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Structural study of $UCuGe_{1.75}$ by X-ray and electron diffraction

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Abstract

The new ternary germanide $UCuGe_{1.75}$ have been isolated. After annealing treatment (under vacuum at 1073 K for 1 month), microprobe chemical analysis and X-ray powder diffraction revealed the presence of several phases: major phase corresponds to $UCuGe_{1.75(5)}$ and traces of UGe_2 and UCu_2Ge_2 were present as impurities phases. The refinement of the crystal structure was performed using a single crystal. It crystallises in orthorhombic system with $a=0.4052(3)$ nm, $b=1.697(1)$ nm and $c=0.4058(1)$ nm. The structure of $UCuGe_{1.75}$ corresponds to the $TbFeSi_2$ structural type. An investigation by transmission electron microscopy (TEM) revealed a substructure $2a\times2b\times2c$ which has been explained by a three-dimensional order of vacancies corresponding to the germanium deficit. Moreover the electrical resistivity and magnetization measurements performed on $UCuGe_{1.75}$ revealed the occurrence of antiferromagnetic ordering below $T_N=133(1)$ K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Uranium; Ternary germanide; TEM investigation; Antiferromagnetism

1. Introduction

Three intermetallic ternary germanides were reported to exist in the U–Cu–Ge system: UCuGe [1], UCu_2Ge_2 [2] and $U_3Cu_4Ge_4$ [3,4]. All these compounds exhibit interesting magnetic properties; UCu_2Ge_2 and $U_3Cu_4Ge_4$ are ferromagnets below $T_C=110$ and 71 K, respectively whereas UCuGe orders antiferromagnetically below $T_N=$ 50 K. During the investigation of this system, we have isolated the new ternary germanide $UCuGe_{1.75}$. We report here on its structural, electrical and magnetic properties investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), resistivity and magnetization measurements.

2. Experimental details

Three samples having different nominal compositions close to the formulae $UCuGe_{1.75}$ were synthesized by direct melting of the pure elements in an induction levitation furnace under purified argon atmosphere. Then they were annealed in quartz tubes under vacuum at 1073 K for 1 month.

The samples were systematically checked by X-ray powder diffraction (Cu Kα radiation; Guinier camera) and electron microprobe (Cameca SX-100 instrument). The latter analysis was based on the intensity measurements of U $M\alpha_1$, Cu $K\alpha_1$ and Ge $K\alpha_1$ X-ray emission lines, which were compared with those obtained for UCu_2Ge_2 used as a reference. The crystal X-ray diffraction data were recorded on an Enraf-Nonius CAD-4 four circle diffractometer (Mo Kα radiation; graphite monochromator; scintillation counter with pulse height discrimination). The examination by transmission electron microscopy were performed using a JEOL 2000FX apparatus.

Magnetization measurements were performed in the temperature range 5–350 K and in applied magnetic fields up to 4 T using a superconducting quantum interference device (SQUID) magnetometer. Electrical resistivity measurements were carried out between 4.2 and 300 K using a standard four probe DC-technique.

3. Results and discussion

3.1. Microprobe analysis

The three samples were checked by electron microprobe. All contain, as main component, the ternary germanide $UCuGe_{\cong 1.75}$ (Table 1). Our results show that it is difficult to obtain this germanide as single phase; parasitic phases as UCu_2Ge_2, 'U_2CuGe_3' and UGe_2 are always

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Table 1
Microprobe analysis of three samples around $UCuGe_{1.75}$ composition

Sample (*n*)	Nominal composition	Microprobe analysis	
		Main phase	Parasitic phases
1	4U + 4Cu + 7Ge	$UCuGe_{1.75(5)}$	UCu_2Ge_2, UGe_2
2	2.8U + 2.4Cu + 4.8Ge	$UCuGe_{1.69(3)}$	U_2CuGe_3, UGe_2
3	1U + 1Cu + 2Ge	$UCuGe_{1.67(2)}$	UCu_2Ge_2, U_2CuGe_3

present. The best sample, sample n°1, corresponds to the nominal composition (4U+4Cu+7Ge), containing the ternary germanide $UCuGe_{1.75(5)}$ with less than 1–2% in mass of UCu_2Ge_2 and UGe_2.

3.2. Single-crystal X-ray diffraction

The examination of the X-ray powder diffraction pattern of sample number 1 indicates: (i) that the major peaks ($UCuGe_{1.75}$ phase) can be indexed on the basis of an orthorhombic unit cell with $a=0.4052(3)$ nm; $b=1.6917(1)$ nm and $c=0.4058(1)$ nm as lattice parameters; (ii) the presence of tetragonal UCu_2Ge_2 [2] and orthorhombic UGe_2 [5] as impurity phases in agreement with the results obtained by microprobe analysis (Table 1). The formula of this new ternary germanide and its unit cell present some analogies with the ternary silicides $UMSi_2$ (M=Fe, Co, Ni, Pt) [6–8] crystallizing with the orthorhombic $CeNiSi_2$-type structure (space group *Cmcm*).

The structural properties of $UCuGe_{1.75}$ were determined from X-ray diffraction carried out on a single crystal. Buerger and Weissenberg diagrams confirm the orthorhombic symmetry and the only systematic extinction (*hkl* observed with $h+k=2n$) present corresponds to a C-centred lattice. The space group of $UCuGe_{1.75}$ is *Cmcm*.

This single crystal was then mounted on an automatic four circle diffractometer. After Lorentz-polarisation and absorption corrections 573 independent reflections in the reciprocal space corresponding to $-8\leq h\leq 8$, $0\leq k\leq 33$, and $0\leq l\leq 8$ with $|F_o|^2>4\sigma\ |F_o|^2$ were measured and kept for the refinement. These data collected using Mo Kα radiation lead to an internal inconsistency index value $R_{int}=0.102$. The values of the lattice constants obtained on the four-circle diffractometer are in good agreement with the powder data. Starting from the hypothesis of a $CeNiSi_2$-type structure, the structure of the present germanide was refined using the SHELX 76 PROGRAM [9].The best result was obtained for the atomic parameters given in Table 2. The conventional residual factor obtained at the final refinement cycle performed with ellipsoidal temperature factors applied to all atoms is 0.079 for 17 variable

Table 2
Atomic parameters of $UCuGe_{1.75}$ (equivalent isotropic thermal parameters B_{eq} given in units of 10^{-2} nm^2)

Atom	Site	Positional parameters			Occupancy	$U_{11}\times10^3$	$U_{22}\times10^3$	$U_{33}\times10^3$	B_{eq}
		x	*y*	*z*					
U	4*c*	0	0.3951(1)	1/4	1	5.84	5.50	5.59	0.45(2)
Cu	4*c*	0	0.7493(2)	1/4	1	12.31	8.65	10.06	0.82(5)
Ge1	4*c*	0	0.0283(4)	1/4	0.77(3)	15.50	12.09	58.09	2.3(2)
Ge2	4*c*	0	0.1690(2)	1/4	1	6.92	21.90	6.14	0.92(4)

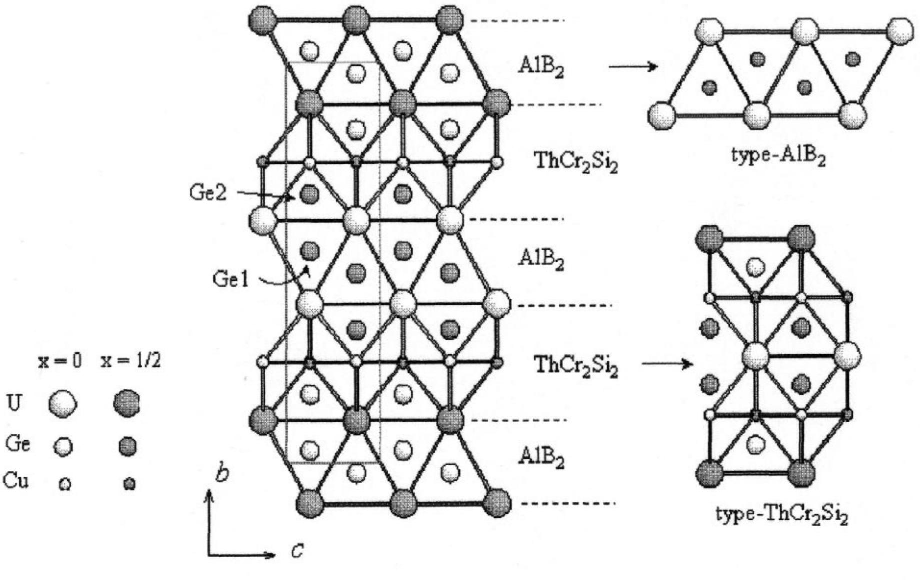

Fig. 1. Crystal structure of $UCuGe_{1.75}$.

parameters. This result leads us to make several comments: (i) we did not be able to get for this phase a single crystal of good quality. In addition the sizes of single crystals founded in our preparation are always very small; (ii) because that uranium atoms are present in this phase the phenomenon of absorption is very important; (iii) the germanium atom Ge1 situated in the site 4*c* partially occupied has a very high value for the anisotropic temperature factor. The equivalent isotropic thermal parameter calculated is $2.3(2)\times10^{-2}$ nm^2. The high value of the composant U_{33} means that the Ge1 atom ($z=1/4$ fixed) reveals a tendency to be delocalisated along the *z*-axis; (iv) the composition $UCuGe_{1.77(3)}$ get by refinement of the structure is very close to that determined by electron micropobe analysis ($UCuGe_{1.75(5)}$).

The structure of $UCuGe_{1.75}$ corresponds to the $TbFeSi_2$ structural type. The latter is closely related to $CeNiSi_2$-type structure by an exchange between the positions occupy by transition metal (Ni,Fe) and that of silicium. The structure of $UCuGe_{1.75}$ can be seen along *b*-axis as a stacking alternated of two arrays of AlB_2 and $ThCr_2Si_2$ type: AlB_2–$ThCr_2Si_2$–AlB_2–$ThCr_2Si_2$–... The site of germanium partially occupied is situated at the centre of a prism $[U_6]$ trigonal prism of AlB_2 type. A projection of the structure along [100] axis is given in Fig. 1. The interatomic distances are listed in Table 3.

3.3. TEM investigation

To get some more structural information an investigation by transition electron microscopy was carried out. Selected-area electron diffraction (SAED) patterns exhibit a lattice of main spots which indexes with the lattice parameters of the unit cell determined by X-ray diffraction. In addition these SAED patterns reveal a second lattice of weak reflections which correspond to a superstructure $2a\times2b\times2c$. Any superstructure reflections corresponding to this superstructure have been seen in the X-ray powder diffraction pattern. For example, the SAED pattern of the [−110] zone direction is shown in Fig. 2. This superstructure could be explained by a three-dimensional order of vacancies corresponding to the germanium deficit in his crystallographic position, a phenomenon similar to that observed before in the silicides YSi_{2-x}, $ErSi_{2-x}$ and Er_3Si_5 [10].

Table 3
Interatomic distances in the structure of $UCuGe_{1.75}$ (standard deviations are all less than or equal 3×10^{-4} nm)

Interatomic distances (nm)		
U–2U 0.4052	Cu–4Cu 0.2868	Ge1–2Ge1 0.2246
–2U 0.4058	–2Ge2 0.2442	–1Ge2 0.2391
–2Cu 0.3183	–2Ge2 0.2459	
–2Cu 0.3200		
–2Ge1 0.3038		Ge2–2Cu 0.2442
–4Ge1 0.3149		–2Cu 0.2459
–4Ge2 0.3068		–1Ge1 0.2391

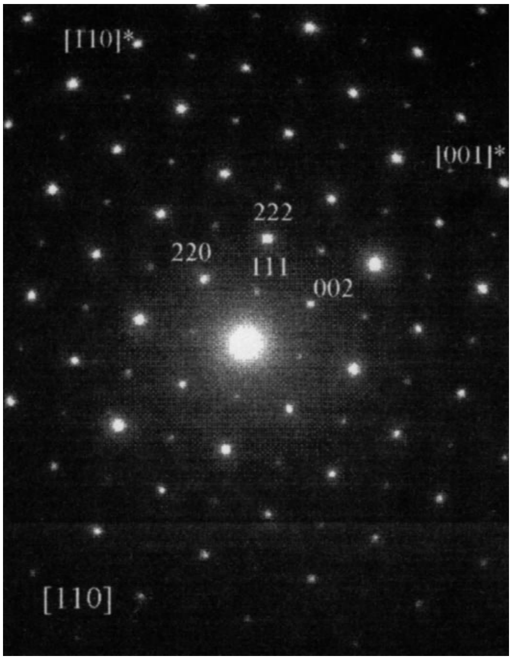

Fig. 2. Selection area electron diffraction pattern along the [−110] zone axis for $UCuGe_{1.75}$ (indexation is given relative to substructure $2a\times2b\times2c$).

3.4. Electrical and magnetic properties

Fig. 3 presents the temperature dependence of the reduced electrical resistivity for $UCuGe_{1.75}$. Above 132 K, this temperature dependence is relatively weak and shows

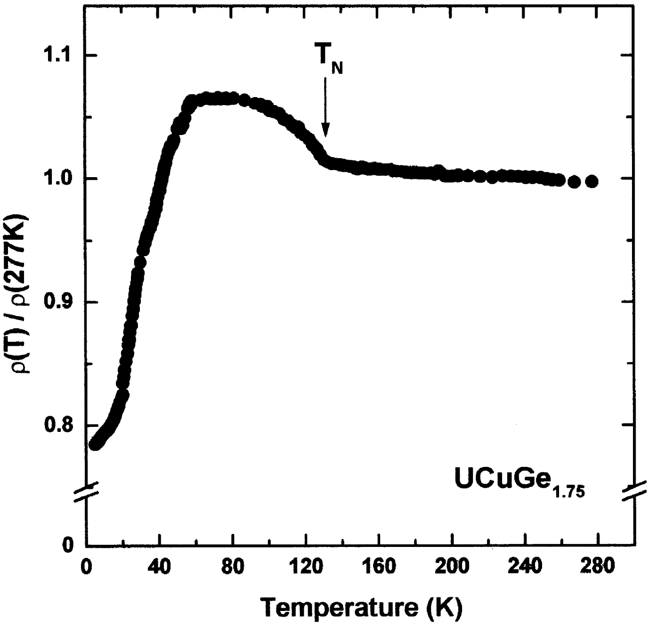

Fig. 3. Temperature dependence of the reduced resistivity of $UCuGe_{1.75}$.

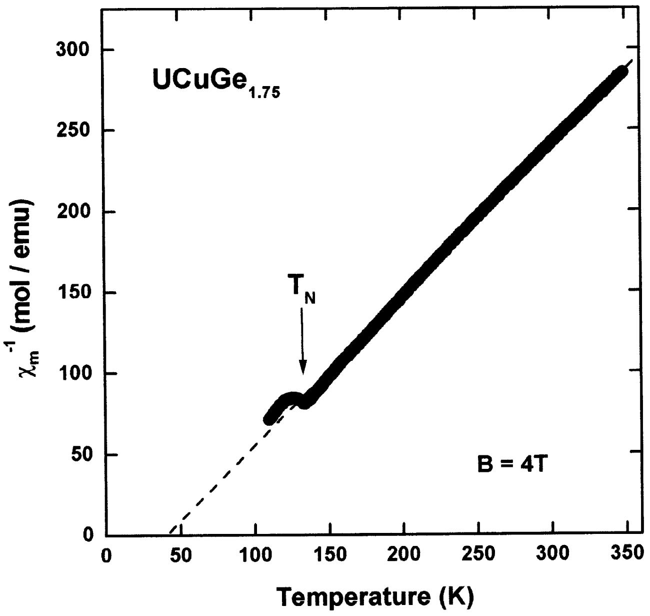

Fig. 4. Temperature dependence of the reciprocal magnetic susceptibility of $UCuGe_{1.75}$.

a negative coefficient $d\rho/dT$. Below $T_N = 132(2)$ K, the reduced resistivity exhibits an anomalous increase, reaches a maximum at about 70 K and then decreases at lower temperatures. This behaviour, observed previously for $U_3Cu_4Si_4$ [11] and UCu_5 [12] characterizes the occurrence at T_N of an antiferromagnetic ordering; the increase below T_N resulting from the reduction of the number of effective conduction electrons due to the gapping of the Fermi surface caused by the magnetic ordering.

Above 140 K, the magnetic susceptibility of $UCuGe_{1.75}$ follows a Curie–Weiss law: $\chi_m = C_m/(T - \theta_p)$ (Fig. 4). A least-squares fit of these data leads to a positive Curie temperature $\theta_p = 44(1)$ K and a Curie constant $C_m = 1.148$ emu K per U-atom corresponding to an effective magnetic moment of $\mu_{eff.} = 3.03(3)$ μ_B per U-atom. The latter value, which is comparable to that determined for the other ternary germanide $U_3Cu_4Ge_4$ ($\mu_{eff} = 3.19$ μ_B) [4], is usually found for uranium in trivalent or tetravalent state.

The temperature dependence of the magnetization of $UCuGe_{1.75}$, under an applied field $B = 4T$, is shown in Fig. 5. The curve exhibits a peak at $T_N = 133(1)$ K indicating an antiferromagnetic transition and two increases appearing near 109(1) and 63(1) K, respectively. These two anomalies can be assigned to the ferromagnetic germanides UCu_2Ge_2 ($T_C = 107$ K) [13] and UGe_2 ($T_C = 52$ K) [5] which are present in the sample. A best understanding of the antiferromagnetic properties of $UCuGe_{1.75}$ requires the synthesis of a sample without impurities phases.

4. Conclusion

A study of both structural, electrical and magnetic properties of $UCuGe_{1.75}$ has been performed. The crystal structure of $UCuGe_{1.75}$ can be considered as an intergrowth of AlB_2- and $ThCr_2Si_2$-type slabs. The electrical

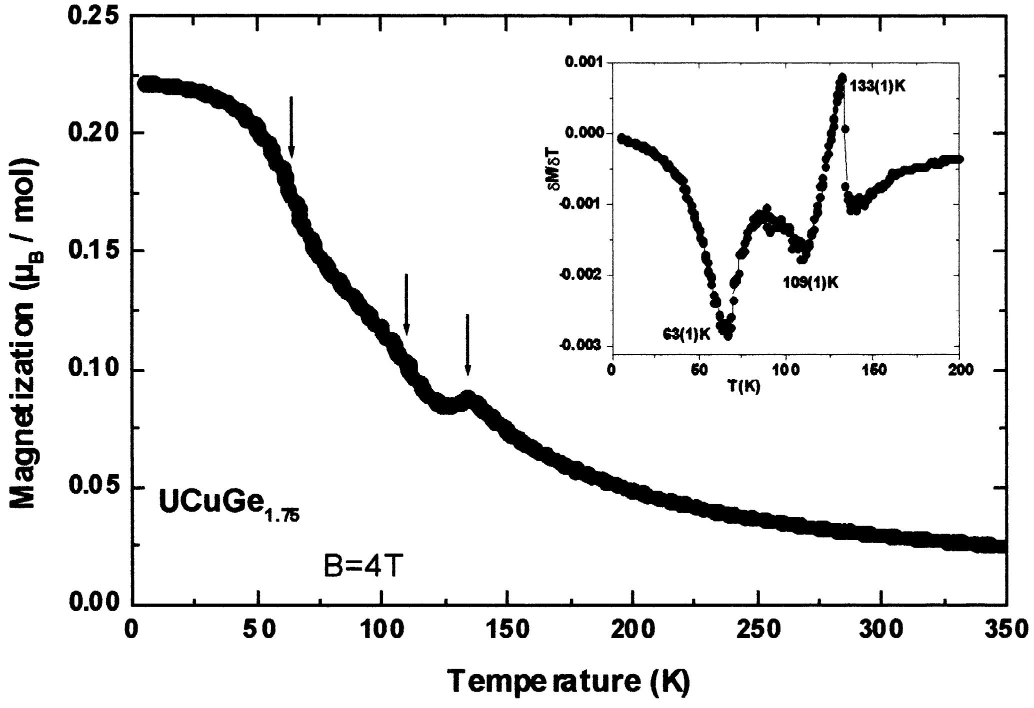

Fig. 5. Temperature dependence of the magnetization of $UCuGe_{1.75}$ (inset: derivative curve).

and magnetic measurements reveal an antiferromagnetic ordering at $T_N = 133(1)$ K.

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