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High Pressure X-ray Absorption Spectroscopy on Uranium Compounds*

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The study of actinide metals and compounds under high pressure can supply information on electronic structure, in particular on the behaviour of the 5f electrons. High-pressure X-ray diffraction (HPXRD) experiments, for instance, have shown that some of these materials transform to low-symmetry crystal structures [1–3]. These phase transitions can, in certain cases, be correlated to a transition from a localised 5f configuration to a situation, where so-called 'itinerant' 5f electrons participate in the chemical bond, or to an increase in the itinerant character of the 5f electrons.

A drawback of HPXRD measurements is that only indirect conclusions for electronic structure are possible from the observed crystal structures. X-ray absorption studies, in contrast, are a more direct probe of electronic structure because of the direct relation of absorption with electronic excitations. Clear shifts of the absorption edges of uranium were observed as a function of 5f configuration [4–6]. Similar shifts can be observed on lanthanide materials when their 4f configuration changes under the action of high pressures [7, 8].

The present study was undertaken in order to check on a few selected uranium compounds whether structural phase transitions under pressure are accompanied by a shift in the absorption edge of uranium. The materials selected were: (i) uranium monocarbide UC which undergoes a first-order phase transition to an orthorhombic structure at about 27 GPa [2]; (ii) uranium monophosphide UP which undergoes a two-stage second-order phase transition that is completed around 27 GPa [1, 9]; and (iii) uranium dialuminide UAl_2 which has a second-order phase transition at 10 GPa [10].

Results of absorption edge studies on actinide materials under high pressure have not been published up to now, with the exception of a short report, by some of the present authors, on preliminary measurements on UC and UP [11]. The latter measurements indicated a slight shift of the L_{III} absorption edge of uranium to higher energy. The present work reports on new measurements of this absorption edge with a different X-ray absorption spectroscopy (XAS) technique. In addition, the same method was applied to the intermetallic compound UAl_2.

Experimental

The energy-dispersive beamline of the synchrotron storage ring of LURE (Orsay, France) was used for the XAS work [12]. The energy-dispersive method has the following advantages for high-pressure applications: (i) it is fast, a spectrum frame can be obtained in 1 s; (ii) the sensitivity is high (0.1 eV); (iii) the beam is focussed, allowing for high diffracted intensity from the small sample volume in the pressure cell; and (iv) the stability of the beam is excellent because of the lack of any mechanical movement during data collection. The main drawback of such a technique is that the spectra are sensitive to sample inhomogeneities such as thickness variations.

A gold-coated mirror was used to eliminate the harmonics. Although the X-ray beam passes through the diamond anvils, the Bragg peaks of the single-crystal diamonds can be shifted out of the studied energy range by rotating the cell perpendicularly to the beam axis. Data accumulation being fast, this tuning of the diamond orientation can be directly controlled on an oscilloscope screen.

For each pressure step, 320 frames were added to obtain a final spectrum with a low statistical error. The final spectra for all pressure steps were normalised to have an intensity difference of $\log (I_0/I) = 1$ between two selected energies on either side of the edge.

The samples were finely powdered and loaded into a diamond anvil cell of the Syassen–Holzapfel type. A 4:1 methanol–ethanol mixture was used as the pressure-transmitting medium. The pressure was measured by the ruby-fluorescence method on a separate optical bench. Centering pins on the cell support allowed the cell to be put back, after pressure

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measurements, at the same place with a precision of 10 μm.

Results and Discussion

Figures 1 and 2 are superpositions of the normalised near-edge absorption spectra for UC and UP for different pressures. Log (I_0/I) is plotted as the ordinate, but the numerical scales of individual spectra are shifted against each other to avoid overlapping of the curves, and thus are not indicated in the graph. The energy origin has been chosen at the maximum of the white line for spectra at low pressure, rather than at the inflexion point which can be affected by white line broadening. The maximum of the white line shifts to higher energy for pressures above about 20 GPa. This is more clearly shown in Figs. 3a and 4a, where the variation of the white line energy is compared to the variation of the relative

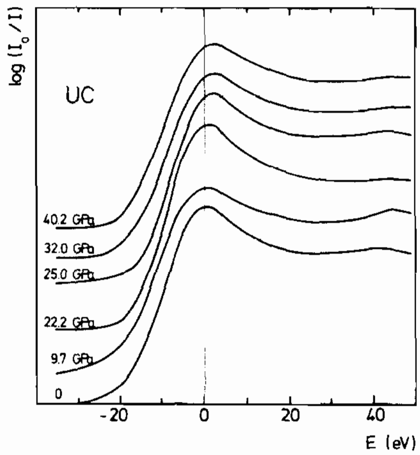

Fig. 1. X-ray absorption spectra of UC near the L_{III} edge of uranium at different pressures. The spectrum for $p = 0$ has been obtained after pressure release. Normalised log (I_0/I) is plotted as the ordinate, but the numerical scales of individual spectra are shifted against each other to avoid overlapping of the curves, and thus are not indicated in the graph.

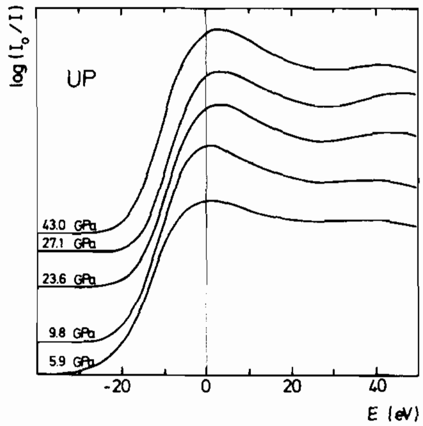

Fig. 2. X-ray absorption spectra of UP near the L_{III} edge of uranium at different pressures. Normalised log (I_0/I) is plotted as the ordinate, but the numerical scales of individual spectra are shifted against each other to avoid overlapping of the curves, and thus are not indicated in the graph.

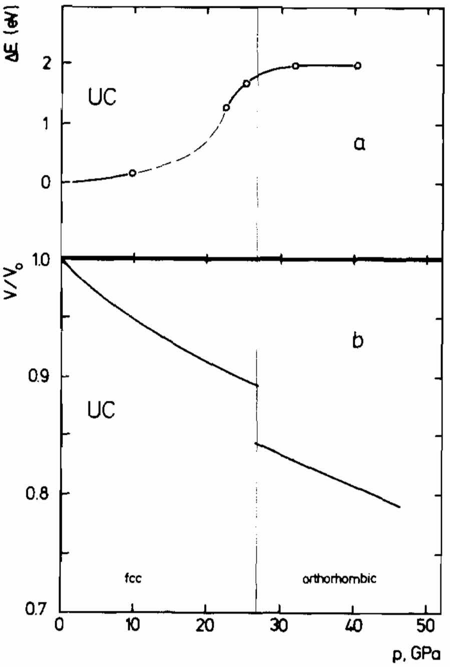

Fig. 3. Comparison of L_{III} edge variation with crystal structure and volume for UC under pressure: (a) energy shift of the maximum of the white line; (b) relative volume in the pressure ranges of the f.c.c. and the orthorhombic phase.

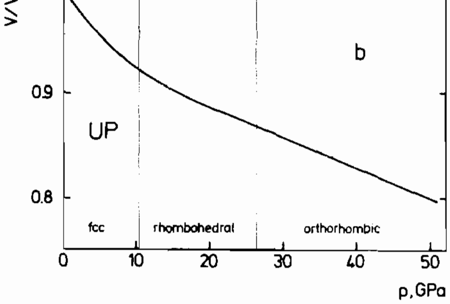

Fig. 4. Comparison of L_{III} edge variation with crystal structure and volume for UP under pressure: (a) energy shift of the maximum of the white line; (b) relative volume in the pressure ranges of the different phases.

volume through the structural phase transitions, Figs. 3b and 4b. The energy difference between the absorption edges for the ambient-pressure and the high-pressure phases is 2 eV for UC and 2.6 eV for UP.

A shift of the absorption edge to higher energy can be expected when, because of 5f delocalisation, the Coulomb interaction between 5f electrons and 2p holes decreases and in turn the 6d–2p interaction increases. Lawrence *et al.* [4], for example, observed that in a series of uranium compounds with increasing U–U distance, thus with increasing 5f localisation, the energy of the L_{III} edge decreased. Along these lines, Kalkowski *et al.* [5] compared the L_{III} edges of uranium in UNi_5 and UCu_5 and suggested that the observed difference of about 2 eV in the white line position between these two compounds was related to a difference in the density of the 6d states due to a 5f–6d hybridisation existing in UNi_5. In the same work, the authors report that the L_{III} edge of trivalent U in UCl_3 is 4 eV lower than that of tetravalent U in UF_4. This shift corresponds to the difference in Coulomb interaction due to the 5f electron which is additional in U^{3+} with respect to U^{4+}.

The shift of L_{III} to higher energy observed under pressure in UC and UP can thus be interpreted as an increase in the itinerant character of the 5f electrons (or as an increase of the uranium valence). In UC, the edge starts shifting already at a certain pressure below the pressure of the structural phase transition. This indicates that f–d mixing already increases before this phase transition, and that the latter occurs suddenly when the f–d mixing has reached a certain value, which could be called a kind of saturating value. For UP, in contrast, the shift of the edge is less progressive, except maybe in the range between 10 and 22 GPa where no experimental data are available. The dashed curve in this area has to be considered as tentative.

For UAl_2, the absorption edge remains constant through the structural phase transition. This can be taken as a confirmation that this phase transition, which was tentatively interpreted as the formation of a modulated lattice of the basic f.c.c. structure [10], is not linked to the 5f electrons.

Conclusions

Positive shifts of the L_{III} absorption edge of uranium under pressure were observed in UC and UP by an energy-dispersive X-ray absorption technique. These occur in the same pressure range as the previously observed structural phase transitions. Both observations, the nature of the phase transitions as well as the shift of the absorption edge to higher energy, allow us to determine that the itinerancy of the 5f electrons increases more or less sharply in a certain pressure range in these two compounds. In constrast, the structural phase transition observed under pressure in UAl_2 does not seem to be connected to changes in the 5f configuration.

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