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Electron Self-trapping in Ge_2Se_3 and its Role in Ag and Sn Incorporation

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ABSTRACT

We present a set of density functional theory (DFT) calculations on the electronic structure of Ag and Sn in Ge_2Se_3 in a periodic model. We show that electron self-trapping is a persistent feature in the presence of many defects. Ag and Sn autoionize upon entering Ge_2Se_3 becoming Ag^+ and Sn^{2+} , respectively, and the freed electrons self trap at the lowest energy site. Both Ag and Sn can substitute for Ge, and we present formation energies as a function of Fermi level that show that Sn can substantially alter the incorporation of Ag into the Ge_2Se_3 network.

INTRODUCTION

Since the seminal article by Chua [1], memristor technology has been exploited using a variety of materials systems and physical principles. Borghetti *et al.* have developed metal oxide-based memristors, wherein positively charged oxygen vacancies migrate under the influence of an applied electric field [2]. Another class of devices exploits electroplating within solid electrolytes. In these devices, positively charged metal ions traverse a thin insulating or semiconducting film to a bottom electrode. Rather than forming a uniform conductive layer, conductive dendrites grow toward a top electrode until complete pathways are formed, lowering the device resistance by orders of magnitude. This dendritic growth can be at least partially reversed, so that the device resistance can be reliably varied over orders of magnitude. Recently, Campbell *et al.* have developed a novel device shown schematically in Figure 1 [3]. Note that the silver is separated

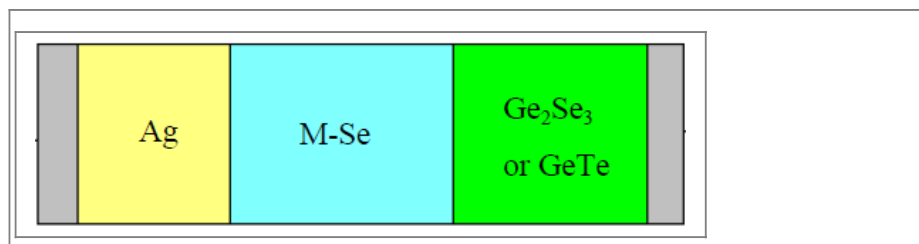


Figure 1: Schematic diagram of layers for device of Campbell *et al.* Gray (outer) is tungsten. In present case, M-Se (blue) is SnSe.

from the active Ge_2Se_3 by a layer of tin selenide. Silver is introduced into the Ge_2Se_3 solely through the influence of an electric field impressed by the top and bottom electrodes. Devasia *et al.* have shown that during heating, tin can enter Ge_2Se_3 from a SnTe layer [4], and Campbell has

inferred from a variety of measurements that tin enters Ge_2Se_3 from the SnSe layer under positive bias. So, to understand the physics of the device in Figure 1, we need to understand the physics of both silver and tin in Ge_2Se_3 , including the interaction between the two. To this end, we report a set of electronic structure calculations, based on density functional theory (DFT), on a crystalline model of Ge_2Se_3 with one or more Ag and/or Sn atoms. We incorporate recent results showing that electrons self-trap in this model system [5]. This is appropriate because in other $\text{Ge}_x\text{Se}_{(100-x)}$ compounds, negatively charged defects have been invoked for the motion of the silver diffusion front in photodoping experiments [6, 7]. Here, we show that, upon entering Ge_2Se_3 , both silver and tin autoionize, losing one and two electrons, respectively, and that these electrons self-trap. Thus, both tin and silver should move under the influence of an electric field. In fact, in the presence of defects, either interstitial or substitutional, there is evidence for single electron self-trapping, similar to the cluster case. Interestingly, for both the interstitial cases, the self trapping site is independent of the interstitial position. The substitutional defects behave differently.

THEORY

Ge_2Se_3 is a metastable stoichiometry, having no crystal structure. Based on EXAFS results [8], showing that the bulk glass is chemically ordered, we use a crystalline model, shown in Figure 2, taken from Si_2Te_3 [9]. We used both periodic supercells and a finite cluster to study

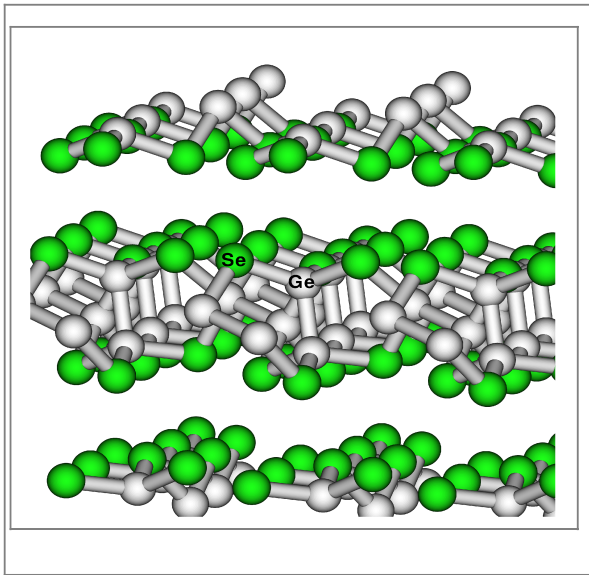


Figure 2: Crystalline model for Ge_2Se_3 .

this system. Details of the construction of the clusters are given in Ref. [5]. We used these in the study of self-trapping, although, as shown below, in periodic calculations single-electron self-trapping is evident in the presence of defects, and paired self-trapping is always present. To calculate defect levels, we used the standard relationship from Ref. [10].

Electron self-trapping

In Figs. 3 (a) and (b), we show the principal distortions for single and paired, self-trapped electron(s) (STE's), respectively, in an abstracted moiety. For the single STE, the salient features are: the lengthening of the $\text{Ge}_1\text{-Ge}_2$ bond by 0.1 Å, the lengthening of $\text{Ge}_1\text{-Se}_1$



Figure 3: Overlaid atoms from the neutral and -1 charge state (a) and from the neutral and -2 charge state (b) showing principal distortions for self-trapping.

and $\text{Ge}_1\text{-Se}_2$ bonds by 0.2 Å, and the increase of $\langle \text{Se}_1\text{-Ge}_1\text{-Se}_2$ bond $\sim 25^\circ$. In Figure 4 of Ref. [5], we showed that the wave function of the single STE is well localized on the moiety shown in Figure 3a. For paired STE's, Figure 3b, the distortion is more dramatic. Here, self-trapping leads to the rupture of a Ge-Se bond. There are strong indications that this is a $-U_{\text{eff}}$ system [11], displaying an effective $e\text{-}e$ attraction. During the relaxation, there is clear indication of an intermediate geometry comprised of two separate, single, self-trapped electrons. As the relaxation progresses, these coalesce into a pair. The energy difference between these two geometries is 0.84 eV. Thus, in equilibrium, single self-trapped electrons will pair.

Neutral interstitial Ag and Sn

In Ref. [12], we presented calculations on interstitial silver. We reported that neutral silver spontaneously autoionizes, dropping an electron into the conduction band of Ge_2Se_3 . This occurs because the 5s-level of atomic silver is above the conduction band edge. We surmised that this could well be a general property of silver, at least in narrow gap semiconductors. Finally, we reported negligible localization of the excess electron near the interstitial silver atom. In the context of our self-trapping calculations, we have revisited those results. In Figure 4, we show the equilibrium conformation (a) and the atom-projected density of states (atom-PDOS) (b) of the neutral, interstitial silver atom, here in an intra layer site. Careful examination of Figure 4 (a) shows that $R_{\text{Ge}_1\text{-Ge}_2}$ has expanded by ~ 0.12 Å, and that the surrounding Ge-Se bond lengths have expanded by ~ 0.13 Å, compared to the perfect crystal.

Turning to the atom-PDOS, several features bear notice. First, there is a broad peak near the bottom of the conduction band comprised predominantly of defect Ge and Se. (The valence and conduction band edges, determined from the bulk Se PDOS, are at 0.0 eV and 1.23 eV.) As this is in the forbidden gap, and as atoms far from the $\text{Ge}_1\text{-Ge}_2$ dimer contribute minimally to this

peak, this is clear evidence for localization. Second, the silver ion contributes very little to the peak in the gap. In fact these features of the PDOS are strikingly similar to those of the single STE in the cluster calculations (see Figure 3 (a) in Ref. [5].)

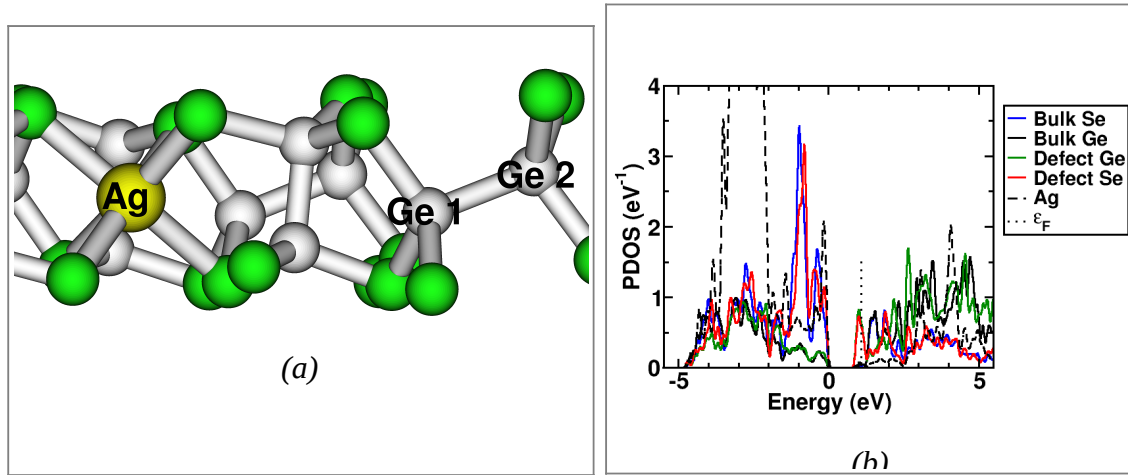


Figure 4: Equilibrium conformation (a) and atom-PDOS (b) for neutral interstitial silver.

Taken together, the atomic relaxations and the electronic structure of the neutral interstitial silver atom imply that in this bulk crystalline model, an isolated silver atom autoionizes, becoming Ag^{+1} , and the excess electron self-traps around a germanium pair.

In Figures. 5 (a) and (b), we show the equilibrium geometry and PDOS of the neutral tin interstitial. In Figure 5 (a), note that far from the Sn interstitial, the atoms surrounding the $\text{Ge}_1\text{-Ge}_2$ dimer are distorted dramatically. In fact the $\text{Ge}_1\text{-Se}_1$ bond has ruptured. This is the fingerprint of a pair of self-trapped electrons. Figure 5 (b) reinforces this contention. As in Figure 4 (b), the valence band edge is at 0.0 eV. Here, however, the conduction band is at about 1.15 eV. Note the very deep level, comprised principally of defect Ge and Se (Ge_1 and Se_1 in Figure 5 (a)). This is completely consistent with the PDOS of the paired STE's (see Figures. 3 (b) and 6 in Ref. [5]). The physics here is analogous to the silver interstitial. Upon entering this system, a tin atom autoionizes, losing two electrons from its outer p-shell, and these electrons self-trap as a pair.

Charged interstitial silver and tin

In Figs. 6 (a) and (b), we show the formation energies for interstitial silver and tin as a function of Fermi level. Note that both species exhibit $-U_{eff}$ consistent with the results on self-trapping. For the silver interstitial, the neutral charge state is excluded and for the tin interstitial, the +1 charge state is excluded because each of these leads to a single STE.

DISCUSSION

Before we discuss further the relevance of self-trapping, several features of Figure 6 bear notice. While we haven't discussed substitutional defects, we report in Figure 6 the energies of formation for both isolated substitutionals and substitutional-interstitial pairs. The latter are

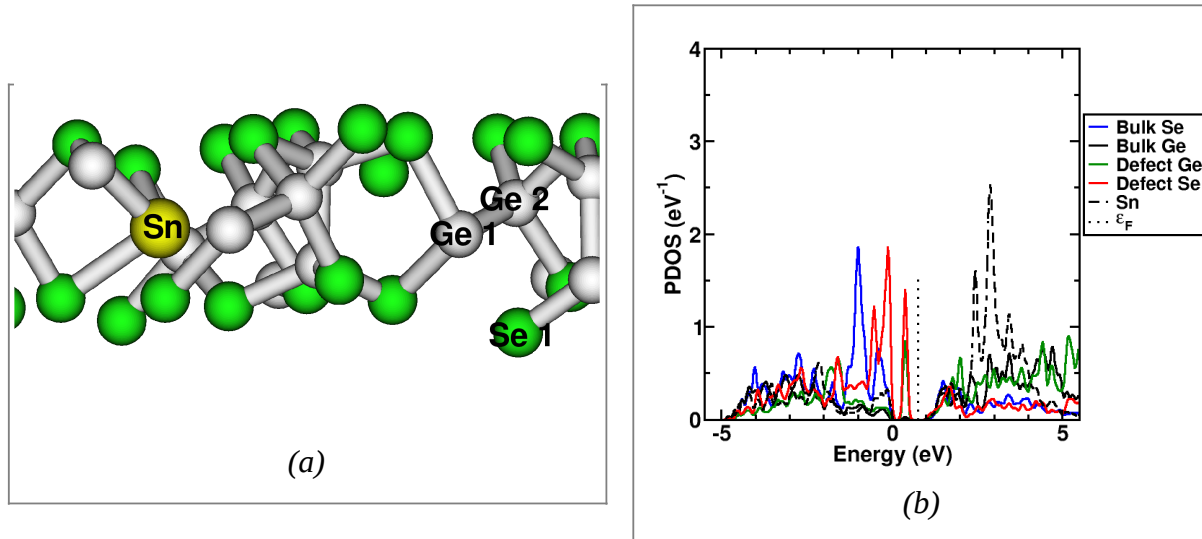


Figure 5: Equilibrium conformation (a) and atom-PDOS (b) for neutral, substitutional tin.

relevant because the extrinsic species are injected at or near room temperature into fully formed Ge_2Se_3 films. In the simplest case, forming a substitutional atom requires the creation of an interstitial. Note that the tin substitutional (Sn_s) has a negative formation energy because

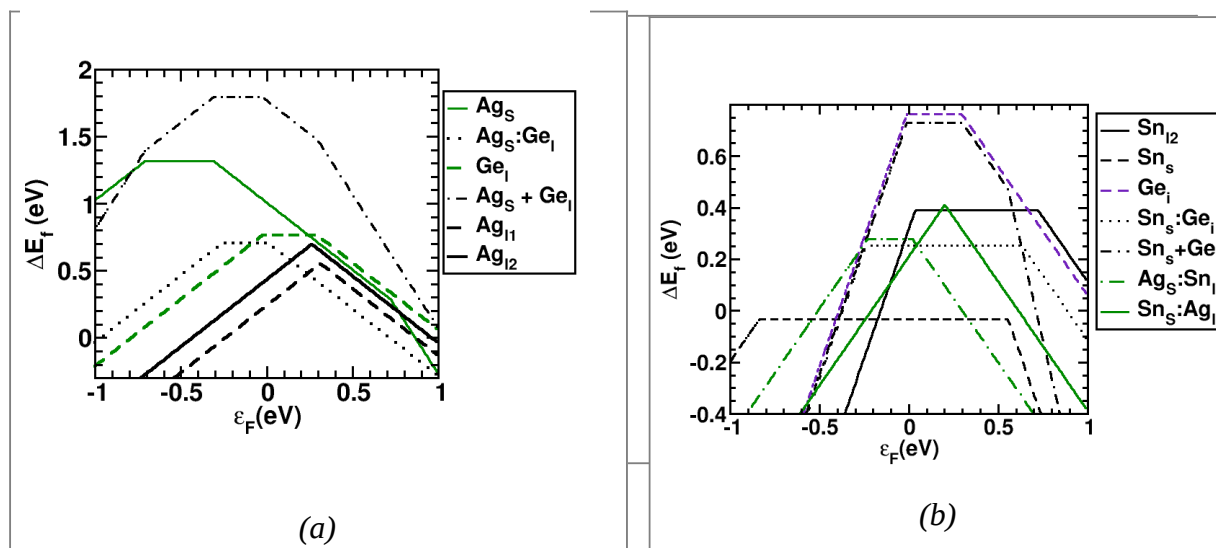


Figure 6: Formation energies for interstitial and substitutional silver (a) and tin (b). In (a) we show both interlayer and intralayer interstitials. $\epsilon_F = 0$ is the Fermi level in the perfect crystal.

elemental Ge, removed from Ge_2Se_3 is more stable than elemental Sn, lost through insertion. We have also found that Sn_s binds STE's. That is, in the -1 charge state, Sn-Se bond lengths grow by 0.1 \AA , while the Ge-Sn bond grows by 0.05 \AA . In the -2 charge state, the Sn-Se bond lengths grow an additional $0.13\text{-}0.3 \text{ \AA}$, and the Ge-Sn bond grows by an additional 0.16 \AA . If we assume that the Fermi level stays near mid-gap, then we see that, in the absence of tin, silver

prefers to be interstitial. For $\epsilon_F > 0.25$, silver prefers to be $\text{Ag}_S:\text{Ge}_I$. However, in the presence of tin, as seen in Figure 6 (b), silver interstitials are predicted to prefer to reside next to $\text{SnS}:\text{GeI}$ pairs. Moreover, for very small perturbations above $\epsilon_F = 0$, these defects are predicted to convert into $\text{Ag}_S:\text{Sn}_I$. Considering the relatively small, predicted ΔE_f for Sn_S , Sn can have a crucial impact on the incorporation of Ag_S .

CONCLUSIONS

To conclude, we have shown that electron self-trapping is persistently predicted in the crystalline model of Ge_2Se_3 , even in the presence of defects. We have shown that STE's are bound to either Ge-Ge or Sn-Ge dimers. This should persist in non-crystalline material because these dimers form the bottom of the conduction band [5]. We have also shown that both Sn and Ag autoionize upon entering Ge_2Se_3 . We can expect, then, that positively charged silver ions could be selectively attracted to these negatively charged dimers, so that these dimers could initiate the formation of conducting pathways. Ge-Sn dimers may be especially important because they can bind silver more efficiently.

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