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Abstract

X-ray diffraction measurements under pressure have been performed on seven different compositions in the $U_xLa_{1-x}S$ system ($x = 0, 0.08, 0.40, 0.50, 0.60, 0.80, 1$). All the compounds have the same structure (NaCl type) at ambient pressure, but show different behaviours under pressure. A transformation into the CsCl-type structure is only observed for $x \leqslant 0.60$. For $x = 0.80$ and 1, the high-pressure phase has yet to be determined. We also observe a difference in bulk modulus (for $x \leqslant 0.50$, $B_0 \leqslant 90$ GPa whereas for $x \geqslant 0.60$, $B_0 \sim 100$ GPa) and in the transition pressure (~ 30 GPa for low-uranium-content compounds and from 45 to 80 GPa for high concentrations).

1. Introduction

The monosulphide of uranium, US, which has the simple NaCl-type structure, is ferromagnetically ordered below 180 K along the easy axis $\langle 111 \rangle$. In spite of many theoretical and experimental studies, a clear understanding of its electronic structure and of the mechanisms responsible for its behaviour is still lacking.

The study of US solid solutions diluted with a diamagnetic element such as lanthanum should give us information about the evolution of interactions and so help us to understand the nature of the fundamental electronic state. From previous neutron diffraction studies [1, 2] and measurements of the macroscopic properties [3], it is clear that in the $U_xLa_{1-x}S$ solid solution, long-range magnetic ordering abruptly disappears at a critical concentration $x_c = 0.57(2)$, far from the percolation limit ($x \sim 0.14$), and the lattice parameter, which follows Vegard's law, increases abnormally around this critical concentration.

The disappearance of the ferromagnetic order could be linked to a delocalization of the uranium 5f electrons, which should influence the value of the compressibility. One way to verify that is to look at the structural behaviour of $U_xLa_{1-x}S$ solid solutions under pressure.
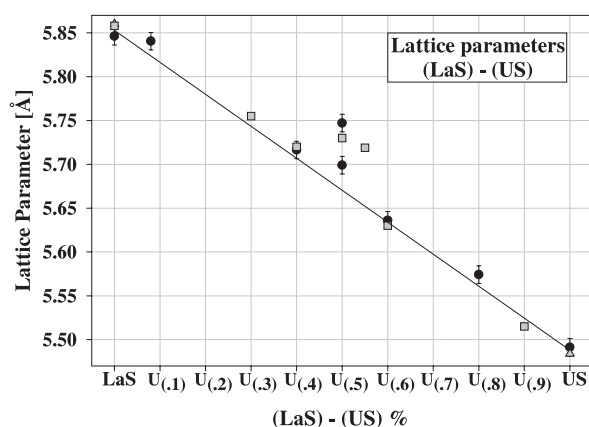
Figure 1. Lattice parameter as a function of U concentration in the $U_xLa_{1-x}S$ system. Black circles: this study; grey squares: [1]; grey triangles: literature.

2. Experimental details

High-pressure x-ray diffraction studies of $U_xLa_{1-x}S$ solid solutions have been carried out on the beamline ID30 at the ESRF and on F3 at Hasylab (one experiment concerning $U_{0.8}La_{0.2}S$). The 15 experiments were performed at room temperature using different types of diamond anvil cell (DAC) (Le Toullec, Chervin, Syassen–Holzapfel or Cornell design) and different pressure-transmitting media (helium, liquid nitrogen, liquid argon for low to medium pressure and silicone oil for very high pressure). The pressure was determined using the fluorescence of ruby for pressures up to 60 GPa. At higher pressure, platinum or gold powder was used as internal calibrant. At the ESRF a focused monochromatic beam of 0.3738 Å, was used with an image plate detector (Fastscan and MAR345), whereas at Hasylab we used a white beam with a germanium detector.

X-ray diffractograms were fitted with the Jandel Peakfit software. Cell parameters were obtained by a least-squares fit (Unit Cell program) of the diffraction data in the cubic setting.

3. Results and discussion

3.1. Structural anomaly at atmospheric pressure

In a solid-solution system, with the parent compounds having the same structure and different lattice parameters, the lattice parameter is expected to evolve linearly with the concentration, according to Vegard's law. As can be seen in figure 1, and in disagreement with previous work published by Schoenes *et al* [3], the $U_xLa_{1-x}S$ system exhibits a strong anomalous behaviour around x_c (0.57). The deviation of the lattice parameter from the linear law is much larger than the experimental error and has been found both with x-rays and neutrons. One could think about non-stoichiometry.

However the mineralization technique [4] used for the synthesis gives a good control of x-values ($\Delta x \approx 1\%$) and is incompatible with the observed deviation that would correspond to $\Delta x \approx 15\%$.

Surprisingly, and contrary to previous observations on $U_{0.5}La_{0.5}S$ and $U_{0.6}La_{0.4}S$ compounds in neutron diffraction experiments [1, 2], we do not see any peak broadening for any of the samples at atmospheric pressure. One explanation could be that with x-rays,
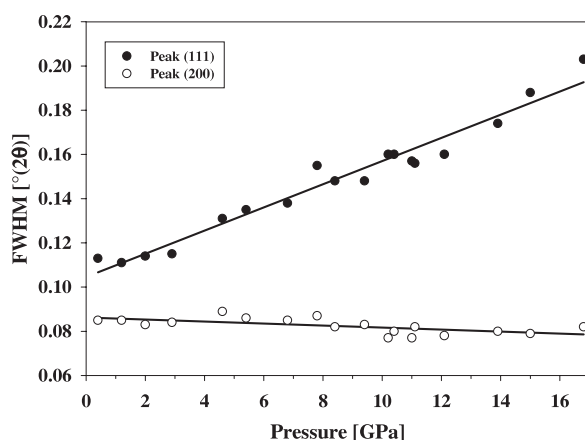
Figure 2. Full width at half-maximum as a function of pressure for the peaks (111) and (002) of the US compound in helium.

U atoms scatter much more than with S atoms, and a small local deformation of the S lattice could be impossible to see, whereas it can be detected with neutrons.

3.2. US

The most recent results concerning the structural behaviour of US under pressure were published by Gerward *et al* [5]. In contrast to USe and UTe which transform at 20 and 9 GPa respectively from the NaCl structure type into the CsCl one, the authors observed a rhombohedral distortion above 10 GPa, stable up to the maximum pressure reached, i.e. 55 GPa. We have found that, actually, this distortion starts as soon as the pressure is applied and increases with the latter. This phenomenon can be followed by observing the value of the FWHM of the (111) and (200) peaks of the NaCl cubic structure (figure 2).

A distortion involving this type of rhombohedral structure leads to a splitting of the (111) peak, transformed into $(111) + (\bar{1}11)$, whereas the (200) remains single. Furthermore, this phenomenon is correlated with the pressure-transmitting medium used in the DAC. For example, silicone oil induces internal stress at much lower pressure than helium gas, liquid nitrogen or argon. Around 70–80 GPa, we have observed another phase transition to a new as yet unidentified structure (figure 3). A similar transformation was also found for the $U_{0.8}La_{0.2}S$ compound with a transition pressure close to 55–60 GPa.

3.3. $U_x La_{1-x} S$

All the other compounds (from $x = 0$ to 0.6) behave in the same way, showing a rhombohedral distortion (peak broadening) followed by a transition to the CsCl structure type. A partial synopsis of the results is given in table 1.

Between $x = 0.50$ and 0.60, we observe a change in the bulk modulus calculated with the Birch–Murnaghan EoS. We expected a linear increase of B_0 with the concentration of U, but as can be seen in figure 4, we reach a minimum for $x = 0.40$ (partially due to a higher B_0'-value compared to those for the other compositions) followed by a strong increase around x_c.

An abrupt change in the value of the transition pressure (T_p) as a function of U concentration, around 0.50–0.60, was also observed. If T_p increases slowly from 28 to 33 GPa for $x = 0$–0.50, it jumps to 47 for $x = 0.60$ and to 80 for $x = 1$.
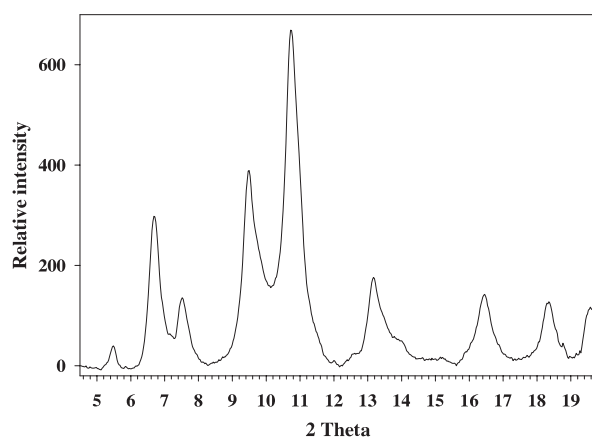
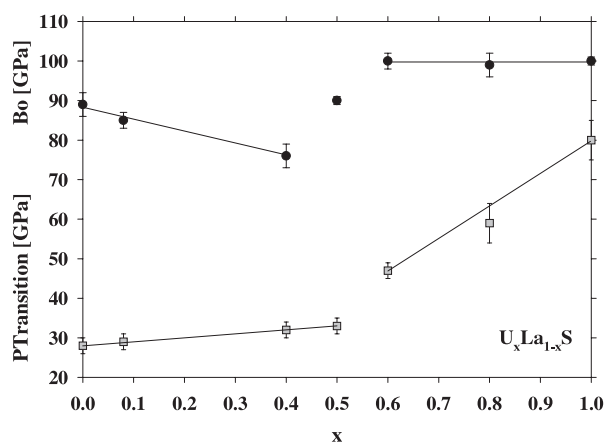**Figure 3.** The diffraction pattern of US at 97(5) GPa.

Figure 4. Transition pressure and bulk modulus B_0 as functions of U concentration.

Table 1. Behaviour of $U_x La_{1-x} S$ solid solution.

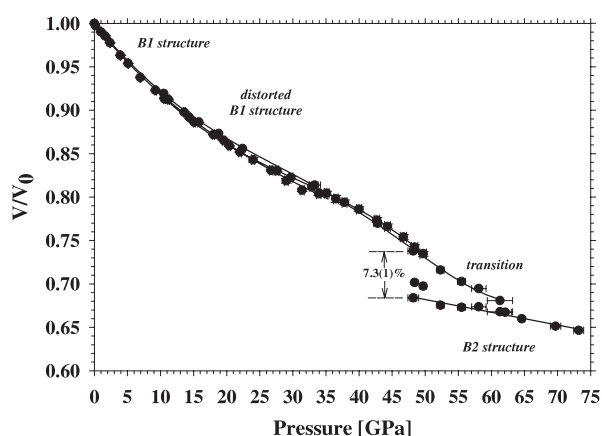| x	Pressure medium	Pressure range (GPa)	B_0 (GPa)	B_0'	Transition pressure (GPa)
0.00	Silicone oil	0–33	—	—	25
0.00	Argon	5–28	89(3)	6.9(8)	28
0.08	Nitrogen	0–45	85(2)	5.3(2)	29
0.40	Silicone oil	0–55	76(4)	7.9(8)	32
0.50	Nitrogen	0–47	90(1)	3.9(1)	33
0.60	Silicone oil	0–75	—	—	45
0.60	Nitrogen	0–50	100(2)	4.0(2)	47
0.80	Alcohol	0–48	99(3)	4.0(3)	N/A
0.80	Silicone oil	0–70	—	—	56
1.00	Helium	0–17	100(1)	5.5(3)	N/A
1.00	Silicone oil	0–100	—	—	80

Figure 5. Relative volume as a function of pressure for $U_{0.6}La_{0.4}S$.

This strange behaviour seen around 0.50–0.60 is in agreement with the disappearance of ferromagnetism at $x = 0.57$ [1, 2].

For all the compounds studied we observe a rather large pressure domain (a few GPa) where the distorted NaCl structure coexists with the CsCl structure (e.g. figure 5). The calculation of the bulk modulus for the high-pressure phase is difficult due to the error in determining an accurate V_0, and therefore we can only estimate that it is about double the value found for the low-pressure phase. This is in agreement with the fact that a volume collapse occurs at the B1–B2 transition, and the U–U distances become smaller than the Hill limit, so the 5f bands can directly overlap and the f electrons delocalize.

3.4. $U_{0.6}La_{0.4}S$

The behaviour of the $U_{0.6}La_{0.4}S$ compound deserves special mention as we observe a change in the slope of the pressure–volume curve above 30 GPa (figure 5).

Analogous changes were measured in similar rare-earth systems [6] and were interpreted as changes in the valence of the lanthanides. The fact that this behaviour occurs only close to the critical concentration could be an indication that for $x_c = 0.57(2)$, the limit between the 3+ and the 4+ valence states for the U ions is not far away. Nevertheless, one has to note that both 3+ and 4+ ground states are magnetic, so a valence change alone does not explain the collapse of the magnetic ordering.

4. Conclusions

We can distinguish two main goals in the reported experiments. The first one was to study the evolution of B_0 versus x, as a change in the electronic localization can be accompanied with a large B_0-variation; e.g. in the isostructural UX_2 systems (X = Co, Fe, Mn, Ir, Al), B_0 jumps from ∼74 to 217 GPa going from localized Al to the more delocalized Co [7]. Our second goal was to study the behaviour of the mixed systems at high pressure and to check whether US behaves like the other uranium monochalcogenides, i.e. whether its high-pressure stable phase is CsCl.

Concerning the first point, even if there is an abrupt change of the B_0-value near $x = 0.57$, the jump is too small to be ascribed to a change in the 5f localization and actually the effects

observed could also be related to a local distortion occurring in the S lattice, also responsible for the reported anomalies. This aspect is at present under investigation [8]. On the basis of the present study, we cannot establish a relationship between the loss of the long-range magnetic ordering and a variation of the electronic localization if any. Concerning the second point, our preliminary measurement allows us to conclude that US and the mixed systems with $x > 0.6$ do not transform into the CsCl structure type at high pressure.

Acknowledgments

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