STRUCTURAL AND MAGNETIC PROPERTIES OF THE $U_3M_4Ge_{13}$ ($M = Ru, Os, Rh, Ir$) TERNARY GERMANIDES

B. Lloret, B. Chevalier, P. Gravereau, B. Darriet and J. Etourneau

Laboratoire de Chimie du Solide du CNRS, 351 cours de la Libération, 33405 Talence Cedex, France

Abstract. – $U_3M_4Ge_{13}$ and $U_3Os_4Ge_{13}$ germanides crystallize in a superstructure of the cubic $Yb_3Rh_4Sn_{13}$ -type structure and exhibit no magnetic order above 4.2 K. On the contrary, $U_3Ir_4Ge_{13}$ orders ferromagnetically near $T_c \simeq 15$ -17 K whereas $U_3Rh_4Ge_{13}$ orders antiferromagnetically at 22 K.

In the last years, many ternary stannides, germanides and silicides with formulae $RE_3M_4X_{13}$ ($RE =$ rare earth, $M = Ru, Os, Rh, Ir$ and $X = Si, Ge, Sn$) were prepared [1, 2, 3]. These compounds crystallize in the cubic $Yb_3Rh_4Sn_{13}$ -type (space group $Pm\bar{3}n$) or in derived structure [4]. Some of these materials have remarkable superconducting properties.

Recently, it was established that URu_2Si_2 shows both a magnetic phase transition at 17.5 K and a superconducting transition at 0.8 K [5]. These interesting results have stimulated us to investigate other new uranium ternary compounds. We report here the structural, magnetic and electrical properties of the new ternary germanides $U_3M_4Ge_{13}$ with $M = Ru, Os, Rh, Ir$.

All samples were prepared by melting stoichiometric amounts of the binary germanide UGe_3 , noble metals Ru, Os, Rh, Ir and germanium. The resulting ingots were annealed in evacuated quartz tubes at 850 °C for two weeks. The samples were characterized by X-ray diffraction and microprobe analysis.

X-ray powder diffraction shows that the $U_3Ru_4Ge_{13}$ and $U_3Os_4Ge_{13}$ germanides crystallize in the cubic $Yb_3Rh_4Sn_{13}$ -type structure. The lattice parameter (a) is respectively equal to 8.939 Å for $M = Ru$ and to 8.949 Å for $M = Os$. However a crystal study performed by Weissenberg and precession photographs on the $U_3Os_4Ge_{13}$ compound reveals a modification of the primitive cubic structure. Splitting of the diffraction spots, well seen at high θ values on Weissenberg films for the three axis, could be explained by a small tetragonal distortion of the lattice and twinning of the crystal. In the family of ternary stannides, $Gd_3Rh_4Sn_{13}$ crystallizes in a tetragonal cell with $a' \sim a\sqrt{2}$ and $c' \sim a$ [4]. As the difference between $a' / \sqrt{2}$ and c' is very small, twin formation has to be expected in this tetragonal phase. In the $Yb_3Rh_4Sn_{13}$ -type or in the derived structure, the Ru and Os atoms occupy the trigonal prism formed by six $Ge(2)$ atoms. The $RuGe_6$ or $OsGe_6$ prisms, share corners, to form a three-dimensional network, which generates icosahedral and cubooctahedral sites which are occupied by the $Ge(1)$ and U atoms. In these ternary germanides,

the U - U distance ($\simeq 4.47$ Å) is greater than the critical value of 3.4-3.6 Å known as the Hill limit [6]. Due to the decrease of the 5f-wave functions overlap, the U atoms bear a stable magnetic moment.

Above 300 K, the thermal variation of the reciprocal susceptibility χ_m^{-1} of $U_3Ru_4Ge_{13}$ and $U_3Os_4Ge_{13}$ can be fitted to a linear Curie-Weiss law with an effective magnetic moment of $2.86 \mu_B / U$ atom for $M = Ru$ and $3.24 \mu_B / U$ atom for $M = Os$. Above 4.2 K, no magnetic order has been detected for $U_3Os_4Ge_{13}$ compound. Below 6-8 K, χ_m tends to saturate for $U_3Ru_4Ge_{13}$ and the thermal variation of the electrical resistivity exhibits a minimum around $T = 10$ -20 K and then increases at lower temperature. These results suggest a Kondo-like behaviour for $U_3Ru_4Ge_{13}$.

The X-ray powder patterns of $U_3Rh_4Ge_{13}$ and $U_3Ir_4Ge_{13}$ show that these germanides adopt a derived structure of $Yb_3Rh_4Sn_{13}$ -type. Some diffraction lines corresponding to the $Pm\bar{3}n$ space group are split including the (222) one, and so a simple tetragonal distortion is excluded. So far, the crystal structure of these two germanides is unknown.

The magnetic susceptibility of $U_3Ir_4Ge_{13}$ follows a Curie-Weiss like dependence in the temperature range $300 K < T < 500 K$ with $\mu_{eff.} = 2.92 \mu_B / U$. This compound orders ferromagnetically near 15-17 K.

The thermal variation of the reciprocal magnetic susceptibility of $U_3Rh_4Ge_{13}$ (Fig. 1) shows a Curie-Weiss behaviour above 250 K with $\mu_{eff.} = 2.96 \mu_B / U$ and $\theta_p = -70 K$. The thermal dependence of the magnetic susceptibility reveals a maximum at 22 K suggesting an antiferromagnetic ordering of the U atoms (Fig. 1). The magnetization curves of $U_3Rh_4Ge_{13}$ observed at $T = 2 K$ and 6 K in fields up to 6 T are displayed in figure 2. A rapid change of the magnetization between 3 and 4 T resembling a metamagnetic transition is observed at 6 K with a hysteresis phenomena. At 2 K, two jumps in the magnetization curve are clearly visible. In addition, the electrical resistivity of $U_3Rh_4Ge_{13}$ decreases at 1.7-1.8 K showing a zero-resistance value close to 1.5 K. The occurrence of this anomaly which depends on the sample preparation could be due to the onset of a superconducting

Fig. 1. - Reciprocal magnetic susceptibility of $\text{U}_3\text{Rh}_4\text{Ge}_{13}$ vs. temperature. Inset: magnetic susceptibility dependence for $4.2 \text{ K} < T < 40 \text{ K}$.

transition. A single crystal study is necessary in order to confirm if this transition is intrinsic or due to small amounts of precipitates not detected by X-rays.

- [1] Espinosa, G. P., Cooper, A. S. and Barz, H., *Mater. Res. Bull.* **17** (1982) 963.
- [2] Venturini, G., Meot-Mayer, M., Malaman, B. and Roques, B., *J. Less-Comm. Met.* **113** (1985) 197.

Fig. 2. - Magnetization curves of $\text{U}_3\text{Rh}_4\text{Ge}_{13}$ versus applied field at 2 K and 6 K.

- [3] Lloret, B., Chevalier, B., Lejay, P. and Etourneau, J., *C.R. Hebd. Séan. Acad. Sci. Paris* **303II** (1986) 1193.
- [4] Miraglia, S., Hodeau, J. L., Marezio, M., Lavi-ron, C., Ghedira, M. and Espinosa, G. P., *J. Solid State Chem.* **63** (1986) 358.
- [5] Palstra, T. T. M., Menovsky, A. A., van den Berg, J., Dirkmaat, A. J., Kes, P. H., Nieuwenhuys, G. J. and Mydosh, J. A., *Phys. Rev. Lett.* **55** (1985) 2727.
- [6] Hill, H. H., plutonium and other actinides, Ed. W. N. Miner (Aime, New York) 1970, p. 2.