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Anomalous Dual-Element Filling in Partially Filled Skutterudites

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Abstract: The existence of a filling fraction limit (FFL) for single-element filling in caged compounds such as $CoSb_3$ has been established as a general phenomenon by both experiment and theory. For dual-element-filled skutterudites, our ab initio results reveal that the filling fraction (FF) of one filler usually decreases linearly as the other increases, and the total FF (the sum of the FFs of the two fillers) lies between the two single-element FFLs. However, the Na–Eu combination manifests an anomalous behavior: the total FF can exceed both the Na-only and Eu-only FFLs and is even likely to reach full filling. Electronic structure analysis shows that the Na–Eu cofilling pushes the s states of Na and Eu closer to the bottom of the conduction band, increases the electron occupancy of these s orbitals, lowers the effective charge states of the fillers, affects the Na–Eu interaction, and finally leads to the anomalous filling behavior.

I. Introduction

In solid-state chemistry, intrinsic lattice voids or cages exist in many groups of compounds, and they can be partially filled with various extrinsic impurities.[1–4] Among those compounds, skutterudite ($CoSb_3$) is a representative example. Cubic $CoSb_3$ possesses two voids in a crystallographic unit cell. The voids can be filled with rare earths (REs),[4–13] alkaline earths (AEs),[14–16] or alkaline metals (AMs),[17–19] and each individual filler has a filling fraction limit (FFL). The study of partial filling in skutterudites has received great interest in recent years,[3–19] mainly because of the fact that the adjustable filling fraction (FF) can tune thermoelectric (TE) properties of the filled skutterudites. It is the partial filling in $CoSb_3$ that reduces the lattice thermal conductivity[20] and greatly enhances the power factor and TE performance, thereby making filled $CoSb_3$ one of the most promising intermediate-temperature TE materials. Recent focus has been devoted to multiple-element filling, which is considered to be an effective way to further optimize the TE performance of filled skutterudites.[23–25]

The FFL of a filler atom in $CoSb_3$ is critical for determining the extent of thermal conductivity reduction as well as the range of electrical performance optimization. FFLs in single-element-filled skutterudites have been shown to follow an electronegativity rule that has been confirmed by both experiment and

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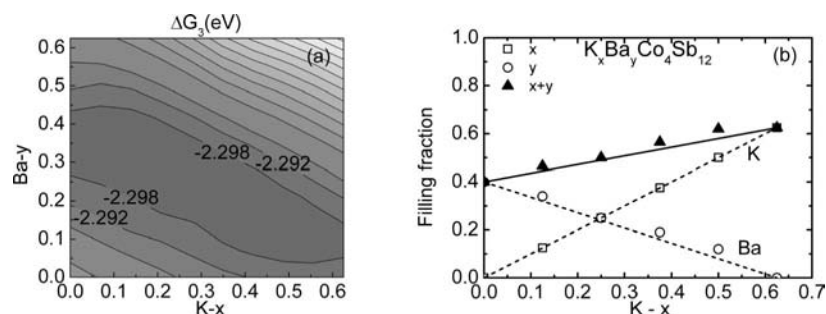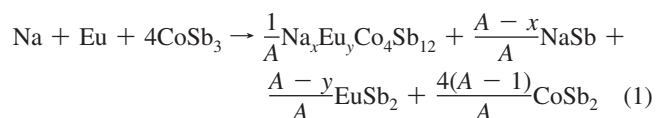
Figure 1. (a) Gibbs free energy pattern for K−Ba-cofilled CoSb₃ at 1000 K. (b) Total FF and the FFs of the two fillers as functions of the K FF, *x*.

theory.[16−19,21] Nevertheless, multiple-element filling has yet to be investigated because of the diversity and complexity of the combinations of filler atoms. We have systematically investigated dual-element filling in CoSb₃ as an example of multiple-element filling in partially filled caged compounds. For most of the dual-element combinations, the cofillings follow the simple rule that inserting one filler type will eliminate the other from the voids in almost a linear way. However, to our surprise, the total FF, defined as the sum of the FFs of the two fillers, is found to exceed both individual FFLs (separated filling) in a few cofilled systems. Analysis of the anomalous dual-element filling behavior suggests that the phenomenon could be universal for multiple-element filling in partially filled caged compounds.

II. Dual-Element Filling Systematics

Our previous work has proven that partial filling in a caged compound such as skutterudite is determined by the competition between the formation of the filled phase and that of secondary phases.[21,19,13] Therefore the actual chemical reaction route to dual-element-filled CoSb₃ (using Na−Eu cofilling as an example to simplify the expression) could be written as

$$Na + Eu + 4CoSb_3 \rightarrow \frac{1}{A}Na_xEu_yCo_4Sb_{12} + \frac{A-x}{A}NaSb +$$
$$\frac{A-y}{A}EuSb_2 + \frac{4(A-1)}{A}CoSb_2 \quad (1)$$

where $A = 4 - x - 2y$ and x and y are the FFs for Na and Eu, respectively, which indicate that fractions x and y of the filler atoms fill into the voids while the rest form secondary phases. The Gibbs free energy corresponding to eq 1 can be expressed as

$$\Delta G_3 = \frac{1}{A}\Delta H_1(x,y) + \frac{A-x}{A}\Delta H_2^{Na} + \frac{A-y}{A}\Delta H_2^{Eu} +$$
$$\frac{1}{A}k_BT[x \ln x + y \ln y + (1-x-y)\ln(1-x-y)] \quad (2)$$

where k_B is the Boltzmann constant, T is the absolute temperature, $\Delta H_1(x, y)$ is the formation enthalpy of the cofilled phase, ΔH_2^{Na} and ΔH_2^{Eu} are the formation enthalpies of secondary phases,[21] and the last term in eq 2 is the configurational entropy contribution caused by the random distribution of the filler atoms in the voids. The two fillers used in this study were selected from groups of different chemical natures, including REs (La, Ce, Eu, Yb), AEs (Ba, Sr), and AMs (Na, K). More than 20 dual-element-filled skutterudites were studied by using the ab initio PAW method as implemented in the VASP package.[26−28]

The reader may refer to our earlier publications on single-element filling for computational details.[13,17,19,21]

Figure 1a shows a typical contour plot of the isoenergy surface of ΔG_3 as a function of both x and y. The lower ΔG_3 values, as indicated by the darker region in the figure, represent more stable dual-element filling at the FFs. Most of the dual-element-filled systems have the linear band pattern shown in Figure 1a. The FF of one filler decreases linearly as that of the other increases, and the total FF, i.e., the sum of x and y, lies between the single-element FFLs (see Figure 1b). This happens for almost all of the AE−AE, AM−AM, and AE−AM combinations. A physical explanation will be given later in the text. For the RE−AE combinations, adding the RE filler into the voids usually increases the Gibbs free energy, leads to the decomposition of the filled systems, and leaves only the dominant AE-filled CoSb₃. Similar behavior exists for the RE−RE combinations, usually with the one having the higher (i.e., smaller absolute value) secondary-phase formation energy dominating the final filled phases.

An unusual behavior is observed in the Na−Eu-cofilled system. In this case, increasing the FF of Na does not decrease that of Eu significantly (see Figure 2). As a result, the total FF of Na−Eu-cofilled CoSb₃ can reach very high values. In Eu-filled CoSb₃ at the FFL (~0.44),[13,22] an extra fractional Na amount of more than 0.30 can still be inserted into the lattice voids to form stable dual-element-filled skutterudites, as shown in Figure 2a. With that, the total FF exceeds the individual FFLs of both Na and Eu. In view of the fact the practical Eu-only FFL in CoSb₃ reaches more than 0.60,[22] it is reasonable to expect that the combination of Na and Eu could reach full filling of the crystal voids in CoSb₃.

III. Electronic Structure Analysis and Discussions

The anomaly in Na−Eu dual-element filling could be attributed to the cofilling-induced electronic structure change. As explained in our earlier work on FFLs of single elements, the screened Coulombic interaction between fillers plays an important role in determining the FFL, and the interaction is determined by the effective charge states of the fillers.[21,13] Comparing dual-element filling with single-element filling, ΔG_3 of the former contains an extra energy term arising from the Na−Eu interaction in the cofilled system, which is determined by the interaction between distinct fillers. This term could be approximately estimated as $\Delta E_2^{Na-Eu} = E_{Na_xEu_yCo_4Sb_{12}} + 4E_{CoSb_3} - E_{Na_xCo_4Sb_{12}} - E_{Eu_yCo_4Sb_{12}}$, where E_X represents the ab initio total

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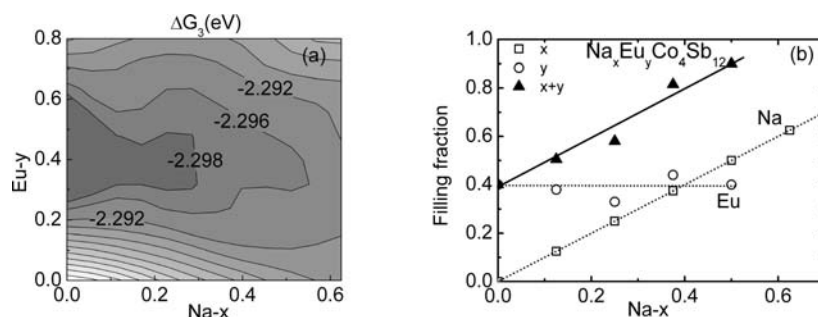
Figure 2. (a) Gibbs free energy pattern for Na−Eu-cofilled CoSb$_3$ at 1000 K. (b) Total FF and the FFs of the two fillers as functions of the Na FF, x.
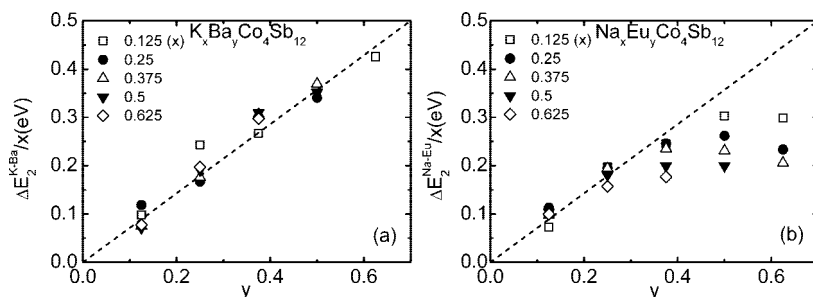
Figure 3. Interaction term $\Delta E_2^{A-B}/x$ as a function of y for various x values in dual-element-filled A$_x$B$_y$Co$_4$Sb$_{12}$: (a) K−Ba system; (b) Na−Eu system. The dashed lines are guides for the eye.
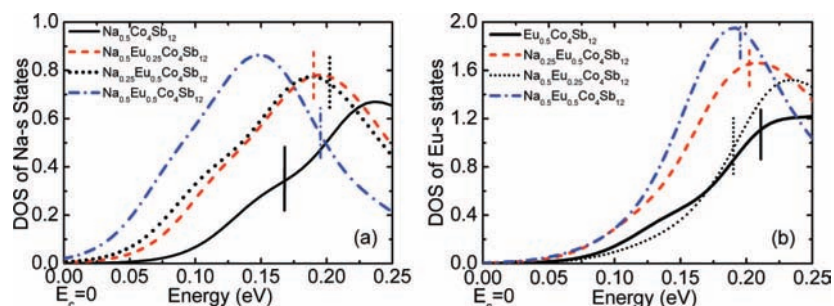
Figure 4. Projected density of states (states/eV per filler atom) on (a) Na 3s and (b) Eu 6s for Na−Eu-cofilled CoSb$_3$. The results for single Na or Eu filling are also plotted for comparison. The energy of bottom of the conduction band is set at zero ($E_c = 0$). The vertical lines represent the Fermi levels.

energy of system X. Calculations without considering the effect of ΔE_2^{Na-Eu} lead to the expected results that the FFs of the two fillers are independent and reproduce the single-element FFLs. The interaction is also related to the distance between fillers and the screening length.[21]

Figure 3a plots calculated values of $\Delta E_2^{K-Ba}/x$ as a function of y for K$_x$Ba$_y$Co$_4$Sb$_{12}$. The data clearly follows a linear relationship, implying that the effective charge states and the surrounding crystal environment for both K and Ba in the cofilled systems change very little, even at very high total FFs. When an effective charge state of +1 for K and a screening length of 12.58 Å (obtained by the single-element filling calculations) are used, the effective charge state of Ba is estimated to be very close to +2, similar to the value for Ba-only filling.[21] All of the AE−AE, AM−AM, and AE−AM combinations show the same behavior as plotted in Figure 3a, which explains why AE and AM atoms could be jointly filled into the crystal voids following the linear correlation rule (Figure 1b).

The calculated values of $\Delta E_2^{Na-Eu}/x$ as a function of y for Na$_x$Eu$_y$Co$_4$Sb$_{12}$ (Figure 3b) shows a different behavior. After following a linear trend at low FFs, $\Delta E_2^{Na-Eu}/x$ starts to level off and deviates from the linear trend with increasing Eu FF, y.

The deviation implies that the effective charge states of filler atoms become different from those in single-element-filled systems. When a +1 charge state for Na at high y values is assumed, the effective charge state of Eu is estimated to be lower than +1, which is much lower than the value of +2 in Eu-filled CoSb$_3$. Assuming +2 for Eu likewise gives a charge state of Na that is also lower than +1.

Figure 4 plots the projected density of states (pDOS) for Na 3s (Figure 4a) and Eu 6s (Figure 4b) states in the Na−Eu-cofilled systems. The most striking characteristic in both figures is that the pDOS of Na 3s/Eu 6s states shift substantially down toward the bottom of the conduction band as the Na FF increases at a fixed Eu FF of 0.50. Together with the slight upshifting of the Fermi levels for Na, as shown in Figure 4a, there is an increasing number of electrons occupying the Na 3s states in Na−Eu-cofilled CoSb$_3$, leading to the reduction of the effective charge states of Na. A similar but relatively weak behavior is also observed for the Eu 6s states (Figure 4b). The pDOS on the Na-surrounding Sb atoms reveals that the Sb-based DOS is also changed a little as a result of the Na−Eu cofilling, which implies that the change in the effective charge states of the fillers in cofilled systems is not just simple electron loss/gain but also

relates to the chemical bonding change in the surrounding Sb atoms. Details will be discussed elsewhere.

A detailed investigation shows that anisotropic local structural distortion induced by the Na−Eu cofilling may be one of the reasons for the charge-state reduction. Our calculations show that the lattice parameter of $Na_xEu_yCo_4Sb_{12}$ is a linear combination of those for $Na_xCo_4Sb_{12}$ and $Eu_yCo_4Sb_{12}$, implying that the distance between fillers in $Na_xEu_yCo_4Sb_{12}$ increases only slightly as the Eu content y increases. However, as y increases, the distances between each Na and its neighboring Sb atoms decrease while the distances between each Eu and its neighboring Sb atoms increase. Differences in the chemical natures of the Na and Eu fillers lead to the anisotropic structural distortion around each filler and thus to the electronic structure change in the cofilled systems. There may also be some other reasons responsible for the change of DOS, and a detailed analysis will be carried out in the future.

IV. Conclusions

In summary, the FFLs for dual-element filling in a typical caged compound, $CoSb_3$, have been systematically investigated by ab initio calculations. Our results show that many dual fillers could jointly fill into the crystal voids following a linear correlation rule, some are dominated by a single-element filling, and a few of them may exhibit anomalous behavior. The Na−Eu-cofilled $CoSb_3$ system is shown to have relatively high total FFs, which obviously exceed the Na-only and Eu-only FFLs and even likely can reach full filling of the crystal voids in $CoSb_3$. The Na−Eu cofilling introduces an anisotropic local structure distortion, moves the Na 3s and Eu 6s states closer to the bottom of the conduction band, increases the number of electrons occupying the Na 3s and Eu 6s states, lowers the Na and Eu charge states and thus the Na−Eu interaction, and leads to the anomalous dual-element filling. On the one hand, this anomalous filling behavior comes from the fact that the chemical bonding between the loosely bound fillers and the surrounding atoms is mainly Coulombic. On the other hand, the difference in the chemical natures of AM and RE fillers, especially the size difference, also plays a role. Since the two aspects usually exist in partially filled caged compounds, it is likely that the anomalous cofilling phenomenon is a general behavior for multielement filling. The cofilling-related FFL enhancement also provides an extra degree of freedom for tuning the physical properties of caged compounds, which calls for further investigation.

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