Investigation by ^{119}Sn Mössbauer spectroscopy, magnetic and electrical resistivity measurements of U_2M_2Sn stannides (M = Fe, Co, Ni, Ru, Rh, Pd)

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Abstract

New ternary stannides U_2M_2Sn with M = Fe, Co, Ni, Ru, Rh and Pd have been prepared. They crystallize in the tetragonal ordered version of the U_3Si_2-type structure (*P4/mbm* space group). A ^{119}Sn Mössbauer spectroscopy study at room temperature shows, the influence of the nature of the M transition element on the Sn environment in these compounds. Magnetic and electrical measurements reveal that U_2Ni_2Sn, U_2Rh_2Sn and U_2Pd_2Sn order antiferromagnetically at $T_N = 25(1)$, $25(1)$ and $42(1)$ K respectively.

1. Introduction

In the uranium-based intermetallic compounds $U_sM_tX_u$, where M is a transition element (3d, 4d or 5d) and X is an element such as silicon, germanium or tin, the magnetic behaviour of uranium is strongly influenced by the size and the number of d electrons of the M component. For instance, the members of the UM_2Si_2 family with M = Fe, Co, Ni or Cu, which crystallize in the tetragonal $ThCr_2Si_2$-type structure, exhibit a large variety of magnetic properties: UFe_2Si_2 is a Pauli paramagnet [1], UCo_2Si_2 orders antiferromagnetically below $T_N = 85$ K [1], whereas three and two magnetic transitions are observed below 123 and 107 K respectively for UNi_2Si_2 and UCu_2Si_2 [2, 3]. The absence of a magnetic moment for uranium in UFe_2Si_2 has been explained by the existence of short U–Fe distances which favour a strong hybridization between the U 5f and Fe 3d orbitals [1].

Recently we had reported the existence of the new U_2Fe_2Sn and U_2Rh_2Sn ternary stannides crystallizing in the tetragonal ordered version of the U_3Si_2-type structure [4]. This family has been extended by preparing the compounds with M = Co, Ni, Ru, Pd, Ir and Pt. In this paper their structural and physical properties are discussed, as determined by X-ray powder diffractometry, ^{119}Sn Mössbauer spectroscopy, magnetic and electrical resistivity measurements.

2. Experimental procedures

All the compounds have been prepared by direct melting of the elements in an induction levitation furnace under a purified argon atmosphere, followed by an annealing treatment under vacuum at 800 °C for one week. Microprobe analysis has been used to check both the homogeneity and the composition of the obtained materials, which have also been examined by conventional X-ray powder diffraction using a Guinier camera (Cu Kα). Their unit cell parameters have been determined by the least-squares refinement method with the use of silicon as an internal standard.

The ^{119}Sn Mössbauer measurements have been performed at room temperature using a $CaSnO_3$ source and a conventional constant-acceleration spectrometer. The isomer shift (IS) values are quoted relative to $CaSnO_3$. Magnetization measurements have been carried out between 4.2 and 300 K using both a pendulum susceptometer and a SQUID (superconducting quantum interference device) magnetometer. The electrical properties have been investigated above 4.2 K by resistivity measurements using a four-probe d.c. technique.

3. Results and discussion

The X-ray powder patterns of the U_2M_2Sn stannides with M = Co, Ni, Ru and Pd can be indexed with the tetragonal U_2Fe_2Sn- or U_2Rh_2Sn-type lattice [4]. A narrow range of homogeneity is detected for the

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$U_2Pd_{2+x}Sn_{1-x}$ compounds. The stannides U_2Ir_2Sn and U_2Pt_2Sn also exist, but their X-ray diffraction patterns show evidence of low intensity peaks that cannot be indexed with a simple structure of the U_2Fe_2Sn or U_2Rh_2Sn original cell. A structural study is now in progress on a U_2Pt_2Sn single crystal.

The projection of this structure on to the (a, b) plane is given in Fig. 1. It can be described as a stacking of two different prisms: (i) a $[U_8]$ tetragonal prism formed by eight uranium atoms surrounding the tin atom (Fig. 2(a)); (ii) a $[U_6]$ trigonal prism containing the M transition element atom (Fig. 2(b)). This type of structure can also be described as a stacking of atomic planes perpendicular to the c axis with the sequence (M, Sn)–U–(M, Sn)–U. These planes are located at $z=0$ and $z=\frac{1}{2}$ respectively.

For these ternary stannides the dependence of the unit cell parameters on the metallic radius r_M (taken from ref. 5) of the M element are given in Fig. 3 and Table 1. While the a parameter increases linearly with r_M, the c parameter decreases with increasing r_M for the stannides containing a 3d transition element but
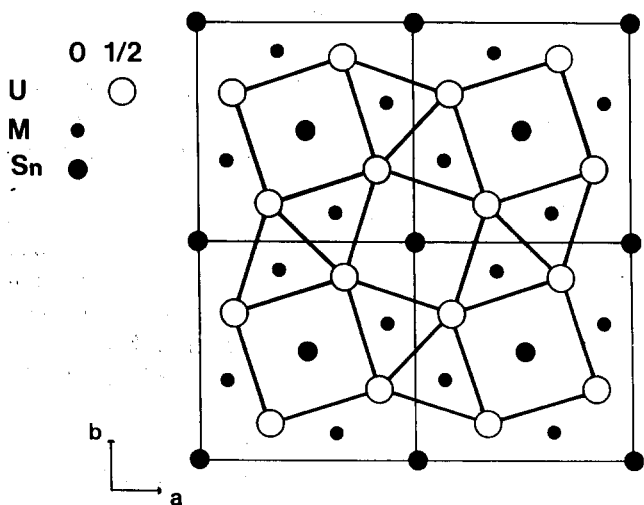

Fig. 3. Dependence of the unit cell parameters on the metallic radius of the M element in U_2M_2Sn.

Fig. 1. Projection of the U_2M_2Sn structure on to the $(x0y)$ plane.

(a) $[U_8]$ prism   (b) $[U_6]$ prism
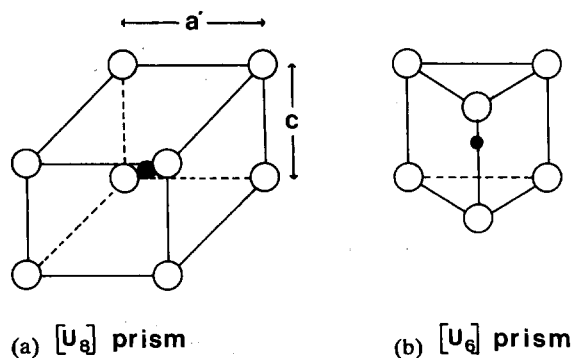
Fig. 2. U prisms surrounding (a) the tin atom and (b) the M transition element atom.
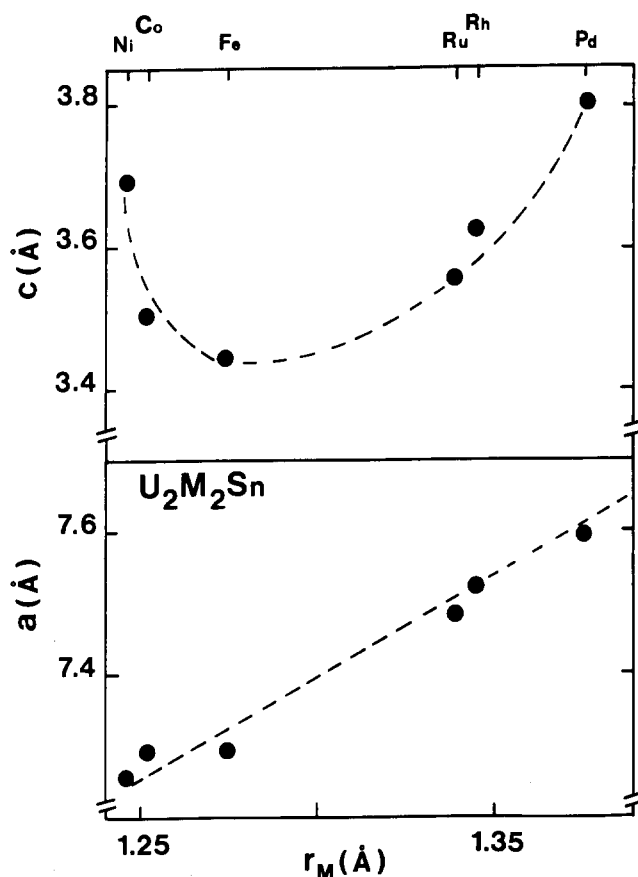
increases for the 4d-based compounds. The presence of a two-dimensional (M, Sn) sublattice perpendicular to the c axis readily explains the dependence of the a parameter. We note that the average distance d_{M-Sn} increases linearly with r_M and is always smaller than the sum of the metallic radii (e.g. for U_2Ni_2Sn $d_{Ni-Sn}=2.838$ Å and for U_2Pd_2Sn $d_{Pd-Sn}=2.966$ Å, whereas $r_{Ni}+r_{Sn}=2.869$ Å and $r_{Pd}+r_{Sn}=2.999$ Å (Fig. 4 and Table 1)). The fact that the c parameter and the unit cell volume decrease in the sequence $U_2Ni_2Sn \rightarrow U_2Co_2Sn \rightarrow U_2Fe_2Sn$ cannot be explained on the basis of steric considerations but suggests that electronic factors are responsible for this behaviour. As seen in Fig. 3 and 4, the c parameter and both the d_{U-Sn} and d_{U-M} average distances exhibit a similar variation as a function of r_M. Such a behaviour suggests a strong hybridization between the uranium 5f orbitals with those of the surrounding atoms, particularly for U_2Fe_2Sn. Similar behaviour has also been reported for the UM_2Si_2 ternary silicides with $M \equiv Fe$, Co and Ni [1]. It can also be seen from Fig. 4 that for all the compounds the d_{U-Sn} distance is always greater than the d_{U-M} distance owing to the smaller size of the M
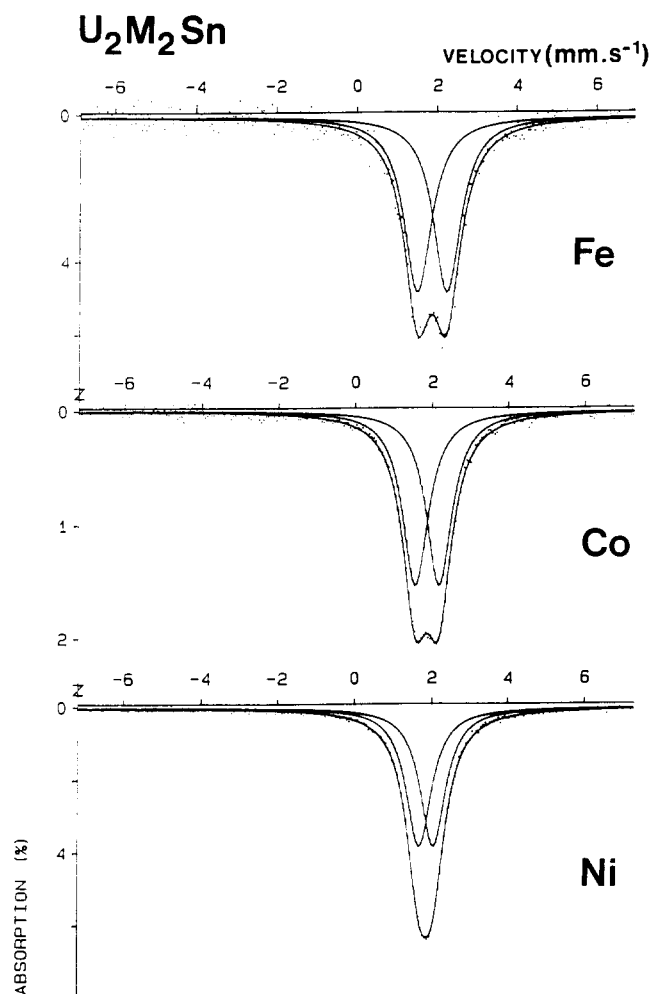
TABLE 1. Crystallographic data for the U_2M_2Sn stannides

Stannide	Unit cell parameters			Average distances (Å)			
	a (Å)	c (Å)	V (Å^3)	d_{U-Sn}	d_{U-M}	d_{M-Sn}	d_{U-U}
U_2Fe_2Sn	7.296(1)	3.446(1)	183.44	3.211	2.764	2.852	2.674
U_2Co_2Sn	7.297(1)	3.506(1)	186.68	3.228	2.783	2.852	3.692
U_2Ni_2Sn	7.261(1)	3.694(1)	194.76	3.269	2.838	2.838	3.732
U_2Ru_2Sn	7.486(2)	3.557(1)	199.33	3.293	2.848	2.923	3.777
U_2Rh_2Sn	7.525(1)	3.624(2)	205.21	3.323	2.878	2.938	3.811
U_2Pd_2Sn	7.595(2)	3.799(1)	219.14	3.393	2.950	2.966	3.887
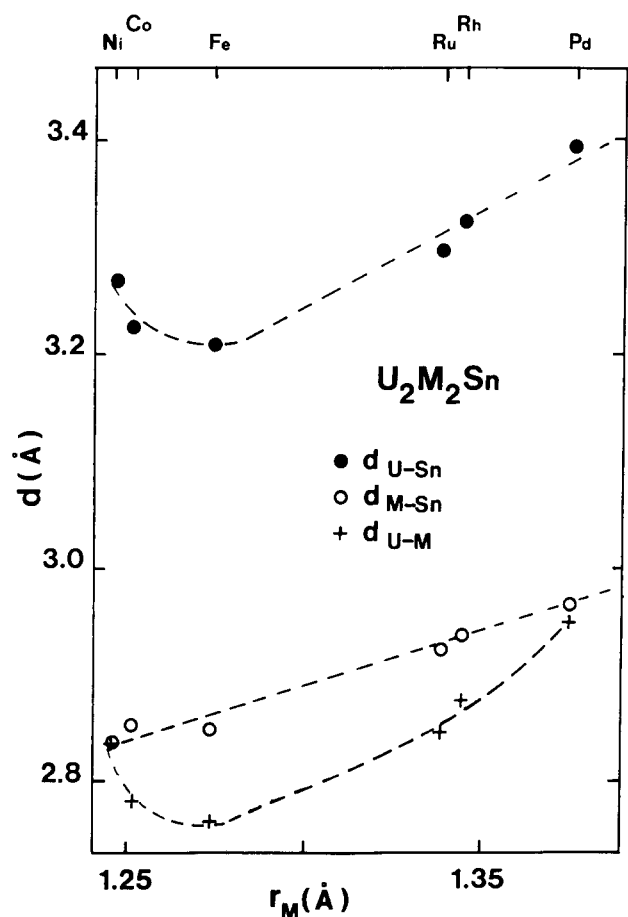
Fig. 4. Dependence of the average distances on the metallic radius of the M element in U_2M_2Sn.

Fig. 5. ^{119}Sn Mössbauer spectra for some U_2M_2Sn compounds at room temperature. The calculation fit is shown by the full curve.

element with respect to that of the tin atom $(r_{Sn} = 1.623$ Å).

In this type of structure each uranium atom has seven uranium nearest neighbours: five in the (a, b) plane and two along the c axis. In all the U_2M_2Sn compounds, the d_{U-U} average distance is greater than Hill's critical distance (about 3.50 Å), beyond which an overlap between the U 5f orbitals can occur, leading to a non-magnetic ground state for uranium [6]. However, it is noteworthy that in U_2Fe_2Sn the d_{U-U} distance along the c-axis (3.446(1) Å) is smaller than this critical distance [4].

The U_2M_2Sn stannides have been studied at room temperature by ^{119}Sn Mössbauer spectroscopy. The spectra have been fitted by one quadrupole doublet corresponding to one site for the tin atom (Fig. 5). The Mössbauer parameters derived from this procedure are given in Table 2. The isomer shift values are close to 2 mm s^{-1} and are comparable with those observed

TABLE 2. Crystallographic and Mössbauer data concerning the Sn environment in the U_2M_2Sn stannides

Stannide	[U_8] prism			Mössbauer data (mm s^{-1})		
	a' (Å)	c (Å)	c/a'	IS	QS	Γ
U_2Fe_2Sn	3.832	3.446	0.899	1.816(15)	0.736(15)	0.837(20)
U_2Co_2Sn	3.833	3.506	0.915	1.874(7)	0.619(7)	0.814(9)
U_2Ni_2Sn	3.814	3.694	0.969	1.859(5)	0.369(5)	0.807(7)
U_2Ru_2Sn	3.919	3.557	0.908	1.992(9)	0.746(9)	0.862(11)
U_2Rh_2Sn	3.939	3.624	0.920	1.935(9)	0.608(9)	0.773(12)
U_2Pd_2Sn	3.976	3.799	0.956	1.908(9)	0.452(9)	0.797(13)

for other ternary stannides such as UPdSn [7]. The experimental linewidth Γ determined at the half-maximum is close to 0.80(5) mm s^{-1} and no significant relationship between the Γ value and the nature of the M element can be deduced. All the spectra show a quadrupole splitting (QS) on account of the Sn located inside the [U_8] prism possessing a tetragonal point symmetry $4/mmm$. The QS value decreases in the sequences $U_2Fe_2Sn \rightarrow U_2Co_2Sn \rightarrow U_2Ni_2Sn$ and $U_2Ru_2Sn \rightarrow U_2Rh_2Sn \rightarrow U_2Pd_2Sn$ in accordance with the electric field gradient, which decreases as the [U_8] prism tends to cubic symmetry, *i.e.* as the c/a' ratio reaches unity (Fig. 2 and Table 2). For the determination of c/a', we have considered that the U_2M_2Sn stannides are isomorphous with U_2Fe_2Sn for M $\equiv$ Co and Ni and with U_2Rh_2Sn for M $\equiv$ Ru and Pd. A linear variation in QS $= f(c/a')$ is observed for these compounds (Fig. 6).

Figure 7 displays the temperature dependence of the reciprocal magnetic susceptibility for U_2Ni_2Sn, U_2Rh_2Sn and U_2Pd_2Sn between 4.2 and 300 K. For the three compounds the $\chi_m^{-1} = f(T)$ curve can be described

Fig. 7. Temperature dependence of the reciprocal magnetic susceptibility of U_2M_2Sn compounds with M $\equiv$ Ni, Rh and Pd (the arrow indicates the Néel temperature).

above 100 K by a Curie–Weiss law with an effective magnetic moment of $\mu_{eff} = 3.2, 3.0$ and 3.1 μ_B (U atom)$^{-1}$ for the Ni, Rh and Pd compounds respectively. These values are lower than that expected for the trivalent or tetravalent free uranium ion. For these stannides the $\chi_m^{-1} = f(T)$ curves exhibit a sharp minimum at low temperatures, which is typical for an antiferromagnet. The Néel transition temperature T_N, determined from the inflection point of the susceptibility curves, are equal to 25(1), 25(1) and 42(1) K for U_2Ni_2Sn, U_2Rh_2Sn and U_2Pd_2Sn respectively.

No magnetic ordering has been detected above 4.2 K for the stannides containing iron, cobalt and ruthenium, suggesting a strong hybridization of U 5f–ligand orbitals in these cases in comparison with the other U_2M_2Sn compounds.

The temperature dependence of the electrical resistivity of U_2Ni_2Sn, U_2Rh_2Sn and U_2Pd_2Sn shows an
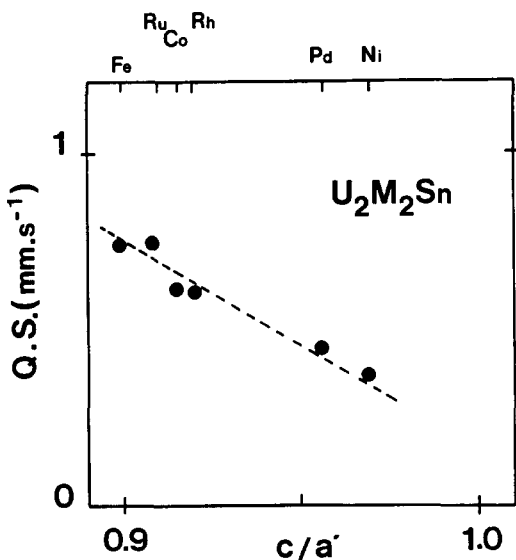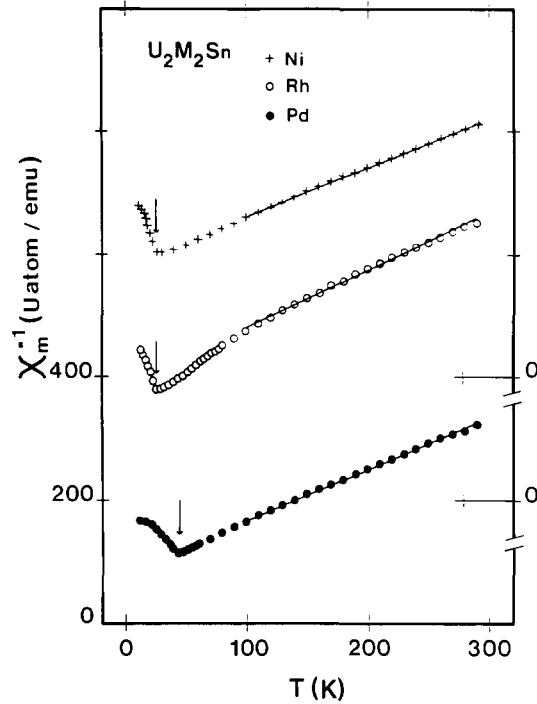

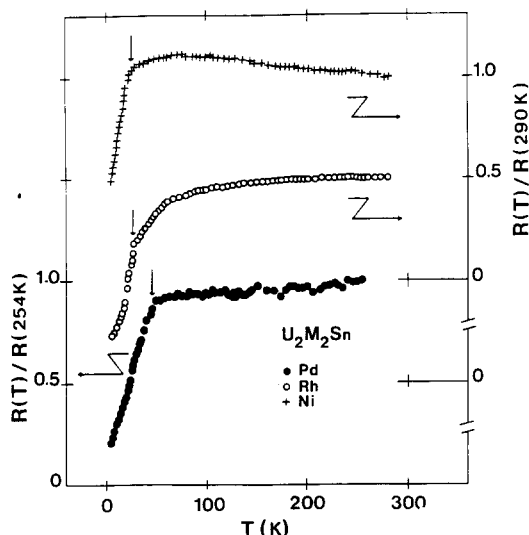Fig. 6. Dependence of the quadrupole splitting of tin in U_2M_2Sn on the c/a' ratio describing the [U_8] prism.

Fig. 8. Temperature dependence of the reduced electrical resistivity of U_2M_2Sn compounds with $M \equiv Ni$, Rh and Pd (the arrow indicates the Néel temperature).

abrupt decrease around the Néel temperature (Fig. 8). These anomalies can be ascribed to the decrease in the spin disorder resistivity resulting from the antiferromagnetic order. These compounds, referring to their $d\rho/dT$ coefficient, exhibit different behaviours above 60–70 K: $d\rho/dT$ is positive for U_2Rh_2Sn, whereas it is negative for U_2Ni_2Sn and constant for U_2Pd_2Sn. Above $T_N = 25(1)$ K the behaviour of U_2Rh_2Sn resembles in many respects that of antiferromagnets where the spin fluctuations are dominant: a pronounced increase in resistivity with temperature in the paramagnetic phase, followed by an approach to saturation at high temperatures [8]. The $\rho = f(T)$ curve for U_2Ni_2Sn shows a flat maximum at around 80 K as a result of the incoherent Kondo scattering of U ions in the presence of crystal field effects. A similar feature is observed for U_2Pd_2Sn.

4. Conclusions

We have prepared polycrystalline samples of the new ternary stannides U_2M_2Sn with $M \equiv Fe$, Co, Ni, Ru, Rh, Pd, Ir and Pt. Except for $M \equiv Ir$ and Pt, all the compounds crystallize in the tetragonal ordered version of the U_3Si_2-type structure. A relationship between the size of the [U_8] prism surrounding the tin atom and the quadrupole splitting determined at room temperature by ^{119}Sn Mössbauer spectroscopy has been established. Magnetic measurements show that U_2Ni_2Sn, U_2Rh_2Sn and U_2Pd_2Sn are antiferromagnetically ordered. Neutron diffraction experiments are now in progress in order to solve their magnetic structure.

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