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Filling Fraction Limit for Intrinsic Voids in Crystals: Doping in Skutterudites

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The doping limit or the filling fraction limit (FFL) of various impurities for the intrinsic voids in the lattice of $CoSb_3$ is studied by the density functional method. The FFL is shown to be determined not only by the interaction between the impurity and host atoms but also by the formation of secondary phases between the impurity atoms and one of the host atoms. The predicted FFLs for Ca, Sr, Ba, La, Ce, and Yb in $CoSb_3$ are in excellent agreement with reported experimental data. A correlation between the FFL of an impurity atom and its valence state and electronegativity is discovered.

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Many physical properties of crystalline solids, such as the electrical or thermal transport, the luminescence, and the magnetic susceptibility, depend pivotally on the presence of impurities [1]. Doping in crystals for performance improvement is an important subject in solid state physics, covering various materials from narrow-gap semiconductors [2], wide-gap semiconductor [3], complex clathrates [2], to ceramics [4], etc. It is known that the doping limit exists for almost all of those materials. Over the years, the mechanisms controlling the doping limit have been discerned for a few typical semiconductors such as GaN and ZnO [3] which have relatively wide band gaps and very low impurity solubilities. For other materials [2,4] with different chemical bondings and electronic structures, no rationale appears yet although the doping limits have been found for years.

Materials that possess the skutterudite structure are typical examples of narrow-gap semiconductors with relatively high impurity solubilities for the interstitial voids [2]. The skutterudite crystal structure contains two large interstitial voids in a conventional unit cell that can be filled with various impurities to form filled skutterudite (FS) [2]. In the past decade, FSs with different filler atoms (Ce, La, Nd, Eu, Yb, Tl, Ca, and Ba) [5–12] have been intensively studied in an effect to search for better thermoelectric materials. One of the most interesting remaining scientific questions is what influences the doping limit or the filling fraction limit (FFL) of each impurity in the host skutterudite structure. It is believed that the FFL is determined simultaneously by several factors such as the charge state, the electronegativity, etc., of the filler. A few theoretical investigations have been done [13,14] to understand the thermodynamic stabilities of FSs; however, to our knowledge, there has yet to be any quantitative model to predict the FFL, to identify crucial physical properties that control the FFL, and to explain the experimental observation. In this Letter, we study the FFLs of Ca, Sr, Ba, La, Ce, and Yb in $CoSb_3$ by density functional method.

The projector augmented wave method [15,16] is utilized for this study. The generalized gradient approximation (GGA) [17] for the exchange-correlation potential is used for all the calculations. Results in the local density approximation (LDA) [18] for the La-doped $CoSb_3$ are also given. Cutoff energy as high as 350 eV is used for the plane wave basis set. All calculations were carried out in a supercell ($2 \times 2 \times 2$ primitive cell) with 128 atoms and 8 voids of pure $CoSb_3$. Lattice constants and ionic coordinates were relaxed to find the most stable states for both the pure and doped $CoSb_3$.

First the formation enthalpy of each impurity (I) atom in $CoSb_3$ is calculated. If the formation enthalpy becomes positive when the filling fraction exceeds a certain limit, the filled $CoSb_3$ is unstable, and hence the FFL could be determined. Formation enthalpy is defined as $\Delta H_1(y) = (E_{I_yCo_4Sb_{12}} - 4E_{CoSb_3} - yE_I)/y$, and it corresponds to the reaction $yI + 4CoSb_3 \rightarrow I_yCo_4Sb_{12}$. $E_{I_yCo_4Sb_{12}}$, E_{CoSb_3}, and E_I are the total energies of $I_yCo_4Sb_{12}$, $CoSb_3$, and I at their most stable states, respectively. y is the filling fraction with $0 < y \leq 1$.

Figure 1 shows ΔH_1 as a function of y between $y = 0.1$ and $y = 0.5$ for all impurities. The formation enthalpies for Ca, Sr, Ba, La, Ce, and Yb in $CoSb_3$ are all negative. In fact, the formation enthalpies are still negative even as all the voids are occupied (not shown in Fig. 1 for $y > 0.5$), which implies that the FSs might be stable at very high filling fractions. This is obviously in contradiction with the reported experimental data [5,6,9,11,12,19].

These results clearly indicate that the FFL of an impurity must also be determined by other factors besides its interaction with the host materials. The most likely reason is the formation of secondary phases between the impurity and the host atoms. The secondary phases could be energetically more favorable than the FS phases, making the FS phases unstable and hence giving rise to FFLs. In the case of $CoSb_3$ with the above filler atoms, $CoSb_2$, ISb_2 are the most likely secondary phases to form based on experimen-

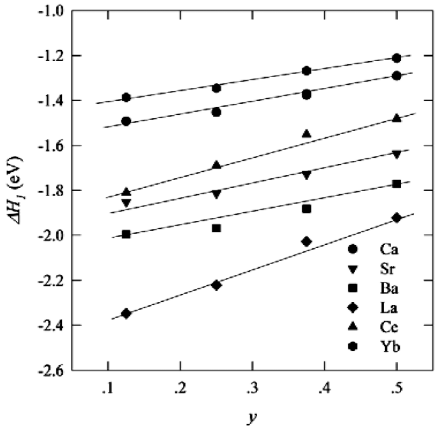

FIG. 1. Formation enthalpy (per impurity atom) as a function of filling fraction y for the filled skutterudites. The lines are the best linear fits to the calculated data (symbols).

tal observations [5,6,9,11,12,19]. *Ab initio* calculations also show that $I\mathrm{Sb}_2$ has the lowest formation enthalpy, at least 0.1 eV lower than those of other possible phases [20]. The secondary phase reaction is taken to be $I + 2\mathrm{CoSb}_3 \rightarrow I\mathrm{Sb}_2 + 2\mathrm{CoSb}_2$, and the corresponding formation enthalpy is $\Delta H_2 = E_{I\mathrm{Sb}_2} + 2E_{\mathrm{CoSb}_2} - E_I - 2E_{\mathrm{CoSb}_3}$. $E_{I\mathrm{Sb}_2}$ and E_{CoSb_2} are the total energies of $I\mathrm{Sb}_2$ and CoSb_2, respectively. Therefore, the reaction route to a system containing both the FS phase and the secondary phases can be described as

$$nI + 4\mathrm{CoSb}_3 \rightarrow \frac{(2-n)}{(2-y)} I_y\mathrm{Co}_4\mathrm{Sb}_{12} + \frac{2(n-y)}{(2-y)} I\mathrm{Sb}_2 + \frac{4(n-y)}{(2-y)}\mathrm{CoSb}_2. \tag{1}$$

At a finite temperature, the corresponding formation energy for an impurity is

$$\Delta G_3 = 2\frac{n-y}{n(2-y)}\Delta H_2 + \frac{(2-n)y}{n(2-y)} \times \left\{\Delta H_1(y) + kT\left[\ln y + \frac{1-y}{y}\ln(1-y)\right]\right\}. \tag{2}$$

Note that only y fraction of the impurity atoms goes into the voids and the rest forms the secondary phases [Eq. (1)]. The second term in ΔG_3 contains the contribution from the configurational entropy due to the random distribution of the impurity atoms at the void positions [21]. k is Boltzmann's constant. Temperature effect on ΔH_1 and ΔH_2 is not considered at the current stage based on the argument that the vibrational free energy contributions to ΔH_1 and ΔH_2 are small [22], and may exhibit systematic cancellation in determining the equilibrium of the reaction represented by Eq. (1). Therefore, the net effect of temperature on the equilibrium point with minimum ΔG_3 is quite small. This is inconsistent with our results that the theoretically predicted FFLs agree well (see later) with the measured values. In fact, the contribution from the entropy term is also small, and only slightly affects the final FFL values.

By minimizing ΔG_3 with respect to the filling fraction y, the FFL values can be obtained in terms of ΔH_1 and ΔH_2. Figure 2 plots the calculated FFLs vs the experimentally measured ones for Ca [11], Sr [19], Ba [12], La [6], Ce [5], and Yb [9] in CoSb_3. They are in excellent agreement with each other. The FFL for La in CoSb_3 calculated in LDA is also shown in Fig. 2, and shows a good consistency with the GGA value.

The aforementioned calculations show that the FFL of an impurity is determined not only by the interaction between the impurity and host materials but also by the formation ability of secondary phases. By taking into account both effects, the FFL can be predicted very accurately. The data in Fig. 1 show that there is a linear dependence of ΔH_1 on the filling fraction y. We may express that as

$$\Delta H_1 = \Delta E_1 + (\Delta E_2)y. \tag{3}$$

This is a good approximation as long as the filling fraction y is not very high. The y independent term ΔE_1 indicates the formation energy of an isolated impurity, determined mainly by the interaction between the impurity atom and its neighboring host atoms. The linear (in y) term comes from the interaction between impurity atoms. Because the shortest possible distance between impurity atoms is still as large as 7.8 Å, a pair interaction approximation can be used, and therefore $\Delta E_2 = wZ$, where w is the interaction energy between a single pair of impurity atoms [23] and Z ($= 8$) is the number of the nearest neighbor voids to an impurity atom.

Based on Eqs. (2) and (3), the FFL of an impurity in CoSb_3 can be given analytically at 0 K as

$$y_{\max} = 2\left(1 - \sqrt{1 + \frac{\Delta E_1 - \Delta H_2}{2\Delta E_2}}\right). \tag{4}$$

According to Eq. (4), the FFL is determined by three

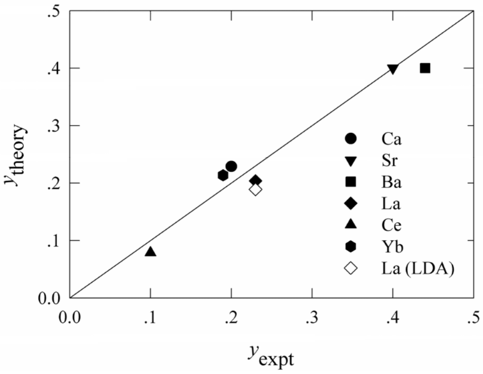

FIG. 2. Calculated filling fraction limits (FFLs, y_{theory}) vs the experimentally measured FFLs (y_{expt}) for Ca [11], Sr [19], Ba [12], La [6], Ce [5], and Yb [9] in CoSb_3. The solid line represents $y_{\mathrm{theory}} = y_{\mathrm{expt}}$.

parameters: ΔE_1, ΔE_2, and ΔH_2. The impurity atom can fill the voids in CoSb$_3$ only when $\Delta E_1 < \Delta H_2$. A high FFL requires a low formation energy of an isolated impurity in CoSb$_3$, high formation energies of secondary phases, and a small interaction between impurity atoms. The interplay amongst these various energies determines $y_{\max}$.

Both ΔE_1 and ΔE_2 can be obtained by fitting Eq. (3) to the calculated ΔH_1. Note that ΔE_2 is always positive for all impurities studied here, indicating a repulsive interaction between filler atoms. This is reasonable, or else it would be energetically more favorable to have high fraction of voids filled. We believe that ΔE_2 is mainly due to the coulomb interactions between impurity atoms. By taking into account the screening effects of the crystal environment, and assuming that the impurity atom has an effective charge q_I, defined as the number of electrons lost from an impurity after being inserted into the void of CoSb$_3$, ΔE_2 can be expressed as

$$\Delta E_2 = \frac{Z q_I^2 e^{-2R/R_0}}{4\pi \varepsilon_r \varepsilon_0 R}, \qquad (5)$$

where R is the distance between filler atoms. ε_0 and ε_r are the dielectric constants of vacuum and CoSb$_3$ [24], respectively, and R_0 is the effective screening length of the CoSb$_3$ crystal around a charged impurity. Because all impurity atoms experience the same crystal environment, it is reasonable to take R_0 as a constant. To estimate q_I for all impurities, the effective charge is taken to be $q_I = +2$ for Ba because of its strong tendency of losing electrons and well-defined valence state for almost all Ba-containing compounds both experimentally [12] and theoretically [14]. The effective charge q_I for other impurities can be obtained using Eq. (5) and comparing the fitted ΔE_2 values to that of Ba. The charge states of all impurities are also estimated by integrating the calculated density of states (DOS) to the Fermi level. The effective charge states calculated by the two methods show good agreement as plotted in Fig. 3(a). A linear dependence of ΔE_2 on the $q_I{}^2$ is also obtained. Therefore, it is reasonable to conclude that q_I can be taken as the real valence charge of the impurity in CoSb$_3$. In fact, our calculated q_I values do agree reasonably well with the valence charges from carrier concentration measurement [5–12]. R_0 is estimated to be 12.58 Å, much larger than those (typically ~2–3 Å) for metals, suggesting a weak charge screening effect in CoSb$_3$. This is consistent with our proposed picture that the impurity-impurity interaction is primarily columbic.

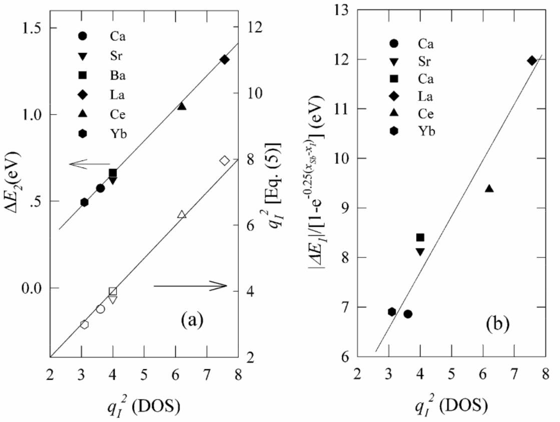

FIG. 3. (a) Relationship between the impurity-impurity repulsive energy ΔE_2 and the effective charge of the impurities (filled symbols). The consistency between the effective charges estimated by Eq. (5) and that from the calculated DOS are also shown in the figure (empty symbols). (b) Relationship among the formation energy ΔE_1 of an isolated impurity, valence charge, and electronegativity of the impurity atom in CoSb$_3$.

Because of the complex structure of Sb and Co atoms around a filler atom in FSs, there is no simple formulation like Eq. (5) for ΔE_1. The electron charge density redistribution due to the insertion of a filler shows that only the electron density around the filler, i.e., the boundary of the irregular dodecahedral cage of Sb atoms surrounding the filler, is significantly affected. Overlap population analysis also gives zero overlap between the valence orbitals of the filler and that of a Co atom at the next-nearest neighbor position to the filler [20]. This leads us to reasonably assume that the ΔE_1 is mainly determined by the I-Sb interactions. The I-Sb bond is more ionic due to the large electronegativity difference between I and Sb atoms and the oversized voids for the impurities. Based on Pauling's definition that the ionic character of a chemical bond is proportional to $[1 - e^{-0.25(x_{\mathrm{Sb}} - x_I)}]$ [25], ΔE_1 is phenomenologically approximated as

$$\Delta E_1 = B_1 q_I^2 [1 - e^{-0.25(x_{\mathrm{Sb}} - x_I)}] + B_2 e^{-0.25(x_{\mathrm{Sb}} - x_I)}. \qquad (6)$$

The first and second terms represent the ionic and covalent parts of chemical bonds around impurity I. x_I and x_{Sb} are the electronegativities of impurity and Sb atoms, respectively. The fitted B_1 and B_2 values according to Eq. (6) are -1.60 V/e and -0.4 eV, respectively. Since B_2 is small, the second term in Eq. (6) can be neglected without changing the physical trend, consistent with the picture that the I-Sb bonds are predominantly ionic in nature. Figure 3(b) plots $\Delta E_1/[1 - e^{-0.25(x_{\mathrm{Sb}} - x_I)}]$ vs $q_I{}^2$ for all impurities. The data show a good linear relationship between the two, suggesting that Eq. (6) (without the second term) is a good approximation.

A careful inspection of the data also reveals that there exists a good linear relationship between the formation enthalpy of the secondary phases (ΔH_2) and $q_I{}^2$ of the impurity atoms. The details will be presented elsewhere [20]. Thus, combining Eqs. (4)–(6) with $\Delta H_2 \propto q_I{}^2$ gives

$$y_{\max} - \left(\frac{y_{\max}}{2}\right)^2 = C_1[1 - e^{-0.25(x_{\mathrm{Sb}} - x_I)}] + C_2. \qquad (7)$$

The constants C_1 and C_2 can be calculated by fitting $y_{\max} - (y_{\max}/2)^2$ vs $1 - e^{-0.25(x_{\mathrm{Sb}} - x_I)}$ shown in Fig. 4, and they are 7.60 and -1.53 at 0 K, and 5.29 and -0.96 at 1000 K, respectively. It is really surprising that FFL turns out to be sensitive to the electronegativity but not directly to the charge state of the impurity atom. The

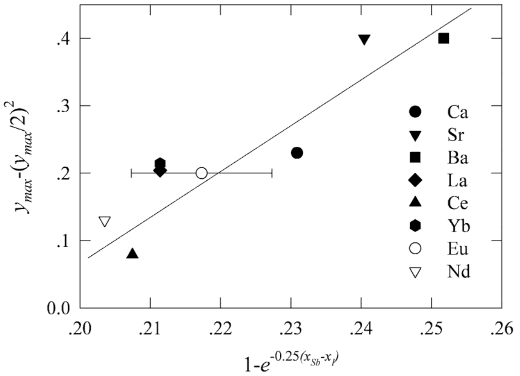

FIG. 4. Correlation between the FFLs of impurities in $CoSb_3$ and their electronegativities. The FFLs for Nd and Eu are taken from Refs. [7,8]. Other FFLs were from references cited in the caption of Fig. 2.

experimental FFL values for Eu and Nd in $CoSb_3$ are also shown in Fig. 4, consistent reasonably well with the linear trend. The error bar for Eu is due to the uncertainty in determining the electronegativity value of Eu [26]. By comparing the exact results in Fig. 2 with the general trend shown in Fig. 4, it is reasonable to believe that we have unveiled the most important factors dominating the FFL. The deviation in Fig. 4 is most likely due to the phenomenological nature of Eq. (6), and the neglect of both the impurity-Co interaction and the covalent part of impurity-Sb interaction although they both are very weak. Note that the importance of elemental electronegativity has also been illustrated by G. A. Slack in predicting and understanding thermoelectric properties of various materials [27].

Because the filling fraction should be greater than zero, i.e., $y > 0$, Eq. (7) leads to a selection rule for a filled $CoSb_3$ to form

$$x_{\mathrm{Sb}} - x_I > 0.80. \tag{8}$$

If $x_{\mathrm{Sb}} - x_I$ is less than 0.80, the FFL for the impurity in $CoSb_3$ is zero. This simple rule [Eq. (8)] is by no means an accurate description, but it provides a general criterion for an impurity to be able to fill the voids in $CoSb_3$. The electronegativities of impurities that have a stable FS without charge compensation satisfy this selection rule except for Tl, which has a reported FFL of 22% in $CoSb_3$ [10]. This breakdown is attributed to the fact that Tl is an unusual element and it is chemically similar to Sb but not to rare-earth or alkaline-earth metals [28].

In conclusion, we studied the FFLs of various impurities in filled skutterudites by density functional method. Formation of secondary phases of an impurity with host atoms is shown to be the key factor to determine the FFL of the impurity. The FFL turns out to be sensitive to the impurity atom's electronegativity but not directly to its charge state. A simple selection rule for forming filled skutterudites is discovered, and it agrees well with experimental observations. Our model could also be applied for the doping limit study of other crystals including other skutterudites with relatively high impurity solubility. The analysis leading to the selection rule is expected to be more accurate for pure ionic systems.

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[1] F. A. Kröger and H. J. Vink, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 307.
[2] G. Chen *et al.*, Int. Mater. Rev. **48**, 45 (2003), and references therein.
[3] S. B. Zhang, S. H. Wei, and A. Zunger, Phys. Rev. Lett. **84**, 1232 (2000).
[4] V. A. Izhevskiy *et al.*, J. Eur. Ceram. Soc. **20**, 2275 (2000).
[5] D. T. Morelli *et al.*, Phys. Rev. B **56**, 7376 (1997).
[6] G. S. Nolas, J. L. Cohn, and G. A. Slack, Phys. Rev. B **58**, 164 (1998).
[7] V. L. Kuznetsov, L. A. Kuznetsova, and D. M. Rowe, J. Phys. Condens. Matter **15**, 5035 (2003).
[8] G. A. Lamberton *et al.*, Appl. Phys. Lett. **80**, 598 (2002).
[9] G. S. Nolas *et al.*, Appl. Phys. Lett. **77**, 1855 (2000).
[10] B. C. Sales, B. C. Chakoumakos, and D. Mandrus, Phys. Rev. B **61**, 2475 (2000).
[11] M. Puyet *et al.*, J. Appl. Phys. **95**, 4852 (2004).
[12] L. D. Chen *et al.*, J. Appl. Phys. **90**, 1864 (2001).
[13] O. M. Løvvik and Ø. Prytz, Phys. Rev. B **70**, 195119 (2004).
[14] L. Bertin and C. Gatti, J. Chem. Phys. **121**, 8983 (2004).
[15] G. Kresse and J. Joubert, Phys. Rev. B **59**, 1758 (1999); P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994).
[16] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[18] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[19] X. Y. Zhao, X. Shi, and L. D. Chen, J. Appl. Phys. (to be published).
[20] X. Shi, W. Zhang, and L. D. Chen (to be published).
[21] D. R. Gaskell, *Introduction to the Thermodynamics of Materials* (Taylor & Francis, London, 1995), 3rd ed..
[22] C. G. Van de Walle and J. Neugebauer, Phys. Rev. Lett. **88**, 066103 (2002); K. Reuter and M. Scheffler, Phys. Rev. B **65**, 035406 (2002).
[23] *Adsorption on Metal Surfaces*, edited by J. Benard (Elsevier Scientific, Amsterdam, 1983).
[24] G. Kliche and H. D. Lutz, Infrared Phys. **24**, 171 (1984).
[25] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960), 3rd ed..
[26] E. Sacher *et al.*, J. Electron Spectrosc. Relat. Phenom. **46**, 173 (1988); A. L. Allred *et al.*, J. Inorg. Nucl. Chem. **5**, 264 (1958).
[27] G. A. Slack, In *CRC Handbook of Thermoelectrics* (CRC Press, Boca Raton, 1995).
[28] A. G. Lee, *The Chemistry of Thallium* (Elsevier, New York, 1971).