PHYSICAL REVIEW B VOLUME 51, NUMBER 22 1 JUNE 1995-II

Occasional appearance of antiferromagnetism in mainly ferromagnetic samples of UCu_2Si_2

Moshe Kuznietz, Haim Pinto, and Mordechai Melamud
Nuclear Research Centre-Negev, P. O. Box 9001, 84190 Beer-Sheva, Israel

(Received 7 February 1995)

UCu_2Si_2 was found by neutron diffraction and magnetization measurements to order ferromagnetically below $T_C=103\pm3$ K. The appearance of antiferromagnetism just above T_C in certain samples of UCu_2Si_2, as suggested by dc and ac susceptibility, is attributed to minor substoichiometry on the copper sublattice, a view supported by our neutron-diffraction study of the magnetic phase diagram of the $U(Ni_{1-x}Cu_x)_2Si_2$ system, with emphasis on the recently prepared solid solution $U(Ni_{0.15}Cu_{0.85})_2Si_2$.

The magnetic properties of the ternary compound UCu_2Si_2 were determined previously[1-8] on different polycrystalline samples (denoted 1–8, similar to the respective reference numbers) by dc- and ac-susceptibility and neutron-diffraction measurements. In these studies UCu_2Si_2 was prepared by induction[1] or arc[2-7] melting, or by casting.[8] All arc-melting preparations were followed by annealing in vacuum in the temperature range of 773–1173 K for 96–700 h. The various preparation conditions are listed in Table I. The polycrystalline UCu_2Si_2 samples were found by x-ray and neutron diffraction to crystallize in the body-centered-tetragonal $ThCr_2Si_2$-type structure (space group $I4/mmm$),[1-7] discovered initially by Ban and Sikirica.[9] The types of magnetic measurements and reported ordering and transition temperatures of the various UCu_2Si_2 samples are summarized in Table I.

The neutron-diffraction studies[1,5,6] on polycrystalline samples of UCu_2Si_2 reveal ferromagnetic (F) ordering of the uranium magnetic moments, aligned along the tetragonal axis, below $T_C=103\pm3$ K. The uranium ordered moment at 4.2 K is reported to be either $1.61\pm0.05\mu_B$ (Ref. 1) or $2.0\pm0.1\mu_B$ (Ref. 5), with no observation of antiferromagnetism above (or below) T_C.[6] However, in the published results compiled in Table I we see occasional appearances of antiferromagnetism in mainly ferromagnetic samples of UCu_2Si_2.

TABLE I. Preparation conditions, types of magnetic measurements [dc- and ac-susc(eptibility), neutron (diffraction)] and reported transition temperatures of polycrystalline samples of UCu_2Si_2.

Sample number (=Ref. No.)	Preparation conditions			Type of magnetic measurement	T_N (K)	T_C (K)
	Fabrication method	Annealing				
		T (K)	t (h)			
1	Induction	None		dc-susc	None	107
				neutron	None	103
2	Arc melt	1073	>500	dc-susc	None	100
3	Arc melt	1073	120	dc-susc	None	101
4	Arc melt	1173	120	dc-susc	None	105
		773	700			
5	Arc melt	1073	120	Neutron	None	(?)
6	Arc melt	1173	168	dc-susc	≈107	≈103
				neutron	none	103
7	Arc melt	1173	96–168	ac-susc	104	≈97
8	Casting	None		dc-susc	110	102

The susceptibility measurements on samples 1–5 of UCu_2Si_2 confirm the ferromagnetism observed by neutron diffraction, with different ordering temperatures, in the 97–107 K range. However, (dc-, ac-, dc-)susceptibility measurements on samples 6,7,8, respectively, reveal the appearance of antiferromagnetism just above T_C. The rather small peak[6] of the dc susceptibility observed in sample 6 suggests an antiferromagnetic (AF) phase in the temperature range 103–107 K, that could not be corroborated by neutron diffraction. The AF ordering in sample 7 in the temperature range 97–104 K, seen as a tiny peak of the ac susceptibility [Fig. 1(b)], and the paramagnetic-to-AF transition at 110 K observed in sample 8 by dc susceptibility, are similar in nature to those in sample 6.

The appearance of antiferromagnetism in certain UCu_2Si_2 samples can be inferred from our investigations of the pseudoternary $U(Ni_{1-x}Cu_x)_2Si_2$ system by x-ray and neutron diffraction and ac susceptibility.[10-12] In these studies polycrystalline samples of the $U(Ni_{1-x}Cu_x)_2Si_2$ solid solutions have been prepared by arc melting of stoichiometric amounts of the constituents in an argon atmosphere, followed by annealing in vacuum at 1023 K for 120 h. The solid solutions crystallize in the $ThCr_2Si_2$-type structure, as do the end compounds UNi_2Si_2 and UCu_2Si_2.[9]

As the copper content varies in the $U(Ni_{1-x}Cu_x)_2Si_2$ system, so does the number of conduction electrons in these metallic materials, affecting the magnetic properties via Ruderman-Kittel-Kasuya-Yosida (RKKY)-like interactions. The oscillatory variation[12] of the paramagnetic Curie temperature (θ) with the copper content (x) is an indication for such behavior. The variations of the magnetic structure and ordering temperature in this system[11,12] are also indicative of the RKKY-like behavior.

In the copper-rich side ($0.50\leq x\leq1$) of the magnetic phase diagram of the $U(Ni_{1-x}Cu_x)_2Si_2$ system[11,12] (see Fig. 2) the ordering temperature decreases from 150 K for $x=0.50$, through 115 K for $x=0.75$, down to 103 K

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for $x=1$. Particularly, in our U$(\mathrm{Ni}_{0.25}\mathrm{Cu}_{0.75})_2\mathrm{Si}_2$ sample, with nominal $x=0.75$, three commensurate magnetic structures are observed,[11] involving variable stacking of ferromagnetic basal planes (i.e., different **k** wave vectors), with uranium moments aligned along the tetragonal axis. These magnetic structures (with sequence of stacking and **k** wave vectors) and their ascribed copper contents and ordering temperatures are

$$\text{AF-I}\ (+-+-)\ ,\ \mathbf{k}=(0,0,1)\ ,\ x<0.75\ ,\ T_N=120\pm3\ \text{K};$$

$$\text{ferrimagnetic}\ (++-)\ ,\ \mathbf{k}=(0,0,2/3)\ ,\ x\approx0.75\ ,\ T_N=115\pm4\ \text{K};$$

$$\text{AF-IA}\ (++--)\ ,\ \mathbf{k}=(0,0,1/2)\ ,\ x>0.75\ ,\ T_N=110\pm3\ \text{K};$$

occupying ≈ 40, ≈ 20, and $\approx 40\,\%$ of the sample volume, respectively.

Furthermore, we have recently prepared the U$(\mathrm{Ni}_{0.15}\mathrm{Cu}_{0.85})_2\mathrm{Si}_2$ solid solution (nominal $x=0.85$), which also crystallizes in the $\mathrm{ThCr}_2\mathrm{Si}_2$-type structure. Our neutron-diffraction results show that it orders mainly ($\approx 93\%$ of the sample volume) in the AF-IA structure below $T_N=110\pm5$ K and down to ≈ 10 K, while the other 7% order ferromagnetically. This result is corroborated by our ac-susceptibility measurements, done from 80 K up to RT [see partial curve in Fig. 1(a)], which show an AF peak at $T_N=108\pm5$ K. An additional F peak is seen in the ac-susceptibility curve at $T_C=95\pm5$ K, arising from smaller parts of the sample. As a comparison, the ac-susceptibility curve of sample 7 of $\mathrm{UCu}_2\mathrm{Si}_2$ is shown in Fig. 1(b).

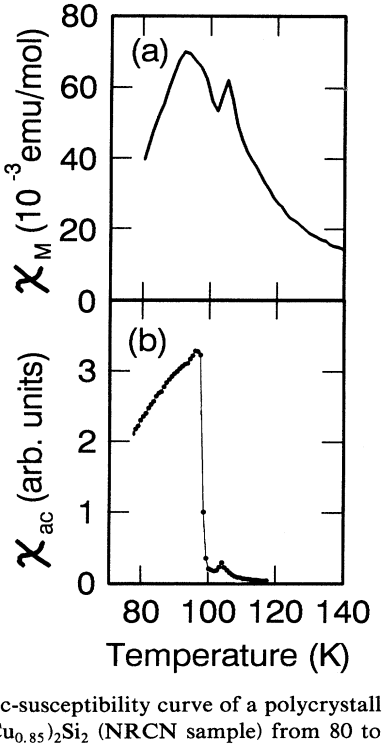

FIG. 1. Ac-susceptibility curve of a polycrystalline sample of (a) U$(\mathrm{Ni}_{0.15}\mathrm{Cu}_{0.85})_2\mathrm{Si}_2$ (NRCN sample) from 80 to 140 K, indicating AF-IA ordering at $T_N=108\pm5$ K and F ordering at $T_C=95\pm5$ K. This sample is paramagnetic above T_N all the way up to RT. (b) $\mathrm{UCu}_2\mathrm{Si}_2$ (sample 7) from 77 to 118 K (taken from Ref. 7), indicating AF ordering at $T_N=104$ K, and F ordering at $T_C=97$ K.

This result indicates that the AF-IA region of the magnetic phase diagram of the U$(\mathrm{Ni}_{1-x}\mathrm{Cu}_x)_2\mathrm{Si}_2$ system extends up to $x\approx 0.90$, and that already at nominal $x\geq 0.85$ the ferromagnetic phase of the Cu-rich end is observed even in well-annealed samples. Similar effects are found in the U$(\mathrm{Ni}_{1-x}\mathrm{Cu}_x)_2\mathrm{Ge}_2$ system[13,14] and in its end compound $\mathrm{UCu}_2\mathrm{Ge}_2$, the latter adopting the AF-IA structure at low temperatures in several samples.[14,15]

Coexistence of several magnetic structures in wide temperature ranges, up to the entire ordered state, can occur in solid-solution systems for certain nominal compositions, in complex regions of their magnetic phase diagrams. This is an inherent property of solid solutions, either polycrystalline or single-crystal materials, due to the existence of finite composition ranges around nominal compositions, throughout the samples. Such composition ranges can even cross magnetic-structure boundaries. Examples for this situation are the NaCl-type systems[16,17] $\mathrm{UAs}_{1-x}\mathrm{Se}_x$ and $\mathrm{UP}_{1-x}\mathrm{S}_x$, discussed in Ref. 11 in connection with U$(\mathrm{Ni}_{0.25}\mathrm{Cu}_{0.75})_2\mathrm{Si}_2$.

Prior to the measurements on the recently prepared sample with $x=0.85$, the magnetic phase diagram of the U$(\mathrm{Ni}_{1-x}\mathrm{Cu}_x)_2\mathrm{Si}_2$ system had a complex region in the vicinity of $x=0.75$, with the AF-I structure for $x<0.75$ (extending also to the lower copper contents of $x=0.50$ and $x=0.25$), AF-IA structure for $x>0.75$, and ferrimagnetic $(+\ +\ -)$ structure in a narrow x range

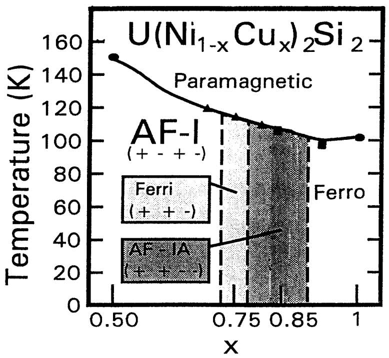

FIG. 2. The copper-rich side ($0.5\leq x\leq 1$) of the magnetic phase diagram (temperature *versus* composition) of the U$(\mathrm{Ni}_{1-x}\mathrm{Cu}_x)_2\mathrm{Si}_2$ system. The boundaries between phases are approximate, and so are the positions of the transitions into the coexisting phases in the samples with nominal $x=0.75$ (three transitions at 120, 115, and 110 K, triangles) and $x=0.85$ (two transitions at 108 and 95 K, squares).

($x \approx 0.75$) in between.[11,12] The magnetic behavior of our recently prepared solid solution $U(Ni_{0.15}Cu_{0.85})_2Si_2$ is compatible with the already published[12] magnetic phase diagram of the $U(Ni_{1-x}Cu_x)_2Si_2$ system. In the amended version of this diagram (Fig. 2) the composition range of the AF-IA structure is extended up to $x \approx 0.90$, beyond which the system is ferromagnetic, as exhibited by stoichiometric UCu_2Si_2.

According to this model the substitution of a small number of atoms ($\approx 10\%$) on the copper sublattice in UCu_2Si_2 by nickel atoms would lead to the appearance of the AF-IA structure in large parts of the sample (but less than 93% found in the sample with nominal $x = 0.85$), with an ordering temperature slightly higher than in stoichiometric UCu_2Si_2. In ac-susceptibility measurements of such a $U(Ni_{1-x}Cu_x)_2Si_2$ sample (with nominal $x = 0.90$) the relative size of the AF-IA and F peaks is expected to change with respect to the sample with $x = 0.85$, shown in Fig. 1(a): The AF-IA peak would decrease while the lower-temperature F peak would increase. This inversion of ac-susceptibility peaks is expected to end with the disappearance of the AF-IA peak in stoichiometric UCu_2Si_2.

Rather minor substoichiometry on the copper sublattice, expected in the absence of annealing (as in sample 8) or in cases of insufficient annealing (as, perhaps, in samples 6 and 7), leads to a decrease in the number of conduction electrons, equivalent to the decrease upon a much larger replacement of copper by nickel, as discussed above. It is this substoichiometry that allows certain parts of samples 6 and 8 of UCu_2Si_2 to order in an AF structure at slightly higher temperatures, with the resulting small AF peaks in the ac-susceptibility curves [Fig. 1(b)]. Such small AF parts of the samples, with small ordered moments at the temperature ranges close to their respective ordering temperatures (T_N), cannot be detected in powder neutron-diffraction measurements.[6]

The crucial role of annealing has been shown in the parallel UCo_2Ge_2 compound.[18,19] Annealed samples crystallize in the $ThCr_2Si_2$-type structure and order in the AF-I structure below $T_N = 175 \pm 5$ K,[18,19] while samples prepared without annealing crystallize in a lower symmetry structure (perhaps of $CaBe_2Ge_2$-type) and do not order magnetically.[19]

We suggest that improved annealing conditions can reduce the extent of substoichiometry in the compound UCu_2Si_2 and the composition range in the solid $U(Ni_{0.25}Cu_{0.75})_2Si_2$ and $U(Ni_{0.15}Cu_{0.85})_2Si_2$, thereby reducing the number of coexisting magnetic structures. The preparation of UCu_2Si_2 samples with controlled (nominal) substoichiometric amounts of copper (1–2 %) can enhance the AF parts of these samples.

We thank Hanania Ettedgui for the sample preparation and help with the measurements.

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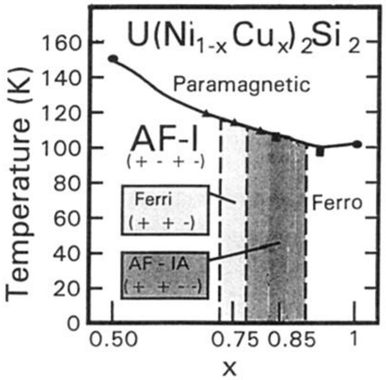

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