Half-metallic-ferrimagnetic Sr_2CrWO_6 and Sr_2FeReO_6 materials for room temperature spintronics: Linear muffin-tin orbital studies

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Abstract: *Complex perovskite-like materials which include magnetic transition elements have relevance due to the technological perspectives in the spintronics industry. In this work, we report the studies of the electronic and magnetic characterizations of Sr_2CrWO_6 and Sr_2FeReO_6 as spintronics materials at room temperature by using the linearized muffin-tin orbitals (LMTO) method through the atomic-sphere approximation (ASA) within the local spin density approximation (LSDA). The interchange-correlation potential was included through the LSDA+U technique. The band structure results at room-temperature predict half-metallic ferrimagnetic ground state for Sr_2CrWO_6 and Sr_2FeReO_6 with total magnetic moment of 1.878 μ_B and 3.184 μ_B per formula unit, respectively, agreement with the previous theoretical and experimental results.*
Keywords: *Complex perovskite; LMTO-ASA method; Half-metallic.*

I.   Introduction

Complex perovskite oxides have the general chemical formula of $A_2BB'O_6$, crystalline in the rock-salt (Na^+Cl^-) structure with alternate perovskites ABO_3 and $AB'O_3$ along three crystallographical axes [1]. The corners of each perovskite unit cell are in turn occupied by different transition-metals B and B', have the mixed valence state $(BB')^{8+}$, with oxygen atoms located in between, forming alternate BO_6 and $B'O_6$ octahedra [1-2]. The large alkaline-earth metal A^{2+} occupied the body-centered site with 12-fold oxygen coordination in each unit cell [3]. The long-range superexchange interactions between magnetic ions in complex perovskite $A_2BB'O_6$ are in the form $(-B-O-B'-)$ instead of double-exchange $(-B-O-B-)$ in single perovskite ABO_3 [4], [5].

Materials with high spin-polarization of the conducting charge carriers, the current, have attracted a great deal of attention owing to their technological applications in spin-electronics (spintronics) [6], in magnetotransport devices, as well as their rich and challenging physical properties [1-6]. In particular, an ideal material with 100% spin-polarization is described as half-metal [7]. Such materials can be found in several materials classes as in; magnetite Fe_3O_4 [8], CrO_2 [9], $LaMnO_3$ [10], Heusler alloy $Co_2(Cr_{1-x}Fe_x)Al$ [11], [12], as well as, in the group of complex perovskites [1],[4-5]. Complex perovskites are of special attention, since within this group half-metals with above room-temperature (RT) transition temperatures are found, such as in A_2FeMoO_6 (A = Ca, Sr, Ba) [13-14] and Sr_2CrMoO_6 [13],[15]. Ordered complex perovskites Sr_2FeMoO_6, Sr_2FeReO_6, Sr_2CrWO_6, etc., are among the very few materials that allow electrons of one spin direction to move through them as though they were passing through a normal metal, while blocking electrons of the opposite spin. Materials that behave this way at RT are even more exotic, so their conduction bands have fully spin-polarized [1]. Sr_2FeReO_6, Sr_2CrWO_6 complex perovskites, in particular, have attracted more attention due to their fairly high transition temperature from a paramagnetic to ferrimagnetic state, which makes them and their family of materials candidates for future spintronics applications.

II.   Materials Characterization

In the present work we report systematic studies on the Cr/Fe (3d) and W/Re (5d) orbitals contributions to the electronic and magnetic structures of two close relative members of strontium complex perovskite oxides Sr_2CrWO_6 and Sr_2FeReO_6. Where, W and Re are neighboring 5d transition-metal elements in the periodic table with the ordinary electronic configurations of [Xe] $4f^{14} 5d^n 6s^2$, where n = 4 for W (Z = 74) or n = 5 for Re (Z = 75), where [Xe] denotes the configurations of the Nobel-gas Xenon core. For chromium and iron Cr/Fe (3d), Cr has an odd electron configuration of [Ar] $4s^1 3d^5$ owing to the lower energy of the high spin configuration, not [Ar] $4s^2 3d^4$ as it might expect, where a half-filled *d* sub-level is more energetically favorable than a half-filled *s* sub-level, so one of the 4*s* electrons is promoted to a 3*d* orbital. On the other hand, iron (Fe) has an ordinary electron configuration of [Ar] $4s^2 3d^6$. Cr and Fe exhibit a wide range of possible oxidation states, where the +3 state is more stable energies [16-18]. Accordingly, the valence configurations of transition-metal ions in Sr_2CrWO_6 are; Cr^{3+} $(3d^3)$ and W^{5+} $(5d^1)$ in the high spin state with valence spin magnetic moments of $S = 3/2$ and $S = 1/2$ according to Hund's rule, respectively. Consequently, the theoretical total magnetic moment is 2.0 μ_B per formula unit cell for the ferrimagnetic ground state. In Sr_2FeReO_6, Fe^{3+} $(3d^5)$ in the high spin state with *S*

= 5/2 and Re^{5+} ($5d^2$) is highly ionized with valence spin magnetic moment of $S = 1$. As a result, the total magnetic moment for the ferrimagnetic ground state is 3.0 μ_B per Sr_2FeReO_6.

For cubic Sr_2CrWO_6 and Sr_2FeReO_6 complex perovskites with space group Fm-3m (No. 225), we used the experimental lattice constants of $a = 7.890$ Å from (Ref. 19) and $a = 7.832$ Å from (Ref. 1), respectively, closed to the theoretical values calculated using SPuDS [18] 7.880 Å and 7.886 Å, correspondingly. The magnetic structure in complex perovskites can be assigned to the AFM superexchange interactions between two very different transition magnetic ions [1],[17], such as Cr/Fe (3d) and W/Re (5d), in this work, via intermediated O^{2-} ions (Cr/Fe – O – W/Re). In addition to, the naturally small magnetic moment at W/Re (5d) is believed to be not intrinsic but is induced by the strong magnetic ions Cr/Fe (3d).

III.   Calculation methods

The first-principles linear muffin-tin orbital (LMTO) method with atomic-sphere approximation (ASA) has been employed to perform self-consistent band structure calculations within the local spin density approximation (LSDA). In LMTO-ASA, which is similar to the multiple-scattering Korringa-Kohn-Rostoker (KKR) method [20] , the potential is approximated by a muffin tin potential, i.e., it is spherically symmetric around the atomic sites and constant in the interstitial volume. Moreover, ASA takes the one-electron potential and charge density to be spherically symmetric inside space-filling Wigner-Seitz (WS) spheres whose overlap is neglected, the interstitial volume, now integrating to zero [20]. The von Barth–Hedin parameterization for exchange-correlation potential is used in the calculations [1], [17]. The Hartree potential is expanded in term of spherical harmonic up to 6, therefore, Sr (5s 4p 4d), Cr/Fe (4s 4p 3d), Mo (5s 5p 4d), W (6s 6p 5d) and O (2s 2p) LMTOs were input as valence states, while Sr (4s), Cr/Fe (3p), Mo (4s 4p), W (5p 4f) fixed as semicore states in the unit cells. It has been established that the structures are close enough, that no empty sphere (ES) is needed to introduce the unit cells [1]. The numbers of divisions along a reciprocal lattice vector which will set up the mesh for integrating valence state are selected as $(6 \times 6 \times 6)$. Special k points of 50 in the irreducible Brillouin zone (IBZ) were used in band structure and density of states calculations. A single kappa LMTOs basis set is expanded in spherical harmonic up to the angular momentum $l_{max} = 6$, was used for the valence-band charge densities and potential inside the non-overlapping muffin-tin spheres [20]. The interchange-correlation potential was included through the LSDA+U technique, where the on-site Coulomb energy (U) has been in used. The correlation parameters, Coulomb energy (U) and Hund's rule exchange (J), were utilized for strongly correlated 3d and weakly 5d electrons in the calculations. The Hubbard parameters ($U = 4.0$ eV, $J = 0.98$ eV) are used for Cr/Fe (3d) states (Refs. 1.0 and 17), even as ($U = 1$ eV, $J = 0.96$ eV) are used for W/Re (5d) states (Refs. 1 and 17). The resolving of spin up and down in total and partial densities of states for Sr_2CrWO_6 and Sr_2FeReO_6 were calculated and obtained from the LSDA+U calculations.

IV.   Results and Discussion

Fig. 1 illustrates the total densities of states (TDOSs) of Sr_2CrWO_6 and Sr_2FeReO_6 from band structure LSDA+U calculations. The obtained results of Sr_2CrWO_6 and Sr_2FeReO_6 are in agreement with previous LSDA+U calculations [1],[17],[22]. In spin-up TDOSs, there are energy gaps of about 1.33 eV in Sr_2CrWO_6 and 2.18 eV in Sr_2FeReO_6 between the occupied Cr/Fe (3d) and unoccupied W/Re (5d) partial bands. Since the energy gap in the spin-up produces from the antiferromagnetic coupling between Cr/Fe (3d) and W/Re (5d) states, as shown in Fig. 2, this situation emerges as peaks of 3d and 5d bands polarized antiferromagnetically demonstrate the Cr/Fe (3d) ↑ and W/Re (5d) ↓ form. Therefore, the spin-up electrons are insulating while the spin-down electrons are metallic, resulting in full (100%) spin-polarized of the conduction electrons at E_F. For that reason, Sr_2CrWO_6 and Sr_2FeReO_6 materials allow electrons of spin-down direction to move through them as though they were passing through a metal, while blocking electrons of the spin-up.
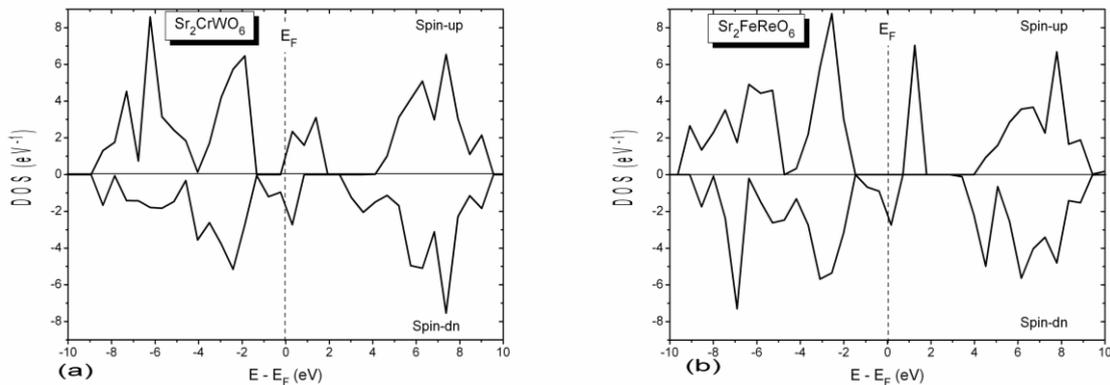
Fig. 1. Total density of states (TDOS) for (a) Sr_2CrWO_6, and (b) Sr_2FeReO_6
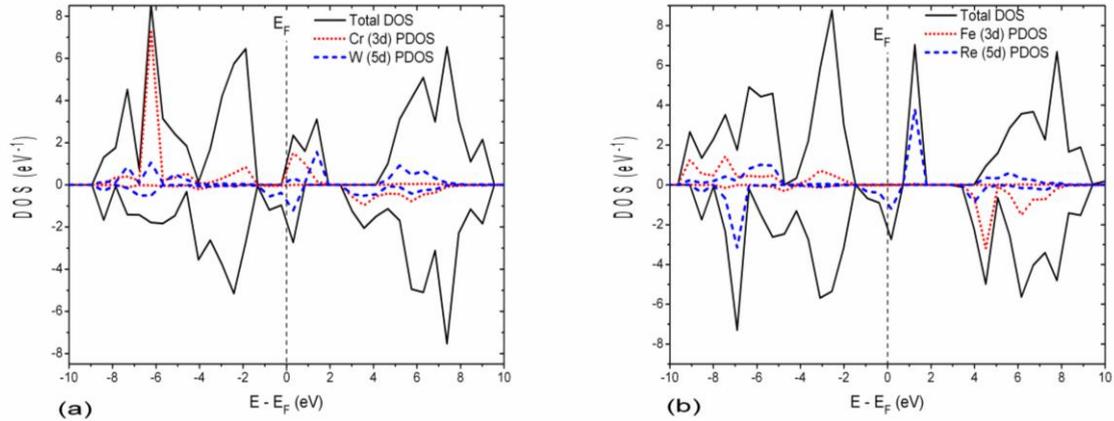
Fig. 2. Total and partial densities of states for (a) Sr_2CrWO_6, and (b) Sr_2FeReO_6

As seen in Fig. 2, the conduction bands in spin-down orientation is attributed mainly to the contributions of W (5d) and Re (5d) ions with tiny contributions of Cr (3d) and Fe (3d), correspondingly. Compare the TDOSs with PDOSs, the level distributions in of Sr_2CrWO_6 and Sr_2FeReO_6 are overall very similar, except a peak between 1.0 eV and 3.0 eV, above E_F, is higher in Sr_2FeReO_6 than in Sr_2CrWO_6. This dissimilarity, as seen in Fig. 2, due to the extra electron in Re ($5d^2$) than in W ($5d^1$).

In order to understand in some more detail the origin of the electronic and magnetic characters of Sr_2CrWO_6 and Sr_2FeReO_6, we critically examine the partial electronic density of states (PDOS) of these systems. The basic critical ingredients in the TDOS are the *d* states of the Cr/Fe and W/Re atoms, which in turn are split into t_{2g} and e_g states by the octahedral crystal field (OCF) produced by the oxygen octahedra. The t_{2g} states having lower energy and place for three electrons per spin channel, whereas the e_g states are higher in energy and have places for two electrons per spin channel. Furthermore, due to the exchange splitting, t_{2g} bands degenerate into double orbitals (d_{xz} and d_{yz}) and one singlet orbital (d_{xy}), while e_g bands degenerate into two singlet orbitals (d_{x2-y2} and d_{z2}), as seen in Fig. 3, which show the partial densities of states of t_{2g}, e_g and 2p orbitals in Sr_2CrWO_6 and Sr_2FeReO_6.

From the PDOS in Fig.3 (a), the threefold degenerate Cr t_{2g} states of the spin-up channel are filled Cr^{3+} ($3d^3$: $t_{2g}^3\uparrow$); consequently the $d_{xy}\uparrow$, $d_{xz}\uparrow$ and $d_{yz}\uparrow$ orbitals are at the energy range, about –7 eV ~ –1.5 eV in the valance bands. Therefore, the E_F ends up in the CF gap of $\Delta_o \approx 1.5$ eV between Cr t_{2g} and e_g states. A similar situation is observed in the half-metallic close-relative Sr_2FeReO_6 [21], [22]. Due to the antiferromagnetic coupling in Cr (3d) – W (5d), it is the spin-down channel in W (5d) which is the occupied one, and it contains one electron in t_{2g} states W^{5+} ($5d^1$: $t_{2g}^1\downarrow$). This means that the W (5d) t_{2g} spin-down states are only filled to about one-two, resulting in high density of states of d_{xy} and d_{yz} at the E_F in spin-down channel. In addition to, due to hybridization between states in Sr_2CrWO_6, Cr $t_{2g}\downarrow$ states achieved small occupation, while W (5d) states in the spin-up channel are essentially empty; hybridization with Cr $t_{2g}\uparrow$ states results nevertheless in a finite, small occupation above E_F.
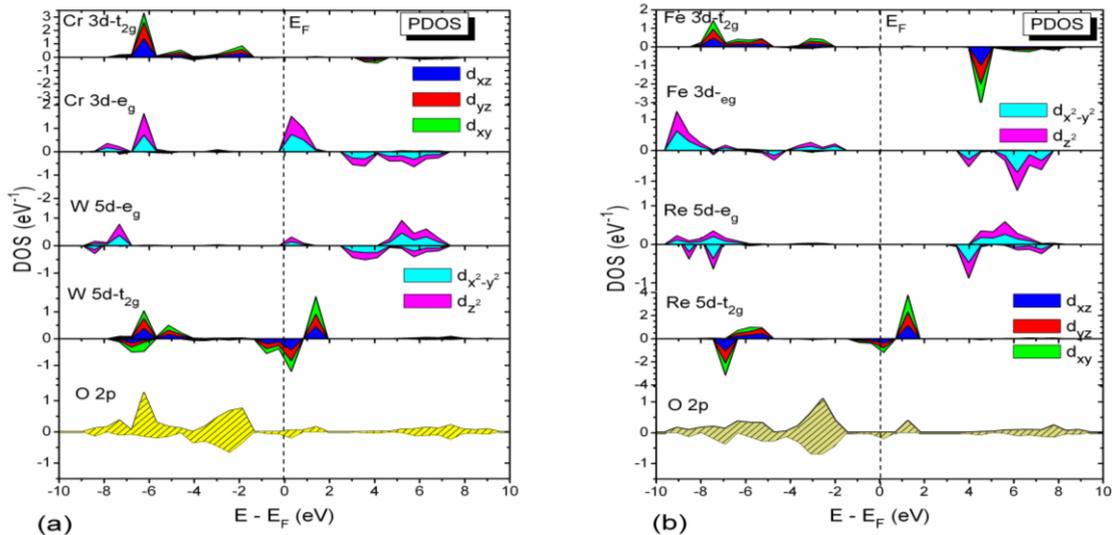
Fig. 3. Partial densities of states of t_{2g}, e_g and 2p orbitals in (a) Sr_2CrWO_6, and (b) Sr_2FeReO_6

On the other hand, from the PDOS in Fig.3 (b), the Fe t_{2g} and e_g states are full-filled in the spin-up orientation; Fe^{3+} ($3d^5$: $t_{2g}^3\uparrow$ $e_g^2\uparrow$) in the high spin state; the electronic configuration can be set of orbitals as $(d_{xy}\uparrow)^1$, $(d_{xz}\uparrow$ and $d_{yz}\uparrow)^2$, $(d_{x2-y2})^1$ and $(d_{z2})^1$ extend from -8.0 eV to -2.0 eV in the valence bands. The exchange splitting is about 7.5 eV, larger than the CF splitting, $\Delta_o \approx 2.25$ eV, resulting in the high-spin of Fe (3d) states. At the same time, spin-down channel in Re (5d) which is the occupied one, and it contains two electrons in t_{2g} states Re^{5+} ($5d^2$: $t_{2g}^2\downarrow$). Therefore, the Re t_{2g} spin-down states are only filled to about two-three, emerged as a high spin-down DOS of d_{xy} and d_{yz} at E_F. Inversely, neither Fe $t_{2g}\downarrow$ nor Re (5d)$\uparrow$ states have contributed to the bands around E_F, while the O (2p) bands are at a much lower energy from -9.0 to -2.0 eV.

Finally, the magnetic structure in Sr_2CrWO_6 and Sr_2FeReO_6 complex perovskites can be assigned to the antiferromagnetic superexchange interactions between Cr/Fe (3d) and W/Re (5d) via intermediated oxygen atoms in the 180° long-chain Cr ($3d$-$t_{2g}\uparrow$) – O ($2p_\pi$) – W ($5d$-$t_{2g}\downarrow$) and Fe ($3d$-$t_{2g}\uparrow$) – O ($2p_\pi$) – Re ($5d$-$t_{2g}\downarrow$), correspondingly. The calculated spin magnetic moments from LSDA+U for Sr_2CrWO_6 are; 2.919 μ_B for Cr, -1.044 μ_B for W with a total magnetic moment of 1.878 μ_B, which is 94% agreement with the later LSDA+U result, 2.01 μ_B [18], [22]. For Sr_2FeReO_6, 4.578 μ_B for Fe, -1.344 μ_B for Re, and the total magnetic moment found to be 3.184 μ_B, also, agree to the LSDA+U result, 3.06 μ_B [1]. The bands scheme for both compounds are illustrated in Fig. 4, the results can be resumed by means the simple model describes the effect of filling t_{2g} and e_g orbitals in $3d$ and $5d$ bands for spin-up and spin-down configurations.
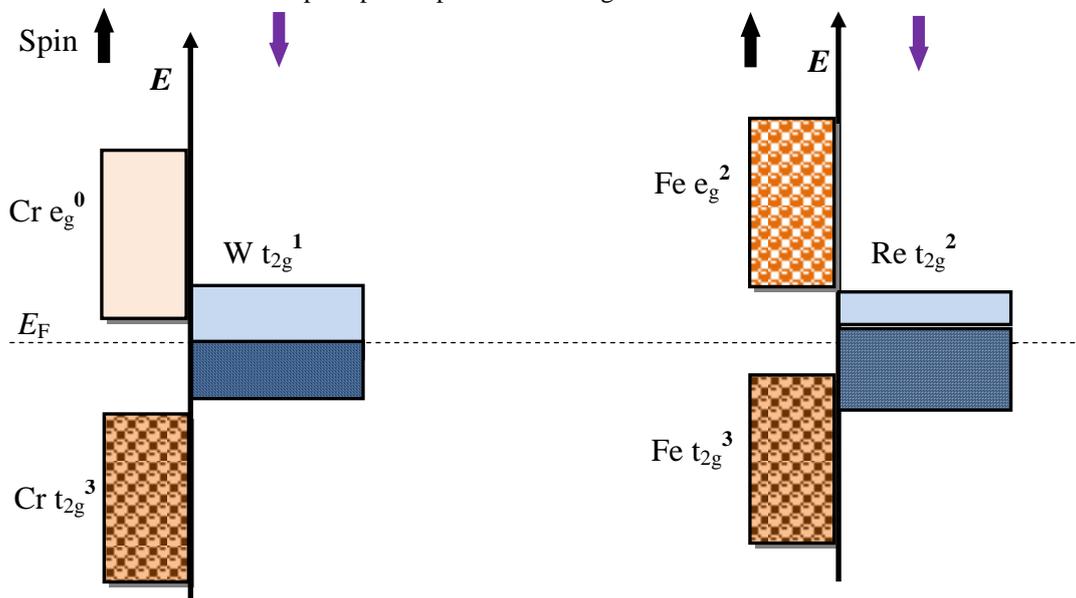
Fig. 4. Representation of the electronic density of spin-up ($\uparrow$) and spin-down ($\downarrow$) states in 100% electronic spin-polarized half metal in the Sr_2CrWO_6 and Sr_2FeReO_6 materials. The quantity of filling signifies the effect of t_{2g} and e_g orbitals in 3d and 5d bands per unit volume and per unit energy E. E_F is the Fermi energy.

V. Conclusion

We have comparatively studied the electronic and magnetic characterizations of complex perovskites Sr_2CrWO_6 and Sr_2FeReO_6 by using the linearized muffin- tin orbitals through the atomic-sphere approximation method within the local spin density approximation, including the interchange-correlation potential through the LSDA+U technique. The band structure results demonstrated half-metallic ferrimagnetic ground state for Sr_2CrWO_6 and Sr_2FeReO_6 with total magnetic moment of 1.878 μ_B and 3.184 μ_B per formula unit, respectively, in exact agreement with the theoretical and experimental results. The obtained HM-FiM feature in complex perovskites Sr_2CrWO_6 and Sr_2FeReO_6 makes these materials suitable for many applications. It established that they have a high degree of electronic spin-polarization which means that they will have the potential spin transport electronics (spintronics), where spin currents are utilized as well as charge currents.

Acknowledgments

References

[1]   Horng-Tay Jeng, and G. Y. Guo, Phys. Rev. B 67, 094438, (2003) 1 – 7.
[2]   L. Brey, M. J. Calderón, S. Das Sarma, and F. Guinea, Phys. Rev. B 74, 094429 (2006) 1-7.
[3]   A. H. Habib, A. Saleem,C. V. Tomya, D. Bahadur, J. Appl. Phys. 97, 10A906 (2005) 1- 4.
[4]   J. Cheng and Z. Q. Yang, Phys. Stat. sol. (b) 243, No. 6 (2006) 1151 – 1158.
[5]   I. V. Solovyev, Phys. Rev. B 65, 144446 (2002) 1-17.
[6]   Tapas Kumar Mandal, Claudia Felser, Martha Greenblatt, and Jurgen Kubler, Phys. Rev. B 78, 134431 (2008) 1 – 8.
[7]   G. Vaitheeswaran, V. Kanchana, and A.Delin, Appl. Phys. Letts. 86, 032513 (2005) 1–3.
[8]   S. Jain, A. O. Adeyeye, and C. B. Boothroyd, J. Appl. Phys. 97, 093713, (2005).
[9]   Joonghoe Dho, Sanghoon Ki, A. F. Gubkin, J. M. S. Park, and E. A. Sherstobitova, Solid State Commun. 150, (2010) 80 – 90.
[10]   L. C. Moreno, J. S. Valencia, D. A. Landinez Tellez, J. Arbey Rodriguez M., M. L. Martinez, J. Roa-Rojas, and F. Fajardo, J. Magnets. Magnet. Mater. 320, (2008) 19-21.
[11]   Koichiro Inomata, Naomichi Ikeda, Nobuki Tezuka, Ryogo Goto, Satoshi Sugimoto, Marek Wojcik, and Eva Jedryka, Sci. Technol. Adv. Mater. 9, 014101, (2008).
[12]   Yoshio Miura, Kazutaka Nagao, and Masafumi Shirai, Phys. Rev. B 69, 144413 (2004)1-7.
[13]   C. M. Bonilla, D. A. Landinez, J. Arbey, E. Vera Lopez and J. Roa-Rojas, Physica B 398, (2007) 208 – 211.
[14]   Akira Isayama, Shogo Kadota, Hideomi Yui, and Takao Sasagawa, Mater. Scien. Engin.: B 173, (2010) 44 - 46.
[15]   Q F Li, X F Zhu, and L F Chen, J. Phys.: Condens. Matter 20, 255230 (2008) 1 – 8.
[16]   M. El-Hagary, J. Alloys and Compounds 502, 2, (2010) 376 – 381.
[17]   Hua Wu, Phys. Rev. B 64, 125126, (2001).
[18]   J. B. Philipp, P. Majewski, L. Alff, R. Gross, T. Graf, M. S. Brandt, J. Simon, T. Walther, W. Mader, D. Topwal, and D. D. Sarma, Phys. Rev. B 68, 144431 (2003).
[19]   J. B. Philipp, D. Reisinger, M. Schonecke, A. Marx, A. Erb, L. Alff, R. Gross, and J. Klein, Appl. Phys. Letts. **79**, 3654 (2001) 1 - 3.
[20]   M. Zwierzycki and O. K. Andersen, Acta Physica Polonica A, 1, V. 115 (2009).
[21]   G. Vaitheeswaran, V. Kanchana, and A.Delin, Appl. Phys. Letts. 86, 032513 (2005) 1–3.
[22]   G. Vaitheeswaran, V. Kanchana and A.Delin, J. Phys.: Confer. Ser. 29 (2006) 50 - 53.
[23]   Yan Zhang, Vincent Ji, Physica B: Condens. Matter 407, 5, (2012) 912 – 917.
[24]   T. S. Chan, R. S. Liu, G. Y. Guo, S. F. Hu, J. G. Lin, J. –F. Lee, L. –Y. Jang, C. –R. Chang and C. Y. Huang, Solid State Commun. 131 (2004) 531 - 535.