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High pressure X-ray diffraction study of UC_2 using synchrotron radiation

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Abstract

UC_2 has been studied under the general topic of X-ray diffraction analysis of pressure-induced structural transitions in actinide compounds and the determination of their ambient pressure bulk moduli. At 17.6 GPa UC_2 shows a phase transition from a tetragonal to a hexagonal structure. The mean values of the bulk modulus and its pressure derivative are 216 GPa and 2.2 respectively.

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1. Introduction

Hill [1] has reported that it is possible to associate the magnetic behaviour of actinide compounds with the inter-actinide distance. Below a certain limit of the inter-actinide distance, called the Hill limit, the compounds are non-magnetic which is correlated with a delocalization of the 5f electrons. Above this limit, the compounds are magnetic and the 5f electrons are localized. This Hill criterion has some exceptions but is a good starting point in the study of actinide compounds. Using Hill plots [1], it can be seen that UC_2 falls in the transition region. With increasing pressure, the shortest U–U distance (352 pm at ambient pressure) may decrease sufficiently to induce a structural transition correlated with 5f electron delocalization.

2. Experimental details

The uranium dicarbide used was prepared by arc melting from a mixture of uranium metal (purity, 99.7%) and graphite (purity, 99.5%) in the atomic ratio 1:2.5. UC_2 crystallizes in the tetragonal CaC_2-type structure, space group *I4/mmm* (no. 139), with two molecules per unit cell. The compound obtained was sealed under a dry atmosphere to avoid reaction with water.

The sample was finely crushed in silicon oil dried over calcium hydride. This same oil was used as the pressure-transmitting medium. The sample was then quickly loaded into an Inconel-gasketed diamond anvil cell of the Syassen–Holzapfel type. A ruby chip was added to the sample for the pressure measurement using the non-linear ruby fluorescence method [2]. The polychromatic X-ray source needed for energy-dispersive diffraction experiments was synchrotron radiation provided by DESY Hasylab. The Bragg angle was determined from an NaCl diffraction spectrum used as reference. For each pressure step, the d_{hkl} values deduced from the energy–dispersive spectrum were used to calculate the lattice parameters and the relative volume V/V_0. The isothermal bulk modulus and its pressure derivative were determined by fitting the $V/V_0 = f(p)$ data (zero indicates ambient pressure) to several equations of state [3–6]. The lattice parameters determined at ambient pressure in the diamond anvil cell were equal to 551.6(6) pm for a and 600.3(6) pm for c, in agreement with the literature [7].

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3. Results and discussion

UC_2 was studied up to 50.1 GPa in 21 steps. Near 17.6 GPa, a stuctural transition occurred as the d_{hkl} variation shows in Fig. 1. The new phase remains stable under pressure up to the highest pressure reached and, on pressure release, down to approximately 5 GPa. The low pressure structure reappears below this pressure value. To determine the structure of the new phase, we made use of two simple mathematical relations observed for the d_{hkl} values at 19.7 GPa (Table 1): $d_1/d_7=1/2$ and $d_1/d_2=(4/3)^{1/2}$.

From the well-known equations used to calculate the d_{hkl} values from the lattice parameters and the *hkl*

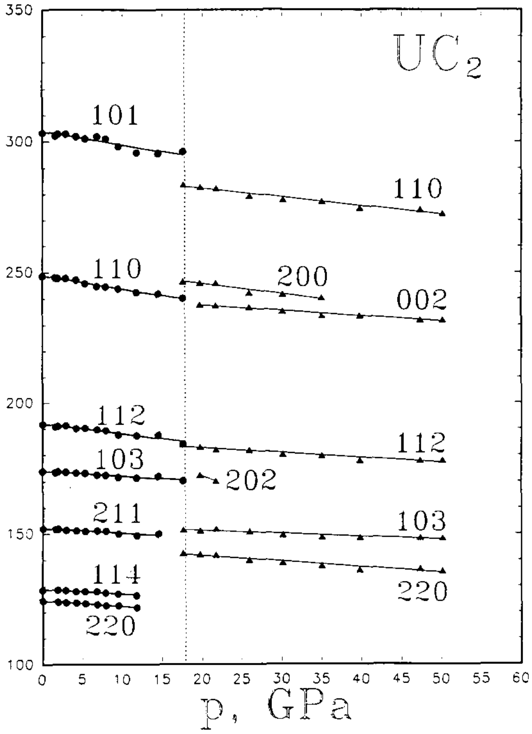

Fig. 1. d_{hkl} of UC_2 *vs.* pressure (filled circles for tetragonal low pressure phase and filled triangles for hexagonal high pressure phase).

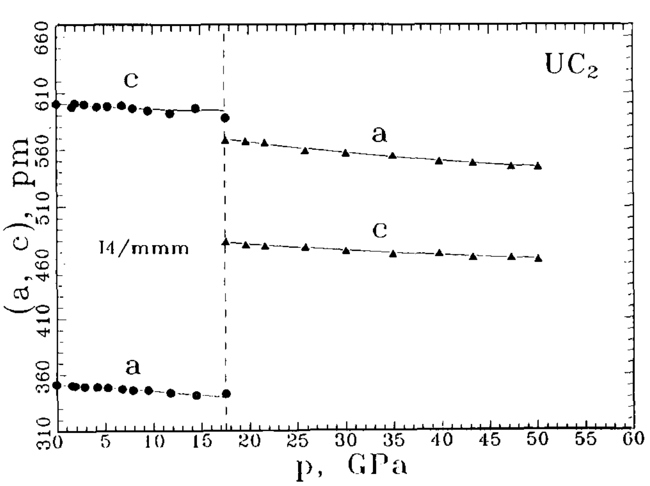

Fig. 2. Lattice parameters of UC_2 *vs.* pressure (filled circles for tetragonal low pressure phase and filled triangles for the hexagonal high pressure phase).

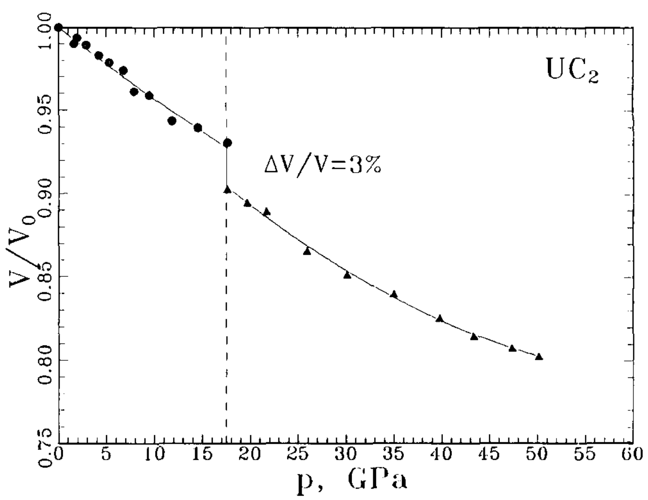

Fig. 3. Relative volume of UC_2 *vs.* pressure (filled circles for tetragonal low pressure phase and filled triangles for the hexagonal high pressure phase).

TABLE 1. Diffraction data of the hexagonal phase of UC_2 at 19.7 GPa. The reliability factor $\Sigma|\Delta d|/\Sigma d_{obs}=0.3\%$ and the lattice parameters are $a=567.4(6)$ pm and $c=476.7(5)$ pm

Peak (intensities)	d_{obs} (pm)	*hkl*	d_{calc} (pm)	$\lvert\Delta d/d\rvert \times 100$
d_1 (w)	282.7	110	283.7	0.35
d_2 (s)	246.1	200	245.7	0.16
d_3 (s)	237.7	002	238.4	0.27
d_4 (m)	182.9	112	182.5	0.20
d_5 (m)	172.3	202	171.1	0.81
d_6 (m)	151.2	103	151.2	0.02
d_7 (w)	142.2	220	141.8	0.27

TABLE 2. Isothermal bulk modulus of tetragonal UC_2 and its pressure derivative determined from several equations of state (Table 3). Average uncertainty is equal to 10 GPa for B_0 and 0.1 for B_0'

Equation	B_0 (GPa)	B_0'
Murnaghan [4]	216	2.2
Birch [3]	215	2.4
Rose *et al.* [5]	216	2.2
General MV*L* [6]	215	2.4
Holzapfel 0*L* [6]	216	2.1
Holzapfel 1*L* [6]	216	2.0
Mean	216	2.2

MV*L*: Modified Vinet form of *L*th order.
H0*L*: Holzapfel form of *L*th order.
H1*L*: Holzapfel form of *L*th order + 1 condition compared to H0*L*.

TABLE 3. Several equations of state (EOS) used to calculate the bulk modulus B_0 and its pressure derivative B_0' ($x=(V/V_0)^{1/3}$ $1 \leq k \leq L$)

Murnaghan [4]	$p=(3/c_2)B_0x^{-c_2}(1-x^{c_2})$ $c_2=3B_0' \neq 0$
Birch [3]	$p=3/2B_0x^{-7}(1-x^2)(1+\Sigma c_{k+1}[(1-x^2)/x^2]^k)$ $c_2=3/4(B_0'-4)$
Rose *et al.* [5]	$p=3B_0(x-1)(\exp(-a^*))[1-0.15a^*+0.05a^{*2}]x^2$ $a^*=(r-r_0)/l$ where r is Wigner–Seitz radius $l=[\Delta E/(12\pi B_0r_0)]^{1/2}$ where ΔE is cohesive energy
General MV*L* [6]	$p=3/nB_0x^{-m}(1-x^n)(\exp[\Sigma c_{k+1}(1-x)^k])$ $p_{FG0}=p_{FG}(Z, V_0)$, Z=atomic number $c_2=3/2[B_0'-(2m-n)/3]$ m and n: adjustable parameters
Holzapfel 0*L* [6]	$p=3B_0x^{-5}(1-x)(\exp[\Sigma c_{k+1}(1-x)^k])$ $c_2=3/2(B_0'-3)$
Holzapfel 1*L* [6]	$p=3B_0x^{-5}(1-x)[\exp(c_0(1-x)+x\Sigma c_{k+1}(1-x)^k)]$ $c_0=\ln p_{FG0}-\ln B_0$ $c_2=3/2(B_0'-3)-c_0$

TABLE 4. Linear compressibilities of UC_2 tetragonal lattice parameters [8]

	a	c
β (GPa^{-1})	$198(18)\times10^{-6}$	$57.0(40)\times10^{-6}$
δ (GPa^{-2})	$23.7(13)\times10^{-6}$	$-25.8(22)\times10^{-6}$

TABLE 5. Estimated interatomic distances of the UC_2 tetragonal phase at ambient pressure and 17.6 GPa

Atom	Neighbour	Distance (pm)	
		Ambient pressure ($a=351.6$, $c=600.3$)	17.6 GPa ($a=343$, $c=588$)
U2(a)	4U	352	343
(0,0,0)	8U	390	381
	2C	233	228
	8C	258	251
	2C	367	360
	8C	422	412
C4(e)	1C	135	132
(0,0,2)	4C	299	255
$z=0.388$	4C	352	343
	4C	376	367
	8C	390	381

values, we found that these relations can be simply related to a hexagonal lattice ($1/d_{hkl}{}^2=(4/3)(h^2+hk+k^2)/a^2+l^2/c^2$ and $l=0$). The complete indexing of the pattern observed (Table 1) confirmed this assumption.

From the variation of d_{hkl} in both phases (Fig. 1), the evolution of the lattice parameters *vs.* pressure was calculated (Fig. 2). Assuming $Z=4$ for the hexagonal unit cell, Fig. 3 shows the pressure dependence of the normalized relative volume for both phases. There is a volume decrease of about 3% at the transition calculated as

$$(V_{hex}-V_{tet})/V_{tet}=-3\%$$

where V_{hex} and V_{tet} are the unit cell volumes of the hexagonal and tetragonal phases divided by Z_{hex} and Z_{tet} respectively at the transition pressure.

The isothermal bulk moduli and their pressure derivatives were obtained by fitting several equations of state to the experimental curve of the tetragonal low pressure phase (Tables 2 and 3). Furthermore, assuming hydrostatic conditions, the linear compressibilities of the UC_2 lattice parameters were calculated as proposed by Fietz *et al.* [8] and reported in Table 4.

X-ray diffraction results do not allow us to obtain the atomic positions from the peak intensities, which are not reliable due to possible preferred orientation of the crystals in the polycrystalline sample. Making the approximation that the atomic positions do not change until transition, we can estimate the interatomic distance variation (Table 5). From this table, it seems possible that the first uranium–uranium distance decreases sufficiently to induce a structural change due to the 5f electrons. However, this phase transition may also be due to the decrease in the shortest C–C distance. To obtain more direct information about the electronic behaviour of UC_2 under pressure, spectroscopic measurements, such as optical reflectivity, and resistivity experiments under pressure seem desirable. Furthermore, considering the strong hysteresis observed, it seems that the lattice energies of both structures are similar.

Acknowledgments

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