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UPd_3 under high pressure: Lattice properties

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The $5f$ electronic states in UPd_3 have a localized $5f^2$ ground state. Our study examining the behavior of the UPd_3 crystal lattice under pressure up to 53 GPa does not reveal any volume anomaly, which could be associated with a delocalization of the $5f$ electronic states, in the entire pressure range. We thus find a disagreement with calculations based on the self-interaction corrected local spin-density approximation, which predict a transition around the pressure of 25 GPa. A bulk modulus of $B_0 = 175(4)$ GPa with $B_0' = 5.0(4)$ was determined.

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The application of pressure to actinide materials increases the degree of itinerancy of the $5f$ electronic states, making them less analogous to the $4f$ (localized) states in regular lanthanides.[1–3] High pressure can be thus a powerful control parameter tuning electronic structure parameters over an interesting regime. This is true especially for the territory of light actinides (U, Np, Pu), relevant for strongly correlated electron physics with diverse exotic phenomena such as heavy fermions, unconventional superconductivity, different types of magnetic order, and in some cases even the unexpected coexistence of superconductivity and magnetism.[4,5] The theory describing such systems is complicated, and complications appear even at the underlying level of simple bonding properties, which are normally well understood in metallic systems by electronic structure calculations in the local spin-density approximation (LSD). For example, one approach to account for volume variations between various allotropic phases of Pu is to consider a variable integral number of localized $5f$ electrons,[6] while part of the $5f$ states remains itinerant (i.e., contributing to bonding). The total energy is then compared for various $5f$ localized configurations, the lowest one being assumed as the ground state. Such theories differ in the way that the energy of the localized f shell is calculated, as this parameter depends on intra-atomic many-body correlations and cannot be obtained from the LSD. One of the possible methods used is to expose the localized electrons to a potential corrected for self-interaction. This so-called self-interaction corrected (SIC) LSD was used to describe rare-earth systems including intermediate-valence ones, in which the variable $4f$ count is the basic ingredient (Ref. 7, and references therein). Such an approach, which is fully *ab initio*, i.e., without adjustable parameters, was also recently applied to actinides, namely, to Pu (Ref. 8) and Am (Ref. 9) monopnictides and monochalcogenides. To give an example, detailed predictions about the valency of Pu could be made for various compounds, ranging from 3+ to 5+ although there is so far no experimental evidence to corroborate these conclusions. Another prediction, based on the SIC-LSD calculations, concerns the possibility for the existence of a pressure induced $5f$ delocalization in UPd_3.[10] Although as a rule the U-based intermetallic compounds exhibit itinerant $5f$ states, UPd_3 represents an exception. Numerous experimental evidence points to UPd_3 having a localized $5f^2$ state.[11–13] The authors of Ref. 10 also concluded the $5f^2$ localized ground state, but this was found to be rather close (in total energy) to the $5f^1$ state, which was then predicted to become energetically favorable when the volume is reduced by an applied pressure of ≈ 25 GPa. Above this critical pressure, UPd_3 should then become similar to the heavy fermion compound UPt_3, for which the same authors deduce the $5f^1$ configuration as the ground state. This situation corresponds to effects also observed in the heavier actinides, which exhibit localized $5f$ states in the ground state, but external pressure leads to their delocalization, manifesting itself as a volume collapse. The delocalization of one $5f$ electron yields a rather dramatic volume effect, due to the fact that localized $5f$ states are rather deep in the ion core and effectively screen the attractive ionic potential felt by the outer electrons. The loss of one $5f$ electron from the core consequently leads to a much stronger attraction of electrons from the outer shells, which then undergo contraction. For example, Am metal under pressure undergoes three phase transitions, two of which are accompanied by volume collapses. These two transitions occur at 10 and 17 GPa, at which the volume collapses by 2% and 7%, respectively.[14,15] Bearing in mind the possibility of $5f$ electron delocalization, it is therefore very interesting to study experimentally the effect of applying high pressure on the structural behavior of UPd_3. Presence or absence of the transition in the given pressure range may be a very good benchmark of a general reliability of the SIC-LSD calculations on a fine energy scale.

High-pressure experiments were performed at room temperature using diamond anvil cells of the Syassen-Holzapfel type. Pressure was determined by means of the ruby fluores-

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cence method[16] and nitrogen was used as the pressure transmitting medium. One series of experiments (pressure range 2–40 GPa) was performed at the European Synchrotron Radiation Facility (ESRF) ID30 beam line in the angular dispersive mode using a double-focused monochromatic beam of $\lambda = 0.3738$ Å. A silicon standard was used for calibrating the sample to detector distance and the diffraction patterns were collected on a SMART 6500 Bruker CCD camera. The two-dimensional diffraction images obtained were then transformed to intensity-vs-2θ diffractograms using the ESRF FIT2D software. For the second set of experiments, covering the pressure range 25–53 GPa, an energy dispersive method at the EDS facility of the positron storage ring DORIS III of Hasylab, DESY, Hamburg was used. The value of the Bragg angle used for these experiments was determined using a gold standard in the exact configuration as employed for the UPd_3 samples and was determined as 5.497°. Lattice spacings were calculated as a function of the applied pressure for each sample using these calibrations and the energy dispersive diffraction data.

UPd_3 crystallizes in the hexagonal structure of the $TiNi_3$ type (space group $P6_3/mmc$), in which U atoms occupy two nonequivalent sites. The UPd_3 sample was prepared by arc-melting stoichiometric amounts of U and Pd under Ar protective atmosphere. The structure at ambient pressure was verified on a small extracted single-crystalline piece by x-ray diffraction using a four-circle diffractometer. The lattice parameters $a = 577.0(1)$ pm, $c = 961.9(4)$ pm, are in reasonable agreement with the literature data, ranging between $a = 576.3$ pm, $c = 954.2$ pm, and $a = 577.5$ pm, $c = 965.4$ pm, depending on slight variations of stoichiometry.[17] However, the high-pressure powder experiments revealed that a small amount of UPd_4 (cubic) impurity was present in all samples studied. An ambient pressure experiment at HASYLAB was also used to obtain lattice parameters of the powder used for the high-pressure studies. The values $a = 576.2(1)$ pm, $c = 961.0(1)$ pm were used as the reference for evaluation of the relative changes induced by pressure. Figure 1 compares the diffraction pattern from the angle-dispersive XRD (ADXRD) method with the energy dependence of diffracted intensity obtained using the energy dispersive XRD (EDXRD) method at approximately the same pressure of about 40 GPa. The ADXRD method has a much better resolution in k space and better statistics, in addition, a number of low angle diffraction peaks are visible as opposed to the EDXRD spectrum where U and Pd fluorescence lines dominate the energy spectrum below 25 keV.

We therefore took the dataset from the ESRF as the primary source for the quantitative evaluation of the pressure dependence of the samples lattice properties. For each pressure step, the lattice parameters and the relative volume V/V_o were calculated.

Figure 2 shows pressure variations of the normalized volume of UPd_3 where it is evident that there are no anomalies in the compression curve. The dependence can therefore be well accounted for by both the Birch[18] and Murnaghan[19] equations of state, yielding the bulk modulus B_0 and its pressure derivative B_0' (the subscript zero indicates ambient pressure).

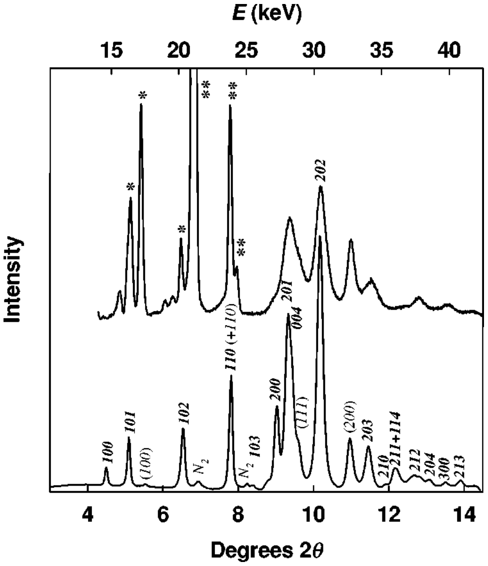

FIG. 1. Comparison of the diffraction pattern obtained from UPd_3 in the angle-dispersive XRD (ADXRD) mode ($p = 40.0$ GPa) with the spectrum (upper line) collected in the energy dispersive XRD (EDXRD) mode ($p = 38.8$ GPa). The peaks originating from the spurious UPd_4 phase have indices in brackets. For the upper (EDXRD) spectrum * and ** denote U and Pd fluorescence, respectively.

The values obtained for the Birch [$B_0 = 175(3)$ GPa, $B_0' = 5.1(2)$] and Murnaghan [$B_0 = 177(4)$ GPa, $B_0' = 4.7(3)$] equations are almost identical. To confirm the reliability of this result additional fitting of the data was carried out with the EOS-FIT program[20] using the Vinet equation[21,22] and gave an almost identical result of 174(3) GPa for B_0 and 5.3(3) for B_0'. Bulk moduli agree rather well with the value obtained from a sound velocity study (167 GPa).[23]

Pressure variations of individual lattice parameters a and c are displayed in Fig. 3 which also includes results from the EDXRD method obtained at higher pressures, for which the uncertainty of the refined parameters is higher (especially for the lattice parameter c). Nevertheless, as the parameters smoothly follow the tendency expected by extrapolating

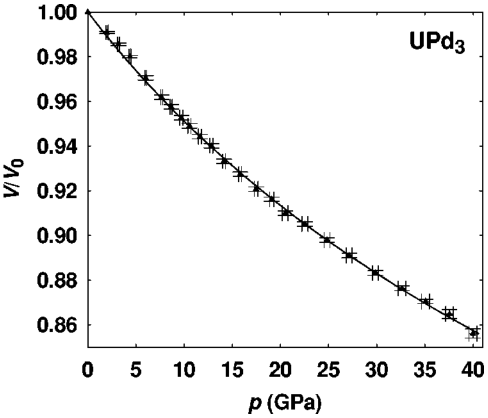

FIG. 2. Pressure dependence of the unit-cell volume. The full line represents the fit to the equation of state. The Birch and Murnaghan equations yield practically identical fit lines.

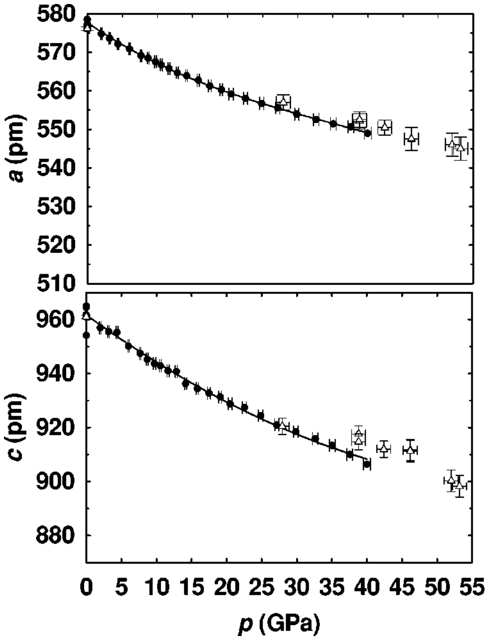

FIG. 3. Pressure dependence of the lattice parameters a and c. The full symbols were obtained from refinement of the data from the angle-dispersive mode, empty symbols from the energy dispersive experiment. The lines are quadratic fits through the data.

from the pressure range where data from both experiments are available, we conclude that no structural phase transition occurs up to $p=53$ GPa.

Figure 4 shows that the linear compressibilities are somewhat anisotropic, with pressure inducing a larger relative compression along the hexagonal c axis than within the basal plane. We have previously shown that in some cases the anisotropic compressibility reflects the anisotropic $5f$ bonding.[24] In the case of localized $5f$ states the reason can be due to crystal electric field (CEF) effects. This CEF model explains the thermal expansion of $\mathrm{UPd_3}$, which exhibits in the room-temperature range larger coefficients of the c-axis expansion than for a-axis expansion.[25]

Individual linear thermal-expansion parameters can be expressed as $\alpha_i = k_i \Gamma_\Theta c_V / V$, where c_V is the specific heat at constant volume, Γ_Θ is the lattice Grüneisen parameter, V is the molar volume, and k_i is the compressibility along the direction i. Hence, the same CEF model can at least qualitatively explain the observed anisotropy. The ground state with the prolate (along the c axis) $5f$ charge distribution becomes less energetically favorable and is gradually depopulated under pressure, which leads to a stronger contraction along c.

The deduced c/a ratio varies in a linear way from 1.667 at ambient pressure to 1.653 at $p=40$ GPa and the relatively small and the smooth change of this ratio indicates that the structure is far from an instability point.

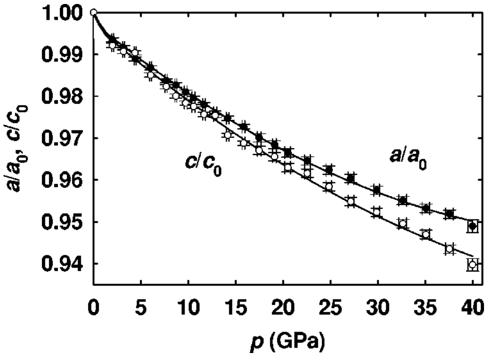

FIG. 4. Pressure dependence of the lattice parameters a and c normalized to the respective zero-pressure values. The lines represent quadratic fits.

The data obtained clearly prove that no volume collapse in $\mathrm{UPd_3}$ occurs in the pressure range up to 53 GPa. The predicted volume compression of about 10%–11%, required by theory for the stabilization of the $5f^1$ state,[10] was achieved experimentally at about 25 GPa. The quality of data allows us to eliminate even a hypothetical possibility that the $5f^1$ and $5f^2$ configurations have identical volumes at the critical pressure. In such circumstances no volume collapse would occur, and even if the type of crystal structure were to remain unchanged, both phases would most probably exhibit different compressibilities. Therefore, an anomaly of the second-order type (sudden change not of lattice parameters but of their pressure derivatives), which would be seen as a point of inflexion in the compressibility curves, would have to appear. No such anomaly is observed in our measurements. A more general conclusion is that other quantitative predictions of SIC-LSD calculations, for example, the localized $5f^1$ configuration for $\mathrm{UPt_3}$, have to be taken with caution. A question remains whether the disagreement is due to approximations inherent to the SIC-LSD approach, or because of the simplified structure of the $\mathrm{AuCu_3}$ type, used to calculate $\mathrm{UPd_3}$ (and $\mathrm{UPt_3}$).[10]

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