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Magnetic ordering in the new ternary stannide $\text{U}_3\text{Rh}_4\text{Sn}_{13}$

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$\text{U}_3\text{Rh}_4\text{Sn}_{13}$ melts noncongruently and crystallizes in the cubic $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ -type structure with $a = 9.6416$ Å. Magnetic, electrical, specific heat measurements and a ^{119}Sn Mössbauer spectroscopy study reveal that this stannide undergoes a magnetic transition near 17.5 K. At low temperature, $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ shows an enhanced electronic specific heat coefficient ($\gamma_0 = 0.225$ J/K²U atom) as observed in magnetically ordered heavy fermions compounds. In addition below the magnetic transition temperature a broadening of the two quadrupole splitting of the Mössbauer spectrum indicates clearly the presence of a hyperfine field at the Sn sites. $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ exhibits a magnetic ordering temperature that is much higher than those already observed for similar stannides containing rare earths.

1. Introduction

The ternary rare earth silicides, germanides and stannides with formulae $\text{M}_3\text{T}_4\text{X}_{13}$ ($\text{M} = \text{Y}, \text{Sc}, \text{Ca}, \text{Sr}, \text{Th}$ or rare earth, $\text{T} = 3\text{d}, 4\text{d}$ or 5d transition element and $\text{X} = \text{Si}, \text{Ge}$ or Sn) have been shown to exhibit very exciting physical properties such as for instance superconductivity or interplay between magnetic ordering and superconductivity [1–4]. These compounds crystallize in the cubic $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ -type or in a derived structure depending on the size of both M and T atoms. For example, two different structures (I and I') have been found for the $\text{M}_3\text{Rh}_4\text{Sn}_{13}$ stannide series [5]. Phase I is cubic ($a_1 \approx 9.7$ Å) and exists only for $\text{M} = \text{Eu}, \text{Yb}, \text{Ca}, \text{Sr}$ and Th whereas the phase I' which is prepared only for $\text{M} = \text{La} \rightarrow \text{Gd}$ shows a tetragonal distortion of the phase I.

Recently we have reported the existence of the uranium-based ternary germanides $\text{U}_3\text{T}_4\text{Ge}_{13}$ with

$\text{T} = \text{Ru}, \text{Os}, \text{Rh}$ and Ir [6]. These compounds exhibit interesting physical properties, as for instance $\text{U}_3\text{Rh}_4\text{Ge}_{13}$ which orders antiferromagnetically at 22 K and shows a metamagnetic transition with a hysteresis phenomena at lower temperatures. We have attempted to extend this family by preparing the $\text{U}_3\text{T}_4\text{Sn}_{13}$ stannides. In this paper, are reported the structural and magnetic properties of $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ investigated by X-ray diffraction, magnetic and specific heat measurements and also by ^{119}Sn Mössbauer spectroscopy.

2. Experimental procedure

Stoichiometric $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ compound has been prepared by direct melting of the pure elements in an induction levitation furnace under a purified argon atmosphere. Then the sample has been annealed in a quartz tube at 800°C under vacuum for two weeks.

The resulting product has been characterized by X-ray powder diffraction using a Guinier camera ($\text{CuK}\alpha$ radiation) and its both composition and chemical homogeneity have been checked by

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microprobe analysis. The structure of $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ has been determined from X-ray powder diffraction data collected on a Philips PW 1050 diffractometer using a Bragg-Brentano geometry with a copper target and a take off angle of 6° . The powder diffraction patterns have been scanned in steps of 0.02° (2θ) from 17° to 110° with a constant counting time of 40 s.

Magnetization measurements have been carried out between 4.2 and 300 K using both a pendulum susceptometer and a SQUID magnetometer. The specific heat has been measured using a standard semiadiabatic heat-pulse method from 1.4 to 40 K. The ^{119}Sn Mössbauer measurements have been performed between 4.2 and 300 K using a CaSnO_3 source and a conventional constant acceleration spectrometer. The isomer shifts have been quoted relative to CaSnO_3 at room temperature.

3. Results and discussion

Both X-ray diffraction and microprobe analysis reveal that the melted and quenched sample corresponding to $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ stoichiometry is indeed a mixture containing USn_3 and URhSn as major components. But after annealing at 800°C , the obtained product is a single phase and its composition checked by microprobe analysis confirm the existence of the new ternary stannide $\text{U}_3\text{Rh}_4\text{Sn}_{13}$.

The X-ray powder pattern of $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ can be indexed on the basis of a primitive cubic unit

Table 1

Atomic positions and isotropic thermal agitation factors for $\text{U}_3\text{Rh}_4\text{Sn}_{13}$. The standard deviations are given in brackets

Atom	Site	Atomic position			B_{eq} ($\text{\AA}^2$)
		x	y	z	
U	6d	1/4	1/2	0	0.58(3)
Rh	8e	1/4	1/4	1/4	0.48(6)
Sn(1)	2a	0	0	0	2.73(15)
Sn(2)	24k	0	0.3081(2)	0.1527(2)	1.54(4)

cell ($a = 9.6416 \text{ \AA}$) corresponding to $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ -type structure [7]. The X-ray powder data have been analyzed by means of the Rietveld profile refinement method. The atomic positions determined from this procedure are given in table 1. After refinement the reliability factor R_1 has a value of 0.091.

It is worthwhile noting that so far no ternary stannide corresponding to the $\text{M}_3\text{Rh}_4\text{Sn}_{13}$ formulae has been prepared with rare earths (RE) having an atomic radius comparable to that of uranium. For example, with $\text{RE} = \text{Ho} \rightarrow \text{Lu}$ another ternary stannide $\text{SnRE}_4\text{Rh}_6\text{Sn}_{18}$ is characterized [5]. Thus the existence of the $\text{M}_3\text{Rh}_4\text{Sn}_{13}$ is strongly influenced by both the size and the oxydation state of the M element. The $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ -type structure is adopted only by ternary stannides containing divalent (Eu^{2+} , Yb^{2+} , Ca^{2+} or Sr^{2+}) or tetravalent (Th^{4+}) M elements. This result suggests that the valence of uranium could be different from three in $\text{U}_3\text{Rh}_4\text{Sn}_{13}$.

In the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ -type structure, the tin atoms occupy two different crystallographic sites

Table 2

Selected interatomic distances in USn_3 , URh_3 , URhSn and $\text{U}_3\text{Rh}_4\text{Sn}_{13}$

Compound	Structure type	Distance ($\text{\AA}$)			Ref.
		U-U	U-Rh	U-Sn	
$\text{U}_3\text{Rh}_4\text{Sn}_{13}$	$\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$	4.821	3.409×4	U-Sn(1) 5.390×6	U-Sn(2) 3.376×8 3.395×4 a)
USn_3	AuCu_3	4.626		3.271	[8]
URh_3	AuCu_3	3.991	2.822		[8]
URhSn	Fe_2P	3.832	3.071×1 2.980×4	3.134×2 3.343×4	[9]

a) This work.

(table 1). The Rh atoms are situated inside trigonal prisms formed by six Sn(2) atoms [7]. The $\text{RhSn}_6(2)$ prisms, share corners, to form a three-dimensional network, which generates icosahedral and cubooctahedral sites containing respectively Sn(1) and Yb or U atoms. The large U-U interatomic distances in $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ ($d_{\text{U-U}} = 4.821 \text{ \AA}$) are far above the Hill's limit ($3.50 \text{ \AA}$) below which the uranium 5f orbitals of neighbouring sites can overlap (table 2). The U-Sn(2) distances which are shorter than the U-Sn(1) ones, are nevertheless larger than those observed in USn_3 (table 2). [8]. In the same way, the U-Rh distances in $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ stannide are much larger than those existing in URh_3 . The strength of the hybridization between the 5f orbitals and the electronic states of the ligand (Rh or Sn) must be reduced in $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ in comparison with that observed in both USn_3 and URh_3 for which no magnetic order is detected: URh_3 shows a Pauli paramagnetism behaviour whereas USn_3 is a highly enhanced paramagnet. On the other hand, the average distances $\overline{\text{U-Sn}}$ and $\overline{\text{U-Rh}}$ observed in $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ are greater than those determined in URhSn which orders ferromagnetically at low temperature [9].

The magnetic susceptibility χ_m of $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ has been analyzed between 20 K and room temperature on the basis of a modified Curie-Weiss law (fig. 1):

$$\chi_m = \chi_0 + C_m / (T - \Theta_p),$$

where χ_0 is a temperature independent term, C_m the Curie constant and Θ_p the paramagnetic Curie temperature. The values of $C_m = 2.123 \text{ emu/mol}$, $\Theta_p = +1.8 \text{ K}$ and $\chi_0 = 3.329 \times 10^{-3} \text{ emu/mol}$ have been deduced from the susceptibility measurements by a least squares method. The effective magnetic moment ($\mu_{\text{eff}} = 2.38 \mu_B/\text{U atom}$) is close to that both calculated for uranium in the $5f^1$ state and reported for USn_3 ($\mu_{\text{eff}} = 2.4 \mu_B/\text{U atom}$) [10]. A peak observed in the thermal dependence of the magnetization curve of $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ centered at around 18 K, suggests the occurrence of an antiferromagnetic ordering (fig. 2).

In the temperature range from 150 to 270 K, the electrical resistivity of $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ weakly

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility of $\text{U}_3\text{Rh}_4\text{Sn}_{13}$.

varies by showing a slight increase with decreasing temperature (fig. 3). Then the resistivity begins to decrease from about 150 K, showing a

Fig. 2. Temperature dependence below 30 K of the magnetization for $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ in two different applied fields.

Fig. 3. Temperature dependence of the electrical resistivity normalized at 270 K for $\text{U}_3\text{Rh}_4\text{Sn}_{13}$. Arrows ($\downarrow$) indicate: the magnetic transition temperature.

shoulder centered around 18–22 K, and finally decreases very rapidly below 18 K. The occurrence of such a behaviour in the thermal dependence of the resistivity is typical of a Kondo effect in the presence of a crystal field splitting in the 5f (or 4f) systems [11]. Thus the broad maximum which appears near 150 K results from the crystalline field effect and the peak which occurs at 18 K is the signature of the magnetic ordering.

Specific heat measurements performed in the 1.4–25 K range are shown in fig. 4. The magnetic transition is discerned through a small, but dis-

Fig. 4. Temperature dependence of the specific heat for $\text{U}_3\text{Rh}_4\text{Sn}_{13}$. Inset: $\Delta C/T$ jump observed at the magnetic transition temperature.

Fig. 5. C/T versus temperature for $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ above ($T > 20$ K) and below its magnetic transition temperature ($T < 5.5$ K).

tinct anomaly which peaks at ≈ 17.5 K in agreement with magnetic and electrical results. The behaviour in the temperature region above the transition is illustrated in fig. 5 by a C/T vs. T^2 representation. Extrapolation of the apparently simple $\gamma_p T + \beta_p T^3$ behaviour yields a large linear term $\gamma_p = 0.75 \text{ J/K}^2 \text{ U atom}$ with $\beta_p = 3.225 \times 10^{-3} \text{ J/K}^4 \text{ mol}$. In the magnetically ordered state, below about 5 K (fig. 5), the experimental data are again consistent with a temperature dependence given by $\gamma_0 T + \beta_0 T^3$, with an extrapolated γ_0 value of $0.225 \text{ J/K}^2 \text{ U atom}$ and a large β_0 value of $1.875 \times 10^{-2} \text{ J/K}^4 \text{ mol}$. The γ_0 value appears as remarkably enhanced like in magnetically ordered heavy-fermion systems as for instance UCd_{11} ($\gamma_0 = 0.250 \text{ J/K}^2 \text{ U atom}$) which orders antiferromagnetically below 5 K [12]. Furthermore we can note that at low temperatures, at least in the explored T -range, the specific heat varies as T^3 which is the form expected for antiferromagnetic magnons. In the inset of the fig. 4, we have plotted the ratio of the contribution excess ΔC (obtained by subtracting the cubic βT^3 term corresponding to $T > 20$ K) over the temperature. The relative discontinuity at the phase transition $\Delta C/T_m$ amounts to $0.14 \text{ J/K}^2 \text{ U atom}$ which corresponds to a jump $\Delta C/(\gamma_p - \gamma_0)T_m$ of only ≈ 0.26 . This small value points towards reduced magnetic moments and also suggests that some heavy electrons survive in the magnetic state. In this view, the part of the Fermi

Fig. 6. ^{119}Sn Mössbauer spectra for $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ at various temperatures.

surface removed by the magnetic ordering may be estimated as $\approx 70\%$ from the fractional change in the temperature linear terms, $(\gamma_p - \gamma_0)/\gamma_p$, a value of the same order magnitude as that observed in other known magnetically ordered heavy-fermion systems [11].

The ^{119}Sn Mössbauer spectrum of $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ measured at various temperatures are shown in fig. 6. At room temperature, this spectrum has been fitted by two quadrupole doublets corresponding to Sn in 2a (Sn(1)) and 24k (Sn(2)) sites. The assignment of the doublets to the crystallographic sites has been done with respect to their relative intensities. The values of the isomer shift (IS) and of the quadrupole splitting (QS) derived from this procedure indicate a large chemical

difference between the two Sn sites. The IS values are (2.55 ± 0.07) and $(2.09 \pm 0.02) \text{ mm s}^{-1}$ and the QS ones are (0.61 ± 0.07) and $(1.34 \pm 0.02) \text{ mm s}^{-1}$ for Sn(1) and Sn(2) respectively. The fact that the quadrupole splitting parameter of the Sn(1) atom is smaller than that observed for the Sn(2) one indicates a decrease of the electrical field gradient at the Sn(1) site. This result is in agreement with the fact that the U-Sn(1) average distance is greater than the U-Sn(2) one (table 2). Also, it is worth noting that the IS value for the Sn(1) site is greater than that observed for the Sn(2) site, thus showing an increase in the s electron density at the Sn(1) Mössbauer nuclei. Below 18 K, the spectrum shows a clear broadening due to a magnetic hyperfine field which confirms the occurrence of a magnetic ordering in $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ (fig. 6). The spectrum at $T = 4.2 \text{ K}$ exhibits a small hyperfine field splitting implying that the Sn atoms see a small magnetic moment localized on uranium site. A detailed investigation of our ^{119}Sn Mössbauer study will be published soon.

4. Conclusion

The present results indicate that the $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ compound orders magnetically around 17.5–18 K. From the specific heat measurements as well as Mössbauer spectroscopy the magnetic moment must be small. This allows us to propose $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ as a magnetically ordered heavy-fermion system in which the magnetic properties can be qualitatively understood within the framework of a competition between the Kondo spin fluctuation and the oscillatory magnetic RKKY interaction [11]. On the other hand, we must mention that the magnetic ordering temperature of $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ is greater than that determined for the isomorphous $\text{Gd}_3\text{Rh}_4\text{Sn}_{13}$ compound which orders magnetically at $T_m = 11.2 \text{ K}$ [4]. This observation which cannot be explained from simple De Gennes factor considerations shows that the magnetic interactions in $\text{U}_3\text{Rh}_4\text{Sn}_{13}$ are not only RKKY type. This behaviour could be due to an unusually strong 5f-conduction electrons hybridization.

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