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Anomalous compression in UAl_3 —an experimental and computational study

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Abstract. High-pressure x-ray diffraction experiments were performed on UAl_3 up to 23 GPa. Anomalous compressibility behaviour of the system was observed in the pressure range 7–14 GPa. The experiments are compared with similar observations in UGa_3 , ULn_3 , UGe_3 and USn_3 . Band structure calculations have been performed to look for a possible explanation of this behaviour through the concept of electron transfer from the f to the d orbitals.

1. Introduction

Systematic studies of the physical properties of actinide intermetallic compounds as a function of pressure are sparse. A survey by Benedict and Holzapfel [1] on high-pressure structural studies of actinide and rare earth compounds has, surprisingly, revealed that very little is known about their high-pressure behaviour. Another recent review by Holzapfel [2] devotes only a small section to compounds and that too only on AB type.

The systematic investigations of pressure induced structural changes in actinide and lanthanide intermetallic compounds were taken up in our laboratory and to begin with U–Al systems were chosen [3]. UAl_3 is one of the three known compounds of the U–Al system. It has a simple cubic structure (space group $Pm\bar{3}m$) with d_{An} about 4.27 Å, which is much above the Hill limit. Here d_{An} is the interactinide distance in the compound. Thus it is expected that the 5f electron states in UAl_3 are localized as per the Hill criterion [4]. But this may not be always true. There are systems like UGe_3 , USn_3 and NpSn_3 in which the 5f states are itinerant although their d_{An} are much above the Hill limit [5]. This has been attributed to the strong hybridization of the 5f orbitals with the orbitals of the other constituent atoms [6]. Recently Benedict [7] has reported that some of the AnB_3 systems display anomalous compressibility behaviour under high pressure. No definite explanation for this anomaly has been given in this paper. But a similar anomaly in YbTe has been explained in terms of valence change from Yb^{2+} to Yb^{3+} involving a $4f \rightarrow 5d$ electron transfer [8]. Low-temperature resistivity and magnetic susceptibility studies on UAl_3 indicate localized spin behaviour. However, the recent magnetic susceptibility and specific heat measurements by Van Maaren *et al* [9] on UAl_3 tend more towards an itinerant nature of their 5f states. Neither band structure calculations nor photoemission studies have been performed on UAl_3 to confirm these aspects.

Our earlier high-pressure experiment on UAl_3 was done using a diamond anvil cell in angle dispersive mode with the film technique. But the experimental data points were very

sparse and did not reveal any anomaly in the pressure–volume behaviour [3]. Therefore the experiment was repeated in the Guinier geometry where we expect results with superior signal to noise ratio and reproducibility. The motivation was (i) to confirm whether UAl_3 , which is also an AnB_3 compound, shows anomalous compressibility behaviour, and (ii) to look for reasons for the possible anomaly and the nature of the 5f state, by performing the band structure calculation.

2. Experimental details

Uranium trialuminide (UAl_3) was prepared in a single phase by the standard arc melting technique. Stoichiometric quantities of U (99.98% pure) and Al (99.999% pure) were melted several times in an inert environment. The arc melted ingots were then sealed in evacuated silica tubes and annealed at 1200 K for about a month. The powdered samples were characterized by x-ray diffraction using a high-precision Guinier diffractometer described elsewhere [10]. The sample was found to be in a single phase and the lattice parameter, $a = 4.265 \pm 0.002 \text{ \AA}$, was in excellent agreement with JCPDS data.

High-pressure x-ray diffraction (HPXRD) was carried out with a Mao–Bell type diamond anvil cell (DAC) in an angle dispersive mode using the Guinier geometry. The detailed description of the Guinier diffractometer set-up for carrying out high-pressure experiments is published in [10]. The Huber–Guinier diffractometer is in the vertical configuration (in symmetric transmission mode) with a Seeman–Bohlin focusing circle of diameter 114.6 mm. It is in combination with a curved quartz crystal monochromator and a linear position sensitive detector (PSD) of length 50 mm. The incident Mo x-ray is obtained from a Rigaku 18 kW rotating anode x-ray generator (RAXRG). This unique combination of apparatus offers an almost truly $K\alpha_1$ molybdenum radiation and reduces the scan time for obtaining a readable HPXRD pattern to as low as $\frac{1}{2}$ h as compared to 20 h with the conventional film method. However, a scan time of about 2 h was required to obtain data with good signal to noise ratio. The overall resolution has been found to be $\delta d/d \approx 0.01\text{--}0.02$. A finely powdered sample mixed with Ag was loaded into the stainless steel gasket hole, along with a mixture of methanol, ethanol and water (MEW) in the ratio of 16:3:1 as the pressure transmitting fluid. The equation of state (EOS) of Ag [11] was used for pressure calibration. In a separate experiment, following the ruby pressure calibration, it was found that the pressure in the cell was truly hydrostatic up to a pressure of at least 20 GPa [12].

3. Results

3.1. High-pressure x-ray diffraction

High-pressure x-ray diffraction experiments were done up to ≈ 23 GPa. Figure 1 shows the high-pressure XRD patterns and figure 2 the variation of the interplanar spacings as a function of pressure. Since the XRD patterns were recorded with a PSD of length 50 mm covering an angular range of 10° , the first peak (100) in the XRD pattern of UAl_3 was not detected as it remained outside the angular range. The P – V data are shown in figure 3. The P – V curve compares very well with those reported for similar compounds by Benedict [7]. The P – V curve clearly shows some change in the slope at about 5 and 10 GPa. Here, it may be noted that the B_0 value obtained by fitting the P – V data to the regular form EOSs may not yield the true values due to the changes in the system associated with the anomalies.

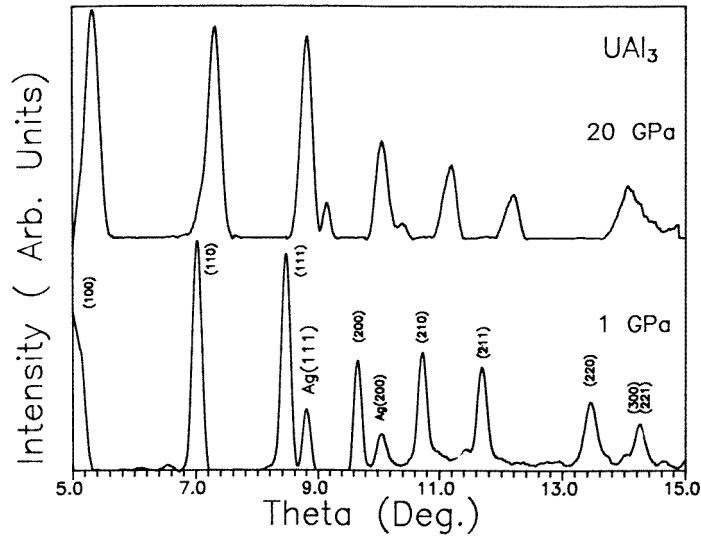


Figure 1. High-pressure x-ray diffraction patterns of UAl_3 at 1 GPa and 20 GPa. Molybdenum $\text{K}\alpha_1$ radiation with $\lambda = 0.70926 \text{ \AA}$ was used. Silver was used as the internal pressure calibrant.

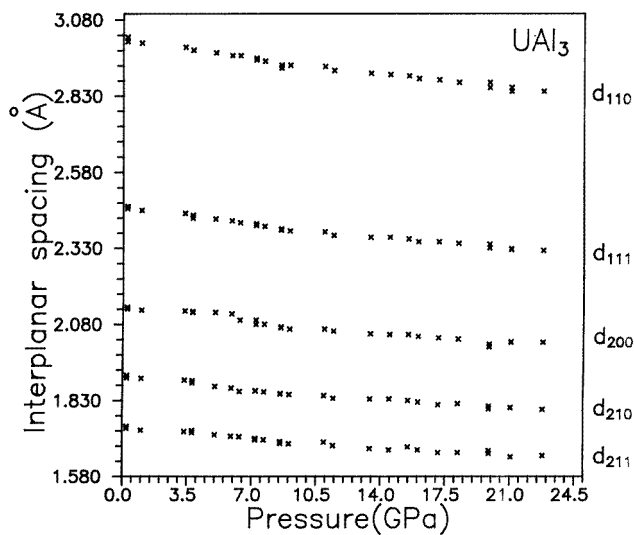


Figure 2. The interplanar spacings of UAl_3 as a function of pressure.

3.2. Band structure calculations

The band structure and the total energies of UAl_3 which crystallizes in the AuCu_3 structure were obtained by means of the tight-binding linear muffin-tin orbital method (TBLMTO) within the atomic sphere approximation (ASA). This is an exact transformation of Andersen's linear muffin-tin orbital method [13] to localized short-range or tight-binding orbitals. The exchange–correlation potential within the local density approximation (LDA) is calculated using the parametrization scheme of von Barth and Hedin [14]. The

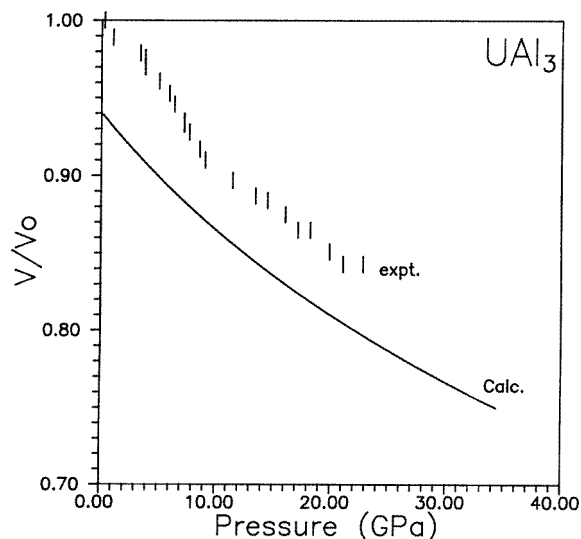


Figure 3. P - V data for UAl_3 . The error bar gives the possible inaccuracies involved in the measurement.

most important corrections, namely, the Darwin correction and mass-velocity terms, were included and the spin-orbit coupling was neglected. The sphere radii for U and Al atoms are chosen in such a way that the potential at the sphere boundary is minimum and there is a small amount of charge transfer from U to Al as per the electronegativity criteria.

The combined correction terms which account for the non-spherical shape of the atomic cells and the truncation of higher partial waves inside the spheres were included so that the error in the LMTO method is minimized. The basis sets chosen to represent the valence states of uranium and aluminium were $(7s7p6d5f)$ and $(3s3p3d)$ respectively.

The band structure calculations were performed for 512 k points in the Brillouin zone. The k convergence was checked by increasing the number of k points. The density of states was calculated by the method of tetrahedra [15].

The total energies were calculated in a manner similar to the earlier technique used by one of the coauthors [16, 17] by changing the volume from $1.1 V_0$ to $0.75 V_0$, where V_0 is the equilibrium cell volume. The variation of total energies with volume is given in figure 4. The calculated total energies were fitted to the Birch EOS [18] to obtain the pressure-volume relation as shown in figure 3 (Calc.). The calculated compression curve does not reproduce exactly the features shown by the experimentally observed changes in the slopes. We presume that this might be due to the inherent limitation of the calculation, since it is known that the volume changes below 1% are difficult to discern. The pressure is obtained by taking the volume derivative of the total energy. The bulk modulus

$$B_0 = -V_0 dP/dV$$

is calculated from the P - V relation. The theoretically calculated value of the equilibrium lattice parameter (4.1805 \AA) and the bulk modulus ($B_0 = 98.07 \text{ GPa}$) are in good agreement with our experimentally observed values. The estimated error in the calculated lattice parameter is 1.9%.

The self-consistent scalar relativistic band structure of UAl_3 along the symmetry direction Γ -X-M-R- Γ at ambient pressure was calculated and is shown in figure 5.

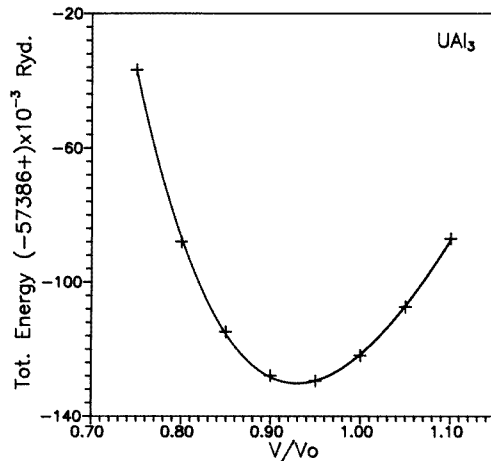


Figure 4. The total energy versus volume for UAl_3 .

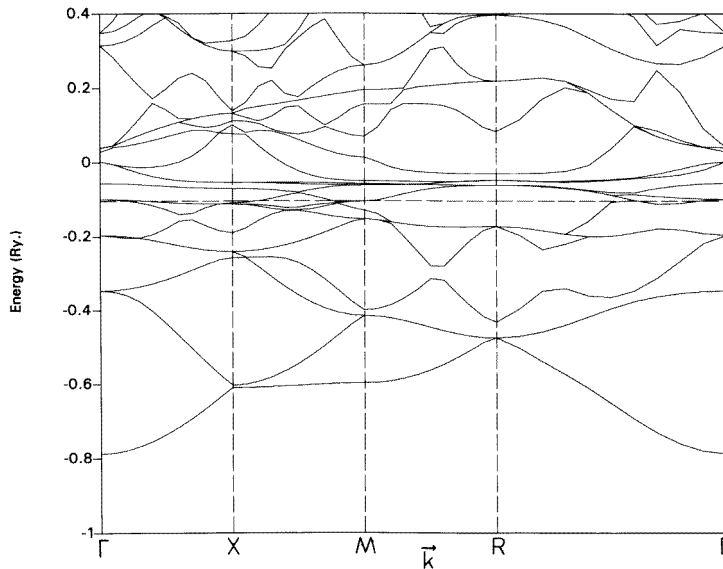


Figure 5. The band structure of UAl_3 at equilibrium volume.

The overall band profile is very similar to those of isostructural compounds such as UGe_3 , UIr_3 and URh_3 . The lowest-lying conduction band is mainly of the U $7s$ type, followed by the Al $3s$ -like and $3p$ -like states. Just above the Fermi level E_F , the U $5f$ states form a narrow band. From the present work, we find that U has 2.621 f -like electrons inside the Wigner–Seitz sphere at atmospheric pressure which agrees well with the other theoretical calculations reported for UGe_3 [19]. The electronic specific heat coefficient (τ) which depends upon the total density of states is obtained by using the expression:

$$\tau = (\pi)^2 N(E_F) k_B^2 N_A / 3.$$

The calculated value of τ at ambient pressure is $3.70 \text{ mJ K}^{-2} \text{ mol}^{-1}$.

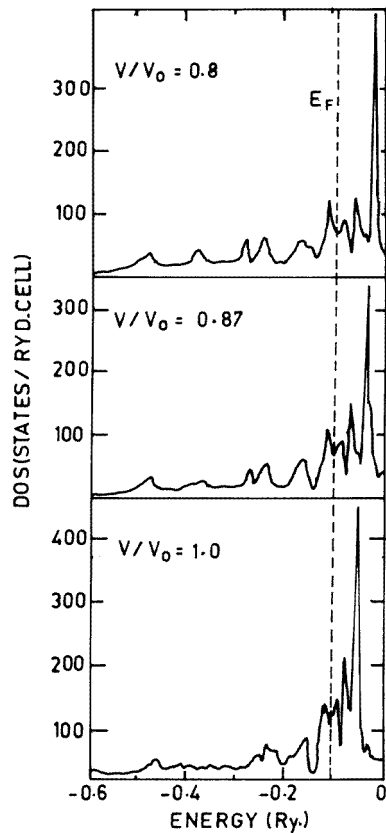


Figure 6. The electron density of states computed at various volume compressions, shifted to the same Fermi energy (at equilibrium volume).

4. Discussion

4.1. Nature of 5f states of uranium in UAl_3

The total densities of states at atmospheric and at two other pressures are presented in figure 6(a)–(c). To our knowledge, no PES (XPS or BIS) studies for UAl_3 are available in the literature. However, such results are available for the isostructural compounds UGe_3 , UIr_3 and URh_3 [19]. In the case of UGe_3 , the PES studies show that the Fermi energy lies on a fairly sharp peak in the density of states which contains a large fraction of f-electron character in the wave function. The occupied portion of the f-electron states in UGe_3 has been reported to be about 1.2 eV below the Fermi energy. It has also been concluded that the f electrons have a tendency towards localization [19]. In the case of UAl_3 , the f-electron states extend up to about 1.19 eV below the Fermi level. In analogy with UGe_3 the f electrons in UAl_3 also may be of localized nature.

Upon further compression, there is a transfer of electrons from the 5f to the 6d states at the U site. The partial numbers of electrons as a function of V/V_0 at both the sites are given in table 1. From the table, it is clear that the amount of d-like electron concentration at U site increases at the expense of f-like electrons. In summary, the calculations do point

Table 1.

V/V_0	Uranium				Aluminium		
	s	p	d	f	s	p	d
1.0	0.490	0.654	2.276	2.621	1.171	1.503	0.311
0.95	0.483	0.662	2.318	2.587	1.151	1.506	0.326
0.90	0.475	0.670	2.360	2.552	1.130	1.508	0.342
0.85	0.466	0.681	2.404	2.516	1.109	1.508	0.360
0.80	0.457	0.694	2.447	2.483	1.086	1.505	0.382

out an overall transfer of electrons from 5f to 6d, but are unable to reproduce the changes in the slope of the observed compression curve.

The cubic $AuCu_3$ structure predominantly occurs in more than 50% of the known AB_3 type of compound existing in the phase diagram. This structure comes under the class of Laves phases which has been found to be stable under a wide compression range like the AB_2 type of compound [20, 21]. Also the present investigation, in combination with the reported structural stability of other AB_3 type compounds, points to the fact that the cubic $AuCu_3$ structure shows a wide structural stability range under compression.

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