Analysis of SnS₂ hyperdoped with V proposed as efficient absorber material

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Abstract

Intermediate-band materials can improve the photovoltaic efficiency of solar cells through the absorption of two subband-gap photons that allow extra electron-hole pair formations. Previous theoretical and experimental findings support the proposal that the layered SnS₂ compound, with a band-gap of around 2 eV, is a candidate for an intermediate-band material when it is doped with a specific transition-metal. In this work we characterize vanadium doped SnS₂ using density functional theory at the dilution level experimentally found and including a dispersion correction combined with the site-occupancy-disorder method. In order to analyze the electronic characteristics that depend on geometry, two SnS₂ polytypes partially substituted with vanadium in symmetry-adapted non-equivalent configurations were studied. In addition the magnetic configurations of vanadium in a SnS₂ 2H-polytype and its comparison with a 4H-polytype were also characterized. We demonstrate that a narrow intermediate-band is formed, when these dopant atoms are located in different layers. Our theoretical predictions confirm the recent experimental findings in which a paramagnetic intermediate-band material in a SnS₂ 2H-polytype with 10% vanadium concentration is obtained.

Keywords: density functional theory, semiconductors, solar cells, tin disulphide

(Some figures may appear in colour only in the online journal)

1. Introduction

In previous works [1–9] transition-metal substituted semiconductors, in which the metal generates a new band in the semiconductor band-gap, have been proposed to develop solar cells with a greater efficiency and lower cost, called intermediate-band (IB) solar cells. The efficiency in IB solar cells is theoretically predicted as high as 63.2% for a semiconductor with 1.98 eV [10, 11]. Therefore, the efficiency in these IB solar cells is enhanced compared with the Shockley–Queisser [12] limit, which determines the highest efficiency of a single-junction solar cell of around 40.7% for a semiconductor with a 1.1 eV band-gap. The predicted mechanism to obtain this enhancement takes place through the absorption of two extra low-energy photons that results in one extra electron promoted from the valence band (VB) to the IB and from there to the conduction band (CB). Therefore, the isolated (disconnected)

IB in this mechanism generates an extra electron-hole pair that provides an enhanced photo-current while voltage in the IB solar cell comes from the host semiconductor band-gap. Furthermore, the IB has a metallic character and contains the Fermi energy level (E_F) while the structure is in equilibrium.

Theoretical approaches regarding the IB materials have focused in the characterization of the nature of the dopant materials, its orbital configurations and the possibility of the particular orbital-splitting while a certain distortion occurs. The need to introduce a high dopant proportion in order to avoid non radiative recombination obtained through the formation of a highly localized discrete energy level of the impurity had also been detailed. The intermediate-band should be narrow, slightly disperse, delocalized and isolated from the host semiconductor bands.

Specifically, dopants are transition-metals which introduce their d orbitals in the band-gap of semiconductors that allow

the formation of the isolated energy band. The basis of this non-bonded crystalline band formation lies in the symmetry of the d orbitals which is different from those s and p-type orbitals that form the VBs and the CBs in almost all III–V and II–VI semiconductors. Therefore the possibility of isolating these orbitals depends on the nature of the semiconductor symmetry which would generate a certain direction in which the p and s orbitals are found.

In addition to the materials that have been proposed to enhance the photon absorption of solar cell through an IB formation [1–9], doped SnS_2 also represents an attractive proposition for an IB material [13].

SnS_2 is similar to a polytypic CdI_2 structure [14]. The octahedrally-coordinated Sn atoms are covalently bonded to six S in an exfoliated sheet, while the atoms of one sheet only encounter the next sheet around 5.8 Å further away. Therefore, in a SnS_2 layered semiconductor, the covalent intralayer bonds are stronger than the *van der Waals* (vdW) interlayer interactions. This gives rise to a deformation of the SnS_2 structure by using a slightly stronger force [15–20] which can be translated as polytypic phase equilibrium. The perpendicular stacking of layers vary in each polytype in such a way that the *2H*-polytype, which is reported as the most stable [21, 22], is the simplest structure with one formula unit in its cell, whereas the *4H*-polytype is the second most stable structure.

SnS_2 *2H* and *4H*-polytypes are described respectively through P_{3m1} and P_{63mc} spatial groups. In its smaller hexagonal unit cell of the *2H*-polytype, the position of the Sn atom is (000) while the S are in (0.33, 0.67, u) and (0.67, 0.33, $-u$) positions, with $u \sim 0.25$ [23]. In the *4H*-polytype a half-bond displacement of the second layer occurs in the perpendicular direction of the layer stacking, therefore the *4H* unit cell structure is made up of two formula units.

Moreover, the SnS_2 - VS_2 solid solution is formed when a large amount of V atoms is thoroughly introduced into the SnS_2 . A layered material with the same P_{3m1} structure of the SnS_2 *2H*-polytype is also in the VS_2 upper-limit. However, even though these two structures share the same crystalline lattice, VS_2 is metallic and magnetic and its cell parameters are smaller [24] than those of SnS_2 [20].

In addition to the previous theoretical optoelectronic characterization of V doped in SnS_2 [13], the interactions between the V atoms are also considered important at this concentration level. The configurational study not only allow the electronic description of V atom interactions in SnS_2 but also the characterization of thermodynamic probabilities.

In this work we study different non-equivalent configurations of vanadium included in a SnS_2 system. In these symmetry-adapted non-equivalent configurations the V atoms are located in different positions of Sn in SnS_2 , and the resulting electronic characteristics related to these configurations are discussed. We also analyze the concentration of vanadium dopant in SnS_2 , the different SnS_2 *2H* and *4H*-polytypes and the resulting spin-coupling behavior through their magnetic configurations. Finally, we detail the geometrical description in the particular doped material in which the IB is obtained.

Figure 1. Configurations of two V atoms in Sn positions in SnS_2 *2H*-polytype ($\text{V}_2\text{Sn}_{10}\text{S}_{24}$) obtained through site-occupancy-disorder.

2. Computational details

Layered SnS_2 *2H* and *4H*-polytypes substituted with V atoms in Sn positions were studied through thermodynamic and electronic calculations. Specifically we described the $\text{VSn}_{11}\text{S}_{24}$, $\text{V}_2\text{Sn}_{16}\text{S}_{36}$ and $\text{V}_2\text{Sn}_{10}\text{S}_{24}$ structures of the corresponding 8.33%, 11.11% and 16.67% vanadium concentrations. Different geometrical and magnetic configurations in addition to the vanadium concentrations were used and in the case of $\text{V}_2\text{Sn}_{16}\text{S}_{36}$ we compared the results of the *2H*-polytype with that of the *4H*-polytype.

All the electronic structures were calculated through Density Functional Theory (DFT). The systems were obtained using the exchange-correlation energy functional of a generalized gradient approximation (Perdew–Burke–Ernzerhof) which is spin-density-dependent, as implemented in the Vienna *ab initio* simulation package (VASP) [25, 26]. However, a Grimme's dispersion-correction, D2 (DFT-D2) [27–30] applied after each auto-consistent cycle allowed the calculation of vdW weak interactions in the geometry optimization, which corrects the geometric parameters of the

Table 1. Characteristics of $V_2Sn_{10}S_{24}$ 2H-polytype configurations: degeneracy (A), initial (d_{VV}^{ini}) and final (d_{VV}^{fin}) V atom distances in the geometry optimization, final cell volume (Vol.) (in parentheses is the volume of a cell with one formula unit), energy difference between magnetic configurations (E_{PS-APS}) and thermodynamic probabilities of each non-symmetrical configuration at 300 K ($p^{300 K}$) and 900 K ($p^{900 K}$), and the probabilities in the non-equilibrium conditions (p^∞).

	A	d_{VV}^{ini} (Å)	d_{VV}^{fin} (Å)	Vol. (Å ³)	E_{PS-APS} (eV)	$p^{300 K}$	$p^{900 K}$	p^∞
c01	6	5.89	5.78	799.75(66.65)	-0.01	0	0.0004	0.0909
c02	6	3.65	3.63	805.73(67.14)	-0.04	0	0.0068	0.0909
c03	6	6.93	6.84	800.61(66.72)	-0.02	0	0.0003	0.0909
c04	12	3.65	3.22	804.66(67.10)	-0.03	0.0364	0.2465	0.1818
c05	12	6.93	6.33	806.35(67.20)	0	0	0.0054	0.1818
c06	12	3.65	3.19	804.67(67.10)	-0.19	0.9636	0.7347	0.1818
c07	12	6.93	6.72	807.19(67.27)	0	0	0.0058	0.1818

V-doped SnS_2 . The interactions between the ionic cores and the valence electrons were introduced using the projector-augmented wave method (PAW) [31]. In this, non-spherical contributions were included in the gradient corrections inside the PAW spheres, which is essential for the accurate total energies of compounds containing atoms with valence d orbitals. Geometry optimizations were accurately obtained with errors of less than 1 meV/atom and the energy cut-off for the plane wave basis set and the k-point grid for the integration into the Brillouin zone of the lattices were selected as 400 eV and $4 \times 4 \times 4$ Γ -centered respectively.

Moreover, the spin polarized calculations allows the description of the different magnetic configurations that are formed in each case and upon this; vanadium antiparallel-spins (APS) and parallel-spins (PS) magnetic configurations were calculated.

The dopant interactions were also analyzed through a symmetry-adapted space of configurations. This was obtained using the Site Occupancy Disorder (SOD) method [32, 33]. Using SOD there is the possibility of describing not only the dopant interactions in different non-equivalent configurations, but also the probabilities of these configurations.

3. Results and discussion

3.1. Symmetry-adapted space of configurations for IB materials

Structures with two SnS_2 layers were selected and one or two V atoms were substituted in Sn positions. Particularly $3 \times 2 \times 2$ (36 atoms) and $3 \times 3 \times 2$ (54 atoms) supercells, which are expansions of the unit cell and contain two layers of SnS_2 were calculated. In the $3 \times 2 \times 2$ expansion one and two V atoms in Sn positions in 36-atom supercells resulted in 8.33% and 16.67% vanadium concentrations, whereas in the $3 \times 3 \times 2$ expansion this dopant concentration was 11.11%, where two V atoms are in Sn positions in the SnS_2 2H and 4H polytypes.

The SOD method [32] allows the reduction of the defective occupied sites by considering the lattice parameters, atom positions and SnS_2 structural symmetry. Hence the symmetry of the defect-arrangement configurations is also information obtained from the symmetry-adapted space created in the supercells. We used the number of symmetry elements, the degeneracy and the relative positions of the V atoms (two V

atoms in the same layer or two V atoms in different layers) in each non-equivalent configuration, in order to compare the geometry of each configuration.

From this point of view, the characteristics of one configuration, from the whole set, might be favored on top of the rest if this configuration is more stable, so its energy is separated (and lower) from the set. The probability of appearance of this structure is one. Therefore, the configurational entropy in the system is zero (towards orderly situation).

On the opposite situation, all the structures have similar characteristics if the energies of all the configurations are very similar ($\Delta E \leq k_B T$) or formally in the limit $T \rightarrow \infty$. Then the probability of the set is $1/K_B$ and the configurational entropy reaches its maximum possible value (toward disorderly situation). This approach is very useful to understand which path will be suitable for obtaining an intermediate band material. A synthesis route which favors the orderly situation will be preferable due to the fact that these types of materials necessarily need a homogeneous system, in which non intermediate band configurations might reduce the photovoltaic efficiency through the appearance of non-radiative recombination. This configurational approach is used for the first time in this work for the understanding dopant positions and the analysis of statistical thermodynamics associated with the symmetry-adapted space of configurations in intermediate band materials. In addition, this approach might be useful not only in this intermediate-band system, but also in other systems of this type, in which the intermediate-band is formed through the alignment of the independent dopant orbitals inside the bulk host-semiconductor.

In next subsections we will explain the different subsets of structures we have found using SOD program at different vanadium concentrations and polytypes. For each concentrations we have labelled each structure as cn where n goes for 1 to the number of possible structures found.

3.1.1. $V_2Sn_{10}S_{24}$ structure. The symmetry-adapted configurational space obtained with SOD for two V atoms in Sn positions in a $3 \times 2 \times 2$ expansion of SnS_2 unit cell ($V_2Sn_{10}S_{24}$) show the formation of seven non-equivalent configurations (figure 1) in this non-isotropic supercell size. The cell parameters of the starting unit cell $a=3.65$ Å and $c=5.89$ Å give a starting cell volume of 942.43 Å³ (78.53 Å³ per unit formula). Degeneracy (A), and initial V atom distances (d_{VV}^{ini}) for each configuration in this set are also shown (table 1).

Figure 2. Configurations of two V atoms in Sn positions in SnS_2 $2H$ -polytype ($\text{V}_2\text{Sn}_{16}\text{S}_{36}$) obtained through site-occupancy-disorder.

For the sake of clarity, two subsets of structures, related to the degeneracy were labeled; the c01–c03 subset and the c04–c07 subset. Within each subset the degeneracy and the total number of symmetry elements are identical. Hence, the resulting symmetry of the c01–c03 subset, which has a smaller degeneracy, is higher than that of the latter. These isodegenerated defect-occupied sites led to c01–c03 and c04–c07 configurations in which electronic structures were comparable, unless the V atoms are located in different layers.

SnS_2 shows a structural anisotropy in all its polytypes, therefore the electronic characteristics of disordered sites will be dependent on the direction in which V atoms are located in the SnS_2 , (e.g.) V atoms in the same layer and V atoms in different layers. If we take this into account the c01–c03 and c04–c07 subsets of two-disordered-site configurations, should be sub-divided in accordance with these criteria.

3.1.2. $\text{V}_2\text{Sn}_{16}\text{S}_{36}$: $2H$ and $4H$ -polytypes. In order to obtain a narrow IB a smaller concentration of V atoms was included in a greater supercell size ($\text{V}_2\text{Sn}_{16}\text{S}_{36}$). The isotropic $3 \times 3 \times 2$ and $3 \times 3 \times 1$ supercell sizes for the SnS_2 $2H$ and

$4H$ -polytypes were obtained respectively and their structures were compared. In these supercells the vanadium concentration was 11.11% which is near the experimental result 10 %. In the comparison of the $2H$ and $4H$ -polytypes, it is demonstrated that both have the same amount of non-symmetrical (and total) configurations at this supercell size.

The total number of combinatorial structures is 153 while the symmetry-adapted configuration spaces reduce this total amount to five (figures 2 and 3). In the $4H$ case the parameters used are similar but slightly different from the $2H$ case and also the doubled c is present in this case. The layer stacking in the $4H$ -polytype is displaced which generates a symmetry breaking which allows a lesser amount of symmetry elements in the structure. Nevertheless even including this displacement among the layers the non-equivalent configurations obtained in the $4H$ -polytype are similar to those of the $2H$ structure. Degeneracy (A) and initial V atom distances for each configuration are also shown (tables 2 and 3).

For the sake of clarity, two subsets of structures related to the V atom positions were labeled; the c01–c02 with V atoms in one layer and the c03–c05 subsets with V atoms in different

Figure 3. Configurations of two V atoms in Sn positions in SnS_2 $4H$ -polytype ($\text{V}_2\text{Sn}_{16}\text{S}_{36}$) obtained through site-occupancy-disorder.

layers. Despite the higher symmetry that appears in $2H$, in $4H$ case the c01–c02 subset shows two V atoms located in the same layer resulting in rather similar $2H$ and $4H$ structures. In addition, degeneracy in both cases also supports this equal local environment for V atoms in these different supercells. Nevertheless, as expected it was found that the amount of symmetry elements are doubled in c01 and c02 configurations of $2H$ compared with that of the $4H$ -polytype.

Furthermore c03–c05 subset includes V atoms in different layers in both the $2H$ and $4H$ -polytypes. Within this subset in the $2H$ -polytype, each configuration has a different degeneracy from the others. As was previously mentioned the electronic characteristics of the disordered sites will be dependent on the direction in which V atoms are located, as well as on the number of symmetry elements (degeneracy). In the $2H$ -polytype (table 2), degeneracy of c01 and c03 as well as that of c02 and c05 are the same. Nevertheless in these cases the localization of the dopants are different, therefore each configuration will present independent electronic characteristics.

Another situation is found in the $4H$ structure in which the displaced layers give the same geometry for all of the iso-degenerated configurations in the c03–c05 subset. In accordance to these criteria, we also should subdivide the c01–c02 and c03–c05 subsets. Therefore, in the $2H$ -polytype each configuration will show independent electronic characteristics while in the $4H$ -polytype c03–c05 they will be identical.

From each vanadium concentration, those cases in which V atoms are located in the same layer and those in the other layer remaining without substitution are considered unlikely

in the experimental conditions. This is because, this vanadium concentration is high enough to substitute the V atom in the Sn positions of each SnS_2 layer and an extended amount of a layer should not be pure SnS_2 under these conditions. Therefore, those configurations with disordered-sites in each layer are more realistic.

3.2. Electronic structures of $\text{Sn}_{12}\text{S}_{24}$ and one V substituting Sn in $\text{VSn}_{11}\text{S}_{24}$

The electronic structures of $\text{Sn}_{12}\text{S}_{24}$ and $\text{VSn}_{11}\text{S}_{24}$ were obtained (figure 4). Grimme's dispersion correction gives a corrected geometry in the direction of the layer stacking when used to obtain the ground-state of the SnS_2 $2H$ and $4H$ -polytypes, as was previously shown [34]. Therefore, if the correction dispersions containing V atoms are also applied in the structures we assume that the distance between the layers, in the direction of the vdW interactions, will also be improved.

In the host SnS_2 $2H$ -polytype (figure 4(a)) the projected densities of states (PDOS) of the Sn and S atomic contributions demonstrate that both the VB and CB are mainly made up of S orbitals with p symmetry. The S orbital contributions with s symmetry are also located around 5 eV below (and above) E_F . The obtained band-gap of the SnS_2 $2H$ -polytype was 1.33 eV.

In figure 4(b) PDOS of V-atom contribution to the total densities of states (DOS) in $\text{VSn}_{11}\text{S}_{24}$ shows that the V d-orbitals are mainly located between the VB and CB of the host SnS_2 band-gap. The $e_g - t_{2g}$ splitting of these V d-orbitals is shown. In the t_{2g} triplet and e_g doublet, *spin-up* is separated from the *spin-down*. *Spin-up* t_{2g} orbitals are interacting with the VB forming a non-isolated IB while spin-down orbitals are empty and bound to the CB. Vanadium 4s orbital-contributions are above in the CB and far from the host's main band-gap.

However, in this $\text{VSn}_{11}\text{S}_{24}$ case one V atom is further away from the other V atoms (7.30 Å distance) in the same layer. Under these conditions, the non-isolated IB is formed through a distortion of vanadium energy levels which is not enough to separate the dopant d-orbital contributions from the host semiconductor orbitals. Therefore, in order to separate the IB, we need to change d level position. Vanadium at different sites produces different interactions between them which modifies bonds. As a result we can obtain a d levels modification which can have an IB. We have study the different possibilities.

3.3. Electronic structures and probabilities of $\text{V}_2\text{Sn}_{10}\text{S}_{24}$ and $\text{V}_2\text{Sn}_{16}\text{S}_{36}$: $2H$ and $4H$ polytypes

3.3.1. $\text{V}_2\text{Sn}_{10}\text{S}_{24}$ structure. DOS obtained for the configurations of $\text{V}_2\text{Sn}_{10}\text{S}_{24}$ (figure 5) and the data resulting from these calculations (table 1) are shown. In all the structures calculated the extra electron in each vanadium atom (with valence V^{5+}) substituting Sn (with valence Sn^{4+}) are located in the V d-orbitals.

We obtained the formation of metallic compounds in cases with V atoms in different layers while the formation of non-metallic compounds appears in those with the atoms in the same layer. The non-metallic structures having V atoms

Figure 4. Total densities of states (DOS) and atomic projected densities of states (PDOS) for (a) SnS_2 2H-polytype ($\text{Sn}_{12}\text{S}_{24}$) and (b) one V atom substituting Sn in SnS_2 2H-polytype, $\text{V}_x\text{Sn}_{1-x}\text{S}_2$ with $x=8.33\%$ ($\text{VSn}_{11}\text{S}_{24}$).

Figure 5. Densities of states (DOS) and V projected densities of states V(PDOS) of non-equivalent configurations of two V in Sn positions in $\text{V}_2\text{Sn}_{10}\text{S}_{24}$. Iso-degenerated configurations with V atoms in different layers in (a) c01–c03 subset, c01 and c03, and (b) c04–c07 subset, c05 and c07.

in the same layer are not shown, because they are unlikely to be formed. Furthermore, the energy difference between magnetic configurations ($E_{\text{PS-APS}}$) obtained for those structures with V atoms in the same layer (c02, c04 and c06) are greater than those of these in different layers (c01, c03, c05 and c07). However, the great $E_{\text{PS-APS}}$ energy difference found in the c06 structure compared with that of the others, demonstrates that a strong spin-coupling appears in c06 case compared with the c02 and c04 cases. We found that there is a relationship between the magnetic behavior and the symmetry of the system. Those cases with V atoms in different layers are less affected by the magnetic coupling. In the experimental

findings [13], the formation of a compound of V-doped SnS_2 2H showed the formation of an IB material with paramagnetic behavior. In the configurations with V atoms located in different layers the magnetic behaviour is consistent with the formation of a paramagnetic material. In the cases with V atoms in the same layer the PS configuration defines the ground-state energy of the structure.

Furthermore, the metallic structures formed in the c01 and c03 cases have the vanadium energy bands interacting with the VB while in c05 and c07 a wide metallic IB is formed. In these c01 and c03 structures the weak spin-coupling that appears might be related to an interaction with the surrounding

Table 2. Characteristics of $V_2Sn_{16}S_{36}$ $2H$ -polytype configurations: degeneracy (Λ), initial (d_{VV}^{ini}) and final (d_{VV}^{fin}) V atom distances in the geometry optimization, final cell volume (Vol.) (in parentheses is the volume of a cell with one formula unit), energy difference between magnetic configurations (E_{PS-APS}) and thermodynamic probabilities of each non-symmetrical configuration at 300 K ($p^{300\text{ K}}$) and 900 K ($p^{900\text{ K}}$) and the probabilities in the non-equilibrium conditions (p^∞).

	Λ	d_{VV}^{ini} (Å)	d_{VV}^{fin} (Å)	Vol. (Å ³)	E_{PS-APS} (eV)	$p^{300\text{ K}}$	$p^{900\text{ K}}$	p^∞
c01	54	3.65	3.18	1221(67.83)	-0.27	0.9744	0.8571	0.3529
c02	18	6.32	6.43	1217(67.61)	-0.04	0.0255	0.1224	0.1176
c03	54	6.93	6.89	1220(67.78)	-0.01	0.0000	0.0050	0.3529
c04	9	5.89	5.84	1220(67.78)	0	0.0000	0.0010	0.0588
c05	18	8.64	8.21	1222(67.89)	0	0.0000	0.0144	0.1176

Table 3. Characteristics of $V_2Sn_{16}S_{36}$ $4H$ -polytype configurations: degeneracy (Λ), initial (d_{VV}^{ini}) and final (d_{VV}^{fin}) V atom distances in the geometry optimization, final cell volume (Vol.) (in parentheses is the volume of a cell with one formula unit), energy difference between magnetic configurations (E_{PS-APS}) and thermodynamic probabilities of each non-symmetrical configuration at 300 K ($p^{300\text{ K}}$) and 900 K ($p^{900\text{ K}}$) and the probabilities in the non-equilibrium conditions (p^∞).

	Λ	d_{VV}^{ini} (Å)	d_{VV}^{fin} (Å)	Vol. (Å ³)	E_{PS-APS} (eV)	$p^{300\text{ K}}$	$p^{900\text{ K}}$	p^∞
c01	54	3.69	3.21	1224(68.00)	-0.25	0.9863	0.8568	0.3529
c02	18	6.39	6.34	1223(67.94)	0	0.0136	0.0989	0.1176
c03	27	6.27	6.25	1223(67.94)	0	0	0.0163	0.1765
c04	27	8.15	8.09	1225(68.05)	0	0	0.0122	0.1765
c05	27	7.27	7.25	1223(67.94)	0	0	0.0159	0.1765

host orbitals which lowers the energies around the V-S bonds, binding the IB to the VB. Therefore, the formation of a wide IB is only allowed when the system is independent of the spin configuration: in the c05 and c07 cases in which the symmetry is less than that of c01 and c03. Hence, there is a dependency of the structure properties on the symmetry of the V-atom configuration and magnetic behavior.

Geometrical parameters are obtained after relaxation in which a contraction of supercells is shown (table 1). It is known that a smaller cell appears in former VS_2 even though the two VS_2 and SnS_2 have the same structure. These former compounds should result in a $V_xSn_{1-x}S_2$ solid solution with the same P_{3m1} symmetry of the host systems. Using this, we infer that the resulting contraction of $V_xSn_{1-x}S_2$ supercells is a consequence of this small VS_2 lattice when compared with the SnS_2 in the form of the $2H$ -polytype. However, the c01 configuration in $V_2Sn_{10}S_{24}$ cases appears with stronger reduction of the cell which is a consequence of the location of each V atom in the same position but different layers (which is exactly the direction of the layer stacking).

According to crystal field theory transition-metal d orbitals lead to a distortion of the metal surrounding bonds either located in octahedral or tetrahedral positions. Nevertheless, despite the great deformation of bonds in all the doped structures, a wide IB is only formed in the c05 and c07 configurations in $V_2Sn_{10}S_{24}$, which demonstrates that not only is the distortion of the lattice necessary but also certain spin coupling and geometric configurations of the V dopant.

3.3.2. $V_2Sn_{16}S_{36}$ $2H$ and $4H$ -polytypes. DOS obtained for the configurations of $V_2Sn_{16}S_{36}$ (figure 6) and the data resulting from these calculations (tables 2 and 3) are shown.

The $2H$ and $4H$ -polytypes are compared under the same conditions and certain situations are also similar to those of 36-atom supercells shown before. Specifically, for the c03 and

c04 configurations in $2H$ -polytype (figures 6(a) and (b)) the results are similar to those of c01 and c03 structures of the $V_2Sn_{10}S_{24}$ supercells (figure 5(a)) while the c05 configuration in the $V_2Sn_{16}S_{36}$ $2H$ -polytype (figure 6(c)) shows a narrow IB which supports the results found experimentally [13].

However, for the $4H$ -polytype the IB is not completely formed in the c03–c05 subset (figure 6(d)). Instead, in these cases the geometric displacement of layers influences the formation of two isolated signals around the Fermi energy level in the electronic structures. This is not a characteristic of a conventional IB but might work as a ratchet IB [35], in which the system is composed by two narrow and very near bands in the middle of the host semiconductor band-gap in which one is empty (the ratched band) and the other one is filled.

The geometrical anisotropy of the lattice of SnS_2 layered materials is what determines the direction of the V-atoms arrangement in order to obtain the IB. The lattice is distorted by the dopant repulsions and the V atoms are in the layer stacking direction in a long-range interaction. Hence, no magnetic coupling appears and the energy of the system is independent of the magnetic configurations.

Furthermore, we demonstrated that the inherent weak vdW interactions in SnS_2 and the type of layer stacking influences the way in which the IB is obtained, e.g. see the differences between figures 6(a)–(c) when these are compared with figure 6(d). Therefore, the IB formation will not only be dependent on the number of symmetry elements (degeneracy) of the disordered-site arrangements in the lattice but also on the host SnS_2 symmetry.

3.3.3. Configuration probabilities. In addition, thermodynamic probabilities associated with each position were obtained from the resulting SOD data. Probabilities of each configuration in 16.67% and 11.11% vanadium concentrations were obtained under equilibrium conditions using

Figure 6. DOS and V(PDOS) of configurations of two V located in different layers in Sn positions obtained in $V_2Sn_{16}S_{36}$ for 2H and 4H-polytypes.

several temperatures, and also non-equilibrium conditions (tables 1–3). In the $V_2Sn_{10}S_{24}$ cases the highest probability is found for the c06 configuration under thermodynamic equilibrium. Therefore, if the temperature is raised, c04 is the second most probable configuration at 900 K while in the total disordered situation the c04–c07 subset has the same probability as expected. This implies that the metallic IB (c05 and c07 configurations) might be synthesized using synthesis routes that include a greater disorder, but it should be noted that under these conditions the other configurations in the c04–c07 subset will also be present.

Nevertheless, structures with close V atoms in the same layer (c02, c04 and c06), leaving one unsubstituted SnS_2 layer, are not formed in great proportions in experimental synthesis. A low diffusion mechanism might also be involved avoiding the formation of V-S-V aggregates. Hence a synthesis route carried out under non-equilibrium conditions only allows the formation of c05 and c07 configurations.

On the other hand, tables 2 and 3 show the probabilities that result from the symmetry-adapted configuration space in the $V_2Sn_{16}S_{36}$ supercell sets for 2H and 4H-polytypes. In the

c03–c05 subset under thermodynamic equilibrium at 900 K, the c05 configuration shows the higher probability, while under non-equilibrium conditions, the c03 configuration competes with it. Our theoretical results support the formation of the IB material in the experimental conditions outside thermodynamic equilibrium.

4. Conclusions

We obtained symmetry-adapted configurations of V atoms at disordered-sites in SnS_2 . The number of symmetry elements, degeneracy and positions of the dopants (e.g. two V atoms in one layer or two V atoms in different layers) were compared and correlated with the electronic results. We demonstrated that these configurations with same degeneracy and disordered sites in the same direction have an equivalent electronic structure. We established that while in the 2H-polytype at 16.67% vanadium concentration c05 and c07 cases (figure 5) shows a wide metallic IB, in the same polytype at 11.11% vanadium concentration, c05 structure (figure 6) shows characteristics of a narrow, isolated and partially filled IB.

Specifically, the IB structure with a V metal concentration of 11.11% has a similar concentration as the 10% achieved in the experimental results in the SnS₂ 2H-polytype [13]. In this configuration the distance between the V atoms is the highest obtained in all the structures with two V atoms substituting Sn, the 8.21 Å and the zero energy difference between the PS and APS spin-configurations of V atoms is consistent with a ground-state independent of the spin-configurations. Therefore, all these theoretical characteristics are coherent with the experimental results that report a paramagnetic material [13].

Moreover, the spin coupling that appears when V atoms have a small d_{VV} avoids the formation of the IB. Therefore, V atoms should have a certain distance between them in order to obtain non-interacting V extra electrons delocalized throughout non-bonded d orbitals.

8.67%, 11.11% and 16.67% vanadium concentrations are high enough to substitute Sn positions within each layer. Therefore in experimental conditions all layer should have vanadium atoms and configurations where this metal is forming clusters leaving pure one layer are less likely than others, where V atoms are located in each layer. The probabilities from the symmetry-adapted configurations showed that V atoms in different layers are likely in the non-equilibrium conditions while at 900 K the configuration with the IB prevails in the lower concentration that was calculated. In this work we have demonstrated that the IB material obtained under these conditions not only depends on the symmetry of the host SnS₂ but also on the symmetry of the dopant arrangement in the lattice.

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References

- [1] Palacios P, Aguilera I, Sánchez K, Conesa J C and Wahnón P 2008 *Phys. Rev. Lett.* **101** 046403
- [2] Palacios P, Wahnón P and Tablero C 2005 *Comput. Mater. Sci.* **33** 118

- [3] Palacios P, Fernandez J J, Sanchez K, Conesa J C and Wahnón P 2006 *Phys. Rev. B* **73** 085206
- [4] Palacios P, Wahnón P, Pizzinato S and Conesa J C 2006 *J. Chem. Phys.* **124** 014711
- [5] Palacios P, Sanchez K, Wahnón P and Conesa J C 2007 *J. Solar Energy Eng.* **129** 314
- [6] Aguilera I, Palacios P and Wahnón P 2008 *Thin Solid Films* **516** 7050
- [7] Palacios P, Sanchez K, Conesa J C, Fernandez J J and Wahnón P 2007 *Thin Solid Films* **515** 6280
- [8] Palacios P, Sanchez K, Conesa J C and Wahnón P 2006 *Phys. Status Solidi* **203** 1395
- [9] Palacios P, Aguilera I and Wahnón P 2008 *Thin Solid Films* **516** 7070
- [10] Luque A and Martí A 1997 *Phys. Rev. Lett.* **78** 5014–7
- [11] Martí A and Luque A 2004 *Series in Optics and Optoelectronics* (Bristol: IOP Publishing)
- [12] Shockley W and Queisser H J 1961 *J. Appl. Phys.* **32** 510–9
- [13] Wahnón P, Conesa J C, Palacios P, Lucena R, Aguilera I, Seminovski Y and Fresno F 2011 *Phys. Chem. Chem. Phys.* **13** 20401–7
- [14] Mitchell R S 1956 *Z. Kristallogr.* **108** 296–315
- [15] Al-Alamy F A S, Balchin A A and White M 1977 *J. Mater. Sci.* **12** 2037–42
- [16] Palosz B and Salje E 1989 *J. Appl. Crystallogr.* **22** 622–3
- [17] Hazen R M and Finger L W 1978 *Am. Mineral.* **63** 289–92
- [18] Nakashima S, Katahama H and Mitsuishi A 1981 *Physica B+C* **105** 343–6
- [19] Mitchell R, Fujiki Y and Ishizawa Y 1974 *Nature* **247** 537–8
- [20] Palosz B, Palosz W and Gierlotka S 1985 *Acta Crystallogr. C* **41** 1402–4
- [21] Mitchell R S, Fujiki Y and Ishizawa Y 1982 *J. Cryst. Growth* **57** 273–9
- [22] Palosz B, Steurer W and Schulz H 1990 *Acta Crystallogr. B* **46** 449–55
- [23] Robertson J 1979 *J. Phys. C: Solid State Phys.* **12** 4753
- [24] Wiegers G A 1980 *Physica B+C* **99** 151–65
- [25] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558–61
- [26] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169–86
- [27] Grimme S 2004 *J. Comput. Chem.* **25** 1463–73
- [28] Grimme S 2006 *J. Comput. Chem.* **27** 1787–99
- [29] Antony J and Grimme S 2006 *Phys. Chem. Chem. Phys.* **8** 5287–93
- [30] Grimme S, Antony J, Ehrlich S and Krieg H 2010 *J. Chem. Phys.* **132** 154104
- [31] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758–75
- [32] Grau-Crespo R, Hamad S, Catlow C R A and de Leeuw N H 2007 *J. Phys.: Condens. Matter* **19** 256201
- [33] Grau-Crespo R and Waghmare U V 2012 *Molecular Modeling for the Design of Novel Performance Chemicals and Materials* ed B Rai (Boca Raton, FL: CRC Press) pp 299–322
- [34] Seminovski Y, Palacios P and Wahnón P 2013 *Thin Solid Films* **535** 387–9
- [35] Yoshida M, Ekins N J, Farrell D J and Phillips C C 2012 *Appl. Phys. Lett.* **100** 263902