High-pressure structural study of UM2Al3 (M = Pd, Ni): evidence for a pressure-induced electronic transition in UPd2Al3

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Angaben zur Veröffentlichung / Publication details:

Krimmel, Alexander, Alois Loidl, K. Knorr, B. Buschinger, C. Geibel, C. Wassilew, and M. Hanfland. 2000. "High-pressure structural study of UM2Al3 (M = Pd, Ni): evidence for a pressure-induced electronic transition in UPd2Al3." *Journal of Physics: Condensed Matter* 12 (41): 8801–8. https://doi.org/10.1088/0953-8984/12/41/305.

High-pressure structural study of UM_2Al_3 (M = Pd, Ni): evidence for a pressure-induced electronic transition in UPd_2Al_3

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Abstract. High-pressure x-ray diffraction studies on the magnetically ordering heavy-fermion superconductors UM_2Al_3 (M = Pd, Ni) have been performed. For UNi_2Al_3 only a smooth reduction of the pressure dependence of the unit-cell volume was observed. In the case of UPd_2Al_3 a structural phase transition takes place around $p \approx 25$ GPa from the high-symmetry hexagonal $PrNi_2Al_3$-type low-pressure structure into a low-symmetry orthorhombic high-pressure phase. The new phase is characterized by space group $Pmmm$ and closely related to the $PrNi_2Al_3$ structure at ambient pressure. Its compressibility is about twice that of the low-pressure phase. The remarkable high-pressure behaviour is discussed with respect to an electronic transition related to the structural high-pressure phase transition.

1. Introduction

UM_2Al_3 (M = Pd, Ni) are magnetically ordered heavy-fermion superconductors [1, 2]. At ambient pressure, both compounds show the $CeCu_5$-derivative $PrNi_2Al_3$-type structure [1, 2]. This crystallographic structure type is characterized by space group $P6/mmm$ in which the uranium, palladium and aluminium atoms occupy the 1(a), 2(c) and 3(g) sites, respectively. Layers of U–Pd ions alternate with Al layers along the c-axis [1, 2]. The crucial parameter in determining the physical properties of these compounds is the strength of the hybridization between the 5f electrons and the band states of conduction electrons which can be tuned by external pressure. On increasing pressure, the unit-cell volume is reduced and the hybridization increases. According to Doniach's model, this leads first to an increase of the Néel temperature. However, above a critical value of the hybridization strength, due to increasing Kondo compensation effects, one expects a continuous suppression of magnetic order, reflected in both the value of the ordered magnetic moment μ_{ord} and the Néel temperature T_N. Indeed, resistivity measurements on UPd_2Al_3 under pressure [3] showed an almost linear decrease of the Néel temperature whereas the superconducting transition temperature T_c remained constant up to $p \approx 6.5$ GPa. For higher pressures, T_c started to decrease while magnetic phase transition temperatures could not be determined any longer [3]. At the highest available pressure of $p = 13.9$ GPa, T_c has shifted from 2 K at ambient pressure down to 1.6 K. Recent high-pressure neutron diffraction experiments on single-crystalline UPd_2Al_3 up to 1.6 GPa revealed that both μ_{ord} and T_N pass through a maximum around $p \approx 0.5$ GPa, and then show a steep decrease for higher pressures with $\mathrm{d}T_N/\mathrm{d}p \approx -0.5$ K GPa^{-1} and $\mathrm{d}\mu_{ord}/\mathrm{d}p \approx -0.16\ \mu_B$ GPa^{-1} [4]. Extrapolating the linear pressure dependence above 0.5 GPa up to 6.5 GPa results in an estimated ordering temperature of $T_N \approx 11$ K and a vanishing ordered magnetic moment [4], in agreement with the resistivity measurements [3].

Here we report on x-ray diffraction experiments on UM_2Al_3 (M = Pd, Ni) under high pressure carried out to look for any relationship between its exciting physical properties and its crystallographic structure.

2. Experimental details and results

The experiments were performed on the multipurpose white-beam station ID09 at the ESRF, Grenoble. The beam line can be equipped for angle-resolved high-pressure diffraction experiments employing an image plate detector. Carefully powdered polycrystalline samples were mounted in a diamond anvil cell (helium membrane type) allowing for pressures up to $p = 40$ GPa (in principle, even higher pressures are available). Methanol–ethanol with a mixing ratio 4:1 was used as the pressure-transmitting medium and ruby fluorescence for the determination of the applied pressure [5]. The fluorescence line broadens upon increasing pressure but its doublet structure could be resolved up to the highest applied pressures thus indicating moderate pressure gradients. The incident wavelength has been determined to be $\lambda = 0.455$ Å by measuring a Si standard. The data were corrected for spatial detector distortion and integrated employing the program FIT2D [6]. The resulting diffraction patterns have been analysed by the standard Rietveld method [7] using the FULLPROF program [8]. All measurements have been performed at room temperature.

For UNi_2Al_3, the application of pressure resulted in a smooth and continuous reduction of the unit-cell volume. No change of its crystallographic structure could be detected up to the maximal pressure of $p = 38.5$ GPa. Within experimental uncertainties, the c/a ratio remained almost constant over the whole available pressure range. Figure 1 shows the corresponding diffraction pattern of UNi_2Al_3 at $p = 18.3$ GPa and at $p = 38.5$ GPa. Figure 3, later, shows the dependence on pressure of the unit-cell volume of UNi_2Al_3. This pressure dependence of the unit-cell volume follows closely the Birch–Murnaghan equation of state (EOS) [9]:

$$V(p) = V(0)\left(\frac{b_0}{b_0'}p + 1\right)^{1/b_0'}. \tag{1}$$

Here, b_0 denotes the isothermal bulk modulus and b_0' its first pressure derivative, both at ambient pressure. The bulk modulus resulting from the fit amounts to $b_0 = 150(5)$ GPa and $b_0' = 4.0(15)$.

As mentioned above, UPd_2Al_3 also crystallizes in the $PrNi_2Al_3$-type structure (at ambient conditions). Similar to what is found in the case of UNi_2Al_3, the unit-cell volume starts to decrease continuously under applied pressure and the pressure dependence again can be well described by the Birch–Murnaghan EOS, as shown in figure 3, later. The corresponding bulk modulus is now $b_0 = 159(6)$ GPa and hence virtually identical with the value found for UNi_2Al_3. Within the experimental accuracy, the pressure derivative of the bulk modulus is again found to be $b_0' = 4$ as in the case of UNi_2Al_3. Up to $p \approx 23$ GPa, also the c/a ratio remained almost constant.

When further increasing the external pressure, a structural phase transition takes place at around $p \approx 25$ GPa into a new high-pressure phase as reflected by the appearance of superlattice reflections. Repeating the experiment with a second loading of the diamond anvil cell

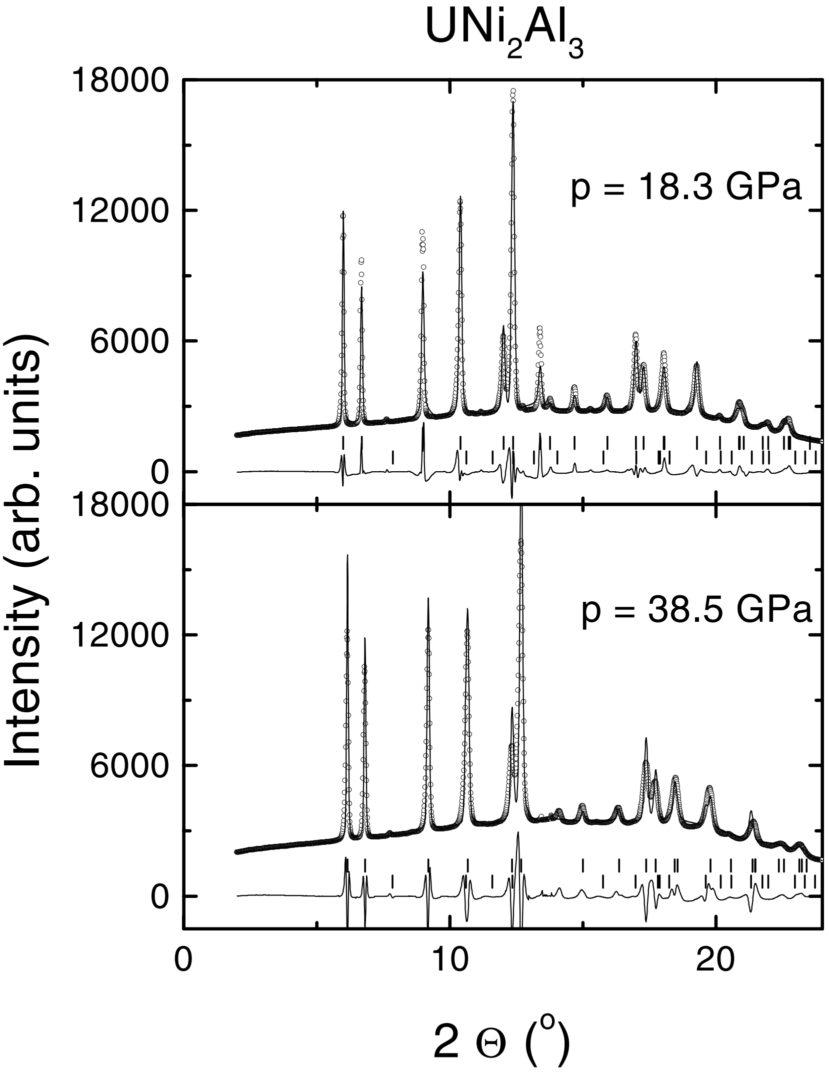

Figure 1. The diffraction pattern of UNi_2Al_3 at $p = 18.3$ GPa and at $p = 38.5$ GPa. Open circles and full lines correspond to observed and calculated intensities within the $PrNi_2Al_3$ structure. In the lower part, the calculated peak positions of UNi_2Al_3 and ruby as well as the difference of the observed and calculated intensities are shown.

yielded reproducible results, thereby confirming the high-pressure phase transition being an intrinsic property of the sample. Within a certain pressure range between 23 and 26 GPa, the two phases coexist, thus indicating a first-order phase transition. Figure 2 shows the corresponding diffraction pattern for the low-pressure and high-pressure phases of UPd_2Al_3. To solve the new high-pressure structure of UPd_2Al_3 we first performed a systematic study of possible space groups to account for the superlattice reflections. We propose an orthorhombic structure of the high-pressure phase closely related to the hexagonal $PrNi_2Al_3$-type structure below $p \approx 25$ GPa. The high-pressure phase can be described by space group $Pmmm$ as a subgroup of $Cmmm$ which in turn is a non-hexagonal non-isomorphic subgroup of $P6/mmm$. Lowering the symmetry further by allowing for a small monoclinic distortion did not result

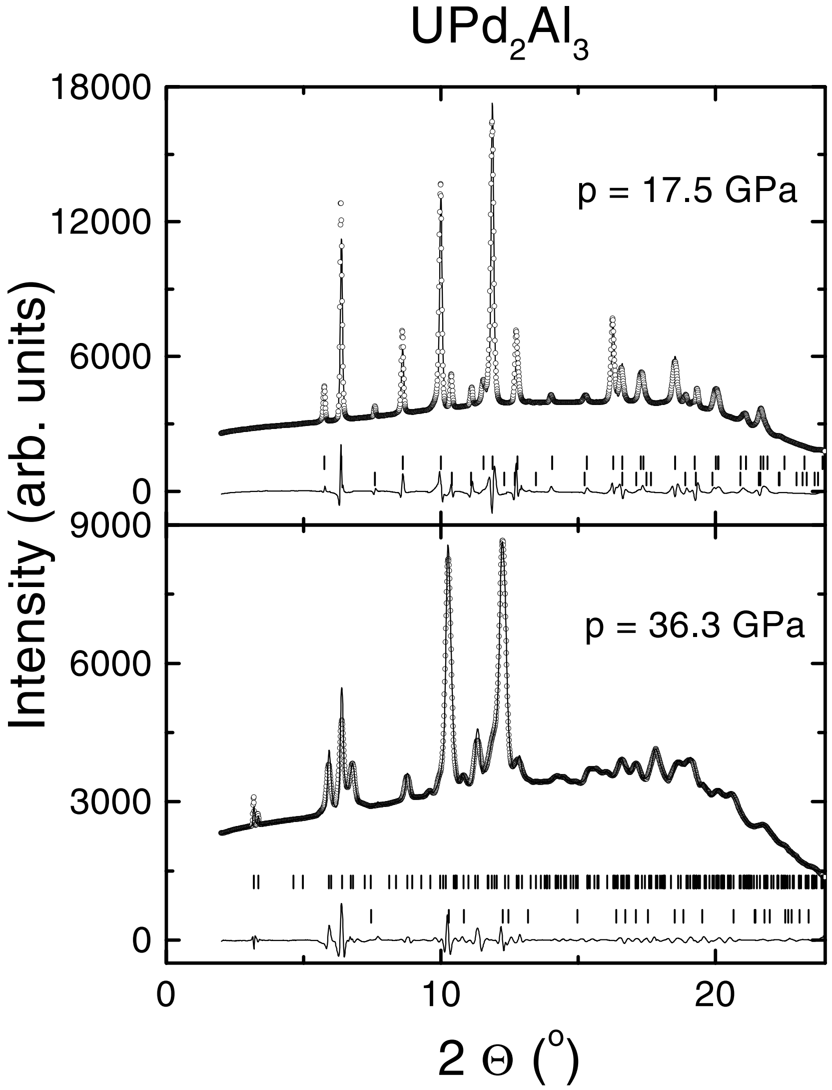

Figure 2. The diffraction pattern of UPd_2Al_3 in the low-pressure phase corresponding to the $PrNi_2Al_3$ structure at $p = 17.5$ GPa (upper part) and in the orthorhombic high-pressure phase at $p = 36.3$ GPa. Observed and calculated intensities, difference and peak positions are shown as in figure 1.

in a significant deviation of the lattice angle β from 90 degrees when refining the unit cell. Therefore we conclude that the new high-pressure phase is of orthorhombic symmetry, at least metrically.

However, with the present data we did not succeed in refining a physically sound structural model. There are several factors which might lead to changes of the intensity profile that have not been taken into account. First, the pressure-transmitting ethanol–methanol mixture solidifies above 1.3 GPa, so we are working with only quasi-hydrostatic pressure conditions. The effect of such non-hydrostatic pressure conditions on polycrystalline samples has been described in detail by Otto *et al* [10]. Second, we may have moderate pressure gradients.

Both effects become more severe with increasing pressure. Furthermore, UPd_2Al_3 is known to display strong preferred-orientation effects as has been inferred by single-crystal susceptibility and dilatation measurements [11], as well as from powder neutron diffraction [12].

In any case, the lattice parameters can be determined with high accuracy. The pressure dependence of the corresponding unit-cell volume of UPd_2Al_3 in its low- and high-pressure phases, normalized to one formula unit, together with the results for UNi_2Al_3, are shown in figure 3. As is evident from the figure, the compressibility of the high-pressure phase is about twice that in the low-pressure phase.

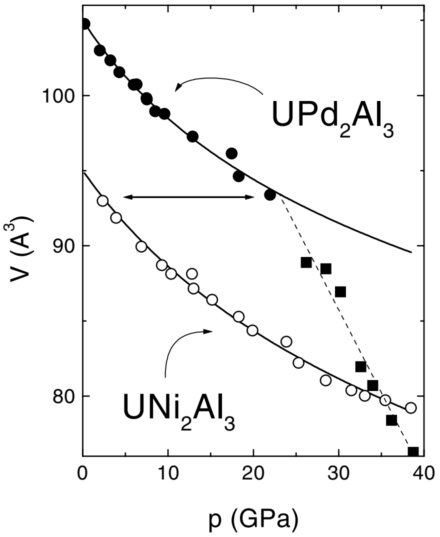

Figure 3. The dependence on pressure of the unit-cell volume of UNi_2Al_3 (open circles) and UPd_2Al_3 (full circles) within the low-pressure phase. Each solid line is a fit to the data according to the Birch–Murnaghan EOS. The arrow indicates the unit-cell volume of UNi_2Al_3 at ambient pressure roughly corresponding with that of UPd_2Al_3 at the beginning of the phase transition. Full squares represent the unit-cell volume of UPd_2Al_3 per formula unit in its orthorhombic high-pressure phase. The dashed line is only to guide the eye.

3. Discussion and conclusions

The Birch–Murnaghan EOS describing the pressure/volume relation of UM_2Al_3 ($M = Pd, Ni$) was originally based on the elastic strain theory for cubic crystals [9]. We therefore conclude that within the pressure range governed by the Birch–Murnaghan EOS, neither steric constraints nor any significant change of the electronic band structure (electronic pressure) inhibits a smooth reduction of the unit cell of UM_2Al_3 ($M = Ni, Pd$). This conclusion is confirmed by the pressure dependence of the metal–metal distances. The shortest metal–metal distance is between U and Pd ions, $d(\text{U–Pd}) = a\cos(30^\circ)/3$ with a being the lattice parameter. The value of a at the critical pressure of $p_c = 23.5$ GPa reveals a U–Pd distance of 1.51 Å. Comparing this value with the effective ionic radii as reported by Shannon [13] reveals that the U–Pd distance at the phase transition pressure corresponds almost exactly to the sum of the ionic radii of U^{4+} and Pd^{4+} ions (in sixfold coordination). Both U^{3+} and Pd^{3+} have significantly larger ionic radii. The ionic radii of Shannon [13] are based on a systematic study of halides and chalcogenides and deviations are expected to occur for intermetallic compounds. However, due to the absence of anions in intermetallic phases, geometrical constraints derived from such ionic radii correspond to a lower limit of the minimal interatomic distances allowed in a given crystallographic structure. Hence the prediction of a critical pressure in terms of simple geometrical constraints agrees surprisingly well with the experimental value. Therefore the present structural data provide evidence for a U^{4+} valence state (for $p \leqslant 25$ GPa), in agreement with susceptibility and specific heat data which also suggested a tetravalent uranium state in the presence of crystal-field effects [14]. Applying the same reasoning to the Ni compound, then extrapolating the Birch–Murnaghan EOS, we can estimate a critical pressure of $p_c \approx 72.5$ GPa for UNi_2Al_3.

The unit-cell volumes per formula unit of UPd_2Al_3 at the phase transition pressure are identical for the two phases. This would be an explanation for the coexistence of the two phases within a small pressure range around the phase transition, indicative of its first-order character. However, it should be noted that the present data cannot rule out the possibility of a small discontinuity of the normalized unit-cell volume (of a few per cent) in the range 23 GPa $\leqslant p \leqslant$ 28 GPa and that the phase coexistence may, at least partly, be due to pressure inhomogeneities.

The properties of uranium-based intermetallic compounds are in general governed by the behaviour of the 5f-electron system. Band-structure calculations (available only for ambient pressure conditions) [15–17] can successfully reproduce the magnetic structure, the value of the ordered magnetic moment, as well as the Fermi surface which has experimentally been determined by de Haas–van Alphen measurements [18, 19]. These spin-density functional calculations reveal a dominant 5f contribution at the Fermi level and a peak of the density of states around 3.5 eV below as arising from Pd 4d states. s- and p-derived states are very weak in intensity and contribute over the entire valence band [15–17]. The Fermi surface is composed of different sheets containing strongly anisotropic bands of almost pure 5f states and rather isotropic bands of strongly hybridized states [17]. A question of ongoing debate is whether to treat the 5f electrons as itinerant band states (as has successfully been done in the band-structure calculations) or as localized moments. Predominantly on the basis of specific heat measurements [20] and μSR experiments [21], it was proposed that UPd_2Al_3 may contain two different 5f-electronic subsystems, one localized part being responsible for the magnetic behaviour and one itinerant part giving rise to the superconducting heavy-fermion state. The occurrence of two markedly different parts of the Fermi surface was interpreted as being in favour of a coexistence of two such electronic subsystems [17]. The high-pressure experiments [3, 4] reveal that the magnetism of UPd_2Al_3, corresponding to the anisotropic and predominantly 5f states, is more sensitively affected by increasing pressure than the already strongly hybridized and rather isotropic parts of the Fermi surface. Hence, the Fermi surface properties of UPd_2Al_3 suggest that the electronic states become more isotropic upon increasing pressure. It is further interesting to note that the onset of magnetic order at low temperatures changes the symmetry from hexagonal to orthorhombic [17]. The structural phase transition of UPd_2Al_3 around $p \approx 25$ GPa also changes the symmetry from hexagonal to orthorhombic. This is in contrast to the general tendency for structures which exhibit high densities to be either fcc or hcp.

It is a well known fact that the application of pressure in 4f materials usually leads to a configurational change from an initial $4f^n$ to a $4f^{n-1}$ state at high pressure [22, 23]. Such valence-fluctuation phenomena are frequently encountered in compounds displaying strong-hybridization effects, i.e. heavy-fermion and mixed-valence compounds [22, 23]. Most of the pressure-induced valence-fluctuation phenomena are based on alloy series corresponding to chemical pressure [23]. An example of changes of the valence state caused by the application of external pressure has been established for Yb, leading to an exceptionally large compressibility

[24]. Hence the sudden increase of the compressibility of UPd_2Al_3 in its high-pressure phase may be interpreted as an indication for the onset of pressure-induced valence fluctuations from a U^{4+} to a U^{5+} configuration, corresponding to a reduction of the ionic radius of uranium by 15% [13]. Such valence-fluctuation phenomena usually take place in a temperature range where the thermal energy $k_B T$ is less than the energy of hybridization between the f electrons and the band states of conduction electrons. In typical mixed-valence compounds, this hybridization energy is of the order of several hundreds of K. In UPd_2Al_3 such a characteristic energy scale was determined by means of inelastic neutron scattering to be only $\approx$50 K [25]. However, a strong increase of the hybridization energy upon application of pressure is expected and evidenced by the results of the high-pressure resistivity [3] and neutron diffraction [4] experiments. Probably, significant effects of hybridization of all s, p, d and f electrons take part in the high-pressure phase transition of UPd_2Al_3.

Our present high-pressure structural study on UM_2Al_3 (M = Ni, Pd) also shows that the behaviour of the Néel temperature and the superconducting transition temperature of UPd_2Al_3 up to $p = 14$ GPa (as determined by electrical resistivity measurements in reference [3]) is indeed solely electronic in nature and not related to any structural changes, such as a possible continuous distortion upon application of pressure. When extrapolating the linear decrease of the superconducting transition temperature T_c starting at $p = 6.5$ GPa [3], a T_c of 1 K is obtained at $p = 25$ GPa. It would be most interesting to know whether UPd_2Al_3 still shows superconductivity above $p = 25$ GPa in its orthorhombic high-pressure phase. Moreover, band-structure calculations depending on the lattice constants are strongly desired.

Acknowledgments

This work was supported by the BMBF under contract numbers 13N6917 (EKM) and 03-LO5AU1-5 (BEO, Verbund 4).

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