Optical dispersion functions of $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ using \textit{ab-initio} calculations

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The magnetic, electronic and optical properties of $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ alloys for selected concentrations ($x = 0, 0.25, 0.50, 0.75$ and $1.0$) were investigated by means of density functional theory (DFT) calculations utilizing full potential linearized augmented plane wave (FP-LAPW) method. It was found that doping the $\text{Co}_2\text{VSn}$ alloy with rare-earth ions like Eu generates the nonstoichiometric $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ and changes its original behavior from half ferromagnetic material to a metallic one. In addition, the total magnetic moment was found to increase with increasing dopant concentration with maximum local magnetic contributions on the Eu-sites. The optical dielectric functions as well as their static value for all the above alloys were also investigated. Moreover, the absorption coefficient, reflectivity and refractive indices were calculated. All the optical calculations were found to agree well with the band structure calculations when determining the alloys’ half-metallic behavior. Finally, the nonstoichiometric metallic compounds found in this series might be useful in the flat panel industry as potential phosphors.

Keywords: Electronic structure; nonstoichiometric system; optical properties; \textit{ab-initio} calculations.

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1. Introduction

The need to find luminescent materials that are resistant to radiation and ion-impact damage is considered the main technological motivation behind the search for new phosphor hosts as any advances in this field may allow the well needed enhancement in the flat panel display applications.\footnote{Corresponding author.} It is a well-known fact that
the role of luminescent rare-earth-metal ions nowadays has become predominant. As there are no reliable theories to predict the relation between phosphor color and composition or efficiency, the short list of known effective commercial phosphor materials have been discovered through sequential synthesis and testing. As the level of advancement in science is rapidly increasing, researchers started focusing on tailoring multi-purpose materials by varying the dopants and/or the combinations of the mixed inorganic hosts for various applications including perfect spin-injectors and-filters, tunneling and giant-magneto resistances (TMRs and GMRs) and storage devices. Since there is no electronic band structural data are published previously for these Co$_{2-x}$Eu$_x$VS$_n$ alloys, nor any optical-property studies conducted on them including their ability to absorb in certain regions within the EM-spectrum for potential applications in the display industry, it was considered reasonable to perform these calculations based on the full potential linearized augmented plane wave (FP-LAPW).

Recently, alloys with a complete spin polarization at the Fermi energy have attracted a great scientific interest since de Groot et al. predicted that some half-Heusler alloys like NiMnSb and PtMnSb exhibit half-metallic (HM) ferromagnetism. The two known types of Heusler systems that can exist are either the $C_{1b}$ or the $L_{21}$ structures. Alloys of first-type, the half-Heusler alloys, is represented by the general chemical formula $XYZ$ and the $C_{1b}$ structure with one of its four sublattices normally unoccupied ($A$-site). The second-type, $(L_{21})$, which is referred to as full-Heusler alloy, is the ternary compounds with 2:1:1 stoichiometry and chemical formula represented by $X_2YZ$, space group 225 (Fm3m), where $X$ and $Y$ (usually located at both $A$ and $C$-sites at $(1/4, 1/4, 1/4)$ and $(1/2, 1/2, 1/2)$, respectively) are transition metals and $Z$ is represented by a main group element. Likewise, the $Y$ and $Z$ atoms are located at $B$ $(3/4, 3/4, 3/4)$ and $D$ $(0, 0, 0)$, respectively. Many studies have been conducted in the last three decades to help understanding the mechanism of their HM behavior and all related physical properties. Reshak et al., studied the influence of varying Ge concentration on the optical properties of Fe$_2$MnSi$_x$Ge$_{1-x}$. They found that the alloys behave as semiconductors in the minority spin and metallic in the majority spin. Furthermore, they calculated the associated reflectivity, refractivity and absorption coefficients. The electronic and magnetic properties of Co-based full-Heusler alloys have been investigated using first-principles calculations. Hence, it was found that many of Co$_2YZ$ are HM and follow a Slater–Pauling behavior, where the total spin magnetic moment per unit cell ($M_t$) in $\mu_B$ scales with the total number of valence electrons ($Z_t$) following the rule:

$$M_t = Z_t - 24.$$  \hspace{1cm} (1)

The effect of defects on the electronic and magnetic properties of Fe$_2$MnSi Heusler alloy was studied. The defects were found to cause narrowing of the band gap as compared to the ideal structure with almost zero in some type of defects.
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Recently, we performed density functional theory (DFT) calculations using FP-LAPW method to investigate the perfect, $\text{Co}_2\text{VSn}$ and nonstoichiometric, $\text{Fe}_{2-x}\text{Co}_x\text{VSn}$, full Heusler alloys.\textsuperscript{14,15} The total magnetic moment of the nonstoichiometric host material was found to increase with increasing Co concentration where the perfect alloy was found to be a ferromagnetic half-metal with a band gap of 0.56 eV and a total magnetic moment of 3.0 $\mu_B$/f.u. We also investigated the effect of defects on the electronic and magnetic structures of the perfect alloy and calculated the formation energies for antisite, swap and vacancy defects. We found that $\text{V}_{\text{Sn}}$ antisite, $\text{V}$, $\text{Co}$ and $\text{Sn}$ vacancies have relatively low formation energies with high probability to occur. We also found in the perfect alloy that the half metallicity is maintained in all structures with band gaps smaller than that of the perfect alloy except for $\text{Co}_x\text{Sn}_{\text{Co}}$ antisite and $\text{Co}$-$\text{Sn}$ swap defected structures, which exhibited a metallic behavior.\textsuperscript{15} Moreover, we concluded that increasing the cobalt concentration in the nonstoichiometric alloy had crucially effected the spin polarization as it is leveled at 100% at $x = 1.50$, $1.75$ and $2.00$ with negative formation energy and hence increased the host total magnetic moment.\textsuperscript{14} However, to the authors’ knowledge, one can barely find a study focusing on exploring the Heusler alloys suitability for being phosphor hosts, and as such the effects of rare-earth dopants are not adequately investigated. Therefore, by this investigation, we extend our previous work starting from the ideal $\text{Co}_2\text{VSn}$ alloy and report the Eu-substitution influence on the cobalt site of the $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ quaternary alloy ($x = 0.25 - 1.00$) in steps of 0.25 aiming to explore any changes on the electronic, magnetic and optical properties of the nonstoichiometric investigated alloys. The rest of the paper is structured as follows: Sec. 2, describes the method of calculation; Sec. 3 is dedicated to the results and discussion, with the concluding remarks being presented in Sec. 4.

2. Calculation Methods

The calculations were performed using DFT\textsuperscript{16} based on FP-LAPW method, as implemented in WIEN2K package.\textsuperscript{17} The electronic exchange-correlation potential is described by the generalized gradient approximation (GGA).\textsuperscript{18} Additionally, we applied the newly modified Becke–Johnson (mBJ) exchange potential approximation to the electronic band structure and density of states (DOS) calculations. The mBJ method is known to provide more accurate energy band gap values.\textsuperscript{19} The ideal structure has closed packed $L_{21}$ cubic structure with a space group $\text{Fm\tilde{3}m}$ (255), which consists of four interpenetrated face-centered cubic (FCC) sublattices. The Co atoms are placed at $A$ (1/4, 1/4, 1/4) and $C$ (3/4, 3/4, 3/4), the V and Sn atoms are placed at $B$ (0, 0, 0) and $D$ (1/2, 1/2, 1/2), respectively. The calculations are performed using a cell with 16 atoms. The basic set parameters are: 16 Ryd cutoff energy for the plane waves in the interstitial region between the muffin tins and 169 Ryd for the potential. The wave function expansion inside the muffin tins are
taken up to $l_{\text{max}} = 10$ and the potential expansion up to $l_{\text{max}} = 4$, while the charge density Fourier is expanded up to $G_{\text{max}} = 12$. The core energy cutoff is taken as $-6.0 \text{ Ryd}$. The radius muffin tin (RMT) is 1.99 a.u. for Co atoms and 2 a.u. for Eu, V and Sn atoms. The $k$-point sampling in the irreducible part of the Brillouin Zone (BZ) is performed using $(30 \times 30 \times 30)$ Monkhorst–pack grid. All structures are fully relaxed until the forces on the atoms are less than 2 mRy/a.u. The convergence of the self consistent calculations is taken with respect to total charge of the system with a tolerance of 0.0001 electron charge. The lattice constant is obtained by optimizing the structure using Murnaghan equation of state.\textsuperscript{20} The calculated DOS are performed using the tetrahedron method with Blöchl corrections.\textsuperscript{21}

3. Results and Discussion

3.1. Structural properties

The structural properties of nonstoichiometric $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ with $x = 0.25, 0.50, 0.75$ and 1.00 are listed in Table 1 and illustrated in Fig. 1. The symmetry and space group of the systems as a function of Eu-concentration are given, where Eu atoms reside on $A$-sites for $x \leq 1$. As expected, increasing Eu-concentration resulted in increasing the lattice parameters’ length and changing formation energy. In fact, according to calculations, the most stable doped structure was the CoEu-VSn with a minimal value of $-721.2 \text{ meV}$. This was true as long as the Eu atoms resided on the $A$-site and $x \leq 1$. The lattice parameter did not show any contraction within the dopant studied limit. This lack of any contraction is explained based on the relatively low dopant concentrations in the host structure even though increasing the Eu-concentration on both the $A$ and $C$-sites might be argued to create stronger bonds between the Eu atoms and their immediate neighbors in comparable to our recent work.\textsuperscript{15} However, because of the known luminescent quenching phenomenon at high dopant concentrations (i.e., $x > 1$) which redeems the material unsuitable for flat panel applications; it was decided to ignore such higher dopant concentrations aside from the high cost of the rare-earth dopants. Therefore, the calculated lattice constants and space groups of the perfect and nonstoichiometric $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ alloys with $0 \leq x \leq 1$ are summarized in Table 1, where all compounds are modeled using a cubic cell of 16 atoms. The total energy as a function

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>$a$ (Å)</th>
<th>Formation energy (meV/Formula)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}_2\text{VSn}$</td>
<td>$\text{Fm}3\text{m}$ (255)</td>
<td>6.022</td>
<td>$-765.3$</td>
</tr>
<tr>
<td>$\text{Co}<em>{0.75}\text{Eu}</em>{0.25}\text{VSn}$</td>
<td>$\text{P}4\text{3}3\text{m}$ (215)</td>
<td>6.031</td>
<td>$-635.7$</td>
</tr>
<tr>
<td>$\text{Co}<em>{1.5}\text{Eu}</em>{0.5}\text{VSn}$</td>
<td>$\text{P}4\text{mm}$ (115)</td>
<td>6.040</td>
<td>$-689.5$</td>
</tr>
<tr>
<td>$\text{Co}<em>{1.25}\text{Eu}</em>{0.75}\text{VSn}$</td>
<td>$\text{P}4\text{3}3\text{m}$ (215)</td>
<td>6.043</td>
<td>$-605.4$</td>
</tr>
<tr>
<td>$\text{CoEuVSn}$</td>
<td>$\text{P}4\text{3}3\text{m}$ (216)</td>
<td>6.045</td>
<td>$-721.2$</td>
</tr>
</tbody>
</table>
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![Fig. 1. The geometrical structures of $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$](image)

(a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$ and (e) $x = 1$.

Table 2. The magnetic moment ($\mu_B$) of both perfect supercell (16 atom) and the nonstoichiometric $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ systems with $x = 0.25, 0.50, 0.75$ and 1.00.

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<tbody>
<tr>
<td>$\text{Co}_2\text{VSn}$</td>
<td>1.10</td>
<td>—</td>
<td>0.87</td>
<td>−0.01</td>
<td>12.00</td>
</tr>
<tr>
<td>$\text{Co}<em>{1.75}\text{Eu}</em>{0.25}\text{VSn}$</td>
<td>1.06, 1.19, 0.86</td>
<td>6.21</td>
<td>0.74</td>
<td>0.0005</td>
<td>17.33</td>
</tr>
<tr>
<td>$\text{Co}<em>{1.5}\text{Eu}</em>{0.5}\text{VSn}$</td>
<td>1.05, 0.95, 0.50</td>
<td>6.28</td>
<td>0.75</td>
<td>0.008</td>
<td>22.5</td>
</tr>
<tr>
<td>$\text{Co}<em>{1.25}\text{Eu}</em>{0.75}\text{VSn}$</td>
<td>0.91, 0.66, −0.016</td>
<td>6.61</td>
<td>1.02</td>
<td>0.19</td>
<td>27.94</td>
</tr>
<tr>
<td>$\text{Co}\text{EuVSn}$</td>
<td>0.45</td>
<td>6.33</td>
<td>1.26</td>
<td>0.015</td>
<td>35.98</td>
</tr>
</tbody>
</table>

of volume is fitted using Murnaghan equation of state and all systems show cubic structures.

3.2. Spin magnetic moments

The total and local spin magnetic moments of $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ are increased according to Eu-concentration. This is consistent with the generalized Slater–Pauling behavior for the stoichiometric structure $\text{Co}_2\text{VSn}$. However, the nonstoichiometric structures follow the modified formula of Slater–Pauling rule, which takes into account the size of the cell in the alloys and has the form $^{22}$:

$$M_{\text{tot}} = Z_V - 24n_Z,$$

Where, $Z_v$ and $n_Z$ are the number of valance electrons and $Z$ atoms in the unit cell, respectively.

In Table 2, we list the total and local magnetic moments, where it is noticed that all values increase as Eu-concentration increases, with a maximum value in $\text{Co}\text{EuVSn}$ alloy of 35.98 $\mu_B$/unit cell (8.99 $\mu_B$/f.u.). The increase of the magnetic moment due to the increase in Eu with average local magnetic moment 6.5 $\mu_B$/atom with electronic configuration $4f^76d^2$ enhances the magnetic moment due to the increase of the valance electrons in the whole structure.

3.3. Band gap and density of states

Using the GGA method, the ideal $\text{Co}_2\text{VSn}$ is found HM with an indirect energy band gap ($E_g$) of 0.56 eV,$^{15}$ see Fig. 2. The nonstoichiometric $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ alloys
are all found to be metals. In Figs. 3(a)–3(d), it can be argued that the valence states shift to higher energy values crossing the Fermi level, which leads to the loss of the half metallicity, where Co and V atoms introduce DOS at the Fermi level close to the energy band gap. In Figs. 4(a)–4(d), we present the partial density of states (PDOS) for the constituent atoms in the nonstoichiometric Co$_{2-x}$Eu$_x$VSn alloys' structures, where $x = 0.25, 0.50, 0.75$ and $1.0$. The spin polarization decreases from 100% for the ideal alloy to 40%, 24% and 17% at $x = 0.25, 0.50$, and 0.75, respectively, after which it increases at $x = 1.0$ to 98%.

Moreover, the absence of the energy band gap ($E_g$) in the alloys was probably introduced from the weak $d–f$ hybridization between Co ($A$- and $C$-sites) atoms and the second neighboring Eu atoms ($A$-site). Additionally, the weak hybridization between V ($d$-state) atoms at $B$-site and first neighbors Eu ($f$-state) at $A$-site enhanced the electron density at Fermi level as a consequence of transformation of the bonding state of Co and V atoms to anti-bonding states. However, the proposed mBJ exchange potential which has been proposed and used to calculate the spin
Fig. 3. Band structure of the minority spin channel of (a) $x = 0.25$, (b) $x = 0.5$, (c) $x = 0.75$ and (d) $x = 1$, using normal GGA.
Fig. 4. Total DOS (state/eV) and PDOS (state/eV) in the minority spin channels for nonstoichiometric Co$_{2-x}$Eu$_x$VSn, (a) $x = 0.25$, (b) $x = 0.5$, (c) $x = 0.75$, (d) $x = 1$, using normal GGA.
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polarized band structure as well as the DOS introduces a variant picture which confirms the semiconducting behavior or the half-metallicity spin dependent in one spin (spin down: minority spin), and the metallicity behavior in the other spin state (spin up, majority spin), for $x = 0, 0.25, 0.5, 0.75$. Nevertheless, at $x = 1$, the DOS

Fig. 5. TDOS of the Ideal $\text{Co}_2\text{VSn}$ Heusler alloy using mBJ method.

Fig. 6. TDOS (state/eV) for the nonstoichiometric $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$: (a) $x = 0.25$, (b) $x = 0.5$, (c) $x = 0.75$ and (d) $x = 1$, using mBJ method.
showed the same previous metallic behavior (Figs. 5 and 6) and hence, the same above metallicity argument is valid.

3.4. Optical functions

The optical properties can be described by the dielectric function $\varepsilon(\omega)$, which is expressed as: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ from the electronic band structure of a solid is\(^{23-25}\):

$$\varepsilon_2(\omega) = \left(\frac{\hbar^2 e^2}{\pi m^2 \omega^2}\right) \sum_{c,v} \int d^3 k \langle c_k | p^\alpha | v_k \rangle \langle v_k | p^\beta | c_k \rangle x \delta (\varepsilon_{c_k} - \varepsilon_{v_k} - \omega),$$

where $p$ is the momentum matrix element between states of bands $\alpha$ and $\beta$ with crystal momentum $k \cdot e_k$ and $v_k$ are the crystal wave functions corresponding to the conduction and the valance bands with crystal wave vector $k$. As such, this imaginary part of the dielectric function $\varepsilon_2(\omega)$ can be utilized to calculate the real part $\varepsilon_1(\omega)$ of the dielectric function from the Kramers–Kroning relation:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{(\omega')^2 - \omega^2} d\omega',$$

where $P$ is the principle value of the integral. The refractive index $n(\omega)$, the extinction coefficient $k(\omega)$, the absorption coefficient $I(\omega)$ and the reflectivity $R(\omega)$ in the crystal are given by the following equations:

$$n(\omega) = \left[\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)}}{2}\right]^{1/2},$$

$$k(\omega) = \left[\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)}}{2}\right]^{1/2},$$

$$I(\omega) = \sqrt{2\omega} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)}\right]^{1/2},$$

$$R(\omega) = \frac{n + ik - 1}{n + ik + 1}.$$
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Fig. 7. Calculated imaginary part of the dielectric constant, $\varepsilon_2(\omega)$, of Co$_{2-x}$Eu$_x$VSn.

Fig. 8. Calculated real part of the dielectric constant, $\varepsilon_1(\omega)$, of Co$_{2-x}$Eu$_x$VSn.

Figure 10 exhibit the reflectivity spectra along $xx$, from this spectra the static reflectivity $R(0)$ is calculated where it varies as a result of increasing Eu-concentration. For the ideal structure at $x = 0$, the static reflectivity index is found
to be 0.37. Adding Eu into the ideal structure increased the static reflectivity index $R(0)$ to 0.61, 0.57, 0.62 and 0.77 for $x = 0.25, 0.50, 0.75$ and 1.00, respectively. This behavior could be attributed to the $f$-orbital influence of the rare earth ion.

The absorption coefficients of all the structures are presented in Fig. 11. The optical absorption edge in spin down for the ideal structure at $x = 0$ is 0.56 eV.
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Fig. 11. Calculated absorption index, $I(\omega)$, of $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$. 

However, it is metallic in the spin up, in agreement with our previous calculations, Fig. 2. Therefore, it is half metal in the spin down case. For the rest of the structures, the absorption starts from the zero energy and this confirms their metallic nature inconsistent with Fig. 3. The resonance of absorption is found to be at 8.0, 9.9, 10.3, 10.5 and 11.1 eV for $x = 0, 0.25, 0.50, 0.75$ and 1.00, respectively which shifted towards higher energy.

4. Conclusion

We investigated the effect of Eu doping in $\text{Co}_2\text{VSn}$, which created a nonstoichiometric $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ systems with $x = 0.25, 0.50, 0.75$ and 1.00, using DFT calculations within FP-LAPW method and GGA functional. The ideal structure is found totally spin polarized at the Fermi level with a band gap of 0.56 eV. The nonstoichiometric $\text{Co}_{2-x}\text{Eu}_x\text{VSn}$ systems are characterised by new structural, electronic, magnetic and optical properties. While using the GGA method, all the doped structures show metallic behavior where the half metallicity is vanished except at $x = 0$, where GGA shows HM behavior. However, the mBJ method established HM behavior for $x = 0, 0.25, 0.5$ and 0.75, but not at $x = 1$. The optical functions are calculated for all the studied systems and found to be consistent with the electronic structure. Even though the HM behavior is favorable for certain applications including spintronic devices, the new investigated alloys might be useful as phosphor hosts where the metallicity might have crucial effect as thermal conductors in releasing the accumulated heat within the pixels of the flat panel displays including the plasma display panels and hence longer panel lifetime.
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References