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 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 thus 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 simple metals, like 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 reasonable mobility and high thermopower in materials with compositions near $(Li,Cu)_4Mo_6Se_8$. [S0163-1829(99)06211-6]

Widespread use of thermoelectric devices, as an alternative technology for power generation and refrigeration, remains a desirable but elusive goal, limited by the performance of existing thermoelectric materials (TEM). In recent years, the center of gravity of the search for new TEM has moved towards crystallographically more complicated compounds. This is motivated in part by the fact that low values of thermal conductivity, required in a good TEM, are more likely in such materials, and partly because such structures provide more avenues for chemical optimization. First principles calculations useful in sorting out the ingredients important to the transport properties in these complex materials and in exploring the effects of chemical modifications on the thermoelectric performance.[1–4]

A good TEM has high thermopower S, low-lattice contribution to the thermal conductivity κ_l, and a sizeable electric conductivity σ.[5] The thermoelectric figure of merit[5] is $ZT = \sigma S^2 T / \kappa$, where $\kappa = \kappa_e + \kappa_l$ is the thermal conductivity. Current TEM have $ZT \approx 1$. Empirical evidence and minimum thermal conductivity theories imply that materials having large numbers of atoms in the unit cell and large atomic masses, are most likely to have low thermal conductivities.[1] Within the kinetic transport theory,[6] the thermopower, for a given doping, is determined by the electronic structure near the Fermi energy E_F

$$S(T) = \frac{1}{eTt(E_F)} \int d\epsilon \epsilon t(\epsilon) \left[-\frac{\partial f(\epsilon, T)}{\partial \epsilon} \right], \quad (1)$$

where f is the Fermi distribution function, and $t(\epsilon)$ is the so-called transport function. In the constant relaxation time approximation this function is proportional to a specific integral over the ϵ-isoenergetic surface, $t(\epsilon) \propto \int v_\epsilon dS_\epsilon$, v being the electron velocity at the isoenergetic surface. Equation (1) allows one to estimate $S(T)$ using the calculated electronic structure. The electric conductivity, σ, is determined by the product of carrier concentration and mobility, or alternatively the product of relaxation time and squared plasma frequency. The latter can be directly calculated from the band structure while information about the scattering time can be obtained by comparing the calculated band structure with substituted or/and displaced ions with that of undisturbed crystal. Large changes near E_F signal short relaxation times and low mobility.

Using the outlined methodology, we investigate here the materials in the family of molybdenum (Mo) cluster compounds known as ''Chevrel phases.'' These are based on the binaries $Mo_6X_8, X=S$, Se, Te. The crystal structure contains large voids, which may be filled to yield a large variety of ternary compounds with the general formula $M_xMo_6X_8$, 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 κ, and experimental evidence indicates that their thermal conductivity is indeed low.[7] In our calculations we used the general potential linearized augmented plane wave (LAPW) method[8,9] with local-orbital extensions[10] to relax linearization errors and treat the $4p$ semicore states of Mo on an equal footing with the valence states. The calculations were performed for $Mo_6Se_8, Mo_4Ru_2Se_8, Mo_2Re_4Se_8$, $A_6Se_8, Li_3Mo_6Se_8, Li_4Mo_6Se_8, Li_6Mo_6Se_8$, and $B_6Mo_6Se_8$ (with A and B being virtual elements with $Z=42.667$ and $Z=2.667$, respectively), in the crystal structures corresponding to experimentally observed Mo_6Se_8, $Li_{3.2}Mo_6Se_8$, and in some cases in the theoretical (relaxed) crystal structures, as summarized in Table I. Well-converged basis set containing ~ 2000 functions was used, with LAPW sphere radii of 2.25 a.u. for Mo and Se, and of 2.0 a.u. for Li. We also performed calculations for several additional compositions (Table I) with the linear muffin-tin orbitals (LMTO)

TABLE I. Systems for which full potential LAPW ($\mathcal{A}$) and/or ASA LMTO ($\mathcal{M}$) calculations have been performed. Unless the full formula is specified, Mo_6Se_8 should be added to all items in the first row.

Structure	Mo_6Se_8	$Mo_4Ru_2Se_8$	$Mo_2Re_4Se_8$	A_6Se_8[a]	$Mo_4Tc_2Se_8$	Li_3	Li_4	Li_6	B_6[b]	Fe_n[c]	Co_3	Ni_3	Cu_4	Zn_2
exptl. Mo_6Se_8	$\mathcal{A}/\mathcal{M}$	$\mathcal{A}/\mathcal{M}$	$\mathcal{M}$	$\mathcal{A}/\mathcal{M}$	$\mathcal{M}$	$\mathcal{A}/\mathcal{M}$	$\mathcal{A}/\mathcal{M}$	$\mathcal{A}/\mathcal{M}$	$\mathcal{A}/\mathcal{M}$	$\mathcal{M}$	$\mathcal{M}$	$\mathcal{M}$	$\mathcal{M}$	$\mathcal{M}$
relaxed LDA structure		$\mathcal{A}$	$\mathcal{A}$											
exptl. $Li_{3.2}Mo_6Se_8$	$\mathcal{A}/\mathcal{M}$					$\mathcal{A}/\mathcal{M}$	$\mathcal{A}/\mathcal{M}$	$\mathcal{A}/\mathcal{M}$						

[a]$Z(A) = 42.667$
[b]$Z(B) = 2.667$
[c]$n = 1,2,3$

method,[8] a much faster but less accurate method. The reliability of the LMTO method for our purposes was established by comparing the LMTO and LAPW results for a number of compounds (see Table I). Our main conclusion, based on all these calculations, is that the most promising from the point of view of TEM are filled Chevrel compounds with Li and Li-Cu combinations.

The band structure of unfilled Mo_6X_8 is relatively simple, despite the crystallographic complexity. Following Ref. 11, the band structure can be described as deriving from a collection of pseudocubic Mo_6X_8 clusters. The chalcogens form a distorted cube X_8 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 (0.2–0.4 eV). These orbitals are strongly hybridized: the hopping amplitude $t_{pd\sigma}$ is $\simeq 2$ 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 $3z^2 - r^2$), altogether 36 states: 12 nonbonding p states, and 12 bonding and 12 antibonding $pd\sigma$ states. In unfilled Mo_6X_8, 24 bonding and nonbonding states (48 in both spin channels) are occupied. The antibonding states are much higher and are never populated. The remaining Mo d orbitals form 18 bands sitting inside the gap between the nonbonding and antibonding $pd\sigma$ bands. The $dd\sigma$ hopping amplitude is also very large, ≈ 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_6X_8 cluster. The total number of electrons in the pd states in Mo_6X_8 is $8 \times 4 + 6 \times 6 = 68$, 4 electrons short of reaching the gap. Thus, doping 4 electrons in the system should make it semiconducting, and then the states of the bottom of the gap should be mostly of Mo d character.

The calculated valence bands of Mo_6Se_8 are shown in Fig 1. There are four holes per unit cell, and the valence states consist primarily of bonding Mo-Mo states along the edges of the Mo octahedra. As a result, relatively small changes in the Mo_6Se_8 cluster geometry lead to dramatic changes in the structure of this band (Fig 2), manifesting strong electron-phonon interaction.[12] This limits the mobility at high temperature. One expects substitutional impurities at the Mo site to scatter strongly the conduction electrons, and indeed our calculations[13] for Mo→Re, Mo→Ru, and Mo→Tc substitution show dramatic changes in the band structure near E_F. Although we did find that doping 4 electrons in such a way produced semiconductors, the carrier mobility in these semiconductors must be low and their thermoelectric performance poor.[14]

Other possible dopings are determined by the crystal structures, which can be described as a collection of such clusters with a small symmetry lowering rhombohedral distortion.[15,11] Several interconnecting interstices, which are empty sites in the binary phases, form channels along the three rhombohedral directions. Besides substituting Mo by metals with higher valencies, doping may be realized by filling these empty sites with small cations: simple (Li, Zn) and transition (Fe, Ni) metals, or by inserting a large cation (Pb) into the largest interstitial site at the origin of the rhombohedral unit cell. Unlike large cations, small cations are distributed over 12 sites arranged as two sets of concentric sixfold rings surrounding the large interstice at the origin.[16,17] In particular, $Li_4Mo_6Se_8$, with the desired electron count, is known to form. For intermediate concentrations ($Li_{4-\delta}Mo_6S_8$), the relative occupancy of these two rings has been a subject of debate,[16,17] but in $Li_4Mo_6S_8$ it is reasonably well established 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, but this ordering is little studied.

Our strategy in studying the filled Chevrels was as follows: first we surveyed a number of potential candidates by doing fast LMTO calculations. We eliminated those compounds which were found to be metals, since high S is not expected there. They were $Fe_nMo_6Se_8$, $n = 1,2,3$, $Co_3Mo_6Se_8$, $Ni_3Mo_6Se_8$. $Li_4Mo_6Se_8$, $Cu_4Mo_6Se_8$, and $Zn_2Mo_6Se_8$ were found to be semiconducting,[18] with the electronic structure of $Li_4Mo_6Se_8$, and to lesser extent of $Cu_4Mo_6Se_8$ and $Zn_2Mo_6Se_8$, near E_F similar to that of unfilled Mo_6Se_8. This suggests that these compounds and their interalloys may have reasonable electronic mobility. Having established that, we proceeded with detailed LAPW calcula-
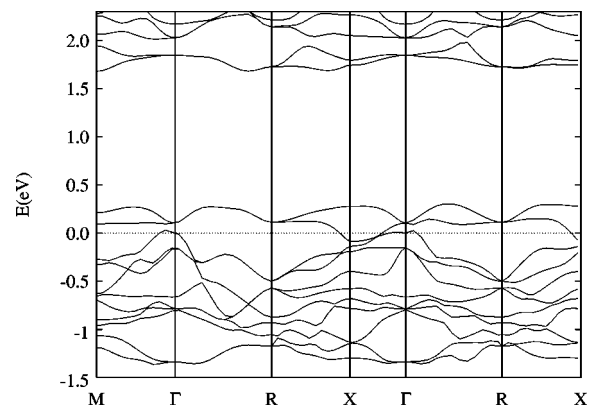

FIG. 1. Band structure of the Mo_6Se_8.

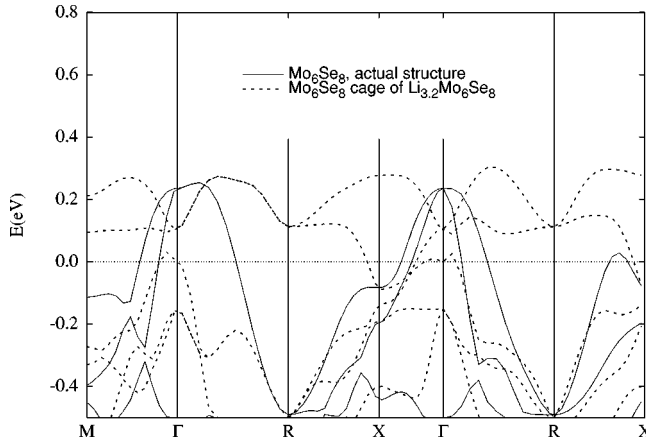FIG. 2. Band structure of the Mo_6Se_8 and of the same compound with the Mo and Se atoms in their position in $Li_{3.2}Mo_6Se_8$ (but without Li). Note the large changes due to relatively small changes in the Mo-Se and Mo-Mo bond lengths, and overall cell geometry.

FIG. 3. Band structure of the ordered rhombohedral $Li_3Mo_6Se_8$ compared with that of a hypothetical rhombohedral $Li_6Mo_6Se_8$.

tions focussing on the $Li_{4-\delta}Mo_6Se_8$ system. Note that in our studies we concentrated on the Se-based compounds, as opposed to more common sulfides. Se has higher mass, favorable for low κ_l. Furthermore, selenides tend to be more covalent,[15] which is better from the point of view of carrier mobility. Experimentally there is a large homogeneity region in the $Li_xMo_6Se_8$ pseudobinary phase diagram near $x=4$.[19]

Most of the calculations were based on the reported crystal structure of $Li_{3.2}Mo_6Se_8$.[16] We do not take, however, into account the trigonal distortion that was reported for $\delta < 0.4$ in Ref. 21. This is probably associated with partial ordering of the Li ions. Transport properties were obtained from the calculated LAPW electronic structures by Eq. (1) and the constant relaxation-time approximation.

In addition to providing the four extra electrons needed to dope the compound to the semiconducting regime, the insertion of Li in the interstitial sites leads to changes in the structure of the Mo-Se frame, e.g., upon saturation of the Mo-Mo bonds, the octahedron contracts and becomes more regular, and the Mo-Se distances increase. The corresponding changes in electronic structure are shown in Fig. 2, where the bands of Mo_6Se_8 near the valence-band edge are compared for two crystal structures: the experimental structure of the binary system and the structure of the Mo-Se frame in $Li_{3.2}Mo_6PSe_8$ (but without Li). Figure 2 indicates that the changes in the Mo-Se frame lead to an enhancement of the band masses. Moreover, the valence-band maxima are shifted to general k points, which implies that a larger number of valleys contribute to the transport integrals, enhancing σ without degrading S. On the other hand, this result again emphasizes the strong electron-phonon interaction in Chevrels, which will reduce mobility at high temperatures. This suggests the optimization as a TEM should be done for lower T operation (below room temperature).

While in the real material Li ions are disordered, we used for $Li_3Mo_6Se_8$ an ordering where the Li ions are in the outer interstitial ring, preserving the rhombohedral symmetry. This band structure is then used to compute the transport integrals for the semiconducting composition, under the assumption that 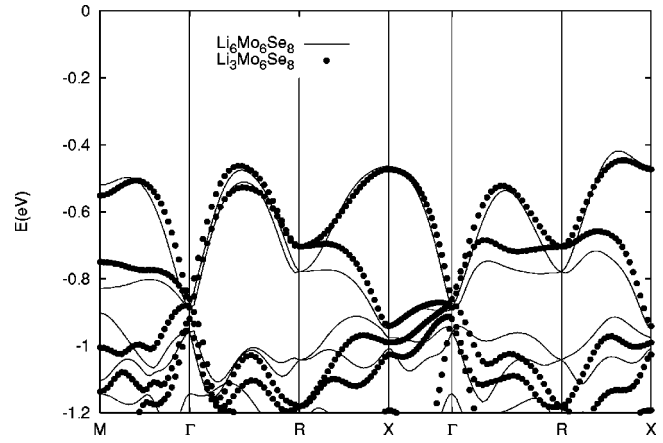the system follows a rigid band behavior as we fill the valence bands. In order to test this assumption, we also computed the band structure of $Li_6Mo_6Se_8$, with the three additional Li atoms in the inner ring, still keeping the rhombohedral symmetry (Fig. 3). The primary contribution to the transport properties is derived from the top of the valence band, which occurs along the R-X line in Fig. 3. The two sets of bands are very similar near the top of the bands, despite the very strong perturbation of the crystal potential by the three additional Li ions and three additional electrons. This indicates weak scattering due to Li disorder and vacancies, which is a prerequisite for 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 Γ-R directions, where the eigenvalues are shifted downwards in the $Li_6Mo_6Se_8$, 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 $x=4$ holds to a good approximation. This also shows that the potential felt by carriers at and near the E_F is only moderately affected by the exact position of the Li ions. The carrier mobility is determined by the electron scattering time, which in turn is defined by the change of the crystal potential upon moving Li atoms. Correspondingly, when the change is small, the carrier mobility is expected to be only weakly reduced by the disorder on the Li site. The negative effect on the mobility will be even further diminished by partial ordering of Li atoms, as occurs in $Li_{4-\delta}Mo_6Se_8$. (A phase transition to a lower symmetry phase has been reported for $\delta < 0.4$.[21]) Furthermore, although the ordering processes in the mixed-filler system $(Cu,Li)_{4-\delta}Mo_6Se_8$ have hardly been studied at all, one might anticipate that, say, $CuLi_3Mo_6Se_8$ (this compound forms), would be better ordered than $Li_4Mo_6Se_8$, and may also have lower κ_l due to Cu rattling.

The calculated thermopower 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 (3×10^{20} holes/cm³) we obtain a maximum Seebeck coefficient of ~ 150 μV/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 com-
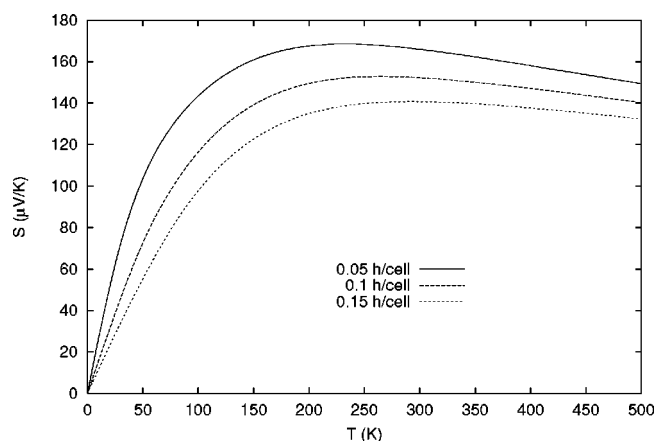
FIG. 4. Calculated thermopower of $Li_{4-\delta}Se_8$ for $\delta = 0.05, 0.1,$ and 0.15.

bined with reasonable κ_{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_6Se_8. The most promising from the point of view of potential thermoelectric applications is $Li_{4-\delta}Mo_6Se_8$, with $\delta \sim 0.1$. This material can possi-

bly 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) how the effects neglected in the current study, namely the local distortion of the Mo_6Se_8 cage near Li and partial ordering of Li atoms will effect the carrier mobility (the former lowers the mobility, and the latter increases it), (2) the role of the electron-phonon interaction, (3) whether the alloying with Li or Li/Cu would be effective in scattering heat conducting phonons, and (3) whether the material will not have compensating defects in Mo_6Se_8 clusters. Cu and Li filled Mo_6Se_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, $(Li,Cu)_{4-\delta} Mo_6Se_8$.

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