

WHERE SHOULD WE LOOK FOR HIGH ZT MATERIALS: SUGGESTIONS FROM THEORY.

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ABSTRACT

The key challenges in discovering new high ZT thermoelectrics are understanding how the nearly contradictory requirements of high electrical conductivity, high thermopower and low thermal conductivity can be achieved in a single material and based on this identifying suitable compounds. First principles calculations provide a material specific microscopic window into the relevant properties and their origins. We illustrate the utility of the approach by presenting specific examples of compounds belonging to the class of skutterudites that are or are not good thermoelectrics along with the microscopic reasons. Based on our computational exploration we make a suggestion for achieving higher values of ZT at room temperature in bulk materials, namely n-type $\text{La}(\text{Ru,Rh})_4\text{Sb}_{12}$ with high La-filling.

INTRODUCTION

The quest for a material with high thermoelectric efficiency consists of optimizing both thermal and electronic properties in order to balance the lattice thermal conductivity κ_L with the electronic conductivity σ , the Seebeck coefficient S and the electronic thermal conductivity κ_e . The goal is to obtain a figure of merit $ZT = \sigma S^2 T / (\kappa_L + \kappa_e)$ as high as possible at the operating temperature of the device, *i.e.* 300 K or below for coolers.

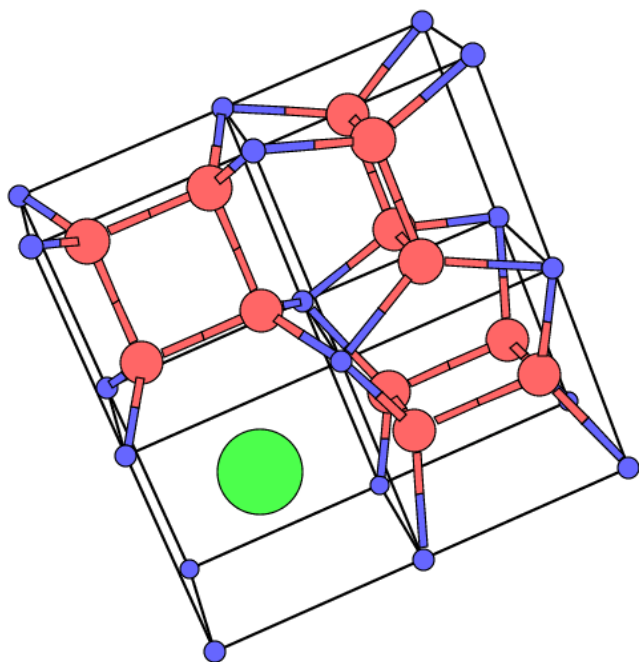


Figure 1

Half of the BCC conventional cell of the skutterudite structure. Three octants are occupied by pnictogen “square” rings. The remaining octant is filled with a rare earth. The metal atoms occupy a cubic sublattice.

The quantities involved in Z are strongly coupled to each other. A good thermoelectric material should be a high effective mass semiconductor (high S) with considerable carrier density after doping (high σ) and with complex unit cell in order to make low κ_L possible. Filled skutterudites are among the promising materials. They satisfy the above criteria and indeed $\text{La}(\text{Fe},\text{Co})_4\text{Sb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$ have shown p-type high figures of merit [1,2], though unfortunately not at temperatures applicable to cooling devices. On the other hand, the skutterudite structure is very stable upon chemical substitutions and alloying and new interesting compounds with low thermal conductivity and optimal electronic properties at lower temperature could be found. Using first principles calculations we performed a systematic computation of the electronic properties of La-filled skutterudites, $\text{LaM}_4\text{Pn}_{12}$ ($M=\text{Fe}, \text{Ru}, \text{Os}$ and $\text{Pn}=\text{P}, \text{As}, \text{Sb}$). The comparison between band structures of different compounds emphasized trends and pointed out a particularly promising composition $\text{La}(\text{Ru},\text{Rh})_4\text{Sb}_{12}$ for which a ZT possibly exceeding unity at room temperature and below may be found [3].

LATTICE STRUCTURE AND COMPUTATIONAL APPROACH

The conventional cubic cell (Fig. 1) of the binary skutterudites, MPn_3 , contains 16 atoms (space group $\text{Im}\bar{3}$). The metal atoms occupy a cubic sublattice; six octants are filled with a Pn_4 ring oriented according to the cubic symmetry and the remaining two are empty. In the filled skutterudites, $\text{RM}_4\text{Pn}_{12}$, the empty octants contain a filling atom, often a rare earth *e.g.* $\text{R}=\text{La}, \text{Ce}$.

We have used linearized augmented plane wave (LAPW) density functional *ab initio* calculations (DFT) in the framework of the local density approximation (see Ref. [3,7] for computational details) to calculate the band structure and density of states (DOS). In order to evaluate the effects of alloying, the virtual crystal approximation (VCA) has been used: the virtual crystal for the alloy has been realized adding one electron in valence and modifying

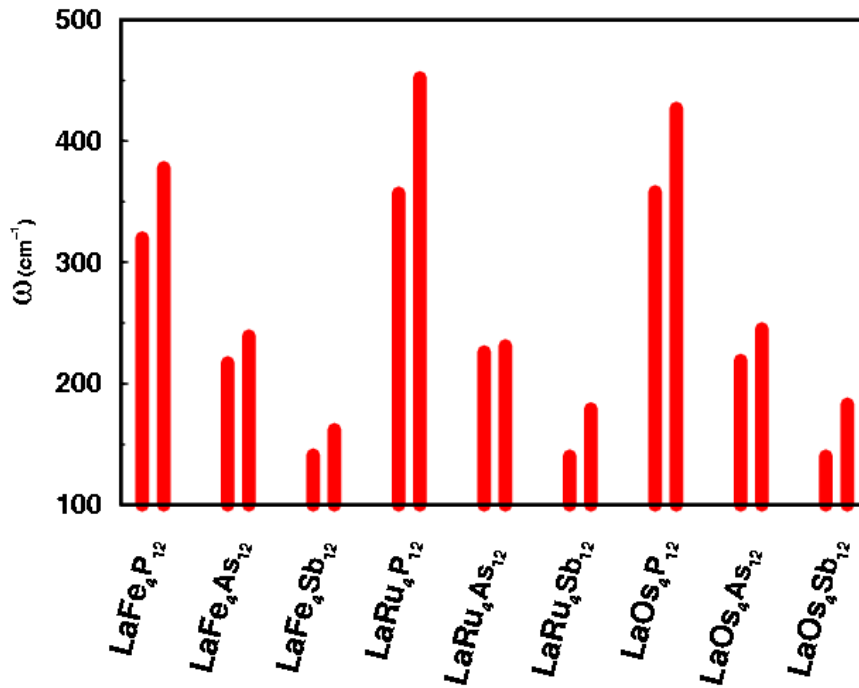


Figure 2

Frequencies of the two A_g modes associated with the full-symmetry pnictogen vibrations. Note the lower frequencies in antimonides.

accordingly the atomic number of the transition metal ($Z \rightarrow Z+0.25$). The validity of VCA is verified *a posteriori* considering the rigid band behavior. Transport properties were studied using kinetic transport theory.

The size and shape of the pnictogen ring is determined by two symmetry independent parameters (x, y). Our calculations are performed using, if available, the experimental structure, otherwise we (A_g modes) that correspond to Raman active modes. Pnictogen ring related

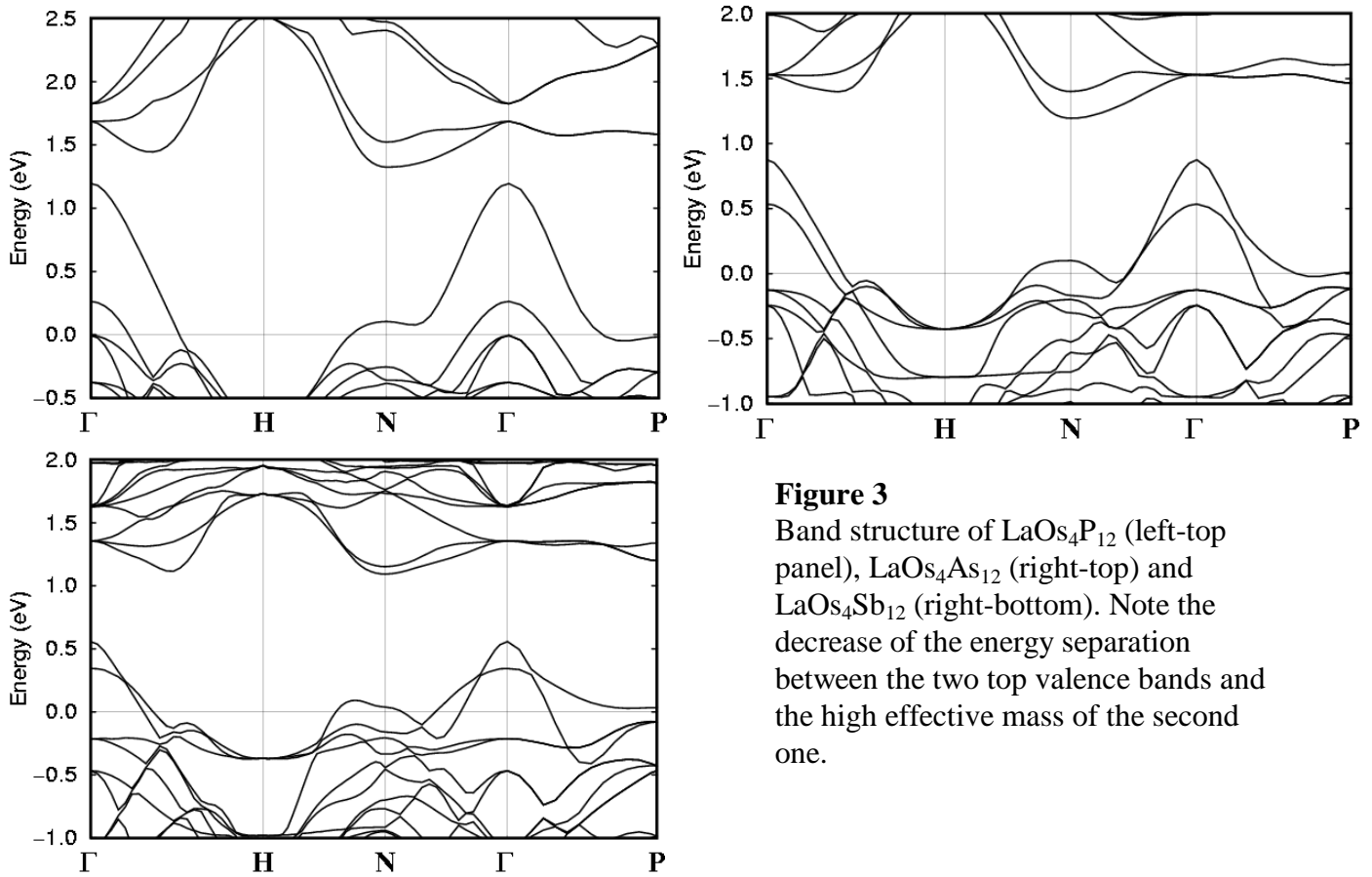


Figure 3
Band structure of $\text{LaOs}_4\text{P}_{12}$ (left-top panel), $\text{LaOs}_4\text{As}_{12}$ (right-top) and $\text{LaOs}_4\text{Sb}_{12}$ (right-bottom). Note the decrease of the energy separation between the two top valence bands and the high effective mass of the second one.

phonons play the main important role in the heat conduction [4].

THE SEARCH

The experimental result that filling the cages in CoSb_3 with La (and alloying with Fe) leads to a drop of about an order of magnitude [1, 2] in the thermal conductivity is our starting point. A clear explanation is still lacking but the comparison between the A_g modes frequencies (Fig. 2) strongly suggests that the lower frequencies of A_g modes in antimonide compounds may favor a coupling with La vibrations ($50\text{-}100\text{ cm}^{-1}$) that does not occur as strongly in the phosphide and arsenide because of the frequency mismatch. In fact, even if La is more tightly bound and has higher frequencies in the P and As compounds because of the cage's smaller volume, the strong coupling with the A_g modes does not seem to occur in the arsenide and phosphide. The overall effect is detrimental in the thermal conductivity, which is substantially higher [5].

In addition La filling has important contributions both on qualitative and quantitative features of the band structure. These effects [6] rest on the interaction between La related f -resonances that appear in the conduction band (about 3 eV above the Fermi level) and that push down, via hybridization, the highest p -Pn band. Depending on the particular starting unfilled material band structure the result can be very different: moving from CoP_3 to $\text{LaFe}_4\text{P}_{12}$ a gap is opened [7], from CoSb_3 to $\text{LaFe}_4\text{Sb}_{12}$ the gap increases and the two highest valence bands become very close in energy (the energy separation at Γ in $\text{LaFe}_4\text{Sb}_{12}$ is about 6 meV, [6]). After p -doping both bands participate in transport. The key point is that the effective mass of the second band is high, favoring high thermoelectric power (S) at reasonable doping levels and hence high values of Z .

Even though LaOs_4Pn_4 compounds have little practical relevance, because of the difficulty in using Os, it is interesting to analyze the effects of pnictogen substitution in the Os pnictides. The phosphide (Fig. 3a) is a semiconductor with a small indirect gap ($E_G=0.15$ eV) that becomes larger in the arsenide ($E_G=0.33$ eV, Fig. 3b) and antimonide ($E_G=0.54$ eV, Fig. 3c). The two top valence bands become energetically closer ($0.93 \rightarrow 0.34 \rightarrow 0.21$ eV), and in $\text{LaOs}_4\text{Sb}_{12}$ the second one shows high effective mass. The material might promise good p -type TE properties. Anyway, in $\text{LaOs}_4\text{Sb}_{12}$ the energy separation between the two top valence bands is still larger than in $\text{LaFe}_4\text{Sb}_{12}$ making this last skutterudite more useful. Also, the conduction band (CB) is subject to considerable changes upon filling and the trend in Os pnictides resembles the main features of all the La filled skutterudites we have investigated. In the unfilled materials the bottom of the CB occurs at Γ point (even if in some cases, e.g. CoSb_3 , this should be interpreted carefully because of the semimetallic or zero gap character of the band structure). In addition to the f -resonance effect, La filling shifts the minimum of the CB from Γ to the zone boundary (generally N). The result is a multivalley multidegenerate CB which is very useful for obtaining high thermopower with high carrier concentrations after n -doping. Although only from a theoretical point of view, $\text{LaOs}_4\text{P}_{12}$ shows the key features of a promising TE material: (i) expected low thermal conductivity, (ii) multivalley bands, (iii) high effective masses.

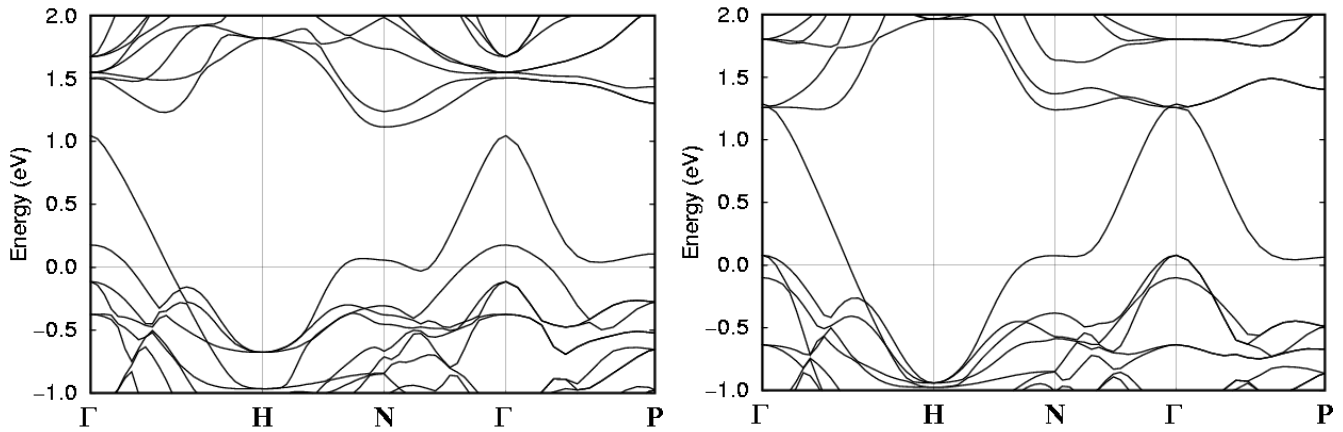


Figure 4

Band structures of $\text{LaRu}_4\text{P}_{12}$ (left) and $\text{LaRu}_4\text{As}_{12}$ (right). In the phosphide the La- f interaction is not enough strong to open a gap.

In Fig. 4 and Fig. 5 we show the effect of pnictogen substitution for $\text{LaRu}_4\text{Pn}_{12}$. The f -resonance

interaction is not enough strong to open a gap in the phosphide, and also when the gap is opened in the arsenide the two highest valence bands are too far apart in energy to be used in transport at a reasonable p-doping. The conduction band seems more interesting because the two minima (occurring at N and in Γ -H direction) are multidegenerate and in $\text{LaRu}_4\text{Sb}_{12}$ are very close in energy resulting in a very promising CB structure for TE n-type applications. Also, since this is an antimonide, κ_L is expected to be quite low and particularly lower than in phosphide and arsenide.

A RESULT: $\text{La}(\text{Ru,Rh})_4\text{Sb}_{12}$

$\text{LaRu}_4\text{Sb}_{12}$ is an indirect gap semiconductor ($E_G=0.16$ eV) with two "degenerate" minima ($\Delta E=10$ meV) in the conduction band occurring at the N (6-fold degenerate) point and just apart from the Γ -H symmetry line (24-fold degenerate). The effective masses in the cubic directions are $m_x^*=1.60$, $m_y^*=0.36$, $m_z^*=2.00$ for the N point and $m_x^*=12.12$, $m_y^*=0.24$, $m_z^*=3.90$ for the other minimum, revealing strong anisotropy. Due to the high effective masses (the average value is $\langle m^* \rangle=3.3$) the maximum Seebeck coefficient will be high and because of the multivalley character also the carrier density and, hence σ is expected to be favorable.

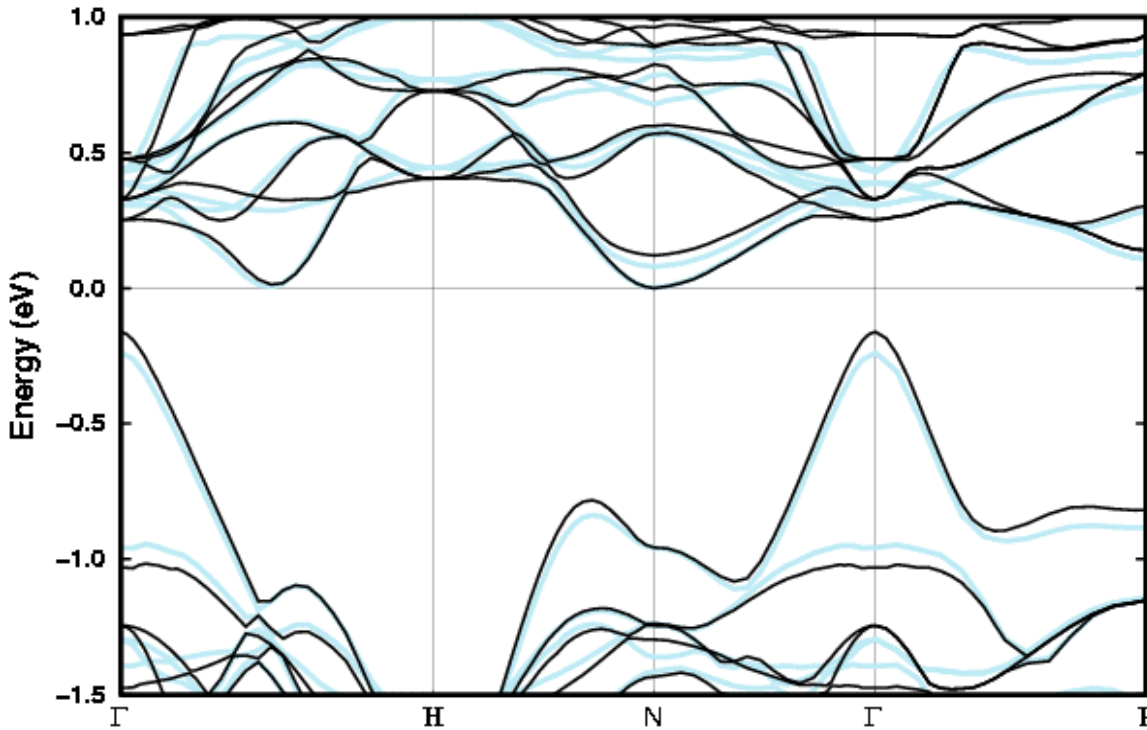


Figure 5
Band structure of $\text{LaRu}_4\text{Sb}_{12}$ (black) and $\text{LaRhRu}_3\text{Sb}_{12}$ (gray). The reference energies are set at the bottom of the respective conduction bands.

To be more quantitative we used standard kinetic theory in the constant scattering time

approximation to compute the temperature dependence of the thermopower at different doping levels for $\text{La}(\text{Ru,Rh})_4\text{Sb}_{12}$. The integration over the Brillouin zone has been performed using a very fine mesh. We computed the DOS, $N(\epsilon)$ and Fermi velocities $v(\epsilon)$ using a smooth Fourier interpolation of the bands.

The results are in Fig. 6. It is clearly shown that the Seebeck coefficient has a quite stable value in excess of $150 \mu\text{V/K}$ in the important temperature window between 100-300 K for a reasonably high carrier concentration of $4.6 \times 10^{19} \text{ cm}^{-3}$. For comparison, $\text{La}(\text{Co,Fe})_4\text{Sb}_{12}$ reaches the same high S but at $T=600 \text{ K}$, [2]. To evaluate the effect on the mobility of the Rh-Ru alloying needed to control the carrier concentration we compare in Fig. 5 the band structures of $\text{LaRu}_4\text{Sb}_{12}$ and $\text{La}(\text{Ru}_{0.75}\text{Rh}_{0.25})_4\text{Sb}_{12}$. They are almost identical for the relevant bands confirming *a posteriori* the validity of VCA and suggesting very low disorder scattering by Ru-Rh alloying and thus high mobility.

As we have shown before, La filling is a key point in the optimization of ZT and in our calculations we have considered a perfect crystal with two La atoms in each conventional cubic cell. In reality, possible La vacancies can strongly affect both the lattice and the electronic properties. To investigate the sensitivity of the mobility to La filling, we have calculated the band structure for the related unfilled material: RhSb_3 (Fig. 7). The band structure is inverted producing a zero gap material and the global features are drastically different from the

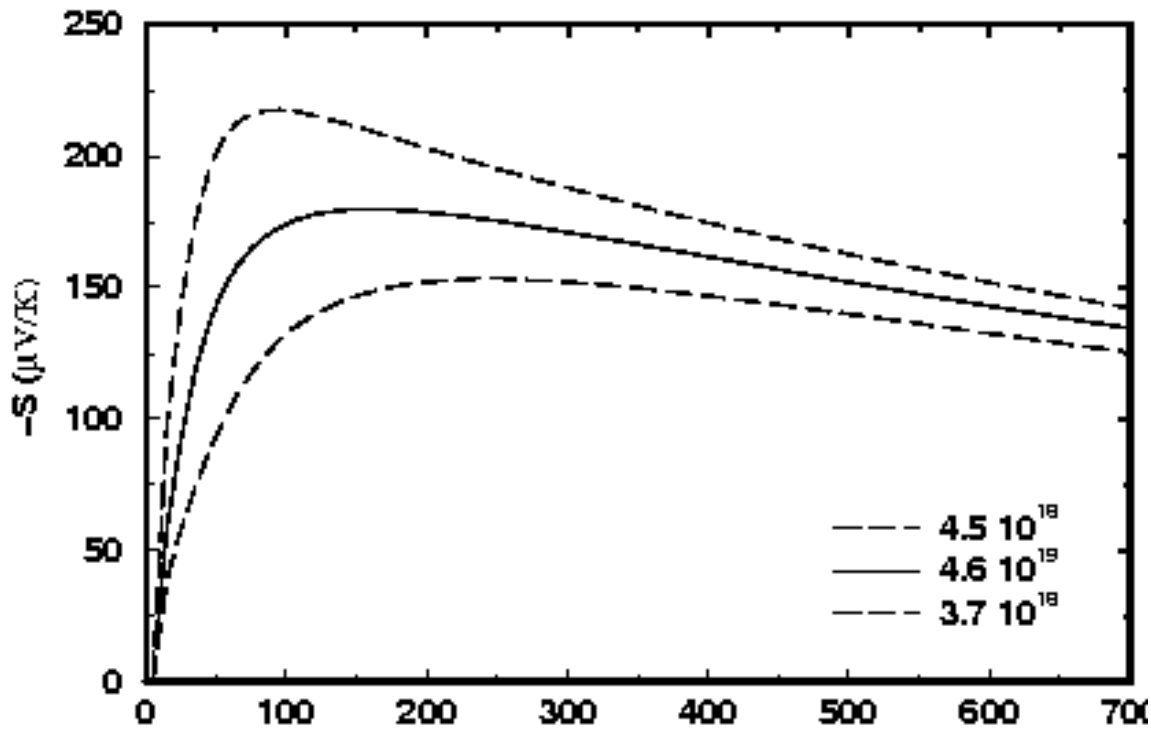


Figure 6
Seebeck coefficient for n-type $\text{LaRhRu}_3\text{Sb}_{12}$ at different carrier densities.
The maximum value occurs below room temperature.

completely filled $\text{LaRu}_4\text{Sb}_{12}$ meaning that high La filling is required in order to maintain a

reasonable mobility. To reach high La filling in $\text{LaCo}_4\text{Sb}_{12}$ new growth techniques have been developed and we are confident that they could also apply to ruthenates. [8]

We like to underline that the drastic difference between the band structures of RhSb_3 (Fig. 7) and $\text{LaRu}_4\text{Sb}_{12}$ is not related to the f-resonance induced by La. The main role in this effect is

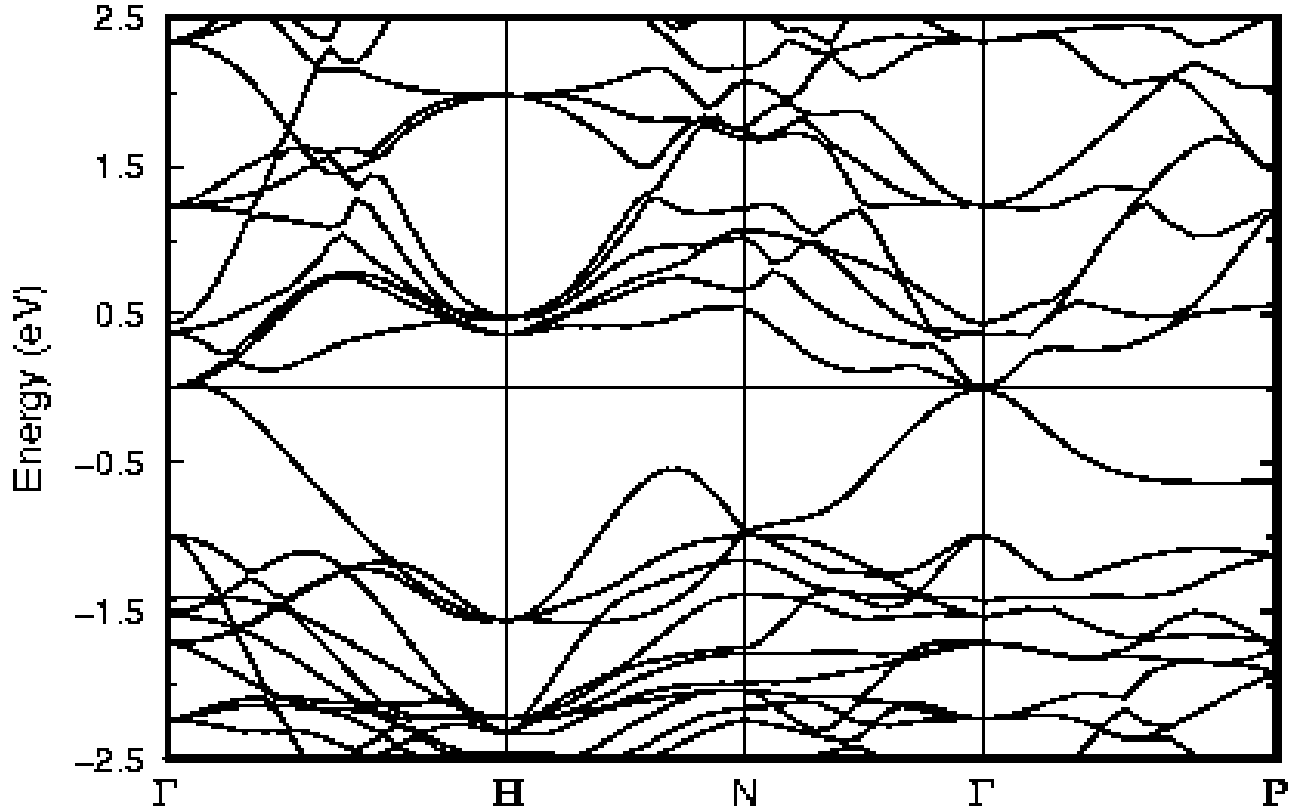


Figure 7

Band structure of RhSb_3 . From comparison with Fig. 5 it appears clear that La filling must be very high in order to avoid detrimental effects on the TE properties.

played by the different ionicity of the bonds involved in the material which causes a charge rearrangement when electrons are transferred from the rare earth to the metal. Thus, a partial substitution of La with other trivalent ions (*e.g.* Yb) should be as good in this case, and this fact could potentially be used to optimize the thermal conductivity.

SUMMARY AND CONCLUSIONS

Comparing the band structures of different skutterudite compounds we have elucidate the effect of La filling and of pnictogen substitutions. These calculations of the band structures of chemically different skutterudites, in addition to a better understanding of trends, point to a new promising specific composition $\text{LaRu}_3\text{RhSb}_{12}$ with an expected ZT about unity below room temperature and at n-type carrier concentration in the 10^{19} cm^{-3} range.

This expectation is based on (1) experimental evidence of low thermal conductivity in similar compounds, (2) the multivalley conduction band structure with high effective masses, and (3) computed thermopowers $S > 150 \mu\text{V/K}$ for T below room temperature. In addition our first principles calculations predict low Ru-Rh scattering and high La-vacancy scattering. The detrimental effect due to incomplete filling needs to be limited using modern growth techniques.

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