Skutterudites for Thermoelectric Applications: Properties, Synthesis and Modelling

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Introduction

Skutterudites are a class of compounds promising in thermoelectric field.

They are among the most studied thermoelectric materials of the last decade because related to the concept of electron-phonon-glass crystal. In literature there are many studies on Co-based skutterudites filled with Rare Earths (RE) (Ballikaya et al. 2012, Daniel et al. 2015, Zhang et al. 2015, Lili et al. 2015, Bhaskar et al. 2015) and Fe,Co-based($REFe_{4-x}Co_xSb_{12}$) (Jacobsen et al. 2014, Zhang et al. 2015, Rogl et al. 2010a), while very feware the studies on Fe,Ni–based skutterudites ($REFe_{4-x}Ni_xSb_{12}$) (Tan et al. 2013a, Kaltzoglou et al. 2012, Morimura et al. 2003).

The name "Skutterudite" comes from a small mining town, Skutterud, in Norway where it was extracted and classified for the first time in 1845. The natural Skutterudite is a cobalt arsenide mineral that contains variable amounts of Ni and Fe, substituting for cobalt, having the general formula: $(Co,Ni,Fe)As_3$. Its orogeny is hydrothermal, in moderate-high temperature; it is often found associatedwith other minerals such asArsenopyrite,nativeSilver,Erythrite,Annabergite,Nickeline,Cobaltite,Silversulfosalts, nativeBismuth,Calcite,Siderite,BariteandQuartz.Its density is about 6.5 g/cm^3 and the Mohs hardness is 6 but these values strictly depend on the composition.

Synthetic skutterudites are now produced in laboratory. They include compounds having the composition MX_3, where M is a transition metal of the VIII, IX, X group andX represents a pnitogen atom belonging to the XV group. Oftedal in 1928 identified $CoAs_3$ as the first synthetic skutterudites and determined its structure as a cubic body-centered cell and space group $Im\bar{3}$.$CoAs_3$ is now reported as the prototype compound for skutterudites.

Prototype and binary skutterudites

The unit cell of $CoAs_3$contains square radicals of the pnicogen atoms, $[As_4]^-$, situatedat center of smaller cubes and oriented along the <100> crystallographic directions. Every radical is surrounded by 8 trivalent transition metal Co^{3+} cations. The unit cell can be described as constituted of 8 small cubes, two of them without the $[As_4]^-$ ring at the center, keeping the compositional ratio Co^{3+}:$[As_4]^{4-}$= 4:3. A characteristic coordination structure is then obtained having$Co_8[As_4]_6$ =$2Co_4[As_4]_3$ composition and 32 atoms per cell.

In electronic terms, each transition metal contributes with 9 electrons and each pnicogen contributes with 3 electrons to the covalent bond, giving a total Valence Electron Count (VEC) of 72 for each smaller cube. Considering, now, one-half of the unit cell and its empty cubes, a general skutterudite formula can be displayed as $\square M_4Pn_{12}$ where $\square$ is the empty cube, M is the transition metal and Pn is the pnicogen atom. Metal atoms are located on 8c sites (1/4,1/4,1/4) while the non-metal ones occupy 24g sites(0,y,z).

Originary Oftedal observed that y+z= ½ leading to formulate the so-called Oftedal relation. This rule allows to hypothesize that the pseudo planar pnicogen "complex" X_4 is a perfect square (Oftedal 1926), where the edges (d_1,d_2) have the same length.Nevertheless, Kaiser andJeitschko (Kaiser and Jeitschko 1999) confirmed that the atomic position of pnictogen atom in the rings fall below this relation but only the unfilled skutterudites include a perfect square X_4; this assumption leads to admit the presence of a small rectangular distortion ($d_1 \neq d_2$).

The experimental values of these parameters, which include the average radius of the voids, are shown in table 1.

Table1:Structural parameters of binary skutterudites

Compound	a (nm)	y	z	d_1(X-X) (nm)	d_2(X-X) (nm)	R(void) (nm)	Ref.
$IrSb_3$	0.92512	0.3376	0.15365	0.2843	0.3005	-	(Snider et al. 2000)
$RhSb_3$	0.92322	0.3420	0.1517	0.2891	0.3000	0.2024	(Arne and Trond 1974)
$FeSb_3$	0.92116	0.3402	0.1578	0.2907	0.2944	-	(Möchel et al. 2011)
$CoSb_3$	0.90385	0.3351	0.1602	0.2891	0.2982	0.1892	(Arne and Trond 1974)
$RhAs_3$	0.84507	0.3482	0.1459	0.2468	0.2569	0.1934	(Arne and Trond 1974)
$CoAs_3$	0.82055	0.3442	0.1514	0.2478	0.2560	0.1825	(Arne and Trond 1974)
IrP_3	0.80151	0.3540	0.1393	0.2233	0.2340	-	(Rundqvist and Ersson 1969)
RhP_3	0.79951	0.3547	0.1393	0.2227	0.2323	0.1909	(Arne and Trond 1974)
NiP_3	0.78157	0.3553	0.1423	0.2281	0.2262	-	(Jeitschko et a . 2000)
PdP_3	0.7705	0.3442	0.1514	0.2333	0.2401	-	(Rundqvist S. 1960)
CoP_3	0.7705	0.3489	0.1451	0.2224	0.2328	0.1763	(Jeitschko et al. 2000)

As reported in the Table 1, the near-neighbor distances in the rectangular rings are comparable to the nearest neighbor distances in the elemental P (≈ 0.22 nm) (Osters et al. 2012), As (≈ 0.25, 0.26 nm) (Ugai et al. 1985) and Sb (≈ 0.28, 0.34 nm) (Lomnytska et Pavliv 2007)

The M-M distance is too large to form a bond; so the only relevant interactions are those among the ions inside the pnicogen ring X_4 (X-X bonds) and those among the M atoms and the pnictogen ions (M-X bonds). Figure 1 illustrates particularly well the binding site of octahedral metal atom and the formation of inclined MX_6 octahedra sharing vertices with octahedra adjacent. The inclination of these octahedra originate the pseudo planar ring structure X_4. Furthermore, it can be easily demonstrate that each pnicogen X is surrounded by two other pnictogens and two M atoms at similar distances. Alogical consequence is that the ring is linked by σ bond where each pentavalent X (ns^2np^3) binds two nearest X sharing two of its own electrons. The other three valence electrons form, instead, bonds with the two closest M atoms. Due to the six bonds formed between the six X atoms and M atom, the pnictogen contributeto the octahedral MX_6 complex is then 3*1/2*6 = 9 electrons. This electronic configuration involve the Co-typemetal one (d^7s^2) to reach the electronic configuration of the noble gas (18 electrons): this promotes diamagnetism and semiconductive behaviour, the main characteristics of binary skutterudites.

This pattern of bonds and the corresponding electron count poses a constraint on the actual existence conditions of binary compound within the skutterudite family. For example, totally replacing the cobalt with iron or nickel does not form the skutterudite. Indeed the hypothetical compound FeX_3having an electron less in the inner d orbitals: should be considered a paramagnetic semiconductor. Similarly for the compound NiX_3; the promotion of an extra non-bonding electron into the conduction band should make it as a paramagnetic compound. A substitution of the metals of group IX is possible and, furthermore, the limits of solubility are remarkably large. Particularly, the cobalt can be substituted with iron and nickel in accordance with the formula:

$$2Co^{3+}(d^6) \leftrightarrow Fe^{2+}(d^6) + Ni^{4+}(d^6)$$

with the consequent preservation of the total number of electrons.

In light of these considerations, the existence of ternary skutterudites is expected, as long as it is maintained the value of Valence Electron Count VEC = 72.

Ternary skutterudites

Starting from the prototype $CoAs_3$, the substitution on both the metal and the pnicnogen sites, can be assumed as feasible and, indeed, several examples of doped ternary skutterudites are reported in the literature. A small list is shown in Table 2 together with the average latticeparameters(Fleurial et al 1997)and the calculated Pauling electronegativity difference.

Table 2: lattice parameter and electronegativity difference of the known ternary skutterudites

Element substitution	Compound	a (A)	$\Delta\chi$
	$CoSb_3$	9.0385	0.17
Pnicogen	$CoGe_{1.5}S_{1.5}$	8.0170	0.41
	$CoGe_{1.5}Se_{1.5}$	8.3076	0.40
	$CoSe_{1.5}Sn_{1.5}$	8.7259	0.37
	$CoSn_{1.5}Te_{1.5}$	9.1284	0.01
Transition metal	$Fe_{0.5}Ni_{0.5}Sb_3$	9.0904	0.18
	$Fe_{0.5}Pd_{0.5}Sb_3$	9.2060	0.03
	$Ru_{0.5}Ni_{0.5}Sb_3$	9.1780	0.00
	$Ru_{0.5}Pd_{0.5}Sb_3$	9.2960	- 0.15

As expected the lattice parameter varies according to the type of substitution:i.e. depending on the dimension of the substituted transition metal, pnicogen atom or both.

The investigation on these ternary skutterudites allowed to define, in addition, the existence more or less extended solid solutions, between the parent binary compounds, which generally obey the Vegard' law.

From the point of view of the physical properties, a relevant behaviour observed in ternary skutterudites thermal conductivity is that there is very low if compared to that of the corresponding binary skutterudites. Unluckily, the decrease of thermal conductivity is consequence of a low carrier mobility: this implies high values of resistivity and small Seebeck coefficient in the ternary skutterudites. The prototipe $CoSb_3$ skutterudite, having cobalt as M, has usually a high electrical conductivity and a large power factor but also a significant thermal conductivity (10 W / m K) (Bhaskar et al. 2015). This value can be decreased by filling the voids of the structure with foreign elements that cause rattling with a consequent amplified effect on the phonon scattering.

Filled skutterudites

The study of the skutterudites structure and the voids identification, as mentioned above, offer the opportunity to add a large number of different species within the lattice. The first "filled" skutterudite $LaFe_4P_{12}$, was synthesized by Jeitschko and Brown in 1977 (Jeitschko and Brown 1977) . Shortly after, filled skutterudites were prepared also for the families of arsenides and antimonides. The general formula for the filled skutterudite is $R^{4+}[M_4X_{12}]^{4-}$, where R is an electropositiveion, the exponent is the balance of charge and T the transition metal of filled skutterudite. It's important to note the difference between the two complexes $[M_4X_{12}]^{4-}$ and $[M_4X_{12}]$ where the first has got a tetravalent negative charge conversely the second appears as a neutral unit: this feature greatly affects the chemical and physical properties of the filled compounds.

Thanks to their physico-chemical properties, alkaline earths and rare earths can be considered the main skutterudites fillers. Indeed, according to (Jacobsen 2014), there are two main conditions that must be respected for a filler to enter the structure: the filler must have a size consistent with the host void and the difference of electronegativity (χ) has to be $\chi_x - \chi_{filler} > 0.8$ Generally, the filler forms weak bonds with x, and their delocalization is responsible for the decrease of thermal conductivity.

With respect to the filler properties, it is very important to considerthat the lattice parameter and the size of the voids consistently increase passing from skutterudites P-based towards those As-based up to those with Sb. In addition, the lattice constants increase with the increase of the mass of metal within a given family of skutterudites. Figure 1 shows the unit cell centred at the position 2a (the position of the atom of filler) to (0,0,0). For many of the compounds the R atoms, frequently rare earths, tend to exhibit exceptionally large thermal parameters corresponding to the rattling of these atoms in an oversized atomic cage, thus causing a strong reduction of their thermal conductivity. (Mochel et al. 2011)

A similar circumstance occurs in the case of $RhSb_3$, where the Rh atoms are replaced by Ru and Pd forming the compound $Ru_2Pd_2Sb_{12}$. The two compounds mentioned above are examples of ternary skutterudites, which are isoelectronic phases with respect to binary compound. Replacing the pnictogen (as pentavalent Sb) with a combination of a tetravalent (eg. Ge, Sn, Pb) and a hexavalent (eg. Se, Te,) stable compounds such as $CoGe_{1.5}Se_{1.5}$ could be obtained. On the other hand, if a

replacement is carried out on both the metal sites and the pnictogen site a ternary skutterudites such as as $Fe_4Sb_8Te_4$ could be generated.The metals of the group 9, Co-type, are often replaced with metals of group 8 such as Fe, Ru and Os; to date no skutterudite with metals of group 8 were obtained most probably due to the obvious imbalance of charge.

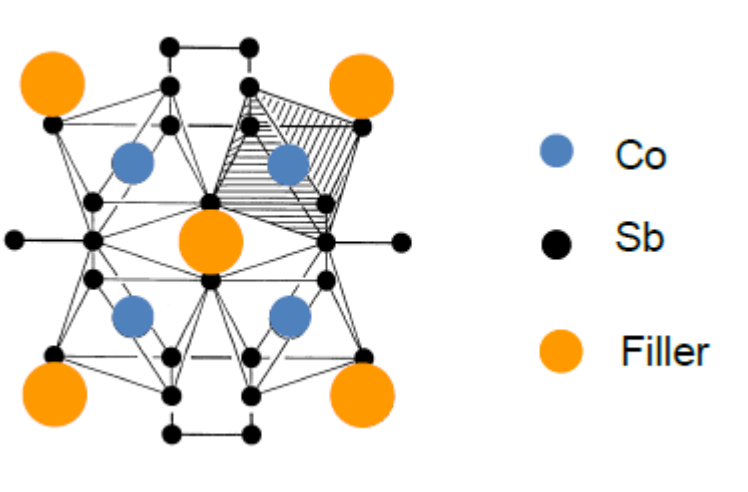


Figure 1: Unit cell of a centered skutterudite at position (0,0,0). The atoms of metal (Co in this case) are coordinated octaedricallyto the pnictogen atoms.

Furthermore, some ternary skutterudites can host varying filler amounts due to the presence of extended solid solutions given by the partial or total substitution of the transition metals. An example is reported by Carlini(Carlini et al. 2016): it is possible to obtain quaternary filled skutterudites having a large range of different compositions. In particular,stable $Fe_{4-x}Ni_xSb_{12}Sm_y$ skutterudites were observed for $0 \lesssim x \lesssim 2.4$ and $0.1 \lesssim y \lesssim 0.8$.

The introduction of a suitable filler R could providethe missing electrons, thus saturating bonds and making electrically semiconductive and diamagnetic neutral structure. The particular "filled" skutterudite having formula $R^{4+}[T_4X_{12}]^{4-}$hasVEC = 72with a consequent behaviour, just like the $CoSb_3$ prototype.A difficulty that often occurs in the synthesis of new filled skutterudites is the choice of a suitable filler. In fact, because of the electronic constraints, generally, only trivalent elements provide stable skutterudites. Most of the rare earths are trivalent, some of them (Yb, Sm) show anintermediate valence, while Eu usually has a divalent state; other species of fillers such as alkaline earth metals are only divalent. Accordingly, the total valence number for skutterudites completely "filled", with ions havinga valence lower than 4+, will be less than 72 units: consequently,these "full" skutterudites will be considered such as paramagnetic metals.From the point of view of thermoelectricity, this is not an optimal condition since the metals has a very small Seebeck coefficient. To take back this type ofcompounds in their semiconductive domain (and so, the total valence to 72 units), a charge compensation is required. The adjustment can be obtained mainly in two ways: by modifyingthe nature of the pnictogenrings (eg. by partial replacement of x atoms with elements of groups III or IV) orby insertion of electronic-richer metals, such as Ni, Cu, etc, in place of metals belonging to the iron group (VIII) at the 8c site. Both approaches considerably expand the compounds range of the skutteruditesfamily(Rowe 2006).

Nowadays, the most studied compounds are today $Ce_yFe_{4-x}Co_xSb_{12}$ and $La_yFe_{4-x}Co_xSb_{12}$. While the total occupancy of the voids is possible when x = 0, the increasing amount of Co implies a decrease of voids occupancy. For x = 4 ($CoSb_3$), the ions of Tllead to an average voids occupation ofabout22%, while itincreases to 100% usingSn. Some values,for $CoSb_3$ rare earths filled, are reported in table 3.

Table 3: Maximum void occupancy in pure CoSb3

Filler Ion	Maximun Void Occupancy (%)	Reference
Yb	44	(Rogl et al. 2010a)
Eu	25	(Berger et al. 2001)
La	23	(Nolas et. Al. 1998)
Ce	10	(Moerelli et l. 1997)

The filler amount and the corresponding charge compensation vary also depending on the type and the composition of skutterudite: i.e $Sm_yFe_{4-x}Ni_xSb_{12}$ shows a maximum at 49 % of void occupancy. (Artini et al. 2016)
In the case of antimony-based skutterudites,the large size of the "cages" pose a constraint on which type of rare earth (or other species) may be trapped in the structure. Using equilibrium conditions for the synthesis, rare earths up to Europium can enter the network. For the lanthanide contraction, the ions of the heavy rare earths are too small and cannot bind with the atoms that constitute the cage of antimony. Therefore, to get Sb-based skutterudities andfilled with heavy rare earths, high pressures or non-equilibrium synthesis are generally required.

As reported by (Okamoto 1991) $Co_4Sb_{12}$is obtained by peritectic reaction at 874 ° C from $CoSb_2$ and melted Sb; a similar behavior is found in the other skutterudites. Furthermore, due to the insertion of fillers, often, these materials are characterized by very long syntheses, which frequently involve the use of rather expensive technologies such as the Spark Plasma Sintering (SPS) or the High Temperature High Pressure (HTHP). The Spark Plasma Sintering is a sintering technique which provides for the simultaneous application of pressure and pulsed continue current. Due to the pressure, the particles of the powderedsample are in intimate contact among them; the current pulses and creates a local raising of the temperature that leads to the melting of the particles surface;a network of microwelding is produced, making compact the sample.

The HTHP synthesis provides, instead, the heating of the samples at high temperature (usually up to 1000 ° C) and at high pressure (usually up to 50 GPa). The high pressure on the sample, thanks to the great mobility due to high temperature, favours the filling process by large elements such as rare earth metals or alkaline earth metals.

Here are just some examples of the main syntheses reported in the literature.

Ballikaya (Ballikaya et al. 2012)reports a preparation of skutterudites rathercomplex: the elements are weighed in the respective stoichiometric amounts, is performed a slow heating (1 °/min) up to 1373 K, annealing for 10hr at that temperature to allow the accurate mixing of the constituents, after a cooling with a rate of 4 °/min to 1000 K and a hold for 10 d for the reaction to favourperitectic reactionfollow. The ingot obtained is pulverized and compacted to be annealed again at 1000 K for another two weeks and finally, re-pulverized to undergo a sintering with SPS. With this synthesis rather long and cumbersome, however, zT valueresults 1.4 at 1073 K, even if the samples are not 100% monophasic.

Also for the preparation of iron-based skutterudites synthesis rather long are required, as reported by Rogl (Rogl et al. 2010b) and Tan (Tan et al. 2013b).

The samples synthesized by Rogl (Rogl et al. 2010b) include the mixing of Fe, Ni and Sb, in the appropriate stoichiometric amounts, at 1230 K and quenching in air. After this, a right amount of didymium is added; the sample is then heated at 873 K for 3 days and at 995 K for 2 days. Subsequently, the sample is melted again at 1230 K, tempered again in water and annealed at 873 K for 5 days. The material obtained finally is pulverized and sintered with High Temperature High Pressure (HTHP) technique.

Tan (Tan et al. 2013b), instead, uses a simplersynthesis but anyway quite long: starting from the pure elements, slow heating and melting at 1273 K, staying at that temperature for 24h, water salt quenching and annealing at 820-870 K for 7 days. The obtained samples are pulverized and sintered using Spark Plasma Syntering(SPS) technique.

Other syntheses often reported(Short et al. 2015) involvesthe "Ball Milling" methods. This method provides a synthesis in several steps. The ball milling, through a proper balance between rotation speed and duration, favours the formation of skutterudites with particular features that make them excellent precursors for nanomaterials. However, to obtain dense samples, it is necessary to use the techniques above described.

Some recent research suggest alternative syntheses as thesolvothermal route using sodium borohydride ($NaBH_4$) as a reducing agent to obtain $CoSb_3$ nanoparticles (Kadel et al. 2014, Li et al. 2013, Bhaskar et al. 2015). The Self-propagating-High-temperature-Synthesis (SHS) technique isalso applied to synthesize $CoSb_3$where a mixtures of Co and Sb powders are compacted into pellets and ignited from one end(Liang et al. 2014).

Physical properties

The large number of possible compositions reported for skutterudites corresponds to a wide range of results for the adimensional figure of merit, ZT. Each strategy applied to the basic compound acts in term of improvement typically on one of the characteristics of the material, trying to preserve the behaviour of the others. For skutterudites containing elements with low electronegativity differences such as $CoSb_3$, a large number of covalent bonding are formed, enabling high carrier mobility resulting in good electronic properties. However, this strong bonding and simple order leads also to high lattice thermal conductivities, due to the reduced scattering mechanisms acting on phonons. As a consequence of the crystal-like electrical behaviour, the main target of materials development is related to the reduction of the lattice thermal conductivity. The introduction of doping in $CoSb_3$ to obtain the carrier concentrations optimizingZT value, adds enough carriers to significantly increaseelectron–phonon interactions reducing the thermal conductivity (Fleurialet al. 1997).Another improvement in reducing lattice component of thermal conductivity comes from the alloying on transition metal site or on the antimony site: this strategy contributes in create lattice disorder able to increase phonon scattering.

Actually the most used, and probably the most effective, solution to improve phonon scattering in skutterudites is related to the presence of the large voids in the structure. Filling these void spaces with rare-earth or other heavy atoms reduces the lattice thermal conductivity: this case, as reported in the previous sections, is widely explored in literature and a large variety of filler has been used to achieve

the larger effect on all classes of skutterudites (Sales et al. 1996). The large database of results obtained allowed to observe a correlation between the size of the filler, and their vibrational motion, and the thermal conductivity of the material: the improvements achieved lead toZT values up to 1 (Nolaset al. 2006; Sales et al.1998). A partial occupation of available voids establishes a random alloy mixture of filling atoms and vacancies introducing effective point-defect scattering. The large space for the filling atom in skutterudites induce local or 'rattling' modes that lower lattice thermal conductivity. This reduction is so drastic that it overcome the modest degradation of the electronic properties of the compounds. The mechanism at the base of this effect is the behaviour of the filler ion which, loosely bonded in a large space, acts as an independent and incoherent oscillator. Its isolated vibration mode is not responsible of heat transfer, but strongly interacts with the phonons of the main framework carrying the heat. This interaction is responsible for the significant reduction of lattice thermal conductivity observed in the filled skutterudites. Spectroscopic and diffractometric experiments and *ab-initio* calculations analyses have been performed to verify and describe in detail the behaviour and the effectsrelated to the filled skutterudites systems (Dordevic et al. 1999, Sales et al.1999, Singh et al. 1999, Mandrus et al.1997,J.L. Feldman et al.2000). The results of these developments show that the motion of the filler is harmonic with large displacements. This induces a filler-antimony interaction not negligible which modifies the characteristic inelastic spectrum of the system: the shifts appearing are only partially related to the bare filler vibrations, the others, typically at high frequencies, are due to antimony modes movement as a result of coupled motion of Sb and filler ion. So, the scenario can be summarized as a consequence of anharmonic scattering of phonons by harmonic motions of the cage fillers (Rowe2003).The employment of different ions to fill the voids, introducing different vibrational modes into the lattice, is at the origin of the multiple filling approach to skutterudites lattice conductivity reduction, resulting in the an improving the 'rattling' effects. In figure 4 (Fleurialet al. 1997, Snyderet al. 2008) the effects of the different solutions described above are summarized: it can be seen how the increase of phonon scattering is able to reduce thermal conductivity among all the range of temperature.

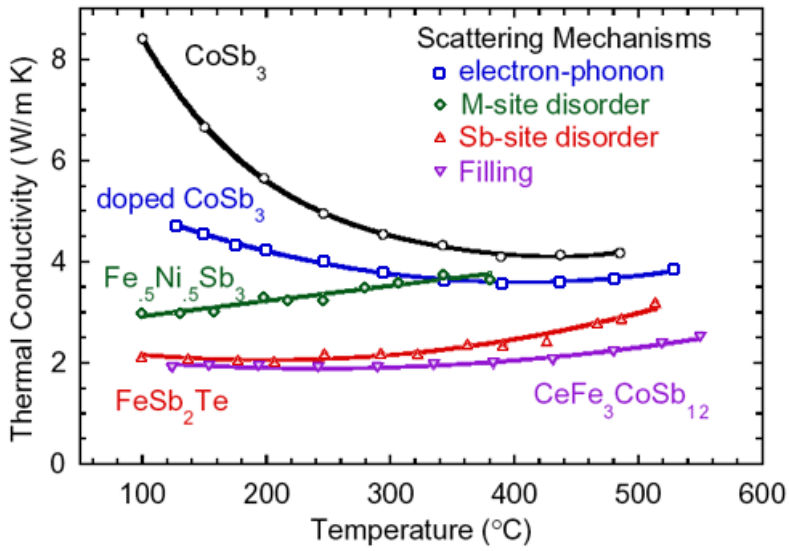


Figure 4: the effects of the different scattering mechanisms on the thermal conductivity of skutterudites: starting from pure $CoSb_3$, the plots display the decrease of heat transfer obtained introducing scattering sources into the system (Fleurialet al. 1997, Snyder et al.2008)

Looking at the effects of fillers on the electronic properties of the materials, these filling ions adds additional electrons that require compensating cations elsewhere in the structure for charge balance,

originating an additional source of lattice disorder. For the case of $CoSb_3$, Fe^{2+} frequently is used to substitute Co^{3+}. A benefit of this partial filling is that the free-carrier concentration may be tuned by moving the composition slightly off the chargebalanced composition. This unbalanced charge corresponds to a slight valence unbalance providing metallic carriers to the compound and improving electrical transport. The main characteristic of pure binary skutterudites from the electrical transport point of view, is the high mobility of the carriers, more similar to the one of metals than to the one typical of semiconductors. This condition is the same for both the cases of *p*- and *n*- type compounds and, for given carrier density, the hole mobility is generally higher than electron one (Uher et al. 2002). The high mobility results to be limited by different scattering mechanisms deriving by material purity, grain size, phonon or impurity interactions, however it exceeds 1000 cm^2/Vs also in polycrystalline samples. As already reported, the presence of fillers introduces charge doping into the system: the partial filling easily produces an increase of few order of magnitude to the carrier density moving the behaviour of the compound from semiconducting to metallic. This effect usually leads to a drastic reduction of Seebeck value, as described in the introduction speaking of the thermoelectric parameters dependence by the carrier density. However, the case of skutterudites is peculiar, due to the large effective mass of carriers. In pure binary compounds Seebeck coefficients are remarkably large with magnitudes of 200-500 □ V/K at 300K typicallyreported. Even for samples with electron density in the order of 10^{21} cm^{-3} the Seebeck coefficient usually results to be more than -100 □ V/K (Rowe2003,Caillat et al. 1996).Increasing temperature the conduction regime passes from extrinsic to intrinsic and the Seebeck coefficient rapidly decreases.The presence of the filler induce a significant change in the electronic bands structure, due to interaction between the fillers electronic configuration with the rigid cage made of covalent bondings, resulting in an increment of carrier density. However, the band derived at the bottom of the conductive band introduced by the filler, are typically 'flat', corresponding to an increase of the effective mass of both type of carriers (electron and holes), leading to a reduction of electrical conductivity, but, at the same time, allowing to escape the drastic suppression expected for Seebeck coefficient at the new 'metallic-like' carrier concentration. Thus, in spite of the degraded mobility, the enhancement of carrier density, coupled with the large Seebeck coefficient, preserves high power factors.

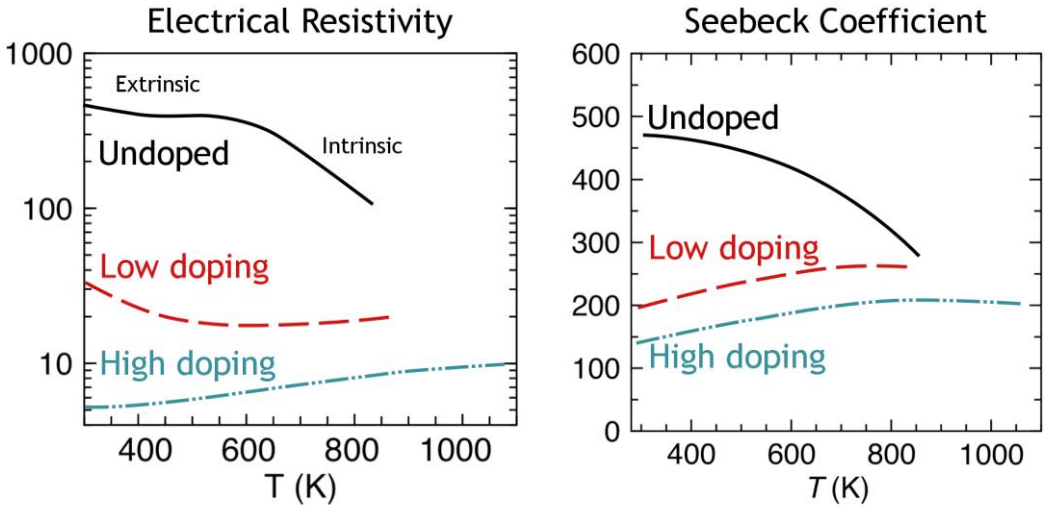


Figure 5: Electrical resistivities and Seebeck coefficients as a function of temperature used as references to display the effects of doping in a skutterudite (qualitative analyses).

In order to visualize and better explain the effects described, an example of electrical resistivity and Seebeck coefficient behaviour as a function of temperature are reported in figure 5.These plots describe the differences in the parameters varying the level of doping of the material.They start with the undoped material having the lower conductivity (high resistivity) and the highest Seebeck coefficient, where is evident the passage from extrinsic to intrinsic regimes of conduction due to the thermal activation of carriers. Gradually increasing the doping level, both absolute values and temperature behaviours change moving towards more metallic-like characteristics: Electrical resistivities and Seebeck coefficients become more constant with the temperature and the shift between extrinsic and intrinsic regimes practically disappears.

The characteristics previously described reflects the high complexity of the scenario related to thermoelectric skutterudites: each available solution, involves an improvement of some parameters and the degradation of the others. The fillers, acting on charge doping, affect the power factor in a detrimental direction, but, on the other side, they reduce significantly the lattice contribution to thermal conductivity. Thus, the target of the development of this class of materials can be summarized by finding the best balance in the final composition of the material in order to obtain the best ZT final value: as previously reported, the high complexity introduced by substitutions and voids filling generally produces greater effects on thermal conductivity than on the final power factor, so recent development are strongly oriented in the direction of filled and multiple-filled skutterudites, often starting from substituted compositions.

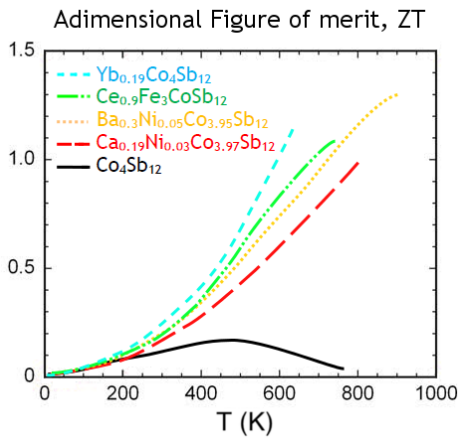


Figure 6: Adimensional figure of merit for different filled-skutterudites starting from basic and substituted $CoSb_3$. The curved reported reflects the effects described in the chapter

Figure 6 reports a collection of ZT values measured on different compounds (Sales et al. 1997, Sales et al. 2003, Sales et al. 1996, Nolas et al. 2000, Tang et al. 2001)showing the improvements achievable from pure $CoSb_3$, where the value is strongly limited by the high thermal conductivity and the temperature behaviour follows the dependence on carrier concentration, to filled and substituted compositions. ZT is highly increased overcoming in many cases the value of 1 and the temperature dependence is totally changed making these materials feasible for technological employments.

To summarize and conclude, table 4 reports some of the recent results obtained on different compounds in terms of ZT: the data are collected in order to easily display how the different strategies for materials improvements have been able to lead this class of thermoelectrics to the important target of being competitive with the best materials currently developed.

Table 4: Collection of data related to ZT maxima and the corresponding temperatures reported in literature for different skutterudite compounds.

Compound	zT_{max}	T(K)	Ref.
$IrSb_3$	0.15	850	(Slack and Tsoukala 1994))
$Mg_{0.4}Co_4Sb_{12}$	0.35	600	(Yan et al. 2013)
$Co_{0.94}Ni_{0.04}Sb_3$	0.5	750	(Katsuyama et al. 2003)
$Sm_{0.7}Fe_{2.8}Ni_{1.2}Sb_{12.8}$	0.55	580	(Carlini et al. 2016)
$Nd_{0.61}Fe_{2.98}Ni_{1.02}Sb_{12}$	0.55	550	(Liu et al. 2014)
$Yb_{0.77}Fe_{2.99}Ni_{1.01}Sb_{12}$	0.7	600	(Liu et al. 2014)
$CeFe_4Sb_{12}$	0.75	800	(Yan et al. 2014)
$Yb_{0.7}Fe_2Co_2Sb_{12}$	0.8	720	(Liu et al. 2014)
$CeFe_{3.9}Ga_{0.1}Sb_{12}$	0.88	800	(Tan et al. 2012)
$CeFe_{3.85}Mn_{0.15}Sb_{12}$	0.98	800	(Qiu et al. 2013)
$Ca_yCo_{4-x}Ni_xSb_{12}$	1	800	(Puyet et al. 2004)
$Yb_{0.8}Fe_{3.4}Ni_{0.6}Sb_{12}$	1	800	(Anno et al. 2002)
$(Ce,Yb)_{0.4}Fe_3Sb_{12}$	1	800	(Berardan et al. 2005)
$DD_{0.63}Fe_{3.5}Ni_{15}Sb_{12}$	1.1	780	(Rogl et al. 2012)
$Ce_{0.28}Co_{2.5}Fe_{1.5}Sb_{12}$	1.1	800	(Tang et al. 2001)
$Ce_xFe_{3.5}Co_{0.5}Sb_{12}$	1.2	870	(Fleurial et al. 1996)
$In_{0.25}Co_4Sb_{12}$	1.2	570	(Chen et al 2006)

In this chapter only the characteristics of the materials related to their thermoelectric performances have been reported and discussed. However, this is only the starting point to produce materials interesting for the development of thermoelectric technologies. In order to use a material to produce a device, other physical properties become really important: the most evident are, obviously, mechanical and thermo-mechanical properties, affecting materials integrity under operating conditions. Other examples are the resistance to the working environment agents or the long term stability, in terms of structure and composition, at operating temperatures. Thermoelectric materials are always operating under thermal gradients, most of the time coupled with a parent material, with the target of supporting the highest delta of temperature achievable without any damage or property degradation: these requirements work as filters for many classes of materials actually available. Recently, more attention is paid to the mechanical characterization of the materials and new ideas for the production of elements useful for applications are under development. However, compiling a state of the art for these characteristics is still difficult due to the lack of data for many of the materials reported and described.

Acronyms

DFT: density-functional theory

EHT: extended Hückel theory

EHTB: extended Hückel tight binding

ELF: electron localization function

FP-APW+lo: full-potential augmented-plane-wave with local orbitals

FP-LMTO: full-potential linear muffin-tin orbital

FLAPW: full-potential linear augmented-plane-wave

GGA: generalized gradient approximation

KKR-CPA: Korringa-Kohn-Rostoker with the coherent potential approximation

LDA: local density approximation

LDA+U: local density approximation with Hubbard corrections

LMTO-ASA: linear muffin-tin orbital-atomic sphere approximation

LSDA: local spin density approximation

QTAIM: quantum theory of atoms in molecules

Property modelling

The modelling of skutterudite properties has been the subject of a large number of publications over the past decades. In this review we will only consider a limited set of results pertaining to Fe- or Ni-based skutterudites. This choice aims at preserving coherence with the experimental section of this chapter that mainly deals with these types of compounds.

1. Structural and mechanical properties

The structural and elastic properties of the ternary skuterrudite based on lanthanum ($LaFe_4A_{12}$, with A=P, As, Sb) have been investigated by ab initio density-functional theory (Hachemaoui et al. 2010)as

a function of an applied external pressure. The FP-APW+lo technique as implemented in the WIEN2k code (Blaha et al. 2001) has been used. At a given pressure, the elastic constants C_{11}, C_{12} and C_{44} and bulk modulus B_0 are found to decrease along the sequence P->As->Sb which is opposite to the cell parameters evolution (772.4, 817.9 and 896.3 pm, respectively). A linear increase of these properties is observed when external pressure increases. The compounds are all stable up to at least 40 GPa. In addition, the bulk, shear and Young moduli, the Poisson ratio, Lamé coefficient, sound velocity and Debye temperature have been calculated for an ideal polycrystalline aggregate as estimated from the Voigt-Reuss-Hill approximation (Hill 1952). It is found that these materials are brittle according to the Pugh empirical rule (Pugh 1954). The Debye temperature is decreasing along the sequence P->As->Sb (849, 619 and 489 K, respectively) which suggests that the $LaFe_4Sb_{12}$ should conduct heat more than the two other compounds. The same properties have been calculated for the UFe_4P_{12} filled skutterudite by Ameri and coll. using DFT (Hohenberg and Kohn 1964, Kohn and Sham 1965) and the FP-LMTO approach (Ameri et al. 2014a). The effect of temperature and pressure on these properties has been investigated through the quasi-harmonic approximation. The compound is found to be stable from at least -10 GPa up to 50 GPa. The Debye temperature θ_D increases systematically with the pressure while remaining almost constant within the range of temperatures 0-500 K. At zero temperature and pressure θ_D amounts to about 607 K. DFT combined with the FP-LMTO methodology has been employed by Benalia and coll. to investigate the mechanical properties of the $CeFe_4P_{12}$ filled skutterudite at absolute zero temperature (Benalia et al. 2008). The Debye temperature is estimated to about 366 K for this compound. Recently, an investigation of the elastic properties has been undertaken for the $EuFe_4P_{12}$ filled skutterudite by Shankar and coll (Shankar et al. 2015a). As with the other compounds mentioned above, $EuFe_4P_{12}$ is brittle. $EuFe_4P_{12}$ possesses bulk and shear moduli of about 116 GPa and 107 GPa, respectively. The Debye temperature amounts to 782.5 K. Finally the $ThFe_4P_{12}$ compound has been investigated using the FP-LAPW+lo technique (Khenata et al. 2007) though only the elastic constants and shear and Young moduli have been reported.

2. Electronic structure

2.1 Unfilled skutterudites

The $Co_{4-x}Ni_xSb_{12}$ phases have been investigated by DFT with *x* an integer parameter varying between 0 and 4 (Christensen et al. 2004). In parallel to this theoretical investigation an experimental one has been conducted using synchrotron and neutron powder diffraction that showed that the compound $Co_{2.9}Ni_{1.2}Sb_{12}$ is in fact a biphasic system with phases $Co_{3.8}Ni_{0.2}Sb_{12}$ and $Co_{0.4}Ni_{3.6}Sb_{12}$. Nevertheless, the density of states of the $Co_{4-x}Ni_xSb_{12}$ compounds has been calculated using DFT. The results show that Co_4Sb_{12} is a narrow band gap semiconductor. By contrast, all the Ni for Co substituted compounds are found to be metallic with a high electron doping character which, according to the authors, confirm that the Ni for Co substitutions are beneficial for the enhancement of the electrical conductivity of the compounds. The chemical bond nature of Co_3NiSb_{12} has been thoroughly investigated using Bader's QTAIM theory (Bertini et al. 2003, Bader et al. 1994). It has been found that the bonding nature of Co_4Sb_{12} is not fundamentally different from that when Ni is substituted for Co. The antimony atoms are bonded to two nearest-neighbour metal atoms and to two antimony atoms involved in the pnictogen ring. Metal atoms are not bonded to each other. The metal-antimony bond is ionic in nature: antimony atoms are cations whereas cobalt and nickel atoms are significantly negatively charged which obviously contradicts Dyck and coll. who have stated that either Ni donate an electron to the conduction band at high temperature or retain it at low temperature (Dyck 2002). The ionicity seems to be reinforced when going from cobalt to nickel (substitution). The electronic

structure of the NiP_3 skutterudite structure has been investigated using the LMTO-ASA method (Llunell et al. 1996). The band structure and density of states show a strong n-doping character with a small pseudo-gap 0.57 eV wide below the Fermi level. An EHTB analysis of the chemical bonds suggests that this compound is mainly metallic in nature, or eventually covalent. $FeSb_3$ skutterudite has been found to be a stable structure as a ferromagnetic compound with magnetization of about 1 μ_B/Fe (Råsander et al. 2015). The ferromagnetic structure is 0.15 eV more stable than the anti-ferromagnetic one which is itself 0.13 eV more stable than the unpolarized structure. The ferromagnetic $FeSb_3$ compound is described as a near half-metal. The spin-up valence bands are almost completely filled and a direct band gap of 0.26 eV shows up at the Γ point. By contrast, the Fermi level is 0.5 eV below the top of the spin-down valence bands with band gap of 0.7 eV separating the valence bands from the conduction ones. Therefore, the density of states of the spin-down bands near the Fermi level is much higher than that of the spin-up bands. Both spin-up and spin-down conduction bands are mainly contributed by Fe-d orbitals (Råsander et al. 2015, Daniel et al. 2015) while for the valence bands, spin-down bands are of Fe-d orbital character and spin-up bands are of Sb-p orbital character.

2.2 Filled skutterudites

To date, a large number of investigations have been reported on iron and nickel-based filled skutterudites a consequence of which the classification given below follows the type of filled skutterudites, namely, $FeAs_3$, FeP_3 and $FeSb_3$.

2.2.1 $FeAs_3$ skutterudite

The Ce-filled $FeAs_3$ skutterudite has been found to be a semiconductor with a small, indirect band gap of about 0.238 eV along the Γ-N line (Hachemaoui et al. 2009, Wawryk et al. 2009, Wawryk et al. 2011). Experimental reports are contradictory on this point: Grandjean and coll. (Grandjean et al. 1984) found this structure to be a semiconductor whereas Maple and coll. found it to be a metal (Maple et al. 2008). According to the theoretical results, the valence bands at the vicinity of the Fermi level are mainly contributed by Fe-d orbitals with little mixing with As-p and Ce-d states whereas the conduction bands are contributed by the Ce-f orbitals. Two very flat and well separated (by about 0.2 eV) conduction bands are visible in band structure (Wawryk et al. 2011). According to the authors, the low-lying bands result from the splitting of the Ce-f orbitals due to spin-orbit coupling.

The band structure as obtained by Harima and Takegahara for the La-filled $FeAs_3$ is very different from that of the previous compound (Harima and Takegahara 2003). $LaFe_4As_{12}$ is found to be a half-metal: some band contributed by the Fe-d orbitals cross the Fermi level. The top of these bands is located at the Γ point whereas the bottom of the conduction bands is between the Γ point and the H point. The Fermi surface around the Γ point is connected through the P point whereas it is closed around the N point.

The magnetism in the hypothetical Na-filled $FeAs_3$ skutterudite has been investigated in detail by Xing and coll. using DFT formalism(Xing et al. 2015). The band structure of $NaFe_4As_{12}$ shows a light band crossing the Fermi level. Hence this compound is a half metal. The maximum of the light band shows up at the Γ point, and a small gap (about 0.2 eV) separates the top of the valence bands from the bottom of the conduction band. The authors report that an instability towards ferromagnetic state

should occur in $NaFe_4As_{12}$ which is evidenced by the high density of states of the Fe-d states near the Fermi level (Stoner theory); The magnetization amounts to about 2.8 μ_B per formula unit.

2.2.2 FeP_3 skutterudite

To our knowledge most of the filled FeP_3 skutterudites have been investigated using lanthanides and actinides as fillers. Only $NaFe_4P_{12}$ has been reported by Xing and coll. using DFT approach(Xing et al. 2015). It has been shown that $NaFe_4P_{12}$ is a half metal with ferromagnetic ground state and magnetization of 1.6 μ_B per formula unit.

For the lanthanide series the La (Jung et al. 1990, Fornari and Singh 1999, Harima and Takegahara 2003, Grosvenor et al. 2006, Takegahara and Harima 2007, Xu and Li 2007, Saeterli et al. 2009, Flage-Larsen et al. 2010), Ce (Nordström and Singh 1996, Grovenor et al. 2006, Khenata et al. 2007, Benalia et al. 2008), Pr (Galvan 2006, Ameri et al. 2014b), and Eu (Shankar and Thapa 2013, Shankar et al., 2014) atoms have been used as fillers.

In $LaFe_4P_{12}$ the lanthanum gives three electrons to the structure leading to La^{3+}. This is evidenced by the projection of the La-4f orbitals from the total density of states that shows that these orbitals are only located well above the Fermi level in the conduction band (around 3 eV above the Fermi level). The structure may be then described as $La^{3+}(Fe_4P_{12})^{3-}$. Considering the large electronegativity of phosphorus compared to that of iron, phosphorus may be considered as the anion P^- hence giving a Fe^{3+} cationic state for iron. However, band structure obtained from EHT calculations suggests that the valence state of iron is close to +2 (Jung et al. 1990). Hence, the charge born by phosphorus would be $11/12 \approx 0.92$. The remaining hole could be associated to one out of the twelve phosphorus atoms. Alternatively the hole could be shared among the iron atoms leading to an average valence state $Fe^{2.25+}$. Reported studies tend to show that the hole is at least partially shared among the phosphorus atoms (Jung et al. 1990, Grosvenor et al. 2006, Shenoy et al. 1982). $LaFe_4P_{12}$ is a half metal compound with a light band crossing the Fermi level. Above this band, which maximum is at the Γ point, a small direct gap is formed (0.098 eV).

By contrast with $LaFe_4P_{12}$, Ce-4f orbitals participate to hybridization with Fe-d and P-p orbitals of the valence band near the Fermi level in $CeFe_4P_{12}$. More specifically, two bands close in energy contribute to the topmost part of the valence band. The highest band is predominantly contributed by the Ce-4f orbitals whereas the second lowest band does not contain Ce-4f contribution. Therefore, the valence state of cerium is not f^0 but rather d^xf^1 with $0.5<x<1$ (Nordström and Singh 1996). The consequence of the strong hybridization of the Ce-4f orbitals in the topmost valence band and lowest conduction one yields an overestimation of the Γ-N indirect energy band gap (0.34 eV versus 0.15-0.25 eV from experiments) as calculated with LDA. Probably that LDA+U technique would correct this behaviour but as far as we know, no such calculations have been undertaken to date.

Very few theoretical studies have been reported on $PrFe_4P_{12}$(Galvan 2006, Ameri et al. 2014b). Using EHT method Galvan has found this compound to be a half metal with very small direct band gap of 0.02 eV. However, this is in contradiction with Ameri and coll. findings of 0.442 eV who used FP-LMTO method. The band crossing the Fermi level is essentially contributed by the Pr-f orbitals with little hybridization with Fe-d and P-p orbitals. Hence, as in $CeFe_4P_{12}$ Pr valence state is of the type f^x with $x>0$.

The Eu-filled Fe_4P_{12} skutterudite has been found to be a ferromagnetic compound with total magnetization of 8.18 μ_B per formula unit (Shankar and Thapa 2013) as calculated with LSDA+U method. The compound is a half metal. The spin-up band structure shows that the Fermi level is crossed by a single, parabolic band at Γ with predominant Eu-f character. This band meets tangentially the conduction band at the Γ point. By contrast, two bands cross the Fermi level and show a maximum at the Γ point though without meeting the conduction band. Hence, a small, indirect gap shows up in the spin-up band structure. The character of these bands is Fe-d and P-p.

Since only thorium and uranium have stable (or very long living) isotopes, only the $ThFe_4P_{12}$(Galvan et al. 2003, Takegahara and Harima 2003, Khenata 2007, Cheng et al. 2008a) and UFe_4P_{12} skutterudites (Galvan et al. 2003, Ameri et al. 2014a) have been investigated using theoretical approaches (EHT, FP-LAPW). According to EHT method both $ThFe_4P_{12}$ and UFe_4P_{12} are metallic compounds which disagree with more elaborated methods such as the FP-LAPW one with which both compounds are described as half-metals with a pseudo bandgap located above the Fermi level. For $ThFe_4P_{12}$ it appears that the shape of the band structure and type of band gap (direct or not) is sensitive to the technical details of the method. To highlight this statement we present in Table 5 the results obtained with various methods. Comparing the effect of the exchange-correlation DFT functional (LDA versus GGA) it appears that LDA yields a direct band gap whereas GGA yields an indirect one. Furthermore, the LDA band gap is slightly wider than the GGA one. The inclusion of spin-orbit coupling allows for the splitting of the Th-f orbitals the consequence of which can be observed in the band structure. Irrespective of the technical details, the bands near the Fermi level barely contain Th-f orbitals that expand over the whole conduction band. The valence bands belong to the hybridization of the P-p and Fe-d orbitals. As to UFe_4P_{12} the calculated band structure shows that this compound is a half metal with an indirect band gap at Γ-N of 0.59 eV (as calculated at the FP-LMTO level). The bottom of the conduction band is made of two, flat bands that are separated by a small gap of about 0.1 eV.

Table 5: **Band structure features of $ThFe_4P_{12}$ obtained with various methods. FP-LAPW: full potential linearized augmented plane waves; lo: local orbitals to treat semi-core electrons if any; SO: spin-orbit coupling.**

Method	FP-LAPW+lo+SO with LDA functional[a]	FP-LAPW+lo with GGA functional[b]	FP-LAPW+SO with LDA functional[c]
Type of band gap	direct	indirect	direct
Band gap (eV)	0.52	0.41	0.45
Comment	Splitting of the f orbitals	No-splitting of the f orbitals	Splitting of the f orbitals

[a]From Khenata 2007.

[b]From Cheng et al. 2008.

[c]From Takegahara and Harima 2003.

2.2.3 $FeSb_3$ skutterudite

The bonding features of $NaFe_4Sb_{12}$ and KFe_4Sb_{12} compounds have been investigated by Leithe-Jasper and coll. using the ELF function (Leithe-Jaster et al. 2003, Leithe-Jaster et al. 2004, Becke and Edgecombe 1990). The resulting picture is that of a covalent frame of Sb and Fe atoms (with on average 1.76e between two Sb atoms and 2.03e between Sb and Fe) in which sodium cations enter into the cavities. The compound can be described as $Na^{0.98+}(Fe_4Sb_{12})^{0.98-}$. The same conclusions can be drawn for KFe_4Sb_{12}. Both compounds have ferromagnetic ground state (Xing et al. 2015). Close to the Fermi level the spin-up density is mainly contributed by Fe-d orbitals whereas the spin-down density is contributed by the Sb-p orbitals. The difference in spin polarization is very close to 1, therefore making XFe_4Sb_{12} (X=Na, K) nearly perfect half metals. There are noticeable similarities and differences in the band structure of $NaFe_4Sb_{12}$ and KFe_4Sb_{12} that have been described in great details by Yang and coll. (Yang et al. 2011) in terms of the band shifting with respect to the Sb-1s core state. The descriptions would be too lengthy to be reproduced in the present review and the interested reader is urged to read the article.

Alcaline-earth metals Ca, Sr and Ba, have been investigated as fillers in $FeSb_3$ skutterudites (Schnelle et al. 2005, Sichelschmidt et al. 2006, Kimura et al. 2007, Yang et al. 2011, Zhou et al. 2011, Yan et al., 2014). These compounds share the same feature of being half metals: the Fermi level is crossed by two, parabolic bands at the Γ point, a light band (antimony) and a heavy one (iron). Below these bands are located several heavy ones around 0.1 eV below the Fermi level. The band gap above the light valence band evolves as 0.47, 0.49 and 0.55 eV for Ca, Sr and Ba containing $FeSb_3$, respectively. The large differences between the conduction bands of the compounds can be exemplified by the energy gap that turns out to change from an indirect one (Γ-N gap) for $CaFe_4Sb_{12}$ and $SrFe_4Sb_{12}$ to a direct one at Γ for $BaFe_4Sb_{12}$.

We treat $InFe_4Sb_{12}$ and $SnFe_4Sb_{12}$altogether as they are consecutive in the periodic table. Indeed, they exhibit very similar band structure (Zhou et al. 2011); they are half metals with two valence bands crossing the Fermi level and they have an indirect band energy gap. The two valence bands have maximum at the Γ point and parabolic shape whereas the minimum of the conduction band is between Γ and N. We can notice that the topmost valence band also shows a marked maximum above the Fermi level at the H point where it has a parabolic shape. This feature is not usually observed for other filled $FeSb_3$ skutterudite. The gap between the valence band maximum and the conduction band minimum is very different though: it is much smaller for $SnFe_4Sb_{12}$ (0.028 eV) than for $InFe_4Sb_{12}$ (0.39 eV). However it could be that, the band gap of the former compound is very underestimated due to the presence of tin. The authors of this review have indeed noticed this feature in other thermoelectric materials such as Mg_2Sn and $Mg_2Si_{1-x}Sn_x$ that are described by DFT methods as metals instead of semiconductors. Nonetheless, this statement needs validation through comparison with experimental data but as far as we know experimental investigations on $SnFe_4Sb_{12}$ have not been reported to date. The hybridization of the orbitals at the vicinity of the Fermi level is as follows. The valence band is as expected mainly composed of the Sb-p and Fe-d orbitals plus a small contribution from the Sn-p orbitals in the case of $SnFe_4Sb_{12}$. The Sn-s orbital contribution is spread over 3 eV of the whole valence band. In $InFe_4Sb_{12}$ no In-p orbitals participate but a small contribution from the In-s orbital appears around 0.5 eV below the Fermi level. The conduction band is mainly composed of the Sb-p and Fe-d orbitals and, in the case of $SnFe_4Sb_{12}$, of the Sn-p orbitals.

Six $FeSb_3$ skutterudites filled with rare-earth metals have been investigated, namely those containing La (Harima and Takegahara 2003, Nouneh et al. 2007, Yang et al. 2011, Xu et al. 2011, Xu et al. 2012, Xing et al. 2015), Ce (Nordström and Singh 1996, Nouneh et al. 2007, Hachemaoui et al. 2009, Xu et al. 2011, Yang et al. 2011), Pr (Yang et al. 2011), Nd (Zhou et al. 2011), Eu (Shankar et al. 2015b), and Yb (Galvan et al. 2003, Schnelle et al. 2005, Sichelschmidt et al. 2006, Zhou et al. 2011, Yang et al. 2011). The band structure

and density of states of the La, Ce and Pr containing compounds show that the charge state of these atoms is +3. Cerium- and praseodynium-$FeSb_3$ skutterudites have very similar band structure, both for the valence and conduction bands. There is a slight discrepancy between several reports regarding the band structure of lanthanum-$FeSb_3$ especially near the Γ point where the maximum of the valence band is located. Following Xu and coll. (Xu et al. 2012) the top of valence band is made of a strongly parabolic (very light effective mass carriers) state. This band is intercepted about 0.15 eV below by a heavier state. By contrast, according to Xing and coll. and Yang and coll. (Yang et al. 2011, Xing et al. 2015) both the heavy and light bands are tangent to each other at the top of the valence band (above the Fermi level). This degeneracy of the states should sensitively increase the density of states and the Seebeck coefficient. Since the methods and technical details used in these studies are of high quality for these types of calculation, the origin of this discrepancy is difficult to trace back. $YbFe_4Sb_{12}$ is also a subject of divergence between the calculations (Zhou et al. 2011, Yang et al. 2011). The authors agree to say that this compound is a half metal and has an indirect band gap but the predicted lines in the Brillouin zone vary. Surprisingly though, the energy band gaps agree with each other and amounts to about 0.42 eV. As expected, the valence state of Yb is +2 in the skutterudite. $NdFe_4Sb_{12}$ is also a half metal compound with heavy p-doping. The band structure, especially the valence band, and the energy band gap (0.37 eV) are very similar to that of $YbFe_4Sb_{12}$(Zhou et al. 2011). Both in the valence and the conduction bands the Sb-p and Fe-d orbitals are hybridized with the Nd-f states. Hence, the valence state of Nd should be of the type s^xd^y with x and y some real numbers between 0 and 2 and 0 and 4, respectively. $EuFe_4Sb_{12}$(Krishnamurthy et al. 2007, Shankar et al. 2014) is described as a half metal compound with a small energy gap of 0.1 eV and is ferromagnetic with a total magnetic moment of 5.02 μ_B, 7 μ_B/Eu and -0.5μ_B/Fe (values from Krushnamurthy and coll.). Hence iron is antiferromagnetically coupled to europium. As with the other filled skutterudites, $EuFe_4Sb_{12}$ possesses a pseudo gap above the valence band. The valence band results from the hybridization of the Eu-f, Sb-p and Fe-d orbitals whereas the conduction band is composed of Eu-d and Fe-d orbitals.

2.3 Substituted skutterudites

A detailed analysis of the bonding structure of the unfilled $Co_{4-x}Ni_xSb_{12}$ skutterudite has been conducted by Bertini and coll. (Bertini et al., 2003) using Bader's QTAIM theory. Each Sb atom is bonded to two metal atoms and to two Sb atoms of the pictnogen ring. The metal atoms are not bonded to each other nor are the antimony ones. The nature of the metal-antimony bond is ionic whereas the Sb-Sb bond is more covalent. The metal-Sb bond is more ionic with nickel than with cobalt, which is in contradiction with the difference of electronegativity between the atoms (i.e. nickel is more electronegative than cobalt). Substitution of Ni for Co leads to a narrowing of the band gap and to an upshift of the Fermi level, which leads to a n-type doping character of Co_3NiSb_{12}, $Co_2Ni_2Sb_{12}$ and $CoNi_3Sb_{12}$ (Christensen et al., 2004). When antimony atoms are replaced by tellurium one, such as in $Co_3NiSb_{11}Te$, the band gap is also narrowed compared to that of $CoSb_3$(Stiewe et al., 2005) and the Fermi level increases in energy leading to an n-doped compound. When Co_3NiSb_{12} is partially filled with calcium, Ca acts as an electron donor; the empty s states of Ca pin the Fermi level in the conduction band yielding a n-doped compound (Puyet et al., 2007).

Other skutterudites based on mixed metals have been theoretically investigated. We find alkaline-earth filled $(Fe,Ni)_4Sb_{12}$ with Ca, Sr and Ba as fillers (Singh and Du, 2010), $Ca(Fe,Co)_4Sb_{12}$(Thomson et al., 2015) and $La(Fe,Co)_4Sb_{12}$(Lu et al., 2010), and $A(Fe,Co)_4P_{12}$ with A=La, Y, Ce (Mangersnes et al., 2008). Using the virtual crystal model, which allows to model site disorder within the density-functional theory approach, Singh and coll. have found that in $(Fe,Ni)_4Sb_{12}$ and $(Fe,Co)_4Sb_{12}$ filling the skutterudite with either Ca, Sr or Ba does not change markedly the band structure and the density of states. These compounds are small energy gap semiconductors with energy gap ranging from 0.36 eV to 0.42 eV. The consequence of these observations is that filling with alkaline-earth metals and mixing Ni and Fe at the metal site could lead to

good p-type thermoelectric materials. Indeed, the authors found that $SrFe_3NiSb_{12}$ may be a good candidate. The behaviour of $Ca(Fe,Co)_4Sb_{12}$ band structure with varying content of Fe and Co is interesting, as shown by Thomson and coworkers. Indeed, the Fe states are much lower in energy than the Co states. Furthermore, the higher the content in Fe, the deeper in energy the Fe states are. Since the Fermi level is pined by the Fe-d states, the density of states at the Fermi level increases with the content in iron. According to Lu and coll., in contrast with the previous skutterudite, the Fe-d states in $LaFe_3CoSb_{12}$ are located higher in energy than the Co-d states. In the skutterudites $A(Fe,Co)_4P_{12}$ where A are the rare-earth elements La, Y or Sc, the Fe/Co ratio affects noticeably the density of states and the electronic behaviour of the compound. For pure iron-based skutterudite the compound is a p-doped semiconductor whereas for an equal mixture of iron and cobalt the compound is a n-doped semiconductor.

3. Thermoelectric properties

The calculations of electronic transport properties (Seebeck coefficient, electrical and electronic thermal conductivities) have been made possible only recently thanks to the increase of computer power. In effect, for these properties the Fermi surface has to be calculated very precisely, which necessitate an extremely large number of k-points for the Brillouin zone sampling. Hence, studies presenting thermoelectric properties of skutterudites are more seldom than those dealing with electronic structure or mechanical properties.

Chaput and coll. investigated both $CoSb_3$ by combining the FLAPW approach and the Boltzmann transport theory and the inclusion of impurities as dopants ($(Ni_xCo_{1-x})Sb_3$, $(Fe_xCo_{1-x})Sb_3$ and Nd_xCoSb_3) using the KKR-CPA approach that allows to account for disordered structures (Chaput et al., 2005). $CoSb_3$ and $(Ni_xCo_{1-x})Sb_3$ are n-type doped compounds whereas $(Fe_xCo_{1-x})Sb_3$ is p-doped. The Seebeck coefficient is largest for the native $CoSb_3$ structure for temperatures below 400 K. The maximum in magnitude is found at around 350 K and amounts to about -420 $\mu V\ K^{-1}$. The same conclusion can be drawn from the experimental findings. It is noted that the calculated maximum of S is about 100 K below the experimental one, but the calculated and measured magnitudes are about the same. Above 400 K, the Nd-doped $CoSb_3$ shows best S characteristics with a maximal magnitude of -400 $\mu V\ K^{-1}$ at 500 K followed by Ni-doped $CoSb_3$ (-300 $\mu V\ K^{-1}$ at 700 K). The iron doped compound shows worst Seebeck coefficient with values below 200 $\mu V\ K^{-1}$ up to 800 K. When cobalt is fully replaced by iron (Daniel et al., 2015) the compound is strongly p-doped (metallic character) and a high electrical conductivity and low Seebeck coefficient is calculated at the Fermi level (intrinsic compound). A slight doping with e.g. an excess antimony concentration of 8 10^{21} cm^{-3} leads to an upshift of the Fermi level (n-doping) which increases the Seebeck coefficient substantially (140 $\mu V\ K^{-1}$ at 500 K). The power factor is also enhanced due to a slight increase of the electrical conductivity. It is concluded that only the n-doping of $FeSb_3$ leads to good thermoelectric properties for this compound which is due to the specific shape of the band structure. Filled $FeSb_3$ properties have also been investigated with alkaline (Na, K), alkaline-earth (Ca, Sr, Ba) and lanthanide metals (La, Ce, Pr, Nd, Eu, Yb) as fillers by Yang (Yang et al., 2011), Zhou (Zhou et al., 2011) Xu (Xu et al., 2011) and Shankar (Shankar et al., 2015b). Generally, the Seebeck coefficients of rare-earth-filled $FeSb_3$ are very low at temperatures below 300K and increase markedly with the temperature (e.g. 150 $\mu V\ K^{-1}$ for Nd Fe_4Sb_{12} at 750 K). In spite of this increase, the power factor of these compounds is rather small due to a small electrical conductivity. Therefore, the decent ZT values obtained for these thermoelectric materials is mainly caused by low lattice thermal conductivity which results from the phonon scattering by the fillers. Indeed, a strong reduction of the thermal conductivity has been observed by filling the voids in $FeSb_3$ by lanthanum atoms (Bernstein et al. 2010). The lowest value obtained amounts to between 1 and 1.6 $W\ m^{-1}\ K^{-1}$ at 900 K, depending on the type of force field parameters used in the molecular dynamics simulations, which is about 2.5 smaller than that for the unfilled skutterudite.

Only a few studies have been reported that deal with the thermoelectric properties of nickel-containing skutterudites. Nickel is present in the structure as a substitutional atom for cobalt or iron or as a filler. The Seebeck coefficient of the unfilled $Co_{4-x}Ni_xSb_{12}$ structure is characteristic of a n-doped materials irrespective of the value of x ranging from 1 to 4 (Christensen et al., 2004). The authors drew the same conclusion for $NiCo_4Sb_{12}$, where Ni fills all the voids. It is noticeable that, the calculated magnitude of the Seebeck coefficient of the $Co_{4-x}Ni_xSb_{12}$ compounds is by far lower than that of the pristine $CoSb_3$ compound for all temperatures except at around 1000 K where |S| is about the same for Co_3NiSb_{12} and $CoSb_3$ (70 $\mu V\ K^{-1}$). $NiCo_4Sb_{12}$ exhibits the smallest Seebeck coefficient magnitude among all the studied compounds. Chaput and coll. (see above) found markedly different results. In particular, above 450 K the $Ni_{0.01}Co_{0.99}Sb_3$ compound exhibit higher Seebeck coefficient than $CoSb_3$. This difference may be due to a different level of doping of the materials. The trends of S with respect to temperature and magnitude for the doubled doped $Co_{1-x}Ni_xSb_{3-y}Te_y$ compound is quite the same as for $Co_{4-x}Ni_xSb_{12}$; |S| increases about linearly with temperature and reaches about 90 $\mu V\ K^{-1}$ at 1000 K (Stiewe et al., 2005). In addition the magnitude of the thermopower decreases as the dopant concentration increases. The best power factor is obtained at 700 K for a ratio Te/Ni of about 0.1. A high magnitude of the Seebeck coefficient (above 200 $\mu V\ K^{-1}$) as been found for the Ca, Ba and Sr alkaline earth-filled Fe_3NiSb_{12}(Singh and Du, 2010). In addition, S is high even for high concentrations of fillers. These high values of S are caused by the presence of flat bands near the Fermi level that are contributed by metal d-orbitals. These observations are valid for both n- and p-doped (Ca,Ba,Sr)Fe_3NiSb_{12} skutterudite. However, the advantage of the p-doped compounds over the n-doped ones is that, a mixing of heavy and light bands comes into play in the valence band, which should be favourable for enhancing the carrier mobility. Indeed, a weaker reduction of the Seebeck coefficient due to bipolar conduction has been observed in p-doped compounds than in n-doped ones. For the same reasons, in $Ca_yCo_{4-x}Ni_xSb_{12}$(Puyet et al., 2007), the electrical conductivity and the thermopower are also enhanced due to the substitution of Ni for Co.

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