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Crystal Structure of UAl_2 above 10 GPa at 300 K

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Abstract

A high pressure X-ray diffraction study on UAl_2 has been done up to ≈28 GPa. It undergoes a structural transition at ≈11 GPa and the structure of the high pressure phase has been identified to be of the $MgNi_2$ type with space group $P6_3/mmc$. The structure of the ambient pressure phase is of the $MgCu_2$ type with space group Fd3m. From the electron per atom ratio *e/a*, it is expected that it may transform back to the $MgCu_2$ type structure at still higher pressures. On the basis of similar arguments, it is expected that most of the AB_2 type Laves phase compounds of the f electron systems with suitable *e/a* ratios may undergo the pressure induced structural transition in the sequence $MgCu_2 \rightarrow MgZn_2$(or $MgNi_2$)$\rightarrow MgCu_2$ due to increased delocalization of their f electron states.

Keywords: High pressure; X-ray diffraction; Phase transition; Laves phases

1. Introduction

In the AB_2 type Laves phase compounds of the actinides, the dialuminides form an interesting family with unusual physical properties. For example, the dialuminides of U, Np and Pu display a variety of magnetic properties ranging from spin fluctuations to ordered magnetism [1]. UAl_2 is a classic spin fluctuation system [2] and has been studied extensively by a variety of techniques. The low temperature specific heat [3], magnetic susceptibility [4–6] and electrical resistivity [5,7] studies clearly indicate ferromagnetic type spin fluctuation behaviour. At ambient conditions, UAl_2 has the C15 ($MgCu_2$ type, space group Fd3m) structure with an interactinide distance $d_{An} \approx 3.38$ Å, very close to the Hill limit. Photoemission studies [8] indicate the itinerant nature of the 5f electron states in it. The high pressure magnetic susceptibility [9] and electrical resistivity studies [10] indicate suppression of spin fluctuation in this system. Itie et al. [11] have performed energy dispersive X-ray diffraction (EDXD) studies on this system up to ≈36 GPa and have reported a structural phase transition to an unidentified structure at ≈10 GPa. The objective of the present investigation was to (i) characterise the high pressure phase of UAl_2 and determine its crystal structure and (ii) obtain the compressibility data to throw more light on the nature of the 5f states.

2. Experimental

Single phase UAl_2 compound was prepared by arc melting the stoichiometric quantities of U (99.98% pure) and Al (99.99% pure) in a He atmosphere. The arc melted buttons were then sealed in quartz tubes under an Ar atmosphere and annealed for about 6 weeks at 1100 K. The annealed buttons were etched in nitric acid to remove any oxide layer and stored in a hexane medium. The powdered samples were characterized by X-ray diffraction (XRD) using a Guinier diffractometer having an overall resolution of $\Delta d/d \approx 0.005$. It was found to be of $MgCu_2$ type structure and in single phase with lattice parameter $a = 7.762(5)$ Å. This compares very well with the JCPDS value of $a = 7.766$ Å.

High pressure X-ray diffraction (HPXRD) was carried out with a Mao–Bell type diamond anvil cell (DAC) in the angle dispersive mode using both the film method and a novel Guinier diffractometer. In the film method the DAC is provided with a cassette of radius 50 mm in which standard 35 mm X-ray films can be loaded to record the diffraction pattern from the sample. The Huber Guinier diffractometer is in 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 Mao–Bell type DAC is fitted to the diffrac-

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tometer such that the position of the sample inside the DAC lies exactly on the Seeman–Bohlin circle.The incident Mo X-ray is obtained from a Rigaku 18 kW rotating anode X-ray generator (RAXRG). This unique combination of apparatus reduces the scan time for obtaining a readable HPXRD pattern to as low as 30 min as compared to 20 h with the conventional film method. However, due to the linear nature of the PSD and other reasons, the overall resolution has been found to be $\Delta d/d \approx 0.01$–0.02. Details of the Guinier set up are published in Ref. [12]. Finely powdered samples of UAl_2 were loaded into the gasket hole along with a mixture of methanol:ethanol:water in a 16:3:1 ratio as the pressure transmitting fluid. The equation of state (EOS) of Ag was used for pressure calibration. While using the film method, with RAXRG operating at 15 kW, an exposure time of 20 h was found to be adequate to obtain a good pattern. But while employing the Guinier diffractometer, the RAXRG was operated only at $\approx$10–12 kW to avoid warming up the quartz crystal monochromator mounted on the X-ray tube shield. At 10 kW, a PSD position scan time of 2 h was sufficient to obtain data with good signal to noise ratio.

3. Results and discussion

The high pressure X-ray diffraction investigations were done on UAl_2 up to $\approx$28 GPa. A reversible structural phase transition was observed at around 11 GPa. Fig. 1 shows a typical raw diffraction spectra of the parent cubic phase at 1 GPa and the high pressure phase at 25 GPa. The angular slot opening of DAC provides a maximum $\theta \approx 200$. As the flat PSD covers 10° in a single scan, two positional scans at 5° and 15° were recorded. Itie et al. [11] observed the above transition at $\approx$10 GPa. In their EDXD spectra taken with synchrotron radiation source, only 5 new peaks could be observed, which along with the parent lines, prevailed up to the maximum pressure of $\approx$36 GPa.They did not identify the structure, but suggested that the new phase could be a modulated structure of the parent cubic phase.

In the present experiment, as can be seen from Fig. 1, more finer features of the high pressure phase with a number of new peaks could be seen. Some of the parent lines were split into multiple peaks and others remained up to maximum pressure. Observation of such fine features are believed to be due to the high efficiency of the PSD and the focusing geometry of the Guinier diffractometer [12]. Appearance of new peaks and splitting of a few parent peaks indicated that the structure of the high pressure phase might be of lower symmetry. Various possible structures were fitted to the high pressure phase and the best fit was found to be with the $MgNi_2$ type structure with space group $P6_3/mmc$ ($Z = 8$). Almost all the lines could be indexed with this new structure (Fig. 1). The cell parameters at a pressure of $\approx$25 GPa were found to be $a = 5.165(15)$ Å, $c = 16.083(15)$ Å and $c/a = 3.114$. Except for the intensities, the calculated d-spacings (Table 1) matched very well with the observed values. In high pressure experiments, such disparity in the intensities is well known [15] and arises mainly due to the preferred orientation of the sample in the DAC.

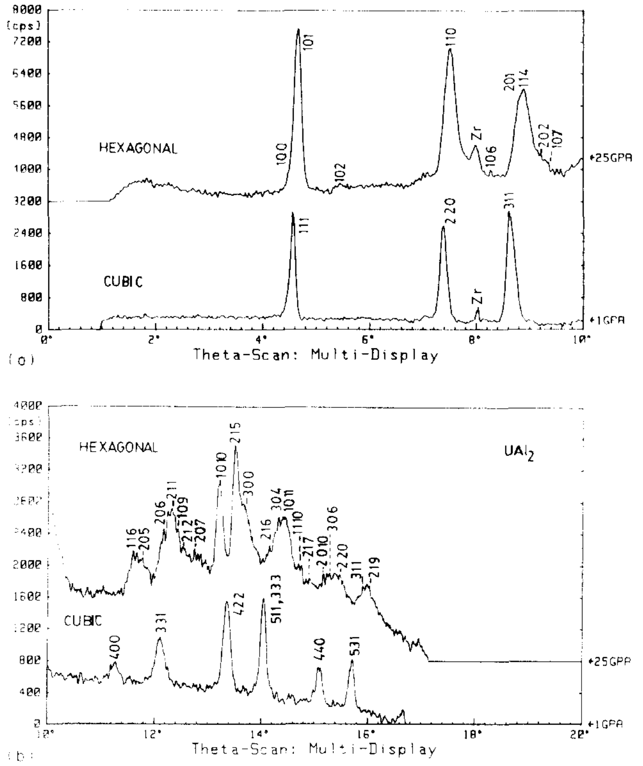

Fig. 1. High pressure X-ray diffraction patterns of UAl_2 at 1 GPa and 25 GPa. The flat PSD covers 10° in a single scan and two positional scans of 10 h duration each at (a) 5° and (b) 15° were taken to cover the θ range 0°–20°. The spectrum at 25 GPa has been indexed to the $MgNi_2$ type hexagonal structure.

The P–V data for UAl_2 is shown in Fig. 2. As it is evident from the figure there seems to be negligible volume change across the transition. The P–V data up to 11 GPa was fitted to both the Murnaghan [13] and the Birch–Murnaghan [14] EOSs, to obtain the bulk modulus B_0 and its pressure derivative B_0'. The values of B_0 and B_0' obtained in this study are: 83.97 ± 7.88 GPa and 8.10 ± 2.34 with the Murnaghan EOS and 82.39 ± 8.99 GPa and 9.29 ± 3.55 with the Birch–Murnaghan EOS respectively. Its high bulk-modulus is consistent with the itinerant nature of 5f states.

It has been found that almost all the known dialuminides of rare earths and actinides (except for $ThAl_2$) have the Laves phase cubic (C15) $MgCu_2$ type structures with space group Fd3m [16,17]. Apart from the dialuminides, other AB_2 type (A: rare earths, B = Ru, Os, Fe, Co, Ni, etc.) also have this structure [18]. The

Table 1
The observed and calculated θ and the d spacings of the hexagonal phase of UAl_2 at ~25 GPa. The wavelength $\lambda = 0.70926$ is used

Peak No.	θ(obs) (°)	θ(cal) (°)	d(obs) (Å)	d(cal) (Å)	*hkl*
1	4.547	4.55	4.4735	4.4730	100
2	4.721	4.72	4.3097	4.3095	101
3	5.356	5.21	3.7992	3.9090	102
4	7.892	7.89	2.5829	2.5825	110
5	8.914	8.87	2.2886	2.2993	106
6	9.121	9.21	2.2370	2.2152	201
7	9.400	9.39	2.1713	2.1729	114
8	9.540	9.47	2.1401	2.1547	202
9	9.980	9.99	2.0463	2.0437	107
10	10.980	10.99	1.8619	1.8598	116
11	11.118	11.14	1.8390	1.8363	205
12	11.884	11.92	1.7220	1.7173	206
13	12.120	12.18	1.6890	1.6814	211
14	12.340	12.34	1.6594	1.6595	109
15	12.381	12.38	1.6539	1.6545	212
16	12.797	12.79	1.6018	1.6026	207
17	13.550	13.55	1.5136	1.5134	1010
18	13.701	13.71	1.4972	1.4965	215
19	13.760	13.76	1.4909	1.4910	300
20	14.353	14.36	1.4306	1.4300	216
21	14.716	14.70	1.3971	1.3980	304
22	14.760	14.79	1.3920	1.3897	1011
23	14.908	15.06	1.3784	1.3652	1110
24	15.160	15.10	1.3560	1.3617	217
25	15.774	15.76	1.3054	1.3057	2010
26	15.815	15.79	1.3012	1.3030	306
27	16.078	15.94	1.2805	1.2912	220
28	16.729	16.66	1.2320	1.2369	311
29	16.77	16.78	1.2294	1.2280	219

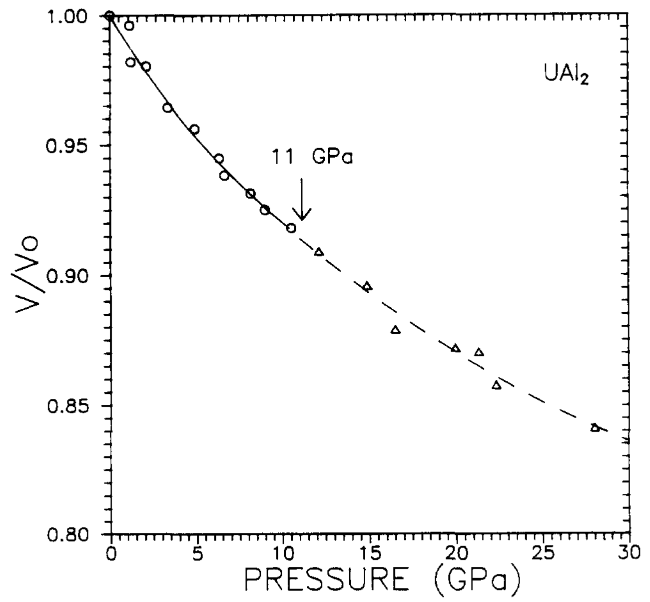

Fig. 2. P–V data for UAl_2 up to 28 GPa. The ○ represents the data for the cubic phase and the △ the hexagonal phase. The continuous line up to 11 GPa is the Murnaghan fit to the experimental data. The dotted line above 11 GPa is a guide to the eye only.

Laves phases are a set of three related complex structures which occur frequently in AB_2 type binary compounds and are isomorphs of $MgZn_2$ (C14, $Z=4$), $MgCu_2$ (C15, $Z=8$) and $MgNi_2$ (C36, $Z=8$) type structures with similar atomic densities [18–20].The first and the third are hexagonal with the same space group $P6_3/mmc$, but with different c/a ratios.

The general opinion is that the geometrical factor (the ratio of atomic radii R_A/R_B) is connected with the existence of the alloys of the Laves phase type [18,19]. Both the cubic ($MgCu_2$) and hexagonal ($MgZn_2$ and $MgNi_2$) should exist at $R_A/R_B=1.225$. In reality, these structures have been found for radii ratios in the range 1.1–1.7. From electronic structure considerations, it has been found that the $MgCu_2$ type structure is stabilised at the free electron concentrations (i.e. number of free electrons per atom e/a) of $e/a<1.8$ and $e/a>2.3$ [21,22]. For intermediate concentrations ($1.8<e/a<2.3$), both $MgZn_2$ and $MgNi_2$ structures are obtained. The connection between free electron concentration and crystal structure is clearly seen in pseudobinary alloys of type $A(B_{1-x}C_x)_2$ (A = rare earth, B = Al, C = Fe, Co, Ni, etc.) [18]. The structure is found to change from the type of $MgCu_2$ to $MgZn_2$ and back to $MgCu_2$ when the concentration of Al increases, in other words, on increasing the free electron concentration from 1–3 per atom.

In UAl_2, the e/a ratio is ≈ 1.66 [23] which corresponds to the region of $MgCu_2$ type structures. In the f electron systems under pressure, increased delocalization of the f electron states lead to an increase in the e/a as well as a decrease in the R_A/R_B due to the contraction of the electronic orbitals in the A (here f) atom. Hence in UAl_2, the transition from $MgCu_2$ to $MgNi_2$ type structure can be understood from the increase in the e/a ratio into a region >1.8 where the $MgZn_2$ or $MgNi_2$ structures are stable. At further higher pressures, it may even transform back to the $MgCu_2$ type structure when its e/a ratio exceeds 2.3. The negligible volume change across the transition in UAl_2 also follows from the almost similar atomic densities of the two structures.

Some of the $REOs_2$ systems like $LaOs_2$, $CeOs_2$ and $PrOs_2$ have also been found to undergo the structural transitions of the type $MgCu_2$ to $MgZn_2$ under pressure [24]. In these systems, the e/a ratios are in the range 1.60–1.68 [23] corresponding to the region of $MgCu_2$ type structures at ambient conditions.

Thus it appears that the structural sequence $MgCu_2$–$MgZn_2$ (or $MgNi_2$)–$MgCu_2$ is the natural outcome of the increased delocalization of the f electron states under pressure. This structural sequence can be expected in other actinide and rare earth based AB_2 type Laves phases with their e/a ratios in the range <1.8.

A systematic high pressure structural investigations on the f electron based AB_2 type Laves phases is desired to establish this pressure induced structural sequence and to correlate the structural boundaries quantitatively with their *e/a* and R_A/R_B ratios. Band structure calculations as a function of pressure would be of much help in understanding the nature and mechanisms of these transitions.

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