The influence of magnetic sublattice dilution on magnetic order in CeNiGe$_3$ and UNiSi$_2$

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Received 5 March 2012, in final form 25 May 2012
Published 19 June 2012
Online at stacks.iop.org/JPhysCM/24/276003

Abstract

Polycrystalline samples of the Y-diluted antiferromagnet CeNiGe$_3$ ($T_N = 5.5$ K) and Th-diluted ferromagnet UNiSi$_2$ ($T_C = 95$ K) were studied by means of x-ray powder diffraction, magnetization and specific heat measurements performed in a wide temperature range. The lattice parameters of the Ce$_{1-x}$Y$_x$NiGe$_3$ alloys decrease linearly with increasing Y content, while the unit cell volume of U$_{1-x}$Th$_x$NiSi$_2$ increases linearly with increasing Th content. The ordering temperatures of the systems decrease monotonically with increasing $x$ down to about 1.2 K in Ce$_{0.4}$Y$_{0.6}$NiGe$_3$ and 26 K in U$_{0.3}$Th$_{0.7}$NiSi$_2$, forming a dome of long-range magnetic order on their magnetic phase diagrams. The suppression of the magnetic order is associated with distinct broadening of the anomalies at $T_N$, $C$ due to crystallographic disorder being a consequence of the alloying. Below the magnetic percolation threshold $x_c$ of about 0.68 and 0.75 in the Ce- and U-based alloys, respectively, the long-range magnetic order smoothly evolves into a short-range one, forming a tail on the magnetic phase diagrams. The observed behaviour of Ce$_{1-x}$Y$_x$NiGe$_3$ and U$_{1-x}$Th$_x$NiSi$_2$ is characteristic of diluted magnetic alloys.

(Some figures may appear in colour only in the online journal)

1. Introduction

Partial substitution of some chemical elements by other ones is one of the methods of modifying and examining the ground states of intermetallic compounds with unique physical properties. Such alloying (or doping) is particularly fruitful in strongly correlated electron systems, in which different sizes and electron configurations of the swapped atoms may significantly influence the exchange integral, this being one of the crucial parameters determining the magnetic properties of these systems [1–3]. Additionally, the chemical doping introduces some structural disorder, which can be another source of non-trivial magnetic behaviour [4].

In the course of our studies of the influence of chemical substitution on the physical properties of selected dense Kondo systems [5–10], we have performed alloying studies of two ternary intermetallic phases, namely CeNiGe$_3$ and UNiSi$_2$, crystallizing in two orthorhombic and—to some extent—similar structures of the SmNiGe$_3$- [11] and CeNiSi$_2$-type [12], respectively. CeNiGe$_3$ orders antiferromagnetically below the Néel temperature $T_N = 5.5$ K and exhibits features of a dense Kondo system with the Kondo temperature $T_K$ being close to $T_N$ [13]. Physical property measurements performed under hydrostatic pressure revealed that the Néel temperature of CeNiGe$_3$ initially increases with increasing pressure up to about 8 K at $P_{\text{max}} \approx 3$ GPa. At higher pressure $T_N$ rapidly decreases and the antiferromagnetic order is suppressed at the critical pressure $P_C = 5.5$ GPa. Simultaneously, the 4f-electrons of cerium become partly delocalized and at about 8 GPa the compound exhibits features of an intermediate valence system. Most importantly, at the critical pressure CeNiGe$_3$ becomes superconducting below $T_c = 0.48$ K [14, 15] and—as revealed by nuclear quadrupole resonance measurements—the superconductivity...
has an unconventional character resulting from the presence of the 4f-electrons of cerium [16–18]. Interestingly, also in YNiGe3, which is an isosstructural non-f-electron reference to CeNiGe3, a superconducting phase transition was found below about 0.48 K, but at ambient pressure [19]. UNiSi2 exhibits in turn a ferromagnetic order of nearly localized magnetic moments of uranium ($T_C = 95$ K) and some features characteristic of Kondo lattices [20, 10]. Our investigations of solid solutions of UNi$_{1-x}$Co$_x$Si$_2$ ($0 \leq x \leq 1$) indicated a very robust nature of the ferromagnetism observed in the parent compound UNiSi$_2$—although the ferromagnetic ordering is gradually suppressed upon stepwise substitution of Ni by Co, the phase transition exhibits clearly the ferromagnetic character up to $x = 0.96$ [21]. Recent pressure experiments performed on UNiSi$_2$ showed that the ferromagnetism of the compound is quenched above 5.5 GPa, where the 5f-electrons of uranium become delocalized [22].

In order to shed more light on the intriguing properties of CeNiGe$_3$ and UNiSi$_2$ we have investigated the physical properties of their solid solutions with their non-magnetic isosstructural counterparts YNiGe$_3$ and ThNiSi$_2$, respectively. Please note that LaNiGe$_3$, which would be a more appropriate reference for CeNiGe$_3$, most probably does not exist [13]. In this paper we present results on the magnetic susceptibility and specific heat measurements, indicating suppression of the long-range magnetic order and its smooth evolution into a short-range one.

2. Experimental details

Polycrystalline samples of the alloys Ce$_{1-x}$Y$_x$NiGe$_3$ and U$_{1-x}$Th$_x$NiSi$_2$ ($0 \leq x \leq 1$) were prepared by conventional arc melting of stoichiometric amounts of the elemental components in the protective atmosphere of an argon glove box. The pellets with Ce were subsequently wrapped in a molybdenum foil, sealed in an evacuated silica tube, and annealed at 800 °C for one week, while the U-based samples were wrapped in a tantalum foil and annealed for four weeks. The quality of the products was checked by means of x-ray powder diffraction, which showed that all the samples were single phase.

The magnetic properties of the alloys were studied using a commercial Quantum Design Magnetic Property Measurement System at temperatures from 1.7 to 400 K and in magnetic fields up to 5 T. The heat capacity was measured at temperatures ranging from 360 mK up to room temperature, using a Quantum Design Physical Property Measurement System.

3. Results

3.1. Crystal structure

Analysis of the x-ray powder diffraction patterns (not presented here) confirmed that CeNiGe$_3$ and YNiGe$_3$ crystallize in the SmNiGe$_3$-type structure (space group $Cmcm$ [11]), while UNiSi$_2$ and ThNiSi$_2$ crystallize in the CeNiGe$_2$-type structure (space group $Cmcm$ [12]).

The refined lattice parameters are $a = 4.1377(5)$ Å, $b = 21.807(3)$ Å and $c = 4.1668(5)$ Å for CeNiGe$_3$, $a = 4.0604(5)$ Å, $b = 21.529(2)$ Å and $c = 4.0627(3)$ Å for YNiGe$_3$, $a = 4.0097(5)$ Å, $b = 16.099(2)$ Å and $c = 4.0089(5)$ Å for UNiSi$_2$, and $a = 4.1256(4)$ Å, $b = 16.388(2)$ Å and $c = 4.1009(5)$ Å for ThNiSi$_2$, all being close to the values reported in the literature [11, 12, 23, 20]. The Rietveld refinement revealed that partial substitution of Ce by smaller Y and U by larger Th does not change the crystal structures of the systems but results, respectively, in linear compression and expansion of the lattice. As can be inferred from figure 1, the observed change of the unit cell volume (in total up to −6% in the Ce phases and +7% in the U alloys) is in both systems monotonic and linear in $x$ in each principal crystallographic direction.

3.2. Magnetic properties

The magnetic susceptibility measurements performed for the parent compounds CeNiGe$_3$ and YNiGe$_3$ confirmed the previous findings [13, 14, 24]. In particular, CeNiGe$_3$ exhibits localized antiferromagnetism below 5.5 K, while YNiGe$_3$ is an itinerant paramagnet with nearly temperature independent magnetic susceptibility $\chi(T)$ (not shown here). Figure 2 displays the $\chi(T)$ of Ce$_{1-x}$Y$_x$NiGe$_3$. As is apparent from the inset to figure 2, the $\chi^{-1}(T)$ curves exhibit linear behaviour above about 100 K and—as normalized per mole of Ce atoms—are nearly superimposed onto each other.
Temperature variations of the magnetic susceptibility $\chi$ of Ce$_{1-x}$Y$_x$NiGe$_3$ in a logarithmic scale. The curves are shifted upward for the sake of clarity; the arrows mark the antiferromagnetic phase transition temperatures $T_N$. Inset: $\chi^{-1}$ versus $T$ for selected compositions. The straight solid lines represent the Curie–Weiss fits.

Least square fits of the Curie–Weiss law (i.e. $\chi(T) = (1/8)\mu_{\text{eff}}^2/(T - \theta_p)$) to the experimental data (see the solid lines in the inset to figure 2) yielded for each alloy an effective magnetic moment $\mu_{\text{eff}}$ of about 2.5(1) $\mu_B$ and a paramagnetic Curie temperature $\theta_p$ ranging between $-20(5)$ and $-10(5)$ K. The values of $\mu_{\text{eff}}$ are close to the theoretical Hund’s-rule magnetic moment calculated for a free Ce$^{3+}$ ion (i.e. 2.54 $\mu_B$), pointing to the presence of well localized cerium magnetic moments in all the alloys studied. The negative $\theta_p$ values are in line with antiferromagnetic exchange interactions, and their relatively large absolute values (in comparison to $T_N$) suggest the presence of Kondo interactions in the alloys. Due to significant scatter in the $\theta_p$ values (not shown here), no clear evolution was found in the $\theta_p(x)$ dependence. The deviation of $\chi^{-1}(T)$ from linear behaviour below 100 K can be ascribed to thermal depopulation of the crystalline electric field levels of the cerium ions. Upon increasing $x$, the cusp visible in the $\chi(T)$ of Ce$_{1-x}$Y$_x$NiGe$_3$ at $T_N$ moves towards lower temperatures and significantly broadens. For $x = 0.50$ the maximum is hardly visible in the magnetic susceptibility above 2 K (figure 2).

Figure 3 presents the magnetic properties of the U$_{1-x}$Th$_x$NiSi$_2$ alloys. UNiSi$_2$ orders ferromagnetically at the Curie temperature $T_C = 95$ K (as reported earlier [20]), while its isostructural non-f-electron reference compound ThNiSi$_2$ is a weak Pauli-like paramagnet. At elevated temperatures, the $\chi^{-1}(T)$ curves appeared to have similar shape and to be nearly parallel to each other (see the inset to figure 3). Such a behaviour suggests that the effective magnetic moment of uranium does not change significantly upon increasing $x$, but its exact value cannot be estimated from the Curie–Weiss fits (due to partial delocalization of the 5f-electrons and the crystalline electric field splitting exceeding the temperature range studied). As is apparent in figure 3(a), the initial Brillouin-shaped $\sigma(T)$ curve significantly broadens and flattens upon diluting the magnetic sublattice and $T_C$ defined as the position of the minimum in the temperature derivative of $\sigma(T)$ (figure 3(b)) decreases monotonically with increasing $x$.

3.3. Thermodynamic properties

Figure 4(a) displays the low-temperature variation of the 4f-electron contribution $\Delta C$ to the total specific heat of Ce$_{1-x}$Y$_x$NiGe$_3$, estimated by subtracting the phonon specific heat of YNiGe$_3$ (cf [13]), normalized per mole of cerium...
and divided by $T$. As seen, the antiferromagnetic ordering of CeNiGe$_3$ at $T_N = 5.5$ K manifests itself as a distinct $\lambda$-shaped anomaly in $\Delta C(T)/T$, being in agreement with the previous reports [13, 25]. Upon diluting the Ce-sublattice with Y, the phase transition anomaly significantly broadens and its position (here defined as a minimum in the second derivative $\Delta C(T)/T$; not presented here) moves to 1.35 K for $x = 0.6$. Finally, in the most diluted alloy studied, i.e. Ce$_{0.1}$Y$_{0.9}$NiGe$_3$, only a very weak signature of the phase transition can be found in the temperature derivative of $\Delta C(T)/T$ at about 0.39 K.

Similar behaviour has been found in the temperature dependence of the 5f-electron contribution to the specific heat of CeNiGe$_3$ at $T_N = 5.5$ K [13, 25]. Upon diluting the Ce-sublattice with Y, the phase transition anomaly significantly broadens and its position (here defined as a minimum in the second derivative of $\Delta C(T)/T$; not presented here) moves to 1.35 K for $x = 0.6$. Finally, in the most diluted alloy studied, i.e. Ce$_{0.1}$Y$_{0.9}$NiGe$_3$, only a very weak signature of the phase transition can be found in the temperature derivative of $\Delta C(T)/T$ at about 0.39 K.

Figure 4. The temperature dependence of the non-phononic contribution $\Delta C$ to the total specific heat of selected Ce$_{1-x}$Y$_x$NiGe$_3$ (a) and U$_{1-x}$Th$_x$NiSi$_2$ (b) alloys, normalized per mole of cerium or uranium, respectively, and divided by $T$. The solid lines serve as guides for the eye and the arrows mark the phase transition temperatures from temperature derivatives of $\Delta C(T)/T$.

Figure 5. Increase of the magnetic entropy $\Delta S$ of selected Ce$_{1-x}$Y$_x$NiGe$_3$ (a) and U$_{1-x}$Th$_x$NiSi$_2$ (b) alloys as a function of temperature $T$. The arrows mark the Neel ($T_N$) and Curie ($T_C$) temperatures from $\Delta C(T)/T$ (figure 4).

In the paramagnetic region, the $\Delta S(T)$ curves calculated for both the Ce$_{1-x}$Y$_x$NiGe$_3$ (figure 5(a)) and U$_{1-x}$Th$_x$NiSi$_2$ alloys (figure 5(b)) nearly superimpose onto each other, suggesting that the entropy contributions of the excited crystalline electric field levels are concentration independent in both systems studied. In other words, the crystalline electric fields in Ce$_{1-x}$Y$_x$NiGe$_3$ and U$_{1-x}$Th$_x$NiSi$_2$ are only weakly altered by the dilution of the magnetic sublattices, which is in line with the magnetic properties of the alloys. In the ordered region, in turn, the temperature dependences of the magnetic entropies of both systems strongly vary with $x$. In particular, upon increasing the Y/Th content up to $x = 0.2$, the kinks visible in the $\Delta S(T)$ of CeNiGe$_3$ and UNiSi$_2$ at the respective ordering temperatures move towards lower
temperatures. For larger $x$ the sharp anomalies at $T_{N,C}$ evolve into broad, featureless curves.

4. Discussion

Figure 6 displays tentative magnetic phase diagrams for the Ce$_{1-x}$Y$_x$NiGe$_3$ and U$_{1-x}$Th$_x$NiSi$_2$ alloys, constructed on the basis of the thus far obtained experimental data. The behaviour of both systems is reminiscent of those reported for diluted magnetic alloys [26]. In particular, in the Ce/U-rich parts of the diagrams one can distinguish a dome of long-range magnetic order, followed by a characteristic tail of short-range magnetic order in the diluted limit. These two concentration regimes are separated from each other by the critical concentration $x_c$. The solid lines serve as guides for the eye and the arrows mark the critical concentrations.

The observed evolution of the magnetic properties of the Ce$_{1-x}$Y$_x$NiGe$_3$ and U$_{1-x}$Th$_x$NiSi$_2$ alloys can be roughly explained as resulting from the nature of the indirect-exchange Ruderman–Kittel–Kasuya–Yosida interactions, which are responsible for the onset of magnetic order in metals. Since these interactions are a function of the distance between the localized magnetic moments, the random occupation of the Ce/Y and U/Th sites by the f-electrons leads most probably to the appearance in the most diluted alloys of magnetic clusters of different sizes and ordering temperatures [26]. As a consequence, the observed anomalies in the physical properties studied become more and more blurred with increasing $x$, and $T_{N,C}$ represent the mean ordering temperatures of the particular alloys. Since the size of the clusters remains finite far below the percolation threshold, a characteristic tail in the magnetic phase diagrams is visible (figure 6). The latter hypothesis needs to be verified by further experiments, e.g. AC magnetic susceptibility, neutron diffraction, etc.

5. Summary

The collected experimental data revealed that the dilution of the magnetic sublattices of CeNiGe$_3$ ($T_N = 5.5$ K) and UNiSi$_2$ ($T_C = 95$ K) leads to rapid decrease of their ordering temperatures down to about 1.35 K in Ce$_{0.6}$Y$_{0.4}$NiGe$_3$ and 29 K in U$_{0.7}$Th$_{0.3}$NiSi$_2$. Further decrease of the Ce/U content results in the loss of the long-range character of the magnetic order at finite temperature and in the formation of a characteristic tail in the magnetic phase diagrams. Therefore, no quantum critical phase transition can be observed in the systems studied. The observed evolution of the magnetic behaviour of Ce$_{1-x}$Y$_x$NiGe$_3$ and U$_{1-x}$Th$_x$NiSi$_2$ is characteristic of diluted magnetic alloys. Interestingly, the observed magnetic behaviour exhibits also some similarities to many solid solutions with fully occupied magnetic sublattices (cf [28]). Further experiments are needed to clarify possible relationships between the latter systems and the two solid solutions studied.

Acknowledgments

APP thanks D Kaczorowski for helpful conversations. This work was supported by the Polish Ministry of Science and Higher Education within research grant no. N N202 102338.
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