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Letter

Crystal structure of the new ternary stannides U_2M_2Sn with $M\equiv Fe$ or Rh

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Abstract

New stannides U_2Fe_2Sn and U_2Rh_2Sn have been prepared and their crystal structures determined by X-ray diffractometry on single crystals. They crystallize in the tetragonal ordered version (*P4/mbm* space group) of the U_3Si_2-type structure with uranium and tin atoms occupying the corresponding U sites and transition element atoms (Fe or Rh) located at the Si sites. This structure has been solved by the heavy atom method with a residual factor R of 0.058 for U_2Fe_2Sn and of 0.039 for U_2Rh_2Sn. The lattice parameters are $a=7.296(1)$ Å and $c=3.446(1)$ Å for U_2Fe_2Sn and $a=7.525(1)$ Å and $c=3.624(1)$ Å for U_2Rh_2Sn.

During recent years, two families of ternary stannides UMSn and UM_2Sn ($M\equiv 3d$, 4d or 5d transition elements) have been intensively investigated due to their interesting physical properties, *e.g.* UNiSn is a "half-metallic" antiferromagnet and UPd_2Sn is a heavy electron system [1, 2]. We have been searching for new ternary stannides in the uranium–transition element–tin system. A new family of compounds U_2M_2Sn with $M\equiv$ Fe, Co, Ni, Ru, Rh, Pd, Ir or Pt have been prepared. In this paper we report the structural properties of U_2Fe_2Sn and U_2Rh_2Sn stannides.

All samples were prepared by melting stoichiometric amounts of the constituent elements in an induction levitation furnace under a purified argon atmosphere. The ingots obtained were annealed in evacuated quartz tubes at 800 °C for 2 weeks. Microprobe analysis performed on annealed samples confirms that U_2Fe_2Sn and U_2Rh_2Sn are obtained as a single phase.

Tiny single crystals of these stannides were isolated by mechanical fragmentation from the annealed samples. Investigation by X-ray photographic techniques reveals that they adopt a primitive tetragonal unit cell of the Laue group *4/mmm*. Systematic extinctions are observed for $0kl$ with $k\neq 2n$ leading to three possible space groups: *P4/mbm*, *P$\bar{4}$b2* or *P4bm*. The lattice parameters, obtained by least-squares refinement of Guinier X-ray (Cu Kα) powder data at room temperature using silicon as internal standard, are $a=7.296(1)$ Å and $c=3.446(1)$ Å for U_2Fe_2Sn and $a=7.525(1)$ Å and $c=3.624(1)$ Å for U_2Rh_2Sn.

The reflection intensities of the U_2Fe_2Sn single crystal were collected using graphite-monochromated Mo Kα radiation on an automatic diffractometer (CAD 4 Enraf-Nonius) in the θ–2θ scan mode. The intensities of 4332 reflections were measured in the reciprocal space corresponding to $-14\leqslant h\leqslant 14$, $-14\leqslant k\leqslant 14$ and $-6\leqslant l\leqslant 6$. After application of both Lorentz and polarization corrections, averaging of the symmetry equivalent reflections and application of a first absorption correction based on azimuthal scans of reflections spanning the θ range, these data lead to 394 reflections with $F_o^2>3\sigma(F_o^2)$ (F_o is the observed structure factor) and to an internal inconsistency index value $R_{INT}=(\Sigma_j\Sigma_i|F_{oi,j}-F_{oj}|)/\Sigma F_o=0.10$. The crystal structure of U_2Fe_2Sn was solved on the basis of the *P4/mbm* group by Patterson function deconvolution with the heavy atom method leading to the position of the U atoms. Sn and Fe sites were obtained by successive difference Fourier syntheses. With the isotropic model thus found, a second absorption correction was performed using the Walker and Stuart method [3] and the ABSORB program [4]. Using anisotropic thermal parameters for all atoms, a weighting scheme $\omega=1/\sigma^2(F_o)$ and an empirical isotropic extinction parameter, the final refinement converges to the residual conventional factors $R=0.058$ and $R_\omega=0.054$. All refinement calculations were performed using SHELX 76 [5]. The atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from the *International Tables for X-Ray Crystallography* [6]. The final positional parameters, equivalent isotropic factors and interatomic distances are given in Tables 1 and 2. The refinements performed in the *P$\bar{4}$b2* and *P4bm* space groups do not improve the R-factor significantly.

A similar investigation carried out on the U_2Rh_2Sn single crystal shows that this stannide is isotypic with U_2Fe_2Sn. In this case, the crystallographic data, listed in Tables 1 and 2 were obtained with the conventional factor values $R=0.039$ and $R_\omega=0.047$.

The U_2Fe_2Sn and U_2Rh_2Sn structures, shown in Fig. 1, consist of an association of infinite columns along the c axis which can be described as follows: (i) a $[U_6]$

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TABLE 1. Atomic coordinates and equivalent isotropic temperature factors for U_2Fe_2Sn and U_2Rh_2Sn (*P4/mbm* space group)

Stannide	Atom	Site	x	y	z	B_{eq} (Å^2)
U_2Fe_2Sn	U	4h	0.1696(1)	0.6696(1)	1/2	0.33(2)
	Fe	4g	0.3678(4)	0.8678(4)	0	0.64(8)
	Sn	2a	0	0	0	0.37(3)
U_2Rh_2Sn	U	4h	0.1725(1)	0.6725(1)	1/2	0.21(1)
	Rh	4g	0.3672(1)	0.8672(1)	0	0.48(2)
	Sn	2a	0	0	0	0.35(2)

TABLE 2. Interatomic distances up to 4 Å in U_2Fe_2Sn and U_2Rh_2Sn

U_2Fe_2Sn (Å)		U_2Rh_2Sn (Å)	
U–4U	3.832(1)	U–4U	3.939(1)
U–1U	3.500(2)	U–1U	3.671(1)
U–2U	3.446(1)	U–2U	3.624(1)
U–4Sn	3.211(1)	U–4Sn	3.323(1)
U–4Fe	2.809(3)	U–4Rh	2.941(1)
U–2Fe	2.674(3)	U–2Rh	2.753(1)
Sn–8U	3.211(1)	Sn–8U	3.323(1)
Sn–4Fe	2.852(2)	Sn–4Rh	2.938(1)
Fe–4U	2.809(3)	Rh–4U	2.941(1)
Fe–2U	2.674(3)	Rh–2U	2.753(1)
Fe–2Sn	2.852(2)	Rh–2Sn	2.938(1)
Fe–1Fe	2.727(8)	Rh–1Rh	2.826(3)

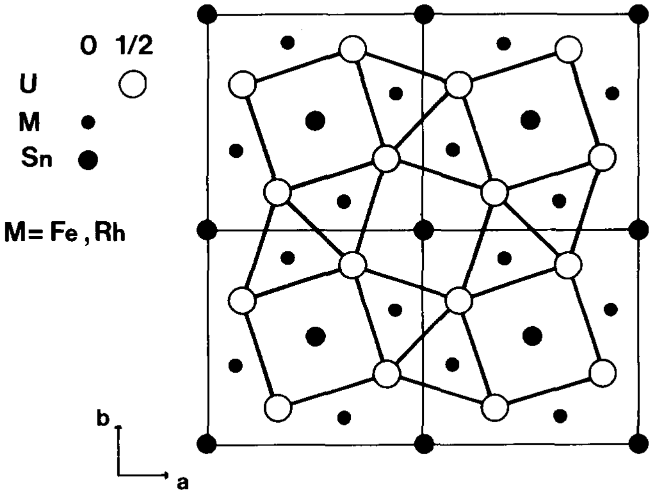

Fig. 1. Projection of the U_2Fe_2Sn and U_2Rh_2Sn structures onto the (*x*0*y*) plane, interpreted as an intergrowth of $[U_8]$ and $[U_6]$ prisms containing the tin and transition element atoms respectively.

trigonal prism formed by six uranium atoms surrounding an iron or rhodium atom; (ii) a $[U_8]$ parallelepiped prism containing the tin atom. This structure is an ordered ternary derivative of the U_3Si_2 type [7]. The two different uranium sites observed in U_3Si_2 are occupied by uranium and tin atoms in U_2Fe_2Sn and U_2Rh_2Sn, whereas the transition elements (Fe, Rh) are located at the silicon site. It should be noted that the $[U_6]$ trigonal prism also exists in the ternary equiatomic stannide UPdSn which crystallizes in an ordered $CaIn_2$-type structure [8].

Each uranium atom is surrounded by seven uranium atoms as nearest neighbours: five located in the same (a, b) plane and two along the c axis (Fig. 1). It should be noted that, in U_2Fe_2Sn, the U–U distance (3.446 Å) along the c axis is slightly smaller than Hill's critical distance of 3.5 Å, beyond which overlap between the U(5f) orbitals can occur leading to a non-magnetic ground state for uranium [9]. In contrast, in U_2Rh_2Sn, all U–U distances are larger than Hill's limit (Table 2). The coordination polyhedron around U can be described by a deformed pentagonal prism which consists of four tin and six transition element atoms. In these stannides, the tin atoms occupy a strongly deformed cuboctahedron formed by eight uranium and four M atoms. The interatomic distances between the central tin atom and the four transition element atoms, which are 2.852 Å and 2.938 Å for U_2Fe_2Sn and U_2Rh_2Sn respectively, are nearly equal to the sum of the metallic radii ($r_{Sn}+r_{Fe}=2.88$ Å and $r_{Sn}+r_{Rh}=2.96$ Å according to Taetum *et al.* [10]). The transition element is in a compressed $[U_6]$ trigonal prism, the height of which (measured here along the c axis) is smaller than the average edge length of its triangular prism base. The relative dimensions of the $[U_6]$ trigonal prism depend on the nature of the element located at the centre [11]. "Elongated" prisms are found for silicides or germanides, whereas "compressed" prisms are observed in compounds containing transition elements inside the prism. For U_2Fe_2Sn for instance, the height h and the average edge length l of the $[U_6]$ prism are 3.446 Å and 3.721 Å respectively leading to a ratio $h/l=0.93$ similar to that observed for binary compounds RE_3Pd_2 (RE ≡ Gd, Dy, Ho, Er) crystallizing in the tetragonal U_3Si_2-type structure [12].

The crystal structure determination of U_2Fe_2Sn and U_2Rh_2Sn shows that the U–U distances are strongly influenced by the nature of the transition element. In particular, some distances in U_2Fe_2Sn are smaller than Hill's critical distance. This may result in interesting physical properties for these new ternary stannides.

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