Crystal Structure, Charge Transport, and Magnetic Properties of MnSb$_2$Se$_4$

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**Dedicated to Professor John D. Corbett on the occasion of his 85th birthday**

**Keywords:** Manganese / Antimony / Selenium / Semiconductors / Magnetic properties / Thermoelectricity

A single phase of MnSb$_2$Se$_4$ was synthesized by combining high-purity elements at 773 K. Single-crystal X-ray diffraction revealed that MnSb$_2$Se$_4$ is isostructural with FeSb$_2$Se$_4$ crystallizing in the monoclinic space group $C2/m$ with $a = 13.076(3)$ Å, $b = 3.965(2)$ Å, $c = 15.236(4)$ Å, $\beta = 115.1(2)^\circ$, $Z = 4$. MnSb$_2$Se$_4$ melts congruently at 790 K and is thermally stable up to 1000 K. Electronic band structure calculations, infrared diffuse reflectance spectroscopy, and low-temperature electronic transport data indicate that MnSb$_2$Se$_4$ is a narrow-bandgap $p$-type semiconductor with an energy bandgap of approximately 0.31 eV and exhibits a sharp increase in the resistivity near 230 K. A large Seebeck coefficient ($S = +945 \mu$V K$^{-1}$), high electrical resistivity ($\rho = 9 \Omega m$), and low thermal conductivity ($\kappa = 1.4$ W m$^{-1}$ K$^{-1}$) were observed at 300 K. Direct current (DC) magnetic-susceptibility measurements indicated that MnSb$_2$Se$_4$ is paramagnetic at 300 K and undergoes an order/disorder antiferromagnetic transition with a Néel temperature of approximately 20 K. Alternating current (AC) susceptibility at various frequencies suggested a spin-glass-like behavior.

**Introduction**

Substantial progress has been made over the past two decades in the chemistry of multinary complex transition-metal chalcogenides, which has led to the discovery of several compounds that exhibit interesting physical properties$^{[1,2]}$ and show potential for applications in thermoelectricity,$^{[3–5]}$ spintronics,$^{[6]}$ nonlinear optics,$^{[7]}$ photoelectronics,$^{[8]}$ and solid-state electrolytes.$^{[9–11]}$ Among known complex transition-metal chalcogenides is the fascinating family of ternary MP$_n$Q$_4$ ($M = Fe, Mn; Pn = Sb, Bi; and Q = S, Se$) compounds with crystal structures that show 1D to 3D connectivity (depending on composition and synthetic method) as well as interesting physical properties.$^{[12–20]}$ For instance, MnSb$_2$S$_4$ synthesized by solid-state reaction crystallizes in the monoclinic lattice ($mC28$)$^{[18]}$ and is isotypic with HgBi$_2$S$_4$,$^{[21]}$ whereas an orthorhombic modification ($oP2_B2_1$) is isostructural with FeSb$_2$S$_4.$$^{[13]}$

was obtained from crystals of the same composition isolated from a hydrothermal preparation method. In the crystal structure of the orthorhombic and the monoclinic MnSb$_2$S$_4$, Mn$_8$ octahedra share edges to form single chains separated by the Sb$_2$S$_3$-type substructure. These isolated chains of Mn$_8$ octahedra represent the substructure that controls the magnetic properties,$^{[1,2,22,23]}$ whereas the electronic properties of the compound are controlled by the Sb$_2$S$_3$-type network that connects adjacent magnetic chains. Because of the unique spatial arrangement of atoms in the MP$_n$Q$_4$ structure, our research group has been very interested in how magnetism and electronic transport respond to modifications of the structure by altering M, P$_n$, and/or Q. For instance, electrical-conductivity and magnetic-susceptibility measurements revealed that MnSb$_2$S$_4$ is a semiconducting antiferromagnet with a Néel temperature ($T_N$) of 26.5 K and an energy bandgap ($E_g$) of 0.77 eV.$^{[15–17]}$ By modifying the nature of the Sb–S bonds that connect the magnetic and semiconducting subunits in MnSb$_2$S$_4$ through isoelectronic substitution of S by Se, we anticipate a significant alteration in electronic charge transport as well as the nature of coupling between adjacent magnetic chains. For instance, an energy bandgap smaller than that of MnSb$_2$S$_4$ ($E_g = 0.77$ eV) and high electrical conductivity are expected for MnSb$_2$Se$_4$ due to an increase in the degree of covalency of the Sb–Se bond.

MnSb$_2$Se$_4$ was first investigated by Kurowski and reported in his doctoral thesis.$^{[15]}$ Based on this work, four
different crystal structure models were proposed. The first model obtained from single-crystal structure refinement in the space group \( C2/m \) revealed the Mn(2a) site to be randomly occupied by Mn and Sb atoms with nearly equal statistical probability, thus leading to a charge-unbalanced distribution in MnSb\(_2\)Se\(_4\). The other three models have been obtained from Rietveld refinement using neutron diffraction data. Two of them considered Mn/Sb mixed occupancies at all the Mn and Sb positions and featured very large atomic displacement parameters for both Mn(2a) and Mn(2d) sites. The last model, which was similar to the ordered structure of HgBi\(_2\)S\(_4\), also showed large atomic displacement parameters for Mn atoms. Therefore, a conclusive structure model for MnSb\(_2\)Se\(_4\) could not be obtained from this early study. Another investigation (from the same research) of the MnSb\(_2\)Bi\(_3\)Se\(_4\) solid solution also revealed large discrepancies in the unit-cell parameters and atomic distribution in MnSb\(_2\)Se\(_4\).[24] Here, we report an accurate determination of the crystal structure of MnSb\(_2\)Se\(_4\) by using high-quality single crystals grown from a solid-state reaction of high-purity elements at 500 °C and discuss results of electronic and thermal transport, electronic structure, as well as direct current (DC) and alternating current (AC) magnetic-susceptibility data.

Results and Discussion

Synthesis and Characterization

A single-phase polycrystalline powder of MnSb\(_2\)Se\(_4\) was obtained through combination of elemental Mn, Sb, and Se at 773 K. Slow heating of the starting mixture to the reaction temperature with intermediate annealing at 573 K was necessary to produce a high-purity phase. Attempts to speed up the reaction by either eliminating the intermediate dwelling step or by slow cooling the starting mixture from the molten state resulted in polycrystalline samples with unreacted selenium as the main impurity phase. Rapid increase of the furnace temperature presumably results in high vapor pressure of the low-melting Se inside the sealed tube, thus leading to a reaction mixture with lower Se content. Upon cooling the furnace to room temperature, the Se vapor ultimately condenses and mixes with the reaction product. X-ray diffraction on polycrystalline powders of the synthesized compound (Figure 1) showed an excellent match with the theoretical pattern simulated from the single-crystal structure refinement. This indicates successful formation of nearly a single phase of MnSb\(_2\)Se\(_4\) and also attests to the accuracy of the proposed structural model. The accuracy of the structural model, as well as the successful synthesis of MnSb\(_2\)Se\(_4\), is also supported by the experimental density of 5.65(2) g cm\(^{-3}\) (measured using helium-gas pycnometry), which represents approximately 99% of theoretical density calculated from single-crystal structure data (Table 1). MnSb\(_2\)Se\(_4\) melts congruently at 790 K and shows no sign of decomposition after heating up to 1000 K (Figure 2). Upon cooling, MnSb\(_2\)Se\(_4\) fully recrystallizes at 771 K, thereby suggesting its high thermal stability. The absence of additional endothermic peaks on heating again suggests the successful synthesis of MnSb\(_2\)Se\(_4\) as a single phase.

![Figure 1. X-ray diffraction pattern of MnSb\(_2\)Se\(_4\) compared with the theoretical pattern calculated from the single-crystal structure refinement data.](image)

![Figure 2. Differential scanning calorimetry (DSC) of MnSb\(_2\)Se\(_4\) showing a single endothermic peak of congruent melting upon heating as well as a single recrystallization peak upon cooling.](image)

<table>
<thead>
<tr>
<th>Crystal system; space group</th>
<th>monoclinic; ( C2/m ) (no. 12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight [g mol(^{-1})]</td>
<td>614.28</td>
</tr>
<tr>
<td>Density (( \rho )) [g cm(^{-3})]</td>
<td>5.70</td>
</tr>
<tr>
<td>Lattice parameters [Å]</td>
<td>a ( = 13.076(3) ) ( b = 3.965(1) ) ( c = 15.236(3) ) ( \beta = 115.1(3) )</td>
</tr>
<tr>
<td>( V ) [Å(^3)]</td>
<td>716(2)</td>
</tr>
<tr>
<td>( Z )</td>
<td>4</td>
</tr>
<tr>
<td>Crystal size [mm]</td>
<td>0.04 × 0.09 × 0.25</td>
</tr>
<tr>
<td>Crystal shape, color</td>
<td>needle, black</td>
</tr>
<tr>
<td>Radiation [Å]</td>
<td>CuK(_\alpha) = 0.71073</td>
</tr>
<tr>
<td>( \mu ) [cm(^{-1})]</td>
<td>295</td>
</tr>
<tr>
<td>Diff. elec. density [e Å(^{-3})]</td>
<td>+1.36 to -1.35</td>
</tr>
<tr>
<td>( R ) ( =</td>
<td>F_o</td>
</tr>
<tr>
<td>( wR )</td>
<td>0.072</td>
</tr>
<tr>
<td>GoF</td>
<td>1.124</td>
</tr>
</tbody>
</table>

\( |F_o| = \Sigma |F_o| - |F_c|/|F_o| \) \( \times 100 \)%

\( wR = \Sigma w(F_o^2 - F_c^2) / \Sigma w(F_o^2)^{1/2} \).

The accuracy of the structural model, as well as the successful synthesis of MnSb\(_2\)Se\(_4\), is also supported by the experimental density of 5.65(2) g cm\(^{-3}\) (measured using helium-gas pycnometry), which represents approximately 99% of theoretical density calculated from single-crystal structure data (Table 1). MnSb\(_2\)Se\(_4\) melts congruently at 790 K and shows no sign of decomposition after heating up to 1000 K (Figure 2). Upon cooling, MnSb\(_2\)Se\(_4\) fully recrystallizes at 771 K, thereby suggesting its high thermal stability. The absence of additional endothermic peaks on heating again suggests the successful synthesis of MnSb\(_2\)Se\(_4\) as a single phase.
Crystal Structure

MnSb₂Se₄ is isostructural with FeSb₂Se₄[14] crystallizing in the monoclinic space group C2/m (no. 12) with lattice parameters, \( a = 13.076(3) \) Å, \( b = 3.965(1) \) Å, \( c = 15.236(3) \) Å, \( \beta = 115.1(3) \)° (Table 1). The observed slight increase in the unit-cell parameters of MnSb₂Se₄ relative to those of FeSb₂Se₄ is consistent with the difference in the effective ionic radii of Mn (0.83 Å) and Fe (0.78 Å) in sixfold coordination.[25] The structure (Figure 3) contains two crystallographically independent Mn atoms located at special positions Mn(3) (2d) and Mn(4) (2a) (Table 2). The Mn(3) position is fully occupied by Mn, whereas the Mn(4) position contains 19% Sb. Both Mn positions are coordinated by six selenium atoms with Mn(3) located in a disordered (1+2+2+1) octahedral coordination (Figure 3, A). Both A and B slabs are linked along the c axis by a rather long Sb–Se bond of 3.116(2) Å 1D \([\text{Mn}(4)\text{Se}_6]\) chains (Figure 3, A). Alternatively, the structure of MnSb₂Se₄ can be better described as a one-dimensional arrangement of \([\text{Mn}\{\text{Sb}_2\text{Se}_4\}]\) chains of edge-sharing octahedra parallel to [010], thus giving the rather long Sb–Se bonds (dashed bonds in Figure 3, a) interconnecting individual chains.

![Figure 3](image_url)

Table 2. Atomic coordinates, Wyckoff positions (W.P.), site-occupancy factors (\(k\)), and equivalent isotropic displacement parameters \(U_{eq}/10^4 \) Å\(^2\) for all atoms in the asymmetric unit of MnSb₂Se₄.

<table>
<thead>
<tr>
<th>Atom</th>
<th>W.P.</th>
<th>(k)</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{eq}[\text{Å}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(1)</td>
<td>4i</td>
<td>0.95</td>
<td>0.2738(2)</td>
<td>0</td>
<td>0.6334(2)</td>
<td>267(3)</td>
</tr>
<tr>
<td>Mn(1)</td>
<td>4i</td>
<td>0.05</td>
<td>0.2738(2)</td>
<td>0</td>
<td>0.6334(2)</td>
<td>267(3)</td>
</tr>
<tr>
<td>Sb(2)</td>
<td>4i</td>
<td>0.96</td>
<td>0.3554(2)</td>
<td>0</td>
<td>0.1260(2)</td>
<td>242(3)</td>
</tr>
<tr>
<td>Mn(2)</td>
<td>4i</td>
<td>0.04</td>
<td>0.3554(2)</td>
<td>0</td>
<td>0.1260(2)</td>
<td>242(3)</td>
</tr>
<tr>
<td>Mn(3)</td>
<td>2d</td>
<td>0</td>
<td>1/2</td>
<td>1/2</td>
<td>265(7)</td>
<td></td>
</tr>
<tr>
<td>Sb(4)</td>
<td>2a</td>
<td>0.19</td>
<td>0</td>
<td>0</td>
<td>252(9)</td>
<td></td>
</tr>
<tr>
<td>Mn(4)</td>
<td>2a</td>
<td>0.81</td>
<td>0</td>
<td>0</td>
<td>252(9)</td>
<td></td>
</tr>
<tr>
<td>Se(1)</td>
<td>4i</td>
<td>0.0123(2)</td>
<td>0</td>
<td>0.1799(2)</td>
<td>269(4)</td>
<td></td>
</tr>
<tr>
<td>Se(2)</td>
<td>4i</td>
<td>0.1143(2)</td>
<td>0</td>
<td>0.4575(2)</td>
<td>228(4)</td>
<td></td>
</tr>
<tr>
<td>Se(3)</td>
<td>4i</td>
<td>0.3446(2)</td>
<td>0</td>
<td>0.2727(2)</td>
<td>243(4)</td>
<td></td>
</tr>
<tr>
<td>Se(4)</td>
<td>4i</td>
<td>0.6549(2)</td>
<td>0</td>
<td>0.0533(2)</td>
<td>246(4)</td>
<td></td>
</tr>
</tbody>
</table>

[a] \(U_{eq}\) is defined as one-third of the trace of the orthogonalized \(U_{ij}\) tensor.

Table 3. Selected interatomic distances [Å] in MnSb₂Se₄ at 300 K.[4]

<table>
<thead>
<tr>
<th>Atom</th>
<th>W.P.</th>
<th>(k)</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{eq}[\text{Å}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(1)(Mn(1))–Se(2)</td>
<td>2.670(2)</td>
<td>Mn(3)–Se(3)(^{\mu})</td>
<td>2.550(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb(1)(Mn(1))–Se(3)(^{\mu})</td>
<td>2.731(2)</td>
<td>Mn(3)–Se(3)(^{\mu})</td>
<td>2.550(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb(1)(Mn(1))–Se(3)(^{\mu})</td>
<td>2.731(2)</td>
<td>Mn(3)–Se(2)(^{\mu})</td>
<td>2.721(2)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Sb(2)(Mn(1))–Se(2)(^{\mu})</td>
<td>3.116(2)</td>
<td>Mn(3)–Se(3)(^{\mu})</td>
<td>2.721(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb(1)(Mn(1))–Se(2)(^{\mu})</td>
<td>3.116(2)</td>
<td>Mn(3)–Se(2)</td>
<td>2.721(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb(2)(Mn(1))–Se(1)(^{\mu})</td>
<td>6.202(2)</td>
<td>Mn(3)–Se(2)</td>
<td>2.721(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb(2)(Mn(1))–Se(1)(^{\mu})</td>
<td>6.202(2)</td>
<td>Mn(4)[Sb(4)–Se(1)]</td>
<td>2.676(2)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Sb(2)(Mn(2))–Se(4)(^{\mu})</td>
<td>2.674(2)</td>
<td>Mn(4)[Sb(4)–Se(1)]</td>
<td>2.676(2)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sb(2)(Mn(2))–Se(1)(^{\mu})</td>
<td>2.718(2)</td>
<td>Mn(4)[Sb(4)–Se(4)] (^{\mu})</td>
<td>2.702(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb(2)(Mn(2))–Se(4)(^{\mu})</td>
<td>2.718(2)</td>
<td>Mn(4)[Sb(4)–Se(4)] (^{\mu})</td>
<td>2.702(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb(2)(Mn(2))–Se(4)(^{\mu})</td>
<td>3.093(2)</td>
<td>Mn(4)[Sb(4)–Se(4)] (^{\mu})</td>
<td>2.702(2)</td>
<td></td>
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<tr>
<td>Sb(2)(Mn(2))–Se(3)</td>
<td>3.138(2)</td>
<td>Mn(4)[Sb(4)–Se(4)] (^{\mu})</td>
<td>2.702(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

[a] Operators for generating equivalent atoms: (i) \(1/2 – x, –1/2 – y, 1 – z\); (ii) \(1/2 – x, 1/2 – y, 1 – z\); (iii) \(1 – x, –y, –z\); (iv) \(1/2 + x, 1/2 + y, –z\); (v) \(1/2 + x, –1/2 + y, –z\); (vi) \(1/2 – x, –1/2 – y, z\); (vii) \(1/2 – x, 1/2 + y, z\); (viii) \(1, 1 + y, z\); (ix) \(–x, –y, 1 – z\); (x) \(1 – x, 1 – z\); (xi) \(1 – x, –y, –z\); (xii) \(1/2 – x, –1/2 – y, –z\); (xiii) \(1/2 – x, 1/2 – y, –z\).
Magnetism

Figure 4(a) shows the magnetic susceptibility and the inverse susceptibility of the synthesized polycrystalline powders of MnSb$_2$Se$_4$ measured at 100 and 1000 Oe. The susceptibility exhibits a broad peak at 20 K, which suggests an ordering of Mn magnetic moments at low temperatures. The susceptibility data above 120 K could be fitted to the Curie–Weiss law with a Curie constant of 5.48 emu K mol$^{-1}$ and a Weiss constant of $-74$ K. The corresponding effective magnetic moment is $\mu_{\text{eff}} = 5.82(2) \mu_B$ per Mn atom. This value is relatively close to the expected theoretical value of $\mu_{\text{eff}} = 5.92 \mu_B$ for Mn$^{2+}$ (3d$^5$) in the high-spin configuration, thereby confirming our assignment of the oxidation state of Mn ions (2+) in the crystal structure. The large negative value of the Weiss constant indicates that the interaction between the Mn$^{2+}$ magnetic moments is predominantly antiferromagnetic (AFM). However, the slight increase in the susceptibility observed below 5 K (Figure 4, inset) also suggests the existence of a small ferromagnetic (FM) ordering in the sample at very low temperatures. In addition, the observed strong dependence of the magnetic susceptibility below 20 K on the applied magnetic field, the shift of the blocking temperature to lower values with the increase in the applied magnetic field, as well as the difference between the ZFC and FC data suggests competing magnetic ordering similar to spin-glass behavior within the sample.[26] To better assess this magnetic behavior, AC susceptibility measurements at various frequencies and different amplitudes of the excitation field were performed. Figure 4(b) shows the in-phase part, $\chi'$, of the AC susceptibility of MnSb$_2$Se$_4$ for selected frequencies between 500 and 10000 Hz. The amplitudes and positions of the peak maxima ($T_{\text{max}}$) depend on the frequency of the applied AC magnetic field (Figure 4, b, inset). $T_{\text{max}}$ gradually shifts to higher temperatures, and the peak intensity decreases with increasing frequency, which indicates that the peaks are associated with the onset of spin freezing. These features are typical for classical spin-glass systems such as Cu$_{1-x}$Mn$_x$ and Au$_{1-x}$Mn$_x$ alloys.[26–29] A quantitative measure of the change in the freezing temperature with frequency in spin-glass materials is obtained by calculating the Mydosh parameter ($K$) defined as the relative shift of the maximum temperature ($T_{\text{max}}$) per decade of frequency.[26] The estimated $K = \Delta T_{\text{m}}/[T_{\text{m}}\log(co)] = 0.013$ is about three times higher than $K$ values found in spin-glass systems such as Cu$_{1-x}$Mn$_x$ ($K = 0.005$) and Au$_{1-x}$Mn$_x$ ($K = 0.0045$) and suggests that the relaxation behavior is consistent with a spin-glass-like behavior. However, in most spin-glass systems, the magnitude of the AC susceptibility below $T_{\text{max}}$ is frequency-dependent and becomes independent of the frequency above $T_{\text{max}}$.[30] Therefore, the observed dependence of the magnitude of the AC susceptibility above and below $T_{\text{max}}$ upon frequencies (Figure 4, b, inset) suggests that the downturn on the magnetic-susceptibility curves (ZFC and FC) of MnSb$_2$Se$_4$ is more complicated in nature. A tentative explanation of this behavior is provided below.

To understand the magnetic behavior of MnSb$_2$Se$_4$, we have carefully analyzed geometrical details of the [MnSe$_6$]$^{2-}$ magnetic chains, their arrangement in the 3D structure, and the coupling (intrachain and interchain) between localized spins on adjacent Mn atoms by using the Goodenough–Kanamori rules.[31–33] As described above, the Mn3 atom is located in a distorted octahedral geometry, [Mn(3)Se$_2$]$_2^-$ with two apical short bonds [2.550(2) Å] and four equatorial long bonds [2.721(2) Å]. Despite the fact that Mn$^{2+}$ (3d$^5$) is not a Jahn–Teller ion, this kind of severe distortion of the octahedral coordination results in a Jahn–Teller-type splitting of the d orbitals, thus leading to an increase in the energy level of $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals. This suggests the orbital and spin distribution ($d_{xy}$),$^1(d_{xz})^1(d_{yz})^1(d_{xy})^1$ leads to a total spin value of $S = 5/2$ (high spin). The more regular octahedral coordination of the Mn(4) atom ($[\text{Mn}(4)\text{Se}_6]$ suggests an octahedral splitting of 3d$^5$ orbitals with spin distribution of ($d_{xz}$, $d_{yz}$, $d_{xy}$)$^1(d_{xz})^1(d_{yz})^1$, which corresponds to a total spin value of $S = 5/2$ (high spin). The total number of spin, $S = 5/2$ for both Mn3 and

![Figure 4](image-url)
Studies on MnSb₂Se₄

Mn₄ atoms, is consistent with the effective magnetic moment calculated from the magnetic-susceptibility data. The structure of MnSb₂Se₄ can therefore be regarded as layers A and B of magnetic chains alternating along the c axis. The magnetic behavior of MnSb₂Se₄ therefore depends on the interactions between adjacent magnetic atoms within a single chain (intrachain) and/or the interchain interactions. The shortest distance between magnetic chains in adjacent magnetic layers is around 7.653 Å, and the intralayer separation between magnetic chains is around 6.832 Å (Figure 3, a). These distances are too long for direct or indirect magnetic exchange interactions between neighboring magnetic chains, thereby suggesting that MnSb₂Se₄ is a quasi-1D magnetic system. Therefore, the magnetic behavior of the compound is controlled by the nature and magnitude of exchange interactions between adjacent magnetic atoms in [[Mn(3)]₆Se₆]⁻ and [[Mn(4)]₆Se₆]⁻ magnetic chains. However, Mn atoms within individual chains (along [010]) are 3.965 Å apart (Figure 3, b). This separation is too long for direct magnetic exchange interactions between the magnetic moments on neighboring Mn atoms. Therefore, adjacent Mn(3) and Mn(4) atoms are magnetically coupled by indirect exchange interactions through the bridging Se atoms. For instance, the observed Mn(3)–Se(2)–Mn(3) bond angle of 93.6° within the [[Mn(3)]₆Se₆]⁻ chain suggests antiferromagnetic or weak ferromagnetic coupling of spins localized on adjacent Mn(3) atoms. Within the [[Mn(4)]₆Se₆]⁻ chain, two Mn(4)–Se(4)–Mn(4) coupling paths with bond angles of 92.3 and 94.4° are possible, thereby indicating competition between AFM and FM ordering of spins localized on adjacent Mn(4) atoms (Figure 3, c). This magnetic frustration within the [[Mn(3)]₆Se₆]⁻ and [[Mn(4)]₆Se₆]⁻ chains are believed to be responsible for the observed broad downturn of the magnetic susceptibility at 20 K as well as the frequency dependence of the peak (T_max) position and amplitude. Upon cooling the sample below 5 K, the FM coupling presumably begins to dominate, thus leading to the observed increase in the DC magnetic susceptibility.

Optical and Charge-Transport Properties

The diffuse reflectance infrared absorption spectrum of MnSb₂Se₄ was recorded at room temperature in the range 0.05–0.5 eV. The bandgap estimated from the absorption coefficient/scattering coefficient (αS) ratio versus energy plot is about 0.32 eV, which indicates that the compound is a narrow-bandgap semiconductor at 300 K (Figure 5, a). The observed value of the energy gap is comparable to the optical bandgap of FeSb₂Se₄ (E_g = 0.33 eV)[14] and is consistent with the black color of the MnSb₂Se₄ crystals. The temperature dependence of the electrical resistivity (ρ) of MnSb₂Se₄ was measured from 100 to 300 K (Figure 5, b). At room temperature, the electrical resistivity is approximately 8.9 Ωm and slightly increases with decreasing temperature down to about 230 K. This trend is consistent with the semiconducting nature of the compound. The observed large value of the electrical resistivity of MnSb₂Se₄ at 300 K presumably originates from the quasi-1D nature of the crystal structure in which individual [[Mn]₆Se₆]⁻ chains parallel to [010] are only weakly interconnected along [100] and [001] through long Sb–Se bonds to the 3D network (Figure 3, a). The resistivity rises rapidly with further decreases in the temperature, and below 180 K, it attained such high
values (>10 kΩm) that the noise precluded collection of the data (Figure 5, b). The rapid increase in the resistivity is similar to the one observed in FeSb₂Se₄[14]. From the Arrhenius plot (Figure 5, b, inset), we calculate the bandgap value to be 0.52 eV. This value is consistent with the observed optical bandgap, thereby confirming again the semiconducting character of MnSb₂Se₄ at 300 K. Figure 5 (c) shows the temperature dependence of the Seebeck coefficient of MnSb₂Se₄ from 200 to 300 K. Positive values of the Seebeck coefficient were observed in the whole measured temperature range, thereby indicating that MnSb₂Se₄ is a p-type narrow-gap semiconductor. The Seebeck data have progressively larger error bars as the temperature decreases due to the noise on the Seebeck voltage contacts associated with the rapid rise in electrical resistivity. The Seebeck coefficient at 300 K is around 950 μVK⁻¹ and gradually increases with the decreasing temperature to a value of about 1050 μVK⁻¹ at 200 K. The temperature dependence of the total thermal conductivity of MnSb₂Se₄ is shown in Figure 5 (d). Because of the large electrical resistivity of MnSb₂Se₄ in the measured temperature range, the electronic contribution to the thermal conductivity (κₑₑc.) is negligible. Therefore, the observed thermal conductivity values essentially correspond to the lattice contribution (κₙₙₙ.). At 300 K, the lattice thermal conductivity of MnSb₂Se₄ is 1.4 Wm⁻¹K⁻¹ (Figure 5, d). This low value of the lattice thermal conductivity of MnSb₂Se₄ can be attributed to the combination of low crystal symmetry and complex structure and chemical composition with heavy elements such as Sb and Se. The lattice thermal conductivity of MnSb₂Se₄ gradually increases with decreasing temperature and a κₙₙₙₙ value of 2.1 Wm⁻¹K⁻¹ was measured at 90 K. The observed increase in the lattice thermal conductivity with decreasing temperature is consistent with a gradual freezing of phonon umklapp processes.

Electronic Structure

Electronic band structure calculations of MnSb₂Se₄ show a small energy gap of around 0.3 eV in a narrow window around the Fermi level (Eₕ) (Figure 6, a). This value is consistent with the observed optical bandgap as well as the activation energy near room temperature, thus further confirming the room-temperature semiconducting character of MnSb₂Se₄. The site-projected density of states (DOS) for one formula unit of nonmagnetic MnSb₂Se₄ (Figure 6, b), shows that the highest-occupied states cross the Fermi level at high density of states, which is attributed to Mn²⁺ t₂g states. The next occupied bands above Eₕ are formed by Mn²⁺ εₐ states. The electron distribution of the d orbital could be t₂g³ (dₓᵧ, dₓz, dᵧz)¹ and εₐ² (dₓ²–y², dₓz, dᵧz)¹, thus confirming the magnetic effective moment calculated from magnetic-susceptibility data. The large broad bands in the energy range from −4 to −1 eV are dominated by bonding p states of Sb and Se, whereas the bottom of the conduction band is based mainly on empty Mn p orbitals. The analysis of bonding interactions between atoms in MnSb₂Se₄ by using the crystal orbital Hamiltonian population (COHP) method[34] showed that the major part of the valence band between −3 and −1 eV is dominated by Mn–Se bonding interactions, whereas at the top of the valence band, Sb–Se and Mn–Se interactions dominate the antibonding interactions (Figure 6, c). The Mn(3)–Se interactions contribute more strongly to the covalent bonding than Mn(4)–Se in the energy range of −3 to −1 eV, and around the Fermi level both Mn(3)–Se and Mn(4)–Se equally contribute to the antibonding. Despite the significant antibonding interactions at Eₕ, the compound is stable because of the positive values of integrants, −ICOHP (Table 4), which predominantly emphasize the bonding character of orbitals below Eₕ. Above the Fermi level, all states are strongly antibond-
ing, which suggests destabilization of the compound upon atomic substitutions by more electron-rich elements if the crystal structure of the phase remained the same.

Table 4. –ICOHP for the Sb(1), Sb(2), Mn(3), and Mn(4) sites in MnSb2Se4.

<table>
<thead>
<tr>
<th>Bond</th>
<th>No.</th>
<th>Bond length</th>
<th>–ICOHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn3–Se2</td>
<td>4</td>
<td>2.721(2)</td>
<td>1.26</td>
</tr>
<tr>
<td>Mn3–Se3</td>
<td>2</td>
<td>2.550(2)</td>
<td>1.86</td>
</tr>
<tr>
<td>Mn4–Se1</td>
<td>2</td>
<td>2.676(2)</td>
<td>1.81</td>
</tr>
<tr>
<td>Mn4–Se4</td>
<td>4</td>
<td>2.702(2)</td>
<td>1.53</td>
</tr>
<tr>
<td>Sb1–Se2</td>
<td>2</td>
<td>3.116(2)</td>
<td>0.21</td>
</tr>
<tr>
<td>Sb1–Se2</td>
<td>1</td>
<td>2.607(2)</td>
<td>2.32</td>
</tr>
<tr>
<td>Sb1–Se3</td>
<td>2</td>
<td>2.731(2)</td>
<td>1.64</td>
</tr>
<tr>
<td>Sb2–Se1</td>
<td>2</td>
<td>2.718(2)</td>
<td>1.77</td>
</tr>
<tr>
<td>Sb2–Se3</td>
<td>1</td>
<td>3.138(2)</td>
<td>0.22</td>
</tr>
<tr>
<td>Sb2–Se4</td>
<td>1</td>
<td>2.674(2)</td>
<td>1.88</td>
</tr>
<tr>
<td>Sb2–Se4</td>
<td>2</td>
<td>3.093(2)</td>
<td>0.32</td>
</tr>
<tr>
<td>Sb1–Se1</td>
<td>2</td>
<td>3.622(2)</td>
<td>0.01</td>
</tr>
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</table>

Finally being cooled slowly to room temperature over 48 h. Several needle-shaped black crystals suitable for single-crystal X-ray structure determination were selected from the resulting polycrystalline product. The remaining sample was ground to a powder, and a high density (>95%) pellet for physical properties measurements was fabricated using a uniaxial hot press.

**Powder X-ray Diffraction (PXRD):** To assess the phase purity of the synthesized polycrystalline powder, PXRD data were collected using curved graphite crystal monochromated Cu-Kα radiation (λ = 1.54056 Å) in reflection geometry with a Philips X-ray powder diffractometer equipped with a position sensitive scintillation counter and operating at 45 kV and 40 mA. The experimental X-ray diffraction pattern was subsequently matched with the theoretical pattern simulated by using single-crystal structure data.

**Single-Crystal Structure Refinement:** A black needle-shaped single crystal of MnSb2Se4 with approximate dimensions of 0.04 × 0.09 × 0.25 mm³ was used for X-ray data collection. Intensity data were recorded at 300 K with a STOE Imaging Plate Diffraction System (IPDS-2T) using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and were indexed in the monoclinic crystal system with cell parameters a = 13.076(6) Å, b = 3.9651(8) Å, c = 15.236(4) Å and β = 115.11(6)°, which are similar to the unit-cell parameters of FeSb2Se4.[14] Therefore, atomic positions of FeSb2Se4 were used as starting model for the structure refinement in the space group C2/m (no. 12) using the SHELXTL package.[35] Initially, Sb atoms were assigned to the general positions M(1)(4) and M(2)(4) located respectively in a distorted octahedral and square-pyramidal coordination, whereas Mn atoms were located in special positions M(3)(2d) and M(4)(2a) with octahedral coordination. The refinement of this model using full-matrix least-squares techniques resulted in R1 = 5% with reasonable thermal parameters for all atoms except Mn(4), which displayed a smaller thermal parameter than those of the Sb atoms. This suggested Mn/Sb mixed occupancy at the M(4) position. To allow for a charge-balanced final composition, Sb/Mn mixed occupancy at the M(1), M(2), and M(3) positions was also considered. The refinement of this model resulted in more uniform thermal parameters for all atoms and an almost neutral composition with about 5% Mn in each of the Sb(1) and Sb(2) sites, whereas the M(3) position remained fully occupied by Mn. In the final refinement cycles, an electro-neutrality restraint was included along with a secondary extinction correction and anisotropic displacement parameters for all atoms. The occupancy factors at M(1), M(2), and M(4) positions were refined to the final values of M(1) = 95%, Sb + 5% Mn, M(2) = 96% Sb + 4% Mn, and M(4) = 81% Mn + 19% Sb, which led to the final charge-balanced composition Mn0.995(3)Sb2.005(3)Se4 assuming 2+, 3+, and 2– oxidation states for Sb and Mn atoms in MnSb2Se4, respectively. The final assignment of Sb and Mn atoms at metal positions and the suggested oxidation state for Sb and Mn atoms in MnSb2Se4 is consistent with the results of bond valence sum (BVS) calculations[36] Mn(1): 2.8; Sb(2): 2.8; Mn(3): 2.3; Mn(4): 2.2. Summary of crystallographic data for MnSb2Se4 are given in Table 1. The atomic coordinates and isotropic displacement parameters of all atoms are given in Table 2. Selected interatomic distances are gathered in Table 3. The software Diamond[37] was utilized to create the graphic representation of the crystal structure with an ellipsoid representation (98% probability level) for all atoms.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Egg-enstein-Leopoldshafen, Germany (fax: +49-7247-808-666; E-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-421940.
**Differential Scanning Calorimetry (DSC):** Differential scanning calorimetry data were recorded with a 404-F1 DSC apparatus (NETZSCH) by using approximately 15 mg of the synthesized compound sealed in a small quartz tube under a residual pressure of ca. $10^{-3}$ Torr. An equivalent mass of alumina (Al$_2$O$_3$) was used as the reference. The sample and reference were simultaneously heated to 1073 K at a rate of 20 K min$^{-1}$, isothermed for 2 min, and then cooled to 423 K at a rate of 20 K min$^{-1}$. DSC data were recorded during two heating and cooling cycles. The endothermic onset temperature is reported as the melting point, and the exothermic onset temperature is the crystallization point.

**Infrared Spectroscopy:** To probe the optical bandgap of MnSb$_2$Se$_4$, room-temperature diffuse reflectance infrared spectroscopy was performed in the 400–4000 cm$^{-1}$ region with a Thermo Nicolet NEXUS 670 FTIR spectrometer. The reflectance data were converted into absorption data by using the Kubelka–Munk function $a/S = (1 - R)^2/2R$ (in which $R$ is the reflectance at a given wavelength, $a$ is the absorption coefficient, and $S$ is the scattering coefficient), and the optical bandgap was estimated from an absorption $(a/S)^{38,39}$ versus energy plot.

**Magnetic Measurements:** DC and AC magnetic-susceptibility measurements were performed on polycrystalline MnSb$_2$Se$_4$ powder (53 mg) with a superconducting quantum interference device (SQUID). DC susceptibility data in FC and ZFC modes were recorded over a temperature range from 2 K to 300 K with an applied field of 100 and 1000 Oe. AC susceptibility data at various frequencies (500 Hz to 10 kHz) were recorded between 2 and 300 K in an applied field of 10 Oe.

**Charge-Transport Measurements:** A rectangular-shaped specimen with dimensions of $2.4 \times 2.6 \times 11$ mm$^3$ cut from a 96% dense hot-pressed pellet of MnSb$_2$Se$_4$ was used for low-temperature measurements of electrical conductivity, the Seebeck coefficient, and thermal conductivity. Electrical conductivity was measured by a four-probe method using a high-sensitivity AC bridge with an excitation frequency of 17 Hz. The Seebeck coefficient and the thermal conductivity at $T \leq 300$ K were measured by using a longitudinal steady-state technique with calibrated Au/Fe/Chromel-P thermocouples (Omega Corp.) traceable to the National Institute of Standards and Technology (NIST) standards and with copper leads serving as voltage probes.

**Electronic Structure Calculations:** The electronic structure of MnSb$_2$Se$_4$ was calculated with the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA) by using the tight-binding program TB-LMTO-ASA.[40] A charge-balanced model was constructed by assigning Sb atoms at M(1) and M(2) positions, whereas Mn atoms were located at the M(3) and M(4) sites. The radii of the Wigner–Seitz (WS) spheres were assigned automatically so that the overlapping potentials would be the best possible approximations to the full potentials, and an interstitial sphere was necessary with the default 16% overlap restriction.[40] Since the structure of MnSb$_2$Se$_4$ is rather open, special care was taken in filling the interatomic space. Using only atom-centered spheres resulted in errors because of overlaps that were too large.

**Acknowledgments**

This work was supported by the National Science Foundation (CAREER Award DMR-0954817), the Louisiana Board of Regents [grant number NSF(2008)-PFUND-126], and the University of New Orleans Office of Research and Sponsored Programs (SoCoRe2009 award). The authors thank Prof. John Wiley (UNO) for granting access to his group’s X-ray powder diffractrometer. Transport measurements at the University of Michigan are supported as part of the Revolutionary Materials for Solid-State Energy Conversion, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Science under award number DE-SC001054.

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Studies on MnSb$_2$Se$_4$


Received: April 5, 2011
Published Online: August 22, 2011