



Structural and transport properties of some UTX compounds where $T = \text{Fe, Co, Ni}$ and $X = \text{Si, Ge}$

F. Canepa, P. Manfrinetti, M. Pani, A. Palenzona*

Istituto di Chimica fisica, Università di Genova, C.so Europa, Palazzo delle Scienze, Genova I-16132, Italy

Received 30 June 1995

Abstract

The ternary intermetallic compounds with general formula UTX ($T = \text{Fe, Co, Ni}$; $X = \text{Si, Ge}$) were analyzed by X-ray methods and some of their physical properties examined. All the studied phases belong to the well known TiNiSi-type structure. The compound UFeGe shows a phase transition at 500 K; at room temperature it crystallizes in a new monoclinic structure with $a = 6.986$, $b = 4.308$, $c = 6.992$ Å, $\beta = 93.71^\circ$ in the space group $P2_1/m$; above 500 K it changes into the orthorhombic TiNiSi-type.

Electrical resistivity measurements were carried out in the range 1.5–300 K for all samples, and up to 600 K for UFeGe. Anomalies in the resistivity behaviour were detected for UNiSi, UFeGe, UCoGe and UNiGe at 19, 80, 46 and 41 K respectively and ascribed to magnetic transitions.

Keywords: Uranium intermetallics; Structural properties; Electrical resistivity

1. Introduction

Ternary uranium intermetallics of composition UTX, when T is a transition element and X a p-block element have been well investigated for their fascinating magnetic and transport properties [1]. Anomalous behaviours such as spin fluctuation, magnetic transition and ordering, itinerant or localized magnetic moment, Kondo effect and heavy fermion state have often been ascribed to the influence of the p or d electrons of the ligands on the behaviour of the uranium 5f electrons [2,3]. It seems, therefore, useful to prepare a great number of these phases and to study their crystal structures and physical properties in order to understand these electron interactions.

In this work we have investigated the compounds for which $T = \text{Fe, Co, Ni}$ and $X = \text{Si, Ge}$. Some of them, namely UCo(Si,Ge) and UNi(Si,Ge) have been studied by Troc and Tran [4] who reported their crystal structures and magnetic properties, while UFe(Si,Ge) have been synthesized for the first time.

2. Experimental details

The elements used in the present investigation were: U depleted 99.8 wt.% purity (Koch–Light Lab., UK); Fe, Co and Ni 99.99 wt.% purity (Aldrich Chem. Co., USA); Si and Ge 99.999 wt.% purity (Koch–Light Lab., UK).

The samples were prepared by direct synthesis from the three elements, pressed together in the form of pellets, in a semilevitation high frequency induction furnace on a water-cooled tantalum heart under an atmosphere of pure and dry argon. The buttons were inverted and remelted three times to ensure complete homogenization and then slowly cooled to room temperature. The alloys were then wrapped in tantalum sheets, closed in quartz tubes under argon and annealed at 1250 K for 3–5 days.

Metallographic examination was carried out with standard techniques; a diluted alcoholic solution of picric acid was used to reveal the phases present. All the samples so obtained were single phase with little grain separation (2–3% at most); they were brittle and some of them showed the presence of more or less evident fractures, which caused some

* Corresponding author.

difficulties in preparing the samples for resistivity measurements.

X-ray analyses were performed on powders in a Guinier–Stoe camera, using silicon as internal standard ($a = 5.4308 \text{ \AA}$).

Single crystals of UFeSi, UCoGe and UFeGe were investigated by means of an automatic four circles diffractometer (Enraf–Nonius CAD–4) using graphite monochromated Mo $K\alpha$ radiation in the θ range 2–30°. The data collection conditions were: ω – θ scan mode, 610 total measured reflections for UFeSi; ω – θ scan mode, 653 total reflections for UCoGe; ω scan, 1311 total reflections for UFeGe. The intensity data were corrected for Lorentz and polarization factors; the absorption effects were taken into account by applying both a spherical and a semiempirical correction [5]. The structure of UFeGe was solved by Patterson methods using SHELXS–86 [6]. Full-matrix least squares refinements based on the F_o^2 values were made by means of SHELXL–93 [7].

Low temperature X-ray powder measurements were carried out using a Huber–Guinier 600 diffractometer (0.002° angular resolution) with Si as internal standard. The diffractometer was operating in the 10–300 K range with a standard cryogenerator from TCI–Cryogenics. A calibrated standard Si diode was used for temperature measurements.

High temperature X-ray experiments were carried out with the powder method using a Rigaku–Denki camera (Cu $K\alpha$ radiation) up to 600 K with a standard Pt–Pt + 10% Rh thermocouple.

Structural transformations were also explored using differential scanning calorimetry, DSC7 from Perkin–Elmer, with a Cr–constantan thermocouple as temperature sensor.

Samples for resistivity measurements with typical dimensions $1 \times 1 \times 8 \text{ mm}^3$ were obtained by cutting the alloys under paraffin oil in order to prevent oxidation.

Electrical resistivity data were obtained in the 1.5–300 K temperature range with an He⁴ cryostat by a standard four-point d.c. method; a calibrated silicon diode sensor from Lake Shore Cryotronics Inc. was used for temperature measurements. A resistance furnace with a Pt–Pt + 10% Rh thermocouple was used for resistivity measurements above room temperature. Additional resistivity data were obtained using a Leybold RG 210 cryocooler between 14 and 300 K. The measurements were performed both on heating and on cooling. In all cases the results were found reproducible within experimental error.

3. Results and discussion

3.1. Crystallographic data

In Table 1 are collected the crystallographic results obtained for the studied phases together with the literature data for the known compounds. The crystal structures of UCoSi, UNiSi and UCoGe were previously determined and reported as CeCu₂-type, while for UNiGe both CeCu₂ and TiNiSi structures have been proposed.

By single crystal analysis we could attribute the orthorhombic TiNiSi-type to UFeSi and UCoGe and correctly define the crystallographic sites of the T and X atoms. The final values of the agreement index ($wR2$) are 0.143 (317 reflections, 19 parameters) and 0.127 (338 reflections, 19 parameters) for UFeSi and UCoGe respectively. Further refinements carried out exchanging X with T gave unreliable displacement parameters and higher $wR2$ values. As can be seen in Table 2, the positional parameters obtained for the two compounds are quite different, especially the x_T values. This reflects in a different coordination around the T and X atoms in the two cases. As already

Table 1
Crystallographic data for the UTX phases (T = Fe, Co, Ni; X = Si, Ge)

Compound	Structure type	Lattice parameters (Å)			Shortest U–U distance (Å)	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
UFeSi	TiNiSi	6.997(2)	4.063(1)	6.867(2)	3.179	this work
UCoSi	TiNiSi	6.842(2)	4.116(1)	7.056(1)	3.253	this work
UCoSi	CeCu ₂	4.104	6.852	7.143	3.47	[4]
UNiSi	TiNiSi	6.959(1)	4.142(1)	7.053(1)	3.260	this work
UNiSi	CeCu ₂	4.107	6.965	7.397	3.53	[4]
UFeGe _{LT}	UFeGe	6.986(1)	4.308(1)	6.992(1)	3.415	this work
				$\beta = 93.71^\circ$		
UFeGe _{HT}	TiNiSi	6.828(2)	4.259(1)	7.286(2)	3.470	this work
UCoGe	TiNiSi	6.852(1)	4.208(1)	7.226(1)	3.478	this work
UCoGe	CeCu ₂	4.205	6.843	7.227	3.46	[4]
UNiGe	TiNiSi	6.999(1)	4.236(1)	7.200(1)	3.553	this work
UNiGe	CeCu ₂	4.238	7.002	7.206	3.54	[4]

Table 2

Atomic coordinates and equivalent displacement parameters for UFeSi and UCoGe, both TiNiSi type; space group *Pnma*, Pearson symbol *oP12*

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
U	4c	0.0106(1)	1/4	0.6782(1)	0.0088(4)
Fe	4c	0.3578(5)	1/4	0.4335(6)	0.0100(8)
Si	4c	0.202(1)	1/4	0.109(1)	0.008(1)
U	4c	0.0101(1)	1/4	0.7075(1)	0.0091(4)
Co	4c	0.2887(5)	1/4	0.4172(5)	0.0129(7)
Ge	4c	0.1967(4)	1/4	0.0870(4)	0.0096(5)

pointed out by Hovestreydt et al. [8], the large variety of compounds crystallizing in the TiNiSi-type (a ternary variant of the PbCl₂-type) show different kinds of bonding situations, varying from ionic-covalent to metallic with corresponding different types of coordination. So, Co and Ge are similarly surrounded by a trigonal prism of U capped by four Ge or Co atoms in UCoGe, while in UFeSi the Si atoms centre tricapped trigonal prisms (formed by 4U + 2Fe) and the Fe atoms are coordinated by a tetrahedron of Si and a tetrahedron of U atoms.

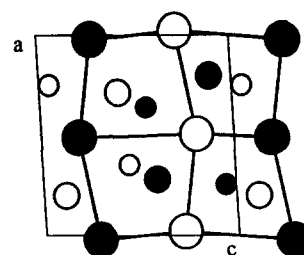
At room temperature UFeGe crystallizes in a new structure type: the results of the anisotropic refinement (*wR*₂ = 0.100 on 686 reflections and 38 parameters) are reported in Table 3. The structure can be easily described as a monoclinic deformation of the TiNiSi structure; a comparison between the two types is made in Fig. 1. The characteristic arrangement of the T–X sublattice is recognized, more or less distorted on going from UFeGe to UFeSi to UCoGe. The similarity between UFeGe and the TiNiSi structure is evident considering the coordination polyhedra around the T and X atoms: Fe2 and Ge1 in UFeGe are surrounded by a tricapped trigonal prism similar to Si in UFeSi, while Fe1 and Ge2 have, respectively, the same polyhedra of Fe in UFeSi and of Co or Ge in UCoGe.

For all the other compounds, the powder patterns were completely indexed on the basis of the TiNiSi type, taking the same positional parameters of UFeSi and UCoGe for the UTSi and UTGe phases respectively.

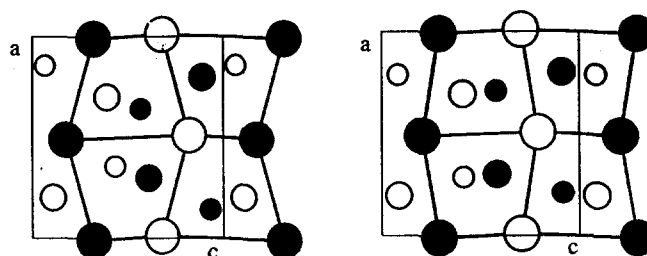
Table 3

Atomic coordinates and equivalent displacement parameters of UFeGe; space group *P2₁/m*, Pearson symbol *mP12*

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
U1	2e	0.0224(1)	1/4	0.7219(1)	0.0108(3)
U2	2e	0.5095(1)	1/4	0.8046(1)	0.0100(3)
Fe1	2e	0.3560(4)	1/4	0.4500(4)	0.0129(7)
Fe2	2e	0.7542(5)	1/4	0.0537(4)	0.0140(7)
Ge1	2e	0.1999(3)	1/4	0.1141(3)	0.0116(5)
Ge2	2e	0.7175(3)	1/4	0.4087(3)	0.0103(5)



(a) UFeGe



UFeSi

UCoGe

(b) TiNiSi - type

Fig. 1. Crystal structures of (a) UFeGe_{LT} and (b) UFeSi, UCoGe (both TiNiSi-type) projected along the *b* direction: large circles, U; medium circles, Si, Ge; small circles, Fe, Co, Ni. Open and filled circles correspond to heights of 1/4 and 3/4 respectively.

3.2. Resistivity data

The electrical resistivities of the examined phases, in the 1.7–300 K temperature range, are reported in Figs. 2, 3 and 4. For all phases, high residual resistivity ρ_0 values were detected, ranging from about 230 $\mu\Omega$ cm for UNiSi up to 2000 $\mu\Omega$ cm for UFeSi. High values of the residual electrical resistivity in several ternary U-intermetallics have been already observed: UIrSi ($\rho_0 \approx 6000 \mu\Omega$ cm) [2], UCuGe ($\rho_0 \approx 700 \mu\Omega$ cm) [9], UAuGa ($\rho_0 \approx 1200 \mu\Omega$ cm), U₂CuGa₃ ($\rho_0 = 930 \mu\Omega$ cm) [10] and UPdSb ($\rho_0 \approx 3500 \mu\Omega$ cm) [11]. For other ternary U-compounds, reduced electrical resistivity (URhGe₂ and UIrGe₂ [12]), electrical resistance (UAlNi, UGa₂Ni, UAlRu and UAlCo [13]) and resistivity data in arbitrary units (U₂Co₃Si₅, U₂Rh₃Si₅ and U₂Ru₃Si₅ [14]) are reported. Different explanations were adopted to justify the obtained results: crystallographic disorder which leads to a strong scattering of electrons [10]; presence of microcracks in polycrystalline samples which prevents the determination of absolute resistivity values [11,13]; high brittleness of the U-compounds for which only samples of irregular

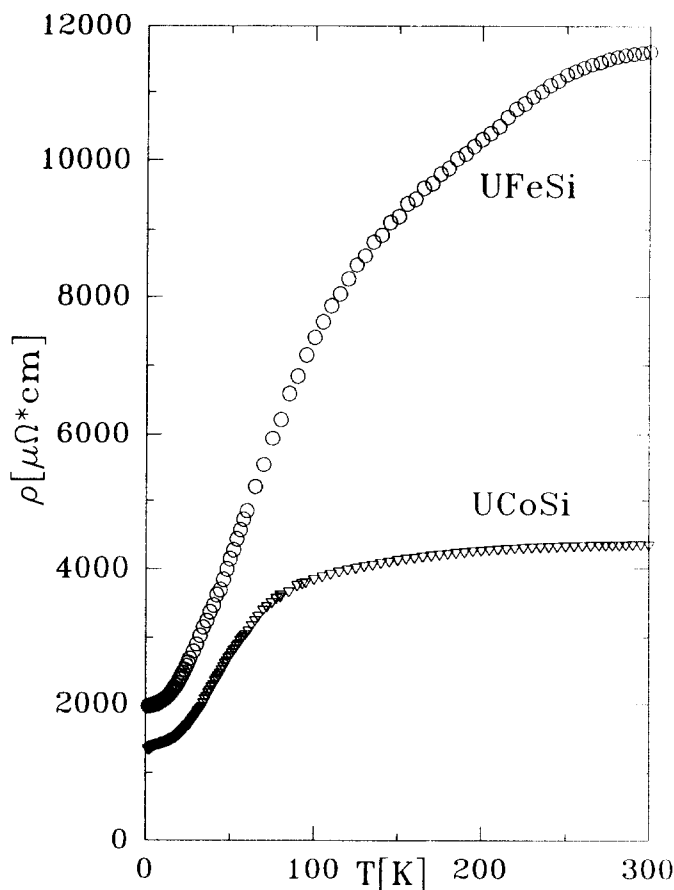


Fig. 2. Electrical resistivity of UFeSi and UCoSi.

shape for electrical resistivity measurements could be obtained [12]. The same analysis can also well apply to our phases. In all cases the obtained compounds (all highly homogeneous) were very brittle and the presence of microcracks could not be excluded.

For UFeSi and UCoSi the electrical resistivity increases monotonically at increasing temperature (see Fig. 2); a strongly negative curvature, however, was observed in the whole temperature range. No evidence of structural or magnetic transitions was detected. In contrast, for the UNiSi phase, reported in Fig. 3, a sharp drop in the electrical resistivity behaviour was observed at about 19 K. Previous magnetic measurements on the UNiSi phase give evidence of two transitions at 7.5 and 80 K [4]. The same authors, however, assert that their electrical resistivity measurements supply different results: they observe only a distinct anomaly at 18 K.

The room temperature absolute value of the electrical resistivity decreases at increasing transition element atomic number: from UFeSi ($\rho_{300\text{K}} = 12000 \mu\Omega \text{ cm}$) to UCoSi ($\rho_{300\text{K}} = 3500 \mu\Omega \text{ cm}$) and UNiSi ($\rho_{300\text{K}} = 350 \mu\Omega \text{ cm}$). Although the existence of microcracks can explain the high values of the residual resistivities for UFeSi ($\rho_0 \approx 2000 \mu\Omega \text{ cm}$) and UCoSi

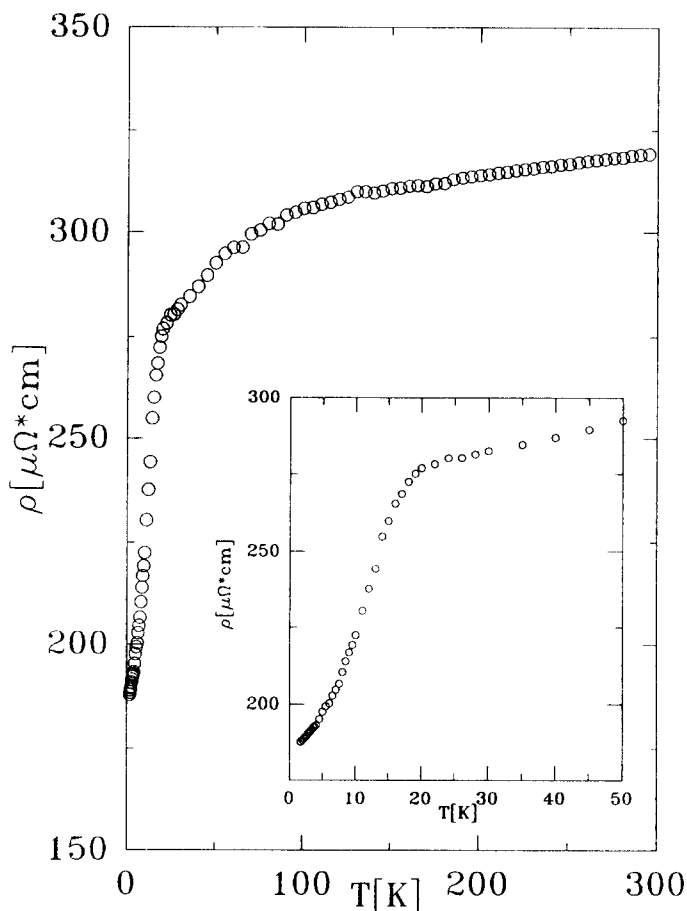


Fig. 3. Electrical resistivity of UNiSi. In the inset, low temperature (0–50 K) electrical resistivity data are reported.

($\rho_0 \approx 1300 \mu\Omega \text{ cm}$), the large magnitude of the resistivity for the two phases with Fe and Co, allows us to suspect that a semiconducting energy gap is present in these compounds at high temperatures. This hypothesis has already been expressed for other equiatomic ternary U-compounds: UPdSn, UPdSb and UAuSn [11].

A maximum in the electrical resistivity thermal behaviour occurs for the UFeGe, UCoGe and UNiGe phases at 80 K, 46 K and 41 K respectively (see Fig. 4).

Previous thermodynamic [14] magnetic [4] and transport [15] measurements performed on the UNiGe compound give evidence of an antiferromagnetic transition at $T_N = 42 \text{ K}$. Our resistivity results are in agreement with the observed ones. Below T_N the resistivity can be described by the equation already adopted for other U-systems [14,16]

$$\rho(T) = \rho_0 + bT \left(1 + \frac{2T}{\Delta} \right) \exp\left(\frac{-\Delta}{T} \right) + cT^2$$

where ρ_0 is the residual resistivity, the exponential term is due to an electron-spin wave scattering and the T^2 term is ascribed to spin fluctuation in the Fermi liquid model. We obtain $\Delta = 30 \text{ K}$ comparable with

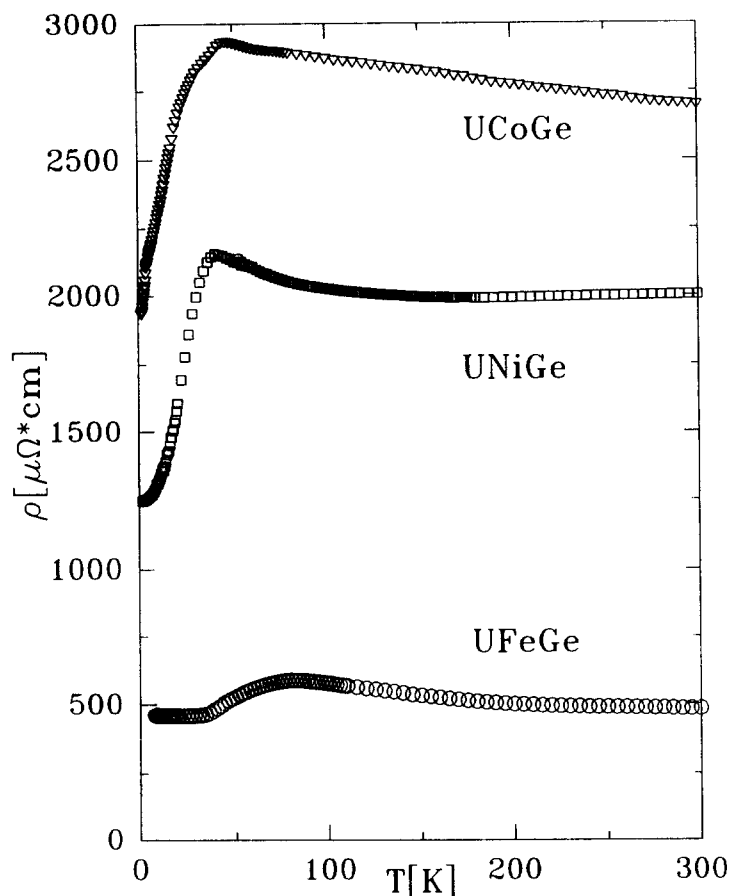


Fig. 4. Electrical resistivity of UFeGe, UCoGe and UNiGe.

$\Delta = 99$ K for URu_2Si_2 [16] and $\Delta = 67$ K for $\text{U}_2\text{Rh}_3\text{Si}_5$ [14].

Previous magnetic susceptibility measurements, performed in the 1.5–300 K temperature range [4], gave no evidence of magnetic transitions in UCoGe, although free-Co impurities affected the experimental values; the compound was described by the authors in terms of ground state paramagnetic behaviour with spin fluctuation effects. On the contrary, since our low temperature X-ray diffraction measurements show no structural transition in the whole temperature range, we hypothesize that the sharp peak observed in the electrical resistivity behaviour can be ascribed to a magnetic transition.

In Fig. 5 electrical resistivity measurements up to 600 K for UFeGe are reported. As described above, a broad maximum in the electrical resistivity trend, centred at 80 K, was detected; after the maximum, the resistivity decreases monotonically with increasing temperature with a $\ln T$ dependence. Since from low temperature X-ray diffraction measurements no evidence of a structural transition was observed in the 10–300 K temperature range, the maximum in the electrical resistivity could be ascribed to a magnetic ordering. A large hysteresis occurs between 430 and

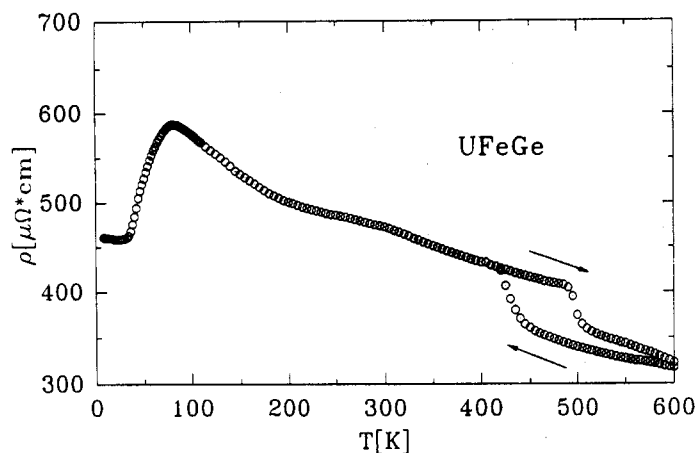


Fig. 5. Electrical resistivity of UFeGe in the 0–600 K temperature range.

530 K; from the middle of the hysteresis cycle we estimate a transition temperature of about 475 K, while the experimental inflection points, on heating and on cooling, are 505 K and 430 K respectively. A thermodynamic analysis performed with a differential scanning calorimeter confirms this transition. As reported in Fig. 6, a rather sharp endothermic peak, with a maximum at about 510 K, was obtained at a heating rate of $20^\circ\text{C min}^{-1}$ which gave an enthalpy change of

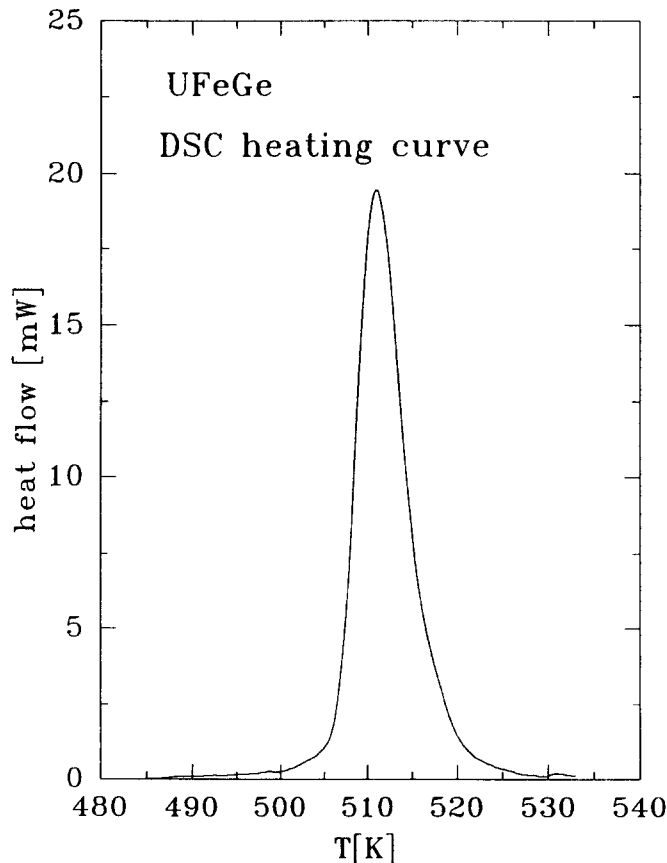


Fig. 6. Differential scanning calorimetry heating curve of UFeGe.

1.7 kJ mol⁻¹. During the cooling run the corresponding thermal effect appears at a lower temperature (about 430 K) and spread over a wide temperature range, indicating undercooling effects. To clarify the nature of the transition, high temperature X-ray diffraction measurements were performed up to 600 K; a structural transition from the room temperature monoclinic UFeGe-type to the orthorhombic TiNiSi-type above 500 K was detected.

Acknowledgements

Financial support from the Italian National Research Council (CNR) is gratefully acknowledged. We thank the Institute of General Chemistry, University of Genoa, for the use of the high temperature X-ray diffraction camera and the Institute of Industrial Chemistry, University of Genoa, for the use of the differential scanning calorimeter.

References

- [1] V. Sechovsky, L. Havela, P. Nozar, E. Brück, F.R. de Boer, A.A. Menovsky, K.H.J. Buschow and A.V. Andreev, *Physica B*, **163** (1990) 103.
- [2] B. Chevalier, B. Lloret, P. Gravereau, B. Buffat and J. Etourneau, *J. Magn. Magn. Mater.*, **75** (1988) 13.
- [3] H. Fujii, H. Kawanaka, T. Takabake, E. Sugiura, K. Sugiyama and M. Date, *J. Magn. Magn. Mater.*, **87** (1990) 235.
- [4] R. Troc and V.H. Tran, *J. Magn. Magn. Mater.*, **73** (1988) 389.
- [5] A.C.T. North, D.C. Phillips and F.S. Matthews, *Acta Crystallogr. A*, **24** (1968) 351.
- [6] G.M. Sheldrick, in G.M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing 3*, Clarendon, Oxford, 1985, p. 175.
- [7] G.M. Sheldrick, SHELXL-93, *Program for refinement of crystal structures*, University of Göttingen, 1993.
- [8] E. Hovestreydt, N. Engel, K. Klepp, B. Chabot and E. Parthé, *J. Less-Common Met.*, **85** (1982) 247.
- [9] V.H. Tran and R. Troc, *J. Magn. Magn. Mater.*, **86** (1990) 231.
- [10] V.H. Tran, R. Troc and D. Badurski, *J. Alloys Comp.*, **199** (1993) 193.
- [11] T.T.M. Palstra, G.J. Nieuwenhuys, R.F.M. Vlaustin, J. van den Berg, J.A. Mydosh and K.H.J. Buschow, *J. Magn. Magn. Mater.*, **67** (1987) 331.
- [12] E. Hickey, B. Chevalier and J. Etourneau, *Mater. Res. Bull.*, **24** (1989) 1111.
- [13] V. Sechovsky, L. Havela, L. Neuzil and A.V. Andreev *J. Less-Common Met.*, **121** (1986) 169.
- [14] S. Kawamata, H. Iwasaki and N. Kobayashi, *J. Magn. Magn. Mater.*, **104–107** (1992) 5.
- [15] S. Kawamata, H. Iwasaki, N. Kobayashi, K. Ishimoto, Y. Yamaguchi and T. Komatsubara, *J. Magn. Magn. Mater.*, **104–107** (1992) 53.
- [16] A.LeR. Dawson, W.R. Datars, J.D. Garrett and F.S. Razavi *J. Phys: Condens. Matter*, **1** (1989) 6817.