Journal of Alloys and Compounds 271–273 (1998) 474–478

Incommensurate and ferrimagnetic phases in $U(Ni,M)_2Si_2$ with minor $M=Co$ or Cu

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Abstract

UNi_2Si_2 orders magnetically at 124±1 K in an incommensurate (IC) phase, undergoes transition at 103±1 K to AF-I (+−+−) phase, and then another transition at 53±1 K to a ferrimagnetic (++−) phase. A.c.-susceptibility and neutron-diffraction studies of polycrystalline $U(Ni,M)_2Si_2$ solid solutions, with minor $M=Co$ and Cu ($U(Co_{1-y}Ni_y)_2Si_2$ with $y=0.75$, 0.90, and 0.95, and $U(Ni_{1-z}Cu_z)_2Si_2$, with $z=0.05$, 0.10, and 0.25) confirm an IC phase for $y=0.90$ below 119±2 K down to 105±2 K and suggest (by a.c.-susceptibility only) IC phases below T_N for compositions between $y\approx0.85$ and $z\approx0.05$. The above ferrimagnetic phase is observed at $T\leq12$ K also for compositions between $y\approx0.93$ and $z\approx0.03$. The magnetic phase diagram in the vicinity of UNi_2Si_2 is redrawn and discussed.

Keywords: Neutron diffraction; A.c.-susceptibility; Solid solutions; Uranium compounds; $U(Ni,M)_2Si_2$; Magnetic phase diagrams

1. Introduction

The metallic ternary UM_2X_2 compounds and pseudoternary $U(M,M')_2X_2$ solid solutions ($M,M'=Co$, Ni, Cu; $X=Si$, Ge) crystallize in the body-centered tetragonal $ThCr_2Si_2$-type structure [1]. In the magnetic phase diagrams of these systems [1,2] the magnetic structures of the U atoms depend on the electron concentration due to the (M,M′) site, which does not order magnetically.

UNi_2Si_2 is unique in these systems, having three different magnetic phases, as observed by neutron-diffraction studies on polycrystalline [3] and single-crystal [4] samples. According to the latter study [4], UNi_2Si_2 orders at $T_N=124\pm1$ K in an incommensurate (IC) phase, with a wavevector $\mathbf{k}=(0,0,k_z)$ varying with temperature: k_z is 0.738±0.002 just below T_N, reaches a maximum of 0.748±0.002 in the temperature range 105–109 K, and drops to 0.732±0.002 around $T_{IC}=103\pm1$ K. UNi_2Si_2 undergoes an incommensurate–commensurate magnetic phase transition at T_{IC} to an AF−I (+−+−) phase with $\mathbf{k}=(0,0,1)$, and undergoes another transition at $T_o=53\pm1$ K to a ferrimagnetic (++−) phase with $\mathbf{k}=(0,0,2/3)$. The uranium ordered magnetic moments are aligned along the tetragonal axis in all three phases.

The same ferrimagnetic phase is observed also in other regions of the magnetic phase diagrams of the $U(Ni,Cu)_2X_2$ systems [2], but the IC phase of UNi_2Si_2 has so far been a unique magnetic phase in these systems [2], being an isolated case in the combined magnetic phase diagram $U(Co,Ni)_2Si_2$–$U(Ni,Cu)_2Si_2$ [2].

We have searched for IC and ferrimagnetic phases in $U(Ni,M)_2Si_2$ solid solutions with minor $M=Co$ and Cu (close to UNi_2Si_2), using a.c.-susceptibility and neutron-diffraction measurements. The observation of LT ferrimagnetic phases in the solid solutions $U(Co_{0.05}Ni_{0.95})_2Si_2$ and $U(Ni_{0.95}Cu_{0.05})_2Si_2$ has been initially reported at the ICM'97 [5].

2. Experimental details

Polycrystalline samples of solid solutions $U(Co_{1-y}Ni_y)_2Si_2$ with $y=0.75$, 0.90, and 0.95, and $U(Ni_{1-z}Cu_z)_2Si_2$ with $z=0.05$, 0.10, and 0.25, were prepared at the Nuclear Research Centre–Negev (NRCN) by arc-melting stoichiometric amounts of the constituents in an argon atmosphere, followed by vacuum-annealing at 1023 K for 120 h. The materials were studied by X-ray diffraction at room temperature (RT=295 K) to determine their quality and crystal parameters.

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0925-8388/98/$19.00
PII: S0925-8388(98)00115-7

A.c.-susceptibility measurements on ~300-mg samples were done at NRCN in the temperature range 10–295 K. The a.c. magnetic field was rather weak (<10 Oe). The a.c.-susceptibility values were calibrated with a 50-mg polycrystalline sample of Ho_2O_3, for which χ_M at 293 K is 89×10^{-3} emu/mol (with $\theta=-14$ K and $\mu_{eff}=10.5\ \mu_B$).

Neutron-diffraction measurements on 20-g polycrystalline samples of all materials (in cylindrical aluminum containers) were done initially in the NRCN IRR−2 reactor, with the single-detector diffractometers ($\lambda=240$–245 pm). A DISPLEX (brand name of a closed-cycle helium cooler made by Air Products Inc.) was used for the NRCN measurements down to 12 K. The materials with $y=0.75$ and 0.90 and $z=0.10$ and 0.25 were studied by neutron diffraction also on the G4.1 diffractometer (800 detectors, 0.1° apart) in the Orphée reactor of the Laboratoire Léon Brillouin (LLB) in CEA/Saclay ($\lambda=244.4$ pm). An Orange (ILL)-type cryostat was used for the LLB measurements down to 1.5 K. The neutron diffractograms were analyzed initially with least-squares fits of observed integrated intensities to the calculated ones. The more recent diffractograms were analyzed by the Rietveld profile analysis program [6].

3. Results

The RT X-ray and neutron diffractograms of the above $U(Ni,M)_2Si_2$ materials contain $\{hkl\}$ reflections with $h+k+l=$even, which are consistent with the space group I4/mmm. The intensities of the RT neutron reflections are consistent with the body-centered tetragonal $ThCr_2Si_2$−type crystal structure.

The RT lattice parameters of the six $U(Ni,M)_2Si_2$ solid solutions in the $U(Co_{1-y}Ni_y)_2Si_2$–$U(Ni_{1-z}Cu_z)_2Si_2$ combined magnetic phase diagram in the vicinity of UNi_2Si_2, are determined from the RT diffractograms. The data for UNi_2Si_2 ($y=1$ or $z=0$) have already been published [3,4]. In this compositional region of the combined system, the parameter a (in the range of 394–397 pm) is rather flat, while the parameter c (in the range of 950–960 pm) has a local minimum around UNi_2Si_2.

The a.c.-susceptibility measurements in the temperature range 80–295 K (Fig. 1) revealed: for $y=0.75$ (Fig. 1(a)) a sharp magnetic transition at 117±2 K; for $y=0.90$ (Fig. 1(b)) a broad magnetic transition at 123±8 K; for $y=0.95$ (Fig. 1(c)) two magnetic transitions, a broad one at 122±5 K, and a sharp one at 108±3 K; for $z=0.05$ (Fig. 1(d)) one sharp magnetic transition at 117±3 K and another weaker at 105±3 K; for $z=0.10$ (Fig. 1(e)) one magnetic transition at 129±3 K; and for $z=0.25$ (Fig. 1(f)) one magnetic transition at 155±5 K. All the transitions observed are associated with antiferromagnetic ordering.

The LT neutron diffractograms of these materials, with the exception of those with $y=0.95$ and $z=0.05$, show additional magnetic reflections for which $h+k+l=$odd (such as {010}, {012}, and {111}), indicating ordering of at least the uranium sublattice in the AF−I structure, i.e. with a wavevector $\mathbf{k}=(0,0,1)$ and alternate (+−+−) stacking of ferromagnetic uranium planes along the tetragonal axis. The absence of $\{00l\}$ reflections with odd l, notably {001}, indicates alignment of ordered uranium magnetic moments along this axis.

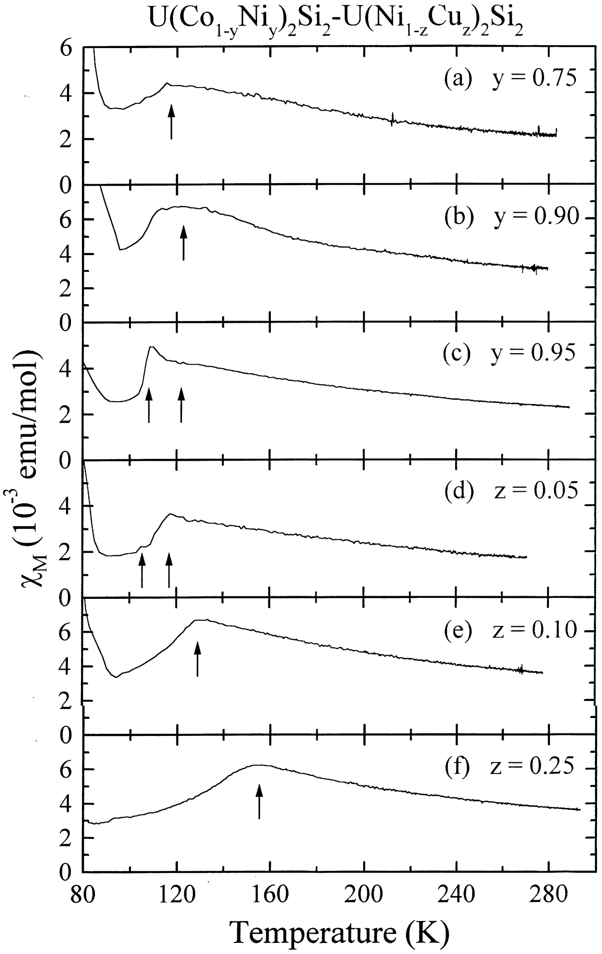

Fig. 1. A.c.-susceptibility curves (with arrows indicating magnetic transitions) in the temperature range 80–295 K of the solid solutions: (a) $U(Co_{0.25}Ni_{0.75})_2Si_2$, depicting one transition at 117±2 K; (b) $U(Co_{0.10}Ni_{0.90})_2Si_2$, depicting one transition at 123±8 K; (c) $U(Co_{0.05}Ni_{0.95})_2Si_2$, depicting two transitions at 122±5 and 108±3 K; (d) $U(Ni_{0.95}Cu_{0.05})_2Si_2$, depicting two transitions at 117±2 and 105±3 K; (e) $U(Ni_{0.90}Cu_{0.10})_2Si_2$, depicting one transition at 129±3 K; (f) $U(Ni_{0.75}Cu_{0.25})_2Si_2$, depicting one transition at 155±5 K. The rise in some curves below ~90 K is due to experimental limitation of the apparatus. However, contributions of LT ferrimagnetic phases cannot be excluded.

For the solid solution with $y=0.95$, the LT neutron diffractogram shows additional magnetic reflections which can be indexed as $\{hk[l\pm(2/3)]\}$ satellites of the nuclear $\{hkl\}$ reflections, indicating ordering of at least the uranium sublattice in a ferrimagnetic structure, i.e. with a wavevector $\mathbf{k}=(0,0,2/3)$ and (++−) stacking of ferromagnetic uranium planes along the tetragonal axis. The absence of $\{00[l\pm(2/3)]\}$ reflections with even l, notably {00(2/3)} and {00(4/3)}, indicates alignment of ordered uranium magnetic moments (1.75±0.11 μ_B at 12 K) along the tetragonal axis. This ferrimagnetic structure exists below T_o=50±4 K, above which the material orders in the AF−I structure with uranium moment of 1.71±0.12 μ_B at 65 K [5]. The ferrimagnetic structure is similar to the one obtained earlier in UNi_2Si_2 [3].

For the solid solution with z=0.05, the LT neutron diffractogram shows two sets of additional magnetic reflections, corresponding to coexisting AF−I (major) and ferrimagnetic (minor) phases. The relative proportions of 70:30 at 12 K were determined by the Rietveld profile analysis [6]. The ordered uranium magnetic moments (1.79±0.15 μ_B at 12 K) are along the tetragonal axis in both phases. Above 37±5 K the material has only AF−I structure with uranium moment of 1.90±0.10 μ_B at 70 K [5].

The ferrimagnetic phase extends at $T \leq 12$ K between the compositions $y \approx 0.93$ and $z \approx 0.03$. This phase forms an enclave in an AF−I region in the combined magnetic phase diagram [5].

Neutron diffractograms for y=0.90 are shown in Fig. 2. The diffractogram at 140 K depicts only nuclear reflections, which indicate a paramagnetic state. The diffractogram at 113 K depicts several additional magnetic reflections, which are not consistent with the AF−I structure. The additional reflections are identified as the $\{hk(l \pm k_z)\}$ satellites of the nuclear $\{hkl\}$ reflections, which are indexed as $\{01(1-k_z)\}$, $\{01(1+k_z)\}$, $\{01(3-k_z)\}$, $\{11(0 \pm k_z\}$, and $\{11(2-k_z)\}$. Except for the first reflection, $\{01(1-k_z)\}$, which is close in position to the {010} reflection of the AF−I phase, all other reflections are quite distinct from those of the AF−I phase. The wavevector $\mathbf{k}=(0,0,k_z)$ is indicative of an incommensurate (IC) phase, with k_z varying slightly with temperature, from 0.795±0.003 at 116 K to 0.803±0.003 at 107 K. The absence of $\{00(l \pm k_z)\}$ satellites, notably $\{00k_z\}$, indicates alignment of the ordered magnetic moments along the tetragonal axis. In the diffractogram at 107 K the IC magnetic phase coexists with traces of the AF−I phase. The temperature variation of k_z in the IC phase is weaker than the variation observed in UNi_2Si_2 [4]. The IC ordered magnetic moment cannot be determined accurately from the rather small powder reflections, due to the small temperature existence range of the IC phase, and its proximity to the ordering temperature T_N. The diffractograms at 104 and 1.5 K indicate the existence of the AF−I phase. Based on these diffractograms and others at intermediate temperatures (not shown in Fig. 2), we conclude that in this material there are two magnetic transitions, one at T_N=119±2 K, from the paramagnetic to the IC phase, and another one, incommensurate–commensurate transition, at T_{IC}=105±2 K, from the IC to the AF−I phase. This two-transition situation is not evident in the a.c.-susceptibility results (Fig. 1(b)), which depict only one broad transition at 123±8 K. The ordered magnetic moment of uranium in the AF−I phase of the solid solution $U(Co_{0.10}Ni_{0.90})_2Si_2$ is included in Table 1.

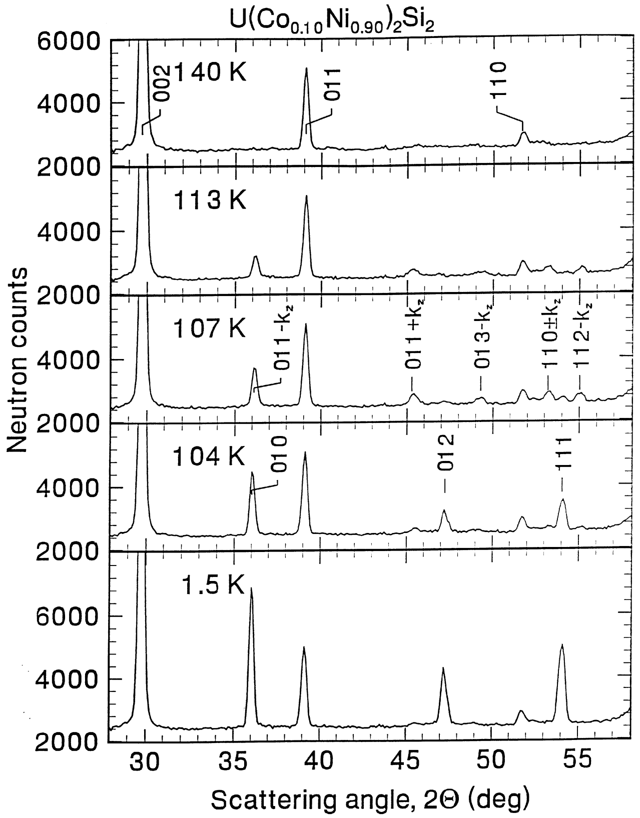

Fig. 2. Neutron (λ=242.49 pm) diffractograms of $U(Co_{0.10}Ni_{0.90})_2Si_2$ at 140 K (paramagnetic state), 113 K (IC phase), 107 K (IC phase, k_z=0.803±0.003, with traces of the AF−I phase), 104 K (AF−I phase), and 1.5 K (AF−I phase).

4. Discussion

Although no neutron diffraction measurements are available for y=0.95 and z=0.05 close to T_N, an incommensurate phase below T_N is probable for y=0.95 and perhaps also for z=0.05. It is therefore suggested that IC phases extend between the compositions $y \approx 0.85$ and $z \approx 0.05$.

The failure of the NRCN neutron measurements to observe an IC magnetic phase in $U(Co_{0.10}Ni_{0.90})_2Si_2$ (y=0.90) and in the new compositions (y=0.95 and z=0.05) is related to lower sensitivity (as compared with the LLB measurements) and to proximity of the {010} and $\{01(1-k_z)\}$ reflections, which are rather small at temperatures close to T_N.

The neutron-diffraction results for the materials of the $U(Co_{1-y}Ni_y)_2Si_2$–$U(Ni_{1-z}Cu_z)_2Si_2$ combined system, searched in the present study, as well as data of UNi_2Si_2 [4], including ordering temperature (T_N), transition temperatures (T_{IC}, T_o), types of ordering, and uranium ordered

Table 1
Neutron-diffraction results for the materials of the $U(Co_{1-y}Ni_y)_2Si_2$–$U(Ni_{1-z}Cu_z)_2Si_2$ combined system, studied in the present work: ordering temperature (T_N), transition temperatures (T_{IC}, T_o), type of ordering below each respective transition, and uranium ordered magnetic moment (m) at LT≤12 K (v% denotes the relative partial volume at LT)

Material	T_N (K)	Order below T_N	T_{IC} (K)	Order below T_{IC}	T_o (K)	Order below T_o(v%)	m at LT≤12 K (μ_B)
$y=0.75$	117±2	AF-I	—	—	—	—	1.86±0.08
$y=0.90$	119±2	IC	105±2	AF-I	—	—	1.84±0.06
$y=0.95$	122±5[a]	IC	108±3[a]	AF-I	50±4	Ferri	1.75±0.11
UNi_2Si_2[b]	124±1	IC	103±1	AF-I	53±1	Ferri	2.2±0.3
$z=0.05$	117±5[a]	IC	105±3[a]	AF-l	37±5	Ferri (30%)	1.79±0.15[c]
$z=0.05$	117±5[a]	IC	105±3[a]	AF-I	—	AF-I (70%)	1.79±0.15[c]
$z=0.10$	135±5	AF-l	—	—	—	—	1.94±0.08
$z=0.25$	151±3	AF-l	—	—	—	—	2.2±0.2

[a] Only a.c.-susceptibility measurements available.

[b] Single-crystal neutron diffraction data (from Ref. [4]).

[c] $m=(m_1^2+m_2^2)^{1/2}$, deduced from LT moments $m_1=0.99\pm0.21$ μ_B (Ferri) and $m_2=1.49\pm0.11$ μ_B (AF-I), assuming that the respective phases are spread out over the entire volume.

magnetic moment at LT≤12 K, are summarized in Table 1. We note that the LT ordered magnetic moments of the six solid solutions investigated (≈1.9 μ_B), are close to those in UNi_2Si_2.

Incommensurate (IC) magnetic phases are rather scarce among metallic uranium compounds, but are somewhat more frequent in uranium-based solid solutions. This is the case of the NaCl-type uranium monopnictides and monochalcogenides which order in commensurate magnetic structures, but their solid solutions, such as $UP_{1-x}S_x$ [7] and $UAs_{1-x}Se_x$ [8], contain several IC magnetic phases. IC magnetic phases are more commonly found in analogous monopnictides and monochalcogenides of the transuranium elements, as observed, for example, in NpAs [9]. UNi_2Si_2 with its IC magnetic phase is a rare example among uranium compounds. The existence of an IC magnetic phase in $U(Co_{0.10}Ni_{0.90})_2Si_2$ is therefore quite reasonable as an extension of the IC phase of UNi_2Si_2, but the narrow range of such a phase, from $y\approx0.85$ to $z\approx0.05$, is rather unusual.

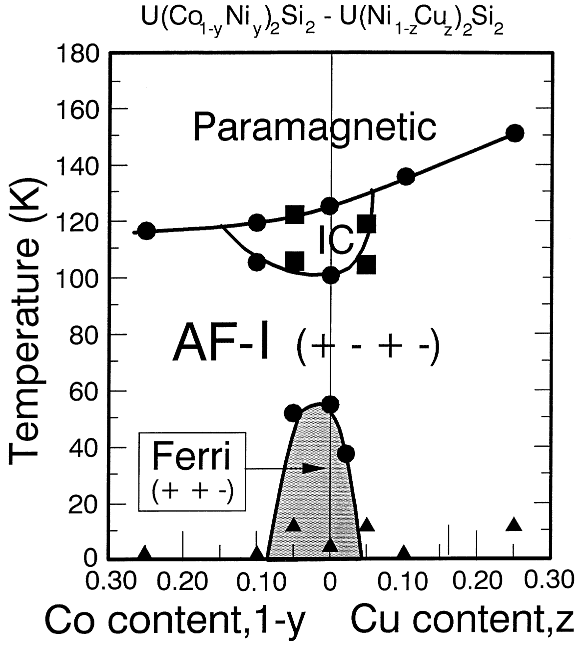

Fig. 3. The region of the magnetic phase diagram of the $U(Co_{1-y}Ni_y)_2Si_2$–$U(Ni_{1-z}Cu_z)_2Si_2$ combined system around UNi_2Si_2, for cobalt content ($1-y$) and copper content (z) up to 0.30. Circles: transition temperatures based on neutron diffraction and a.c.-susceptibility; Squares, transition temperatures based only on a.c.-susceptibility; triangles, lowest temperatures of neutron-diffraction measurements.

In Fig. 3 we have redrawn (compared to Ref. [2]) the magnetic phase diagram of the combined $U(Co_{1-y}Ni_y)_2Si_2$–$U(Ni_{1-z}Cu_z)_2Si_2$ system in the region around UNi_2Si_2, according to the present results. This diagram amends slightly the combined magnetic phase diagram published recently [2], regarding the IC phase below T_N and the LT ferrimagnetic phase. The ferrimagnetic enclave around UNi_2Si_2 is quite unique, being surrounded completely by the AF−I phase.

The appearance of the ferrimagnetic (++−) phase is therefore not confined only to UNi_2Si_2, as known before the present study, and is found to exist in the composition range between $y\approx0.93$ to $z\approx0.03$, with an intermediate composition of existence at $y\approx0.98$. The RKKY-like interactions, that give rise to the various magnetic structures in the $U(M,M')_2X_2$ systems [2], will probably account for the abrupt appearance and disappearance of the ferrimagnetic phase upon minor change in the number of conduction electrons in compositions in the vicinity of UNi_2Si_2 [3].

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