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Spin-glass-like behaviour in U_2TSi_3 (T≡Fe, Co, Ni or Cu) intermetallics with disordered AlB_2- and α-$ThSi_2$-type structures

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Abstract. A new series of ternary uranium intermetallics U_2TSi_3 (T≡Fe, Co, Ni or Cu) has been discovered. All these phases crystallize in the hexagonal AlB_2-type structure, except for U_2CuSi_3 which is of the tetragonal α-$ThSi_2$ type. The magnetic properties of the new compounds were investigated by means of DC magnetization and AC susceptibility measurements. The results show all the main characteristics of a re-entrant spin-glass behaviour at low temperatures in all the ternaries studied. Owing to some structural properties of these compounds they could be classified as non-magnetic atom disorder spin glasses.

1. Introduction

Ternary uranium–transition-metal silicides and germanides have attracted much interest in the last decade because of the great variety of their unusual magnetic properties. However, most previous studies were devoted to the 1:2:2 series, exemplified by the heavy-fermion superconductor URu_2Si_2 [1]. When searching for new phases existing in the U–T–Si systems (T≡late transition metal), we found recently [2] a family of compounds with the composition 2:1:3. To our knowledge the existence of only two uranium compounds with this stoichiometry, namely U_2FeSi_3 [3] and U_2PtSi_3 [4, 5], has been reported to date. However, in the very final stage of this study, we became aware of some investigations on similar ternaries recently undertaken by other workers [6]. The magnetic properties have been published only for U_2PtSi_3. They caused some controversy, being interpreted as either spin-glass behaviour [4] or weak itinerant ferromagnetism [5].

In the present paper we report some structural and magnetic data for the U_2TSi_3 compounds with T≡Fe, Co, Ni or Cu. The observed properties are discussed here in terms of a re-entrant spin-glass behaviour.

2. Experimental details

The samples were prepared by arc melting the appropriate amounts of the elements (all metals with nominal purities greater than 99.9%; 99.999% pure silicon) in a titanium-gettered argon atmosphere. The buttons were flipped over and remelted a number of times

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to ensure good homogeneity of the materials. Then, they were wrapped with tantalum foil and annealed in an evacuated quartz ampoule at 800 °C for 10 days.

X-ray diffraction patterns were taken for both the as-cast and the annealed specimens using a Stoe powder diffractometer with CuK_α radiation. All the samples were found to be single phase and no significant differences were seen between the patterns taken before and after the annealing procedure. The only exception was U_2CuSi_3 where the as-cast sample and to a less extent even the sample annealed at 800 °C showed the presence of a few weak extra lines which were easily indexable in a hexagonal system with the lattice parameters $a = 4.013$ Å and $c = 3.954$ Å. However, this additional phase, which was probably UCuSi [7], disappeared completely after annealing at 1000 °C for 14 days. It is worthwhile noting that no supplementary lines corresponding to the formation of any superstructure were observed for the annealed specimens, contrary to the case of the rare-earth RE_2TSi_3 intermetallics [8–10]. It appears that the U_2TSi_3 compounds with T≡Fe, Co or Ni, like U_2PtSi_3 reported previously [4], crystallize in the hexagonal AlB_2-type structure. In contrast, U_2CuSi_3 is of the tetragonal α-$ThSi_2$ type. The lattice parameters for all the phases studied were evaluated by a least-squares method, and they are listed in table 1.

Table 1. Crystallographic data for the uranium silicides U_2TSi_3.

Compound	Structure type	Lattice parameters		
		a (Å)	c (Å)	c/a
U_2FeSi_3	AlB_2	4.004	3.864	0.965
U_2CoSi_3	AlB_2	3.988	3.883	0.974
U_2NiSi_3	AlB_2	3.979	3.949	0.992
U_2PtSi_3 [5]	AlB_2	4.084	3.973	0.973
U_2CuSi_3	α-$ThSi_2$	3.971	13.926	3.507

DC magnetic measurements were performed in the temperature range 5–300 K using a SHE SQUID magnetometer. The low-temperature complex magnetic susceptibility was measured employing a LakeShore AC susceptometer.

3. Results

The results of our DC magnetization and magnetic susceptibility measurements are presented in figures 1–4. The inverse magnetic susceptibility for U_2FeSi_4 is displayed in figure 1. It appears that this compound remains paramagnetic down to 5 K. Its $\chi(T)$ dependence above 50 K exhibits a modified Curie–Weiss (MCW) behaviour given by

$$\chi = \chi_0 + C/(T - \Theta_p) \qquad \mu_{eff} = (8C)^{1/2} \tag{1}$$

with the parameters $\chi_0 = 732 \times 10^{-6}$ emu mol^{-1}, $\Theta_p = -86$ K and $\mu_{eff} = 2.77\ \mu_B$/U atom. Below 50 K a deviation from the MCW law is observed but the magnetic susceptibility of U_2FeSi_3 measured at 5 K is field independent (see inset to figure 1). Thus, a small step-like change in the susceptibility occurring at about 3.5 kOe can be attributed to a sample reorientation effect (for the SQUID measurements a well crystallized polycrystalline piece of U_2FeSi_3 was freely placed in a container).

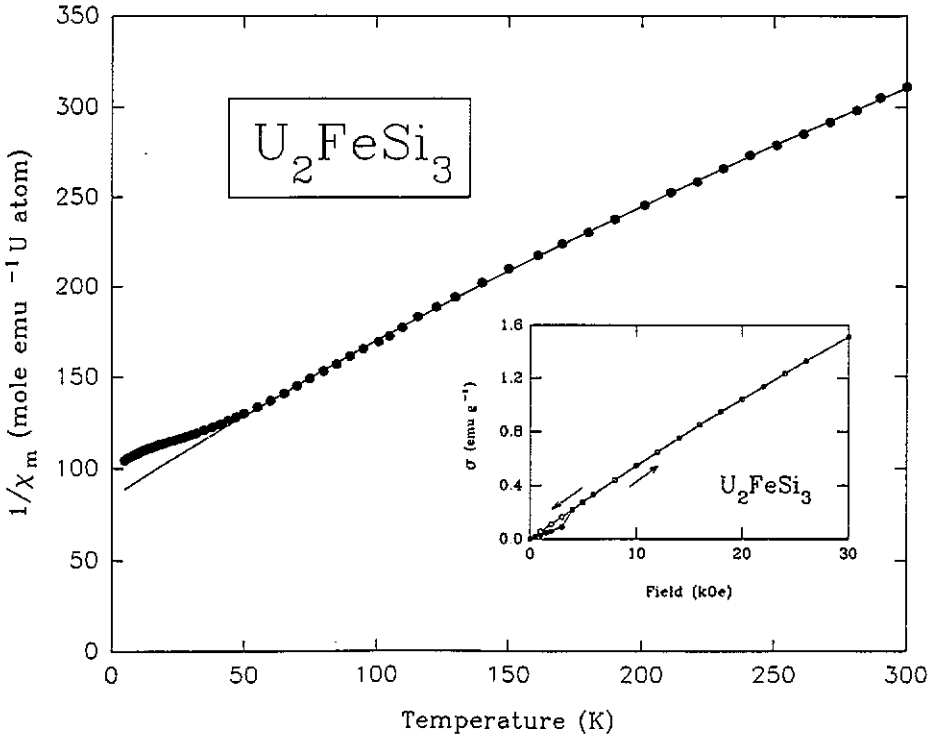

Figure 1. Inverse magnetic susceptibility versus temperature for U_2FeSi_3:——, fit of $\chi^{-1}(T)$ to the MCW law. The inset shows the field dependence of the magnetization of U_2FeSi_3 measured at 5 K.

The other compounds studied exhibit all the main characteristics of ferromagnetic materials. Their magnetization shows a hysteresis effect and remanence (see insets to figures 2–4), although the $\sigma(H)$ curves do not saturate up to 30 kOe, reaching only $0.28\mu_B$/U atom, $0.67\mu_B$/U atom and $0.52\mu_B$/U atom for U_2CoSi_3, U_2NiSi_3 and U_2CuSi_3, respectively, and the remanence magnitude μ_R is also very small, being only $0.05\mu_B$/U atom, $0.31\mu_B$/U atom and $0.25\mu_B$/U atom, respectively. The temperature variation in the magnetization was measured in magnetic fields of 200 Oe and 2 kOe, in two regimes of the sample cooling: with an applied field (FC) and without an applied field (ZFC). The magnetizations of U_2NiSi_3 and U_2CuSi_3 appear to be strongly dependent on the magnetic history of the samples, and the ZFC curves for these compounds exhibit characteristic cusp-like maxima which shift to lower temperatures as the magnetic field increases (see figures 3 and 4). Moreover, a strong time dependence of the magnetization was observed. In turn, the magnetization of U_2CoSi_3, U_2NiSi_3 and U_2CuSi_3 measured in the FC regime decreases rapidly with increasing temperature in a manner as for ferromagnets with inflection points of 10 K, 25 K and 30 K, respectively. Surprisingly, U_2NiSi_3, besides such a low-temperature phase transition at 25 K, shows an additional ferromagnetic-like anomaly in the $\sigma(T)$ curves located at about 95 K. At present we cannot distinguish whether this latter feature is an intrinsic effect or is due to a very small admixture of $UNiSi_2$ (which is certainly undetectable by x-ray diffraction) which orders ferromagnetically just at 95 K [11]. In the paramagnetic region the magnetic susceptibilities of U_2CoSi_3, U_2NiSi_3 and U_2CuSi_3 follow the MCW law (see figures 2–4) with the parameters listed in table 2.

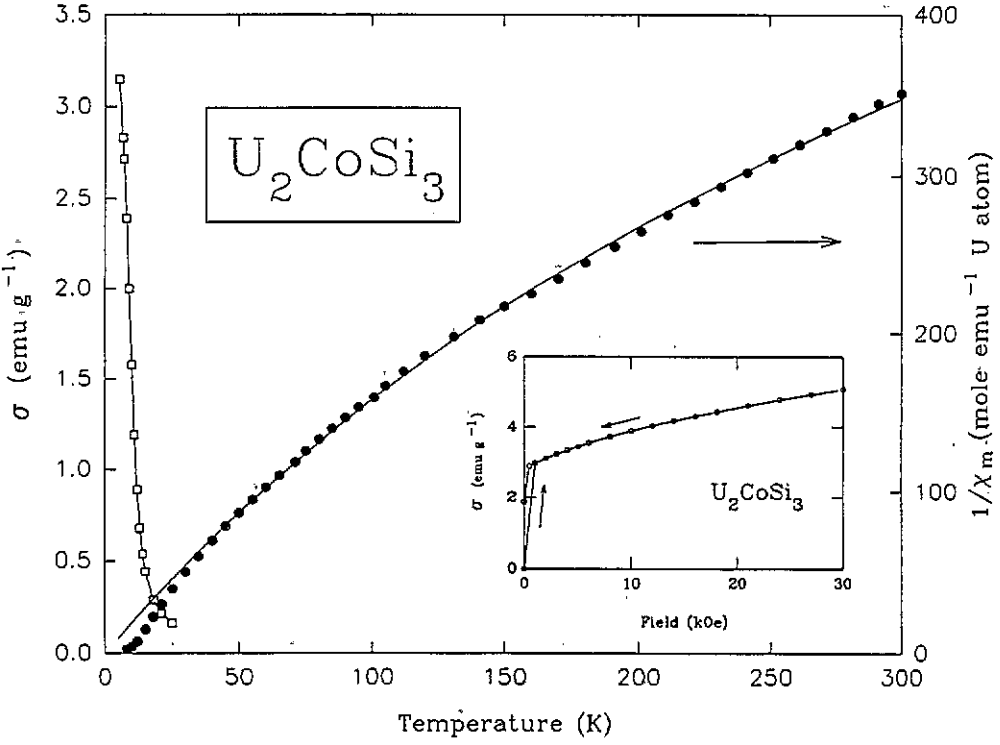

Figure 2. Temperature dependence of the magnetization (left-hand scale) and the reciprocal magnetic susceptibility (right-hand scale) for U_2CoSi_3 measured in a magnetic field of 2 kOe: ——, fit of $\chi^{-1}(T)$ to the MCW law. The inset shows the field dependence of the magnetization of U_2CoSi_3 measured at 5 K with increasing (●) and decreasing (○) magnetic field.

It may be of great interest to compare our present results with those reported previously for U_2PtSi_3 [5]. Such a comparison is made in table 2. It appears that the U_2TSi_3 compounds with T≡Co, Ni or Cu behave in a very similar manner to the Pt-containing silicide. In particular, all the main characteristics of U_2PtSi_3 (T_C, μ_R and μ_{eff}) are of the same order of magnitude as those of the compounds studied here. It seems likely that the physical origins of the magnetic properties in all the U_2TSi_3 ternaries should be similar. Interestingly, from the results obtained in [5] it was concluded there that U_2PtSi_3 is a weak itinerant ferromagnet. On the other hand, the same compound has been characterized in [4] as a spin-glass material.

To clarify this controversy, the complex susceptibilities of U_2CoSi_3, U_2NiSi_3 and U_2CuSi_3 were studied in AC fields of 1 and 10 Oe at several frequencies ranging from 15 to 800 Hz. As an example, figure 5 displays the temperature variations in the AC susceptibility obtained for U_2CoSi_3. It is clear from this figure that the results obtained indicate a spin-glass-like behaviour in this compound. Both the real and the imaginary components of the susceptibility show pronounced maxima, the positions of which are field and frequency dependent. It appears that the freezing temperature T_f, defined by a peak in χ'' [12], rises as the field decreases or as the frequency increases. However, because the susceptibility maxima are rather rounded and not cusped, they occur in χ' and χ'' at slightly different temperatures, and χ'' does not vanish just above T_f; it seems likely that U_2CoSi_3 is not a simple spin glass but a re-entrant spin glass (ferroglass) [12, 13], exhibiting first a

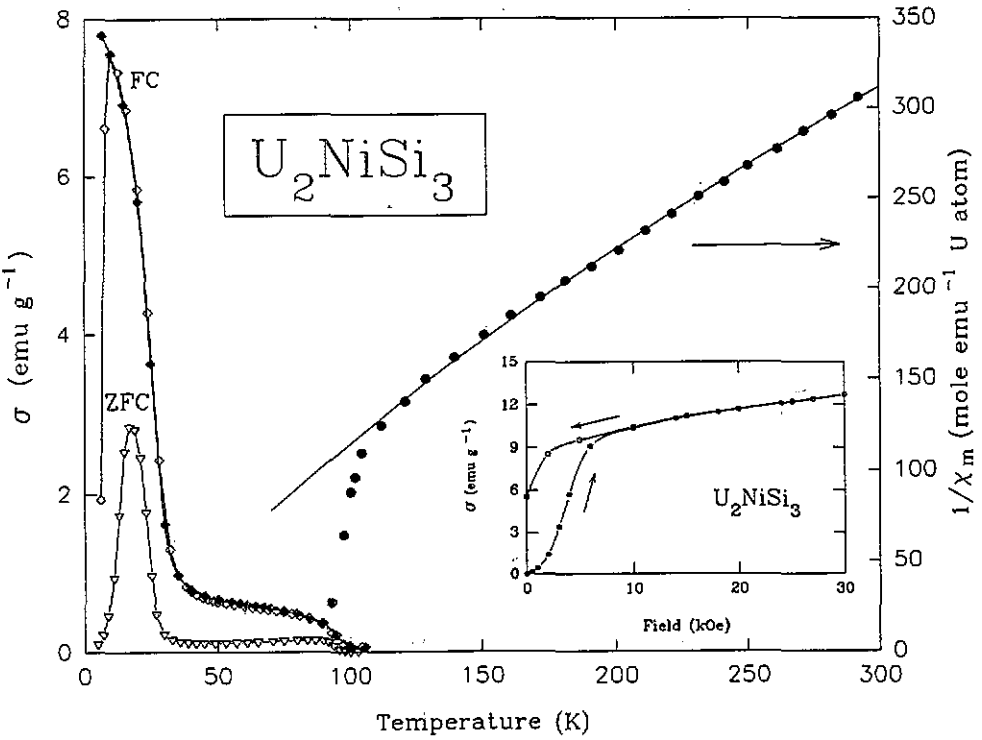

Figure 3. Temperature dependence of the magnetization (left-hand scale) and the reciprocal magnetic susceptibility (right-hand scale) for U_2NiSi_3: ——, fit of $\chi^{-1}(T)$ to the MCW law. *The magnetization was measured in the FC regime (see the text) in a field of 2 kOe* (■) *and in* the ZFC regime in fields of 200 Oe (▽) and 2 kOe (□). The inset shows the field dependence of the magnetization of U_2NiSi_3 measured at 5 K with increasing (●) and decreasing (○) magnetic field.

ferromagnetic transition at 10 K and then showing spin-glass properties below about 8 K (see figure 5).

The temperature dependence of the AC susceptibility of U_2CuSi_3 is displayed in figure 6. The $\chi'(T)$ and $\chi''(T)$ curves shown were taken at $f = 15$ Hz in an AC field H of 10 Oe, but very similar results were obtained at several other frequencies and magnitudes of H. The main feature seen in figure 6 is a two-peak behaviour of both the real and the imaginary components of the AC susceptibility. Whereas the first maximum, occurring at about 26 K, shows significant field and frequency dependences which are of the same kind as that found for U_2CoSi_3, the other peak, at about 28 K, appears to be much less f and H dependent. It is worth noting that such behaviour of χ'' was claimed [12, 14] to be typical for re-entrant spin glasses where the low-temperature maximum in χ'' defines T_f, and the second maximum occurs just below the ferromagnetic phase transition. Indeed, as seen from figure 6, the imaginary susceptibility χ'', upon going through these two pronounced maxima, finally falls to zero at 30 K, i.e. at the Curie temperature found in our DC measurements. Interestingly, in U_2CuSi_3, as in U_2CoSi_3, the characteristic temperatures T_C and T_f do not differ very much, suggesting that both these materials are close to the multicritical point on their magnetic phase diagrams [13].

A two-peak behaviour of the AC susceptibility was also found for U_2NiSi_3 (figure 7).

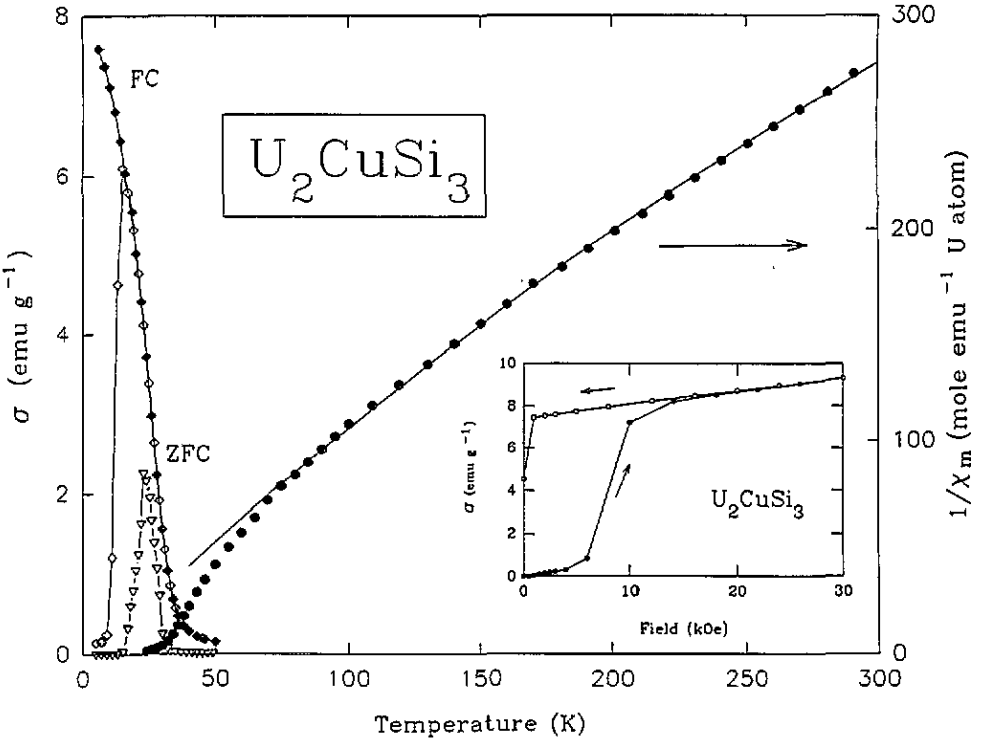

Figure 4. Temperature dependence of the magnetization (left-hand scale) and the reciprocal magnetic susceptibility (right-hand scale) for U_2CuSi_3: ——, fit of $\chi^{-1}(T)$ to the MCW law. The magnetization was measured in the FC regime (see the text) in a field of 2 kOe (■) and in the ZFC regime in fields of 200 Oe (▽) and 2 kOe (□). The inset shows the field dependence of the magnetization of U_2CuSi_3 measured at 5 K with increasing (●) and decreasing (○) magnetic field.

Table 2. Magnetic data for the U_2TSi_3 compounds.

	T_C (K)	T_f (K)	$\mu_{30\ kOe}$ (μ_B/U atom)	μ_R (μ_B/U atom)	μ_{eff} (μ_B/U atom)	Θ_p (K)	χ_0 (10^{-3} emu mol^{-1})
U_2FeSi_3	—	—	—	—	2.77	−86	0.732
U_2CoSi_3	10	8	0.28	0.05	2.03	≃0	1.150
U_2NiSi_3	25(?)	22	0.67	0.31	2.38	11	0.769
U_2CuSi_3	30	26	0.52	0.25	2.56	5	0.812
U_2PtSi_3 [5]	8	?	0.6[a], 0.2[b]	0.19[a]	2.1	19[a], −7[b]	0.9

[a] For the $H \parallel a$ axis at 1.3 K.
[b] For the $H \parallel c$ axis at 2.0 K.

In this case, however, the high-temperature maximum in χ'' is located at 95 K, i.e. at a much higher temperature than $T_f \simeq 22$ K. This second maximum which corresponds clearly to the anomaly in the $\sigma(T)$ variations (see figure 3) appears to be two orders of magnitude lower than the low-temperature maximum and its position exhibits much smaller field and frequency dependences. Unfortunately, as mentioned above, at present we cannot distinguish whether ferromagnetism below 95 K has an intrinisic effect in U_2NiSi_3, and thus

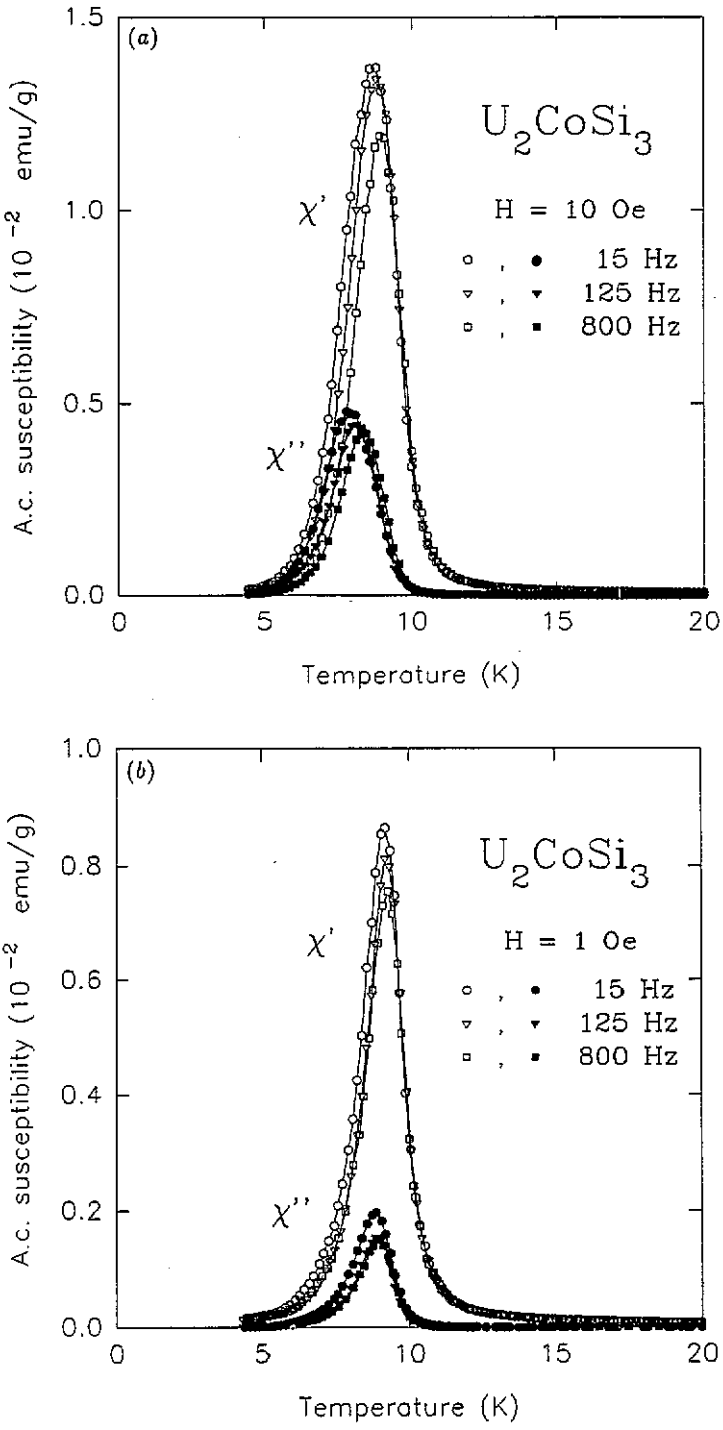

Figure 5. Complex susceptibility versus temperature for U_2CoSi_3 measured at frequencies of 15 Hz (○, ●), 125 Hz (△, ▲) and 800 Hz (□, ■) in AC fields of (*a*) 10 Oe and (*b*) 1 Oe.

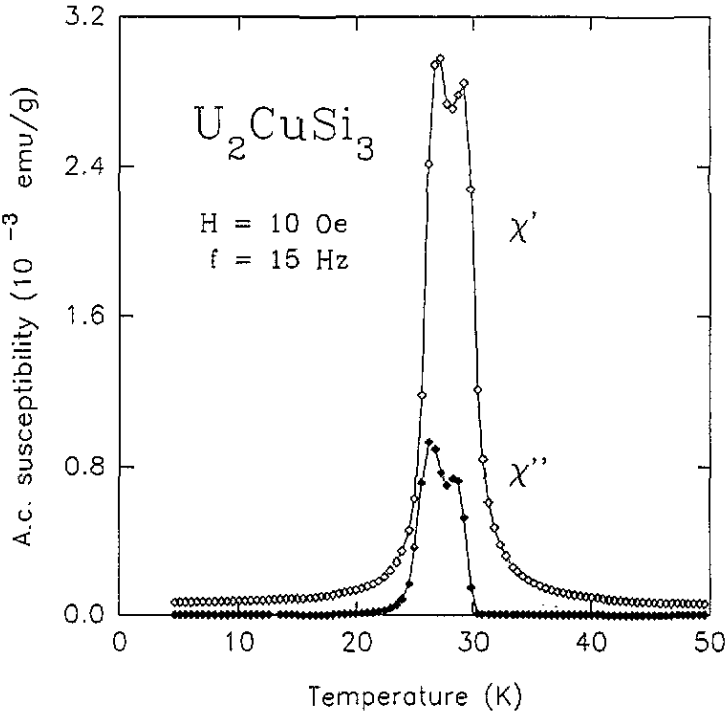

Figure 6. Complex susceptibility versus temperature for U_2CuSi_3 measured at a frequency of 15 Hz in an AC field of 10 Oe.

any interpretation of the magnetic properties of this interesting silicide must await further preparation efforts.

4. Discussion

4.1. Structural chemistry

The ternary U_2TSi_3 (T≡Fe, Co or Ni) compounds crystallize in the hexagonal AlB_2-type structure. This structure consists of alternating Al and B layers built of triangular nets of the respective atoms. Many years ago [15], the AlB_2-type structure was reported to be adopted by a binary silicide USi_2 which recently turned out to be a defective compound $USi_{1.67}$ (U_3Si_5) [16, 17]. It appears that in the U_2TSi_3 intermetallics the transition-metal atoms first fill the crystallographic sites which are left unoccupied by the Si atoms in $USi_{1.67}$ and then replace about one tenth of the Si atoms in the silicon networks of the latter compound. Such a replacement has been observed previously [18–22] for some ternary lanthanoid–transition-metal silicides and germanides crystallizing in the AlB_2-type structure. It is worth noting that rather a large homogeneity range has been reported [18] for these latter compounds, yielding a general composition $RET_{0.3-0.5}Si_{1.7-1.5}$. Moreover, for the Pd- and Rh-containing intermetallics the formation of a superstructure due to ordering of the transition-metal atoms has been discovered [8–10], which results in doubling of the AlB_2-type unit cell along all three crystallographic axes. Interestingly, the very same behaviour has also been recently observed for a new ternary uranium gallide U_2CuGa_3 [23]. In contrast, as mentioned above,

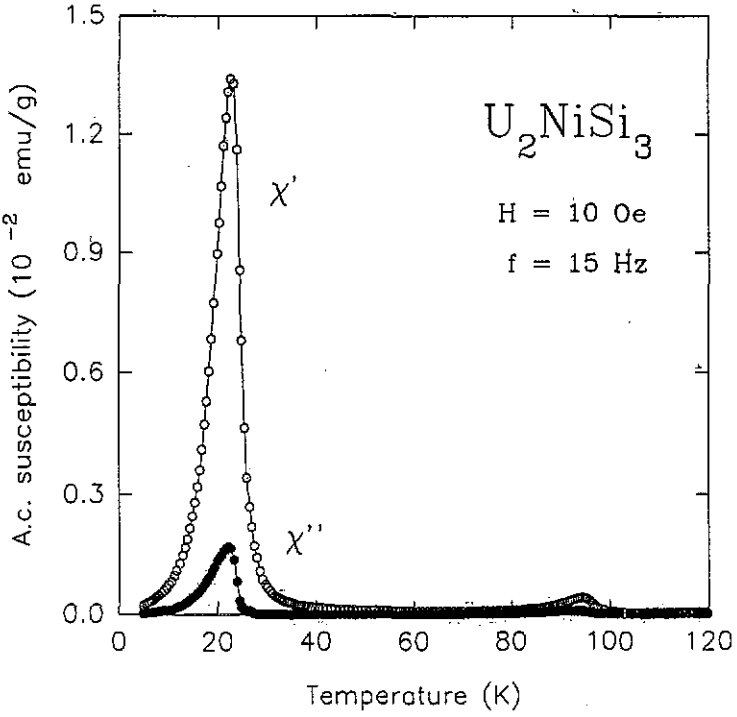

Figure 7. Complex susceptibility versus temperature for U_2NiSi_3 measured at a frequency of 15 Hz in an AC field of 10 Oe.

no evidence of any superstructure was seen for the U_2TSi_3 compounds studied in the present work.

The AlB_2-type structure has also been reported for some Cu-containing rare-earth silicides $RECu_{0.67-1}Si_{1.33-1}$ [20]. Interestingly, within the above composition range there exist some uranium–copper silicides with the same hexagonal structure, as exemplified by $UCu_{0.67}Si_{1.33}$ [24] and UCuSi [7]. On the contrary, the compound studied here, namely U_2CuSi_3, adopts a tetragonal structure of the α-$ThSi_2$ type. As reported previously [16, 17], another defective uranium silicide $USi_{1.88}$ crystallizes in the latter structure type. As in the hexagonal $USi_{1.67}$, the uranium atoms in $USi_{1.88}$ form graphite-like layers but, in contrast with the AlB_2 type, the Si atoms in the latter compound are arranged in three-dimensional networks. It seems that U_2TSi_3 can be derived from the above binary phase, filling the unoccupied Si atom positions and replacing about 17% of the Si atoms in $USi_{1.88}$. To our knowledge, the only ternary compound that has been reported to be isostructural with α-$ThSi_2$ is Er_2CuSi_3 [25]. Interestingly enough, erbium behaves here in a very similar manner to uranium, forming a tetragonal silicide with 1:0.5:1.5 stoichiometry, but adopting the hexagonal AlB_2-type structure for compounds with a larger Cu content such as $ErCu_{0.67-1}Si_{1.33-1}$ [20, 25].

4.2. Magnetic properties

Many uranium compounds exhibit ZFC and FC magnetization behaviours similar to those observed for the U_2TSi_3 compounds in the DC magnetic measurements. This phenomenon is usually interpreted as a domain effect due to the thermal activation of the movement

of Bloch walls in highly anisotropic materials. However, our AC susceptibility results for the U_2TSi_3 silicides with T≡Co, Ni or Cu seem to rule out such an interpretation for these compounds, suggesting spin-glass-like behaviour at low temperatures. Because of the rapid decrease observed in the freezing temperature T_f when going from Cu to Co (see table 2) we expect that U_2FeSi_3 is also a spin glass but only below 5 K. It is worthwhile noting that our finding of the spin-glass properties for these new U_2TSi_3 silicides seems to support the idea of the low-temperature spin-glass state in U_2PtSi_3 given by Geibel *et al* [4]. However, from the characteristic behaviour of the AC susceptibility we suggest that the U_2TSi_3 intermetallics are not simple spin glasses but re-entrant spin glasses which exhibit ferromagnetic-like properties between the high-temperature paramagnetic and low-temperature spin-glass region.

In principle, the magnetism in the U_2TSi_3 compounds may originate from both the uranium and the transition-metal sublattices. However, the idea that the T atoms contribute to the magnetic behaviour seems to be unlikely in view of the very similar properties shown by U_2CoSi_3 and U_2NiSi_3 on the one hand and the Cu-containing silicide on the other hand. Hence, we expect that, in the ternaries studied, only the uranium atoms carry magnetic moments. This conclusion is in line with the results obtained for the closely related phases $REFe_{0.67}Ge_{1.33}$ (RE≡Nd or Sm) and $NdNi_{0.67}Si_{1.33}$ [21, 22] where the rare-earth atoms are magnetically ordered while the Fe or Ni sublattices are diamagnetic.

The low-temperature spin-glass behaviour in the U_2TSi_3 compounds results presumably from the statistical distribution of the T and Si atoms at crystallographically equivalent lattice sites, giving some randomness in U–U exchange interactions. In this respect these new materials resemble the so-called non-magnetic atom disorder spin glasses [26], exemplified by $CeCu_{6.5}Al_{6.5}$ [27], $CePd_3B_{0.3}$ [28] and $CePtGa_3$ [29]. In all these compounds, the cerium atoms form a fully periodic lattice but the remaining constituent atoms exhibit some disorder in their arrangement in the respective unit cell. It is this varying electronic environment around the Ce atoms that introduces some variation in the RKKY-type exchange interactions, and thus a contradictory ordering between the Ce magnetic moments takes place. We believe that a very similar mechanism of spin-glass-like frustration is also essential to the formation of the spin-glass state in the U_2TSi_3 intermetallics.

Acknowledgments

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