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Crystal Structure of the First Uranium Oxyarsenide $U_2Cu_2As_3O$

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The crystal structure of $U_2Cu_2As_3O$ was determined from single-crystal X-ray data and refined to a residual of $R = 0.037$, $R_w = 0.034$, for 443 reflections with $I > \sigma(I)$ and 22 variables. It is of a new type with tetragonal space group $P4/nmm$, $Z = 2$, and lattice parameters $a = 3.9111(2)$ Å and $c = 17.916(4)$ Å. A close relationship between the crystal structures of $U_2Cu_2As_3O$ and $UCuAs_2$ is discussed. $U_2Cu_2As_3O$ appears to be the first known oxypnictide among uranium compounds. However, in view of the results obtained for $U_2Cu_2As_3O$, another uranium compound, previously denoted as "$U_4Cu_4P_7$," is believed now to be $U_2Cu_2P_3O$, closely related to the arsenide. © 1994 Academic Press, Inc.

1. INTRODUCTION

Ternary uranium—transition metal–pnictides have attracted much interest in recent years because of their remarkable physical properties. In the course of our continuous search for new phases existing in the U–Cu–As system we have reported already on $UCuAs_2$ (1), $U_2Cu_4As_5$ (2), and UCu_3As_2 (3). The former two compounds crystallize with a tetragonal symmetry and their crystal structures were refined (2, 4) from single-crystal X-ray data. The magnetic and electrical properties of these two ternary phases were also investigated (2, 5 and references therein). The other known arsenide, UCu_3As_2, was briefly communicated (3) to be hexagonal and the primary aim of this study was to refine its crystal structure from single-crystal data. However, our attempts to grow single crystals of this compound failed. Instead we discovered a new uranium–copper arsenide which, however, was found to contain also oxygen in its unit cell. Thus, in the present paper we address the determination and subsequent refinement of the crystal structure of a quaternary compound $U_2Cu_2As_3O$.

2. SAMPLE PREPARATION

The powder sample of UCu_3As_2 was prepared by heating a mixture of UAs_2 + 3Cu in an evacuated sealed quartz ampoule at 900°C for 2 weeks. The product was analyzed by X-ray diffraction and found to be single phase. It was used as a starting material for the single-crystal growth by the chemical vapor transport method with iodine as a transporting agent. As a result, numerous small single crystals which had the form of either cubo-octahedrons or thin platelets were obtained. Energy-dispersive analysis in a scanning electron microscope revealed the former crystals to be U_3As_4, but the plates were found to be a new uranium compound with an approximate composition "$U_2Cu_2As_3$."

3. CRYSTAL STRUCTURE DETERMINATION

A small single crystal with dimensions 90 μm × 80 μm × 8 μm was isolated from a gently crushed platelet of "$U_2Cu_2As_3$" and used for the intensity data collection on a four-circle diffractometer (Nonius CAD4) with graphite-monochromated Mo$K\alpha$ radiation. Least-squares refinement of the diffraction angles of 25 reflections resulted in the tetragonal lattice parameters $a = 3.9111(2)$ Å and $c = 17.916(4)$ Å. The observed systematic extinctions of $h + k \neq 2n$ for $hk0$ reflections were compatible with the space groups $P4/n$ and $P4/nmm$. During the structure determination, the higher symmetry group $P4/nmm$ was found to be correct.

A total of 827 reflections were measured in the reciprocal sphere up to $\theta = 40°$ within the limits $0 < h < 7$, $0 < k < 7$, and $0 < l < 32$. An absorption correction was made by the program ABSCOR (6). The main crystallographic and experimental data are summarized in Table 1.

The uranium atom positions were determined from the Patterson function and the Cu and As atoms were located in difference Fourier syntheses. The structure was refined by full-matrix least-squares cycles using the SDP program system (6). The conventional and weighted residuals were $R = 0.046$ and $R_w = 0.051$, yielding the formula $U_2Cu_2As_3$, with atomic positions as given in Table 2. However, a final Fourier difference analysis showed still a rather high residual density of 24 e Å^3 at site $2a$: 0.75, 0.25, 0. Placing additional arsenic atoms As(4) at this position resulted in a significant decrease of the residuals ($R = 0.036$ and $R_w = 0.034$) but the occupancy for this

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TABLE 1

Crystallographic and Experimental Data for $U_2Cu_2As_3O$

Lattice constants	
a (Å)	3.9111(2)
c (Å)	17.916(4)
V (Å^3)	274.06(6)
Formula units/cell	$Z = 2$
Space group	$P4/nmm$ (No. 129)
Formula weight	843.91
Calculated density (g cm^{-3})	10.23
Absorption coefficient (cm^{-1})	813.7
Crystal dimensions (μm^3)	90 × 80 × 8
$\theta/2\theta$ scans up to	$\theta = 40°$
Range in hkl	$0 < h,k < 7$, $0 < l < 32$
Absorption correction	ABSCOR (6)
min/max	0.56/1.80
Total No. of Reflections with $I > \sigma(I)/2$	827
Unique reflections	511
Merging R	0.061
Reflections with $I > \sigma(I)$	443
No. of variables	22
Conventional residual	0.037
Weighted residual	0.034
Statistical weight	$\omega = 4F_0^2/\sigma^2(F_0^2) + (PF_0^2)^2$ with $P = 0.02$
Goodness of fit	1.057
Maximum density in final difference Fourier	$\pm 5\ e^-/\text{Å}^3$ near U atom
Ratio of maximum shift to eds	<0.01

site was found to be only 0.155(6). Moreover, the U–As(4) distances were unusually short, about 2.35 Å, i.e., almost the same length as the uranium–oxygen bonding in such compounds as UOSe (2.357 Å (7)) and UO_2 (2.369 Å (8)). Further calculations with substitution of oxygen for As(4) gave the same final residuals and reasonable values of the thermal factors for the $2a$ position being fully occupied by the oxygen atoms (see Table 3). The crystallochemical formula corresponding to these results is $U_2Cu_2As_3O$.

Although no oxygen was introduced specifically to form such an oxyarsenide, a small amount necessary to form some single crystals of this compound can be easily obtained from a slight oxidation in air of the starting materials or from outgassing the silica tubes at high temperatures during the crystal growth process. So, although we cannot give any arguments from either physical or chemical analysis (the sensitivity of the EDAX spectrometer used in our electron microprobe studies was not sufficient to determine an oxygen content), the above crystallographic calculations seem to give convincing indications that oxygen is present on the $2a$ site rather than an As(4) atom with a strongly reduced occupancy parameter.

The interatomic distances in $U_2Cu_2As_3O$ are listed in Table 4. The structure factor tables are available from the authors.

4. DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of $U_2Cu_2As_3O$ is displayed in Fig. 1. It is of a new type and consists of a few blocks of

TABLE 2

Positional Parameters in $U_2Cu_2As_3O$

Atom	Site	x	y	z
U(1)	$2c$	0.25	0.25	0.07312(4)
U(2)	$2c$	0.25	0.25	0.62539(4)
Cu	$4f$	0.75	0.25	0.23092(9)
As(1)	$2c$	0.25	0.25	0.3213(1)
As(2)	$2b$	0.75	0.25	0.5
As(3)	$2c$	0.25	0.25	0.8520(1)
O	$2a$	0.75	0.25	0.0

TABLE 3

Anisotropic and Isotropic Equivalent Thermal Parameters for $U_2Cu_2As_3O$

Atom	Site	β_{11}	β_{22}	β_{33}	B_{eq} (Å^2)
U(1)	$2c$	0.32(1)	β_{11}	0.36(2)	0.334(6)
U(2)	$2c$	0.33(1)	β_{11}	0.40(2)	0.354(6)
Cu	$4f$	0.75(6)	0.97(6)	0.76(5)	0.83(3)
As(1)	$2c$	0.48(4)	β_{11}	0.59(5)	0.52(2)
As(2)	$2b$	0.64(4)	β_{11}	0.46(5)	0.58(2)
As(3)	$2c$	0.48(3)	β_{11}	0.56(5)	0.50(2)
O	$2a$	1.1(3)	β_{11}	0.5(3)	0.9(1)

Note. The form of the anisotropic thermal parameters is $\exp(-\frac{1}{4}\Sigma_{ij}h_ih_ja_i^*a_j^*\beta_{ij})$, where a_i^* is a reciprocal lattice parameter.

TABLE 4
Interatomic Distances (in Å) in $U_2Cu_2As_3O$

U(1)–4O	2.354(1)	As(1)-4Cu	2.539(2)
4As(3)	3.074(1)	4U(2)	2.926(1)
4Cu	3.438(2)	4As(2)	3.751(2)
4U(1)	3.809(1)	4As(1)	3.911(1)
		As(2)-4As(2)	2.766(1)
U(2)–4As(1)	2.926(1)	4U(2)	2.978(1)
4As(2)	2.978(1)	4As(1)	3.751(1)
4Cu	3.233(2)		
4U(2)	3.911(1)		
		As(3)-4Cu	2.456(2)
Cu–2As(3)	2.456(2)	4U(1)	3.074(1)
2As(1)	2.539(2)	4O	3.294(2)
4Cu	2.766(1)	4As(3)	3.911(1)
2U(2)	3.233(2)		
2U(1)	3.438(2)	O–4U(1)	2.354(1)
		4O	2.766(1)
		4As(3)	3.294(2)

alternating atomic layers which are typical for many ZrSiS(PbFCl)-related compounds. Thus, for example, the slab U(2)–As(2)–U(2), marked in Fig. 1 as block B, has its clear correspondence in UAs_2, $UCuAs_2$, and $U_2Cu_4As_5$, and the U–U distance of 5.275 Å within this slab is almost the same as that in the other arsenides (5.380 Å (9), 5.267 Å (4), and 5.286 Å (2) for UAs_2, $UCuAs_2$, and $U_2Cu_4As_5$, respectively). In turn, block A, i.e., the slab U(2)–As(1)–Cu–As(3)–U(1), with a uranium interatomic spacing of 6.068 Å (across the slab), is characteristic of $UCuAs_2$, where this U–U distance amounts to 5.809 Å (4). Finally, the slab U(1)–O–U(1), i.e., block C, is a building element in uranium oxychalcogenides UO*Y* (*Y* = S, Se, Te). The shortest U–U distance of 3.809 Å within this block is very close to that found, for example, in UOSe (3.821 Å (7)).

A close similarity between the unit cell of $U_2Cu_2As_3O$ and that of $UCuAs_2$ is clearly evident from Fig. 1, where both structures are drawn with their origins shifted by (0.75, 0.75, $-z_{U(1)}$) and (0.75, 0.75, $-z_U$), respectively. One sees easily that $UCuAs_2$ may be considered to consist of alternating blocks A and B, while our new quaternary compound can be represented by the sequence –ABAC–.

The above relationship is also reflected in very similar coordination polyhedra of all the constituent atoms in both structures. Both uranium atoms U(1) and U(2) in $U_2Cu_2As_3O$ are located in sites of C_{4v} point symmetry but they have somewhat different coordination spheres. Whereas U(2) is surrounded by four As(1) and four As(2) atoms forming a square antiprism with the base sides equal to *a* and $a\sqrt{2}$, the U(1) atoms are placed inside such a square antiprism but formed by four O and four As(3) atoms. Thus, the U(2) atoms are coordinated in the very same manner as the uranium atoms in $UCuAs_2$, while the coordination polyhedron of U(1) resembles that one characteristic of the UO*Y* compounds with the only difference being that the chalcogen atoms are replaced here by arsenic.

Then, the nearest-neighbor coordination sphere of the copper atoms consists of two As(3) and two As(1) atoms which together form a distorted tetrahedron. This coordination polyhedron is completed by four Cu atoms placed in a square arrangement with a base side $a/\sqrt{2}$.

Coordination spheres very similar to that of the Cu atom apply also to the As(2) and O atoms. In these cases, however, the tetrahedron is regular and it is formed by four U(2) or four U(1) atoms for As(2) and O, respectively, and the square consists of four As(2) and four O atoms, respectively.

Finally, the As(1) and As(3) atoms have a coordination sphere like that of the uranium atoms but a square antiprism is formed here by four Cu and four U(2) atoms or four Cu and four U(1) atoms, respectively.

It may be of some interest to discuss the interatomic distances in $U_2Cu_2As_3O$, collected in Table 4. Considering

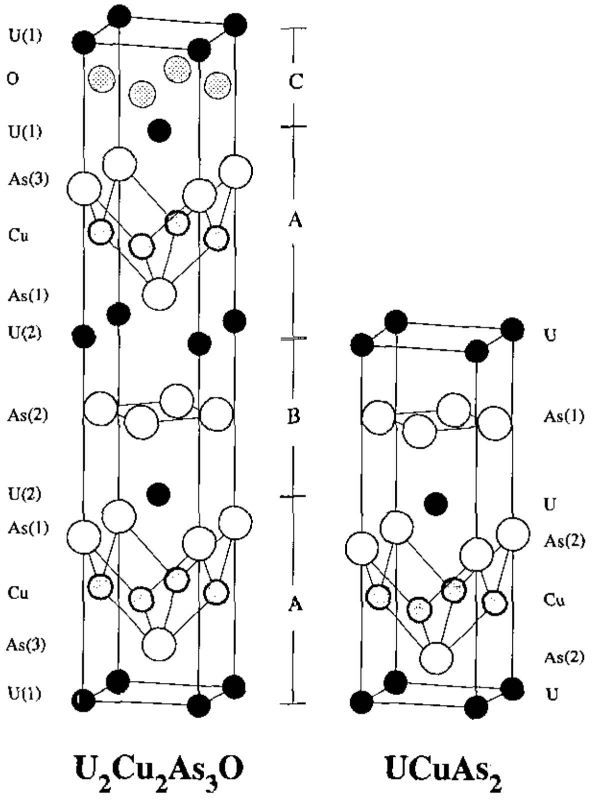

FIG. 1. Crystal structure of $U_2Cu_2As_3O$ (the origin was shifted by 0.75, 0.75, $-z_{U(1)}$). Thin solid lines show a pyramidal arrangement of the Cu, As(1), and As(3) atoms and a planar arrangement of the As(2) atoms. Characteristic blocks in the structure (see text) are denoted A, B and C. For comparison, the unit cell of $UCuAs_2$ is also shown (the origin was shifted by 0.75, 0.75, $-z_U$) in real proportion to that of $U_2Cu_2As_3O$.

the uranium–arsenic and uranium–oxygen spacings, one sees readily that they are close to the sum of the atomic radii of the U^{4+} and As^{3-} or O^{2-} ions (10). Thus, one expects mostly ionic bonding between these atoms. In contrast, a strong covalent character of the Cu–As(1) and Cu–As(3) bondings can be deduced from rather short distances between the copper and arsenic atoms. These covalent interactions yield the formation of characteristic pyramidal layers, built of transition metal and pnictogen atoms, which are typical for $UCuAs_2$ (see Fig. 1) but also for many other rare-earth and actinide ternary phases with ZrSiS- or $BaAl_4$-related structures (*11*). Another feature characteristic of these pnictides is a layer of pnictogen atoms coupled to each other by strong covalent intralayer interactions (11). Such a covalent bonding is seen, for example, in $UCuAs_2$ and $U_2Cu_4As_5$ and is anticipated to occur also in $U_2Cu_2As_3O$, where the As(2)–As(2) separation of 2.766 Å is much shorter than the sum of the atomic radii of the As^{3-} ions. This interaction leads to the reduction of the oxidation number of these arsenic atoms. Following the idea of Johnson and Jeitschko (12) of the formal charge compensation in ZrSiS–related compounds, we proposed previously (4) for $UCuAs_2$ the valence scheme $U^{4+}Cu^{+}[As(1)]^{2-}As(2)^{3-}$, where the brackets indicate the intralayer bonding between the arsenic atoms. According to the same simple model one may represent the new oxyarsenide by the formula $U(1)^{4+}U(2)^{4+}Cu^{+}Cu^{+}As(1)^{3-}[As(2)]^{2-}As(3)^{3-}$. However, in view of the aforementioned bonding between the copper and arsenic atoms, this compensation scheme should be taken as a first approximation only. Moreover, a semimetallic conductivity of $UCuAs_2$ (13) which seems likely also in $U_2Cu_2As_3O$ indicates unambiguously that the charge balance in these compounds is made also by the conduction electrons and the valence-band holes.

Finally, it is worth noting that $U_2Cu_2As_3O$ appears to be the first known example of a uranium oxyarsenide. To our best knowledge, to date only one actinide oxypnictide has been reported, namely $Th_4Fe_{17}P_{10}O$ (14), which crystallizes in monoclinic *C2/m* space group. On the other hand, a few compounds with the formula M_4X_2O (M = Ca,Sr,Ba; X = P,As,Sb,Bi) have recently been communicated (15) which crystallize with the tetragonal K_2NiF_4-type structure (space group *I4/mmm*). However, the oxygen atom in these latter phases exhibits an octahedral environment, in contrast to $U_2Cu_2As_3O$, where it is located in the center of a $U(1)_4$ tetrahedron. Moreover, the coordination spheres of the metal atoms in M_4X_2O are very different from the square antiprismatic surrounding of uranium in the present case.

Yet, considering the main crystallographic results obtained for $U_2Cu_2As_3O$, we think that another uranium–copper pnictide reported by us several years ago (16) and denoted $U_4Cu_4P_7$ may be in fact an oxyphosphide $U_2Cu_2P_3O$. A characteristic feature of the crystal structure of this compound was partial occupancy of the P(4) phosphorus atom sites (53%) and an anomalously short separation of only 2.336 Å between the U(2) and P(4) atoms (16). It appears that this latter distance is very close to the U(1)–O spacing in $U_2Cu_2As_3O$ (see Table 4), which strongly suggests that in that case also one is dealing with oxygen instead of a defected phosphorus sublattice. The electron density at the 4*d* position, yielding the 53% occupancy parameter for the P(4) atom, corresponds nicely to the full occupation of this site by oxygen. The unit cells of $U_2Cu_2As_3O$ and $U_4Cu_4P_7$ are very closely related and all the coordination polyhedra are essentially the same in both structures. Hence, we believe that the latter compound may also be a quaternary oxypnictide with the real composition $U_2Cu_2P_3O$.

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