Complex doping of group 13 elements In and Ga in caged skutterudite

CoSb₃

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The complex doping behavior Ga and In in CoSb₃ has been investigated using *ab initio* total-energy calculations and thermodynamics. The formation energies of void filling, Sb-substitution, and complex dual-site occupancy defects with different charge states, and their dependence on chemical potentials of species were studied. Results show that Ga predominantly forms dual-site 2Ga_{VF}-Ga_{Sb} defects and substitute for Sb only at very high Fermi levels or electron concentrations. In, on the other hand, can play multiple roles in skutterudites, including filling in the crystalline voids, substituting for Sb atoms, or forming dual-site occupancy, among which the fully charge-compensated dual-site defects (2In_{VF}-In_{Sb} and 4In_{VF}-2In_{Sb}) are dominant. The equilibrium concentration ratio of impurities at void-filling sites to those at Sb-substitution sites for Ga-doped CoSb₃ is very close to be 2:1, while this value markedly deviates from 2:1 for In-doped CoSb₃. The 2:1 ratio of Ga-doping in CoSb₃ leads to low electron concentration ($\sim 2 \times 10^{19} \text{ cm}^{-3}$) and makes the doped system a semiconductor.

Key words: Defect; Thermoelectric; Ab initio calculations; Skutterudites

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1. Introduction

There has been great progress in filled-skutterudite thermoelectric (TE) materials in recent years [1,2]. Studies on filling fraction limits (FFLs) for various impurities in skutterudite CoSb_3 are important not only for understanding the transport properties but also for predicting novel systems and compositions. The FFLs for rare-earths (REs), alkaline-earths (AEs), and alkaline metals (AMs) single-element-filled skutterudites have been studied using the density functional *ab initio* methods and the results show good agreement with experiments [3-15]. A simple electronegativity rule ($x_I - x_{\text{Sb}} > 0.8$, x 's are the electronegativities of the filler, I , and Sb) was proposed to determine whether a filler impurity can be stably filled into the crystal voids [3]. This rule has predicted ultra-high FFLs for certain AMs in CoSb_3 , and these have been confirmed experimentally [13-15]. FFLs in multiple-element-filled CoSb_3 have also been investigated [16,17]. The calculated and measured FFLs are in good accord for these electropositive filling elements. In any case, the effect of filling with these elements includes electron-doping, partially compensated by defects, strong thermal conductivity reduction, and modification of the band structure including opening of the gap [18], though not by enough to completely eliminate bipolar effects at low doping [19]. This last fact among others suggests that further optimization is possible leading to still higher ZT .

Interestingly, there are elements that can be incorporated in skutterudites but do not satisfy this electronegativity rule, including Ga and In. Specifically, based on electronegativity one would predict that these elements are not stable fillers in CoSb_3 , there are several reports that Ga and In can be doped into the CoSb_3 structure. Furthermore, it is reported that these elements affect the electrical and thermal transport properties, and that these doped skutterudites even show improved TE performance. Harnwungmoung *et al.* investigated Ga-filled CoSb_3 and results showed that only a

small amount of Ga can be filled into the crystal voids [20]. He *et al.* and Mallik *et al.* reported the In-filled skutterudites, seemingly showing a FFL of 0.22 [21-23]. Grytsiv *et al.* investigated the phase equilibria of In-doped CoSb₃, and the maximum solubility of In in skutterudites was reported to be 0.22 when the compound is in equilibrium with CoSb₂ and InSb, while the solubility limit is reduced to 0.09 when it coexists with Sb [24]. The maximum reported thermoelectric figure of merit ZT value of single In-filled CoSb₃ is 1.2 at 575 K [21]. There have also been reports of double-filled CoSb₃ with In. These give FFLs of In in CoSb₃ of less than 0.2 and ZT values of 1.43, 1.4, and 1.3 for In-Ce, In-Yb, and In-Ba double filled CoSb₃ at 800 K respectively [25-27]. Recently Sesselmann *et al.* found that besides the void sites, In can also occupy the Sb sites [28]. In contrast, electropositive elements such as AM, AE and RE clearly cannot substitute for Sb. This is in accord with our first-principles calculations and experiments, which showed that Ga and In atoms could occupy both the voids and Sb sites in CoSb₃ and that these two elements behavior differently with respect to carrier doping [29-31].

Here we extend this work to develop understanding of the substitution, filling and doping behavior of these group 13 elements in CoSb₃ based on thermodynamic doping theory and energetics obtained from first principles defect calculations. We systematically study the single impurity induced complex doping properties for Ga- and In-containing CoSb₃ skutterudites. The formation energies of many complex defects with different structure and charge states are studied. The results show that both Ga and In mainly form complex dual-site defects. The defect concentrations are studied by using the grand canonical ensemble approximation. We find that the carrier concentration of Ga- and In-doped skutterudites should be very low due to the charge compensation by Sb-substitution.

2. Theoretical methods

The present calculations were carried out within density functional theory using the projector augmented wave (PAW) method, as implemented in the Vienna *ab initio* Simulation Package (VASP) [32] and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) [32]. The narrow band gap of CoSb_3 is reasonably reproduced with this functional, unlike oxides or other common semiconductors where gap corrections or hybrid functionals need to be used for defect calculations. The calculations with Ga and In doping are carried out on a supercell ($2 \times 2 \times 2$ primitive cell) containing a total of 128 atoms and 8 voids from the CoSb_3 plus the additional dopant atoms. A $3 \times 3 \times 3$ Monkhorst-Pack uniform k-point sampling is used for supercell energy calculations, and $15 \times 15 \times 15$ Monkhorst-Pack uniform k-point sampling is used for other compounds. Lattice constants and ion positions were optimized, and the configuration that has the lowest energy is chosen for further analysis. Details are similar to our prior work on related systems [16,17].

3. Results and discussions

3.1 Crystal structures and complex defect structures

The skutterudite compounds TMX_3 (TM= Co, Rh, Ir, and X=P, As, Sb), are body centered cubic materials, spacegroup Im3. The conventional cubic cell contains 8 formula units, for a total of 32 framework atoms and two voids. The TM occupy the 8c sites and the pnictogen atoms X occupy the 24g sites. The voids at the 2a positions are the 12 fold coordinated by X atoms. It is these sites that can be filled with RE, ME, and AM satisfying the electronegativity selection rule [3]. As mentioned, Ga and In do not satisfy the electronegativity selection rule and furthermore ionic radii of trivalent Ga and In would seem to be too small for these void sites [33]. Thus other sites, including framework substitutions for Co and Sb, should also be considered. Additionally, more complex compound

defects such as void filling-substitution complexes are possible. Here we consider a wide range of possible defect structures including void filling, Co and Sb substitution, and complex defects containing different numbers of void fillers and substitution atoms. The detailed structures of these defects are described below.

Four of the possible defect types are particularly favorable. The first of these is filling of the void sites (labeled as M_{VF} , $M=Ga, In$), and the second is the Sb substitution defect (M_{Sb}). The third and fourth are complex defects, all involving dual-site occupancy of doping atoms but at different ratios. One has a 1:1 ratio for void-site to Sb-site occupancy (labeled as $M_{VF-M_{Sb}}$), and the other has a ratio of 2:1 (labeled as $2M_{VF-M_{Sb}}$). The other complex defects can be obtained by combining these four defects. Figure 1 depicts the stable structures of these four defects. Note that these defects may show different charge states as discussed below. The simple void filling, M_{VF} and the Sb substitutional, M_{Sb} have only one configuration. However, for those defects with dual-site occupancy, there are several possible configurations due to the different occupations of M_{VF} and M_{Sb} and thus varying distances between doping atoms. Based on the total energy calculations, we find that the complex defect has the lowest energy when the distance between the Sb-substitution impurity M_{Sb} and the void-filling impurity M_{VF} is minimized (Fig. 1c), regardless of the charge states of the defects. This is reasonable both because of the Coulomb interactions between the negative acceptor-like M_{Sb} and the positive donor-like M_{VF} and also from the point of view of lattice strain (Ga and In take space upon void filling, but are smaller than Sb). Our calculations show that the Co substitutional, M_{Co} defect gives much higher formation energy than the other types of defects. Thus this defect type is excluded and is not considered further. Native point defects in ideal $CoSb_3$ were recently studied by Park et al [34]. Their results showed that all possible native defects in $CoSb_3$ have high positive formation energies,

among which the Co interstitial (Co_i) defect has the lowest. We hence include consideration of Co_i here.

Skutterudite structure CoSb_3 is cubic with equivalent 12 Sb atoms icosahedrally coordinating the void site. However, the symmetry is greatly reduced when defects are added. With one M impurity replacing a Sb (M_{Sb}), the void distorts and the symmetry is thus reduced. The filler impurity (M_{VF}), shifts away from the center reflecting the small sizes of In and Ga. In the complex defects it moves to a position that is relatively closer to the impurity substituting for Sb than to other Sb atoms. The distance of this shift depends on the radius of impurity elements as well as on the chemical bonding between M_{VF} and M_{Sb} . The structure distortion is especially severe for doping with Ga which has a very small size compared both to the available volume of the void and the Sb size. Fig. 2 shows the relaxed positions of several atoms surrounding one specific void site with both the void-filling and Sb-substitution impurities (Ga or In) indicated. It can be observed that Ga_{VF} significantly shifts away from the void center and moves very close to the Ga_{Sb} , leading to a severe distortion of the void and a much shorter $\text{Ga}_{\text{VF}}\text{-Ga}_{\text{Sb}}$ distance comparing to those between Ga_{VF} with other Sb atoms. In fact, the two impurities, Ga_{VF} and Ga_{Sb} , form direct bond with partial covalent character, consistent with the expectation that a complex compound defect may have stable structure due to the intra-defect interaction [29,31]. The complex defect with In doping shows a qualitatively similar distortion pattern, but the shift of In_{VF} is small. The underlying reasons are the more spatially extended valence orbitals and larger size of In.

3.2 Formation energies and relative stabilities of defects

The formation energies and relative stabilities of the Ga-, and In-related defects in CoSb_3 were systematically investigated by *ab initio* calculations combined with thermodynamics. The approach is

as described previously [35,36]. We mainly focus on M_{VF} , M_{Sb} , and the associated complex compound defects with different charge states, including $M_{VF}(0, +1)$, $M_{Sb}(0, -1, -2, +1)$, $M_{VF}-M_{Sb}(0, -1, +1)$, $2M_{VF}-M_{Sb}(0, -1, +1)$, $3M_{VF}-M_{Sb}(0, +1)$, $4M_{VF}-M_{Sb}(0, +1, +2)$, $4M_{VF}-2M_{Sb}(0)$, $5M_{VF}-2M_{Sb}(0, +1)$, and $6M_{VF}-3M_{Sb}(0)$. The numbers in the parentheses indicate the charge states of defects. One specific complex defect, $M_{Sb}-Sb_{VF}(0, +1, +2, -1)$, is also included to examine the possibility of M substituting for host atom Sb accompanied one Sb occupying the void center. The native defect Co_i in $CoSb_3$ was also considered, since this was previously reported to be the lowest energy intrinsic defect. We also investigated other defects including M_{Co} and $V_{Sb}-M_{Sb}(V = \text{vacancy})$, but found them to have relatively high formation energies, and do not discuss them further (see Table 1 for a detailed list).

We use (D, q) to label a defect complex $M_xCo_{32-y}M_ySb_{96-z}M_z$ with q being the charge state of the defect. The defect formation energy $\Delta G_f(D, q)$ per impurity atom can be written as follows [35,36]

$$\Delta G_f(D, q) = [E_{tot}(D, q) - E_{tot}(bulk) + y\mu_{Co} + z\mu_{Sb} - (x + y + z)\mu_M + q(\varepsilon_F + E_v + \Delta V)] / (x + y + z), \quad (1)$$

where $E_{tot}(D, q)$ is the total energy of the defect-containing supercell $M_xCo_{32-y}M_ySb_{96-z}M_z$ with doping element M, and $E_{tot}(bulk)$ is the total energy of the defect-free supercell. x is the number of void-filling impurity atoms, y of Co-substitution atoms, and z of Sb-substitution impurities. Here μ_{Co} , μ_{Sb} , and μ_M are the chemical potentials of the different elements. ε_F is the Fermi level referring to the valence band maximum (VBM) E_v of the defect-free bulk $CoSb_3$, and ΔV is the defect-induced correction of the electrostatic potential aligning the valence band maxima (VBM) in all systems [35].

The chemical potentials of Co, Sb, and impurity M (μ_{Co} , μ_{Sb} , and μ_M) in Eq. (1) are dependent

on experimental environment [37]. These are constrained by condition of thermodynamic equilibrium with stable bulk CoSb₃ requiring $3\mu_{Sb} + \mu_{Co} = \mu_{CoSb_3}$; this is the physically meaningful range of the effective chemical potential for element Sb (or Co) have to satisfy $0 \geq \Delta\mu_{Sb} \geq \frac{1}{3}\Delta H_{CoSb_3}$ (or $0 \geq \Delta\mu_{Co} \geq \Delta H_{CoSb_3}$), limited by Co-rich ($\Delta\mu_{Co} \leq 0$) and Sb-rich ($\Delta\mu_{Sb} \leq 0$) conditions. ΔH_{CoSb_3} is the formation enthalpy of CoSb₃. The effective chemical potentials for elements are defined by $\Delta\mu_{Co} = \mu_{Co} - \mu_{Co}^0$ and $\Delta\mu_{Sb} = \mu_{Sb} - \mu_{Sb}^0$, referring to the zero-temperature potentials μ_{Co}^0 and μ_{Sb}^0 , i.e. the total energies of bulk Co and Sb from *ab initio* calculations in our model. The calculated formation enthalpy of CoSb₃ is -0.99 eV per formula unit, reasonably agreeing with available experimental data and earlier calculations [34,38]. The chemical potential μ_M of impurities is set to be $\mu_M = \mu_M^0$ in estimating $\Delta G_f(D, q)$. Experimentally, the value of μ_M should be one that gives absence of both impurity the *M* and the compound MSb (GaSb, InSb) phases. Here we normalize the formation energies on a per impurity atom basis. Thus the μ_M variation within the small range allowed experimentally does not affect the general trends and conclusions of this work. The electronic chemical potential, the Fermi level ε_F , also affects doping behavior in CoSb₃, but because of the small gap and heavy bands, the range is limited.

Table 1 lists the formation energies of the corresponding zero-charged defects per impurity by using eq. (1). The numbers in the parentheses, such as 2-1, 3-2, and 4-2, are the abbreviations to denote these complex dual-site occupancy defects, and will be used in the following. The native defects, Co-substitutional defects M_{Co} , M_{Sb} -Sb_{VF}, and V_{Sb} -M_{VF} have much higher formation energies than other defects. The complex dual-site defects with different ratios always have very low formation energies. Therefore, we mainly focus on these complex dual-site defects and two single-element defects M_{VF} and M_{Sb} for further analysis.

Fig. 3 shows the formation energies of different defects as a function of the Fermi level for Ga- and In-doped CoSb_3 in the Co-rich and Sb-rich limits. Here, the zero corresponds to the valence band maximum (VBM). The shaded regions in the figures show the theoretical band gap areas. The configurational entropy $T\Delta S$ contribution to the defect formation energies was treated by assuming a random distribution of impurity atoms at all possible sites with T taken at 1000 K. Each kink in the curves indicates a transition of the corresponding defect types with different charge states.

We find that the dominant defects in both Ga- and In- doped CoSb_3 depend on the chemical potentials of Sb or Co, i.e. experimental synthesis conditions, as well as on the position of the Fermi level, i.e. carrier concentration. For Ga-doped CoSb_3 , the dominant defect is always the complex dual-site occupancy defect with the ratio of 2:1 over the entire band-gap area for both the Co-rich and Sb-rich conditions. Only at very high Fermi levels, does the single Ga_{Sb} defect with a charge state of -2 and the complex defect $\text{Ga}_{\text{VF}}\text{-Ga}_{\text{Sb}}$ with a charge state -1 become more stable than other defects. This is when the electrons in conduction band stabilize the defect-related dangling bonds. Our calculations indicate that In doping leads to a complicated situation. As shown in Fig. 3b and d, In can potentially form either a single filling (M_{VF}), or complex dual-site doping defects at different ratios, or Sb-substitutional defects for both the Co-rich and Sb-rich limits. Complex dual-site occupancy defects at different ratios have very close formation energies for In doped CoSb_3 , which means that all these defects will coexist.

Previous experimental results have shown that Ga prefers to form complex dual-site occupancy defects with a ratio of 2:1 in CoSb_3 , consistent with the above formation energy results. The doping behavior of In in CoSb_3 is complicated based on our results. Experimental results also show that In-related defects usually have more complex behavior than found in Ga-containing CoSb_3 [30].

Based on our calculations, In can fill into the void at low Fermi level, form dual-site occupancy defects with the increasing Fermi level, and become Sb-substitution defect with charge state -2 at very high Fermi levels. For Fermi levels in the middle of the gap, In prefers complex dual-site occupancy defects with different ratios. Our calculations basically indicate that doping behavior of In is very sensitive to experimental conditions in CoSb₃. The filling site, Sb-site, and dual-site doping are all realizable depending on synthesis conditions, consistent with the variety of observations and resulting controversy in literature regarding the doping behavior and site preference of In in CoSb₃.

3.3 Defect concentrations

Here we adopt the grand canonical ensemble thermodynamic model to describe Ga- and In-doping in CoSb₃. The details are given in the Appendix A. The defect concentration can be estimated by minimizing the Gibbs free energy of an approximate grand canonical ensemble containing the host CoSb₃ and various isolated but complex defects. The theoretical band gap value ($E_g = 0.17$ eV) is used in determining the Fermi level by requiring overall charge neutrality. Fig. 4 plots the concentration of all possible defects with different charge states and their dependence on Sb chemical potential in Ga- and In-doping CoSb₃. The figures are divided into two regions by the dotted red vertical lines. The left part is for results with the effective chemical potential of impurity atom (Ga, or In) set to 0 eV. The right region is for the cases that the effective chemical potentials of impurity atoms are constrained by the formation of secondary phases MSb (M=Ga, In), i.e. $\mu_{Sb} + \mu_M = \mu_{MSb}$. In experiments, it is very hard to precisely control the effective chemical potential. Typically, in the growth of CoSb₃ the ratio of Sb and Co is slightly lower than the nominal 3:1 ratio. So the variations of effective chemical potential of Sb are most likely confined in a small range from the Sb-rich limiting conditions in experiments. The experimental results always fall into

very small range in the right parts of Fig. 4.

The calculated carrier concentration from the charge neutrality requirement is shown in Fig. 4. The concentration of those charge-compensated compound defects with dual-site occupancy (M_{VF} : $M_{Sb} = 2:1, 4:2, 6:3$) is also plotted for comparison. Our results show that Ga-doped $CoSb_3$ could exhibit weak p-type behavior but only at very low Sb chemical potentials and that it quickly becomes n-type as the Sb chemical potential increases. The crossover from p- to n-type is actually at very low Sb chemical potential (-0.28 eV). No doubt, achieving such a low value of the Sb chemical potential will require a precise control of Sb compositions at levels noticeably below the nominal 3:1 (Sb: Co ratio). This is likely to be very hard to achieve when one considers the narrow synthesis conditions for obtaining the bulk $CoSb_3$ phase. Meanwhile, in almost the whole physical range of Sb chemical potential, the electron concentration ($\sim 2 \times 10^{19} \text{ cm}^{-3}$ at 1000K) is always slightly higher than the hole concentration ($\sim 4 \times 10^{18} \text{ cm}^{-3}$ at 1000 K), leading to the conclusion that the Ga-doping of $CoSb_3$ usually yields n-type behavior. Due to the strong compensation effect among donor-like and acceptor-like defects, the maximum achievable electron concentration is found to be low, less than $\sim 2 \times 10^{19} \text{ cm}^{-3}$ in theory, indicating that Ga-doping of $CoSb_3$ always yields low electron concentrations. This result is in accord with recent experiments [29].

In-doped $CoSb_3$ shows n-type behavior. The electron concentration is always higher than the hole concentration over the entire achievable Sb chemical potential range. This reflects the fact that In has more probability than Ga of taking the void filling site. The maximum carrier concentration of In-doped $CoSb_3$ is $4.3 \times 10^{19} \text{ cm}^{-3}$ at 1000 K. This value is higher than that of Ga-doped $CoSb_3$, which suggests that In-doped $CoSb_3$ is not completely charge compensated as Ga-doped $CoSb_3$, consistent with recent experiment results [30]. These show that the electron concentrations of In-containing

skutterudites are indeed higher than those of Ga-containing ones. This further corroborates the conclusion In-containing skutterudites are not fully charge-compensated by defects. The single-filling defect may coexist with dual-site complex defects. The maximum electron concentration (about $2 \times 10^{20} \text{ cm}^{-3}$) of In-doped CoSb_3 in experiments is slightly higher than our theoretical result. This may be because of the complexity of synthesis processes, defect equilibrium at a different temperature than that assumed or possibly non-equilibrium conditions in growth.

The n-type or p-type behavior of the doped compound is dependent on the concentration of different charge defects. As shown in Fig. 4, the complex dual-site occupancy defects are the major defects for both the Ga- and In-doping CoSb_3 . The completely charge-compensated compound defects especially the 2-1 defects are the dominant ones in Ga-containing CoSb_3 . The concentrations of other defects, such as the 1-1(-1) and dual-site occupancy defects with ratio of 3-1, 4-1, or 5-2, are much lower. For In-doped CoSb_3 , the dual-site defects 2-1 and 4-2 are the two dominant defect types, and 1-1(-1) could exist at low Sb chemical potentials. The other defects with different dual-site ratios (5-2, 6-3, 4-1, 3-1) have very similar concentrations. This is consistent with the formation energy results as discussed in relation to Fig. 3. Their concentrations are also substantially lower than that of the dual-site defects 2-1 and 4-2. Interestingly, unlike the Ga-doped CoSb_3 with only one type of charge-compensated dual-site 2-1 defect, In-doping leads to the formation of many complex defect clusters with different dual-site occupancy ratios even though their concentrations are lower than those of the 2-1 and 4-2 defects. Except for the charge compensated dual-site defects (4-2, 2-1, 6-3), all the other dual-site defects donate electrons to the systems. This is why the carrier concentration of In-doped CoSb_3 is significantly higher than that of Ga-doped system on one hand; and on the other hand, the achievable total concentrations of In impurities are higher than that of Ga in CoSb_3 , which

is also an electron donor defect.

In experiments, one can measure the total concentration of impurities, but it is difficult to quantitatively identify the separate contributions of different defects. Nonetheless, this information is helpful for understanding doping and carrier transport. So we calculate the concentrations of impurities in voids and at the Sb-substitution sites. Fig. 5 shows the atomic concentrations as a function of Sb chemical potential. Similar to Fig. 4, Fig. 5 is divided into two regions by the vertical lines with different values of impurity effective chemical potential. For the Ga-doped system, the ratio of defect concentrations at void-sites to Sb-substitution sites is very close to 2:1 at both low and high Sb chemical potential. This means that Ga tends to form dual-site charge-compensated defects. With Sb-rich conditions, the doping limit of Ga in CoSb_3 is 0.12. This is consistent with the recent experiment results [29]. As Sb chemical potential decreases, the doping levels of Ga in both the void site and the Sb-site increase. The maximum doping level of Ga in the void sites is 0.9 at the low Sb chemical potential limit. Such high doping levels of Ga in CoSb_3 are not found in experiments because the low Sb chemical potentials are very hard to realize. For the In-doped system, the ratio of concentration of defects in the voids and that at the Sb-substitution sites obviously deviates from 2:1, and the overall defect concentration is higher than that estimated by assuming only the dual-site charge-compensated 2:1 defects, again consistent with the higher electron concentration in both theory and experiments. For the Sb-rich limit, the solubility of In in CoSb_3 is about 0.2. This value is lower than recent experimental data (0.27) [30]. But when the In solubility is 0.27, the Sb compositions in CoSb_3 are lower than those of Ga-containing systems. The Sb chemical potential of In-containing CoSb_3 , when the In solubility is 0.27 is lower than 0, the value for Ga-containing CoSb_3 . When chemical potential of Sb marginally departs from the Sb-rich limit, such as $\Delta\mu_{\text{Sb}}=-0.05$

eV, the solubility of In in CoSb_3 is 0.272, and this value is very close to the experimental results. The above results show that the high impurity solubility can be obtained by controlling the chemical potential of Sb, even though this is hard to achieve experimentally. At the low Sb chemical potential limit, the solubility of In in the void site can also reach a very large value (0.7).

The above results mean that group-13 elements Ga and In do not form only the single-filled or Sb-substituted CoSb_3 compounds, but rather they enter both the voids and the Sb sites. This is key to understanding the doping behavior of these additions and also clearly has implications for the thermal conductivity and carrier mobility. Further support for this is given in Fig. 6, which shows a comparison of the theoretically predicted and experimental Sb composition as a function of the Ga and In composition. Purely substitutional Ga or In would imply a one to one decrease in Sb content with Ga or In, while void filling would imply no change. Experimentally, we synthesized Ga- and In-doping systems at different conditions. The microscopic compositions were analyzed by different techniques, mainly by SEM and TEM with the nominal composition $(\text{Ga}_{\text{VF}})_{0.1}\text{Co}_4\text{Sb}_{11.95}(\text{Ga}_{\text{Sb}})_{0.05}$. Experimental details are as reported previously [31]. The theoretical predictions for the Ga/In atomic percentage based on the total solubility of Ga and In in both void sites and Sb-sites at different Sb chemical potentials near the Sb-rich limit. The line (black) of $m_{\text{Sb}}=75\%-5/6 n_{\text{M}}$ ($\text{M}=\text{Ga}, \text{In}$) in Figure 6 represents the expected relationship between Sb atomic composition and the concentration of Ga/In impurities if the doped system has only the ideally charge-compensated compound defects $2\text{M}_{\text{VF}}-\text{M}_{\text{Sb}}$. As seen, when the concentration of Ga or In increases in CoSb_3 , the Sb concentration decreases and reasonably follows the behavior that would be expected for fully charge-compensated dual-site defects. Although the measured data are not from single crystals, they are all from single-phase samples. While the agreement is not perfect in that some points deviate

from the line, the experimental results do support the theoretical conclusion that Ga and In impurities occupy both the void-filling sites and the Sb-substitution sites and form complex dual-site occupancy defects in CoSb₃.

3.4 Possibility of high level Ga/In doping and metastability of defects

As discussed above, and shown in Fig. 5, Ga/In have high solubility in CoSb₃ at low Sb chemical potentials. Also as shown in Table I, the defect formation energies are positive at 0 K, which means that the defects are metastable at low temperature. As temperature increases, the configurational entropy plays an important role in stabilizing Ga/In-containing CoSb₃. Fig. 7 shows the formation energies of the charge compensated defects 2-1, 4-2 and 6-3 in CoSb₃ at different Sb chemical potentials. Here the chemical potential of impurities $\Delta\mu_M = 0$ is used. The contribution of the configurational entropy $T\Delta S$ to defect formation energies is considered at $T=1000$ K. The defect formation energy is related to the Sb chemical potential. For Ga-containing skutterudites, the formation enthalpy of defect 2-1 has a negative value due to the contribution of configurational entropy, but are positive for the 4-2 and 6-3 defects. Unlike Ga-doped CoSb₃, the formation enthalpies are very close to each other and are positive for the three fully charge-compensated defects in In-containing CoSb₃. At the low Sb chemical potential limit, the formation energies are very low for all the defects (2-1, 4-2, 6-3), and for both Ga- and In-containing CoSb₃. By controlling the chemical potential of Sb and considering the contribution of configurational entropy, it is clear that high solubility for Ga and In in skutterudites can be obtained. The reason is that at low Sb chemical potentials, defects that involve Sb deficiency become more favorable.

4. Conclusions

We investigated the doping behavior of group 13 elements Ga, In in CoSb₃ skutterudites by combining density functional theory and thermodynamics. Incorporation of these elements is energetically disfavored at low temperature. At finite temperature complex behavior involving compensating defects at void filling and Sb substitutional sites is found. The calculated doping behaviors of Ga and In at finite temperature are dependent on the experimental conditions, and in particular the Sb chemical potential plays an important role. Both Ga and In doping are shown to result in complex defects that combine interacting donor-like void-filling and acceptor-like Sb-substitution impurities. The calculated defect formation energies show that Ga can form dual-site doping defects and Sb substitution defect with charge state -2, while In forms either void filling, or dual-site doping, or a Sb-substitution defects depending on experiment conditions. For Ga, the concentration ratio in void-site and Sb-site is about 2:1. For In, the concentration ratio departs slightly from 2:1 between the void-sites and the Sb-sites. The ionic radii of Ga and In affect the defect behavior in CoSb₃. Our calculations also reveal that Ga-containing CoSb₃ always has very low electron concentrations ($\sim 2 \times 10^{19} \text{ cm}^{-3}$), while the In-containing system can have higher n-type carrier concentrations. The predicted solubility of Ga/In in CoSb₃ at Sb rich conditions is consistent with recent experiments. We predict that at Sb-poor conditions they have very high solubility at elevated temperature although the positive formation energies imply that this high defect concentration state is metastable. Turning to thermoelectric applications, as mentioned, even the best n-type multiple-filled-CoSb₃ that has the highest ZT value may not yet be fully optimized. For example, as mentioned bipolar effects may still be reducing the achievable ZT, and of course further thermal conductivity reduction would also be beneficial. The complex behavior of Ga, In impurities in particular suggests that its incorporation in combination with other strategies, in particular rare earth

filling, may provide needed chemical degrees of freedom for further optimization of the n-type CoSb₃ based thermoelectric.

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Appendix A. Grand Canonical Ensemble

By assuming that the doped system is thermodynamically open and that the formed defects, even with complex defect structure, have no interaction with each other (isolated defect approximation), the grand canonical ensemble can be used to estimate the concentrations of defects.

Given that N is the number of *single-void-containing unit* with one lattice void, 12 Sb atoms, and 4 Co atoms. The unit is to be used as the coarse-grained lattice site to count the configurations of defects. n_i labels the number of the defect type i existing in the ensemble, and m is the total number of defect types. The number of defect Co_i is n_0 . The number of defects M_{VF} , M_{Sb} , $M_{VF-M_{Sb}}$, $2M_{VF-M_{Sb}}$, ..., $aM_{VF-bM_{Sb}}$ is labeled as $n_1(1-0)$, $n_2(0-1)$, $n_3(1-1)$, $n_4(2-1)$, ..., and $n_m(a-b)$, respectively. a and b are the number of impurities at the void sites and the Sb-substitution sites for a given dual-site occupancy defect. When defect concentration is low, and defect-defect interaction can be neglected, the total Gibbs free energy of the ensemble can be written as:

$$J = U - TS - N_M \mu_M - N_{Sb} \mu_{Sb} - N_{Co} \mu_{Co} \quad .$$

Where U is the internal energy, N_M , N_{Sb} , and N_{Co} are the number of M , Sb , and Co atoms in the

ensemble, respectively. For the doping system studied in the present work, we have,

$$U = E_0 + \sum_{i=0}^m n_i \varepsilon_i^{def}, N_M = \sum_{i=0}^m n_i a_i, N_{Sb} = 12N - \sum_{i=0}^m n_i b_i, N_{Co} = 4N + n_0$$

$$\varepsilon_i = E_i^{def} - E_0 + q(\varepsilon_F + E_v + \Delta V)$$

Where E_i^{def} is the total energy of the supercell with a specific defect i , and E_0 is the total energy of

CoSb₃ supercell free of defects. By assuming that there is only one defect M_{Sb} around one M_{VF} in one

void, the total configuration entropy of the ensemble can be expressed as

$$S = k_B \ln \Omega, \Omega = \prod_i \Omega_i$$

$$\Omega_0 = C_{3N}^{n_0},$$

$$\Omega_1(1-0) = C_N^{n_1},$$

$$\Omega_2(0-1) = C_N^{n_2} (C_{12}^1)^{n_2},$$

$$\Omega_3(1-1) = C_N^{n_3} (C_{12}^1)^{n_3},$$

$$\Omega_4(2-1) = C_N^{2n_4} (C_{24}^1)^{n_4},$$

.....

$$\Omega_i(a_i-1) = [C_N^{a_i n_i} (C_{12a_i}^1)^{n_i}],$$

$$\Omega_i(a_i-2) = [C_N^{a_i n_i} (C_{12a_i}^1)^{n_i} (C_{12a_i-12}^1)^{n_i}],$$

$$\Omega_i(a_i-3) = [C_N^{a_i n_i} (C_{12a_i}^1)^{n_i} (C_{12a_i-12}^1)^{n_i} (C_{12a_i-24}^1)^{n_i}]$$

In the condition of thermodynamic equilibrium, the defect concentration can be obtained by

minimizing the total Gibbs free energy of the ensemble with respect to the number of defect i

$$\frac{\partial J}{\partial n_i} = 0$$

By defining,

$$\begin{cases} g_0 = E_{Coi}^{def} - E_0 + q(\varepsilon_F + E_v + \Delta V) - \mu_{Co}, i = 0 \\ g_i(a_i - b_i) = E_i^{def} - E_0 + q(\varepsilon_F + E_v + \Delta V) - a_i \mu_M + b_i \mu_{Sb}, i > 0 \end{cases}$$

When $n_i \ll N$, the concentration of defects is obtained to be

$$C_0 = n_0 / N \approx 3 \exp(-g_0 / kT)$$

$$C_1(1-0) = n_1 / N \approx \exp(-g_1 / kT)$$

$$C_2(0-1) = n_2 / N \approx 12 \exp(-g_2 / kT)$$

$$C_3(1-1) = n_3 / N \approx 12 \exp(-g_3 / kT)$$

$$C_4(2-1) = n_4 / N \approx \frac{\sqrt{24}}{2} \exp(-g_4 / (3kT))$$

.....

$$C_i(a_i - 1) = n_i / N \approx \frac{(a_i * 12)^{\frac{1}{a_i}}}{a_i} \exp(-g_i / (a_i kT))$$

$$C_i(a_i - 2) = n_i / N \approx \frac{(a_i * 12)^{\frac{1}{a_i}}}{a_i} (a_i * 12 - 12)^{\frac{1}{a_i}} \exp(-g_i / (a_i kT))$$

$$C_i(a_i - 3) = n_i / N \approx \frac{(a_i * 12)^{\frac{1}{a_i}}}{a_i} (a_i * 12 - 12)^{\frac{1}{a_i}} (a_i * 12 - 24)^{\frac{1}{a_i}} \exp(-g_i / (a_i kT))$$

For an ensemble with many charged defects, the carrier concentration depends on the Fermi level in the following way

$$n_e = N_C \exp[-(E_g - \varepsilon_F) / k_B T], n_h = N_V \exp(-\varepsilon_F / k_B T),$$

where N_C and N_V are the effective density of states of conduction and valence band edges. E_g is the band gap of the system.

The Fermi level can be determined by overall charge neutrality, i.e.

$$n_e - n_h = \sum_i q(i) C_i N_s$$

Where $q(i)$ is the charge state of defect type i . N_s is the number of sites (per unit volume) at which defect i can be formed.

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Table 1. Formation energies of different defects at 0 K. Values are given for the chemical potentials in the Co-rich ($\Delta\mu_{\text{Sb}} = -0.33$ eV) and Sb-rich ($\Delta\mu_{\text{Sb}} = 0$ eV) limits. The formation energies of the several native defects are also shown in the table for comparison. Only zero charge state defects are listed. The charge state dependence is given in Fig. 3.

Figure Captions

Fig. 1. Local atomic structures for the four types of defects in M-doped CoSb₃, with the defect-related atoms red cycled. (a) Void-filling, M_{VF} , (b) Sb-substitution, M_{Sb} , (c) Complex defect with void-filling and Sb-substitution atoms at a 1:1 ratio, $M_{\text{VF}}-M_{\text{Sb}}$, (d) Complex defect with void-filling and Sb-substitution complex atoms at a 2:1 ratio, $2M_{\text{VF}}-M_{\text{Sb}}$. Each defect may have different charge states. The green icosahedron indicates void site in the skutterudite lattice.

Fig. 2. Stable configurations of the $M_{\text{VF}}-M_{\text{Sb}}$ (1:1) complex defect. The distances between M_{VF} (central atom) and some of the 12 neighbor atoms are indicated to illustrate the structure distortion. The figures correspond to Ga- (a) and In-filling (b). The $2M_{\text{VF}}-M_{\text{Sb}}$ (2:1) defect (not shown) has practically the same distances as those indicated in the above figures.

Fig. 3. Defect formation energies (per impurity atom) as a function of the Fermi level at the Co-rich and Sb-rich limits. The defect types are labeled on the figure, with the number on each curve indicating the charge state of the defect.

Fig. 4. Equilibrium defect concentrations for (a) Ga- and (b) In- doped CoSb₃ at 1000 K. The defect types are labeled in the figure, with the number in parentheses indicating the charge state of the defect. The calculated concentrations of electrons (n) and holes (p) are also plotted. The figure is divided to two parts by red lines with different chemical potentials of impurity atoms Ga/In for the formation of GaSb or InSb.

Fig 5. Total impurity atomic concentration (with respect to numbers of voids) as a function of Sb chemical potential for Ga- and In-containing CoSb₃ skutterusites. The black lines are the total

impurity concentrations. Green lines indicate the total concentration for Ga and In impurities occupying the void sites, and red lines for impurities occupying Sb-substitution sites. The blue lines are the estimated concentrations of impurities at the Sb-substitution sites from the Ga_{VF} or In_{VF} curves assuming only the dual-site 2-1 defects.

Fig. 6. Theoretical and experimental Sb atomic percentages as a function of Ga/In atomic percentages in Ga- and In-doped CoSb_3 . Open symbols are experimentally measured results. Solid stars are theoretical data. The statistical composition data from Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) analysis are plotted for the samples with nominal composition $(\text{Ga}_{\text{VF}})_{0.1}\text{Co}_4\text{Sb}_{11.95}(\text{Ga}_{\text{Sb}})_{0.05}$. The black line represents the expected Sb atomic composition variation as a function of Ga or In doping based on the ideal defect $2\text{M}_{\text{VF}}-\text{M}_{\text{Sb}}$.

Fig. 7. Formation energies of a few different fully charge-compensated defects under different Sb chemical potentials at 1000 K. The lines are guides to the eye to connect the points for related defects.

Fig. 1.

Fig. 2.

Fig. 3a.

Fig. 3b.

Fig. 3c.

Fig. 3d.

Fig. 4a.

Fig. 4b.

Fig. 5a.

Fig. 5b

Fig. 6a.

Fig. 6b.

Fig. 7.

Table 1. Formation energies of different defects at 0 K. Values are given for the chemical potentials in the Co-rich ($\Delta\mu_{\text{Sb}}=-0.33$ eV) and Sb-rich ($\Delta\mu_{\text{Sb}}=0$ eV) limits. The formation energies of the several native defects are also shown in the table for comparison. Only zero charge state defects are listed. The charge state dependence is given in Fig. 3.

M	Ga (eV)		In (eV)	
Defect	$E(\Delta\mu_{\text{Sb}}=0)$	$E(\Delta\mu_{\text{Sb}}=-0.33)$	$E(\Delta\mu_{\text{Sb}}=0)$	$E(\Delta\mu_{\text{Sb}}=-0.33)$
M_{VF}	0.594	0.594	0.471	0.471
M_{i}	0.896	0.896	1.458	1.458
M_{Sb}	0.676	0.346	0.898	0.568
$M_{\text{VF}}-M_{\text{Sb}}(1-1)$	0.436	0.271	0.534	0.369
$2M_{\text{VF}}-M_{\text{Sb}}(2-1)$	0.309	0.199	0.368	0.258
$3M_{\text{VF}}-M_{\text{Sb}}(3-1)$	0.373	0.290	0.382	0.299
$4M_{\text{VF}}-M_{\text{Sb}}(4-1)$	0.414	0.348	0.398	0.332
$5M_{\text{VF}}-2M_{\text{Sb}}(5-2)$	0.397	0.303	0.363	0.269
$4M_{\text{VF}}-2M_{\text{Sb}}(4-2)$	0.314	0.204	0.359	0.249
$6M_{\text{VF}}-3M_{\text{Sb}}(6-3)$	0.337	0.227	0.352	0.242
$M_{\text{Sb}}-\text{Sb}_{\text{VF}}$	0.920	0.920	1.476	1.476
M_{Co}	1.007	1.997	1.715	2.705
$V_{\text{Sb}}-M_{\text{Sb}}$	2.678	2.078	2.777	2.117
Co_{i}	0.897 (0.8) ^a	1.887(2.19) ^a		
Sb_{i}	2.46 ^a	2.0 ^a		
V_{Co}	2.89 ^a	1.5 ^a		
V_{Sb}	2.75 ^a	3.21 ^a		

^aPark et al., Phys. Rev. B. **81**, 085206 (2010).