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HfMoSb$_4$, the first nonmetallic early transition metal antimonide

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HfMoSb$_4$, isostructural with the isoelectronic NbSb$_2$, exhibits nonmetallic properties, as predicted *via* electronic structure calculations made before the actual discovery of HfMoSb$_4$.

All known antimonides of the valence-electron poor (early) transition metal elements are metallic. This includes the most antimony-rich binary and ternary examples, *e.g.* TiSb$_2$ and VSb$_2$,[1,2] ZrSb$_2$,[3] Zr$_{11}$Sb$_{18}$,[4] Hf$_5$Sb$_9$,[5] Zr$_2$V$_6$Sb$_9$[6] and Mo$_3$Sb$_7$.[7] Since small band gaps are essential for thermoelectric energy conversion,[8–10] the metallic character prohibits using these materials for this purpose. Aside from that, these antimonides appear to be good candidates for thermoelectrics. Hence we are interested in modifying the antimonides to render them nonmetallic.

We carried out LMTO[11,12] band structure calculations for all of the above-mentioned antimonides. Mo$_3$Sb$_7$ is the only compound of this family whose band structure exhibits a gap in the vicinity of (albeit not directly at) the Fermi level. We recently succeeded in replacing part of the Sb atoms of Mo$_3$Sb$_7$ with Te atoms, thereby raising the Fermi level (E_F) into the band gap, which resulted in semiconducting properties of the antimonide–telluride Mo$_3$Sb$_5$Te$_2$.[13,14] On the other hand, the densities of states of both ZrSb$_2$ and NbSb$_2$ exhibit a local minimum directly at E_F, which is more pronounced in the Nb case. Therefore we turned our attention to NbSb$_2$, planning to render it semiconducting by chemical modification.

NbSb$_2$ forms a structure of the OsGe$_2$ type, with the Nb atoms surrounded by eight Sb atoms in the form of a bicapped trigonal prism, and one Nb–Nb bond of 3.14 Å occurs as a consequence of the condensation of two (bicapped) NbSb$_8$ prisms *via* a common rectangular face (Fig. 1).[15,16]

While the Sb1 atoms do not participate in any homonuclear contacts <3.3 Å, the Sb2 atoms form puckered layers with one short Sb–Sb bond of 2.77 Å and two intermediate ones of 3.04 Å per Sb atom. Typical Sb–Sb single bond distances are around 2.8 Å,[17–19] and Sb–Sb distances of 3.0 Å–3.1 Å are often considered to have a bond order of ½.[6,20–22] Treating the former as a full bond and the latter as a half bond, one can assign the oxidation states to be Nb^{+4}, Sb1^{-3} and Sb2^{-1}. According to this, one 4d electron per Nb atom is available for the Nb–Nb bond. However, the Nb–Nb distance of 3.14 Å is much longer than expected for a single bond (*cf.* Pauling's single bond radius of 1.34 Å[23]). This indicates that the counting scheme may only be a crude approximation, also considering that additional Sb–Sb contacts of the order of 3.3 Å may exhibit (weak) bonding character as well.[24]

According to our LMTO calculations, NbSb$_2$ is metallic, since a few bands of mostly Nb d character cross the Fermi level (E_F, arbitrarily placed at 0 eV in Fig. 2) along several directions, regardless of which structure model (Kjekshus[15] or Kauzlarich[16]) is used.

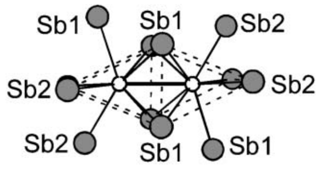

Fig. 1 Nb-centered bicapped trigonal prism pair of NbSb$_2$. White circles: Nb; grey: Sb. The dashed lines indicate the edges of the trigonal prisms.

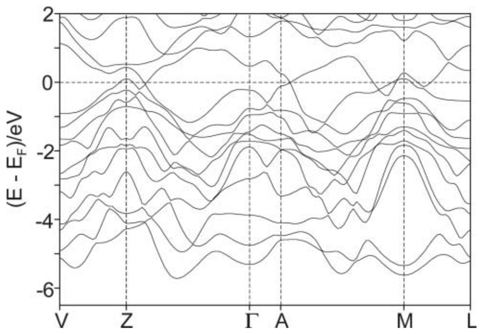

Fig. 2 Band structure of NbSb$_2$.

Can the band crossing of E_F be avoided, *e.g.* by polarizing the M–M interaction? A model calculation, based on replacing the Nb atom pair with one Hf and one Mo atom, resulted in a very small band gap of the (then-hypothetical) Hf$_{0.5}$Mo$_{0.5}$Sb$_2$ ≡ HfMoSb$_4$. Subsequently we successfully synthesized HfMoSb$_4$ by reacting the elements in the stoichiometric ratios at 850 °C in ceramic crucibles sealed in evacuated fused silica tubes. According to our single crystal data measured at room temperature on an Apex CCD (Bruker), HfMoSb$_4$ is isomorphous with NbSb$_2$: it crystallizes in the monoclinic space group *C2/m*, with lattice dimensions of a = 10.321(3) Å, b = 3.6475(9) Å, c = 8.393(2) Å, and β = 119.895(5)°, with residual factors of $R(F)$ = 0.043 and $R(F^2)$ = 0.088. The one metal atom site M present in this structure is mixed; occupied by 50.1(5)% Hf and 49.9% Mo, with no evidence of long range ordering. In part mixed Hf/Mo occupancies were also found in the metallic phosphide Hf$_{5.08}$Mo$_{0.92}$P$_3$.[25] A tentative refinement in *Cm* yielded no difference between the therein two symmetry-independent metal sites. Further details of the structure studies can be obtained from the Fachinformations-zentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-414284.

According to our experiments, HfMoSb$_4$ is not accessible below 800 °C. Changing the synthesis conditions, *e.g.* to long-time tempering at lower temperatures such as 500 °C after heating to 800 °C, did not yield noticeable changes according to an additional single crystal structure study, *i.e.* again no long-range ordering of the Hf and Mo atoms. Preliminary investigations indicated a very small phase range. Thus far, we were unable to synthesize the Zr/Mo and Hf/W analogue.

The (formal) replacement of two Nb atoms with one Hf and one Mo atom results in an increase of all lattice parameters, for a total volume increase of 2.1% at room temperature. The sums of Pauling's single bond radii concur with this observation: $2 \times r_{\mathrm{Nb}}$ = 2.68 Å < $r_{\mathrm{Hf}} + r_{\mathrm{Mo}}$ = 1.45 Å + 1.29 Å = 2.74 Å. Correspondingly, the M–M distance is larger in the ternary antimonide (3.18 Å *vs.* 3.14 Å). Somewhat smaller increases were found for the M–Sb and Sb–Sb bonds.

We calculated the band structure of HfMoSb$_4$ assuming the most simple ordering, namely an Hf–Mo pair in each trigonal prism pair as shown in Fig. 1, using the structural parameters from

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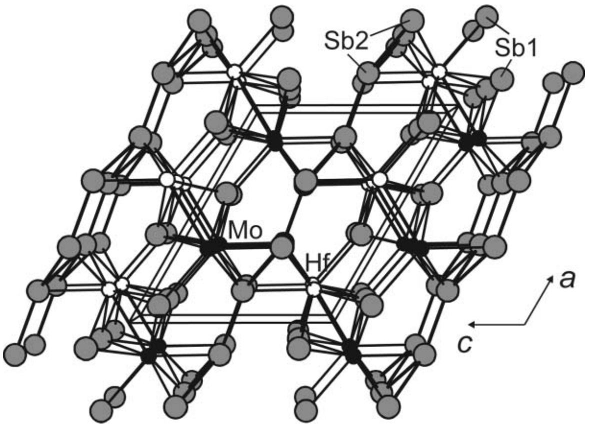

Fig. 3 Crystal structure of $HfMoSb_4$ in *Cm*. White circles: Hf; black: Mo; grey: Sb.

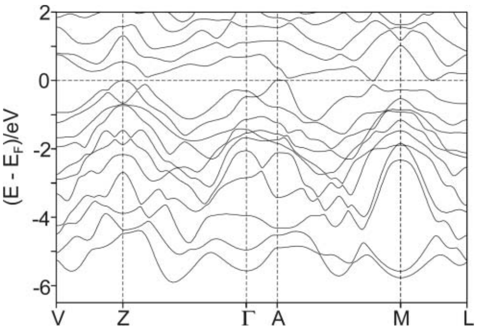

Fig. 4 Band structure of $HfMoSb_4$.

the refined single crystal data. This ordering destroys the 2-fold rotational axis, resulting in the space group *Cm* (Fig. 3).†

While the band structure exhibits strong similarities to that of $NbSb_2$, no bands actually cross (but touch) the Fermi level (Fig. 4). Therefore, $HfMoSb_4$ is predicted *not* to be a metal, in contrast with $NbSb_2$ and the other early transition metal antimonides.

We obtained phase-pure $HfMoSb_4$ and $NbSb_2$ samples by heating the elements in the stoichiometric ratios at 920 °C over a period of three weeks, interrupted midway for grinding to enhance homogeneity. We checked for homogeneity and purity using an X-ray powder diffractometer with a position-sensitive detector (INEL) and an electron microscope (LEO 1530) with an additional EDX device (EDAX Pegasus 1200). The samples were thoroughly ground, and then pressed into bar-shaped pellets of the dimensions $6 \times 1 \times 1$ mm. We used a four-point method to measure the voltage drops applying currents between 5 mA and 10 mA under vacuum over a temperature range between 180 K and 295 K, utilizing a homemade device.

As shown in Fig. 5, $NbSb_2$ exhibits the expected linear, positive temperature dependence of the specific electrical resistance that is typical for metallic materials. On the other hand, the curve for $HfMoSb_4$ is typical for nonmetals, *i.e.* the resistance decreases with increasing temperature because of the increase in charge carriers (while the curvature is opposite to semiconducting behavior). The absolute values differ by a factor of 4–6 over the temperature range investigated. We verified with a repetition of the $HfMoSb_4$ measurement of a different sample that the slope is reproducible, and not an artefact. That $HfMoSb_4$ is not a metal suggests local Hf/Mo ordering, since the presence of Mo–Mo pairs would lead to metallic conductivity as an additional model calculation in *P*2/*m* (same unit cell as before) with Hf–Hf and Mo–Mo pairs alternating along the *a* axis indicated.

To summarize, both resistance measurements prove the

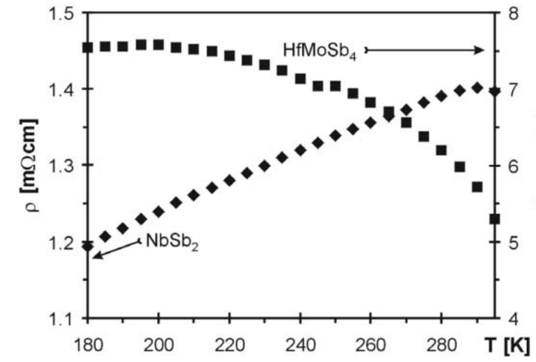

Fig. 5 Specific electrical resistances of $NbSb_2$ (◆) and $HfMoSb_4$ (■).

electronic structure calculations to be correct. Hence, we succeeded in synthesizing the first nonmetallic early transition metal antimonide, guided by theory. It will be interesting to investigate its thermoelectric properties (in dependence of the exact Hf : Mo ratio), noting that both the band structure and the specific electrical resistances resemble those of the low-temperature thermoelectric material $CsBi_4Te_6$.[26,27]

Notes and references

† CCDC 242777. See http://www.rsc.org/suppdata/cc/b4/b409225b/ for crystallographic data in .cif or other electronic format.

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