THEORETICAL PREDICTION OF POSSIBLE COEXISTENCE OF SUPERCONDUCTIVITY AND ANTIFERROMAGNETISM IN NOVEL $SrFeRuBi_2$, $SrRu_2Bi_2$ AND PARENT $SrFe_2Bi_2$ COMPOUNDS

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The optimized properties of the $SrFe_2Bi_2$ compound are compared with its iso structural compounds by gradual replacing of Ru in Fe position, namely $SrFeRuBi_2$, $SrRu_2Bi_2$ compounds by means of first principles calculation. Energies of the reported compounds at various magnetic orders, stability nature and electrical resistivity at ambient temperature are calculated. All the observed parameters with its conducting behaviour are used to analyze the superconducting nature of the reported compounds. In this group $SrFe_2As_2$ compound, is reported as an antiferromagnetic coexisting superconducting compound. This leads our main interest to focus the magnetic and superconducting nature of the proposed compounds.

Keywords: Intermetallic compounds; Fermi surface; Anti ferro magnet; High Tc superconductors; DFT.

1. Introduction

Among the recently discovered iron-based high-temperature superconductors, two main groups are identified as iron pnictides and iron chalcogenides. The parent compounds of these iron-pnictides are metallic, while the parent compounds of cuprates are Mott insulators. From the literature [1] it is understood that several structural families are possible for iron (Fe) pnictides (Pn), such as ternary 111 (e.g. LiFePn), 122 (e.g. $BaFe_2Pn_2$), quaternary 1111 (e.g. LaFePnO) and five-component 32225 (e.g. $Sr_3Sc_2Fe_2Pn_2O_5$), etc., Of which the present study deals with the band structure study of newly proposed Iron(Fe)/Ruthenium(Ru) replaced 122 pnictide compounds. AT_2Pn_2 Materials with $ThCr_2Si_2$ type structure (122 compounds) have attracted interest of solid state community for decades for the diverse bonding patterns and dimensionality that give rise to exotic physical properties. In the vicinity of room temperature, 122 (AFe_2Pn_2) compounds crystallize in tetragonal symmetry with no magnetic T(Fe)Pn layer, where Fe atoms form a 2D square sublattice with Pn atoms sit at

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the centre of these square, but off the Fe plane (above and below the plane alternately) [2,3].

Some $ThCr_2Si_2$-type compounds exhibit superconductivity and other physical properties are enhanced under chemical doping or under the application of external pressure. Upon doping or compressing, there is a transition in the magnetic order and the same support for superconducting state. Also in $Ba_{1-x}K_xFe_2As_2$, $BaFe_{2-x}Co_xAs_2$ and $SrFe_{2-x}Ru_xAs_2$ an unconventional superconductivity was discovered by doping at alkaline metal (A) or transition metal (T) site [4,5].

This motivates us to study about Ru substituted $SrFe_2Bi_2$ compound namely $SrFeRuBi_2$ compound. To provide a complete description, this study leads a comparative band structure study on $SrFe_2Bi_2$, $SrRu_2Bi_2$ and $SrFeRuBi_2$ compounds. In our previous work, $SrFe_2Bi_2$ is proposed as an unconventional superconductor [6]. In addition from the literature it is observed that superconducting transition temperature (T_C) can be enhancing in the presence of large concentration of the magnetic Fe in these layered compounds has provided an avenue to investigate the interplay of magnetism and superconductivity which may help in unraveling a long standing mystery of high temperature superconductivity and the same motivates us to do the present study [7].

2. Materials and Methodology

The calculations are carried out by means of Full Potential – Linearized Augmented Plane Wave (FP – LAPW) method as implemented in the WIEN 2K code [8].The Generalized Gradient Approximation parameterized by Perdew et al. [9] has been applied to calculate the exchange correlation potential [10,11]. These compounds exist in $ThCr_2Si_2$ type tetragonal structure, with the space group 139 (I4/mmm). The atomic positions for Sr is (0, 0, 0), for Fe/Ru is (0, 0.5, 0.25) and for Bismuth is (0, 0,Z_{Bi}). Here Z_{Bi} (variable position parameter) is the so-called internal coordinate governing the Fe/Ru–Bi distance (d). Muffin tin spheres of radius RMT are chosen in such a way that there is minimal charge leakage from the core. The calculations are performed with 1000 K-points in the Brillouin zone. The plane wave expansion (R_{MT} * K_{MAX}) is taken as 7. The self consistent calculations are carried out to an accuracy of 0.0001 Ry, 0.1 mRy and 0.001 |e| for energy, force and charge respectively. The theoretically calculated equilibrium lattice parameters form the optimized volume [12] are used to optimize c/a ratio, which are then used to optimize position of the (Z_{Pn}) pnictogen atoms in non magnetic (NM) order. The same optimization procedure has been done in ferromagnetic (FM) and anti-ferro magnetic (AFM) order with spin calculation. The optimized structural, positional, electronic, magnetic parameters and the total energy (E_{Total}) in Rydberg for non magnetic, ferro magnetic and antiferro

magnetic order of the compounds under study are calculated and reported. The resistivity calculation of the compounds is performed by using Boltzmann transport theory interfaced to the Wien2k program [13].

3. Results and Discussion

3.1 Replacing a single Fe by Ru in $SrFe_2Bi_2$ compound

The structural, electronic, magnetic, Bulk modulus and energy parameters of $SrFe_2Bi_2$ compound [6] are reported in Table 1 and are compared with available results [14]. The motivation to extend our study is prevailing literature [15] shows that the isovalent substitution of heavier element in lighter element provides an internal chemical pressure to the compound which could help in inducing superconductivity. As reference, substitution of As (Z = 33) in P (Z = 15) site at Eu 122 compound and Ru (Z = 44) in Fe (Z = 26) site at $BaFe_{2-x}Ru_xAs_2$ (x = 0.75) compound shows superconductivity in increased order of transition temperature (T_c~20 K). Qi et al. [16] reported that Ru substitution on the Fe site in $Ba(Fe_{1-x}Ru_x)_2As_2$ compound exhibit properties similar to the electron-doped $BaFe_2As_2$ series, at higher doping compositions. Hence we replace Fe in $SrFe_2Bi_2$ compound with its isovalent Ru by which the electronic environment of the compound will not be affected.

The volume, c/a ratio and positional parameters are optimized for $SrFeRuBi_2$ at ambient condition and the corresponding values are tabulated in Table 1. The corresponding crystal structure of $SrFeRuBi_2$ compound is shown in Fig.1. It has a tetragonal structure and it is iso structure with its parent $SrFe_2Bi_2$ compound with similar 139 (I4/mmm) space group. The observed bulk modulus is very high in Ru substituted Fe compound and the same depicts from the literature [17]. DOS at Fermi level ($N(E_F)$) and electron density plots are plotted to study the transport behavior of electrons and the bonding property of $SrFeRuBi_2$ are shown in Figs.2 and 3 respectively.

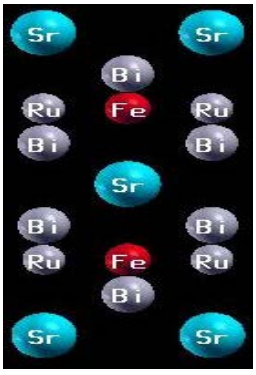


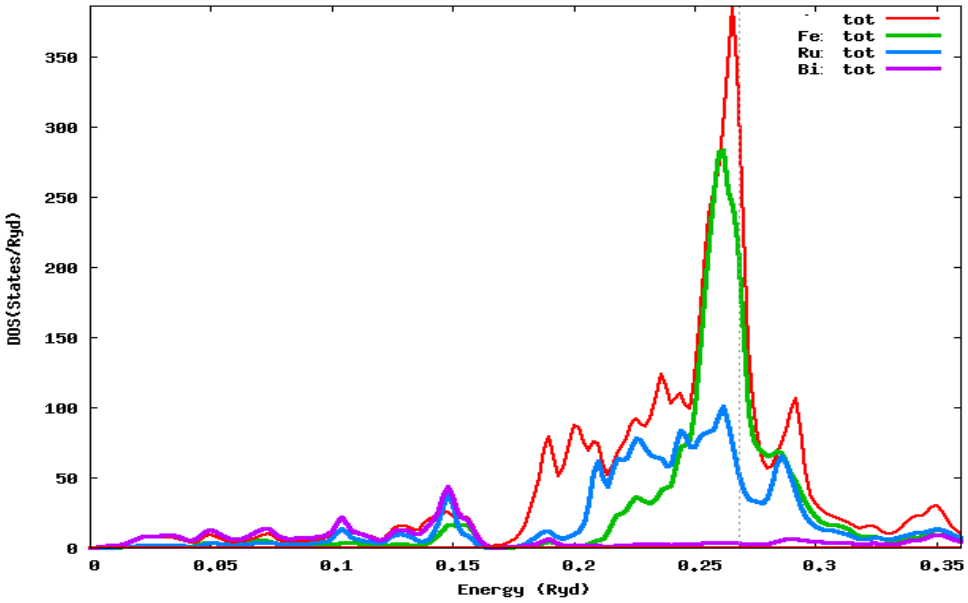
Fig. 1 crystal structure of $SrFeRuBi_2$ compound

Table 1

The optimized structural, electronic and magnetic parameters of $SrFe_2Bi_2$, $SrFeRuBi_2$ and $SrRu_2Bi_2$ compounds

Phase/Parameter	**$SrFe_2Bi_2$**	**$SrFeRuBi_2$**	**$SrRu_2Bi_2$**
a [a.u.]	8.4354 [6]	8.628	8.7078
c [a.u.]	23.3562 [6]	21.9262	22.1804
Z_{Bi}	0.3595 [6]	0.3606	0.3642
d[T-Bi] Bohr	4.9325 [6]	5.0167 (T-Ru) 4.5687 (T-Fe)	5.0372
d[Bi-Bi] Bohr	6.5631 [6]	6.3707	6.0237
Bulk modulus [GPa]	46.68	77.18	91.9025
Electronic specific heat coefficient [Gamma in mJ/(mol cell K**2)]	7.54 [6]	6.59	4.12
Fermi energy [Rydberg]	0.5465 [6]	0.2685	0.4062
$N(E_F)$ (states/Rydberg f.u)	43.50 [6]	38	23.75
Resisitivity (ρ) (μΩ-cm)	0.66	0.07	1.08
Total energy (Ryd.)	– 97777. 0525^{NM} – 97777. 0812^{FM} -102867.8728^{AFM}	– 108631.7899 ^{NM} -108585.9973^{FM} -118767.4120^{AFM}	-110813.2399^{NM} -110813.2399^{FM} -110813.23994^{AFM}
Magnetic Moment of the compound (Bohr magneton)	NA^{NM} 4.8261^{FM} 2.7055^{AFM} [Fe- I site – 2.66 (2.45)[13] Fe- II site – 1.99 (1.95)][13]	NA ^{NM} 2.01 ^{FM} –0.00003 ^{AFM}	NA ^{NM} 0.0053 ^{FM} 0.0001 ^{AFM}

^{NM} Non Magnetic; ^{FM} Ferro Magnetic; ^{AFM} Anti ferro Magnetic



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(b)

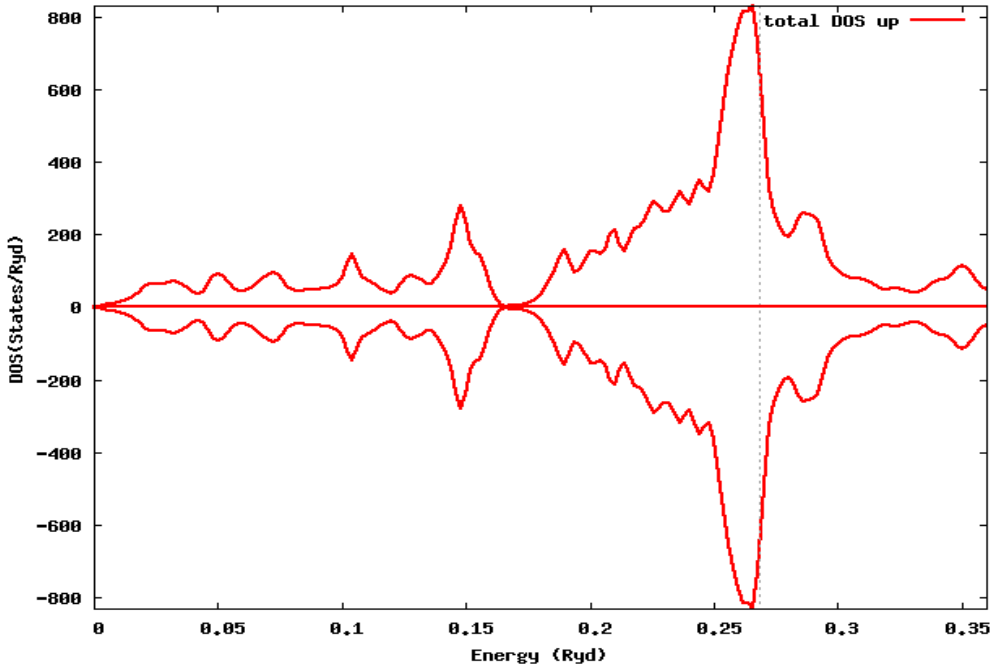


Fig. 2 $SrFeRuBi_2$ (a) Total and partial density of states (b) Comparative spin up and spin down density of states.

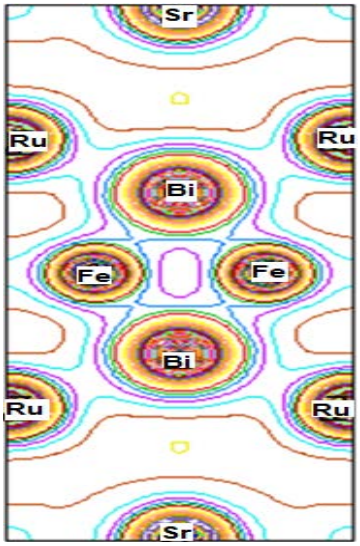


Fig. 3 Electron density plot of $SrFeRuBi_2$ compound

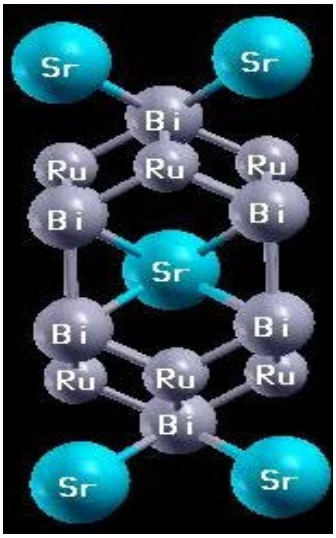


Fig. 4 $SrRu_2Bi_2$ crystal structure

3.1.1. Electron transport properties of $SrFeRuBi_2$ compound

To know the electron transport behavior, the total and partial DOS histograms and spin up and spin down density of states are drawn for $SrFeRuBi_2$ compound (Fig. 2a). In Fig. 2b, it is observed that Fe and Ru contributes the most to the total DOS at the Fermi level consistent with a general tendency that the DOS at the Fermi level are dominated by the d-band of the T atom and the contribution from Sr towards the Fermi level in DOS is found to be comparatively less [18]. Replacement of Fe by Ru, in $SrFe_2Bi_2$ compound leads decrement of $N(E_F)$; hence it is substantiated that Fe play a vital role towards metallic than Ru in present compound. The resistivity value is 0.07 (μΩ-cm), and it is one of the evidence for the possibility of superconductivity in this compound similar to its parent compound $SrFe_2Bi_2$ (0.66 μΩ-cm) listed in Table 1.

3.1.2. *Bonding properties of $SrFeRuBi_2$ compound*

To probe into the bonding properties of these compound charge density plots along (100) plane are plotted and are analysed, shown in Fig. 3. Directionality contours exist between Fe and Bi atoms, whereas no such covalent interaction is seen between Bi–Bi atoms in $SrFeRuBi_2$ compound. In $SrFeRuBi_2$ compound strong covalence is found between Ru and Fe (T) – Bi (Pn), and in both parent ($SrFe_2Bi_2$) [6] and novel ($SrFeRuBi_2$) compounds. Spherical charge density contours are exists around Sr atom which is an indication of metallic

nature of the compound. To extend and compose the comparative studies this work also concentrates over $SrRu_2Bi_2$ compound.

3.2 Replacing transition element Fe by Ru in $SrFe_2Bi_2$ compound

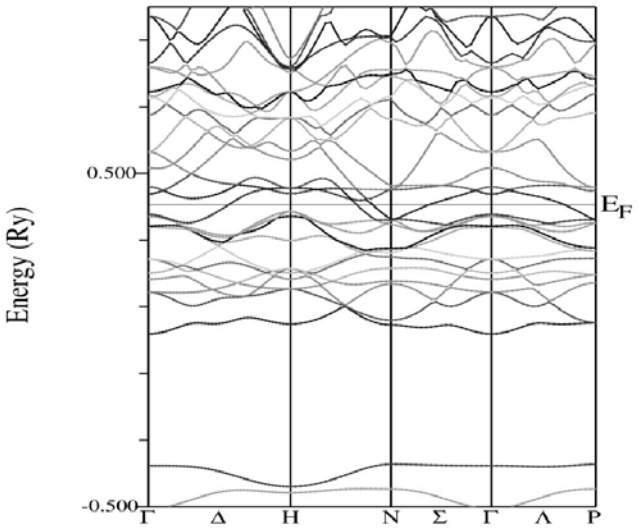
To explore the superconductivity beyond copper and iron as transition element, literature is available with Ru as a transition element. $LaRu_2(P/As)_2$ has been reported as a superconductor with transition temperature from 3.84 to 5.77 K using a pressure of 1.74 GPa [19]. Hence, in further study extends the replacement of Fe by Ru in $SrFe_2Bi_2$ compound.

The volume, c/a ratio and positional parameters of $SrRu_2Bi_2$ compound are optimized and derived from its respective parent compound $SrRu_2As_2$ [20]. The optimized structural parameters along with the distances (d) between the transition metal (Ru) - pnictogen (Bi) atoms, pnictogen - pnictogen (Bi) atoms, Fermi energy and DOS at Fermi level at ambient condition are given Table 1. The corresponding crystal structure of $SrRu_2Bi_2$ compound is shown in Fig.4.

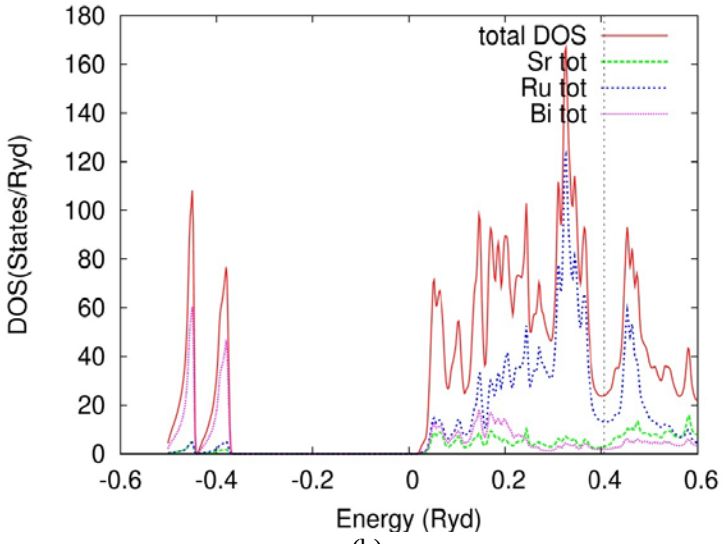
3.2.1. Electron transport properties in $SrRu_2Bi_2$ compound

To analyze the electron transport behaviour, the band structure plots and DOS histograms are drawn and shown in Fig.5. Band structure (Fig.5a) of Ru-based hypothetical compound reveals that several bands cross the Fermi level depicting the metallic nature of these compounds. The lowest lying bands around –0.45 Rydberg arise mainly from Bi-6s states and are separated by a gap; the energy bands located near the Fermi level at 0.4 Rydberg are formed predominantly by Ru-4d states and Bi-6p states. In Fig. 5b, Ru-4s states and Bi-p states are contributing more to the total DOS. Here, further $N(E_F)$ is reduces from $SrFe_2Bi_2$ compound due to Ru role and the same Ru role leads to increment of bulk modulus. Bulk modulus is one of the parameter which decides the hardness of the material and compressibility is the inverse of bulk modulus. Hence in $SrRu_2Bi_2$ compound the compressibility is very less/ hardness is high because of its bulk modulus.

Besides, it is noteworthy that the contribution from the valence states of Ba is negligible in the near Fermi region. Total and partial density of States of $SrRu_2Bi_2$ is being contributed from Ru-4d states. In addition, the Fermi level lies exactly at pseudo gap in $SrRu_2Bi_2$. Hence the crystal structure of $SrRu_2Bi_2$ could be more stable. Moon et al. [21] described that the pseudo gap is universally regarded as an essential part of the physics of unconventional superconductors and it is the one of the manifestations in the class of high T_C materials [22]. This is an evidence to achieve superconductivity in $SrRu_2Bi_2$ compound and its resistivity value 1.08 (μΩ-cm) is substantiate the same.



(a)



(b)

Fig. 5 $SrRu_2Bi_2$ (a) Band structure and (b) Electronic Density of States

3.2.2. Bonding properties of $SrRu_2Bi_2$ compound

To probe into the bonding properties of $SrRu_2Bi_2$, charge density plots along (100) plane is plotted and analyzed, shown in Fig.6. From the plot one can observe (i) directional contours exist between Ru and Bi atoms; whereas no such covalent interaction is seen between Bi–Bi atoms; there are spherical charge

density contours around Bi atoms which is an indication of metallic nature of the compound (ii) Electron clouds around [Ru_2Bi_2] blocks are separated from that of Sr atom and it is a sign of ionic interaction between [Ru_2Bi_2] blocks and Sr atom. Thus the charge density plots exits a mixed covalent, ionic and metallic behavior alike their parent compounds [23].

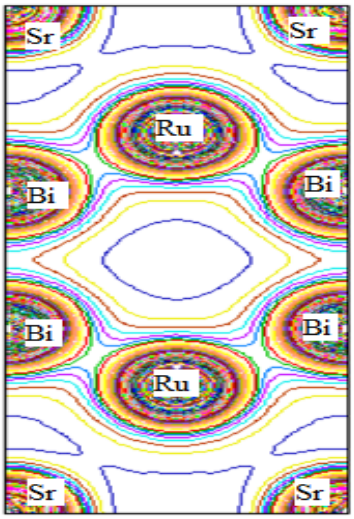


Fig. 6 Electron Density plot of $SrRu_2Bi_2$ compound

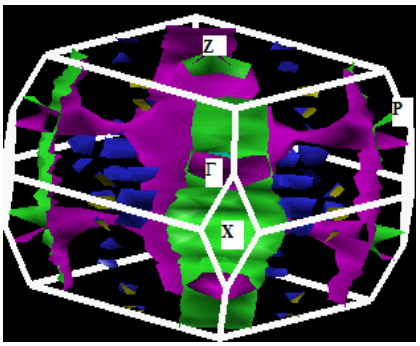
3.3. Magnetic properties of $SrFe_2Bi_2$, $SrFeRuBi_2$ and $SrRu_2Bi_2$ compounds

It is intriguing that superconductivity and antiferromagnetism compete for the same electrons which were not expected, especially when it is known that the magnetism is generally detrimental for superconductivity [24,25]. But in FeAs superconductors the antiferromagnetism is coexists with superconductivity. In the FeAs-based superconductors, antiferromagnetism is originates from conduction electrons and also form the cooper pairs when T below T_c. In '122' compound superconductivity could be induced from its antiferromagnetic parent compound by external pressure or by substitution of isovalent element. By taking it has a clue; we checked the total energy of the compounds namely $SrFe_2Bi_2$, $SrFeRuBi_2$ and $SrRu_2Bi_2$ for various magnetic orders and are given in Table 1, to extend our research towards their possibility for occurrence of superconductivity nature. It shows that $SrFe_2Bi_2$ and $SrFeRuBi_2$ compounds are stabled in antiferromagnetic order and total energy of $SrRu_2Bi_2$ compound is approximately same at all its magnetic order.

3.4. *Fermi surface plots of newly proposed $SrFeRuBi_2$ and $SrRu_2Bi_2$ compounds*

The Fermi surface plot of newly proposed compounds namely $SrFeRuBi_2$, $SrRu_2Bi_2$ are drawn and are depicted in Figure 7 and 8 respectively to validate the clues regarding the superconducting nature of the compounds. The observations from the Fermi surface plot of $SrFeRuBi_2$ compound (Fig. 7) are (i) Fermi surface plot is drawn by using the bands that crosses the Fermi level which are indexed as 48-52. This FS plot matches well with the plot reported in the literature [26] for the compounds $CaFe_2As_2$ which has been reported as a high T_C superconductor (ii) Electron sheet-like structures are seen at each of the four corners of the BZ at 'X', 'P' points (iii) hole cylinder-like structure is seen at 'Γ–*Z*' point along *Kz* direction of the Brillouin Zone (BZ).

The observations from the Fermi surface plot of $SrRu_2Bi_2$ compound (Fig. 8) are (i) two large distorted sheets of electron pockets around X and P points at each corner of the BZ (ii) flat pillow-like electron sheets at the top of the zone is observed at *Z* point along *Kz* direction, which arises due to Fermi crossings (bands 36, 37) and it is interconnected from a zone centre to the zone corner. These observations are similar with that of its $BaFe_2As_2$ compound [26].



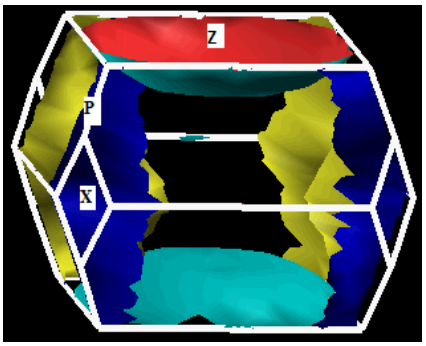


Fig. 7 Fermi surface plot of $SrFeRuBi_2$ compound Fig. 8 Fermi surface plot of $SrRu_2Bi_2$ compound

4. Conclusion

The observations from the comparative analysis of $SrFe_2Bi_2$, $SrFeRuBi_2$ and $SrRu_2Bi_2$ compounds are substitution of Ru in $SrFe_2Bi_2$ compound decreases the contribution of transition metal towards density of states at fermi level and increases the Bulk modulus. In $SrRu_2Bi_2$ compound, strong directional contours are exist between Ru and Bi atoms in the same layer, whereas no such strong interaction is seen between Bi-Bi atoms of adjacent layer. Fermi energy

lies in the deep valley (pseudo gap) for $SrRu_2Bi_2$, which suggests the more stable nature of the compound and also it supports for the evidence of superconductivity. In this study, it is shown that $SrFeRuBi_2$ and $SrFe_2Bi_2$ are stable in antiferromagnetism and these compounds also exhibits approximate zero resistivity, which supports for superconductivity. Hence it stated that antiferromagnetism is induced in $SrRu_2Bi_2$ by the substitution of Fe at 'T' site. From our results we can provide a clue for the existence of superconductivity in $SrFe_2Bi_2$ and $SrFeRuBi_2$ compounds for the experimentalist and it is to be verified by the experimentalist. In over all the electronic, structural, bonding and magnetic behaviour of $SrFe_2Bi_2$, $SrFeRuBi_2$ and $SrRu_2Bi_2$ compounds at ambient condition are analysed and their possibilities to become a superconductor is observed by comparing with their parent compounds.

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