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Structural stability of URh_3 at high pressure

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ABSTRACT

URh_3 stabilizes in the cubic $AuCu_3$ type structure at normal temperature and pressure. High-pressure angle-dispersive X-ray diffraction experiments were performed on URh_3 up to 25 GPa using a diamond-anvil cell. URh_3 remains in its cubic $AuCu_3$ type structure up to the maximum pressure studied. The Birch–Murnaghan equation of state fit to the P–V data yields the bulk modulus to be 133 GPa. The Villars structural stability map gives a clue of a possible high pressure phase transition to a Ni_3Sn type structure. The electronic structure calculations were carried out for both the ambient $AuCu_3$ type cubic phase and the expected Ni_3Sn type hexagonal high pressure phase. However, the total energy curves of these two structures do not intersect even at pressure as high as 360 GPa, removing the possibility of transition to Ni_3Sn type structure.

1. Introduction

Study of uranium intermetallics is very interesting for basic sciences as well as relevant for nuclear energy [1]. In a recent report, the phase transition behavior of uranium intermetallics has been reviewed [2]. Among various uranium intermetallic compounds (U-IMCs), UX (where X belongs to p or d block metal) mostly show phase transition from B1 to B2 type structure under pressure [3]. The UX_2 compounds stabilize either in the $MgCu_2$ type cubic or AlB_2 type hexagonal structure and show interesting structural transitions under pressure [4,5]. The UX_3 compounds on the other hand stabilize in $AuCu_3$ type cubic structure and showed high structural stability under pressure [6,7]. Earlier, high pressure structural studies on UGa_3 up to 30 GPa show that the ambient phase ($AuCu_3$ cubic type structure) remains stable [8]. Moreover, the electronic structure calculations on UGa_3 as a function of reduced volume show very little change in Density of States (DOS) at the Fermi level E_F, supporting the structural stability of this compound under pressure.

URh_3 stabilizes in the cubic $AuCu_3$ type structure at ambient conditions. Although, the U–U distance is much larger than the Hill limit (∼3.5 Å), the 5f states in the URh_3 system exhibit itinerant nature due to strong hybridization between the U-f and Rh-d electron orbitals [9–11]. Transport, mechanical and thermal properties of URh_3 compound are well studied [12–15]. Several computational studies have been carried out investigating the electronic structure of URh_3 [16–22]. Recently, Petit et al. [23] have done electronic structure calculations on URh_3, UPt_3, UPd_3 and UAu_3 compounds using the self-interaction corrected local-spin-density approximation. In general, these experiments and computations help understand the stability of the structure and the change in hybridizations under compression and across the phase transition. In URh_3, the DOS shows that the E_F is situated below the f peak, and intersects a strongly hybridized f–d band. Although there are several reports on the electronic structure of URh_3 for ambient conditions, no such reports exist at high pressure conditions.

In order to understand the structural stability and bonding nature of f-electrons on UX_3 type systems, Kathirvel et al. [24] carried out the electronic structure calculations on URh_3 up to 40 GPa [24]. In this case the self-interaction correction was not used since the interest was in the compression and structural stability rather than magnetism. Their calculations show that the position of the Fermi level E_F lies on a small peak in the DOS curve and it remains pinned at the same position even at 40 GPa. The charge density plots indicate increase in metallic character under pressure. The small changes of the DOS at E_F support the structural stability of the URh_3 at least up to 40 GPa [24]. In order to look for possible high pressure phases, they have made use of an empirical method of using 2-D structural stability maps for AB_3 type (where A belongs to lanthanide or actinide metals and B belongs to p or d block metal) compounds [25,26].

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The stability maps are used to explore the occurrence of different domains of structure as a function of parameters like average valence electron (*VE*), average electronegativity (ΔX) and average Zunger-pseudo-potential radii (ΔR) [26]. These maps correlate the crystal structure and the electronic configuration of the constituents of several thousands of known compounds. However, construction of such stability maps for the high pressure phases has not been explored yet, because of inadequacy of high pressure structural data. In general, one can expect the increase in *VE* and decrease in ΔR with pressure and this is consistent with the predicted increase in the metallic character of UX_3 compounds [24]. Moreover, the electronegativity values of metals are expected to increase monotonously with pressure [27]. With this information, one can determine candidate high pressure phase (structure). Recently, we have validated the 2-D structural stability maps for f-electron based AB_2 type compounds for several high pressure phases obtained from the experimental results [25].

For URh_3, the calculated ΔX, ΔR, and *VE* values are -0.232, 1.2 (a.u) and 7.5 respectively. In 2-D stability maps (AB_3 type compounds), the important observation is that the domain belonging to Ni_3Sn type structure overlaps with that of the domain with $AuCu_3$ type structure (where the URh_3 system is located). The range of values of the three parameters for the $AuCu_3$ type and Ni_3Sn type structure is listed in Table 1. The overlap indicates that URh_3 may transform to the Ni_3Sn type structure at very high pressures due to the changes in its ΔX, ΔR and *VE*.

In this paper, we report the results of the HPXRD studies on URh_3 up to 25 GPa and also electronic structure and the total energy of the URh_3 compound in $AuCu_3$ and Ni_3Sn type structure as a function of reduced volume to compare their structural stability and understand the bonding nature of the f electron states.

2. Experimental and calculation details

2.1. Sample preparation

URh_3 was prepared by using a standard arc melting technique. Stoichiometric quantities of U (99.98%) and Rh (99.999%) were melted in He atmosphere and the melted ingot was flipped 2–3 times to obtain a homogenous compound. The ingots were then vacuum sealed in Ar atmosphere in silica tube and annealed for about 4 weeks at temperature of 1100 K. In order to remove any oxide layer, the annealed ingots were etched in 1:1 mixture of nitric and sulfuric acid for about 2 min. The annealed sample was powdered and XRD pattern showed single phase compound with cubic structure [28].

2.2. High pressure X-ray diffraction

In-situ high pressure X-ray diffraction experiment (HPXRD) was carried out using a Mao–Bell type diamond anvil cell (DAC) in the angle dispersive mode. The sample in the powder form was loaded into a 200 μm diameter hole drilled in pre-indented stainless steel (SS) gasket along with the pressure calibrant material. An internal X-ray collimator of size 100 μm was used to avoid SS gasket peak. For pressure calibration the material is chosen in such a way that its diffraction lines of the calibrant do not overlap with that of the sample. In this experiment, equation of state (EOS) of platinum was used for pressure calibration. Pt, having higher bulk modulus than URh_3, does not see the pressure easily and its (1 1 1) peak shifts slower with pressure than the sample peak thereby preventing overlap of Pt and URh_3. A mixture of methanol, ethanol and water (MEW) in the volume ratio 16:3:1 was used as the pressure transmitting medium. The pressure medium MEW freezes at about 14 GPa. However, the X-ray diffraction patterns do not show any discernable change in the pressure range. The collection time for each spectrum was 2 h.

The incident Mo X-ray beam obtained from a Rigaku ULTRAX18 (18 kW) rotating anode X-ray generator was monochromatised with a graphite monochromator which gives Mo $K\alpha_1$ radiation with wavelength 0.7107 Å. An image plate based mardtb345 diffractometer was used to carry out the HPXRD experiments. The overall resolution of the diffractometer system is $\delta d/d \sim 0.001$. The sample to detector distance was calibrated using LaB_6 as standard.

2.3. Calculations

The electronic structure calculations of URh_3 were carried out using WIEN2k code [29] implemented with Full Potential–Linear Augmented Plane Wave (FP–LAPW) method. The exchange-correlation interaction was treated within GGA approximation of Perdew et al. [30]. Previous work suggests that the FP–LAPW methodology provides more reliable insights into the electronic structure of these compounds, as compared to Tight-Binding based approaches [31].

Fig. 1a and b shows the structures of URh_3 in $AuCu_3$ and Ni_3Sn type structures. In order to find out the equilibrium volume for URh_3 system in Ni_3Sn type structure (hexagonal structure), approximate volume was calculated from the equilibrium volume of $AuCu_3$ type structure. Hereafter, the cubic $AuCu_3$ (SG Pm-3m) and Ni_3Sn (SG $P6_3$/mmc) type structures will be mentioned as C and H type structures respectively. Standard crystallographic data and atomic positions are available for C type structure. C type structure has only one formula unit per unit cell (i.e. 4 atoms per unit cell). But, the H type structure has two formula units per unit cell (i.e. 8 atoms per unit cell). Hence, the unit cell volume of the *H* type structure is two times that of the C type structure. The following procedure was adopted to estimate the approximate lattice parameters and cell volume for H type structure.

Equilibrium unit cell volume of the C type structure [24] is 64.843 $Å^3$.

Unit cell volume of the H type structure (V_H)=2* equilibrium volume of the C type structure:

$$V_H = 2*64.843 = 129.687\ \text{Å}^3;\ a = 5.714\ \text{Å};$$
$$c = 4.587\ \text{Å};\quad c/a\ \text{ratio} = 0.802$$

Further, these approximated lattice parameters were fed into the WIEN2K code to optimize the lattice parameters. The calculation was performed in two steps. The first step was to optimize *a* and *c* values by varying volume and keeping the *c*/*a* ratio as constant. The lattice parameters *a* and *c* were derived from the

Table 1
Ranges of values of *VE*, ΔR, ΔX of $AuCu_3$ (cubic) and Ni_3Sn (hexagonal) type structures from the 2-D stability maps.

Structure type	Average valence electron (*VE*)	Average Zunger pseudo-potential radii ΔR (a.u)	Average electronegativity ΔX
$AuCu_3$ (cubic) (where URh_3 is located)	(7.25–7.75)	(0–1.25)	[(−0.5)–(−0.1)]
Ni_3Sn (hexagonal)	≥ 9.75	(+1.0)–(−0.9)	(−0.2)–(+0.15)