

Preparation, Crystal Structures and Properties of Two Modifications of UCr_6P_4

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Tin Flux, Crystal Structure, Magnetic Properties, Structural Relationships

UCr_6P_4 was prepared from a tin flux in two forms at low (α) and high (β) temperatures (880 °C and 1000 °C), respectively. The crystal structures of both modifications were determined from single-crystal data. $\alpha\text{-UCr}_6\text{P}_4$: $\text{P}\bar{6}m2$ (No. 187), $a = 698.5(3)$ pm, $c = 350.8(1)$ pm, $Z = 1$, $R = 0.052$ for 18 variable parameters and 410 structure factors; $\beta\text{-UCr}_6\text{P}_4$: Pmmn (No. 59), $a = 698.6(1)$ pm, $b = 350.85(4)$ pm, $c = 1196.1(2)$ pm, $Z = 2$, $R = 0.047$ for 21 variables and 656 structure factors. Although the lattice constants of both modifications are closely related, the two forms can be transformed into each other only by a very sluggish, reconstructive phase transformation. Nevertheless, both structures have very similar coordination polyhedra. The U atoms have 6 P neighbours in trigonal prismatic arrangement. Half of the Cr atoms have tetrahedral, the other half square pyramidal P coordinations. As is typical for phosphides with high metal content, all metal atoms additionally have many metal neighbours. The P atoms are located in trigonal prisms of metal atoms with two or three additional metal atoms outside the rectangular faces of the prisms. Both modifications of UCr_6P_4 show relatively high, almost temperature independent paramagnetism, as is frequently observed for intermetallic phases of uranium.

During the investigations of ternary systems lanthanoid(Ln)-transition metal(T)-phosphorus numerous phosphides were found with a metal:phosphorus ratio close to or at exactly 2:1. Examples are the series $\text{Ln}_2\text{Fe}_{12}\text{P}_7$, $\text{Ln}_2\text{Co}_{12}\text{P}_7$ [1, 2], $\text{Ln}_2\text{Ni}_{12}\text{P}_7$ [3], $\text{Ln}_2\text{Rh}_{12}\text{P}_7$ [4], LnFe_5P_3 [5], LnCo_5P_3 [6–8], LnNi_5P_3 [9, 10], LnCo_8P_5 [11, 12], $\text{Ln}_6\text{Ni}_{20}\text{P}_{13}$ [13], LnCo_3P_2 [8, 14, 15], $\text{Ln}_5\text{Co}_{19}\text{P}_{12}$ [8, 16], $\text{Ln}_5\text{Ru}_{19}\text{P}_{12}$ [17], LnNi_4P_2 [18], and $\text{Ln}_3\text{Ni}_7\text{P}_5$ [19]. A few corresponding actinoid transition metal phosphides have also been reported: $\text{Th}_6\text{Co}_{20}\text{P}_{13}$ [20], $\text{U}_6\text{Rh}_{20}\text{P}_{13}$ [21] and UMn_4P_2 [22]. Here we give a detailed account of our work on two modifications of UCr_6P_4 . Preliminary reports about their crystal structures were given before [23, 24].

Sample Preparation and Properties

Both modifications of UCr_6P_4 were prepared from the elemental components using tin as a flux [25, 26]. Starting materials were small platelets of uranium (Merck, “nuklearrein”), chromium powder (150 mesh, nominal purity 99.99%), red phosphorus in the form of small pieces (Höchst AG, Knapsack, “ultrapure”), and granules of tin (Rie-

del-de Haën, “reinst”). The best results were achieved by preparing first UP_2 (with about 10% excess of phosphorus) by reaction of the components in evacuated silica tubes for 20 h at 450 °C. The excess (white) phosphorus was separated from the main product by a temperature gradient in the furnace. The resulting UP_2 sample was crushed to a powder under argon and not allowed to contact air prior to the reactions. Appropriate amounts of UP_2 were then reacted with chromium powder and red phosphorus in a tin flux. The atomic ratios U:Cr:P:Sn varied between 4:19:9:68 and 5:17:8:70. The samples were placed in alumina containers, which were sealed in evacuated silica tubes and slowly heated (50 °C/h) to 450 °C, where they were held for about 10 h to allow reaction of the excess phosphorus. They were then annealed for ten days at temperatures between 880 and 1000 °C. The tin-rich matrix of the samples was dissolved in moderately diluted (1:1) hydrochloric acid. The Guinier powder patterns showed the samples annealed at 1000 °C to be single phase $\beta\text{-UCr}_6\text{P}_4$. The samples annealed at 880 °C consisted of the α modification with minor amounts of the β modification.

Both modifications crystallize in the form of black needles with metallic lustre. They are stable in air and only very slowly attacked by hot concentrated hydrochloric acid.

Magnetic susceptibility measurements were made with a Faraday balance between liquid ni-

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trogen and room temperature as described earlier [27]. Both modifications show almost temperature-independent paramagnetism. At room temperature the susceptibility of the β -modifications is $\chi = 4.3(\pm 0.1) \times 10^{-3} \text{ cm}^3/\text{mol}$; it increases to $\chi = 4.7(\pm 0.1) \times 10^{-3} \text{ cm}^3/\text{mol}$ at 77 K. The values for the low temperature modification are about 10% higher, but could not be determined accurately because the sample contained the high temperature modification as a second phase. The magnitude of these susceptibilities is considerably higher than the Pauli paramagnetism of ordinary metals and similar to that of “heavy fermion systems” [28].

Structure Determinations

Indices for the interpretation of the Guinier powder data could be assigned on the basis of the single-crystal data and the intensities calculated [29] from the refined structure. Lattice constants were refined by least-squares fits using α -quartz ($a = 491.30 \text{ pm}$, $c = 540.46 \text{ pm}$) as standard. They are listed in Table I together with other data of the structure determination.

Needle-shaped single-crystals of both UCr_6P_4 modifications were investigated in Weissenberg cameras. In both cases the needle axes turned out to be the short axes, as is usually the case. The crystals had the Laue symmetries 6/mmm and mmm and the structures were eventually determined in the space groups $\text{P}\bar{6}\text{m}2$ (No. 187) and Pmmn (No. 59), respectively. Intensity data were

collected with a four-circle diffractometer. The positions of the uranium atoms were obtained from the Patterson syntheses; those of the other atoms were found on difference Fourier maps. For the full-matrix least-squares refinements atomic scattering factors [30] were used, corrected for anomalous dispersion [31]. Weights reflected the counting statistics. Parameters accounting for isotropic secondary extinction were refined and applied to the calculated structure factors. To check for deviations from the ideal compositions, we refined occupancy parameters together with the thermal parameters, while the scale factors were held constant. No significant deviations from the ideal occupancies were observed. In the final cycles the ideal occupancies were assumed. The correct handedness of the crystal used to determine the structure of the hexagonal crystal was found by refining both enantiomorphic settings. The residual value for the correct setting was lower by 4 relative % (0.052 vs. 0.054). The final residuals, positional parameters and interatomic distances are given in Tables I–III. The anisotropic thermal parameters and structure factor tables are available [32, 33]*.

* Further details may be obtained from: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information mbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the Registry No. CSD 55861, the names of the authors and the journal citation.

| | $\alpha\text{-UCr}_6\text{P}_4$ | $\beta\text{-UCr}_6\text{P}_4$ |
|---|--|--|
| Space group | $\text{P}\bar{6}\text{m}2$ (No. 187) | Pmmn (No. 59) |
| Cell-constants (pm) | $a = 698.5(3)$ $c = 350.8(1)$ $c/a = 0.5022$ | $a = 698.6(1)$ $b = 350.85(4)$ $c = 1196.1(2)$ |
| Cell volume (nm^3) | $V = 0.1482$ | $V = 0.2932$ |
| Formula units per cell | $Z = 1$ | $Z = 2$ |
| Formula weight | 673.90 | 673.90 |
| Calculated density (g/cm^3) | $\rho_{\text{calc}} = 7.55$ | $\rho_{\text{calc}} = 7.63$ |
| Crystal size (μm) | $13 \times 18 \times 150$ | $10 \times 13 \times 100$ |
| Radiation | graphite monochromated $\text{MoK}\alpha$ | |
| Detector | scintillation counter, pulse height discriminator | |
| Scan type | $\theta/2\theta$ | $\theta/2\theta$ |
| Scan range (2θ) | 100° | 80° |
| $\pm h, \pm k, \pm l$ | $\pm 13, \pm 13, \pm 7$ | $\pm 12, \pm 6, \pm 21$ |
| Absorption corr. from | psi scan data | psi scan data |
| Total no. of data | 6123 | 7239 |
| Data after averaging | 648 | 1108 |
| Data with $I > 3\sigma(I)$ | 410 | 654 |
| Residual (on F values) | $R = 0.052$ | $R = 0.039$ |
| Weighted residual | $R_w = 0.060$ | $R_w = 0.047$ |
| No. of variables | 18 | 40 |

Table I. Crystallographic data for the low (α)- and high (β)-temperature modification of UCr_6P_4 .

Table II. Atomic parameters for α - and β - UCr_6P_4 . The last column lists the equivalent isotropic thermal parameter B_{eq} ($\times 100$ in units of nm^2). Standard deviations in the positions of the last listed digit are given in parentheses throughout this paper.

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | B_{eq} |
|--|----------|-----------|------------|---------------------|
| α - UCr_6P_4 $\text{P}\bar{6}\text{m}2$ (No. 187) | | | | |
| U | 1a | 0 | 0 | 0.423(6) |
| Cr(1) | 3k | 0.7989(3) | 0.2011 1/2 | 1.47(6) |
| Cr(2) | 3j | 0.4624(3) | 0.5376 0 | 0.55(3) |
| P(1) | 3k | 0.1863(5) | 0.8137 1/2 | 0.78(5) |
| P(2) | 1e | 2/3 | 1/3 0 | 1.2(1) |
| β - UCr_6P_4 Pmmn (No. 59) | | | | |
| U | 2b | 1/4 | 3/4 | 0.68048(6) 0.359(7) |
| Cr(1) | 2a | 1/4 | 1/4 | 0.8834(2) 0.70(4) |
| Cr(2) | 2a | 1/4 | 1/4 | 0.2830(2) 0.43(4) |
| Cr(3) | 4f | 0.0550(3) | 1/4 | 0.0897(2) 0.38(2) |
| Cr(4) | 4f | 0.5574(3) | 1/4 | 0.5746(2) 0.72(3) |
| P(1) | 2a | 1/4 | 1/4 | 0.4906(4) 0.63(7) |
| P(2) | 2b | 1/4 | 3/4 | 0.0107(4) 0.51(6) |
| P(3) | 4f | 0.5281(5) | 1/4 | 0.7715(3) 0.41(4) |

Discussion

The structures and coordination polyhedra of the two modification of UCr_6P_4 are shown in Fig. 1. Both represent new structure types, and although both structures have much in common, the phase transformation taking place somewhere between 880 and 1000 °C must be of the sluggish, reconstructive type as opposed to the displacive, ferroic type, because the connectivity of the atoms is different. The high-temperature (β) modification for a given composition can usually be described with a smaller number of positional parameters. UCr_6P_4 represents one of the few exceptions from this rule.

In both modifications of UCr_6P_4 all atoms are placed on mirror planes, which extend perpendicular to the short axes. In both structures the U atoms have six P neighbours forming trigonal prisms at (average) distances of 285.6 pm and 284.7 pm in the α - and β -modification, respectively. These coordination polyhedra are augmented by twelve Cr atoms at average distances of 326.0 pm and 323.7 pm. Two U atoms a translation period above and below at (the same distances in both structures of) 350.8 pm complete these coordination polyhedra, although these interactions can hardly be considered as bonding. Two types of different coordinations for the Cr atoms occur in

Table III. Interatomic distances (pm) in α - and β - UCr_6P_4 . All metal–metal and metal–phosphorus distances shorter than 360 pm are listed. The shortest P–P distances are all greater than 300 pm. Standard deviations are all less than 0.5 pm in the α - and less than 0.6 pm in the β -modification.

| α - UCr_6P_4 | | | β - UCr_6P_4 | | |
|-------------------------------------|--------|-------|------------------------------------|--------|-------|
| U: | 6P(1) | 285.6 | U: | 4P(3) | 283.5 |
| | 6Cr(1) | 299.9 | | 2P(1) | 287.0 |
| | 2U | 350.8 | | 2Cr(1) | 299.5 |
| | 6Cr(2) | 352.2 | | 4Cr(4) | 304.8 |
| | | | | 2Cr(4) | 333.5 |
| Cr(1): | 2P(1) | 234.8 | | 2Cr(3) | 347.8 |
| | 2P(2) | 237.4 | | 2U | 350.8 |
| | 2Cr(1) | 277.2 | | 2Cr(2) | 352.0 |
| | 4Cr(2) | 279.1 | | | |
| | 2U | 299.9 | Cr(1): | 2P(2) | 232.3 |
| | 2Cr | 350.8 | | 2P(3) | 235.9 |
| | | | | 4Cr(3) | 277.9 |
| Cr(2): | 4P(1) | 242.9 | | 2Cr(3) | 281.9 |
| | 1P(2) | 247.1 | | 2U | 299.5 |
| | 2Cr(2) | 270.4 | | 2Cr(1) | 350.8 |
| | 4Cr(1) | 279.1 | | | |
| | 2Cr(2) | 350.8 | Cr(2): | 4P(3) | 243.0 |
| | 2U | 352.2 | | 1P(1) | 248.3 |
| | | | | 2Cr(3) | 268.4 |
| P(1): | 2Cr(1) | 234.8 | | 4Cr(4) | 279.1 |
| | 4Cr(2) | 242.9 | | 2Cr(2) | 350.8 |
| | 2U | 285.6 | | 2U | 352.0 |
| | | | | | |
| P(2): | 6Cr(1) | 237.4 | Cr(3): | 2P(2) | 241.4 |
| | 3Cr(2) | 247.1 | | 2P(3) | 242.3 |
| | | | | 1P(2) | 244.6 |
| | | | | 1Cr(2) | 268.4 |
| | | | | 1Cr(3) | 272.5 |
| | | | | 2Cr(1) | 277.9 |
| | | | | 1Cr(1) | 281.9 |
| | | | | 2Cr(3) | 287.6 |
| | | | | 1U | 347.8 |
| | | | | 2Cr(3) | 350.8 |
| | | | Cr(4): | 2P(1) | 234.4 |
| | | | | 1P(3) | 236.4 |
| | | | | 1P(1) | 237.1 |
| | | | | 2Cr(4) | 262.8 |
| | | | | 1Cr(4) | 269.1 |
| | | | | 2Cr(2) | 279.1 |
| | | | | 2U | 304.8 |
| | | | | 1U | 333.5 |
| | | | | 2Cr(4) | 350.8 |
| | | | P(1): | 4Cr(4) | 234.4 |
| | | | | 2Cr(4) | 237.1 |
| | | | | 1Cr(2) | 248.3 |
| | | | | 2U | 287.0 |
| | | | P(2): | 2Cr(1) | 232.3 |
| | | | | 4Cr(3) | 241.4 |
| | | | | 2Cr(3) | 244.6 |
| | | | P(3): | 1Cr(1) | 235.9 |
| | | | | 1Cr(4) | 236.4 |
| | | | | 2Cr(3) | 242.3 |
| | | | | 2Cr(2) | 243.0 |
| | | | | 2U | 283.5 |

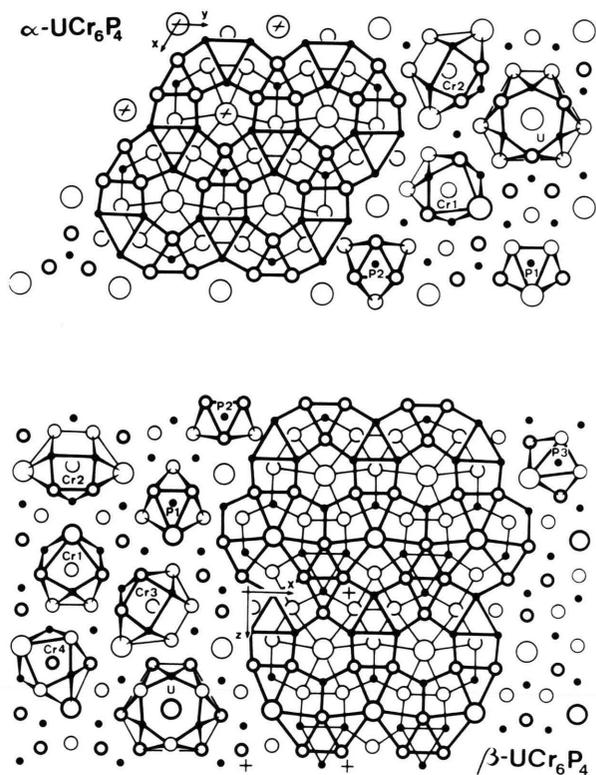


Fig. 1. Crystal structures and coordination polyhedra of the low (α -) and high (β -) temperature modifications of UCr_6P_4 . Atoms connected by thick and thin lines are separated from each other by half a translation period of the projection direction.

both structures. Half of the Cr atoms (the Cr(1) atoms in the α - and the Cr(1) and Cr(4) atoms in the β -modification) have four P neighbours forming a distorted tetrahedron (at average distances of 236.1 pm, 234.1 pm and 235.4 pm), the other half has five P neighbours forming a distorted square pyramid (with average distances of 243.7 pm, 244.1 pm, and 242.4 pm for the Cr(2) atoms of the α - and the Cr(2) and Cr(3) atoms of the β -modification, respectively). The average Cr–P distances are larger for the Cr atoms with five P neighbours than the average Cr–P distances of the Cr atoms with four P neighbours, as it should be for these strong interactions. In addition both types of Cr atoms have ten metal neighbours with Cr–Cr distances ranging between 262.8 pm and 350.8 pm and Cr–U distances between 299.5 pm and 352.2 pm. The larger ones of these distances can hardly be counted as bonding interactions,

these neighbouring atoms are “needed”, however, to complete the coordination polyhedra.

As is usually observed for phosphides with high metal content the phosphorus atoms have six metal neighbours forming trigonal prisms (Fig. 2). In phosphides with a metal:phosphorus ratio of exactly 2:1 the phosphorus atoms have three additional metal neighbours outside the rectangular faces of the prisms, thus increasing the coordination number to nine. In UCr_6P_4 the metal:phosphorus ratio is slightly lower and therefore in both modifications one quarter of the P atoms is coordinated to nine metal atoms, while the others have only eight close metal neighbours.

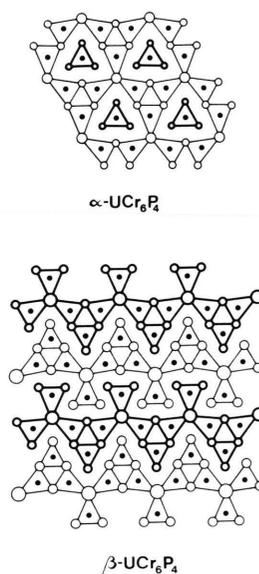


Fig. 2. Arrangement of the trigonal metal prisms around the phosphorus atoms in the two modifications of UCr_6P_4 . Atoms connected by thick and thin lines are separated from each other by half a translation period of the projection direction. Large and small circles: U and Cr; filled circles: P.

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