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Lattice anisotropy in uranium ternary compounds: UTX

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ABSTRACT

Several U-based intermetallic compounds (UCoGe, UNiGe with the TiNiSi structure type and UNiAl with the ZrNiAl structure type) and their hydrides were studied from the point of view of compressibility and thermal expansion. Confronted with existing data for the compounds with the ZrNiAl structure type a common pattern emerges. The direction of the U–U bonds with participation of the 5*f* states is distinctly the "soft" crystallographic direction, exhibiting also the highest coefficient of linear thermal expansion. The finding leads to an apparent paradox: the closer the U atoms are together in a particular direction the better they can be additionally compressed together by applied hydrostatic pressure.

1. Introduction

One of the most striking features of the light-actinide compounds is a giant magnetic anisotropy, originating from sizeable orbital magnetic moments induced in the system of bonding itinerant electrons by a strong spin–orbit interaction. Such a situation leads to the so-called hybridization-induced anisotropy, which is two-ion by nature, and is therefore qualitatively different from a single-ion anisotropy due to CEF phenomena [1,2]. This bonding directionality manifests itself mainly at low occupancy of the *f*-states; more *f*-electrons lead to a wider directional spread of occupied m_j states. U-systems with less than three 5*f* electrons per atom carry a hallmark of such phenomena in the orientation of 5*f* moments perpendicular to the shortest U–U bonds. It is most apparent in the case of uniaxial anisotropy, arising for a planar coordination of U, as in the ternary UTX compounds with the ZrNiAl structure type [3]. If U atoms are coordinated in linear chains (TiNiSi or GaGeLi structure types from the UTX compounds), a hard-magnetization axis is equivalent to the chain direction, with in-plane anisotropy perpendicular to the chain direction being weaker [3]. In this sense, the magnetic anisotropy reflects the bonding anisotropy in U-based compounds.

The UTX compounds with the ZrNiAl structure type were also found to exhibit a large elastic anisotropy [4]. Applying a hydrostatic pressure, the compression along the hexagonal basal-plane sheets (with shorter U–U spacing) is much higher than that along the *c*-axis. Such an effect observed for all studied U-based compounds and absent in rare-earth analogues indicates that the 5*f* states and 5*f*–5*f* bonds are the main culprit. It can be related to the sensitivity of the 5*f* states with highly variable degrees of delocalization to all control parameters. Ref. [4] also showed that the same pattern as the difference in linear compressibilities is followed by thermal expansion; the "soft" lattice directions also have the highest coefficients of linear thermal expansion. Such an elastic anisotropy has not yet been studied in other structure types, so its general validity (for U compounds) is uncertain.

Here we present results of high-pressure and thermal-expansion studies of several types of UTX compounds and their hydrides, which were selected to test a more general validity of the above mentioned rules, pointing out the specifics of light actinides. The crystallographic parameters of all investigated and some referenced UTX compounds are presented in Table 1. Hydrogenation is used as a tool to achieve a volume expansion. One has to be, however, cautious to interpret it as a negative pressure. The expansion due to the H absorption can be, as we observe, also highly

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Table 1
Structure type and lattice parameters of UTX compounds and their hydrides.

Compound	Structure type	a (Å)	b (Å)	c (Å)	V (Å^3/f.u.)	$\Delta V/V$ (%)	$d_{U–U}$ (Å)
UCoAl[a]	ZrNiAl	6.686		3.966	51.18		3.50
UPtAl[a]		7.012		4.127	58.58		3.60
UNiGa[a]		6.733		4.022	52.63		3.50
UCoGa[a]		6.693		4.019	51.97		3.50
URuGa[b]		7.115		3.836	54.40		3.73
UNiAl[a]		6.751		4.048	53.26		3.50
$UNiAlD_{2.1}$		7.189(2)		3.972(1)	59.26	11.3	3.98
UCoGe	TiNiSi	6.848(1)	4.207(1)	7.230(1)	52.07		3.48
$UCoGeH_{0.1}$		6.851(1)	4.201(1)	7.254(1)	52.19	0.2	3.48
$UCoGeH_{1.0}$	ZrBeSi	4.125(1)		7.517(2)	55.38	6.4	3.76
$UCoGeH_{1.7}$		4.095(1)		7.937(1)	57.64	10.7	3.97
UNiGe	TiNiSi	7.000(3)	4.233(2)	7.197(2)	53.31		3.56
$UNiGeH_{1.0}$	ZrBeSi	4.108(1)		7.714(2)	56.38	5.8	3.86
UIrGe	TiNiSi	6.867(1)	4.302(1)	7.576(1)	55.96		3.51
$UIrGeH_{0.1}$		6.880(2)	4.304(1)	7.609(2)	56.33	0.7	5.52

[a] [4].
[b] [22].

anisotropic, but the anisotropy can sometimes be different from that obtained by a hydrostatic pressure.

2. Experimental details

Polycrystalline samples of UNiAl, UNiGe, UCoGe, and UIrGe were prepared by arc melting of stoichiometric amounts of the constituent metals. The crystal structure was checked by means of XRD-3003 Seifert diffractometer (Cu-Kα radiation). In the case of UNiGe a certain amount (7–8%) of spurious phase (UNi_2Ge_2) was detected.

After initial preparation, hydrides of these compounds were synthesized. Prior to exposing a bulk material to hydrogen/deuterium, it was crushed into sub-millimeter particles and placed into a reactor. The surface of the sample was activated by heating up to $T = 523$ K under high-vacuum conditions (pressure of 10^{-6} mbar). Subsequently the activated material was exposed to a hydrogen (or deuterium) atmosphere. Depending on its pressure, various H/D stoichiometries can be achieved. The last step was thermal cycling of the sample up to $T = 773$ K at a given hydrogen/deuterium pressure to promote the absorption. The absolute amount of absorbed H/D can be determined by thermally induced desorption into an evacuated calibrated volume.

The temperature dependence of the lattice parameters of $UNiAlD_{2.1}$, UIrGe, UNiGe and one of its hydrides ($UNiGeH_{1.0}$) were studied using a Siemens-D5000 diffractometer (Co-Kα radiation). The X-ray diffraction (XRD) data were collected at ambient pressure and temperature decreasing gradually down to 5 K (or down to 80 K for $UNiAlD_{2.1}$). Low-T diffraction data for $UNiAlD_{2.1}$ were collected by means of the time of flight method at LANSCE LANL.

The high-pressure XRD experiments were performed at room temperature up to 22 GPa using a modified Bruker D8 diffractrometer with focusing mirror optics, installed on a Mo rotating anode source ($\lambda = 0.70926$ Å). The microsample of $UNiAlD_{2.1}$ was placed in a diamond anvil cell (DAC) into the gasket (in our case mainly Be). High-pressure XRD data were collected on a Bruker Smart APEX II detector. Pressure was determined by means of the ruby fluorescence method and silicone oil was used as the pressure-transmitting medium. The diffraction images were processed using ESRF FIT2D software. The crystal structure refinements were done using the FullProf software suite.

3. Experimental results and discussion

3.1. Switching over the soft direction in the ZrNiAl family

The hexagonal ZrNiAl-type of structure (space group P-62m), which is the ordered ternary variant of the Fe_2P-type, has a distinct layered character. It is built up of U–T and T–X basal-plane layers alternating along the c-axis. The shortest U–U distances ($d_{U–U}$) are found within the U–T layers, where each U-atom has four nearest U neighbours. The U–T layers are separated by the lattice parameter c. Hydrides/deuterides of hexagonal UTX usually adopt the same type of structure as their precursors, but exhibit a large volume expansion. UNiAl was the first such compound, in which a large hydrogen absorption was detected, which leads to a large expansion in the basal plane, and a small compression in the c-direction [5]. More detailed structure studies [6,7] indicated that the U–U spacing within the basal plane increases enormously ($d_{U–U} \approx 3.48$ Å in UNiAl and $d_{U–U} \approx 4.15$ Å in its deuteride) so that it becomes higher than the c-axis spacing (3.98 Å). This would lead, provided the two-ion anisotropy model is correct, to a swapping of the anisotropy type from c-axis to the basal plane. This assumption could not be corroborated by neutron diffraction, as the magnetic structure could not be resolved from a small amount of magnetic reflections [8]. Neither single-crystal could be synthesized to determine the anisotropy of bulk susceptibility.

Therefore we undertook the high-pressure crystal-structure study of $UNiAlD_{2.1}$ with the aim to find a possible change of the soft crystallographic direction from the a-axis (basal plane) to the c-axis direction. Results of the room temperature XRD study under applied pressure up to 22 GPa are displayed in Fig. 1, together with similar data for UCoAl from Ref. [4]. The high-pressure XRD experiment was not performed for pure UNiAl, but because of the uniformity of behaviour of U compounds with the same structure type [4] one can expect close similarity of UNiAl and UCoAl.

The experiment was performed with gradually increasing pressure. After reaching the maximum pressure, a few data points were taken also during unloading. The agreement of lattice parameters of initial and final ambient-pressure state excludes that the H concentration would change during the high-pressure experiment.

The pressure variations of individual lattice parameters and volume were fitted to a quadratic polynomial dependence ($g_i(p) = g_i(0) - k_i g_i(0)p + k_i{}' g_i(0)p^2$) which yielded the linear compressibility k_i along each lattice direction i (Table 2). The bulk modulus can be expressed as $B_0 = 1/k_V$, where k_V is the volume

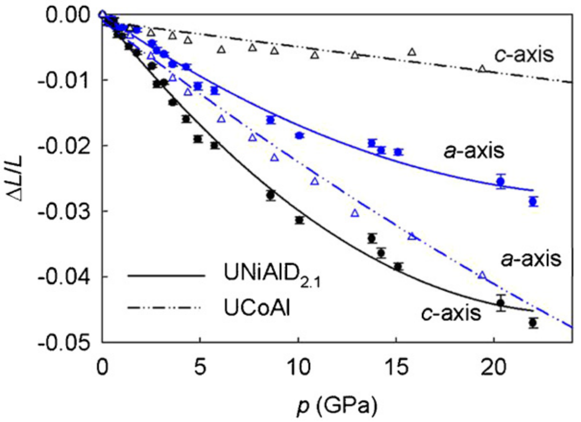

Fig. 1. Pressure variations of the relative change of the lattice parameters a and c for $UNiAlD_{2.1}$ compared with UCoAl [4].