ELSEVIER

Journal of Alloys and Compounds 216 (1994) 117–121

Journal of
ALLOYS
AND COMPOUNDS

Crystal structure and complex magnetic behaviour of a novel uranium oxyphosphide UCuPO

D. Kaczorowski[a,*], J.H. Albering[b], H. Noël[c], W. Jeitschko[b]

[a]*W. Trzebiatowski Institute for Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 937, PL-50950 Wrocław, Poland*
[b]*Anorganisch-Chemisches Institut, Universität Münster, Wilhelm-Klemm-Strasse 8, D-48149 Münster, Germany*
[c]*Laboratoire de Chimie du Solide et Inorganique Moléculaire, Université de Rennes, U.R.A./C.N.R.S. 1495, F-35042 Rennes, France*

Received 15 April 1994

Abstract

The crystal structure of UCuPO was determined from single-crystal X-ray data and refined to a residual of $R=0.033$ for 192 structure factors and 12 variables. It has a tetragonal ZrCuSiAs-type structure: $P4/nmm$, $a=379.3(1)$ pm, $c=823.3(2)$ pm, $Z=2$. Magnetisation and magnetic susceptibility measurements of a powder sample in the range 5–300 K show UCuPO to order antiferromagnetically at $T_N=220\pm2$ K. Its $\chi(T)$ dependence appears to be highly anomalous with a strong upturn at low temperatures. The close relationship between UCuPO and $U_2Cu_2P_3O$ with respect to their crystal structures and their magnetic behaviour is discussed.

Keywords: Uranium pnictides; Crystal structure refinement; Magnetic properties; Antiferromagnets

1. Introduction

Ternary uranium pnictides containing a transition metal form an interesting family of compounds, which exhibit pronounced structural similarities but show a great variety of magnetic behaviour (see for example Refs. [1,2]). Some of these phases have already been thoroughly characterised with respect to their magnetic and transport properties. The best examples here are $UCuP_2$ and $UCuAs_2$ for which detailed measurements of the magnetisation, the magnetic susceptibility, the electrical resistivity, the Hall effect, the magnetoresistivity, the thermal conductivity, the heat capacity, the elastic effects, the optical and the magnetooptical behaviour were performed on both powder and single-crystalline specimens ([3,4] and references cited therein). In all these investigations the role of metalloids surrounding the uranium atoms on the observed properties was strongly emphasized. It is clear that such physical mechanisms as magnetic exchange interactions, crystal field effects and 5f-s,p,d, hybridisation are directly related to main crystallochemical characteristics of the compound, such as details of its crystal structure and nature of the chemical bonds.

Very recently we reported [5] on the discovery of a new compound, $U_2Cu_2As_3O$, that turns out to be the first known example of any uranium oxypnictide. Thus $U_2Cu_2As_3O$, being structurally very closely related to the 1:1:2 phases, offers an unique possibility to study magnetic behaviour of the uranium atom coordinated jointly by the pnictogen and oxygen ions.

In the present paper we report on the synthesis, crystal structure and magnetic properties of a quaternary uranium–copper oxyphosphide UCuPO, which appears to be another representative of this new group of compounds.

2. Experimental details

After the first observation of the uranium oxyphosphide UCuPO, a polycrystalline sample of this compound was prepared by reaction of a stoichiometric mixture of UP and CuO in an evacuated silica tube at 1000 °C. Crystals suitable for the single-crystal X-ray investigations were grown from microcrystalline UCuPO by an isothermal transport reaction at 900 °C using iodine as a transporting agent. The compound crystallizes in the form of shiny square and rectangular platelets. An energy dispersive analysis in a scanning

---

*Corresponding author.

0925-8388/94/$07.00 © 1994 Elsevier Science S.A. All rights reserved
SSDI 0925-8388(94)01251-C

Table 1
Crystallographic and experimental data for UCuPO

Lattice parameters[a]	*a* (pm)	379.3(1)	(378.7(1))
	c (pm)	823.3(2)	(822.8(5))
	V (nm^3)	0.1184	(0.1180)
Formula units/cell		$Z=2$	
Space group		*P*4/*nmm* (no. 129)	
Formula weight		348.54	
Calculated density (g cm^{-3})		9.78	
Crystal dimension (μm^3)		10×50×50	
$\theta/2\theta$ scans up to		$2\theta=80°$	
Range in *hkl*		±6, ±6, +14	
Transmission coefficient (highest/lowest)		6.44	
Total number of reflections		1534	
Unique reflections		267	
Inner residual		$R_i=0.043$	
Reflections with $I_o>3\sigma(I_o)$		192	
No. of variables		12	
Conventional residual		$R=0.033$	
Weighted residual		$R_w=0.039$	

[a] The lattice parameters given in parentheses were derived from the single crystal investigated on the four-circle diffractometer; they are less accurate than those obtained from the powder data due to systematic errors from absorption effects.

electron microscope showed no impurities (e.g. silicon or iodine) in the crystal used for the structure refinement. The lattice parameters were determined by least-squares fits of the Guinier powder data using α-quartz ($a=491.3$ pm, $c=540.46$ pm) as an internal standard. The lattice constants obtained from the crystal investigated on a four-circle diffractometer are in good agreement with those from the powder data (Table 1).

Magnetic measurements were performed on a powder sample in the temperature interval 5–300 K with a SQUID magnetometer.

3. Crystal structure

A single crystal of UCuPO was examined in a Weissenberg camera to establish its symmetry and suitability for an intensity data collection. The intensity data were recorded on an automated four-circle diffractometer with monochromated Mo Kα radiation, a scintillation counter and a pulse-height discriminator. The background was determined at both ends of each $\theta/2\theta$ scan. A first absorption correction was made on the basis of psi scan data.

From the dimensions of the unit cell it was guessed originally that UCuPO might have an anti-PbFCl-type structure and the positions of the uranium atoms were assumed accordingly. The positions of the other atoms were obtained from difference Fourier syntheses. The structure was refined by a full matrix least-squares program with atomic scattering factors [6,7], corrected for anomalous dispersion [7]. The weighting scheme, which included a term that accounted for the counting statistics and a parameter correcting for isotropic secondary extinction, was included in the calculations. The refinement of the occupancy parameters resulted in the percentage values: 100.5(2), 92.9(7), 103(2) and 86(4) for the U, Cu, P and O positions. The refinement of the anisotropic thermal parameters showed that the U_{11} values of the non-oxygen atoms were between 1.5 and 10 times greater than the U_{33} values. This was ascribed to a systematic error of the data resulting from an insufficient absorption correction and we therefore made another correction for absorption using the DIFABS program [8] for a model with the ideal occupancy parameters and the isotropic thermal parameters as obtained before. This resulted in smaller standard deviation and it lowered the residual from $R=0.052$ to $R=0.033$ for 12 variable parameters and 192 structure factors. A subsequent refinement of the occupancy parameters showed as the most significant deviation from the ideal values an occupancy of the copper position of 95.8% with a standard deviation of 0.8%. Nevertheless, we considered the refinement with the ideal occupancies as the final one. A final difference Fourier synthesis gave no indication of the occupancy of additional atomic sites. Further crystallographic data, atomic parameters and interatomic distances are given in Tables 1–3. A listing of the structure factors is available from the authors.

Table 2
Positional and thermal parameters for UCuPO[a]

Atom	*P*4/*nmm*	*x*	*y*	*z*	$U_{11}=U_{22}$ (pm^2)	U_{33} (pm^2)	B_{eq} (nm^2)
U	2*c*	1/4	1/4	0.6656(1)	36(1)	38(2)	0.287(6)
Cu	2*a*	3/4	1/4	0	89(6)	122(10)	0.79(3)
P	2*c*	1/4	1/4	0.1784(8)	69(11)	45(18)	0.48(5)
O	2*b*	3/4	1/4	1/2	124(37)	65(49)	0.8(1)

[a] The positional parameters were transformed to a standard setting by the program STRUCTURE TIDY [9]. The anisotropic thermal parameters U_{ij} are defined by: $U_{hkl}=\exp[-2\pi^*(U_{11}h^2a^{*2}+\ldots)]$; the values U_{12}, U_{13} and U_{23} are zero for this structure. The right-hand column lists the equivalent isotropic thermal parameters B_{eq} (×100).

Table 3
Interatomic distances in UCuPO[a]

Atoms	Distance (pm)	Atoms	Distance (pm)
U–4O	233.6(1)	Cu–4P	239.9(4)
U–4P	297.4(3)	Cu–4Cu	268.2(1)
U–4Cu	334.3(1)	Cu–4U	334.3(1)
U–4U	379.3(1)	P–4Cu	239.9(4)
U–4U	382.5(1)	P–4U	297.4(3)
		O–4U	233.6(1)

[a] All distances shorter than 500 pm (U–U, U–Cu, Cu–Cu), 400 pm (U–P, U–O, Cu–P, Cu–O), 320 pm (P–P, P–O) and 260 pm (O–O) are listed.

4. Discussion

4.1. Crystal structure description

The crystal structure of UCuPO is shown in Fig. 1. It is isotypic with ZrCuSiAs [10] with the atomic positions of the Zr, Cu and As atoms being occupied by the U, Cu and P atoms, while the oxygen positions of UCuPO correspond to the silicon positions of the prototype. Interestingly there are also several ternary compounds with related compositions, where the same atomic positions are occupied. $UCuAs_2$ (Fig. 2) was the first one of this series [11], which now comprises ten ternary uranium transition metal pnictides UTX_2 with T = Fe, Co, Ni, Cu and X = P, As, Sb, Bi [1]. The recently reported compound $U_2Cu_2As_3O$ [5] also has a closely related structure. It can be seen from Fig. 2 that the crystal structure of $U_2Cu_2As_3O$ consists of three types of atomic layers named A, B and C, stacked in the sequence A + B + A + C. It appears now that the fragment A + B is identical with the unit cell of $UCuAs_2$, whereas the upper part of the structure of $U_2Cu_2As_3O$, i.e. the fragment A + C, corresponds to the unit cell of a hypothetical compound UCuAsO (not yet synthesized), which would be isostructural with UCuPO.

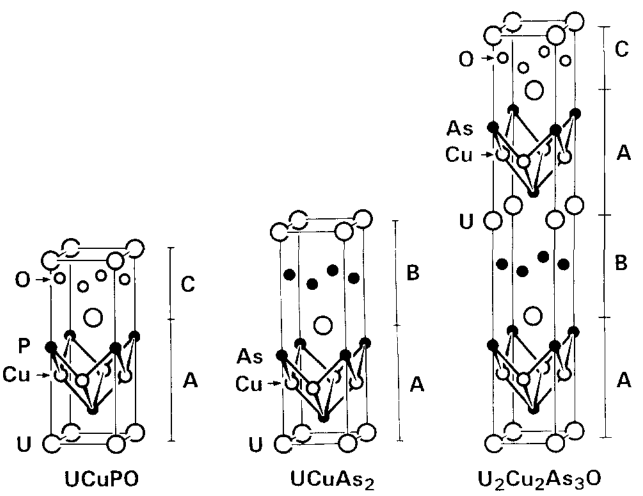

Fig. 2. Comparison of the unit cells of UCuPO, $UCuAs_2$ and $U_2Cu_2As_3O$. The origins of the cells were shifted to the uranium positions to facilitate comparisons. Characteristic blocks in the structures are denoted by the capital letters A, B and C.

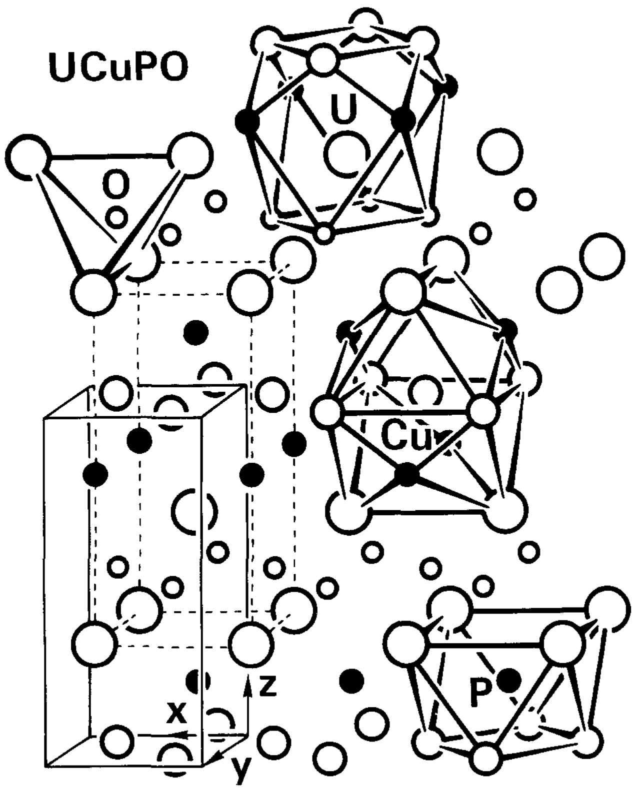

Fig. 1. Crystal structure and coordination polyhedra of UCuPO. The unit cell as given in Table 2 is outlined with solid lines. The cell indicated with dashed lines corresponds to the setting of Fig. 2.

Moreover, the unit cell of UCuPO appears to be a building block of the structure of $U_2Cu_2P_3O$, the compound which was previously denoted [12] as "$U_4Cu_4P_7$" (for discussion see Ref. [5]). Thus, all the coordination polyhedra in UCuPO have their counterparts in the $U_2Cu_2P_3O$ structure. The uranium atoms have the coordination number 12 with strongly bonded oxygen (4×) and phosphorus (4×) neighbours, forming a square antiprism, while the four copper atoms are completing the coordination shell, although the bonding character of the uranium–copper interactions is questionable. The copper atoms are primarily bonded to four phosphorus atoms in tetrahedral arrangement. This coordination is augmented by four copper and four uranium neighbours forming a square and a disphenoid, respectively, again with at best little bonding character. The phosphorus atoms are situated in a square antiprism formed by four uranium and four copper atoms, while the oxygen atoms have a tetrahedral coordination of uranium atoms. The interatomic distances in UCuPO and $U_2Cu_2P_3O$ are almost the same. For example, the shortest U–O spacing in both compounds amounts to 233.6 pm. This can be compared with the strongly ionic U–O bonding of 236.9 pm in UO_2 [13], 235.7 pm in UOSe [14] and 235.4 pm in $U_2Cu_2As_3O$ [5]. The U–P distances of 297.4 pm and 299.1 pm in UCuPO and $U_2Cu_2P_3O$ respectively are also quite similar; however, they are considerably larger than those in more covalent uranium phosphides like UP_2 (289 pm and 277 pm [15]), UPS (288 pm [15]) or $UCuP_2$ (279.4 pm and 289.9 pm [16]) with similar crystal structures. Hence, it seems likely that UCuPO can be described in a first approximation as a normal valence compound with the formula $U^{4+}Cu^{+}P^{3-}O^{2-}$. In this respect UCuPO resembles the oxychalcogenides UOY (Y = S, Se, Te), which also show a full charge compensation and behave at low temperatures as antiferromagnetic semiconductors.

4.2. Magnetic properties

The results of the magnetic measurements are shown in Fig. 3. As deduced from a pronounced maximum in the susceptibility $\chi(T)$, UCuPO orders antiferromagnetically below 220 ± 2 K. In the paramagnetic region the susceptibility follows the Curie law with an effective magnetic moment of 2.68 μ_B.

The most striking feature of the $\chi(T)$ variation, displayed in Fig. 3, is a strong rise in the susceptibility below about 80 K with a pronounced inflection around 75 K. Moreover, in the region of the susceptibility upturn at low temperatures there appears additionally some difference between the $\chi(T)$ curves measured with the sample cooled with (FC, field cooled) and without (ZFC, zero field cooled) an applied magnetic field. This difference becomes more and more pronounced as the temperature is being lowered, suggesting that it may originate from some ferromagnetic impurities present in the sample. Indeed, the field dependence of the magnetisation (see the inset to Fig. 3) exhibits a slight deviation from a straight-line behaviour and shows a small remanency σ_R of about 1.7×10^{-2} emu g^{-1}. An inspection of all the binary and ternary phases of the system U–Cu–P–O known to date leads to the conclusion that the only possible compound that might act as a ferromagnetic impurity in the studied sample of UCuPO is $UCuP_2$ because it orders ferromagnetically at $T_c = 75$ K [3], i.e. at the temperature where the inflection in the $\chi(T)$ dependence for UCuPO occurs. From the comparison of the aforegiven σ_R and the ordered magnetic moment in $UCuP_2$ ($\mu_o = 0.98$, $\mu_B = 15$ emu g^{-1} [3]), an amount of about 0.1% $UCuP_2$ in the measured sample of UCuPO can be estimated. Of course, such a small admixture of the foreign phase would be by far undetectable by X-ray powder diffraction.

It is worth remembering at this point that a very similar behaviour of the magnetic susceptibility, with an upturn at low temperatures and a mysterious step-like change in the magnitude of the susceptibility at about 80 K, has previously been observed [17] for "$U_4Cu_4P_7$", i.e. $U_2Cu_2P_3O$ (see remark above). As proposed in Ref. [17], the characteristic behaviour of the susceptibility in this latter compound may result from crystal field interactions, in the case when the magnetic exchange strength is of comparable magnitude with the energy splitting of the lowest-lying crystal field levels (for theoretical discussion see Ref. [18]). More recently [19], a detailed structure analysis of the "$U_4Cu_4P_7$" single crystals showed that the regular stacking sequence of the unit cells of "$U_4Cu_4P_7$" can be interrupted by single layers corresponding to one-half of the unit cell of the $UCuP_2$-type. This finding raised the question of whether the step-like change in $\chi(T)$ may not be due to this intergrowth of the unit cells of "$U_4Cu_4P_7$" and $UCuP_2$. Now, in view of the close relationship between the crystal structures of UCuPO

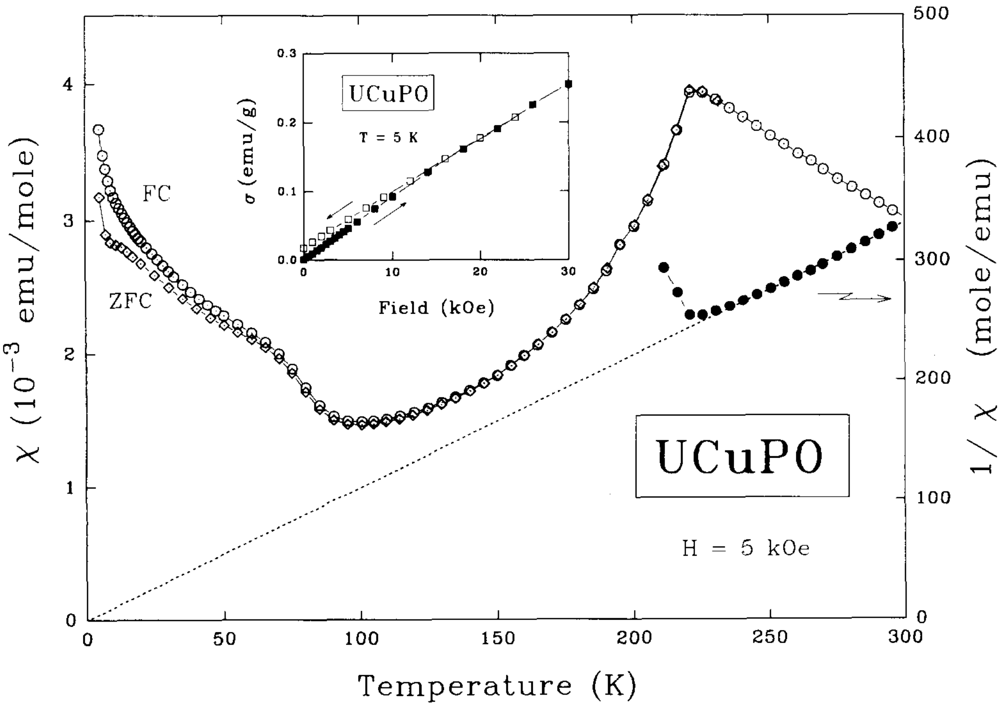

Fig. 3. Temperature dependence of the magnetic susceptibility (left-hand scale) and the inverse magnetic susceptibility (right-hand scale) of UCuPO. The susceptibility was measured in the ordered region with cooling the sample with (FC) and without (ZFC) an applied magnetic field of 5 kOe. The thin dotted line is the fit of $\chi^{-1}(T)$ by the Curie law. The inset shows the magnetisation of UCuPO as a function of the magnetic field, measured at 5 K with increasing (■) and decreasing (□) field strength.

and $U_2Cu_2P_3O$, it seems very likely that also in the present case the $\chi(T)$ inflection around 75 K may result from the occurrence of an intergrowth of the unit cells of UCuPO and $UCuP_2$. However, at the present stage of this work we cannot exclude the possibility that the observed behaviour of the susceptibility is an intrinsic property of UCuPO and reflects some canting of the antiferromagnetic structure of this compound taking place at about 80 K. Yet it should be emphasized that whatever the origin is of the ferromagnetic component in the susceptibility of the studied samples of UCuPO and $U_2Cu_2P_3O$, it cannot explain the rise in $\chi(T)$ at low temperatures but only the anomalies around 75 K. Instead, as mentioned above it seems very likely that the observed properties are determined mainly by crystal field interactions and result from a special square antiprismatic coordination of the uranium atom surrounded in both compounds by four phosphorus and four oxygen ions.

Acknowledgements

We thank Dipl.-Ing. U. Rodewald and Dr M.H. Möller for the collection of the four-circle diffractometer data and Mr K. Wagner for the work using the scanning electron microscope. We are grateful for the generous gift of silica tubes (Dr G. Höfer, Heraeus Quarzschmelze, Hanau) and ultrapure red phosphorus (Hoechst AG, Werk Knapsack). One of us (D.K.) is indebted to the Alexander von Humboldt Foundation and the French Ministry of Research and Technology for supporting his stays at the University of Münster and the University of Rennes, respectively, during which this work was mainly done. We also wish to thank the Stiftung Stipendienfonds des Verbandes der Chemischen Industrie for a stipend to J.A. This study was also supported by the Committee for Scientific Research (Poland) under Grant No. 202969101 and the Deutsche Forschungsgemeinschaft.

References

[1] D. Kaczorowski, *J. Alloys Comp., 186* (1992) 333.
[2] D. Kaczorowski and R. Troć, *J. Phys.: Cond. Matter, 2* (1990) 4185.
[3] D. Kaczorowski, R. Troć and H. Noël, *J. Phys.: Cond. Matter, 3* (1991) 4959.
[4] J. Mucha, H. Misiorek, D. Kaczorowski and A. Jeżowski, *J. Alloys Comp., 189* (1992) 217.
[5] D. Kaczorowski, M. Potel and H. Noël, *J. Solid State Chem.*, (1994) in press.
[6] D.T. Cromer and J.B. Mann, *Acta Crystallogr. A, 24* (1968) 321.
[7] D.T. Cromer and D. Liberman, *J. Chem. Phys., 53* (1970) 1891.
[8] N. Walker and D. Stuart, *Acta Crystallogr. A, 39* (1983) 158.
[9] L.M. Gelato and E. Parthé, *J. Appl. Crystallogr., 20* (1987) 139.
[10] V. Johnson and W. Jeitschko, *J. Solid State Chem., 11* (1974) 161.
[11] J. Stępień-Damm, D. Kaczorowski and R. Troć, *J. Less-Common Met., 132* (1987) 15.
[12] H. Noël, Z. Żołnierek, D. Kaczorowski, R. Troć and J. Stępień-Damm, *J. Less-Common Met., 135* (1987) 61.
[13] L. Lynds, *J. Inorg. Nucl. Chem., 24* (1962) 1007.
[14] D. Kaczorowski, R. Pöttgen, Z. Gajek, A. Zygmunt and W. Jeitschko, *J. Phys. Chem. Solids, 54* (1993) 723.
[15] F. Hulliger, *J. Less-Common Met., 16* (1968) 113.
[16] H. Noël, Z. Żołnierek, D. Kaczorowski and R. Troć, *J. Less-Common Met., 132* (1987) 327.
[17] D. Kaczorowski, R. Troć and H. Noël, *J. Less-Common Met., 161* (1990) 239.
[18] Y.L. Wang and B.R. Cooper, *Phys. Rev. B, 2* (1970) 2607.
[19] J. Schoenes, D. Kaczorowski and C. Beeli, *Z. Phys. B – Cond. Matter, 88* (1992) 135.