Electronic structure of URh$_3$ up to 40 GPa

V Kathirvel$^{1,2}$, Sharat Chandra$^1$, N V Chandra Shekar$^1$, P Ch Sahu$^1$ and S Moorthy Babu$^2$

$^1$Condensed Matter Physics Division, Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam - 603102, Tamil Nadu, India.
$^2$Crystal Growth Centre, Anna University, Chennai – 600025, Tamil Nadu, India.

Abstract. Full potential linear augmented plane wave (FP-LAPW) method is used to calculate the electronic structure of URh$_3$ in its AuCu$_3$ type structure as a function of reduced volume. The Fermi level lies near a maxima in the DOS and it remains pinned at the same position even at 40 GPa. The charge density plots show that the charge distribution becomes more uniform, the directional bonding decreases at very high pressure and the system becomes more metallic. The present analysis suggests that the AuCu$_3$ structure might remain as the ground state for URh$_3$ up to quite high pressures. A 2-D structural stability map constructed for the AB$_3$ type system indicates a wide structural stability regime for URh$_3$ under high pressure.

1. Introduction

The f-electron based intermetallics (f-IMCs) are quite interesting and the f-orbital is sensitive to influence of external factor such as pressure. The systematic high-pressure studies on f-electron based intermetallic compounds and the electronic structure calculations as a function of pressure help us to understand the contribution of f-electrons in bonding [1]. In this paper, we have carried out the detailed electronic structure calculations on URh$_3$ in its AuCu$_3$ type cubic structure as a function of reduced volume. Though the U-U distance is much larger than the Hill limit [2], the 5-f states in this system exhibit itinerant nature due to the strong hybridization between the f and d electron orbitals [3, 4]. The electronic structure of URh$_3$ has been calculated earlier by using several codes [3-9]. Dunlap et al [7] have done band structure calculations for URh$_3$ and URh$_3$B by using relativistic linear augmented - plane – wave method. The dehybridization occurs between U-f electron states and Rh-d electron states when boron atom is added in the URh$_3$ system. However, there are no reported electronic structure calculations as a function of reduced volume for this system. In this study, the objective is two fold. Firstly, calculate the electronic structure of URh$_3$, predict its structural stability behaviour as a function of pressure and see whether it falls within the criterions for stability of f-electron based compounds. Secondly, we have tried to discuss the stability of UX$_3$ systems (AuCu$_3$ type) in general and understand the stability in terms of a 2D map.

2. Methodology: Full potential linear augmented plane wave (FP-LAPW) method as implemented in WIEN2k code [10] is used to calculate the total energy and the electronic structure of URh$_3$ as a function of pressures. It is
believed that FP-LAPW calculations are more reliable to predict the position and width of the $f$-band in $f$-electron based systems when compared to the TB method [11]. The band structure and the density of states are calculated using 455 k-points in the irreducible Brillouin zone (IBZ) for the non-magnetic state. Spin orbit interaction and the improved version of generalized gradient approximation (GGA – PBE96) [12] are used. The plane-waves with a cut off of $R_{MT} K_{\text{max}} = 10$ are used, where $R_{MT}$ denotes the smallest atomic sphere radius and $K_{\text{max}}$ is the magnitude of the largest k-vector in the plane wave expansion. The relaxed lattice parameter is found to be equal to 4.0175 Å in close agreement with the experimental value of 4.0998 Å for the ambient structure [13].

3. Results and Discussions:
The band structure is obtained along the Brillouin zone path R-Γ-X-M-Γ. The band dispersion curves at ambient pressure are shown in figure 1. For comparison, the density of states (DOS) is also shown along with band structure and it is constructed for the energies ranging from -8 eV to +8 eV. The Fermi level ($E_F$) lies very close to a maximum in the DOS curve. Below the Fermi level, the band dispersion curves show that lower energy region is mostly dominated by Rh $d$ band states. About ~0.6 eV above the Fermi level, there is a sharp narrow peak due to the U-$f$ band and the tail of the $f$ band extends towards lower energy below the Fermi level. This is a clear evidence for strong hybridization U-$f$ band in URh$_3$.

![Figure 1. Band dispersion curves along with DOS at 0.1 MPa](image1)

![Figure 2. Band dispersion curves along with DOS at 40 GPa](image2)

The band dispersion curves at 40 GPa are shown in figure 2. The bands show movement under the influence of pressure. From the DOS curve, it is clear that there is not much change in the electronic structure around the Fermi level. Even at 40 GPa, the $E_F$ lies on the same maxima in the DOS curve. At higher pressures, the Rh $d$ like band becomes more dominant than U-$f$-like band at the Fermi level.

The DOS at various pressures are displayed in figure 3. At higher pressures the width of the U-$f$ band increases and the total DOS of URh$_3$ decreases. The enlarged portion shows that the Fermi level is pinned in the same position even at higher Pressures. This implies that the URh$_3$ system is more stable. The theoretical P-V data is computed and fitted with Birch-Murnaghan equation of states. The calculated bulk modulus and its pressure derivative are 216.4 GPa and 5.6 respectively. In figures 4a and 4b we have shown charge densities at different pressures for the (001)

![Figure 3. DOS at various high pressures. Inset shows the magnified view of $E_F$.](image3)
plane. In the (001) plane, the uranium atoms are placed at the corners and the rhodium atom is at the centre of the square. The darker regions are of higher valence electron density.

Even though the $\text{URh}_3$ system is metallic, the charge density plot at ambient and at high pressures show that the bonding between uranium and rhodium is somewhat directional, indicating partial covalent bonding, which is in agreement with an earlier work [5]. In figures 4a and 4b, a line from (0,0) to (1,1) in the (001) plane is shown along which the percentage of increase in the valence charge density is computed and the plot is shown in figure 4c. At a distance equal to quarter of the diagonal, there is ~26% increase in the valence charge density at 40 GPa, which is expected at higher pressure due to decrease in the interatomic distance. Also, it can be noticed that the charge distribution becomes more uniform around the atoms, indicating reduction of directional bonding and the system becoming more metallic in nature.

To predict high pressure phase, one can approach Villars 3D structural stability map which has been prepared for binaries by using the three parameters: Zunger-pseudo potential radii ($\Delta R$), average valence electron ($\text{VE}$), and electro negativity ($\Delta X$) [14]. If the plots are made for selected compounds separately, then it will be helpful to predict the high pressure phase easily. Earlier we have generated the two dimensional structural stability map for selected $\text{AB}_2$ [$\text{MgCu}_2$, $\text{CeCu}_2$, $\text{AlB}_2$, $\text{ThSi}_2$, $\text{ZrSi}_2$, $\text{SmSb}_2$, $\text{CaIn}_2$, and $\text{SbCu}_2$] type compounds with which may help to correlate and predict the structural sequences at high pressures [15]. With the success of 2D stability map for $\text{AB}_2$ type compounds, we have generated a 2D map for $\text{AB}_3$ type compounds that may be helpful in understanding the large structural stability regime of $\text{UX}_3$ type compounds. Figure 5 shows that 2D structural stability map for $\text{AB}_3$ type compounds. The plot is prepared for selected $\text{AB}_3$ [$\text{CFe}_3$, $\text{AuCu}_3$, $\text{BeFb}_3$, $\text{NiSn}$, $\text{CoGa}_3$, $\text{Cr}_3\text{Si}$, $\text{AsNa}_3$ and $\text{NdTe}_3$] type compounds with $\Delta X$ and $\Delta R$ as the X and Y axes. The calculated $\Delta X$, $\Delta R$, $\text{VE}$ values for $\text{URh}_3$ are -0.232, 1.2 and 7.5 respectively.

**Figure 4.** (a) Charge density of $\text{URh}_3$ in the plane (001) at 0.1 MPa , (b). at 40 GPa and (c) percentage increase in valence charge density at 40 GPa between two U atoms located at (0,0) and (1,1) in the plane (001) (distance is divided into 100 equal parts).

**Figure 5.** 2-D structural stability maps for $\text{AB}_3$ type compounds at NTP.
To construct the 2D map, the clusters with more than 10 systems are considered and the map is divided into two parts for the convenient viewing. From the 2D map, it is clear that the AuCu$_3$ type structures are occupying more area than the other structures. In this map the black colour box indicates the position of the URh$_3$ system in this map. The average valence electron for URh$_3$ lies in the range of 7.25 – 7.75. In general, one can expect the VE to increase and ∆R to decrease with pressure. At higher pressures, URh$_3$ system is expected to move to the next cluster which is also belongs to AuCu$_3$ type structure. The above observations confirm that URh$_3$ system has a wide stability regime under high pressure. However, under very high pressure, it may transform from the AuCu$_3$ type to Be$_3$Nb type structure, which has similar VE values.

4. Conclusions:
Electronic structure of URh$_3$ is carried out as a function of reduced volume. Our calculation shows that in the DOS curve, the position of the Fermi level lies on a peak and it remains pinned at the same position even at higher pressures. The charge density plot indicates decreased covalency or increase in metallic character under high pressure. Moreover, although the 2D stability map predicts a large stability regimes for this structure, there is a possibility of phase transition from AuCu$_3$ type to Be$_3$Nb type structure at very high pressures. Further, calculations on URh$_3$ in Be$_3$Nb type structure and high pressure experiments are being carried out to verify the theoretical prediction.

5. Acknowledgement
The authors thank Dr. N. Subramanian, Shri M. Sekar, Shri N.R. Sanjay Kumar for useful discussion and Shri L.M. Sundaram for his help. They thank Dr. A. K. Arora, Dr. C. S. Sundar, and Dr. Baldev Raj for their encouragement and support. VK expresses his gratitude to the IGCAR authorities for granting permission to carry out his Ph.D. research work at the Condensed Matter Physics Division of IGCAR.

6. References
[1] Chandra Shekar N V and Sahu P Ch 2006 J. Mat. Sci. 41 3207
[2] Hill H H 1970 Plutonium 1970 and Other Actinides, ed W N Miner (Newyork: Met. Soc. AIME) p 2
[3] Arko A J, Brodsky M B, Crabtree G W, Karim D, Koelling D D, Windmiller L R and Ketterson J B 1975 Phys. Rev. B 12 4102
[4] Eriksson O, Johansson B, Brooks M S S and Skrivar H L 1989 Phys. Rev. B 40 9508
[5] Trygg J, Wills J, Johannsson B and Eriksson O 1994 Phys. Rev. B 50 9226
[6] Petit L, Svane A, Temmerman W M and Szotek Z 2002 Phys. Rev. Lett. 88 216403
[7] Dunlap B D, Crabtree G W, Jorgensen J D, Kierstead H A, Koelling D D, Kwok W K, Lam D J, Malik S K, Mitchell A W and Strite S C 1989 Phys. Rev. B 39 5640
[8] Crabtree G W 1985 J. Mag. Mag. Mat. 52 169
[9] Arko A J, Koelling D D and Schirber J E 1985 Handbook on the Physics and Chemistry of the Actinides vol 2, ed A J Freeman and G H Lander (Amsterdam: North-Holland) p 175
[10] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 WIEN2k ISBN 3-9501031-1-2 Schwarz K (Austria: Vienna University of Technology)
[11] Divis M 1994 Phys. Stat. Sol. (b) 182 K15
[12] Perdew J P, Burke K and Ernzerof M 1996 Phys. Rev. Lett. 77 3865
[13] Kathirvel V, Chandra Shekar N V, Meenakshi Sundaram L and Sahu P Ch 2008 Powder Diffraction File W26208
[14] Villars P, Mathis K and Hulliger F 1989 The Structures of Binary Compounds vol 2, ed F R De Boer and D G Pettifor (Amsterdam: North-Holland) p 2
[15] Chandra Shekar N V, Sanjay Kumar N R, Sekar M, Subramanian N, Kathirvel V, Sarat Chandra and Rajagopalaman M 2009 Solid State Phenomena. 150 123