

New filled P-based skutterudites—promising materials for thermoelectricity?

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New Journal of Physics **10** (2008) 053004 (16pp)

Received 7 February 2008

Published 6 May 2008

Online at <http://www.njp.org/>

doi:10.1088/1367-2630/10/5/053004

Abstract. The crystal structure, thermodynamic stability and electronic structure of the 75 filled and unfilled skutterudite compounds $M_x\text{Co}_{4-y}\text{Fe}_y\text{P}_{12}$, with M being La, Y and Sc, $x = \{0, 0.125, 0.25, 0.50, 1\}$ and $y = \{0, 1, 2, 3, 4\}$ are predicted from periodic density functional calculations. The rattling amplitude of the filling atom M , which is important for the thermal conductivity of the compounds, is found to depend mostly on the type of filling element and only to a small extent on the filling fraction, or the fraction of Fe in the structure. The calculated ground state stabilities show that none of the Sc-filled skutterudites are thermodynamically stable at 0 K, while the only stable combination of x and y among the studied Y-filled ones is $\text{YCoFe}_3\text{P}_{12}$. The La-filled skutterudites, on the other hand, are thermodynamically stable in a variety of combinations, with maximum stability when $y = 3x$, that is three Fe atoms per filling atom. Based on the calculated electronic structure we also expect filled skutterudites with $y = 3x$ to be most interesting for thermoelectric applications.

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1. Introduction

Materials with the skutterudite structure have been the subject of considerable interest because of their relevance for thermoelectric applications. The skutterudites have the general formula TX_3 with T being a transition metal (e.g. Co, Rh or Ir) and X a pnictogen (As, Sb or P). These materials, which crystallize in the cubic $Im\bar{3}$ space group, contain two rather large dodecahedral (12-fold) voids corresponding to the $2a$ sites in Wyckoff notation.

The thermoelectric figure of merit, $Z = \frac{S^2\sigma}{\lambda}$, is a measure of the quality of a thermoelectric material. A high value for Z indicates that a given material will be suitable for thermoelectric applications. S is the Seebeck coefficient, while σ and λ are the electrical and thermal conductivities. Binary skutterudites usually display both high Seebeck coefficient and electrical conductivity, but their thermal conductivity is also high, often making them unsuitable for thermoelectric applications.

In 1994, Slack and Tsoukala [1] predicted that filling the large voids of the skutterudite with foreign atoms could lower the thermal conductivity through a disruptive influence on the thermal phonons by the rattling of the filler atom in the oversized box. This effect has indeed been demonstrated for several different filling elements [2]–[6]. Rare earth metals, e.g. La, Ce, Nd, Sm, Eu, etc, are typically used for filling. A strong correlation was found between the rattling amplitude and the thermal conductivity. For instance, an increase in rattling amplitude from 15 pm in $CeFe_4P_{12}$ to 29 pm in $CeFe_4Sb_{12}$ lowered the thermal conductivity by as much as an order of magnitude [7].

In parallel to this, theoretical modeling of skutterudites for thermoelectricity has been the subject of a number of papers [8]–[19]. In one such study, it was predicted that the filling fraction limit of La, Y and Sc in pure CoP_3 would be a few percent at most [20]. In addition it is known that filled CoP_3 is not suitable for thermoelectric applications because of the relatively high charge carrier concentration. However, the maximum filling fraction of these elements is expected to increase significantly if Fe is substituted for Co, since this should compensate for the extra charge carriers contributed by the rattling atom. Also, this would possibly reduce the charge carrier concentration, making the compounds more useful for thermoelectric applications.

In this work, we investigate the hypothetical compounds $M_xCo_{4-y}Fe_yP_{12}$, with M being La, Y and Sc, $x = \{0, 0.125, 0.25, 0.50, 1\}$ and $y = \{0, 1, 2, 3, 4\}$. The only previously

described [21] compounds in this series are CoP_3 and $\text{LaFe}_4\text{P}_{12}$. We use density functional calculations within the generalized gradient approximation (GGA), and employ a full relaxation of the atomic coordinates, the unit cell size and shape. The thermodynamic ground state stability is also investigated by comparing the calculated total electronic energies of various competing compounds to those of the skutterudites. Finally, the electronic structure is analyzed to study how the electric conductivity may be affected by the filling of the voids and by the substitution of Co by Fe.

2. Computational method

The calculations were performed using periodic density-functional calculations at the GGA level as implemented in the Vienna *ab initio* simulation package (VASP) [22, 23]. The projector augmented wave (PAW) method was used to span out the electron density [24], and the gradient correction was PW91 [25]. The PAW method may be seen as a generalization of augmented wave methods and the pseudopotential approach. It has similar reliability as full-potential all-electron methods, whereas the efficiency is comparable to that of the pseudopotential approach [26]. When two consecutive total energies differed by less than 0.01 meV the electronic structure was considered self-consistent. A plane-wave cutoff energy of 650 eV was used throughout, and the largest minimum distance between \mathbf{k} points in the irreducible wedge of the Brillouin zone was 0.05 \AA^{-1} , sufficient to ensure that the overall error due to the mentioned numerical sources was of the order of 1 meV per unit cell. Smearing of partial electronic occupancies was for most of the compounds done using the tetrahedron method with Blöchl corrections, except in a few cases where large unit cells lead to less than three \mathbf{k} points in one or more directions; we then used a Gaussian smearing with a width of 0.2 eV. All calculations allowed for spin polarization, and in unit cells with both Co and Fe we used an atomic arrangement giving maximum Co–Co and Fe–Fe distances. This distribution of Co and Fe in the structures was chosen after performing test calculations of both distributed and clustered metal atoms, which showed an effective repulsion between atoms of the same kind. One typical unit cell with such a distribution of Co and Fe is shown in figure 1.

Relaxations were performed using the residual minimization method direct inversion in iterative subspace implementation of the quasi-Newton algorithm [27]. The ionic coordinates and the unit cell size and shape were optimized simultaneously to eliminate structures with internal stress. A structure was considered relaxed when all forces were less than 0.05 eV \AA^{-1} . A single calculation using high accuracy was performed after the completion of the relaxation in order to determine the total electronic energy more accurately.

3. Results and discussion

3.1. Crystal structure

The starting point for all our models was the cubic skutterudite unit cell, which has also been observed to persist when the structure is filled. However, since we use periodic boundary conditions in the calculations, some symmetry is necessarily broken when the models are constructed. Thus, the model with 25% filling is made from a $1 \times 1 \times 2$ conventional (cubic) unit cell, while the model with 12.5% has been created using a $2 \times 2 \times 2$ primitive (rhombohedral) cell in order to preserve cubic symmetry. The models for other fillings used the conventional

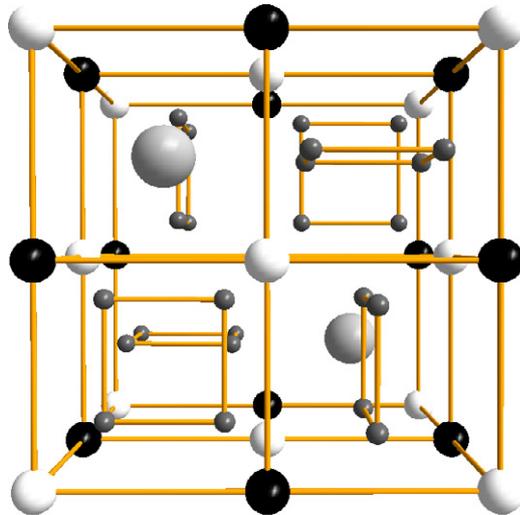


Figure 1. The filled skutterudite unit cell with the origin translated by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ along the diagonal, here represented by $\text{YCo}_2\text{Fe}_2\text{P}_{12}$. Y is represented by large gray balls, while P is represented by small (darker) gray balls. Co and Fe (white and black balls, respectively) are distributed in the cubic lattice so that there is a maximum distance between equal metal atoms. Based on the calculated ground state energy, this is the configuration of metal atoms that is most likely to occur.

unit cell. The resulting symmetry of these constructions is shown in table 1 by specifying the space group of each model. We can see how some symmetry is lost when Fe substitutes for Co on the $8c$ sites, since some of the symmetry operators transforming Co sites among each other are no longer valid. In a similar vein symmetry is broken when the filling fraction is less than one. We do, however, expect both metal and filling atoms to be randomly distributed in the real compounds, and it is therefore reasonable to talk about skutterudite structures also for the models with lower symmetry.

The unit cell shape and size as well as the ionic positions were simultaneously allowed to relax during the calculations. Nevertheless, none of the models changed space group in the course of the relaxations. Furthermore, the relaxed unit cells retained cubic or rhombohedral symmetry for the models with 100 and 50% filling and for the rhombohedral cells with $y = 0, 2$ and 4. However, in the models where cubic symmetry is intrinsically broken, the relaxed lattice constants were not of the same length. The largest difference between the lattice constants was 1.7 pm in $\text{Y}_{0.25}\text{Co}_4\text{P}_{12}$, followed by 1.4 pm in $\text{Y}_{0.25}\text{Fe}_4\text{P}_{12}$. The other deviations were between 0.3 and 1.2 pm. Does this point to broken symmetry in the real materials? Previous calculations for other compounds have shown that lattice constants of equivalent structures may differ by up to 3 pm when starting from different input models [28]. Thus, all the relaxed structures are cubic within the inherent uncertainty of the method. Similarly, the resulting angles may differ by up to 0.17° in such calculations [28]. None of the angles in our relaxations differed by more than 0.15° from orthogonality. We hence believe that the broken symmetry of the models is entirely due to the restrictions imposed by the periodic calculations. Our calculations leave no reason to suspect that the cubic symmetry in the real material is broken, and we conclude that experiments most probably will find the structure of the filled $\text{Co}_{4-y}\text{Fe}_y\text{P}_{12}$ to be cubic with the skutterudite structure.

Table 1. The resulting space groups of the relaxed structures $M_x\text{Co}_{4-y}\text{Fe}_y\text{P}_{12}$. The relaxed structure had in all cases the same space group as the initial structure. M is La, Y and Sc, x is the filling fraction, and y represents the fraction of Fe in the structure. The number of atoms in the unit cell, N_{atoms} , and the SG have also been listed. The results with $y = 0$ are from Løvvik and Prytz [20].

Compound	x (%)	y	N_{atoms}	SG
Fe_4P_{12}	0	4	32	$Im\bar{3}$
$M_{0.125}\text{Fe}_4\text{P}_{12}$	12.5	4	129	$Im\bar{3}$
$M_{0.25}\text{Fe}_4\text{P}_{12}$	25	4	65	$Pmmm$
$M_{0.5}\text{Fe}_4\text{P}_{12}$	50	4	33	$Pm\bar{3}$
$M\text{Fe}_4\text{P}_{12}$	100	4	34	$Im\bar{3}$
$\text{CoFe}_3\text{P}_{12}$	0	3	32	$R\bar{3}$
$M_{0.125}\text{CoFe}_3\text{P}_{12}$	12.5	3	129	$C2$
$M_{0.25}\text{CoFe}_3\text{P}_{12}$	25	3	65	$P\bar{1}$
$M_{0.5}\text{CoFe}_3\text{P}_{12}$	50	3	33	$R\bar{3}$
$M\text{CoFe}_3\text{P}_{12}$	100	3	34	$R\bar{3}$
$\text{Co}_2\text{Fe}_2\text{P}_{12}$	0	2	32	$Pn\bar{3}$
$M_{0.125}\text{Co}_2\text{Fe}_2\text{P}_{12}$	12.5	2	129	$I23$
$M_{0.25}\text{Co}_2\text{Fe}_2\text{P}_{12}$	25	2	65	$P222$
$M_{0.5}\text{Co}_2\text{Fe}_2\text{P}_{12}$	50	2	33	$P23$
$M\text{Co}_2\text{Fe}_2\text{P}_{12}$	100	2	34	$Pn\bar{3}$
$\text{Co}_3\text{FeP}_{12}$	0	1	32	$R\bar{3}$
$M_{0.125}\text{Co}_3\text{FeP}_{12}$	12.5	1	129	$C2$
$M_{0.25}\text{Co}_3\text{FeP}_{12}$	25	1	65	$P\bar{1}$
$M_{0.5}\text{Co}_3\text{FeP}_{12}$	50	1	33	$R\bar{3}$
$M\text{Co}_3\text{FeP}_{12}$	100	1	34	$R\bar{3}$
Co_4P_{12}	0	0	32	$Im\bar{3}$
$M_{0.125}\text{Co}_4\text{P}_{12}$	12.5	0	129	$Im\bar{3}$
$M_{0.25}\text{Co}_4\text{P}_{12}$	25	0	65	$Pmmm$
$M_{0.5}\text{Co}_4\text{P}_{12}$	50	0	33	$Pm\bar{3}$
$M\text{Co}_4\text{P}_{12}$	100	0	34	$Im\bar{3}$

3.2. Lattice parameters and rattling amplitude

Figure 2 shows the relaxed unit cell volume of $\text{Y}_x\text{Co}_{4-y}\text{Fe}_y\text{P}_{12}$ as a function of the filling fraction x . The cell volume increases monotonically with x for all the models, but the slope decreases as the amount of Fe (y) increases. Thus, while CoP_3 has the lowest volume among the unfilled models, it is the opposite for the 100% Y-filled models: fully Y-filled CoP_3 has a larger volume than all the other fully Y-filled $(\text{Co,Fe})\text{P}_3$ compounds. The same trend is also seen for the La-filled compounds.

Figure 3 shows the cell volume as a function of filling fraction, every second Co atom has been substituted by Fe. We observe a strong dependence of the volume on the amount of filling, and also on the type of filling atom, clearly reflecting the difference in size between the three atomic species.

In figure 4, the cell volume in the case of partial filling ($x = 0.25$) is shown for various degrees of substitution. The most striking feature here is that the relative change in cell volume

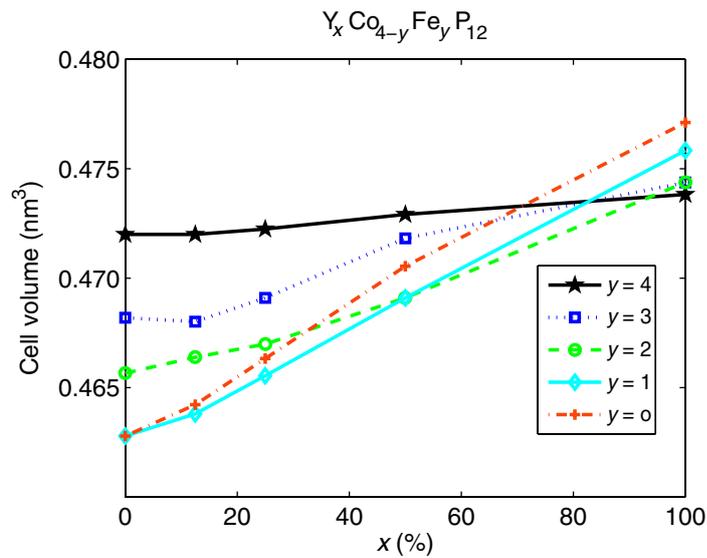


Figure 2. The relaxed unit cell volume of $Y_xCo_{4-y}Fe_yP_{12}$. $y = 4$ is represented by the solid line with stars, $y = 3$ by the dotted line, $y = 2$ by the dashed line, $y = 1$ by the solid line with diamonds, and $y = 0$ is represented by the dashdot line.

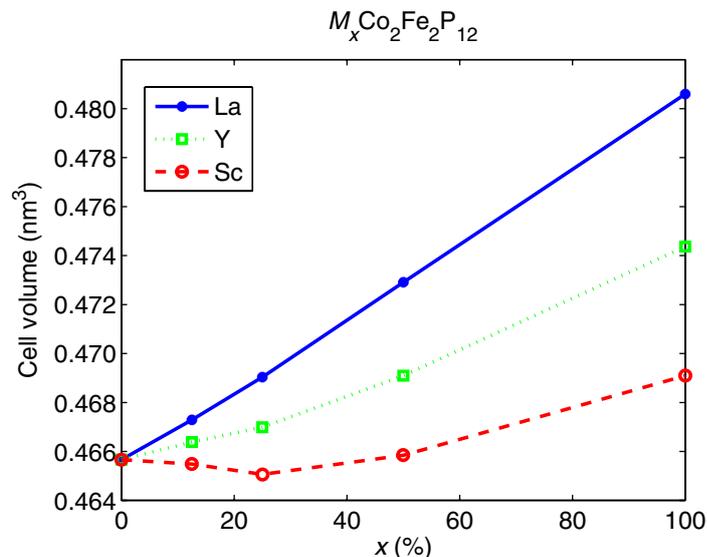


Figure 3. The relaxed unit cell volume of $M_xCo_2Fe_2P_{12}$. La is represented by the solid line, Y by the dotted line, and Sc by the dashed line.

as the iron content increases, is very similar for the three types of filling atoms. Furthermore, the minimum volume is found for $M_{0.25}Co_3FeP_{12}$ for all filling elements.

To explain these results we start by assuming that Fe is in the Fe^{2+} valence state while Co is present as Co^{3+} . Our calculations predict that the lattice parameter of FeP_3 is 778.6 pm; more than 5 pm larger than that of CoP_3 (773.5 pm). The covalent radii of Co^{3+} and Fe^{2+} are 122 and 123 pm, which explains quite well the difference in lattice parameter [21]. Counting the

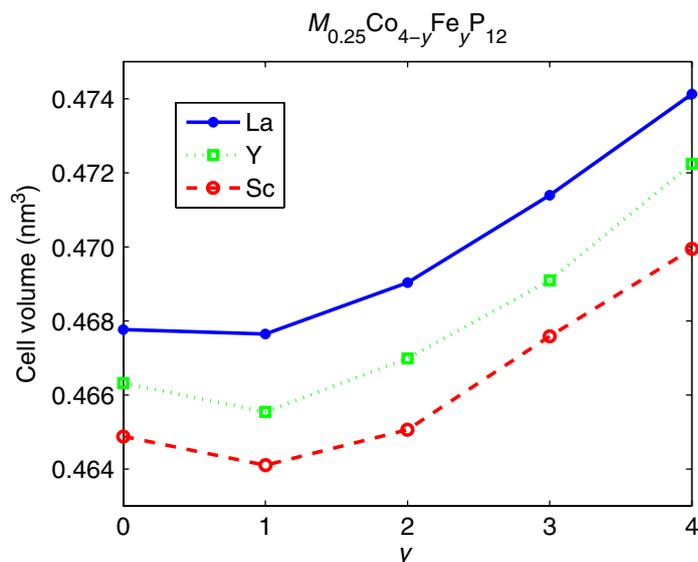


Figure 4. Volume of the relaxed unit cell of $M_{0.25}\text{Co}_{4-y}\text{Fe}_y\text{P}_{12}$. La is represented by the solid line, Y by the dotted line, and Sc by the dashed line.

number of valence electrons implies that the covalent bonds of CoP_3 will be saturated, while the covalent bonds of FeP_3 will be electron deficient. A more detailed study of the relaxed structures also shows that the Fe–P distances in FeP_3 are significantly larger than the corresponding Co–P distances in CoP_3 . However, in the models containing both Co and Fe the situation is reversed: the Co–P distances are now longer than the Fe–P distances! This seems to indicate that the valence state of both Co and Fe is changed when going from the pure to the mixed (Co, Fe) models. The most probable rationalization of the results for the mixed models seems to be that Fe and Co enter a shared valence state, in which the valence electrons are shared equally between Co and Fe in the unit cell. The listed covalent radii for Co^{2+} and Fe^{3+} are 132 and 122 pm [29], respectively, which means that the hypothesized shared valence state readily explains the increased Co–P distances of the mixed (Co, Fe) models.

The different filling elements La, Y and Sc each carry three valence electrons, thus contributing to saturate the electron deficient bonds in structures containing Fe; they will be superfluous in Co-based skutterudites, however. The bonds will be exactly saturated when $y = 3x$, that is when three Co atoms are replaced by Fe per filling atom.

An effect of this relationship between the number of filling atoms and the degree of substitution can be observed in figure 4. Here the structure is partially filled ($x = 0.25$), and a small decrease in cell volume can be seen as the iron content is increased from $y = 0$ to 1. This agrees well with the relationship above, which predicts fully saturated bonds for $y = 0.75$. For larger degrees of substitution, the cell volume increases as an increasing number of Fe–P bonds remain unsaturated.

The rattling amplitude, A_{ratl} , is defined as the radius of the dodecahedral (12-fold) void of the skutterudite, R_{void} , minus the covalent radius of the filler atom, R_{cov} :

$$A_{\text{ratl}} = R_{\text{void}} - R_{\text{cov}}. \quad (1)$$

The radius of the void is found by taking one half of the distance between two P atoms situated in opposite corners (the shortest diagonal distance), minus one half of a P–P bond. Even though

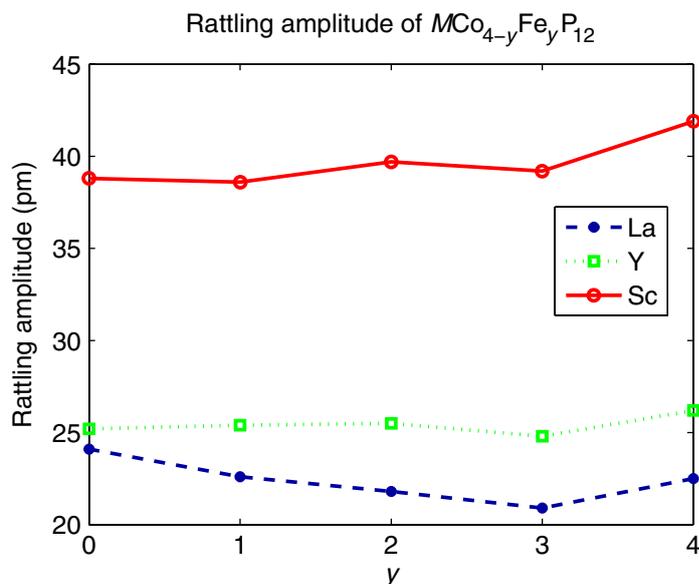


Figure 5. Rattling amplitude of $M\text{Co}_{4-y}\text{Fe}_y\text{P}_{12}$, with M being La (solid line), Y (dotted line), and Sc (dashed line).

this is a simple model, in previous studies it has proved to be a successful indicator of the reduction, and we will use it here as an indicator in this sense.

We have found that the difference in the covalent radius of the filler atoms is significantly larger than the difference in lattice parameters in the filled skutterudites. Thus, we expect the rattling amplitude of Sc and Y-filled skutterudites to be larger than that of those filled with La. As an example, the lattice parameters of 100% La, Y and Sc-filled FeP_3 are 783.8, 779.2 and 776.1 pm, resulting in quite significant differences in rattling amplitude. In figure 5 the rattling amplitude of 100% filled skutterudites is plotted versus y , the content of Fe. The rattling amplitude varies very little with the filling fraction, and the same trend is observed for the other filling fractions (not shown). The amplitude is, as expected, between 5 and 20 pm larger for Y- and Sc-filled compounds than for those equally filled with La. If the results of Chen *et al* [7] are directly transferable to this case, we can expect a decrease in thermal conductivity by an order of magnitude when going from La-filled to Sc-filled compounds. This analysis neglects, however, the role of mass on the rattling effect. Since heavier atoms contribute more efficiently to the scattering of phonons, the actual decrease of thermal conductivity may be smaller than estimated above, since La is heavier than Y and Sc.

3.3. Phase stability

The compositions studied above show a predictable behavior with regard to cell volume, and display a rattling amplitude that suggests that a reduction in thermal conductivity can be achieved. Furthermore, all the investigated compositions retain the skutterudite structure regardless of filling and substitution.

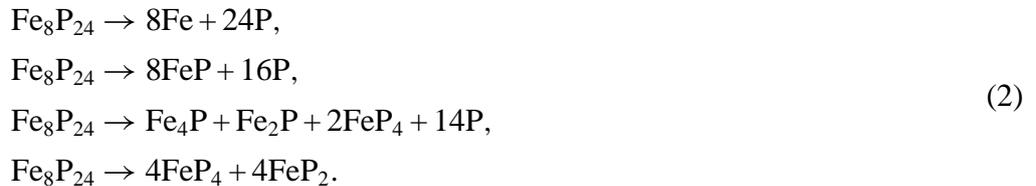
However, this does not indicate that the structures are thermodynamically stable relative to competing phases. In order to quantify the thermodynamic stability of these hypothetical compounds, we have compared the calculated ground state energies of the skutterudites to

Table 2. The different compounds and elements used in the phase stability calculations.

Co	ScFe ₄ P ₂
Fe	FeP ₄
P	Fe ₂ Y
La	Fe ₂ Sc
Y	Fe ₅ Y
Sc	LaP
CoFe	YP
CoP	ScP
CoP ₂	LaP ₅
CoP ₃	Sc ₃ P ₂
FeP	YCo
Fe ₂ P	YP ₅
Fe ₃ P	LaFe ₂ P ₂
Fe ₄ P	

those of the competing compounds of various possible decomposition routes. The compounds considered in these calculations are listed in table 2. The electronic energy was found in the same way as for the skutterudite structures: by a full relaxation of both the unit cell and the ionic positions, followed by a final high precision calculation. The stability of Co based skutterudites ($y = 0$) was already presented in [20], but is included here for completeness.

Zero point motion and temperature effects are not included in the calculations. We assume, however, that the effect of the zero point motion will more or less cancel out when comparing different structures. Temperature and entropy often contribute to a relative stabilization of complex materials, which means that the following results probably lead to conservative estimates of the stability of the filled models. In each case the most stable decomposition route was chosen to evaluate the stability of the skutterudite compound. As an example, some of the different decomposition routes investigated for Fe₈P₂₄ were



To calculate the decomposition enthalpy we have compared the total electronic energy, in this case of Fe₈P₂₄, with that of the possible decomposition routes. For instance,

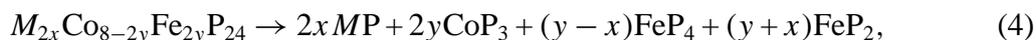
$$\begin{aligned}
 H_{\text{decomp}}(\text{Fe}_8\text{P}_{24}) &= - [E(\text{Fe}_8\text{P}_{24}) - 8E(\text{Fe}) - 24E(\text{P})] \\
 &= 12.82 \text{ eV},
 \end{aligned}
 \tag{3}$$

for the first line of equation (2). A positive enthalpy indicates that the skutterudite is thermodynamically stable compared to the end products, which in this case are the pure elements. In table 3, we show the most stable decomposition routes of Y-filled (Co, Fe)P₃. From the table it can be seen that the last line of equation (2) gives the most stable end product, with negative enthalpy. The unfilled iron based skutterudite will therefore, as suspected, not be

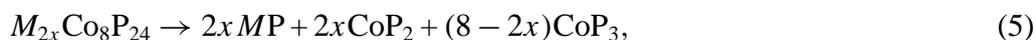
Table 3. The most probable decomposition routes and enthalpies of $Y_xCo_{4-y}Fe_yP_{12}$. A positive decomposition enthalpy means that the skutterudite will be stable compared with its end products.

Decomposition route	H_{decomp} (eV)
$Fe_8P_{24} \rightarrow 4FeP_4 + 4FeP_2$	-2.95
$Y_{0.25}Fe_8P_{24} \rightarrow 0.25YP + 3.875FeP_4 + 4.125FeP_2$	-2.37
$Y_{0.50}Fe_8P_{24} \rightarrow 0.5YP + 3.75FeP_4 + 4.25FeP_2$	-2.30
$YFe_8P_{24} \rightarrow YP + 3.5FeP_4 + 4.5FeP_2$	-1.67
$Y_2Fe_8P_{24} \rightarrow 2YP + 3FeP_4 + 5FeP_2$	-0.25
$Co_2Fe_6P_{24} \rightarrow 2CoP_3 + 3FeP_4 + 3FeP_2$	-2.11
$Y_{0.25}Co_2Fe_6P_{24} \rightarrow 0.25YP + 2CoP_3 + 2.875FeP_4 + 3.125FeP_2$	-1.57
$Y_{0.50}Co_2Fe_6P_{24} \rightarrow 0.5YP + 2CoP_3 + 2.75FeP_4 + 3.25FeP_2$	-1.45
$YCo_2Fe_6P_{24} \rightarrow YP + 3CoP_3 + 2.5FeP_4 + 3.5FeP_2$	-0.86
$Y_2Co_2Fe_6P_{24} \rightarrow 2YP + 2CoP_3 + 2FeP_4 + 4FeP_2$	0.08
$Co_4Fe_4P_{24} \rightarrow 4CoP_3 + 2FeP_4 + 2FeP_2$	-1.22
$Y_{0.25}Co_4Fe_4P_{24} \rightarrow 0.25YP + 4CoP_3 + 1.875FeP_4 + 2.125FeP_2$	-0.75
$Y_{0.50}Co_4Fe_4P_{24} \rightarrow 0.5YP + 4CoP_3 + 1.75FeP_4 + 2.25FeP_2$	-0.66
$YCo_4Fe_4P_{24} \rightarrow YP + 4CoP_3 + 1.5FeP_4 + 2.5FeP_2$	-0.17
$Y_2Co_4Fe_4P_{24} \rightarrow 2YP + 4CoP_3 + FeP_4 + 3FeP_2$	-1.41
$Co_6Fe_2P_{24} \rightarrow 6CoP_3 + FeP_4 + FeP_2$	-0.43
$Y_{0.25}Co_6Fe_2P_{24} \rightarrow 0.25YP + 6CoP_3 + 0.875FeP_4 + 1.125FeP_2$	-0.13
$Y_{0.50}Co_6Fe_2P_{24} \rightarrow 0.5YP + 6CoP_3 + 0.75FeP_4 + 1.25FeP_2$	-0.14
$YCo_6Fe_2P_{24} \rightarrow YP + 6CoP_3 + 0.5FeP_4 + 1.5FeP_2$	-0.83
$Y_2Co_6Fe_2P_{24} \rightarrow 2YP + 6CoP_3 + 2FeP_2$	-3.01

thermodynamically stable. The decomposition routes of the La- and Sc-filled compounds have been calculated in a similar way. The La- and Sc-filled skutterudites containing Fe ($y = 1-4$) decomposed following the general route

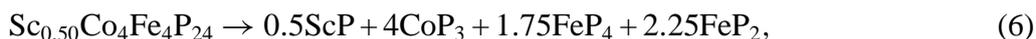


with a few exceptions for the La-filled compounds. The La- and Sc-filled skutterudites with solely Co on the metal sites ($y = 0$) decomposed according to the formula



with M being La and Sc only for these two last equations.

As an example for the case $y = 2$,



in agreement with equation (4).

The ground state stability of the unfilled skutterudites is shown in the upper left corner of figure 6. None of the compounds $Co_{4-y}Fe_yP_{12}$ with $y \geq 1$ are thermodynamically stable, but a linear extrapolation of the data points shows that an unfilled skutterudite with less than around 12.5% Fe will most probably be stable.

The thermodynamic ground state stability of filled skutterudites is shown in the other panels of figure 6. The Sc-filled compounds are clearly seen to be thermodynamically unstable,

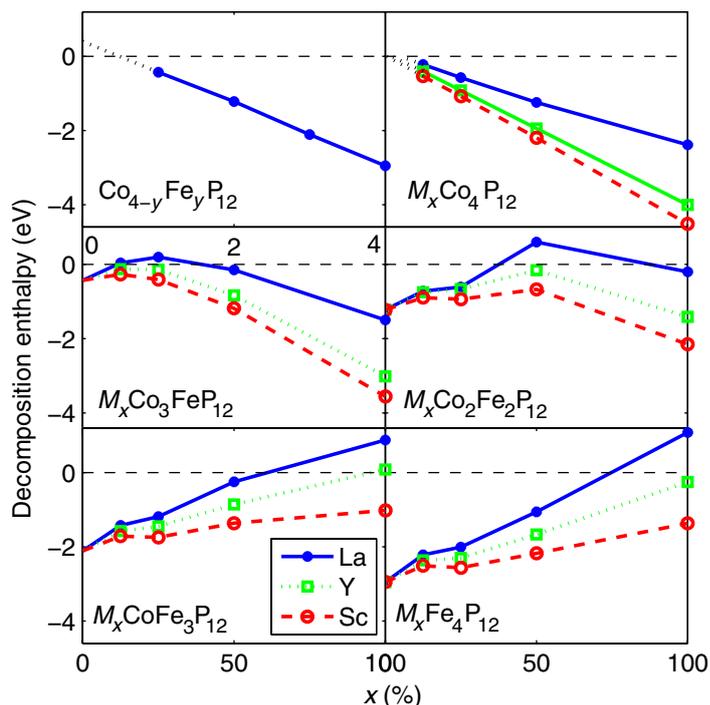


Figure 6. The upper left corner shows the decomposition enthalpy of $\text{Co}_{4-y}\text{Fe}_y\text{P}_{12}$ as a function of y , the Fe content. The other figures show the decomposition enthalpy of $M_x\text{Co}_{4-y}\text{Fe}_y\text{P}_{12}$ as a function of the filling fraction. A positive decomposition enthalpy means that the skutterudite will be stable compared to its most favorable end points. The energy has been normalized to the conventional cubic unit cell. The dotted oblique lines in the two upper figures are extrapolations based on linear fits of the data points. La is represented by solid lines and filled circles as markers, Y by dotted lines and squares, and Sc by dashed lines and open circles.

while the only stable Y-filled compound among the ones investigated in this work is $\text{YCoFe}_3\text{P}_{12}$. La, on the other hand, can be filled into several different skutterudite compounds.

The possible filling fractions decrease with increasing amount of Co in the structure. From the discussion on lattice parameters we know that the three valence electrons from the filling elements contribute to the saturation of the covalent bonds. We therefore believe that the compounds will have maximum stability when there is one void filler per three Fe atoms.

In other words, $M_{0.67}\text{Co}_2\text{Fe}_2\text{P}_{12}$ and $M_{0.33}\text{CoFe}_3\text{P}_{12}$ will be the optimal stability solutions for $y = 2$ and 3 , respectively. Even if these compounds have not been studied directly, this conclusion seems to be consistent with the observations in figure 6. This also implies that $\text{Y}_{0.67}\text{Co}_2\text{Fe}_2\text{P}_{12}$ and $\text{Y}_{0.33}\text{CoFe}_3\text{P}_{12}$ may be thermodynamically stable. It is also possible that temperature and entropy can stabilize some of these filled compounds.

3.4. Electronic structure

In the previous sections, it was shown that Y-filled skutterudites display a rattling amplitude larger than the correspondingly La filled materials, which suggest that they may have a lower

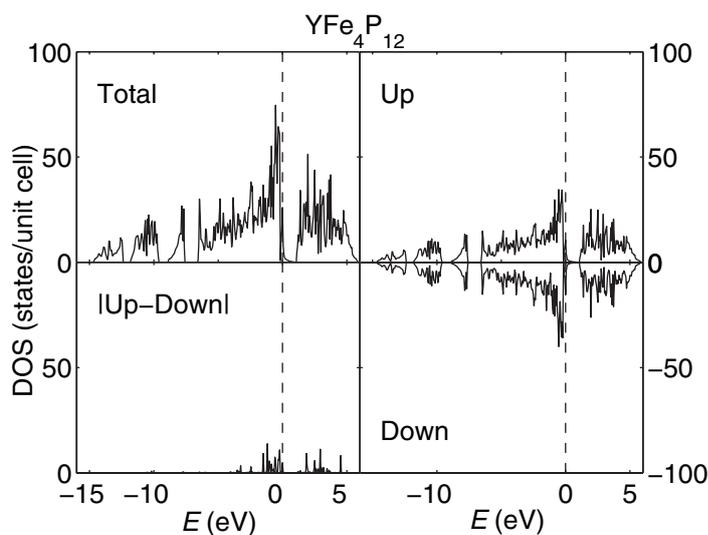


Figure 7. Spin polarized density of states (DOS) of $\text{YFe}_4\text{P}_{12}$. The figure shows the total DOS, the DOS of spin up and spin down, and the absolute difference between spin up, and spin down DOS. The energy is in electron volt relative to the Fermi level.

thermal conductivity. Furthermore, our investigations indicate that several of these hypothetical compounds may be thermodynamically stable.

In addition to having a low thermal conductivity, a material considered for thermoelectric applications should have high values of the Seebeck coefficient S and the electrical conductivity σ , both of which are to a large part determined by the band structure of the material. In particular, the Seebeck coefficient can be shown to depend strongly on gradients in the density of states (DOS) $N(\epsilon)$ close to the Fermi-level. Thus, as a rule of thumb, we are looking for materials where the Fermi-level is located in a band gap, but close to the onset of either the conduction or valence bands, or in general close to sharp features in the DOS.

To aid these evaluations, we have calculated the total electronic DOS for all the materials considered in this study. As an example, we show in figure 7 the total and spin polarized DOS of $\text{YFe}_4\text{P}_{12}$. The DOS for this compound displays features typical for skutterudite compounds [9, 20, 30, 31]. The Fermi-level is located close to a pseudo-gap of approximately 1 eV where the DOS is very small. Below this gap, the transition metal 3d states are sharply peaked, while above a rather uniform distribution of states is seen. In this particular case, the Fermi-level is located at the very bottom of the pseudo-gap close to the valence band. Figure 7 also shows the spin polarized DOS, and the absolute difference in the spin up and down DOS. As can be seen, there is a net magnetic moment, indicating that this compound is ferromagnetic, which is reasonable given a valence electron count of 71 in the formula unit.

The DOS for the La- and Sc-filled compounds are very similar to that of the Y-filled skutterudite, and is not shown. However, both the degree of filling, and the relative amount of Co versus Fe affect the DOS significantly. In figure 8, we have demonstrated the changes in the DOS by three examples. The top panel shows the calculated total DOS in the case where half of the voids are filled by Y, and all Co atoms are substituted by Fe. In the middle is shown the fully filled and Fe substituted case (as in figure 7); this moves the electron bands to lower energies, but the overall shape of the bands is not significantly changed. Finally, the bottom

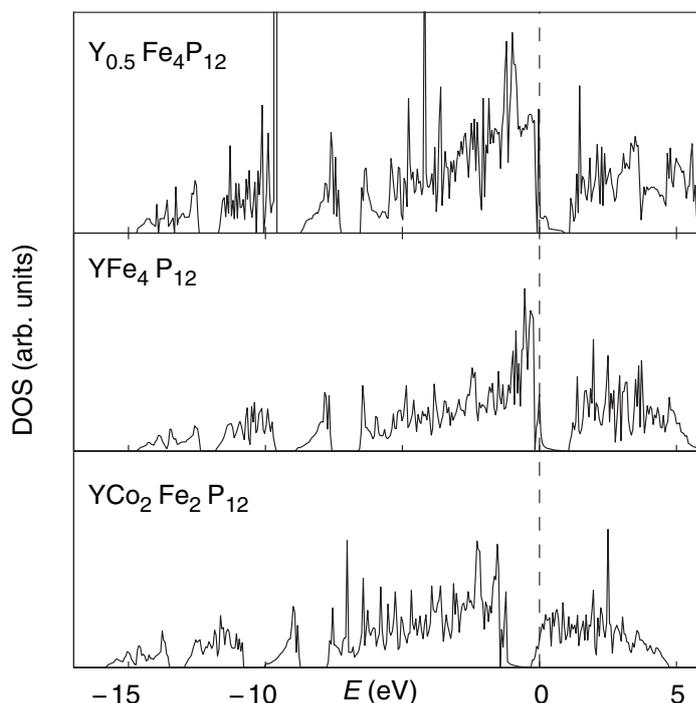


Figure 8. The total DOS of $\text{Y}_{0.5}\text{Fe}_4\text{P}_{12}$ (top), $\text{YFe}_4\text{P}_{12}$ (mid) and $\text{YCo}_2\text{Fe}_2\text{P}_{12}$ (bottom). Both increasing the filling fraction and increasing the amount of Co in the compound raises the Fermi level without any other significant influence on the overall shape of the DOS.

panel shows the DOS for the situation with an equal mix of iron and cobalt at the metal site, still with all voids occupied by yttrium. It is clear that this moves the Fermi-level across the pseudo gap and into the bottom of the conduction band. Thus we expect that by carefully choosing the right relation between the degree of filling and the relative Fe content we can bring the Fermi level into the band gap or into the area with low values of DOS, thus tailoring the material for thermoelectric applications.

It seems that compounds with $y = 3x$, three Fe atoms per filling atom, are best suited. These compounds should hold no unpaired spins and hence be semiconductors or semimetals. Indeed, in figure 9 it is illustrated that the Fermi level of $\text{YCoFe}_3\text{P}_{12}$ is located in an area with low values of DOS, and that it holds no unpaired spins, as predicted. Also, it is seen that the DOS exhibits a very promising asymmetry at the Fermi level, with a rather large derivative of the DOS at the onset of the conduction band. This should lead to large Fermi velocities, which are crucial to obtain a high Seebeck coefficient.

The promising DOS of $\text{YCoFe}_3\text{P}_{12}$ encouraged the calculation of the electronic band dispersion relation to elucidate the band structure further; a plot of this is provided in figure 10. It is seen here that the Fermi-level is crossed by a single band. The DOS is very low at the Fermi level, and a closer look at the local DOS (not shown) suggests that the crossing band is of d-character from Y, Co and Fe and p-character from P.

It is well known that density functional theory (DFT) at the GGA level underestimates or in some cases even fails to predict band gaps of semiconductors. As an example, experiments have found CoP_3 to be a diamagnetic semiconductor [32], while two independent modeling studies

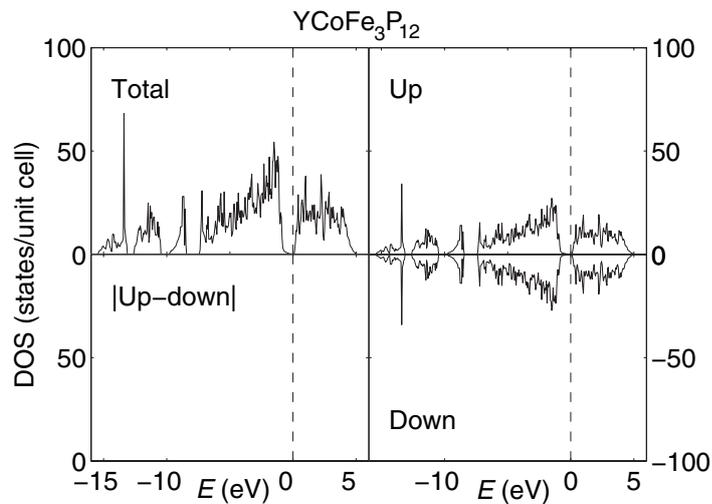


Figure 9. The spin polarized DOS of $\text{YCoFe}_3\text{P}_{12}$. The figure shows the total DOS, the DOS of spin up and spin down, and the absolute difference between spin up and spin down DOS. The energy is in electron volt relative to the Fermi level.

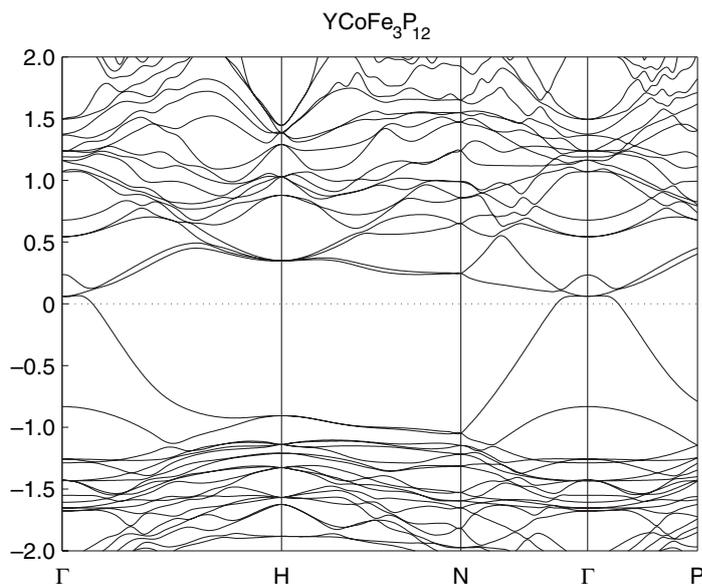


Figure 10. The electronic band structure of $\text{YCoFe}_3\text{P}_{12}$. The energy is in electron volt relative to the Fermi level.

of CoP_3 using DFT found it to be metallic due to a single band crossing the Fermi level [9, 20]. Since the calculated electronic structure of $\text{YCoFe}_3\text{P}_{12}$ is not too different from that of CoP_3 , we can suppose that this compound actually has a small band gap. This is promising for the thermoelectric properties of this compound, and is also valid for many of the other compounds of this study.

In the work of Meisner *et al* [33] it is argued that the reduction of lattice thermal conductivity results not only from rattling of the filler atom, but also from mass scattering

between filled and unfilled voids. Minimum lattice conductivity was found at a filling fraction just above 60%. We may therefore believe that $x \sim \frac{2}{3}$ will lead to a minimum lattice conductivity for our skutterudites, and that compounds with a stoichiometry in the vicinity of $Y_{0.67}Co_2Fe_2P_{12}$ (or $La_{0.67}Co_2Fe_2P_{12}$) will be especially interesting for thermoelectric applications.

$LaCoFe_3Sb_{12}$ is today the skutterudite with the highest reported ZT value [2]; 1.4 at 900 °C. La has a rattling amplitude of 29 pm in this skutterudite, not very different from that of Y in $YCoFe_3P_{12}$ predicted in this work. Thus, $YCoFe_3P_{12}$ is a very interesting compound for thermoelectric applications, and $Y_{0.67}Co_2Fe_2P_{12}$ will probably be even more interesting if it is possible to synthesize.

An obvious extension of the present study would be to investigate corresponding Sb-based skutterudites. (A number of studies have done this already with other filling elements; see, e.g. [6], [34]–[38].) If it is possible to synthesize compounds like $YCoFe_3Sb_{12}$ with $y = 3x$, they might be even better suited for thermoelectric applications than P-based skutterudites, because of the increased rattling amplitude due to the large Sb-surrounded 12-fold voids.

Also, it would be very interesting to investigate how the thermopower of these materials behaves as a function of temperature. Together with estimates of their thermal conductivity, this would give valuable additional information about which materials are most promising for thermoelectric applications. Such investigations are in progress.

4. Conclusions

We have shown that all the hypothetical compounds $M_xCo_{4-y}Fe_yP_{12}$, with M being La, Y and Sc, $x = \{0, 0.125, 0.25, 0.50, 1\}$ and $y = \{0, 1, 2, 3, 4\}$ have the (filled) skutterudite structure within the uncertainty of our methodology. That is, if all metal sites and voids are considered equivalent, the structure will belong to the space group $Im\bar{3}$, no. 204. The Sc-filled compounds exhibit very large rattling amplitudes, but they are all thermodynamically unstable relative to the competing phases. The Y-filled compounds have larger rattling amplitudes than the La-filled, but are less stable; only the completely filled $YCoFe_3P_{12}$ is predicted to be stable at 0 K. Many other Y-filled compounds are close to being stable, however, and could possibly be stabilized by temperature and entropy effects. The La-filled compounds have the smallest rattling amplitudes of this study, but could still be interesting for thermoelectricity due to the larger mass of La. Also many of these compounds can probably be synthesized, according to our 0 K thermodynamics assessments.

Fe and Co contribute two and three electrons to the covalent bonds of the structures containing only Fe or Co, but enter a shared valence state in compounds with both Fe and Co on the metal sites. Filling the voids helps to saturate the covalent bonds if they are not already saturated. The optimal relation between the filling fraction, x , and the degree of substitution of Fe for Co, y , is $y = 3x$. This relation also gives the most thermodynamically stable compounds and the compounds with the most promising DOS. Based on these results we expect P-based skutterudites like $(La,Y)CoFe_3P_{12}$ and $(La,Y)_{0.67}Co_2Fe_2P_{12}$ to be very interesting for thermoelectric applications, as well as their corresponding antimonides.

Acknowledgments

We thank Johan Taftø for feedback, support and useful discussions. Numerous hours of computing time from the NOTUR project are also greatly appreciated.

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