A COMPARATIVE STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF TRANSITION METAL COMPOUNDS OF $ThCr_2Si_2$ TYPE

SUBMITTED BY

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UNDER THE GUIDANCE OF

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CERTIFICATE

This is to certify that the project thesis titled, "A Comparative Study Of Structural And Electronic Properties Of Transition Metal Compounds Of $Thcr_2si_2$ Type" being submitted by Padmavati Murmu in partial fulfillment to the requirement to the one year project course (PH-592) of M.Sc Degree in physics of National Institute of Technology, Rourkela has been carried out under my guidance. The result analyzed in the thesis has been reproduced by TB-LMTO code.

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Date :

Prof. Biplab Ganguli

Dept. of Physics

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ABSTRACT

The electronic structures of transition metal compounds of $ThCr_2Si_2$ type were studied by means of self-consistent TB-LMTO (Tight Binding Linear Muffin Tin Orbital) band structure calculations. The structural parameters such as lattice constant, space group number, nuclear charge are used to operate TB-LMTO method. And different bonding interactions in transition metal compounds ($SrRh_2P_2$, $SrRu_2P_2$, $LaRu_2P_2$) are analyzed and their dependence on the electron count are discussed in terms of formal substitution of elements. Particularly the evolution of interlayer bonding between nonmetal atoms by changing the transition metal is examined in more detail.

Contents

Introduction

Since $SrTh_2P_2$, $SrRu_2P_2$ and $LaRu_2P_2$ have $ThCr_2Si_2$ type structure which is reported by Ban and Sikirica in 1965. More than 700 compounds have been found to adopt this structure. In the formulation AM_2X_2, A generally corresponds to an alkaline earth or a lanthanide element, M is a transition metal and X an elements from group 3b-6b.

The aim is to draw a picture of electronic structure of the $ThCr_2Si_2$ type compounds, based on first principle TB-LMTO band calculations in order to achieve a better understanding of bonding and physical properties.

By changing the base-metal component and transition-metal component the effect of electronic properties are shown by calculating band structure of $ThCr_2Si_2$-type compounds ($SrRh_2P_2$, $SrRu_2P_2$ and $LaRu_2P_2$). A comparative study of electronic property of $ThCr_2Si_2$-type compounds ($SrRh_2P_2$, $SrRu_2P_2$ and $LaRu_2P_2$) has been done by changing their base-metal component (A) and transition-metal component (M).

2. Computational Method

There are different approaches for the choice of the basis set and hence to find the solution of the one electron band structure.

(a) Fixed basis method (LCAO method)

(b) Partial wave method (KKR method)

The approach (a) is straight forward and versatile but less accurate. The approach (b) is sophisticated and time taking but highly accurate. There is another approach called linear muffin tin orbital method (TB-LMTO). The TB-LMTO method not only establishes the connection with both LCAO and KKR-ASA method but also combines the desire features of both. Here basically one derives an energy independent basis set from the energy dependent partial waves in the form of muffin-tin orbitals. Then this gives a fast efficient and reasonably accurate prescription for computing one electron energies and wave functions for all the elements in the periodic table.

2.1 TB-LMTO Method

TB-LMTO is the linearized version of KKR multiple scattering method which is the most accurate partial wave band structure method. It leads to the smallest Hamiltonian andoverlap matrices and hence faster from the computational point of view. In this method it is also possible to define a localized basis such that the Hamiltonian can be recast in atight binding form (TB-LMTO). This can be solved in reciprocal as well as in real space.

This TB-LMTO method gives very good result for the compounds having localized d and f orbitals. For the first principle calculations of the electronic structure of solids, LDA based TB-LMTO-ASA is the most handy tool and it is also known as “minimal basis set” method. This is

the only method which can be implemented at different levels of sophistication and can be run even on PC. Density of states (DOS), band structure, electron density and total energy can be calculated easily for non-magnetic, ferromagnetic, antiferromagnetic solids in bulk, surface or interface/multilayer.

3. LITERATURE SURVEY

3.1 Transition metal compounds

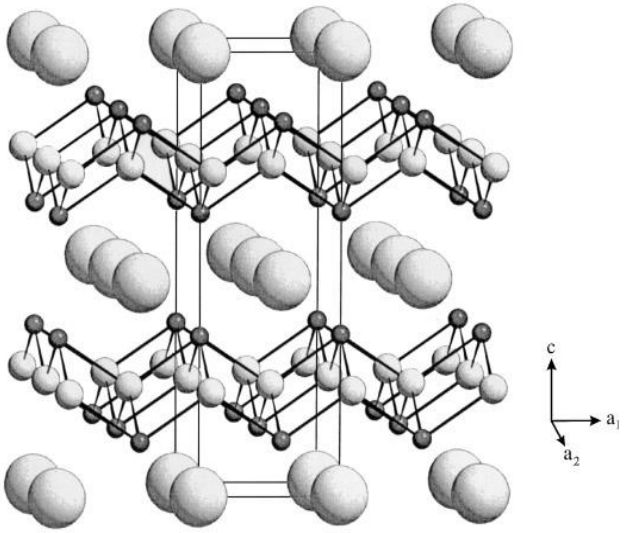
The three rows of periodic table extending from the alkali earths (Calcium, Strontium, Barium) to the noble metals (Copper, Silver and Gold) each contain nine transition elements, in which the d-shell that is empty in the alkali earths and completely filled in noble metals is gradually filled in. The stable room temperature forms of the transition elements are either monatomic fcc or bcc Bravias lattices structures. All are metals, but their properties are to a considerable degree dominated by the d-electrons.

Calculated transition band (as in the noble metals) structures indicate that the d-band not only lies high up in the conduction band but general extends through the Fermi levels.

The d-bands are narrower than typical electron conduction bands, and contain enough levels to accommodate ten electrons. Since the d-bands contain more levels in a narrower energy range, the density of levels is likely to be substantially higher than the free electron density of levels throughout the energy region where the d-band lies. This effect can be observed in the electronic contribution to the low temperature specific heat which is proportional to the density of levels at the Fermi energy that reveals the transition metal electrons specific levels are induced significantly higher than those of the simple metals.

3.2 $ThCr_2Si_2$ type structure

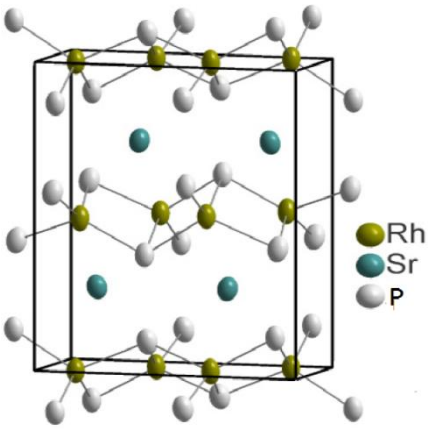
The tetragonal body-centered $ThCr_2Si_2$ structure (space group I4/mmm) is mainly characterized by layers of edge-sharing MX_4 tetrahedra parallel to the xy plane, separated by planes of the base metal atoms (*A*). The atomic distances within the 2 layers are found to be slightly smaller than the sum of the covalent radii (indicating strong M-X bonding within the layers), whereas the interlayer distances between the X atoms show a great variety of values. The $ThCr_2Si_2$ type is frequently described as an ordered ternary variant of the $BaAl_4$ structure, which is somewhat unreasonable regarding the representatives with interlayer X-X distances of more than 3 A°. In fact, we have two different branches of this structure type, one building a real three-dimensional network with X-X bonds and another with a two-dimensional layered character. This is supported by the behavior of the lattice constants with respect to different *A* components. The substitution of Ca by larger Sr or Ba leads to longer axis in the compounds with short X-X distances, whereas in the second branch the MX_4 tetrahedra are remarkably rigid. Here the substitution causes a drastic increase of the interlayer distance without changing the atomic distances within the layers. This emphasizes the distinct layer character of this $ThCr_2Si_2$ structure branch.



(The ThCr2Si2 structure: large spheres, *A*; medium spheres, M; small spheres;X.)

3.3 Structure of $SrRh_2P_2$

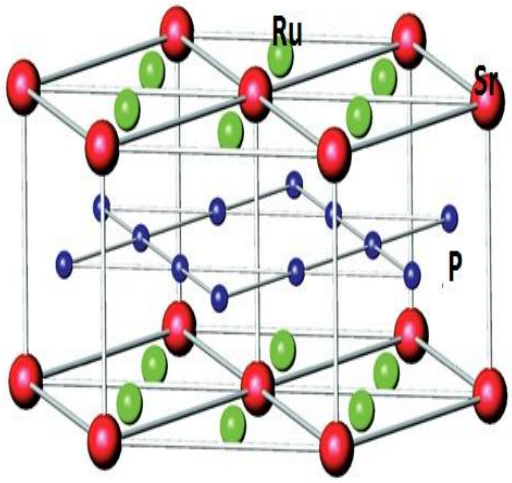
$SrRh_2P_2$ compound is having $ThCr_2Si_2$ type structure which is tetragonal body-centered structure having space group number 139 and space group I4/mmm. The elements of the compound Sr, Rh, P are alkali earth metal, transition metal and nonmetal respectively. Sr has nuclear charge 38, Rh has 45 and P has 15. The lattice parameters of $SrRh_2P_2$ compound are a: 3.937 A^o, c: 11.713 A^o, z/c: 0.3598 and the atomic positions of the elements are Sr (0,0,0), Rh (0.5,0,0.25), P (0,0,0.5).



Crystal structure of $SrRh_2P_2$

3.4 Structure of $SrRu_2P_2$

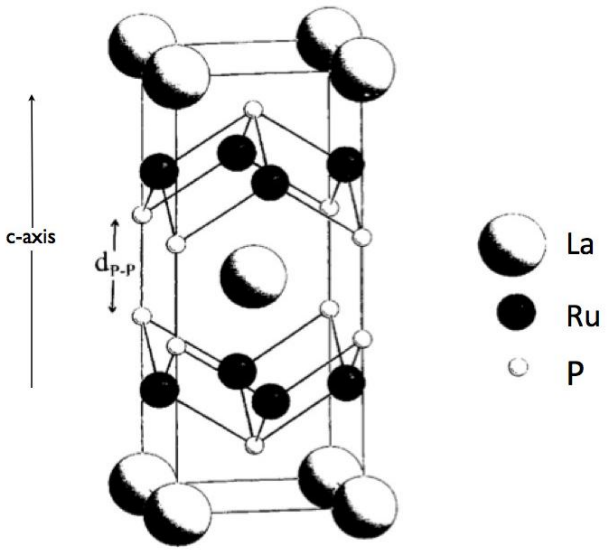
$SrRu_2P_2$ compound is having $ThCr_2Si_2$ type structure which is tetragonal body-centered structure having space group number 139 and space group I4/mmm. The elements of the compound Sr, Ru, P are alkali earth metal, transition metal and nonmetal respectively. Sr has nuclear charge 38, Ru has 44 and P has 15. The lattice parameters of $SrRu_2P_2$ compound are a: 4.032 A^0, c: 11.122 A^0, a/c: 2.758 and the atomic positions of the elements are Sr (0,0,0), Ru (0,0.5,0.5), P (0,0,0.3529).



Crystal structure of $SrRu_2P_2$

3.5 Structure of $LaRu_2P_2$

$LaRu_2P_2$ compound is having $ThCr_2Si_2$ type structure which is tetragonal body-centered structure having space group number 139 and space group I4/mmm. The elements of the compound La, Ru, P are lanthanide, transition metal and nonmetal respectively. La has nuclear charge 57, Ru has 44 and P has 15. The lattice parameters of $LaRu_2P_2$ compound are a: 4.031 A^0, c: 10.675 A^0, a/c: 2.648 and the atomic positions of the elements are La (0,0,0), Ru (0,0.5,0.25), P (0,0,0.3593).



Crystal structure of $LaRu_2P_2$

Results and Analysis

4.1 $SrRh_2P_2$

The electronic band structure of $SrRh_2P_2$ was calculated.

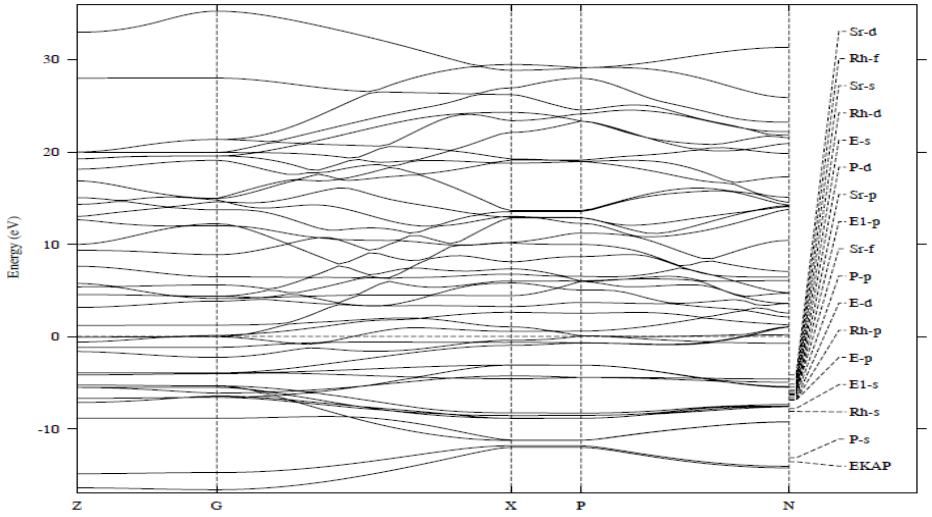


Fig.1 Electronic band structure of $SrRh_2P_2$

From the above structure it is clear that $SrRh_2P_2$has no band gap.

The density of states of $SrRh_2P_2$was calculated.

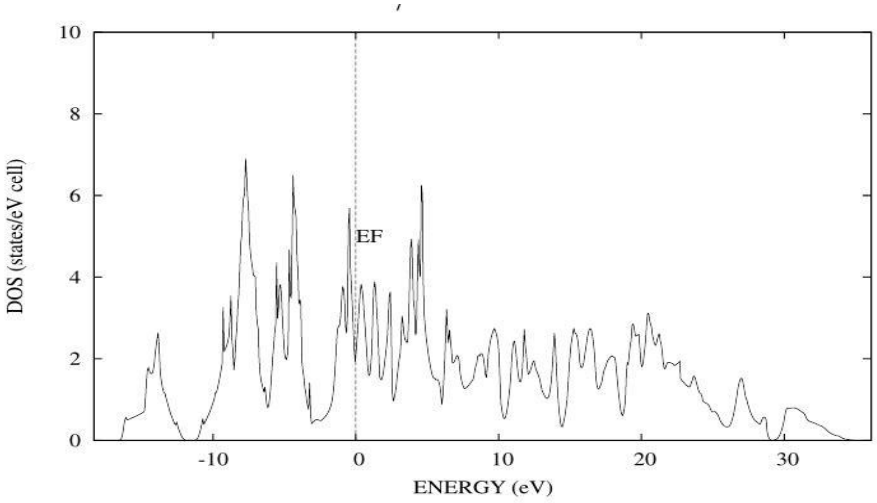


Fig.2 Density of States of $SrRh_2P_2$

Since $SrRh_2P_2$is a metal, so near the Fermi level there is no energy gap. Separation between the valence band and conduction band is found to be zero.

4.2 $SrRu_2P_2$

Electronic band structure of $SrRu_2P_2$ was calculated.

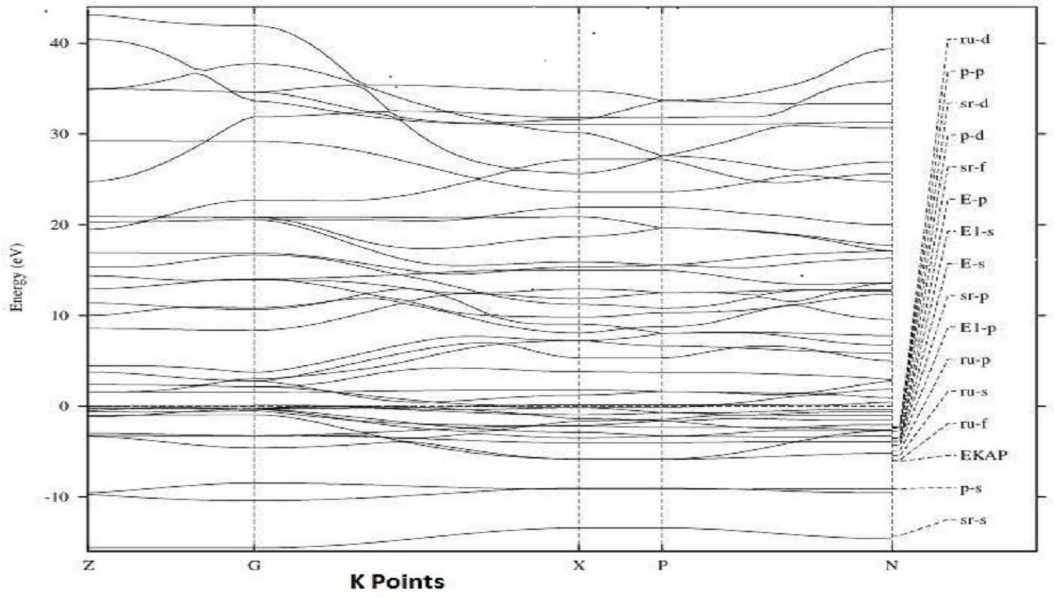


Fig.3 Electronic band structure of $SrRu_2P_2$

From the above structure it is clear that $SrRh_2P_2$has no band gap.

Density of states of $SrRu_2P_2$ was calculated.

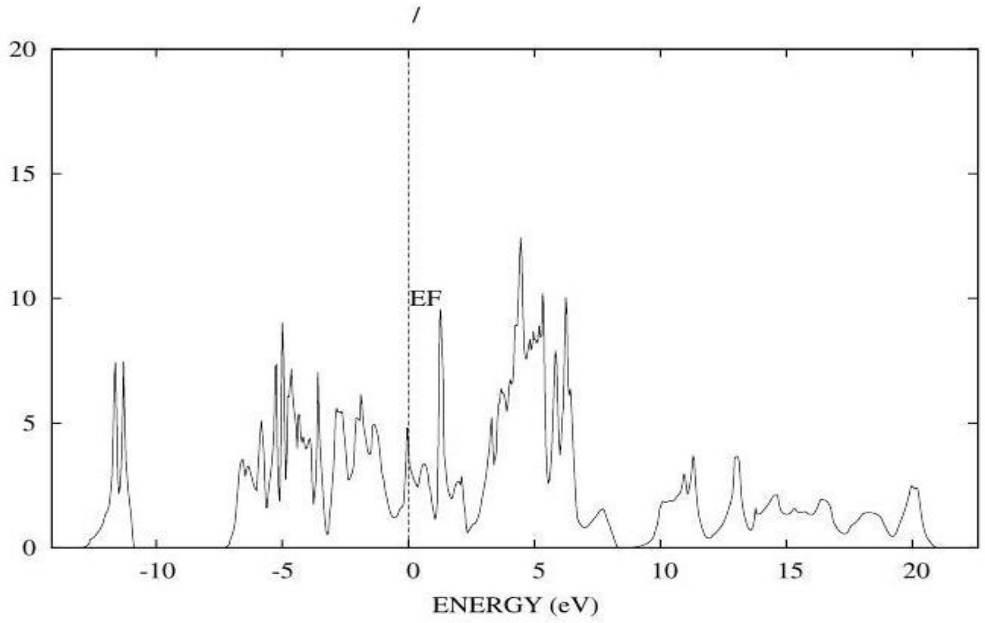


Fig.4 Density of states of $SrRu_2P_2$

Since $SrRu_2P_2$ is a metal, so near the Fermi level there is no energy gap. Separation between the valence band and conduction band is found to be zero.

4.3 $LaRu_2P_2$

Electronic band structure of $LaRu_2P_2$ was calculated.

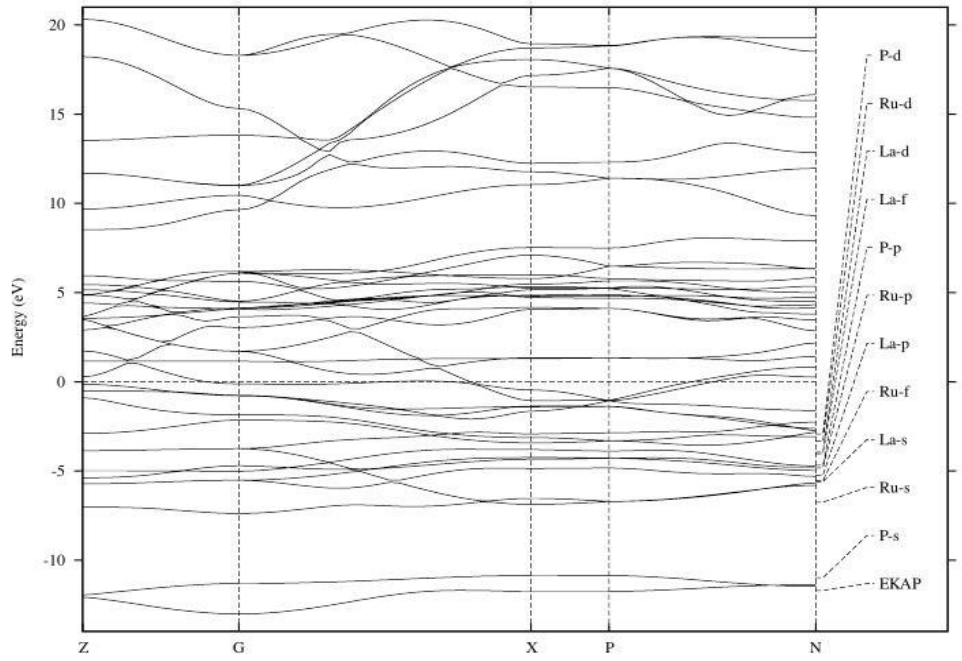


Fig.5 Electronic band structure of $LaRu_2P_2$

From the above structure it is clear that $LaRu_2P_2$ has no band gap.

Density of states of $LaRu_2P_2$ was calculated.

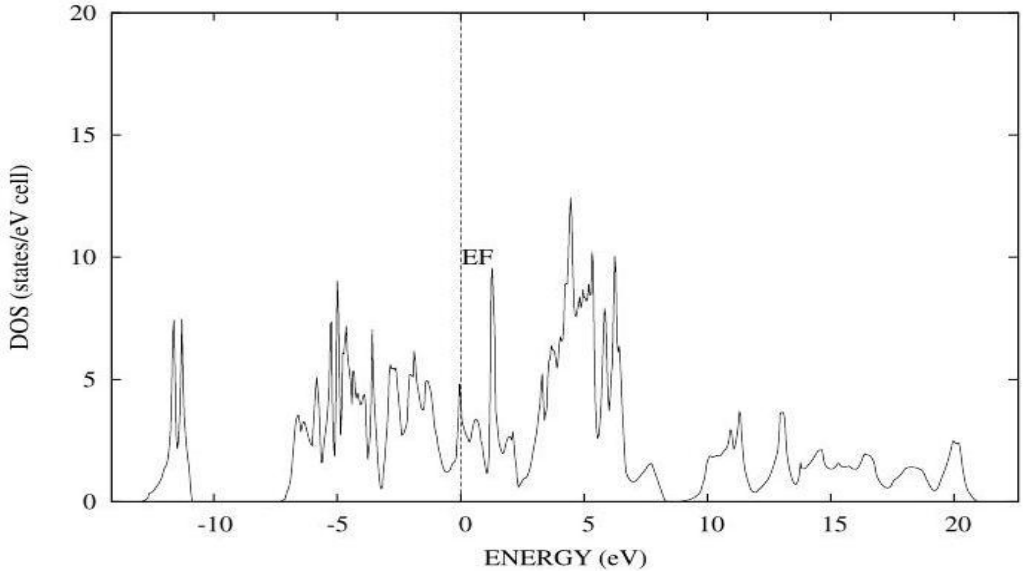


Fig.6 Density of states of $LaRu_2P_2$

Since $LaRu_2P_2$is a metal, so near the Fermi level there is no energy gap. Separation between the valence band and conduction band is found to be zero.

4.4 Comparison between Band Structure of $SrRh_2P_2$and $SrRu_2P_2$

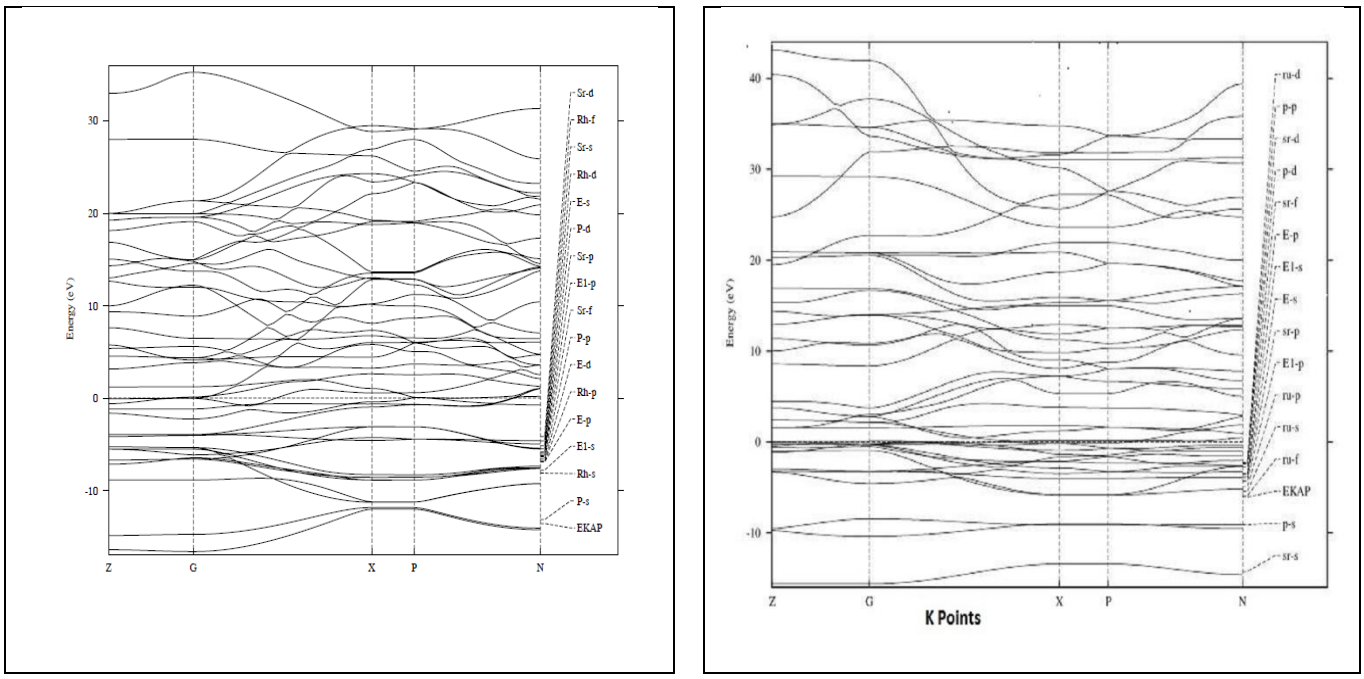


Fig.7 The band structure of $SrRh_2P_2$ (left) and $SrRu_2P_2$ (right)

By changing the transition metal component (M) the electronic effect has been shown. Here by changing the transition metal component Rh and Ru the electronic band structure has been calculated. The increasing d-band occupation on going from left to right in the periodic system leads to weaker M-M and M-P bonds and therefore the layers becomes less rigid within the plane. The metal-metal anti-bonding band is empty for Ru and partially filled for Rh. Hence the metal-metal bonding decreases strongly with band filling. So $SrRh_2P_2$ compound has weaker bonding than $SrRu_2P_2$.

4.5 Comparison between Band Structure of $SrRu_2P_2$and $LaRu_2P_2$

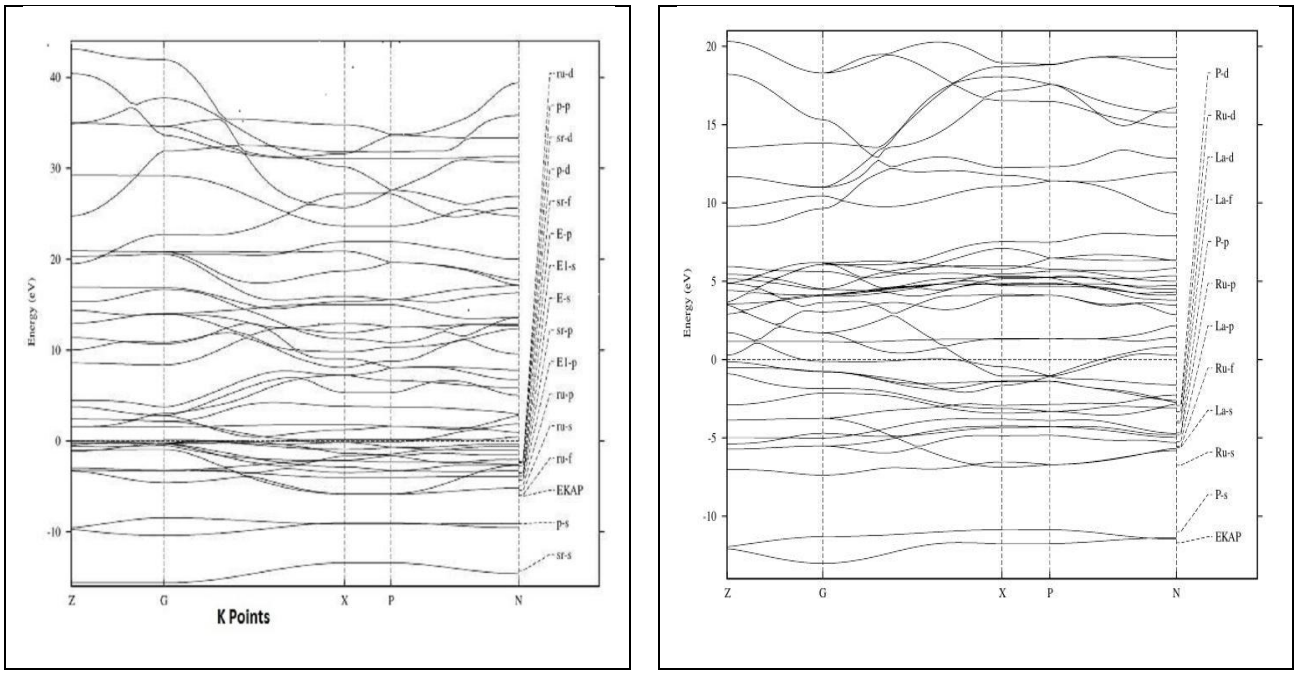


Fig.8 The band structure of $SrRu_2P_2$ (left) and $LaRu_2P_2$ (right)

By changing the base metal component (A) the band structure of $SrRu_2P_2$ and $LaRu_2P_2$ are calculated. Here the Fermi level is nearly the same for the La substituted compound compared with $SrRu_2P_2$. The substitution of Sr by La would have nearly no influence on bonding in this structure and geometric effects regarding the smaller atomic radii of La has of greater influence. The La d-shell is partially occupied. This indicates some covalent La-La interaction. This bonding is extremely weak and therefore neglected. So here it is supposed to say that the elements having smaller atomic radii have weak bonding. So $LaRu_2P_2$ has weaker bonding than $SrRu_2P_2$.

Conclusion

The electronic properties of $ThCr_2Si_2$-type compounds ($SrRh_2P_2$, $SrRu_2P_2$ and $LaRu_2P_2$) were by the tight binding linear muffin tin orbital method included in the TB-LMTO-ASA program. The band structure and density of states were calculated for all the three compounds.

Metal-metal bonding plays an important role in the $ThCr_2Si_2$ structure and influences indirectly the X-X distances. When the transition-metal d-shell gets completely filled, the attractive metal-metal interaction vanishes and the distance is elongated. As a consequence of the larger metal squares, the interlayer distance becomes smaller for geometric reasons and the X-X interaction gets stronger.

Since $SrRh_2P_2$, $SrRu_2P_2$ and $LaRu_2P_2$ are metals, there is no energy gap near the Fermi level. The band gap calculated through the density of states is found to be zero.

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