₆S₈ is relatively simple, despite the crystallographic complexity. Following Ref. the band structure can be described as deriving from a collection of pseudocubic Mo₆X₈ clusters. The chalcogens form a distorted cube, X₈, and the Mo’s occupy the face centers of the cube. The on-site energies of the X-p and Mo-d orbitals are close; for instance, in Mo₆S₈ $E_d - E_p \approx 0.2 - 0.4$ eV (in Mo₆S₈ it is larger, about 0.9 eV). These orbitals are strongly hybridized: the hopping amplitude $t_{pd\sigma}$ is of the order of 2 eV. Two out of five d-orbitals for each Mo atom are affected by the $pd\sigma$ bonding (for the xy face they are xy and $3z^2 - r^2$). The total number of affected states is $8 \times 3 + 6 \times 2 = 36$, of which there are 12 non bonding $p$ states, 12 bonding, and 12 antibonding $pd\sigma$ states. In unfilled Mo₆X₈, 24 bonding and nonbonding states (48 in both spin channels) are all occupied, and the antibonding states are
much higher and are never populated in the real compounds. The remaining Mo $d$ orbitals form 18 bands sitting inside the gap between the non-bonding and antibonding $pd\sigma$ bands. The $dd\sigma$ hopping amplitude is also very large, $\approx 1.5$ eV, and as a result these 18 bands also form bonding and antibonding combinations (there are no nonbonding states for $d$-orbitals on an octahedron). It can be shown that the number of bonding states is 12, and of antibonding states 6, so there is a gap between 36th and 37th state in the Mo$_6$X$_8$ cluster.

The total number of electrons in the $pd$ states in Mo$_6$X$_8$ is $8 \times 4 + 6 \times 6 = 68$, 4 electrons short of reaching the above mentioned gap. Thus, one conjectures that doping 4 electrons in the system will make it semiconducting, and that the states of the bottom of the gap would be predominantly Mo $d$. In particular, one expects the bands below the gap to be sensitive to substitution on the metal site, but not to filling the voids. However, the desired doping requires substantial filling, e.g. with 4 monovalent atoms (Li, Cu), or 2 divalent ones (Zn) per formula unit.

In our calculations, the lithium (Li) filled selenide, Li$_{1-\delta}$Mo$_6$Se$_8$, is found to be particularly favorable for thermoelectric applications from an electronic point of view. Other favorable choices include Cu$_{1-\delta}$Mo$_6$Se$_8$ and Zn$_{2-\delta}$Mo$_6$Se$_8$, while transition metal fillers or alloying on the Mo site are found to have too low carrier mobilities to be candidates for thermoelectric applications. We concentrate on the Se based compounds, as opposed to more common sulfides. Se has higher mass, favorable to low lattice heat conductance. Furthermore, selenides tend to be more covalent which is better from the point of view of carrier mobility. Experimentally there is a large homogeneity region in the Li$_2$Mo$_6$Se$_8$ pseudobinary phase diagram near this composition.

We use a density-functional approach within the local-density approximation (LDA) for the exchange and correlation to calculate the electronic structures. In accord with considerations presented above, Li$_4$Mo$_6$Se$_8$ was indeed found to be a semiconductor with an LDA gap of about 1.4 eV. For most calculations we used the general potential linearized augmented plane wave (LAPW) method with local-orbital extension to relax linearization errors and treat the 4p semi-core states of Mo on an equal footing with the valence states. We employ a well-converged basis set containing \~2000 basis functions, with muffin-tin sphere radii of 2.25 a.u. for Mo and Se, and of 2.0 a.u. for Li. The calculations were based on the reported crystal structure of Li$_{1.2}$Mo$_6$Se$_8$. In the present work, we do not take into account the trigonal distortion that was reported for $\delta < 0.4$ in Ref. 13. This is probably associated with partial ordering of the Li ions.

We also considered several other dopants to the Mo$_6$Se$_8$ phase, to add four electrons per formula unit and make it a semiconductor. These include doping with zinc, copper, and some transition metals at the interstitial sites, as well as substitution of ruthenium, technetium, and rhenium on the metal (Mo) site. Zn and Cu fillings were found to be favorable, but the Chevrel phases with the needed concentration have not been synthesized experimentally. Transition metal substitutions were found to be unfavorable due to strong carrier scattering (as discussed above, the states below the gap are predominantly of Mo-Mo bonding character, thus substitution at the Mo site has a drastic effect on these states). A detailed account of these studies will be published elsewhere.

Transport properties were obtained from the calculated LAPW electronic structures using kinetic (Bloch-Boltzmann) transport theory. The only further approximation was that of an isotropic and energy independent relaxation time for electrons. Unless there is particularly sharp structure of the density of states near the Fermi level (e.g. Pd or heavy fermion materials), this approximation is quite good.

The structure of Chevrel compounds can be described as a collection of the above mentioned pseudocubic Mo$_6$X$_8$ clusters with a small symmetry lowering rhombohedral distortion. Several interconnecting interstices, which are empty sites in the binary phases, form channels along the three rhombohedral directions. A large variety of ternary compounds may be synthesized by filling these empty sites, e.g. Li$_{2}$Mo$_6$Se$_8$, and also the prototype large-cation compound PbMo$_6$Se$_8$, which is obtained by placing Pb into the largest interstitial site at the origin of the rhombohedral unit cell. PbMo$_6$Se$_8$ and similar materials have been extensively studied due to their interesting superconducting properties but semiconducting compositions have attracted less interest. Unlike large cations, like Pb, small cations such as Li are distributed over 12 sites arranged as two sets of concentric sixfold rings surrounding the large interstice at the origin of the rhombohedral cell. For intermediate concentrations ($1 < x < 4$), the relative occupancy of these two
rings has been a subject of debate, at least in the case of the sulfide. However, for $x = 4$ it is commonly accepted that three Li atoms occupy the outer ring, with the fourth Li atom occupying the inner ring. There is a tendency for Li atoms to order partially, however, this ordering is very little studied.

Bonding in these compounds is understood to derive from covalent bonds between the Mo atoms in the octahedral cluster, and between Mo and X (Ref. 19). The latter bond has mixed ionic/covalent character. As mentioned, the Mo-Se bonds are less ionic than Mo-S bonds. The valence bands of Mo$_6$Se$_8$ shown in Fig. 1 are thus composed of covalent Mo-Mo and Mo-Se bonds. The conduction band is partially occupied (four holes per unit cell) at the top of the valence band manifold. As mentioned, the top states in this band consist primarily of bonding Mo-Mo states along the edges of the Mo octahedra.

In addition to providing the four extra electrons needed to dope the compound to the semiconducting regime, the introduction of three additional Li ions and three additional electrons. This is key because it indicates weak scattering due to Li disorder and vacancies, which is a prerequisite for obtaining reasonable mobilities and thermoelectric performance. The most pronounced difference between these two sets of bands near the top of the bands is found along the $\Gamma$-$R$ directions, where the eigenvalues are shifted downwards in the Li$_3$Mo$_6$Se$_8$ (but without Li). The two sets of bands are very similar near the top of the bands, despite the very strong perturbation of the self-consistent potential, upon the introduction of three additional Li ions and three additional electrons. This is key because it indicates weak scattering due to Li disorder and vacancies, which is a prerequisite for obtaining reasonable mobilities and thermoelectric performance. The most pronounced difference between these two sets of bands near the top of the bands is found along the $\Gamma$-$R$ directions, where the eigenvalues are shifted downwards in the Li$_3$Mo$_6$Se$_8$, with respect to the band maxima. Nevertheless, given that the perturbation in this case is substantially stronger than in the composition of interest ($x = 4$), we see Fig. 3 as an indication that rigid band behavior between the $x = 3$ and $x = 4$ compositions holds to a good approximation. The observed rigid-band behavior also shows that the crystal potential felt by carriers at and near the Fermi level is only moderately affected by the exact position of the Li ions. The carrier mobility is determined by the electron scattering time, which in turns is defined by the change of the crystal potential upon moving Li atoms. Corre-
spondingly, when the change is small, the carrier mobility is expected to be only weakly reduced by Coulomb scattering due to the disorder on the Li site. The negative effect on the mobility will be even further reduced by partial ordering of Li atoms, which is known to occur in Li$_{1-x}$Mo$_6$Se$_8$. (A phase transition to a lower symmetry trigonal phase has been reported for $\delta < 0.4$ in this compound.) Furthermore, although the ordering processes in the mixed-filler system (Cu, Li)$_{1-x}$Mo$_6$Se$_8$ have hardly been studied at all, one might anticipate that, say, CuLi$_3$Mo$_6$Se$_8$ (this compound forms), would be better ordered than Li$_4$Mo$_6$Se$_8$.

The calculated thermopower as a function of temperature is shown in Fig. 4 for three different doping levels. All three curves reach a maximum at around 200 K. At a doping of about 0.1 hole/cell hole/cell (corresponding to a concentration of $3\times10^{20}$ holes/cm$^3$) we obtain a maximum Seebeck coefficient of $\sim 150$ $\mu$V/K at $T \sim 250$ K. Without quantitative data on the lattice thermal conductivity and carrier mobility it is not possible to determine $ZT$, but it is worth mentioning that these high values at high carrier concentration, if combined with reasonable $\kappa_{\text{latt.}}$, are compatible with $ZT \geq 1$, when the material is optimized.

In summary, we present first principles calculations of filled Chevrel phases based on Mo$_6$Se$_8$. The most promising from the point of view of potential thermoelectric applications is Li$_{1-x}$Mo$_6$Se$_8$, with $\delta \sim 0.1$. This material can possibly have values of $ZT$ of the order of 1 or larger. Among the most important questions about this and other filled Chevrel compounds, from the point of view of thermoelectric applications are: (1) whether the effects neglected in the current study, namely the local distortion of the Mo$_6$Se$_8$ cage near Li and partial ordering of Li atoms will not adversely affect the carrier mobility (the former effect lowers the mobility, and the latter increases it), and (2) whether the alloying with Li or Li/Cu would be sufficiently effective in scattering heat conducting phonons. In this regard Cu and Li filled Mo$_6$Se$_8$ are similar electronically but presumably very different vibrationally, so the Li/Cu ratio may be a useful "knob" for controlling the thermal conductivity. We hope that our calculations will encourage experimentalists to look closer at this promising system, (Li,Cu)$_{1-x}$Mo$_6$Se$_8$.

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1 G. Mahan, B. Sales, and J. Sharp, Phys. Today, March 1997, p. 42.
2 D. J. Singh and W. Pickett, Phys. Rev. B 50, 11235 (1994).
3 D. J. Singh and I. I. Mazin, Phys. Rev. B 56, R1650 (1997).
4 S. G. Kim, I. I. Mazin, and D. J. Singh, Phys. Rev. B 57, 6199 (1998).
5 CRC Handbook of Thermoelectrics, D. M. Rowe, ed., Chemical Rubber, Boca Raton, Fl. (1995), chap. 34.
6 T. Caillat, private communication.
7 Roche et al [J. Phys. Cond. Mat. 10, L333, 1998] have recently reported recursion LMTO-ASA calculations for Cu$_2$Mo$_6$Se$_8$ and Zn$_2$Mo$_6$Se$_8$. They identified the latter compound as a semiconductor, but did not report thermopowers or estimates of the effect of Zn disorder on mobility. Our calculations for the same compound show favorable results in both aspects, but Li/Cu filling appears to be more advantageous from the electronic point of view.
8 K. Yvon, Cur. Top. Mater. Sci. 3, 53 (1979).
9 L.S. Selwyn and W.R. McKinnon, J. Phys. C21, 1905 (1988).
10 O. K. Anderson, Phys. Rev. B 12, 3060 (1975).
11 D. J. Singh, Planewaves, Pseudopotentials and the LAPW Method (Kluwer, Boston, 1994).
12 D. J. Singh, Phys. Rev. B 43, 6388 (1991).
13 R. J. Cava, A. Santoro, and J. M. Tarascon, J. Sol. State Chem. 54, 193 (1984).
14 J. R. Dahn, W.R. McKinnon, and S.T. Coleman, Phys. Rev. B 31, 484 (1985).
15 J.M. Ziman, Principles of the Theory of Solids, Cambridge University Press, Cambridge, 1972.
16 H. Nohl, W. Klose, and O.K. Andersen, in Ref. [15], p. 165.
17 C. Ritter, E. Gocke, C. Fischer, and R. Scho"llhorn, Mat. Res. Bull., 27, p. 1217 (1992).
18 Superconductivity in ternary compounds, O. Fischer and M.B. Maple, eds., p. 165, Springer, Berlin, 1982.