

# Density-functional band-structure calculations for La-, Y-, and Sc-filled CoP<sub>3</sub>-based skutterudite structures

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The crystal structure, thermodynamic stability, and electronic structure of La-, Y-, and Sc-filled CoP<sub>3</sub> are predicted from density-functional band-structure calculations. The size of the cubic voids in the skutterudite structure is changed much less than the difference in size between the different filling atoms, and we expect that the larger rattling amplitude of the smaller Sc and Y atoms may decrease the lattice thermal conductivity of Sc- and Y-filled structures significantly compared to La-filled structures. The solubility of La, Y, and Sc in CoP<sub>3</sub> is calculated to be around 5, 3-6 %, and below 1% at 0 K, respectively. Based on similar systems, this is expected to increase considerably if Fe is substituted for Co. Fe substitution is also expected to compensate the increased charge carrier concentration of the filled structures that is seen in the calculated electron density of states. In conclusion, Sc- or Y-filled (FeCo)P<sub>3</sub> skutterudite structures are promising materials for thermoelectric applications.

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## I. INTRODUCTION

There has recently been considerable interest in materials with the skutterudite structure because of their newly discovered potential for thermoelectric applications.<sup>1,2</sup> These materials have the general formula  $TX_3$ , with  $T$  being a transition metal (typically Co, Rh, Ir, etc.) and  $X$  a pnictogen (P, As, Sb, with possible substitution by Sn, etc.). They crystallize in the cubic  $Im\bar{3}$  space group (No. 204), with a unit cell consisting of eight smaller cubes with the transition metal on the cube corners, six of which are filled with mutually perpendicular “rings” of four pnictogens. This leaves a rather large void in each of the two unoccupied cubes, corresponding to the  $2a$  sites in Wyckoff notation.

Thermoelectric materials are usually rated based on the thermoelectric figure of merit  $Z=S^2\sigma/\lambda$ , where  $S$  and  $\sigma$  are the Seebeck coefficient and electrical conductivity, and  $\lambda$  is the thermal conductivity of the material. A high value for  $Z$  indicates that a given material is suitable for thermoelectric applications. The skutterudite materials usually display a high value for  $S$  and  $\sigma$ , but unfortunately they also exhibit a high thermal conductivity, thus reducing their suitability for thermoelectric applications.

In 1994, Slack and Tsoukala predicted that filling the voids in the skutterudite materials could reduce their lattice thermal conductivity through scattering of the thermal phonons by the rattling of the filling atoms in an oversized “box” in the structure.<sup>3</sup> This effect has been thoroughly demonstrated for several compositions, with the filling elements typically being a rare-earth metal, e.g., La, Ce, Nd, Sm, Eu, Th, etc. Depending on the rattling amplitude, this filling atom lowers the lattice thermal conductivity by as much as an order of magnitude, with a strong correlation between the rattling amplitude and the thermal conductivity.<sup>4-8</sup> When all the empty boxes in the structure have been filled (filling fraction 100%), the general formula is  $MT_4X_{12}$ , where  $M$  is the rare-earth filling element. The possibility of “tailoring” the thermal conductivity in this way has caused great interest

in the skutterudite materials for thermoelectric applications. The filled skutterudite crystal structure is shown in Fig. 1.

Based on the “rattling box” picture of this effect, it can be expected that a large ion in a relatively small box has a smaller effect on the thermal conductivity than a small ion in a relatively large box. Indeed, this has been confirmed in the case of Ce filling of the (CoFe)P<sub>3</sub> and (CoFe)Sb<sub>3</sub> systems.<sup>9</sup> The antimony based skutterudite structures have much larger lattice constants ( $a=903-913$  pm) than the phosphorus based system ( $a=770-779$  pm), leaving more free space for the Ce ion in which to “rattle.” This results in a 90% reduction of the thermal conductivity of the antimony-based skutterudite structure compared to only a 20% reduction for the

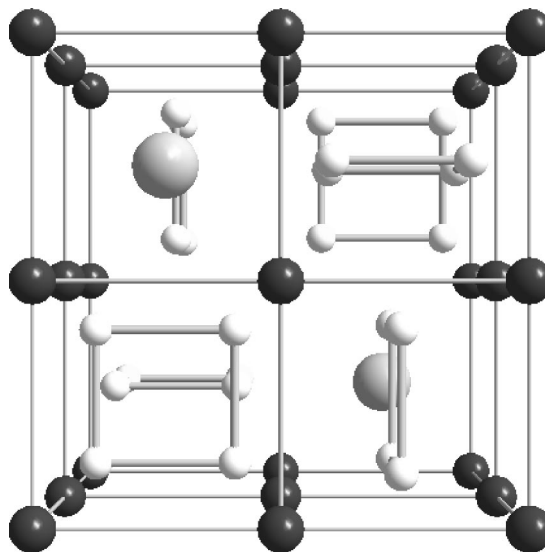


FIG. 1. The filled skutterudite crystal structure. The composition is  $MT_4X_{12}$ , where  $M$  is the rare-earth filling atom (large grey balls),  $T$  is the transition metal (black balls), and  $X$  is the pnictogen (white balls). The conventional cubic unit cell containing two formula units is shown, only with the origin translated by (0.25,0.25,0.25).

phosphorus-based structure when filling with Ce.<sup>9</sup> This trend is general, and even for several different materials the thermal conductivity decreases by an order of magnitude almost monotonically when the rattling amplitude increases from 15 pm (in CeFe<sub>4</sub>P<sub>12</sub>) to 29 pm (in CeFe<sub>4</sub>Sb<sub>12</sub>).<sup>2</sup>

It is evident that the smaller unit cell of the phosphorus-based skutterudite structures requires a smaller filling element to achieve a comparable reduction in thermal conductivity to that seen in the larger antimony based materials. In this article we explore the feasibility of filling the CoP<sub>3</sub> structure with La, Y, and Sc. The rattling amplitude is defined as the difference between the void filler covalent radius and the radius of the cage.<sup>10</sup> Since the covalent radius decreases from 169 to 144 pm when going from La to Sc, we may expect that the rattling amplitude decreases in the order of 25 pm, even though the cell parameters may be slightly different in those materials. Following the general trend for filled skutterudites,<sup>2</sup> we may thus expect that Sc-filled skutterudites have a lattice thermal conductivity of at least an order of magnitude smaller than corresponding La-filled structures. The covalent radius of Y is 162 pm, not too different from La; the expected reduction in lattice thermal conduction is from this around a factor of 2. To explore the feasibility of filling with Y or Sc, we calculated the thermodynamical stability of such filled skutterudite structures by comparing the calculated free energy of various compounds. At the same time we calculate their optimized cell parameters by performing full relaxation of unit cell size and shape, as well as optimization of ionic positions.

The detailed electronic structure of these hypothetical materials is also investigated in this work to clarify how the electronic conductivity may be influenced by the filling atoms. Both the density of states (DOS), local DOS, and band structure of the materials are presented, and for unfilled CoP<sub>3</sub> the results are compared to previous calculations.<sup>11,12</sup>

A number of theoretical studies have previously investigated various properties of skutterudite-type materials. The semiempirical extended Hückel tight-binding method has been used to calculate the electronic structure of filled and unfilled skutterudite structures.<sup>13–15</sup> CoP<sub>3</sub> and NiP<sub>3</sub> have been investigated by using the linear muffin-tin orbital method in the atomic sphere approximation.<sup>11</sup> Singh and co-workers have used the linearized augmented plane wave method within the local-density approximation to calculate various properties of IrSb<sub>3</sub>, CoSb<sub>3</sub>, and CoAs<sub>3</sub>;<sup>16</sup> CoP<sub>3</sub> and LaFe<sub>4</sub>P<sub>12</sub>;<sup>12</sup> and (La,Ce)Fe<sub>4</sub>Sb<sub>12</sub>.<sup>17,18</sup>

## II. COMPUTATIONAL METHOD

Periodic density-functional calculations within the generalized-gradient approximation as implemented in the Vienna *ab initio* simulation package (VASP)<sup>19,20</sup> was used in all the calculations, except the DOS mentioned below. The projector augmented wave (PAW) method was used to span out the electron density,<sup>21</sup> and the gradient correction was PW91.<sup>22</sup> The PAW method is a generalization of the linearized augmented plane-wave method, and gives access to the full wave function;<sup>23</sup> meanwhile, it has comparable effi-

TABLE I. The models being used to create the compounds  $M_x\text{Co}_4\text{P}_{12}$ , where  $M$  is La, Y, and Sc and  $x$  is the filling fraction of  $M$ . The number of atoms in the unit cell  $N_{\text{atoms}}$  and the space group (SG) have been listed in addition to the filling fraction  $x$ .

$x$	$N_{\text{atoms}}$	SG	SG No.
0	32	$Im\bar{3}$	204
12.5	133	$Im\bar{3}$	204
25	65	$Pm\bar{m}m$	47
50	33	$Pm\bar{3}$	200
100	34	$Im\bar{3}$	204

ciency to the pseudopotential approach. The criterion for self-consistency in the electronic structure determination was that two consecutive total energies differed by less than 0.01 meV. A cutoff energy of 500 eV was used throughout, and the density of  $k$  points in the irreducible wedge of the Brillouin zone was sufficient to ensure that the overall error due to the mentioned numerical sources was of the order of 1 meV per unit cell. The number of irreducible  $k$  points in the Brillouin zone varied between 24 for the smallest unit cells, consisting of eight CoP<sub>3</sub> units, to 7 for the largest unit cells, consisting of 32 CoP<sub>3</sub> units. Some of the smaller unit cells for calculating the thermodynamical stability had even more  $k$  points, up to the CoP structure, with 216 irreducible  $k$  points in the Brillouin zone. This latter structure has four formula units in the conventional unit cell. For the DOS calculations the number was increased further, to a total of 76 irreducible  $k$  points in the Brillouin zone for the Co<sub>8</sub>P<sub>24</sub> model. The smearing of partial occupancies of the wave functions are done using the tetrahedron method with Blöchl corrections.

Relaxations have been performed by using the RM-DIIS implementation of the quasi-Newton method. The ionic coordinates and the unit cell size and shape were optimized simultaneously to eliminate structures with internal stress. The structure was considered relaxed when all the forces were less than 0.05 eV/Å. A single calculation using high accuracy was performed after the completion of the relaxation, to determine the accurate total free energy.

The electronic density of states (DOS) was calculated both using VASP and the ADF-BAND<sup>24,25</sup> packages. The latter is based on linear combinations of numeric and Slater-type atomic orbitals, and is, in principle, exact (at the GGA level) when all numerical issues such as basis sets, integration accuracy, etc., have been taken care of. This thus serves as a convenient check of the calculated DOS by using VASP.

## III. RESULTS AND DISCUSSION

### A. Crystal structure

When creating periodic models with various filling fractions, some symmetry is necessarily broken. Table I lists the symmetry of the unit cells used to represent the filling fractions of this study. The model with 25% filling is made from

TABLE II. The resulting lattice constants for the different models in study in the form  $M_x\text{Co}_4\text{P}_{12}$ . The resulting cell angles were all  $90^\circ$ , and the resulting space groups were as in Table I. The experimental lattice constant of  $\text{CoP}_3$  (no filling) is 771.1 pm (Ref. 27).

Filling atom $M$	Filling fraction (%)	$a_{\text{latt}}$ (pm)	$b_{\text{latt}}$ (pm)	$c_{\text{latt}}$ (pm)
	0	773.5	773.5	773.5
La	12.5	774.8	774.8	774.8
La	25	776.5	776.4	775.9
La	50	779.7	779.7	779.7
La	100	784.6	784.6	784.6
Y	12.5	774.3	774.3	774.3
Y	25	776.1	775.7	774.6
Y	50	777.8	777.8	777.8
Y	100	781.4	781.4	781.4
Sc	12.5	773.7	773.7	773.7
Sc	25	775.2	774.7	774.1
Sc	50	775.8	775.8	775.8
Sc	100	778.2	778.2	778.2

a  $1 \times 1 \times 2$  conventional (cubic) cell, and is thus the only model that has intrinsically broken the cubic symmetry and the isotropic distribution of the filling atoms. The model with  $x=12.5\%$  has been constructed using a  $2 \times 2 \times 2$  primitive (rhombohedral) cell in order to preserve cubic symmetry. The other models use the conventional cubic cell.

The relaxation procedure allowed the unit cell to change size and shape and the ionic positions to relax. None of the models changed space group during the relaxation, but all the models with 25% filling lost the cubic shape of their unit cells. The resulting lattice constants are shown for all the models in Table II. We can see that the models with isotropic distribution of the filling atoms (i.e., all except the 25% filled), retained the cubic shape of their unit cells. The 25% La-filled model is also not far from cubic; the difference between the smallest and largest lattice constants is only 0.6 pm. This difference has grown to 1.5 pm and 1.1 pm for Y and Sc, respectively. These structures are still cubic within the uncertainty of our relaxation method, however: When starting from different input structures, the lattice constants of the same resulting structure may differ by up to 3 pm with our current accuracy.<sup>26</sup> Since there is no reason to expect that symmetry in the real material is broken in the same way as in the 25% models, we conclude that the real structure of filled  $\text{CoP}_3$  will most probably be cubic.

The lattice constants increase with increasing filling fraction, and most for the larger filling atoms. This has been depicted in Fig. 2, where the cubic cell volume has been plotted as a function of filling fraction for the three filling elements La, Y, and Sc. The volume expansion is very close to linear, and the small deviations from linearity are within the error limits of our calculations. The expansion is more than twice as large for filling with La than for Sc, with Y in the middle, reflecting the variation in their size. But the difference in size of the cubic voids (around 6 pm for 100% filling, and not more than 1 pm for more realistic filling

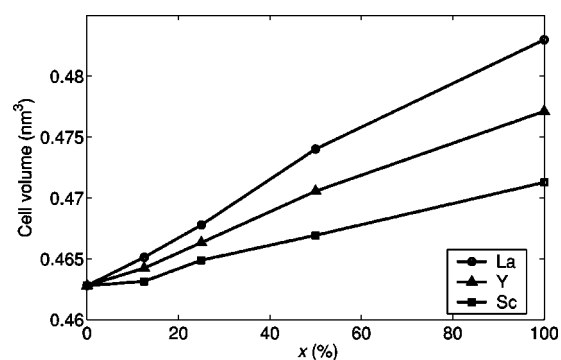


FIG. 2. The relaxed volume in  $\text{nm}^3$  of the models  $M_x\text{Co}_4\text{P}_{12}$  as a function of the filling fraction  $x$ , with  $M=\text{La}$ ,  $\text{Y}$ , and  $\text{Sc}$ . The experimental volume of  $\text{CoP}_3$  is  $0.4585 \text{ nm}^3$  (Ref. 27).

fractions) is not nearly as large as the size difference of 25 pm between La and Sc.<sup>28</sup> Our founding hypothesis has thus been confirmed, and based on the general trend of fully filled skutterudite structures,<sup>2</sup> we may expect an order of magnitude decrease of the lattice thermal conductivity of Sc-filled skutterudite structures compared to that of La-filled structures. Similarly, the lattice thermal conductivity of Y-filled skutterudite structures should be approximately halved compared to the La-filled ones. This is, of course, speculative and depends, among several other things, on the thermodynamic solubility of the filling atoms.

## B. Phase stability

The thermodynamic stability of the current models has been calculated by checking different decomposition routes from the filled structure. The total free energy of all the compounds participating in these hypothetical reactions has been calculated in the same manner as the skutterudite structures; by a full relaxation of both the unit cell and ionic positions, followed by a final high precision calculation. The most stable end point was chosen in each case to evaluate the stability of the filled structure. The investigated decomposition routes have been presented for the 50% filled models in Table III. The possible routes are similar for the other filling fractions, except for the 100% Y-filled  $\text{CoP}_3$ , where  $\text{YP}_5$  cannot form together with Co-P compounds. The most favorable route is similar for all the filling atoms; for  $M$ -filled  $\text{CoP}_3$  it is to  $\text{MP}$ ,  $\text{CoP}_3$ , and  $\text{CoP}_2$ .

This has been used to calculate the decomposition enthalpy  $H_{\text{decomp}}$  defined as

$$H_{\text{decomp}}(M\text{T}_8\text{X}_{24}) = E(M\text{T}_8\text{X}_{24}) - 8E(\text{TX}_3) - E(M) \quad (1)$$

for the first decomposition route, etc. Here  $E(\text{TX}_3)$  and  $E(M\text{T}_8\text{X}_{24})$  are the uncorrected total free energy of the unfilled and filled skutterudite-type structures as provided by VASP and  $E(M)$  is that of the filling metal in its standard state. This has been used to create a plot of the decomposition enthalpy as a function of filling fraction for the three filling elements in Fig. 3. None of the models in this study are stable compared to the end products, implying that the solubility of La, Y, and Sc is less than 12.5% in  $\text{CoP}_3$  at 0 K assuming ordered distribution of the filling element. Apart

TABLE III. Possible decomposition routes for 50% filled  $\text{CoP}_3$ . The decomposition enthalpy  $H_{\text{decomp}}$  is given for each route in eV per formula unit. A negative decomposition enthalpy means that the filled  $\text{CoP}_3$  is unstable compared to the end products.

Decomposition route	$H_{\text{decomp}}$ (eV)
$\text{LaCo}_8\text{P}_{24} \rightarrow \text{La} + 8\text{CoP}_3$	1.579
$\text{LaCo}_8\text{P}_{24} \rightarrow \text{LaP} + 7\text{CoP}_3 + \text{CoP}_2$	-1.243
$\text{LaCo}_8\text{P}_{24} \rightarrow \text{LaP} + 7.5\text{CoP}_3 + 0.5\text{CoP}$	-1.210
$\text{YCo}_8\text{P}_{24} \rightarrow \text{Y} + 8\text{CoP}_3$	0.107
$\text{YCo}_8\text{P}_{24} \rightarrow \text{YP} + 7\text{CoP}_3 + \text{CoP}_2$	-2.825
$\text{YCo}_8\text{P}_{24} \rightarrow \text{YP} + 7.5\text{CoP}_3 + 0.5\text{CoP}$	-2.792
$\text{YCo}_8\text{P}_{24} \rightarrow \text{YP}_5 + 3\text{CoP}_3 + 5\text{CoP}_2$	-1.282
$\text{YCo}_8\text{P}_{24} \rightarrow \text{YP}_5 + 5.5\text{CoP}_3 + 2.5\text{CoP}$	-1.119
$\text{ScCo}_8\text{P}_{24} \rightarrow \text{Sc} + 8\text{CoP}_3$	0.445
$\text{ScCo}_8\text{P}_{24} \rightarrow \text{ScP} + 7\text{CoP}_3 + \text{CoP}_2$	-2.198
$\text{ScCo}_8\text{P}_{24} \rightarrow \text{ScP} + 7.5\text{CoP}_3 + 0.5\text{CoP}$	-2.166

from the behavior of the Y-filled models, which crosses the linear curve of Sc filled  $\text{CoP}_3$  between 25 and 50 % Y, all the curves closely follow a linear behavior, and we thus feel relatively safe to linearly extrapolate the curves to  $H_{\text{decomp}} = 0$  which is indicative of a stable filled structure. This has been done in Fig. 3 by extrapolating linearly from the 25 and 12.5 % data points. The point from the 25% Y-filled model is higher than should be expected from the linear behavior, and a linear extrapolation using the 50% point instead of the 25% point would cross the abscissa at a higher value. We do not have a reasonable physical explanation for this deviation from linearity; most probably it is reflecting the numerical uncertainty of our procedure. The predicted solubility in  $\text{CoP}_3$  at 0 K may hence be read out of Fig. 3: 5% La, 3-6 % Y, and less than 1% Sc.

Our results could be slightly altered if the zero-point motion of the ions were included. This has not been done for two reasons. We expect that this effect would more or less be canceled when comparing different systems. In addition,

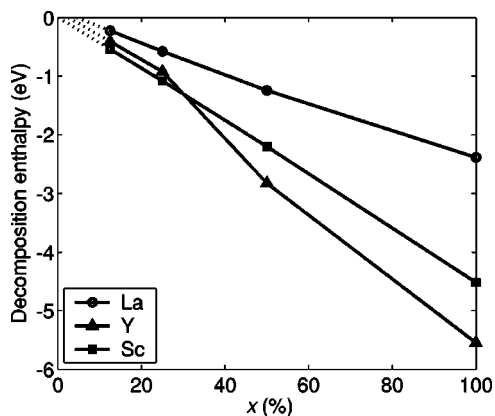


FIG. 3. The decomposition enthalpy of filled  $\text{CoP}_3$  as a function of filling fraction  $x$ . The enthalpy has been normalized to the conventional cell, that is,  $\text{Co}_8\text{P}_{24}$ . The dotted lines are linear extrapolations of the data points at 25 and 12.5 %.

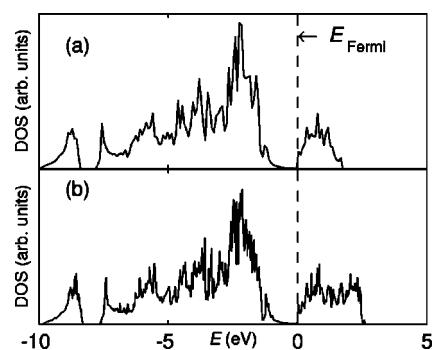


FIG. 4. The total DOS of  $\text{CoP}_3$  calculated by ADF-BAND (a) and VASP (b). The energy is in eV relative to the Fermi level.

such calculations would be prohibitively expensive, particularly for the large systems in study.

Furthermore, we expect both temperature effects and entropy to increase the solubility of the filling atoms when moving to room temperature. Since no experimental investigations of these compounds have yet been published, we must compare to another system: The solubility of Ce in  $\text{CoSb}_3$  is around 7%,<sup>2</sup> increasing to 100% when Co is fully substituted by Fe. Similarly, it is known that the solubility of La and Y is 100% in  $\text{FeP}_3$ .<sup>29,30</sup> From this we expect that it is possible to fill mixed  $(\text{FeCo})\text{P}_3$  skutterudite structures with both La, Y, and Sc.

The substitution of Fe for Co in skutterudite-type structures is usually motivated by charge compensation for the filling. We shall see how this can be understood from the electronic structure in what follows.

### C. Electronic structure

The electronic density of states (DOS) and the band structure are important to judge whether a material is promising for thermoelectric applications—the optimal charge carrier concentration for a thermoelectric material is around  $10^{19} \text{ cm}^{-3}$ , which means that it should be a semiconductor or a semimetal.<sup>2</sup> Calculated electronic structures have already been published for  $\text{CoP}_3$  by two previous studies using different techniques and achieving very different results.<sup>11,12</sup> Llundell and co-workers used the atomic sphere approximation within the linearized muffin tin orbital method (LMTO-ASA), and found that the band structure exhibited a pseudogap separating the valence and conduction bands.<sup>11</sup> Fornari and Singh, using the linearized augmented plane wave (LAPW) formalism, found that this gap is crossed by a phosphorus  $p$  band above the Fermi level, so that  $\text{CoP}_3$  is expected to be metallic.<sup>12</sup> The two studies also presented DOS plots that were relatively similar, but they also differed in some important details, particularly around the Fermi level.

We have calculated the total DOS of  $\text{CoP}_3$  using two other approaches: the planar augmented wave method of VASP (Refs. 19,20) [shown in Fig. 4(a)] and the linear combination of numeric and Slater-type atomic orbitals as implemented in ADF-BAND [shown in Fig. 4(b)]. These two plots do not differ by more than details, even though the methods used are quite

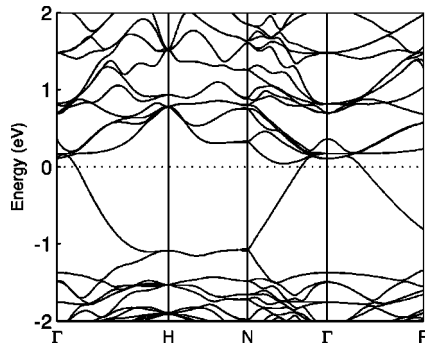


FIG. 5. The band structure of  $\text{CoP}_3$ . The energy is in eV relative to the Fermi level.

different. Both methods should in principle be able to produce results close to the DFT limit, without any further important approximations than the description of the exchange-correlation potential. It is important to note that, while VASP calculates the electron density within the generalized gradient approximation, the electron density has been found self-consistently within the local-density approximation in the ADF-BAND. The VASP curve was produced using spin-polarized calculations, while the ADF-BAND curve did not; this is actually the reason for the difference in the valence band far from the Fermi level. We have performed VASP test calculations with spin polarization and without, and the only non-negligible difference in the DOS was found at the high end of the valence band. Our results are quite similar to the DOS curves for  $\text{CoP}_3$  presented by the previous LMTO-ASA study<sup>11</sup> and LAPW study,<sup>12</sup> apart from a range of details.

When turning to the band structure, however, the differences are much clearer. We have plotted the band structure for  $\text{CoP}_3$  in Fig. 5. There is no indirect gap at the Fermi level, as was found in Ref. 11, and we find the same band crossing the Fermi level close to the  $\Gamma$  point as was found in Ref. 12. In most of the overall features, our results correspond nicely with those of the latter study. There are a number of details that differ, though, particularly around the  $H$  point. This does not change the main picture, however; that of a metallic  $\text{CoP}_3$  with relatively low DOS directly below the Fermi level.

We now turn to the effect on the electronic structure from adding the rattling atom. The effect on the DOS of adding La to  $\text{CoP}_3$  is shown in Fig. 6. First of all, it is noted that the overall shape of the DOS is changed only to a small extent when filling with La. The main difference when increasing the filling fraction is that the Fermi level is moved upwards into what used to be the conduction band. The same effect is seen for Y- and Sc-filled  $\text{CoP}_3$  (not shown) with a quantitatively similar impact on the Fermi level. This indicates that the same electronic changes are caused by filling with either of the three elements. In all cases the DOS plots show that filled  $\text{CoP}_3$  has a larger carrier concentration than the unfilled structure, giving a higher electrical conductivity and thus contributing to a higher figure of merit. However, it is likely that the change in DOS also will have a detrimental effect on the Seebeck coefficient, thereby reducing the figure of merit.

This is even more visible in the band structure, shown for 50% La-filled  $\text{CoP}_3$  in Fig. 7. Here we see that the higher

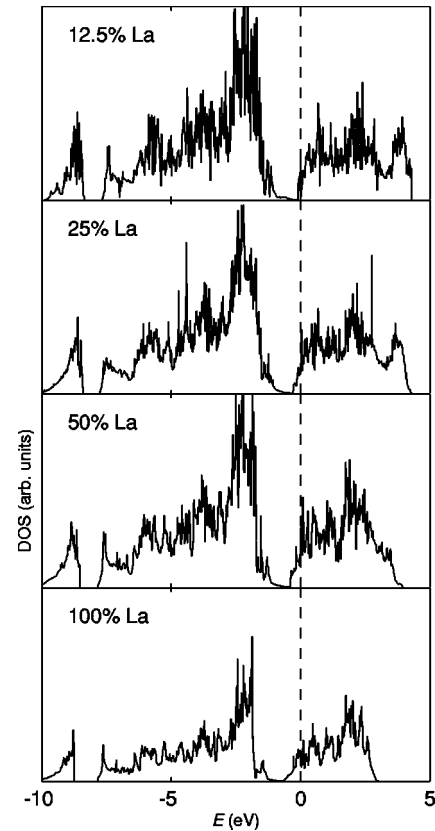


FIG. 6. The total DOS of 12.5, 25, 50, and 100 % La-filled  $\text{CoP}_3$ . The energy is in eV relative to the Fermi level.

Fermi level pushes the band that previously crossed the Fermi level down into the valence band. Meanwhile, several bands that previously belonged to the conduction band are now crossing the Fermi level from above. Most of the other qualitative properties of the band structure are unchanged, so the main effect of adding La has been to increase the carrier concentration. We know from La-filled  $\text{FeP}_3$  that this situation may improve when substituting Fe for Co. By carefully choosing the optimal Fe content, it should be possible to move the Fermi level back down to the area with scarcely populated electron states, just below the point where the DOS increases dramatically, that is, around  $-0.4$  eV. If this may be done without destroying the other benign properties of the band structure, we would expect that Y- or Sc-filled

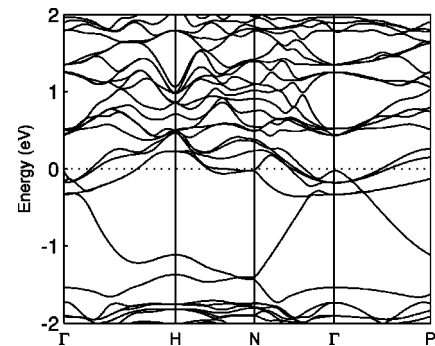


FIG. 7. The band structure of  $\text{LaCo}_8\text{P}_{24}$ . The energy is in eV relative to the Fermi level.

(FeCo)P<sub>3</sub> should have a thermoelectric figure of merit superior to that of La-filled structures. This is the subject of a forthcoming study.

#### IV. CONCLUSIONS

Accurate density-functional band-structure calculations have been performed to predict the crystal structure and solubility of La, Y, and Sc in CoP<sub>3</sub>. A number of models were used to vary the content of the filling atoms in CoP<sub>3</sub> from 12.5 to 100 %. Full structural relaxations showed that cubic symmetry was, within the accuracy of the method, maintained in all cases. The lattice expansion due to increasing filling fraction was linear, with the La-filled models expanding more than twice as much as the Sc-filled models, and Y-filled CoP<sub>3</sub> in between. The difference in expansion is negligible compared to the difference in size between the filling atoms, and we expect that Sc- and Y-filled structures may have significantly reduced thermal conductivities because of the larger rattling amplitude of the filling atoms.

The thermodynamic solubility of the filling atoms in CoP<sub>3</sub> was found by extrapolating curves of the decomposition enthalpy of the filled models to stable filling. The present calculations were performed at 0 K, and at this temperature we predict a solubility of La, Y, and Sc in CoP<sub>3</sub> of 5%, 3-6 %, and less than 1%, respectively.

Similarly to Ce in CoSb<sub>3</sub>, we expect this to increase if substituting Fe for Co.

The calculated DOS and band structures show that the electronic effect of adding La, Y, or Sc is quite similar. It causes the Fermi level to move into the conduction band, effectively increasing the charge carrier concentration and thus the electrical conductivity. It may also, however, decrease the Seebeck coefficient, hence reducing the figure of merit. Based on this, we do not expect the hypothetical materials of this study to be too promising for thermoelectric applications. This may easily change, however, if the increased charge concentration is compensated by replacing Fe for Co—we then expect that the Sc- or Y-filled structures may have thermoelectric performances superior to that of La-filled structure. We therefore propose that synthesis of Sc- or Y-filled (FeCo)P<sub>3</sub> skutterudite-type structures is attempted, and that their thermoelectric properties be investigated.

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