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Structural and physical properties of actinide materials at high pressure

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Abstract

Selected results of *in situ* high pressure studies of actinide metals and compounds are described. A comparison is attempted between the pressure-induced structural phase transitions of UAs, UO_2 and Th_3P_4 and the optical response of these compounds at high pressure. The structural properties of UTe, USe and PuSb at high pressure are compared with their electrical and magnetic properties. In certain cases a clear correlation could be established between a structural phase transition at room temperature and changes in reflectivity at the same temperature or in electrical resistance at temperatures between room temperature and 1.3 K. However, for some of the materials discussed the evolution of the physical properties is largely independent of the structural phase transitions.

1. Structural *vs.* physical studies

Work at JRC-ITU has used high pressure X-ray diffraction (HPXRD) to obtain basic information on phase transitions at high pressure in actinide materials, such as the nature of the high pressure phases, the volume change at phase transitions and the compressibilities. Energy-dispersive X-ray diffraction (EDXRD) methods were applied with conventional X-ray tubes [1] and with X-rays from synchrotron radiation at DESY, Hamburg [2]. Groups from the Universities of Paderborn, Copenhagen and Lyngby and from the Oak Ridge National Laboratory have cooperated with us in various parts in this X-ray work.

Over the past 13 years a relatively complete systematics of the pressure-induced structural phase transitions has evolved from these and similar studies of other laboratories for the actinide metals and the B1-type actinide compounds. Attempts have been made to correlate these crystallographic results with changes in electronic structure that were expected to accompany the observed phase transitions. This comparison was in general based on semiempirical approaches, such as a proposed correlation between low symmetry structures in metals and delocalized f-electrons.

It was felt that the structural methods should be complemented by the study of pressure effects on other properties more directly linked to the electronic processes, such as optical properties or electrical resistance. Facilities for pressure studies of electrical resistance and optical reflectivity were set up at ITU in recent years. First results of resistance studies of UTe, USe, PuSb and Am have been published [3–7] or are being published along with this paper [8, 9].

High pressure absorption spectroscopy (HPAS) has been applied to actinide halides in a collaboration with the Oak Ridge National Laboratory [10, 11]. High pressure reflection spectroscopy (HPRS) was applied to uranium and thorium compounds of semiconducting or metallic character in a collaboration with the Max-Planck-Institut für Festkörperforschung, Stuttgart [12, 13].

In a first approach, one was tempted to associate the changes in crystal structure, *i.e.* the phase transitions, with synchronous changes in other properties. Electrical resistance and optical properties were expected to undergo relatively abrupt changes at the pressure of the structural phase transition. Such a situation was found to exist in the variation in optical reflection of some B1-type compounds with pressure. For 10 uranium and thorium compounds the variation in reflectivity with pressure and with the energy of the incident light was measured [13]. Peaks in the reflection spectrum correspond to electronic excitations in the solid caused by the incident light. Many of these peaks could be correlated with either the high pressure or the ambient pressure phases of compounds, supplying information about the electronic structures of these phases. The optical reflection spectra of UAs at various pressures are given in Fig. 1 as an example. Maxima A and C in reflectivity, around 1.2 and 3.5 eV respectively, seem to be characteristic of the B1-type phase, since they

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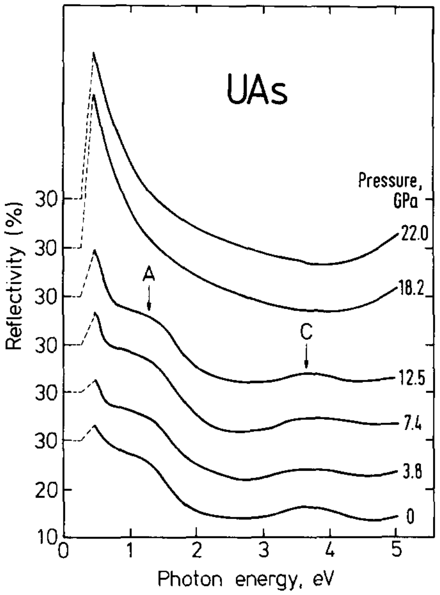

Fig. 1. Optical reflectivity of UAs at various pressures. The figures for reflectivity (%) only apply to the 0 GPa curve; all other curves are shifted by a constant amount with respect to the curve of next-lower pressure. The dashed lines indicate, for each reflectivity curve, the corresponding (shifted) 30% reference value. Note disappearance of maxima A and C above the structural phase transition which occurs around 18 GPa.

disappear at pressures above 18 GPa where the transition to the B2-type phase occurs. Other examples are phase transitions in UC and UP to less symmetric high pressure structures, which are accompanied by a shift of the L_{III} X-ray absorption edge [14].

However, in other cases the changes in electrical, magnetic and optical properties are not synchronous with the crystallographical phase transitions. Certain physical properties can start to change at pressures where a structural phase transition is not indicated. On the other hand, a physical phenomenon such as magnetic order can persist *through* a structural phase transition. We shall see from a few selected examples that each material has to be discussed separately and that even within the same family of compounds (*e.g.* the B1-type compounds) the relationship between the structural phase transition and other physical changes may vary considerably. We shall successively discuss the results obtained on UTe, USe, PuSb, Th_3P_4 and UO_2.

A large number of actinide compounds of the B1 structure type were studied under high pressure by X-ray diffraction [15–22]. Those with the heavy anions Se, Te, As and Sb in general transform to the B2 structure type under pressure.

2. Uranium monotelluride

UTe was observed to successively transform from the B1 to the B2 structure type in the pressure range 10–20 GPa at room temperature [21]. This phase transformation is indicated in Fig. 2(a) by a thick line around 298 K and an arrow in the direction of increasing pressure.

Let us compare this with the results obtained with respect to magnetic ordering under pressure in a study of the pressure-induced variation in the electrical resistance of UTe [3, 5]. In this case the derivative d*R*/d*T* of the electrical resistance *R* has a sharp maximum

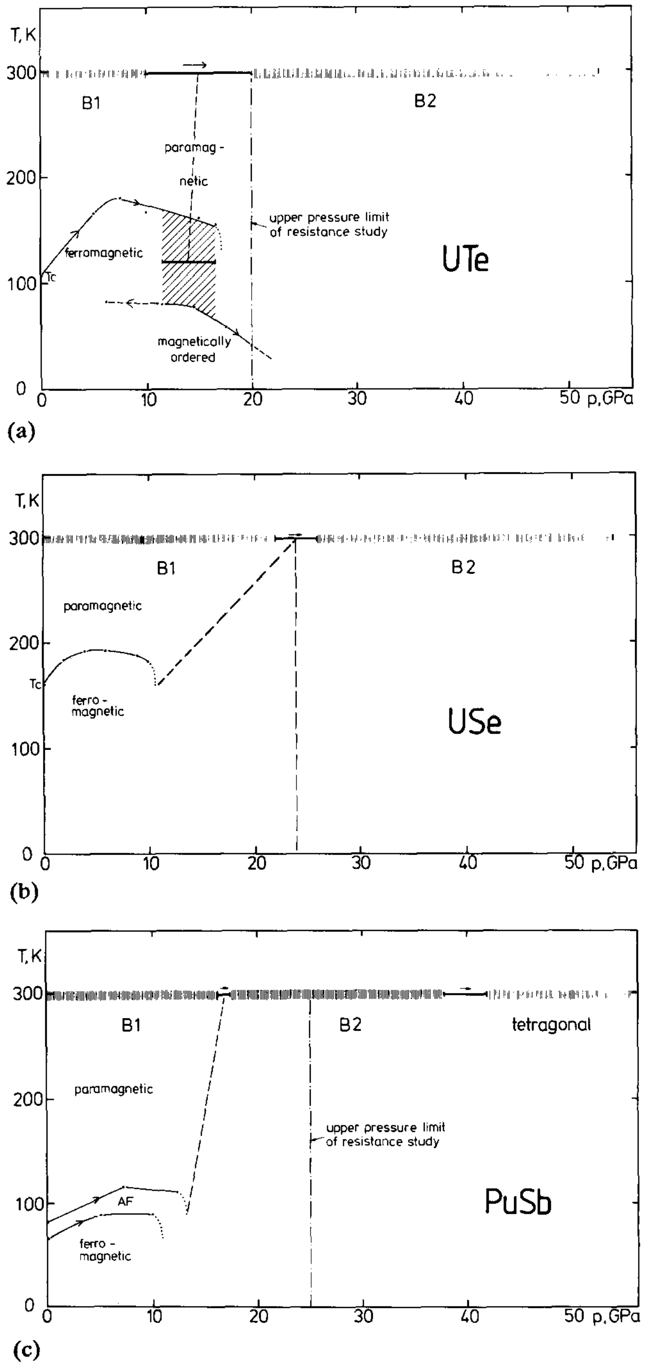

Fig. 2. Known elements of structural and magnetic phase diagrams for (a) UTe, (b) USe and (c) PuSb. Arrows indicate direction of pressure variation. AF, antiferromagnetic.

at the ferromagnetic ordering temperature T_C. This allowed us to plot in Fig. 2(a) the upper limit of the ferromagnetic area of the magnetic phase diagram. In the pressure range 11.5–16.5 GPa the maximum in dR/dT corresponding to T_C successively disappears, but another maximum grows at lower temperature (about 80 K) and persists up to the upper pressure limit reached in this experiment. The temperature variation in this second maximum with pressure is shown by the lower line in the left part of Fig. 2(a). The second maximum was also tentatively interpreted as corresponding to magnetic ordering. This will have to be confirmed by direct determination of magnetic properties under pressure; in particular, we do not know what kind of magnetic order may exist below this line in the diagram.

The transition between the two regimes of assumed magnetic order takes place in the same pressure range where the structural transition from B1 to B2 was observed. Although the structural transition was only studied at room temperature and could in principle occur at a different pressure (or even not at all) at lower temperatures, the agreement between the two pressure ranges makes us believe that the best interpretation is the following. At temperatures below 200 K the B1-type phase transforms to the B2 type in roughly the same pressure range as at room temperature, but the structural change does not destroy magnetic order. The only effects on magnetic behaviour induced by the structural phase transition are a large decrease in the ordering temperature and possibly a transition to a different type of order. Thus UTe seems to be a case where magnetic order is not independent of structure but survives the structural phase transition. Since the upper pressure limit in the resistance experiment was 20 GPa – at which pressure the maximum in dR/dT assumed to indicate magnetic order still existed – we cannot determine at present to which pressure magnetic order may persist.

Another strong argument for the given interpretation is based on the hysteresis observed for the structural transition of UTe. The backward transition from B2 to B1 does not occur on pressure release at room temperature. Instead, the B2-type phase is preserved in a metastable condition at ambient pressure. In the resistance measurements we have also been able to follow the variation in the magnetic ordering temperature on pressure release down to 6 GPa (dashed line, with arrow pointing towards low pressure, in Fig. 2(a)). At this pressure, which is distinctly below the pressure range where the change in magnetic regime was observed upon pressure increase, the maximum in dR/dT, and thus the assumed magnetic transition, is still at 83 K, which perfectly fits with the temperature range where the second maximum was first observed on pressure increase. (This is corroborated by another data point at 11 GPa, 81 K, also determined on pressure release.) This hysteresis in the assumed magnetic ordering very clearly shows that in the case of UTe the two different ordering temperatures correspond to the two different crystallographic structures, NaCl (B1) type and CsCl (B2) type.

3. Uranium monoselenide

Figure 2(b) is a representation of the pressure behaviour of USe analogous to that given in Fig. 2(a) for UTe. USe has been studied up to 54 GPa by X-ray diffraction at room temperature [21]. The B1–B2 transition was also observed but occurred at a higher pressure, in the range 22–26 GPa. This is again indicated by a thick line and an arrow at room temperature in Fig. 2(b). The ferromagnetic transition of USe, deduced from the dR/dT curve in the same way as for UTe [4], is shown as the curved line between 160 and 192 K in the left part of Fig. 2(b). Although the variation in electrical resistance in USe was followed up to 22 GPa, no indication of magnetic order was obtained above 10 GPa.

Two interpretations are possible for the USe behaviour. Firstly, the disappearance of ferromagnetism above 10 GPa might indicate that the structural transition from B1 to B2 takes place around 10 GPa in the temperature range of ferromagnetic ordering and that there is no magnetic order in the high pressure B2-type phase. This would mean a quite oblique limit between B1 and B2 in the structural phase diagram, as shown in Fig. 2(b) by the thin dashed line. Alternatively, we assume that the pressure range of the structural transition, as in the case of UTe, undergoes only a small variation when the temperature is lowered (thick dashed line) and that magnetic order is destroyed by volume effects only, without any influence of crystal structure.

In view of the good coincidence in pressure ranges for the structural and electrical–magnetic changes in UTe, indicating a nearly vertical line in the phase diagram for the B1–B2 transition, we tend towards the second explanation. It seems unlikely that in two closely similar systems such as USe and UTe the phase transition lines would have such different slopes.

4. Plutonium antimonide

This system is again a bit more complicated, since two successive magnetic transitions are observed as a function of temperature. At ambient pressure PuSb is ferromagnetic below 65 K and antiferromagnetic between 65 and 82 K. Figure 2(c) shows, based on the electrical resistance under pressure [5, 6, 9], how the temperatures of the two magnetic transitions vary with pressure. As in the two cases of UTe and USe described above, the magnetic ordering temperatures appear as clear maxima in the derivative d*R*/d*T*. No maximum corresponding to an antiferro–ferro transition is observed above 10 GPa and the maximum associated with the para–antiferro transition also disappears at higher pressures, *i.e.* above 12 GPa.

Reference 9 correlates the disappearance of the maxima in d*R*/d*T* with the structural phase transition from the B1 to the B2 type that was observed earlier [15]. This view is presented in Fig. 2(c) by the thick dashed line, which would mean that (1) the B1–B2 phase transition is accompanied by the loss of magnetic order and (2) the transition pressure for the B1–B2 transformation decreases slightly with decreasing temperature.

5. Summary for the B1-type compounds

The three examples seem to show that magnetic order, which certainly has strong links to crystal structure, is nevertheless more independent of structure than one may think. In these three compounds, if our hypotheses are confirmed, we have one example (USe) where within the same crystal structure we have or do not have magnetic order depending on the volume and interatomic distances, while we have another case (UTe) where even with a severe structural change the magnetic order survives the phase transition.

6. Trithorium tetraphosphide, Th_3P_4

This compound and the isostructural U_3P_4 were studied by X-ray diffraction up to 40 GPa [23]. No structural phase transition was observed in this pressure range for either these two compounds. The evolution of optical reflectivity, optical conductivity and dielectric constant with pressure was determined for Th_3P_4 and U_3P_4 [24, 25]. In the thorium compound, which is a semiconductor at ambient pressure, indications of the appearance of metallic character were obtained at a pressure of 38 GPa, whereas the X-ray diffraction spectra did not show any sign of a structural phase transition up to 40 GPa. This means again that an important physical process, *i.e.* metallization, occurs without an accompanying change in crystal structure. This process seems to depend only on the volume and interatomic distances.

Th_3P_4 and U_3P_4 are typical members of the family of Th_3P_4-type compounds which comprises a large number of lanthanide and actinide pnictides and chalcogenides of 3:4 stoichiometry. Triuranium tetraphosphide is a diamagnetic semiconductor, while the uranium compound is ferromagnetic below 138 K. Their optical reflectivity at ambient pressure has been determined by Schoenes *et al.* [26]. These authors also derived densities of states for the compounds.

The electronic properties and magnetic anisotropy of U_3P_4 were explained on the basis of hybridization between 5f orbitals of uranium and 3p orbitals of phosphorus. This p–f mixing raises the energy of the p-valence states, which then overlap the conduction band.

Comparing the spectra of the two compounds at ambient pressure [26] or at moderate pressure as obtained in our own work, the most prominent difference is the upturn in reflectivity and conductivity towards the lowest energies observed for U_3P_4, which contrasts with a steady decrease in the same energy range for Th_3P_4. This upturn in reflectivity supports the metallic character of U_3P_4.

Optical reflection under pressure was measured in the spectral range 0.5–4 eV up to 38 GPa for Th_3P_4 and up to 39 GPa for U_3P_4. Reflectivities were determined at the sample–diamond interface. The evolution of optical reflectivity of Th_3P_4 with pressure is shown in Fig. 3(a). Figures 3(b) and 3(c) show, for the selected pressures of 10.1 and 38.2 GPa (highest pressure

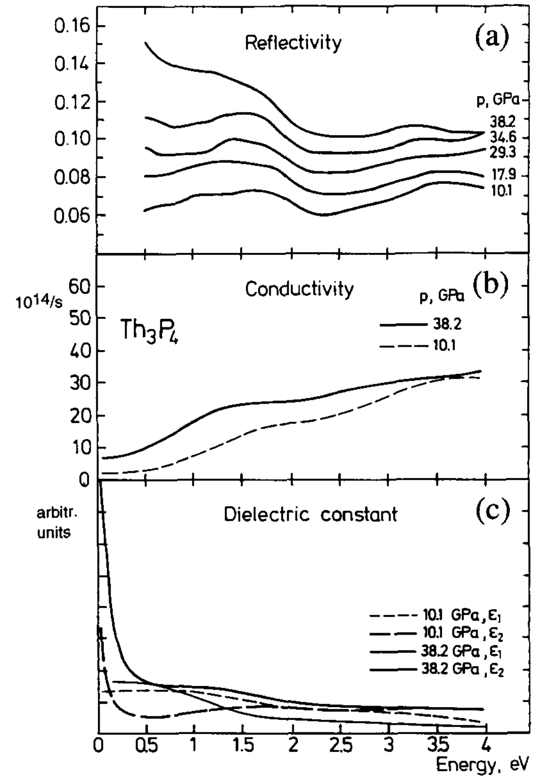

Fig. 3. Evolution with pressure of (a) optical reflectivity, (b) optical conductivity and (c) real and imaginary parts of dielectric constant for Th_3P_4.

reached), the optical conductivity and the real and imaginary parts of the dielectric constant respectively.

At low pressures the reflectivity of Th_3P_4 decreases when going from 1.5 to 0.5 eV, as can be expected for a semiconductor. With increasing pressure, intraband transitions, whose energy is typically around 0.5 eV, are enhanced. The high reflection of photons with energy 0.5 eV reached at 38.2 GPa indicates that Th_3P_4 has metallic properties above this pressure. For U_3P_4 the high reflectivity at low energies over the whole pressure range studied shows that this compound is already metallic at low pressures.

The decrease in energy of certain features in the conductivity curve when going from Th_3P_4 to U_3P_4 was considered by Schoenes *et al.* [26] as an indication of p–f mixing. Along the same lines, the energy decrease with pressure in the conductivity features of Th_3P_4 (Fig. 3(b)) supplies additional evidence of a pressure-induced increase in f-occupation and, as a consequence, of metallic character in the latter compound.

The most important pressure effect observed is the appearance of metallic character in Th_3P_4 at 38 GPa, indicated by a marked upturn in reflectivity towards low energies and by a shift of two steps in the conductivity curve to lower energy under the action of pressure. Since 5f levels are assumed to be empty in Th_3P_4 at ambient pressure, this might indicate that a pressure of 38 GPa creates sufficient 5f occupation to allow p–f mixing and thus induce metallic character in a similar way as this has been assumed for U_3P_4 at ambient pressure.

7. Uranium dioxide

The optical response of UO_2 was studied up to 36 GPa [12]. At pressures above about 15 GPa, excitations within the $5f^2$ multiplet of UO_2 became observable in the reflection spectra and seem to indicate an increasing admixture of presumably d-like character to the $5f^2$ ground state. In addition, the optical reflectivity of UO_2 at 0.5 eV was found to increase sharply above 20 GPa (Fig. 4).

An X-ray diffraction study of UO_2 up to 38 GPa [27] showed that cubic fluorite-type UO_2 successively transformed to an orthorhombic structure in the range 29–38 GPa.

The above-mentioned intraband transitions and the sharp increase in reflectivity appear at pressures much below that of the structural phase transition. They seem to be structure independent and to be a consequence of the volume compression and the accompanying band overlap. The fact that the reflectivity of ThO_2 does not exhibit similar features [12] may suggest that the excitations in UO_2 are 5f related.

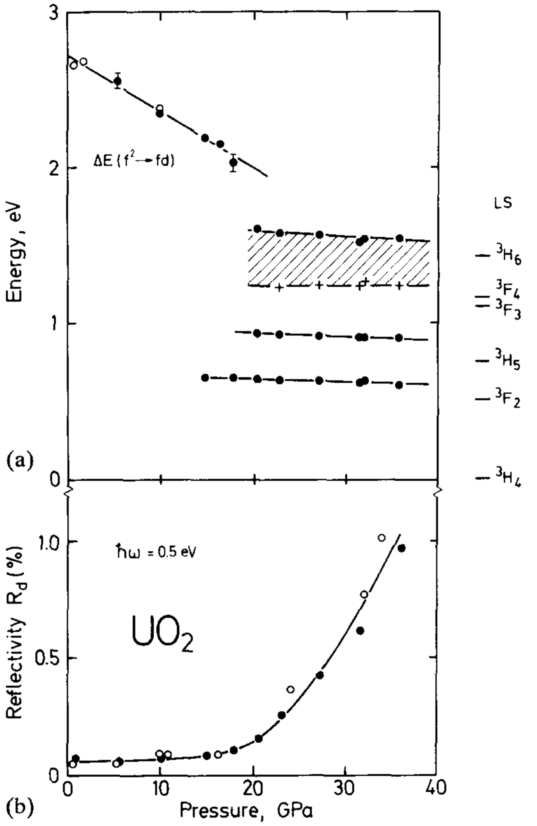

Fig. 4. Optical response of UO_2 *vs.* pressure up to 36 GPa [27]: (a) energy of reflectivity maxima; (b) reflectivity at 0.5 eV.

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