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Electronic band profiles and magneto-electronic properties of ternary XCu_2P_2 (X = Ca, Sr) compounds: insight from *ab initio* calculations

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Abstract: Full-potential augmented plane waves (FP-APW) method is applied to determine the electronic band profiles and magneto-electronic properties of XCu_2P_2 (X = Ca, Sr) compounds. We have adopted Perdew, Burke and Ernzerhof's generalized gradient approximation (PBE-GGA) along with GGA plus Hubbard *U* parameter method (GGA+*U*) as exchange correlation potentials. The physical properties of interest for XCu_2P_2 (X = Ca, Sr) compounds were analyzed for the first time in the Zintl phase of tetragonal structure with space group I4/mmm (No. 139). From the structural parameters we have found that ferromagnetic phase is more stable as compared to paramagnetic and antiferromagnetic phase. Electronic band profiles predict the metallic nature of these compounds in FM phase. The projected densities of states computed in this work recognize that the bonding is accomplished through hybridization of Cu-3*d* with P-*p* states. The evaluated magnetic moments support weak ferromagnetism in these compounds. The compounds of interest are thermodynamically stable. In addition, the cohesive energies and Curie temperatures of the studied compounds were also predicted. Metallic and ferromagnetic nature of XCu_2P_2 (X = Ca, Sr) compounds predict the important of these compounds in spintronic devices.

Keywords: DFT calculations; electronic structures; ferromagnetic properties; FP-LAPW.

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1 Introduction

The AB_2C_2 type ternary compounds with $ThCr_2Si_2$ structure have great importance due to their novel electronic and magnetic properties. Important among these compounds are the iron-based pristine compounds AFe_2As_2 (*A* = Ca, Sr, Ba, Eu) [1]. Several attempts have been focused in the past on Mn based arsenides, for studying the difference between the properties of pristine $ThCr_2Si_2$-type high-*T*c superconductors and doped $BaMn_2As_2$ systems [2–4]. It was reported that when the temperature of semiconducting $BaMn_2As_2$ is below the Neel temperature (T_N = 625 K), it exhibits G-type antiferromagnetic arrangement and deviates the direction along *c* axis. The compounds having composition AB_2C_2 pnictides (*A* = Ca, Sr, Ba, *B* = transition metal, *C* = P, As, Sb) show unique properties as well as spacious range of doping potential either by electrons or holes [5], therefore the investigation of these compounds are highly desirable.

It is recommended that this type ($ThCr_2Si_2$) of a material is situated at the border-line of an interlayer C–C bonding instability, and breaking and forming of the C–C bond will alter the shape of the tetrahedron as well as the charge rearrangement within the A–B–C bonded layers [5].By changing the choices of A or B element possibly affect the formation of C–C bond in these phases; further influences occur on the crystal structures, magnetism, and the presence of superconductivity in these pnictides. Being after this assumption, a lot of investigations and some motivating behaviors other than the high-temperature superconductivity of these pnictides (122-type) have been carried out, e. g., itinerant ant ferromagnetism are found in $CaCo_2P_2$ [6] and $BaCr_2As_2$ [7]. $BaMn_2As_2$ are examined as an antiferromagnetic insulator [8], Pauli paramagnetic metallic behavior in $CaNi_2P_2$ [9] and $CaFe_2P_2$, [9], the compounds XCu_2Pn_2 (X = Sr, Ba; Pn = As, Sb), [10–12] show almost T-independent diamagnetism with metallic nature. Further superconductivity displayed in $SrNi_2P_2$ (T_C < 4 K), [13] and $BaNi_2P_2$, [14]. Zeng et al. [15] reported that in Cu-based materials that it (Cu^{2+}) is responsible for the super exchange interaction; however, the magnetic interactions are negligible or extremely weak.

Different attempts have been made in the past to investigate the structural and magneto-electronic properties of compounds with structure type AB_2C_2, although there is no notable theoretical work mainly on the magneto-electronic electronic properties of XCu_2P_2 (X = Ca, Sr) compounds by purposing density functional theory (DFT). The GGA+U method give us relatively better results as compared to PBE-GGA. Presently, our concentration is mainly focused on the electronic and magnetic properties of $CaCu_2P_2$ and $SrCu_2P_2$ compounds to cover up the lack of theoretical information of these compounds by purposing Full-potential augmented plane waves (FP-APW) method. We expect that our results will provide a platform for further experimental and theoretical test.

2 Method of calculation

The $CaCu_2P_2$ and $SrCu_2P_2$ compounds are classified as Zintl phase and exist in tetragonal structure (Figure 1) with space group I4/mmm (No. 139) [16]. Calculations are done for these compounds by employing DFT [17, 18] based on FP-APW approach as follow up in WIEN2K code [19]. For the treatment of exchange (E_{ex}) and correlation (E_{co}) potential, we have applied different approximation techniques, named as Perdew, Burke and Ernzerhof's generalized gradient approximation (PBE-GGA) [20] and GGA+U [21, 22]. Spherical harmonics are formed with the help of these two primary functions electron densities and potential by a circular atomic sites with a cutoff of l_{max} = 10, although the charge density was Fourier expanded up to G_{max} = 12 atom unit (au)$^{-1}$, where G_{max} is leading vector in Fourier expansion. The wave functions are increased in the extent of interstitial domain (ID) to plane waves with a cutoff of K_{max} = 7.0/RMT, Whereas, average radius of muffin-tin spheres gives us RMT and K_{max} represents the higher magnitude value of K vector in the plane wave. The Hubbard U value is taken 0.58 Ry for Cu d-states in the DFT+U calculations. We have taken the value of non-overlapping muffin-tin radii as (2.5, 2.1, 1.8) au For (Ca/Sr, Cu, P) elements respectively. We have used 1000 k points Monkhorst–Pack mesh [23, 24] in the Brillion zone for these compounds in ferromagnetic phase.

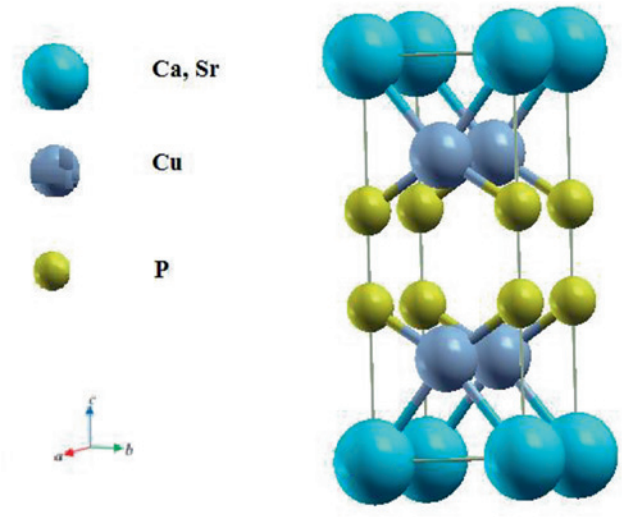

Figure 1: Crystal structure of XCu_2P_2 unit cell of the tetragonal structure.

3 Results and discussion

3.1 Structural properties

In this section XCu_2P_2 (X = Ca, Sr) compounds are optimized in the tetragonal structure with space group $I4/mmm$ (139). Along with this section we have purposed in addition to GGA, the GGA+U formalism in the FM phase. We have optimized our studied compounds in three different phases, namely paramagnetic (PM), ferromagnetic (FM), and antiferromagnetic (AFM). Interestingly, the studied compounds stabilize in the FM phase as predicted from Figure 2. To further determine the material structure performance, we have computed the structural parameters such as lattice parameter a (Å), bulk modulus, B (GPa), and pressure derivative (B^p) through the volume optimization process in the Birch Murnaghan's equation of state [25] in Table 1. The lowest energy state is called the ground state (stable state) energy and the volume correspond to this energy is called optimized volume. It is seen from Table 1 that the computed lattice constants and bulk moduli increases if we move down the group from Ca to Sr, which means that the size of the unit cell increases and the substitution of Ca with Sr forced the hardness of the materials. The negative values of the energy difference between ferromagnetic and anti-ferromagnetic phase predicted in Table 1 also support the ferromagnetic phase of these compounds. To the date there is no experimental/theoretical data available in the literature for the studied compounds to be compared with our present results, therefore further experiment could test these results.

3.2 Electronic properties

The electronic nature of XCu_2P_2 (X = Ca, Sr) compounds are investigated by computing the electronic band structure and

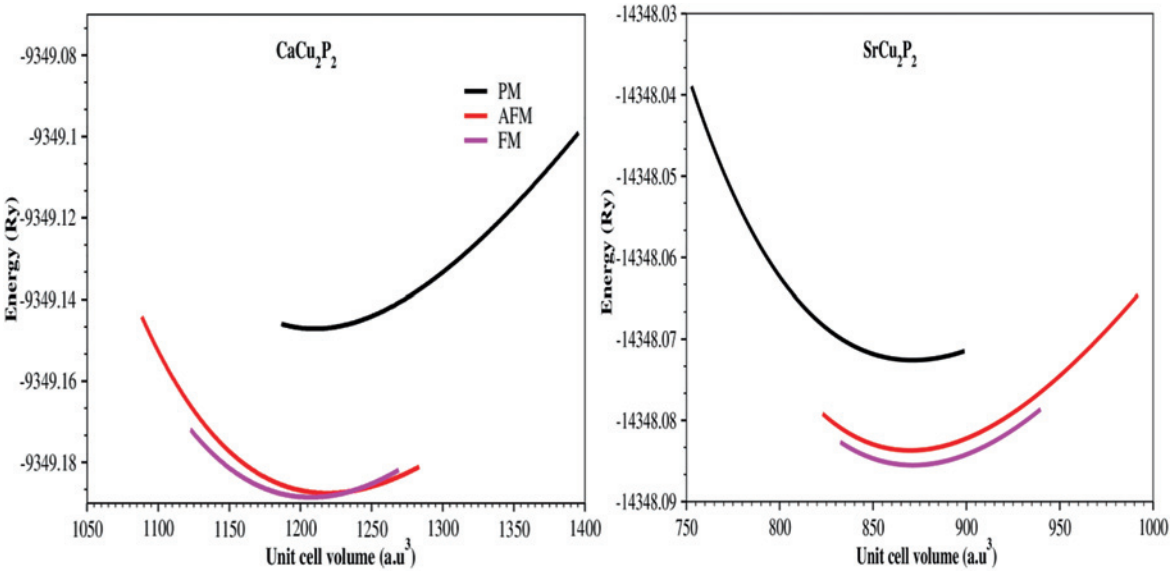

Figure 2: Optimization plots showing energy verses volume for XCu_2P_2 (X = Ca, Sr).

Table 1: The ground state structural parameters a/c, B, B^p, E_{FM}, E_{AFM} and E_{NM} for XCu_2P_2 (X = Ca, Sr) compounds.

Compounds	Lattice constant (Å)		V_0 (a.u)^3	B (GPa)	B^p	E_0 (Ry)			
	a	*c*				FM	AFM	NM	$\Delta E = E_{FM} - E_{AFM}$
$CaCu_2P_2$	4.9	10.26	837.17	48.33	3.85	−9349.19	−9349.18	−9349.16	−0.01
$SrCu_2P_2$	5.0	10.28	871.36	43.73	5.0	−14348.09	−14348.08	−14348.07	−0.01

density of states (DOS). For the analyses of band structure of these compounds GGA+*U* scheme in the ferromagnetic phase were adopted. The electronic energy band structure of XCu_2P_2 (X = Ca, Sr) compounds in the tetragonal structure of both spin channels with optimized lattice parameters along with the high symmetry points within the first Brillion zone are exhibited in Figures 3a and 3b respectively. Majority (spin up) and minority (spin dn) spin states in both figures are indicated on left side and right side respectively. In view of Figure 3a, the conduction band (CB) minimum and valance band (VB) maximum of $CaCu_2P_2$ crosses the Fermi level E_f along Γ and H direction in both spin channels. While in Figure 3b for $SrCu_2P_2$ compound many of them just cross the Fermi level in both spin channels. Moreover, the conduction bands overlap with the valence band near the Fermi level for both compounds. As a result, clearly no noticeable band gap are examined and these compounds behave as a metal, in the ferromagnetic phase. The gross features of the band structures of $CaCu_2P_2$ and $SrCu_2P_2$ are nearly same.

To further extend the electronic properties of these compounds we have evaluated the total (TDOS) and partial (PTDOS) densities of states of XCu_2P_2 (X = Ca, Sr) compounds. The TDOS and PTDOS of XCu_2P_2 are shown in Figure 4. As can be seen form Figure 4 that the TDOS has a fixed value at the Fermi level E_f, around 1.0 and 1.8 states per electron volt per unit cell, for $CaCu_2P_2$ and $SrCu_2P_2$ compound respectively. $CaCu_2P_2$ is small contribution as compared to $SrCu_2P_2$ at the E_f. The DOS at the E_f increases considerably due to the substitution of Ca by Sr. The facts of the peak structures in the TDOS and PDOS for $CaCu_2P_2$ and $SrCu_2P_2$ are nearly comparable. One remarkable difference is that the relative heights in the DOS at the VB and Fermi level E_f for $SrCu_2P_2$ are dominated as compared to $CaCu_2P_2$. The dominant states in these compounds are due to Ca-*d*, Cu-*d*, P-*p* and Sr-*d*, Cu-*d*, P-*p* states for $CaCu_2P_2$ and $SrCu_2P_2$ respectively in both spin channels (up and down). Cations (Ca, Sr) and anion (P) are situated in CB and VB dominantly in both spin types. The occupied valence bands (VB) usually spread from −7.8 eV to the Fermi level E_f for $CaCu_2P_2$ compound, while for $SrCu_2P_2$ compound the VB spreads from −6 eV to −4 eV dominantly in both spin types.

The TDOS are not symmetrical due to exchange splitting occur in both of the compounds. The contributions of

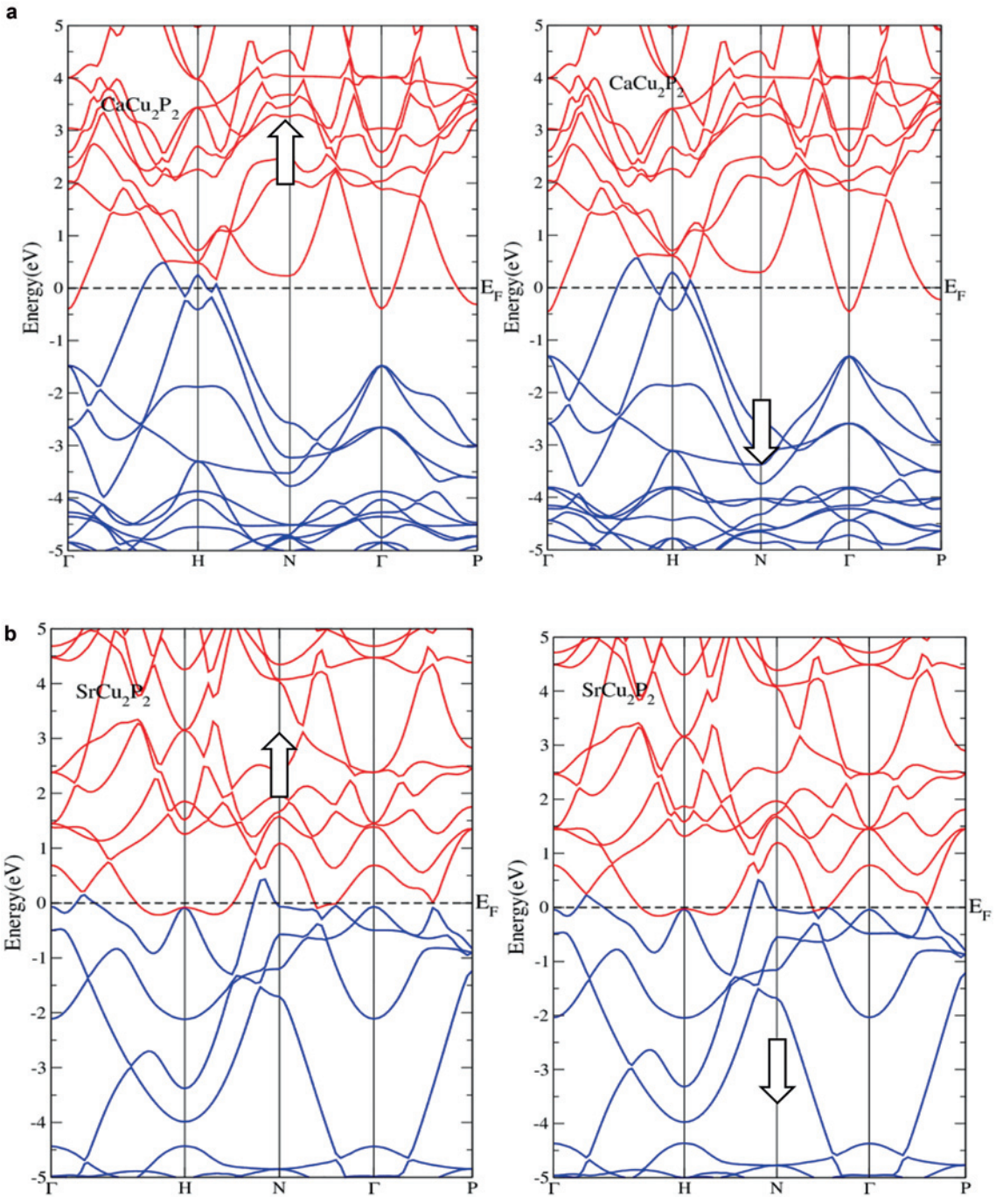

Figure 3: a. Band structure of $CaCu_2P_2$ in spin polarized calculations in both modes calculated using GGA+*U*. b. Band structure of $SrCu_2P_2$ in spin polarized calculations in both modes calculated using GGA+*U*.

d (Cu) states are dominantly buried in VB for both compounds which are not the same like the DOS of rare earth metal (Ca, Sr). High sharp peaks of *d* (Cu) states are observed in VB in both compounds. In the VB regime, we determine the existence of hybridization occur between Cu *3d* and P *3p* states. Examination of the PDOS shows that the DOS for XCu_2P_2 at the Fermi level originates mainly from the hybridized contributions from the Cu *3d* and P *3p* electronic orbitals. Hybridization for FM is important for partial *d*-band filling on account of the super or double exchange. In these FM states super exchange couplings occur due d states which are isolated from the E_f level [15]. These plots show metallic character in both spin directions.

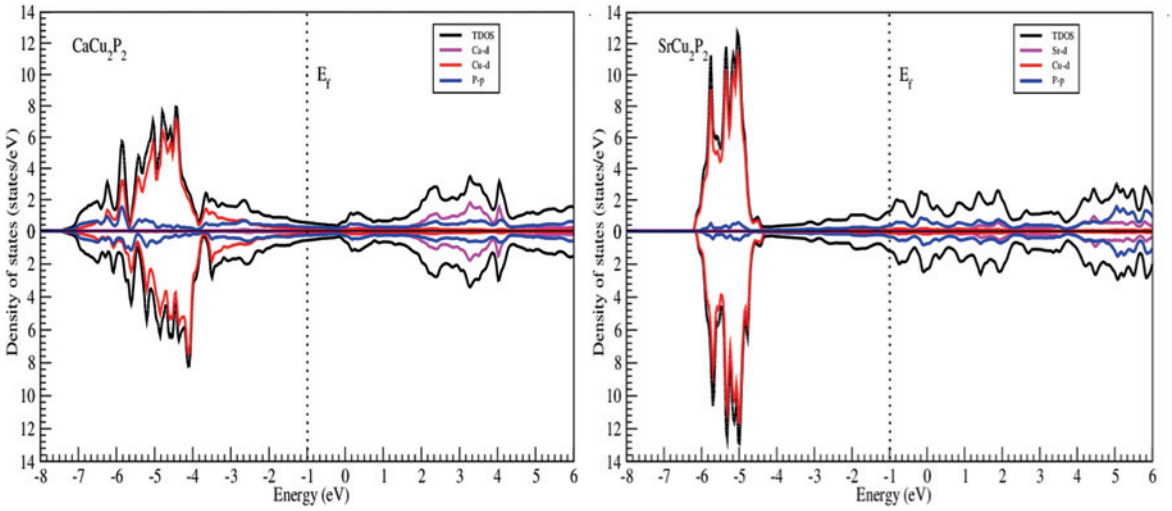

Figure 4: DOS plots for ternary compound $CaCu_2P_2$ and $SrCu_2P_2$ in both the spin directions using GGA+*U*.

3.3 Magnetic properties

To get more information about the magnetic properties of XCu_2P_2 (P = Ca, Sr) compounds, we have computed the total and atomic magnetic moments of XCu_2P_2 (P = Ca, Sr) in Table 2. Here we have used GGA+*U* scheme, so the function of the *U* parameter appears to improve the localization of transition-metal element (Cu). It is evident from Table 2 that in both compounds, $CaCu_2P_2$ and $SrCu_2P_2$ the most important regions of the total magnetic moments are due to *d* (Cu), *p* (P) and *d* (Sr), *p* (P) orbitals respectively. To obtain insight into the atomic magnetic moments, it can be seen that the magnetic moments of the Cu and P atoms in $CaCu_2P_2$ are 0.10940 μ_B and 0.00546 μ_B, respectively which are parallel to the magnetic moments of Ca atom, and $SrCu_2P_2$ compound the magnetic moment of Cu atom is –0.00286 μ_B, which is anti-parallel to the magnetic moments of Ca and P atoms. As a result of the magnetic moment analysis given in Table 2. The total magnetic moment of each cell, m_c, for each of the compound, as well as their individual atomic magnetic moments, are given in Table 2. The magnetic moments of these compounds show weak Ferromagnetic behavior.

Moreover, it is clear from FM phase that magnetism are mostly arises in the DOS plots due to the strong spin coupling of the Cu-*d* and P-*p* states near the Fermi level. To get insight into the Cu exposed that it is the unfilled 3*d* (e_g) orbitals that play significant role in the magnetic nature of these compounds. The *d*-orbitals of these commonly split into $e_g(dz^2, dx^2\text{-}y^2)$ states. For $CaCu_2P_2$ and $SrCu_2P_2$ the electronic configuration will lead to valence electrons filling the lower *d*-orbitals, giving rise to a total magnetic moment of 0.17 and 0.1 μ_B for both compounds respectively.

3.4 Formation energy

From thermodynamic point of view there is no inclusive experimental work on XCu_2P_2 compounds. Therefore, we required to check their thermodynamic stability by determining the energy of formation and cohesion energy [26, 27] of these compounds like in our previous work [28]. The formation energy (E_f) is defined as a required energy quantum which dissociates the links between atoms to form the solid. From the computed negative values of E_f in Table 3, we can predict that these compounds are thermodynamically stable.

3.5 Cohesive energy

The cohesion energy (E_C) determines the value of the strength of the force that holds atoms together in the materials, which predict the structural stability in the ground

Table 2: Magnetic moments of the interstitial region, individual atoms and total unit cell of XCu_2P_2 (X = Ca, Sr) compounds for spin ferromagnetic configurations.

Compounds	m^{Inst}	$m^{Ca/Sr}$	m^{Cu}	m^{P}	m^{c}
$CaCu_2P_2$	–0.04182	–0.01272	0.10940	0.00546	0.17517
$SrCu_2P_2$	0.08000	0.00604	–0.00286	0.00813	0.09661

Table 3: Calculated total energy (E_0), individual energies of Ca, Sr, Cu, and P and formation energy (E_f) of XCu_2P_2 are given in Ry unit.

Compound	E_0	E_{Ca}	E_{Cu}	E_P	E_f
$CaCu_2P_2$	−9349.19	−1360.659389	−6619.371498	−1367.88612	1.27
$SrCu_2P_2$	−14348.09	−6359.595248	−6619.371498	−1367.88612	1.24

state. The cohesion energy E_C of these compounds is computed using the following relation [29].

$$E_C = E^{isol}_{Ca} + 2E^{isol}_{Cu} + 2E^{isol}_{P} - E_{CaCu_2P_2}{}^{total} \quad (1)$$

$$E_C = E^{isol}_{Sr} + 2E^{isol}_{Cu} + 2E^{isol}_{P} - E_{SrCu_2P_2}{}^{total} \quad (2)$$

where $E_{CaCu_2P_2}{}^{total}$ and $E_{SrCu_2P_2}{}^{total}$ are the equilibrium total energy per formula unit of XCu_2P_2 (P = Ca, Sr) compounds respectively determined by first principles and E^{isol}_{Ca}, E^{isol}_{Sr}, E^{isol}_{Cu} and E^{isol}_{P}, are the energies of isolated Ca, Sr, Cu and P atoms, respectively. This is the energy needed to dissociate the crystal in to fragments, which is not only an indicator of the bond strengths but also an indicator of the mobility of atoms in the crystal. The computed values of E_C are −127 eV and −124 eV for the $CaCu_2P_2$ and $SrCu_2P_2$ respectively. The high value of cohesion energies of these compounds predict the strong chemical binds in these compounds.

3.6 Curie temperature

The Curie temperature (TC) of XCu_2P_2 compounds are also calculated for XCu_2P_2 compounds by the method introduced in our previous work [30].The Curie temperature was evaluated having in hands the total magnetic moments μ_B, using the following expression [31–32].

$$T_C\,(\mathrm{K}) = 2/3 + 181\,\mathrm{m_c}\,(\mu_B) \quad (3)$$

where

$$\mu_B = 9.27 \times 10^{-24}\ \mathrm{A{-}m^2}$$

The calculated values of Curie temperature for $CaCu_2P_2$ and $SrCu_2P_2$ are 54.70 K and 40.49 K respectively. The higher value of Curie temperature for $CaCu_2P_2$ shows strong interaction among the magnetic atoms as compared to $SrCu_2P_2$.

4 Conclusion

In this article we have carried out first-principles DFT calculations to predict the electronic and magnetic properties of XCu_2P_2 compounds by employing FP-APW approach within the WIEN2K code with PBE-GGA and GGA+*U* techniques as exchange correlation potentials. We have observed that the ferromagnetic arrangement is more suitable than the PM and AFM phase configurations. The electronic properties reveal the metallic nature for both compounds in ferromagnetic phase. Upon applying GGA+*U* method, the compounds show metallic behavior with overlapping bands in both spin channels. It has been cleared in electronic properties that d states of Cu atoms are buried in VB completely. DOS shows that the contribution of the valence and conduction bands are dominated by the *d* (Ca, Sr, Cu) and *p* (P) states elements in these compounds. The strong hybridization occurred between *d* (Cu) and *p* (P) states in both compounds. Also, the studies on magnetism suggested that *p* (Cu) and *p* (Sr), atoms are chief contributors to the magnetic moments of $CaCu_2P_2$ and $SrCu_2P_2$ compounds respectively. The compounds of interest are thermodynamically stable. In addition the cohesive energies and Curie temperatures of the studied compounds were also predicted. The electronic and magnetic properties of XCu_2P_2 (X = Ca, Sr) compounds predict the important of these compounds in spintronic devices.

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References

[1] N. S. Sangeetha, A. Pandey, Z. A. Benson, and D. C. Johnston, *Phys. Rev. B*, vol. 94, no. 9, 094417, 2016.
[2] Y. Singh, A. Ellern, and D. C. Johnston, *Phys. Rev. B*, vol. 79, 094519, 2009.
[3] Y. Singh, M. A. Green, Q. Huang, et al., *Phys. Rev. B*, vol. 80, p. 100403(R), 2009.
[4] D. C. Johnston, R. J. McQueeney, B. Lake, et al., *Phys. Rev.*, vol. B84, p. 094445, 2011.

[5] L. Li, D. Parker, M. Chi, G. M. Tsoi, Y. K. Vohra, and A. S. Sefat, "Metallicity of Ca_2 Cu_6P_5 with single and double copper-pnictide layers," *J. Alloys Compd.*, vol. 671, pp. 334–339, 2016.
[6] R. E. Baumbach, V. A. Sidorov, X. Lu, et al., *Phys. Rev. B*, vol. 89, 2014.
[7] D. J. Singh, A. S. Sefat, M. A. McGuire, et al., *Phys. Rev. B*, vol. 79, 094429, 2009.
[8] Y. Singh, A. Ellern, and D. C. Johnston, *Phys. Rev. B*, vol. 79, 094519, 2009.
[9] S. Jia, S. Chi, J. W. Lynn, and R. J. Cava, *Phys. Rev. B*, vol. 81, 2010.
[10] V. K. Anand, P. K. Perera, A. Pandey, R. J. Goetsch, A. Kreyssig, and D. C. Johnston, *Phys. Rev. B*, vol. 85, 214523, 2012.
[11] B. Saparov, and A. S. Sefat, *J. Solid State Chem.*, vol. 191, 213, 2012.
[12] S. F. Wu, P. Richard, A. van Roekeghem, et al., *Phys. Rev. B*, vol. 91, 235109, 2015.
[13] F. Ronning, E. D. Bauer, T. S. Park, H. Baek, H. Sakai, and J. D. Thompson, *Phys. Rev. B*, vol. 79, 2009.
[14] T. Mine, H. Yanagi, T. Kamiya, Y. Kamihara, M. Hirano, and H. Hosono, *Solid State Commun.*, vol. 147, 111, 2008.
[15] J. Zeng, S. Qin, C. Le, and J. Hu, "Magnetism and superconductivity in the layered hexagonal transition metal pnictides," *Phys. Rev. B*, vol. 96, no. 17, 174506, 2017, doi: 10.1103/PhysRevB.96.174506.
[16] A. Mewis, "Der $ThCr_2Si_2$-Typ und verwandte Strukturen bei APd_2X_2-verbindungen (A = Ca, Sr, Ba; X = P, As)/ the $ThCr_2Si_2$-type and related structures of APd_2X_2-compounds (A—Ca, Sr, Ba; X = P, As)," *Z. Naturforsch. B*, vol. 39, no. 6, pp. 713–720, 1984, doi: 10.1515/znb-1984-0603.
[17] P. Hohenberg and W. Kohn, *Phys. Rev.*, vol. 136, pp. B864–B871, 1964.
[18] W. Kohn and L. J. Sham, *Phys. Rev.*, vol. 140, pp. A1133–A1138, 1965.
[19] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2K, an augmented plane wave plus local orbitals program for calculating crystal properties*, Vienna: Vienna University of Technology, 2001.
[20] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, vol. 77, 3865, 1996.
[21] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, *Phys. Rev. B*, vol. 52, R5467, 1995.
[22] O. Bengone, M. Alouani, P. Blochl, and J. Hugel, *Phys. Rev. B*, vol. 62, 16392, 2000.
[23] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, vol. 13, pp. 5188–5192, 1976.
[24] J. D. Pack and H. J. Monkhorst, *Phys. Rev.B*, vol. 16, pp. 1748–1749, 1977.
[25] K. M. Wong, M. Irfan, A. Mahmood, G. Murtaza, *Optik*, vol. 130, 517, 2017.
[26] J. Wang and Y. Zhou, *Phys. Rev. B*, vol. 69, no. 21, 214111, 2004.
[27] G. Chen, X. Q. Wang, K. Fu, et al., *Appl. Phys. Lett.*, vol. 104, no. 17, 172108, 2014.
[28] M. E. Monir, H. Ullah, H. Baltach, M. G. Ashiq, and R. Khenata, *J. Magn. Magn Mater.*, vol. 442, pp. 107–117, 2017.
[29] X. P. Wei, Y. Zhang, T. Wang, et al., *Mater. Res. Bull.*, vol. 86, 139, 2017.
[30] H. Ullah, F. S. Kayani, and R. Khenata, *Mater. Res. Express*, vol. 6, 12, 2019.
[31] S. Wurmehl, G. H. Fecher, H. C. Kandpal, et al., *Phys. Rev. B*, vol. 72, 184434, 2005.
[32] A. Candan, G. Ugur, Z. Chari, H. Baaziz, and M. R. El-lialtioglu, *J. Alloys Compd.*, vol. 560, 215, 2013.