Structural properties and magnetic structure of the heavy-fermion compound UCu$_5$Sn

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Abstract. The heavy-fermion compound UCu$_5$Sn has been studied by means of neutron powder diffraction. This compound exhibits the hexagonal CeNi$_5$Sn-type structure with space group $P6_3/mmc$. We have determined the lattice parameters and atomic positions at room temperature, using a high-resolution diffractometer. The neutron diffraction diagrams were also measured at various temperatures between 1.4 and 61 K, using an 800-cell position-sensitive diffractometer. The observed minimum in the unit-cell volume at temperature of 30 K, being rather far below the magnetic ordering one ($T_C = 53$ K), may suggest a change in the strength of the 5f–conduction electron hybridization which probably takes place at low temperatures. It was found that the magnetic phase transition at T_C corresponds to the onset of a ferrimagnetic order. The magnetic structure is characterized by forming the ferromagnetic planes (001) with the $(+ - + -)$ stacking sequence, where the U moments are oriented parallel to the hexagonal c-axis. However, the size of the U moments arranged in the $z = 0$ plane (M_{U1}), and formed by the sites 2(a), is substantially larger than these arranged in the adjacent $z = \frac{1}{4}$ plane (M_{U2}), and formed by the sites 2(c). At 1.4 K, they are $M_{U1} = 2.14(2)$ μ_B/atom U and $M_{U2} = 0.18(4)$ μ_B/atom U. We discuss several mechanisms leading to a reduction of the magnetic moment at the one site compared to the other one.

1. Introduction

The discovery of heavy-fermion properties in the orthorhombic CeCu$_6$ system [1] and the non-Fermi-liquid (NFL) behaviour in its solid solutions CeCu$_{6-x}$Au$_x$ around $x \approx 0.1$ [2] has inspired us to investigate uranium-based compounds with similar stoichiometry and crystal structure. Along this direction, we have recently discovered three new, intermetallic uranium-based compounds UCu$_5$M, (M = Al, In and Sn), which show an enhanced linear specific heat coefficient $\gamma(0)$. The $\gamma(0)$-value was found to be 180 mJ K^{-2} mol^{-1} for UCu$_5$Al [3], 210 mJ K^{-2} mol^{-1} for UCu$_5$In [4] and 330 mJ K^{-2} mol^{-1} for UCu$_5$Sn [5] all at $T = 0.4$ K. Surprisingly, each of these compounds crystallizes in the different crystal structure. UCu$_5$Al possesses a tetragonal structure [6] of own type, UCu$_5$In adopts the orthorhombic CeCu$_5$Au type [7] while UCu$_5$Sn crystallizes in the hexagonal structure of CeNi$_5$Sn type [5, 8].

In this work, we shall focus on the structural properties and magnetic structure of UCu$_5$Sn. Previously, except for the single-crystal x-ray refinement of crystal structure

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[8], this compound has also been studied by means of ac and dc magnetic susceptibility, magnetization, electrical resistivity, magnetoresistance and specific heat measurements [5]. All these measurements indicate that UCu_5Sn is a heavy-fermion compound, which undergoes transition into magnetically ordered state at $T_C = 53.5$ K. The occurrence of the strongly correlated electron state observed in this compound at low temperatures is believed to be associated with the Kondo-type interactions with the Kondo temperature $T_K = 15$ K in the presence of the crystalline electric field effect. Here, we will prove that the magnetic transition at T_C is due to the onset of a ferrimagnetic order, which is caused by the presence in the unit cell of two different U sublattices. The other striking result is the presence of an anomalous temperature dependence of the lattice parameters observed below T_C.

2. Experiment

The sample being about 15 g was synthesized by arc-melting stoichiometric mixtures of high-purity elements (U—3 N, Cu—4 N, Sn—5 N) in an argon atmosphere. The resulting buttons were wrapped in Ta foil, sealed in evacuated quartz ampoules and then annealed at $800\,^{\circ}$C for two weeks. After annealing the buttons were ground into fine powder under an argon atmosphere. The quality of the sample was checked by x-ray diffraction and microprobe analysis. The results indicate a single phase and that its composition corresponds to the nominal concentration.

Neutron diffraction measurements were performed at the Orphée reactor at Laboratoire Léon Brillouin, Saclay. For crystal structure determination the 3T2 diffractometer ($\lambda = 1.227$ Å) was used at room temperature. The collected data allow us to refine crystallographic parameters, using the Rietveld-type FULLPROF program [9]. The scattering lengths employed in the refinement were taken from [10]. The shape of the Bragg peaks was described by a four-term pseudo-Voigt function. The low-temperature measurements were performed on G4.1 diffractometer ($\lambda = 2.426$ Å) at nine temperatures between 1.4 and 61 K to determine the lattice parameters versus temperature. The magnetic structure of UCu_5Sn was refined from the difference of diagrams collected below and above the ordering temperature. In this case, a magnetic form factor of U^{3+}, calculated in the dipolar approximation by Freeman *et al* [11], was used.

3. Results

3.1. Structural properties

Figure 1 shows the neutron diffraction pattern of UCu_5Sn collected at room temperature. Apart from the observed intensities (open circles), we show also the best fit (solid line) and the difference between the calculated and observed intensities (solid line at the bottom of the figure). The vertical bars refer to calculated reflection positions. All Bragg peaks could be indexed based on the hexagonal unit cell with the lattice parameters $a = 4.9837(2)$ and $c = 20.2944(9)$ Å at room temperature.

Previously, based on x-ray diffraction refinements on a single crystal of UCu_5Sn, the crystal structure of this compound has been found to have a hexagonal unit cell with the space group $P6_3/mmc$ [8]. There are four uranium atoms per unit cell occupying two inequivalent U sites: two atoms U1 occupy the 2(a) sites, while the remaining two atoms U2 locate the 2(c) sites. There are as many as 20 Cu atoms being distributed respectively on the 12(k), 4(f), 2(d) and 2(b) sites. The four Sn atoms are located on the 4(f) sites. Thus, UCu_5Sn belongs to the hexagonal $CeNi_5Sn$-type structure reported by Skolozdra *et al* [12] from x-ray study.
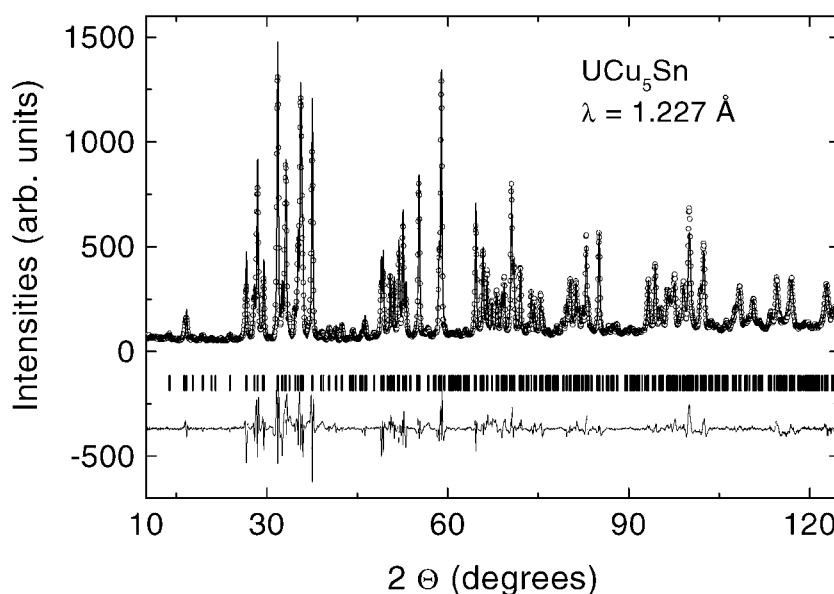
Figure 1. Observed and calculated powder diffraction patterns of UCu₅Sn at room temperature ($\lambda = 1.227$ Å). The open circles represent the experimental points, the solid lines the calculated profile. The difference between observed and calculated profiles is shown at the bottom of the figure.

However, Moze *et al* [13] have recently claimed on the basis of powder neutron diffraction results that the Sn atoms in the unit cell of CeNi₅Sn are distributed randomly among the 4(f) and 12(k) sites. Therefore, in order to check such a possibility, we have taken into account two alternative models of the crystal structure of UCu₅Sn: one corresponding to the ordered and the other to the random distribution of the Cu and Sn atoms in the unit cell, respectively.

With the help of the ordered model, the refinement with 300 reflections for a maximum of 16 parameters (containing the scale factor, lattice parameters, positions of the atoms, isotropic temperature factors) converged to a reasonable level. This yields a good agreement between the observed and calculated intensities ($R_B < 5.8\%$) and diffraction profiles ($R_f < 5.5\%$). The refinement of the disordered model with as many as 18 free parameters, containing the occupancy parameters of Cu and Sn atoms over the 4(f) and 12(k) sites as additional parameters, gave no distinct improvement compared with the previous refinement. Therefore, we have chosen the ordered crystal structure as the proper one for the UCu₅Sn compound.

The refined structural parameters of UCu₅Sn are collected in table 1 and the interatomic distances in table 2. These parameters are in excellent agreement with previous x-ray single-crystal data [8].

It follows from the crystal structure shown in figure 2(a) that the network of the U1 atoms is formed in the $z = 0$ plane, while that of the U2 atoms is formed in the $z = 0.25$. Interestingly, in each sublattice the central U atom has six nearest U neighbours in the *ab* plane at the distance $d_{U-U} = 4.984$ Å. This is much shorter than the distance between the U1 and U2 atoms in different sublattices ($d_{U1-U2} = 5.833$ Å). Both U1 and U2 form a similar U sublattice and their coordination number (CN) is 18 and 20, respectively (figure 2(b)). However, the difference is evident in the interatomic distances inside each coordination polyhedron. The mean interatomic distance towards the central U2 atoms, $d_{U-ligand}$, is about 0.07 Å smaller,

Table 1. Structural parameters of UCu_5Sn at $T = 297$ K. The space group is $P6_3/mmc$ and lattice parameters are: $a = 4.9837(2)$, $c = 20.2944(9)$ Å.

Atom	Position	x	y	z	B (10^{-2} Å)
U1	2a	0	0	0	1.03(8)
U2	2c	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.07(6)
Cu1	12k	0.8335(8)	0.3329(8)	0.1468(2)	0.57(3)
Cu2	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.5433(2)	0.92(6)
Cu3	2d	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	0.38(8)
Cu4	2b	0	0	$\frac{1}{4}$	0.29(9)
Sn	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.0855(2)	0.32(6)

Table 2. Interatomic distances and coordination numbers in UCu_5Sn.

	Interatomic distances (Å)
U1–6Cu	2.994
6Cu	3.323
6Sn	3.335
U2–6Cu	2.873
6Cu	3.249
6Cu	3.249
2Sn	3.373
Cu–2U	3.249
1U	3.323
2Cu	2.418
1Cu	2.513
1Cu	2.551
3Cu	2.558
2Sn	2.800
Cu–3U	2.994
3Cu	2.551
3Cu	3.331
1Sn	2.535
3Sn	2.997
Cu–3U	2.873
6Cu	2.513
3Cu	2.873
Cu–3U	2.873
6Cu	2.558
3Cu	2.873
Sn–3U	3.335
1U	3.373
1Cu	2.535
6Cu	2.800
3Cu	2.997

compared to that in the case of U1. On this basis one may expect a stronger coupling between the 5f electrons and those of surrounding ligands in the case of the U2 polyhedron. In other words, the interactions between those atoms in these two uranium sites may lead in consequence
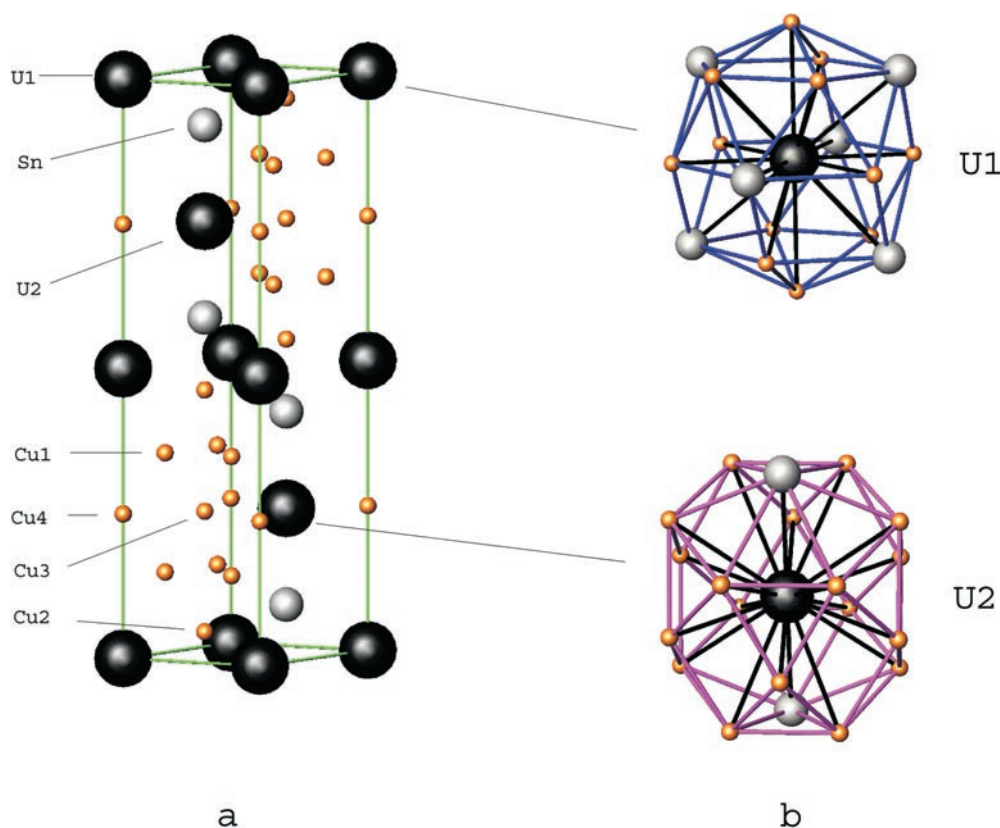
Figure 2. (a) Crystal structure of UCu$_5$Sn with (b) coordination polyhedra of U1 and U2 atoms.

to their different behaviour. This may suggest that there appears some difference either in the valence of uranium ions and/or in the local density of conduction electrons around the U1 and U2 atoms.

Upon decreasing temperature the a and c parameters decrease steadily, as shown in figure 3. There is seen only a weak anomaly near T_C. Within the experimental error we found a pronounced minimum in the dependence of the lattice parameters around $T_{min} = 30$ K, i.e. relatively far below the ordering temperature of 53.5 K. At present, the origin of this anomaly is not quite clear. This appears to be somewhat correlated with the temperature dependence of the electrical resistivity [5], where below T_{min} the resistivity increases logarithmically with decreasing temperature. The observed increase in the unit-cell volume with decreasing temperature below T_{min} may be caused by a change in the hybridization of the 5f and conduction electrons which finally drives the development of the Kondo state in this compound with T_K about 15 K [5].

3.2. Magnetic structure

In figure 4 we show the difference between the 1.4 K and 61 K neutron powder diffraction patterns. We observe very strong contribution to (012), (100) and (014) and little one to (011), (103) and (105) Bragg reflections. All these reflections can be indexed in a magnetic unit cell identical to the crystallographic one, i.e. the propagation vector is $k = (0, 0, 1)$.
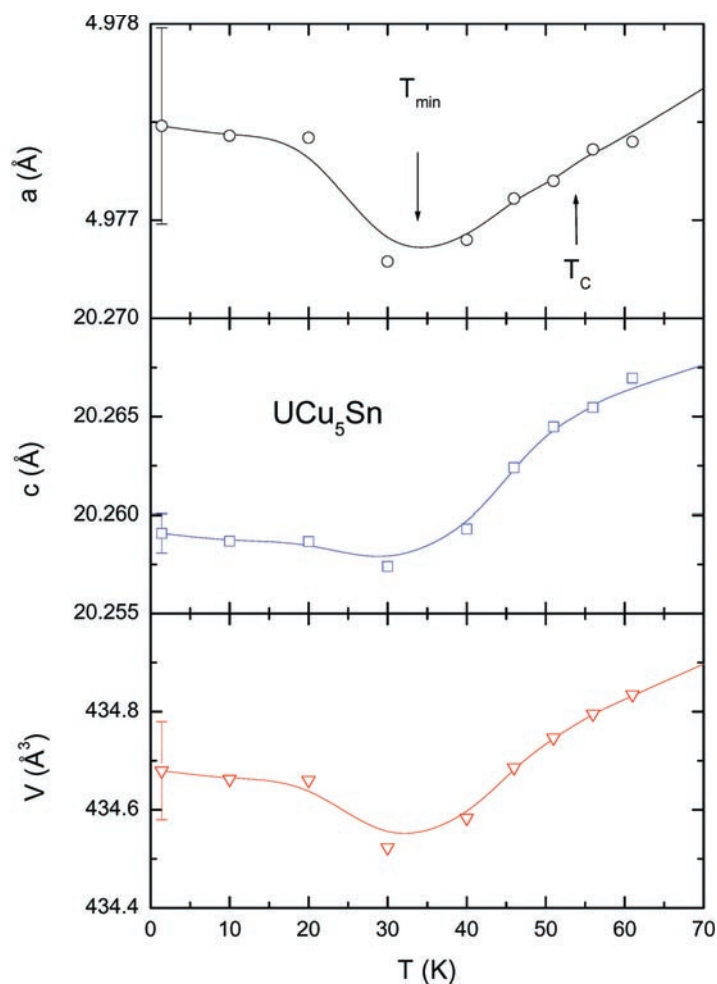
Figure 3. Temperature dependence of the lattice parameters. The solid lines represent a polynomial fit.

Thus, the magnetic unit cell contains four U magnetic moments with the following positions: $M_{U1}(0, 0, 0)$, $M'_{U1}(0, 0, \frac{1}{2})$ and M_{U2} $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and M'_{U2} $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$. Since no intensity appears in the $00l$ reflections, the magnetic structure must be collinear with the magnetic U moments arranged parallel to the hexagonal c axis. Therefore, the four magnetic moments are expected to be coupled antiferromagnetically or ferromagnetically in the one of the following sequences: $M_{U1} + M_{U2} - M'_{U1} - M'_{U2}$, $M_{U1} - M_{U2} + M'_{U1} - M'_{U2}$, $M_{U1} - M_{U2} - M'_{U1} + M'_{U2}$ or $M_{U1} + M_{U2} + M'_{U1} + M'_{U2}$. The results of a best refinement are shown in figure 4 as the solid line, and this corresponds to the stacking sequence $(+ - + -)$ being of the second type, i.e. $M_{U1} - M_{U2} + M'_{U1} - M'_{U2}$ with the following magnitudes of the uranium magnetic moment: $M_{U1} = 2.14(2)$ μ_B/atom U and $M_{U2} = 0.18(4)$ μ_B/atom U at $T = 1.4$ K. A schematic representation of the magnetic structure of UCu_5Sn is illustrated in figure 5. We note from this figure that the indicated difference in the magnitude of the magnetic moments, and the occurrence of the ferrimagnetic order, is due to the presence of the two crystallographically inequivalent U sites in the unit cell of the $CeNi_5Sn$-type structure.
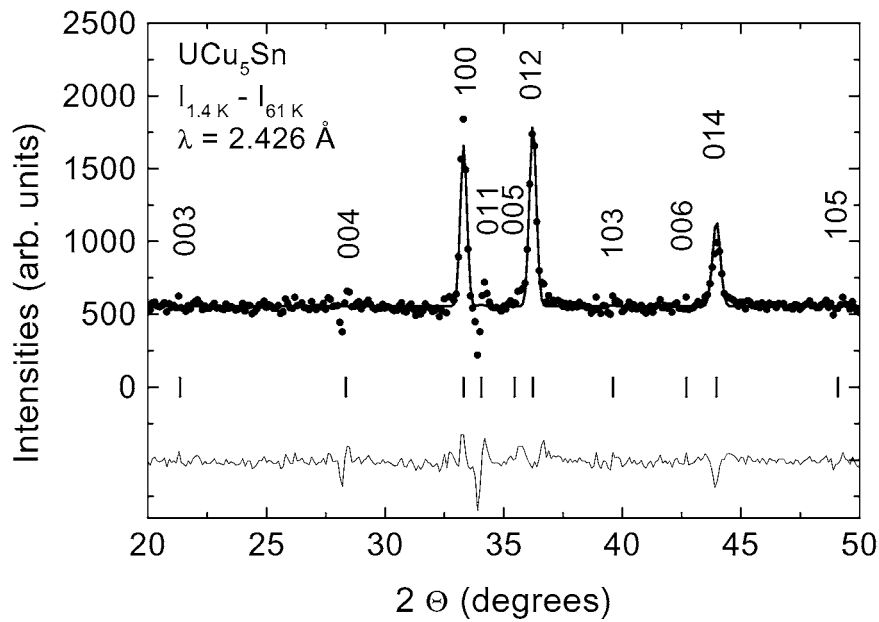
Figure 4. Neutron powder diffraction difference pattern between those taken at 1.4 and 61 K. Closed points and solid line represent observed and calculated data, respectively. The solid line at the bottom is the difference between them.
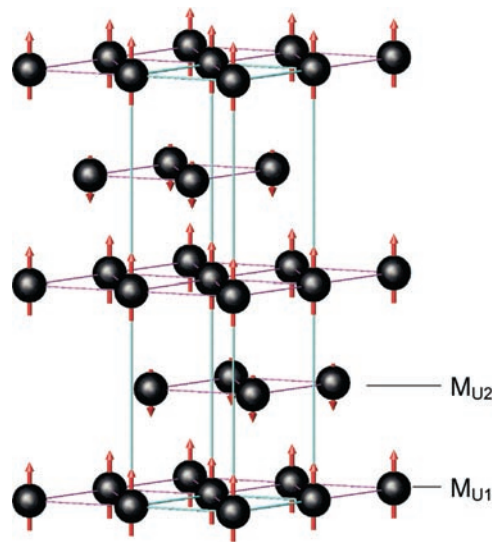

Figure 5. Magnetic structure of UCu₅Sn. Only the uranium atoms are drawn.

Furthermore, we show in figure 6 the temperature dependences of the magnetic moments M_{U1} and M_{U2}. These moments exhibit similar temperature dependences and they simultaneously vanish at 54 K, just at a temperature that is close to that found in the magnetic susceptibility and electrical resistivity measurements [5]. Surprisingly, as the temperature is lowered below 15 K, these moments show some decreasing tendency in their magnitudes. This is probably due to the Kondo screening effect.
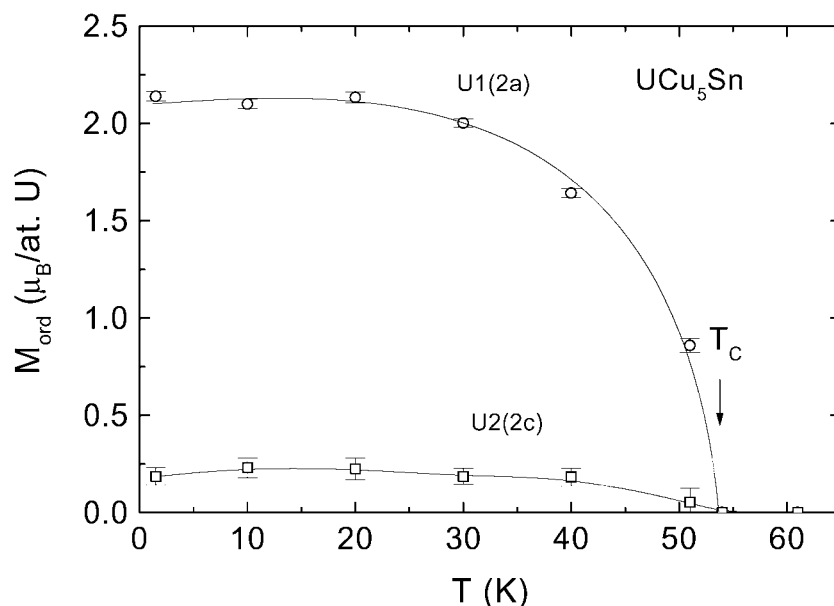
Figure 6. Temperature dependences of U1 and U2 moments in UCu_5Sn.

4. Discussion

As shown above, the most remarkable finding here is a strong reduction in the magnitude of the uranium magnetic moment U2 located at the 2(c) sites. Earlier investigations of other uranium compounds possessing at least two crystallographically inequivalent U sites in the unit cell have pointed out that a reduction of the moment magnitude at the one of the U sites can really be observed. For instance, Burlet *et al* [14] have studied a $U_4Cu_4P_7$ single crystal by means of neutron diffraction and found different temperature dependences and different values of magnetic moment for uranium atoms occupying two different sites. These differences have been explained by taking into account a difference in valence of the uranium ions in these sites. Furthermore, Troć *et al* [15] have also observed different temperature dependences of two moment values for uranium ions in $UNi_{1.6}As_2$. The authors have arrived at a similar explanation to that given in the case of $U_4Cu_4P_7$ [14].

In some other antiferromagnetic uranium compounds, one observes that the uranium atom at one of the sites does not carry any magnetic moment. Such a vanishing of magnetic moment at one of the sites is frequently found in compounds where there exists a frustration in the exchange interactions. This is for example the case of UNi_4B [16]. In this compound, two-thirds of the uranium moments order in the basal hexagonal plane, forming magnetic vortices, while the remaining one-third of the moments at the 2(b) sites have zero ordered moment, due to the zero molecular field at this site. The same mechanism leading to zero ordered moment at one of the uranium sites is working in $U_{14}Au_{51}$ [17], in the hexagonal unit cell of which there are as many as three crystallographically inequivalent U sites, namely 6(k), 6(j) and 2(e). It was found that the moments at the 6(k) and 6(j) sites have comparable values and are arranged opposite each other, while that at the 2(e) site has a zero value. The non-ordered uranium moments located on the last site are again due to zero molecular field at this position. Probably the same mechanism is also valid in the case of the germanides $U_3Al_2Ge_3$ and $U_3Ga_2Ge_3$ [18], crystallizing in the tetragonal ordered antitype-Cr_5B_3 structure, where

there are also three different sites of uranium atoms. However, in this latter case there are only two U atoms at different sites, which carry ordered magnetic moments. These moments are aligned ferromagnetically to each other and have different magnitudes.

Our present results concern a ferrimagnet UCu$_5$Sn. This case provides a new example of quite unusual behaviour. There is not only a strong reduction of the magnetic moment magnitude at one of two possible sites but in addition this reduction may be relevant exclusively to the Kondo effect. Moreover, we have previously shown that UCu$_5$Sn is a medium heavy-fermion compound with enhanced $\gamma(0)$-value of 330 mJ mol^{-1} K^{-2} at 0.4 K [5]. This value may be treated as an average of the two magnetically different U atoms. Thus, one can suppose that the U atoms at the 2(a) and 2(c) sites do not contribute equally to the density of states (DOS) at the Fermi level. On the basis of the large value of the moment of the U1 atom we expect a fully localized character of its 5f shell, and hence this shell gives little addition to the total DOS. On the other hand, the small moment value of the U2 atom indicates that the major contribution to DOS may originate thus from this kind of atom. Therefore, the effective electronic specific heat coefficient associated only with these atoms (50% in the unit cell) may be in consequence much higher than that measured as a mean value.

5. Conclusion

The high-resolution neutron-diffraction data show that the ternary uranium compound UCu$_5$Sn crystallizes in the ordered hexagonal structure with space group $P6_3/mmc$. To our best knowledge, UCu$_5$Sn is the first uranium isotypic compound to the CeNi$_5$Sn phase. The results obtained in this work indicate that the two U sublattices order ferrimagnetically at low temperatures, where each of two sublattices has ferromagnetically coupled uranium moments, but they are oppositely arranged to each other.

The magnetic structure is collinear with the uranium moments confined to the c axis. The most surprising feature of this structure is a very large difference in the magnitudes of the magnetic moments leading to their ratio of 12 for the 2(a) and 2(c) sites. This is believed to be caused by a Kondo screening effect acting strongly first of all in the 2(c) site. The latter effect is probably also responsible for the development of the heavy-fermion state in UCu$_5$Sn. On the basis of both the earlier bulk result [5] and the neutron diffraction data obtained in this work for UCu$_5$Sn, we can conclude that all these results provide the sole example as yet among uranium compounds of the coexistence of ferrimagnetism and heavy-fermion behaviour at low temperature.

Acknowledgment

References

[1] Amato A, Jaccard D, Flouquet J, Lapierre F, Tholence J L, Fisher R A, Lacey S E, Olsen J A and Phillips N E 1987 *J. Low Temp. Phys.* **68** 371
[2] von Löhneysen H 1996 *J. Phys.: Condens. Matter* **8** 9689
[3] Troć R, Andruszkiewicz R, Pietri R and Andraka B 1998 *J. Magn. Magn. Mater.* **183** 132
[4] Troć R, Kaczorowski D, Tran V H and Zaremba V I 1999 *Physica* B **259–261** 233
[5] Tran V H, Troć R, Pietri P and Andraka B 1999 *Phys. Rev.* B **60** 4696
[6] Troć R, Tran V H, Wołcyrz M, André G and Bourée F 1998 *J. Magn. Magn. Mater.* **190** 251
[7] Zaremba V, Stępień-Damm J, Troć R and Kaczorowski D 1998 *J. Alloys Compounds* **280** 196

[8]   Stępień-Damm J, Zaremba V, Tran V H and Troć R 1999 *J. Alloys Compounds* **289** 32

[9]   Rodriguez-Carvajal J 1993 *Physica* B **192** 55

[10] Sears V F 1992 *Neutron News* **3** 26

[11] Freeman A J, Desclaux J P, Lander G H and Faber J Jr 1976 *Phys. Rev.* B **13** 1168

[12] Skolozdra R V, Mandzyk V M, Akselrud L G 1981 *Sov. Phys.–Crystallogr.* **26** 272

[13] Moze O, Kockelmann W, Brück E and Buschow K H J 1998 *J. Alloys Compounds* **279** 110

[14] Burlet P, Troć R, Kaczorowski D, Noël H and Rossat-Mignod J 1994 *J. Magn. Magn. Mater.* **130** 237

[15] Troć R, Burlet P, Noël H, Kaczorowski D and Rossat-Mignod J 1994 *Physica* B **202** 167

[16] Mentink S A M, Nieuwenhuys G J, Menovsky A A, Mydosh J A, Drost A and Frikkee E 1995 *Physica* B **206/207**
        473

[17] Brown P J, Crangle J, Neumann K-U, Smith J G and Ziebeck K R A 1997 *J. Phys.: Condens. Matter* **9** 4729

[18] Rogl P, André G, Bourée F and Noël H 1999 *J. Magn. Magn. Mater.* **191** 291