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COMMENT

Commented review: UCu_2Ge_2 and UCu_2Si_2—compounds with only ferromagnetic ordering

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Abstract
The slow acceptance by the scientific community of only ferromagnetic ordering below T_C in UCu_2Ge_2, and the general acceptance of the same magnetic situation in UCu_2Si_2, both with the BCT $ThCr_2Si_2$-type crystallographic structure, are reviewed chronologically. Observations by neutron diffraction on annealed polycrystalline samples of UCu_2Ge_2 have finally overcome many conclusions of antiferromagnetic (AF) ordering at low temperatures (LT), deduced from the magnetization overlooking the ferromagnetic domain structure. Observations by magnetization measurements on Cu-flux-grown UCu_2Si_2 single crystals, claiming 'a 50 K AF transition below the 100 K ferromagnetic transition', published recently in this journal (2003 *J. Phys.: Condens. Matter* **15** S1917), are shown to have been misinterpreted by omitting any reference to ferromagnetic domain structure. Comments are made on other features disputing the LT ferromagnetism of UCu_2Si_2.

1. Introduction—the case of UCo_2Ge_2

The ternary uranium compounds UCu_2Ge_2 and UCu_2Si_2 crystallize in the body-centred tetragonal $ThCr_2Si_2$-type structure (space group $I4/mmm$), with two formula units per tetragonal unit cell. These compounds are part of the large group of UM_2X_2 compounds and $U(M, M')_2X_2$ solid solutions ($M, M' = $ 3d transition element: Co, Ni, Cu; X = Si, Ge) studied at Nuclear Research Centre–Negev (NRCN), Beer-Sheva, Israel, on annealed polycrystalline samples, crystallizing mostly with the $ThCr_2Si_2$-type structure. X-ray and neutron diffractograms of samples with this structure taken at room temperature (RT) contain only $\{hk\ell\}$ diffraction lines ('nuclear lines') with $h + k + \ell =$ even.

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The studies at the NRCN started in 1988 with neutron-diffraction and ac-susceptibility measurements on the compound UCo_2Ge_2, crystallizing with the $ThCr_2Si_2$-type structure [1]. UCo_2Ge_2 was found to have antiferromagnetic (AF) ordering of uranium magnetic moments only below $T_N = 175(5)$ K, aligned along the tetragonal c axis perpendicularly to the ferromagnetic basal planes. In this AF–I structure the ferromagnetic planes are stacked alternately $(+ - +-)$ along the tetragonal axis. The low-temperature (LT) neutron diffractograms of samples with this magnetic structure, such as UCo_2Ge_2, contain additional $\{hk\ell\}$ diffraction lines ('magnetic lines') with $h + k + \ell =$ odd, excluding $\{00\ell\}$ diffraction lines with odd ℓ, notably {001}. The latter exclusion is related to magnetic moments aligned along the tetragonal axis, as in UCo_2Ge_2.

In recent years two other groups, one in Poland [2] and another one in The Netherlands [3–5], studied UM_2X_2 compounds and published different results for UCo_2Ge_2. Chełmicki *et al* [2] reported that their UCo_2Ge_2 sample, which was not annealed after casting, showed additional small neutron diffraction lines at RT (considered by them as bound to an unidentified phase), besides those of the major $ThCr_2Si_2$-type phase. Their sample remained paramagnetic down to 4.2 K. Three consecutive publications by the group from The Netherlands [3–5] claimed that their UCo_2Ge_2 sample, which was also not annealed after casting, crystallized with the $ThCr_2Si_2$-type structure, but with lattice parameters of $a = 403.60$ pm and $c = 937.78$ pm, quite different from the NRCN values of $a = 402.0$ pm and $c = 986.8$ pm (notably the value of c). Their sample did not show any sign of magnetic ordering down to 1.7 K (being a Pauli paramagnet (PP)), in agreement with the results of Chełmicki *et al* [2]. The Dutch authors even built theories to explain the changes in magnetism among the UT_2Ge_2 compounds (T = Mn, Fe, Co, Ni, Cu) with the PP role of UCo_2Ge_2.

At this stage the NRCN group published a 'Note on the magnetism of UCo_2Ge_2' [6], disputing the other authors, mainly those of The Netherlands [3–5] and suggesting that they did not find the AF ordering of UCo_2Ge_2 below $T_N = 175$ K, probably due to a different crystallographic structure and absence of $I4/mmm$ symmetry (and a reduced c parameter) in their unannealed samples.

The response of the Dutch group was immediate. They prepared an annealed sample of UCo_2Ge_2 and confirmed [7] the NRCN result of AF ordering of UCo_2Ge_2. Endstra *et al* [7] admitted that their original unannealed sample of UCo_2Ge_2 had lower symmetry, initially overlooked, giving rise to the additional small diffraction lines, as reported also by Chełmicki *et al* [2]. Indeed, the nonmagnetic unannealed sample of UCo_2Ge_2 had the primitive tetragonal $CaBe_2Ge_2$-type crystallographic structure (space group $P4/nmm$), characterized by a reduced c parameter. The dispute was resolved. Annealed UCo_2Ge_2 crystallizes with the $ThCr_2Si_2$-type structure and has AF ordering below a rather high transition temperature (175 K). Those theories based on the PP behaviour of UCo_2Ge_2 among the $ThCr_2Si_2$-type materials have been subsequently amended.

2. Ferromagnetism observed at NRCN for UCu_2Ge_2 and UCu_2Si_2 and domain effects

The NRCN studies on 'Magnetic phase diagrams of the $U(M, M')_2X_2$ systems' were presented at the SCES'95 Conference held in Goa, India, and summarized in an article in the Proceedings [8]. The magnetic phase diagrams, determined by neutron diffraction (as well as by ac susceptibility for some compositions), state clearly that the magnetic ordering of the compounds UCu_2Ge_2 and UCu_2Si_2 below the ordering temperature (T_C) is just ferromagnetic. The ferromagnetic ordering of UCu_2Ge_2 persists in adjacent solid solutions in the $U(Co_{1-x}Cu_x)_2Ge_2$ system, while that of UCu_2Si_2 persists in adjacent solid solutions in the $U(Co_{1-x}Cu_x)_2Si_2$ system, both systems crystallizing with the $ThCr_2Si_2$-type structure.

The LT neutron diffractograms of ferromagnetic samples such as UCu_2Ge_2 and UCu_2Si_2 depict magnetic contributions on top of the RT $\{hk\ell\}$ diffraction lines ('nuclear lines') with $h+k+\ell =$ even, except for the $\{00\ell\}$ lines with even ℓ, notably $\{002\}$. The latter exclusion, as in the case of AF–I materials, indicates that the uranium magnetic moments are aligned along the *c* axis. Any AF structures at LT in both UCu_2Ge_2 and UCu_2Si_2 and their above adjacent solid solutions would be seen as separate magnetic lines in the neutron diffractograms, more clearly visible with respect to the ferromagnetic contribution. However, this was not the case and UCu_2Ge_2 and UCu_2Si_2 below T_C are just ferromagnetic.

Magnetic materials in zero applied magnetic fields, the normal situation encountered in neutron-diffraction measurements, contain magnetic domains. In AF materials, such as UCo_2Ge_2 and most other $U(M, M')_2X_2$ solid solutions studied at the NRCN [8], the AF domains with domain walls as narrow as the separation of consecutive uranium basal planes still lead to overall AF materials with zero bulk magnetic moment (with plane stacking: $\cdots + - + - + - - + - + - + - + \cdots$). The AF materials have a minor response to applied magnetic fields at all temperatures, but with a slightly enhanced response at the magnetic transitions, and even high magnetic fields generally affect moderately the AF character. In ferromagnetic materials, such as UCu_2Ge_2 and UCu_2Si_2 and adjacent $U(Co_{1-x}Cu_x)_2Ge_2$ and $U(Co_{1-x}Cu_x)_2Si_2$ solid solutions, respectively, studied at the NRCN [8], the ferromagnetic domains, again with domain walls as narrow as the separation of consecutive uranium basal planes, lead to bulk materials with reduced ferromagnetic character and ultimately to zero bulk magnetic moment (with plane stacking: $\cdots + + + + - - - - - - - - \cdots$). The ferromagnetic materials have a strong temperature-dependent response to applied magnetic fields. At the ferromagnetic transition temperature and at temperatures just below such a transition low magnetic fields normally align the domains into a full ferromagnetic state. On zero-field cooling (ZFC) of such materials, only high magnetic fields, above a value depending on temperature, are able to align the domains into a single ferromagnetic domain. When alignment is still impossible, the bulk material has a low magnetic moment and resembles an AF material.

In the $ThCr_2Si_2$-type systems $U(Co_{1-x}Cu_x)_2Ge_2$ and $U(Co_{1-x}Cu_x)_2Si_2$ the ferromagnetic materials contain ferromagnetic basal planes. Adjacent ferromagnetic domains in a crystallite of a polycrystalline sample, and eventually in a monocrystalline sample, involve reversal of the direction of the basal-plane moments, thereby reducing the total moment of the crystallite or the single crystal. In the latter the effect of an external magnetic field, at suitable temperatures, should be stronger when applied along the *c* axis rather than in the *ab*-basal plane.

In either AF or ferromagnetic materials the distribution of the magnetic domains has only a minor effect on the neutron-diffraction measurements. The NRCN observation of ferromagnetic structure in UCu_2Ge_2 and UCu_2Si_2 and adjacent solid solutions is rather certain and leaves no room for any AF phase at LT.

3. The case of UCu_2Ge_2

The ferromagnetic structure of UCu_2Ge_2 aroused wider controversy with respect to the minor dispute on the character of UCo_2Ge_2, before the AF structure of the latter was widely accepted. The NRCN neutron-diffraction observation of just ferromagnetic ordering of UCu_2Ge_2 below $T_C = 107(5)$ K and down to 10 K was published in 1990 [9, 10] and was supported by a similar finding [9] in the adjacent solid solution $U(Co_{0.25}Cu_{0.75})_2Ge_2$.

Around the time of the NRCN publications, four other groups, in Poland [2, 11], in Canada [12], in The Netherlands [4, 5] and in England [13], studied polycrystalline UCu_2Ge_2 samples (with other UM_2X_2 compounds in some cases [2, 4, 5]) and published different results for UCu_2Ge_2. Except for the sample of the Dutch group [4, 5], which was annealed in conditions similar to those used at the NRCN [9, 10], all other samples were as-cast, without any annealing.

Leciejewicz *et al* [2, 11] reported that their UCu_2Ge_2 sample, which was not annealed after casting, showed from their neutron-diffraction study that UCu_2Ge_2 ordered ferromagnetically below $T_C = 100(3)$ K and underwent a magnetic transition to the AF–IA $(++--)$ structure below 25–40 K. They correlated their neutron-diffraction observation with their magnetization measurements in an applied field of 0.086 T, showing a sharp rise below T_C, a 10 K plateau around 53 K and a sharp drop at 43 K, attributed by them to a transition into the AF–IA structure. They reported that, in fields up to 0.55 T, the above drop in magnetization persisted (leading to the AF phase) while in higher fields, up to 5 T, the sample behaved as a ferromagnet.

McAlister *et al* [12] reported that their UCu_2Ge_2 sample, which was not annealed after casting, showed from their magnetization study that it ordered ferromagnetically below $T_C = 110(2)$ K and underwent an AF transition at 65(1) K, as indicated by the magnetization measured in applied fields of 0.0019–0.1 T. In the highest field applied by them, 2 T, the AF transition moved to a lower temperature and would have probably disappeared in applied fields approaching 5 T.

Dirkmaat, Endstra *et al* [4, 5] reported that their UCu_2Ge_2 sample, which was annealed, showed, from their magnetization measurement in an applied field of 0.3 T, that it ordered ferromagnetically below $T_C = 105$ K and underwent an AF transition at 43 K. These authors did not see any trace of the LT transition in their specific heat study [5] and hinted for the first time [4] that domain effects in the behaviour of the LT magnetization could not be ruled out.

The three groups of authors mentioned above [2, 4, 5, 11, 12] could not refer to the NRCN neutron-diffraction observation [9, 10] of ferromagnetic ordering only in annealed UCu_2Ge_2, due to the late publication date of the NRCN papers. However, Roy and Coles submitted in May 1991 a paper (published in December 1991) [13] on 'Magnetic and electrical properties of UCu_2Ge_2', with no reference to the NRCN work on this material, published early in 1990 [9, 10]. Roy and Coles [13] reported that their UCu_2Ge_2 sample, which was not annealed after casting, showed, from their magnetization study in an applied field of 0.01 T, ferromagnetic ordering below $T_C = 107$ K and 'a gradual transition from a ferromagnetic to an AF state over a large temperature range (around 43 K)', the latter having no trace in their ac-susceptibility measurements.

With two additional NRCN publications [14, 15] on the ferromagnetic ordering of UCu_2Ge_2 in the pipeline, the conclusions of Roy and Coles [13], that took two months to be accepted for publication, brought about a sharp reaction by the NRCN group in a 'Note on the magnetism of UCu_2Ge_2' that took, however, eight months to be accepted for publication [16]. The NRCN group ascribed the absence or appearance of an AF phase at LT in the ferromagnetic UCu_2Ge_2 to different annealing conditions (or their absence) that might produce variations in stoichiometry, a viewpoint supported by NRCN neutron-diffraction studies of the magnetic phase diagram of the $U(Ni_{1-x}Cu_x)_2Ge_2$ system [14, 15]. The AF behaviour of the magnetization, reported by the other groups, was ascribed to ferromagnetic-domain effects (as outlined in section 2 of the present paper).

The long delay in publication of the NRCN Note [16] allowed Roy and co-workers to report on spin-glass behaviour in UCu_2Ge_2 [17] and again on the gradual ferromagnetic to AF transition, this time using magnetoresistance [18], still without any reference to the NRCN work on ferromagnetism in UCu_2Ge_2 [9, 10].

Meanwhile a fifth group, from Taiwan [19], joined the authors that were not aware of the NRCN neutron-diffraction observation of only ferromagnetism in UCu_2Ge_2 [9, 10, 14, 15]. Tien *et al* [19] reported that their polycrystalline sample of UCu_2Ge_2, which was not annealed after casting, showed, from a SQUID magnetization study in an applied field of 0.05 T and electrical resistivity measurements, that it ordered ferromagnetically below $T_C = 110$ K and underwent a second magnetic transition, presumably AF, at 45 K. However, the LT transition did not appear in the SQUID magnetization study in an applied field of 1 T and in the specific-heat measurements.

Together with other contributions on the metastable response and character of UCu_2Ge_2, published with some co-workers [20, 21], Roy finally reacted to the NRCN Note [16] in "Comments on 'Note on the magnetism of UCu_2Ge_2'" [22]. He stood firmly behind the appearance of an AF phase at LT, as he inferred also from some unrefereed incomplete neutron-diffraction study of the Dutch group [23] on an annealed polycrystalline sample of UCu_2Ge_2, claimed to be 'very detailed'. The other point in Roy's comment [22] was that 'since of six different samples from five different groups only that of (the NRCN group) fails to show AF character at LT, we find it difficult to believe that non-stoichiometry is playing a central role in its appearance', or in other words *vox populi vox Dei*.

Following Roy's comments [22], the NRCN group published in the same issue of the journal "Countercomments to Roy's comments on 'Note on the magnetism of UCu_2Ge_2'" [24]. Examining the paper of Endstra *et al* [23] and evaluating the neutron-diffraction results there, the NRCN group found the Dutch results rather inconclusive with respect to its own neutron-diffraction measurements and adhered to the NRCN observation of only ferromagnetic ordering below T_C in UCu_2Ge_2 [9, 10, 14, 15].

In spite of the minority opinion of the NRCN group on only ferromagnetic ordering of UCu_2Ge_2 [9, 10, 14, 15], which was very little referred to, its persistence finally paid off. The group coordinated by Madhav Rao at the Bhabha Atomic Research Centre (BARC), Mumbai, India, made proper neutron-diffraction measurements on annealed polycrystalline samples of UCu_2Ge_2 [25–27] and the adjacent solid solution $(U_{0.95}Th_{0.05})Cu_2Ge_2$ [28] and confirmed the NRCN observation of only ferromagnetic ordering of UCu_2Ge_2, against all the other groups. Yusuf *et al* [25] used ac-susceptibility, neutron-depolarization and neutron-diffraction measurements that revealed that UCu_2Ge_2 remained ferromagnetic at all temperatures below $T_C = 107$ K, but in the temperature range of 25–45 K the ferromagnetic moments seemed to be randomly canted with respect to the *c* axis. Adding to the just-mentioned techniques of magnetization measurements, Yusuf *et al* [26] stated that their measurements indicated ferromagnetic ordering at all temperatures below T_C, ruled out the transition to an AF state at LT and suggested below about 45 K random canting of the ferromagnetic moments with respect to the *c* axis. The full BARC report on the study of the magnetization, by Chandrasekhar Rao *et al* [27], ascribed the various magnetic features of UCu_2Ge_2 to the 'intrinsic domain-wall pinning associated with the narrow domain walls in this highly anisotropic compound' (as narrow as the separation of consecutive uranium basal planes). Their studies completely ruled out any AF phase, spin-glass or cluster-glass spin freezing at LT and confirmed the existence of the ferromagnetic state down to the lowest temperatures, with random canting of the ferromagnetically coupled moments below about 30 K. In the adjacent solid solution $(U_{0.95}Th_{0.05})Cu_2Ge_2$ Yusuf *et al* [28] found only ferromagnetic ordering down to the lowest temperatures, with no canting of the ferromagnetic moments.

An independent study of the susceptibility and magnetization of an annealed polycrystalline sample of UCu_2Ge_2 carried out in France by Pechev *et al* [29] found only ferromagnetic ordering below $T_C = 108(1)$ K, in agreement with the NRCN neutron-diffraction results [9, 10, 14, 15] and showed the crucial role of heat treatments on the chemical homogeneity, structural and magnetic properties of the UCu_2Ge_2 compound.

The BARC papers [25–28] and the paper of Pechev *et al* [29] confirmed the original NRCN observation of only ferromagnetic ordering in UCu_2Ge_2 [9]. Following the first NRCN study of the $U(Co_{1-x}Cu_x)_2Ge_2$ solid solutions [9], and its follow-up [8], Dubman *et al* [30] have recently studied annealed polycrystalline samples with $x = 0$, 0.25, 0.50, 0.60, 0.70, 0.75 and 1 by means of SQUID-magnetization and ac-susceptibility measurements. They confirm the previous results of only ferromagnetic ordering in Cu-rich compositions ($x = 0.70$, 0.75, 1), as compared to intermediate compositions ($x = 0.50$, 0.60), which order ferromagnetically but do undergo transitions to the AF-I state at lower temperatures.

4. The case of UCu_2Si_2

The ferromagnetic structure of UCu_2Si_2 was hitherto well accepted and aroused only certain disagreements with respect to the magnetic structure around the ordering temperature. The structure was first determined by Chełmicki *et al* [2] in studying a polycystalline sample of UCu_2Si_2 which was not annealed after casting. Their neutron-diffraction study showed ferromagnetic ordering below $T_C = 103(3)$ K and down to 4.2 K, with uranium magnetic moments along the *c* axis. They correlated their neutron-diffraction observations with their magnetization measurements in an applied field of 1 T, which also indicated ferromagnetic ordering below a comparable temperature of 107 K. Shortly afterwards Hiebl and Rogl [31] studied an annealed polycrystalline sample of UCu_2Si_2 by magnetization measurements (shown for applied fields of 1.00 and 1.18 T) and found only ferromagnetic ordering below $T_C = 105$ K and down to 1.8 K. At the same time Giorgi *et al* [32] studied a polycrystalline sample (with no annealing details) of UCu_2Si_2 by neutron-diffraction and magnetization measurements and confirmed its ordering as a simple ferromagnet. Later on Hiebl *et al* [33] studied an annealed stoichiometric polycrystalline sample of UCu_2Si_2, which was well characterized, by magnetization measurements (shown for an applied field of 0.1 T) and found only ferromagnetic ordering below $T_C = 105(5)$ K and down to 2 K. They emphasized the role of movements of the narrow domain walls in the magnetization processes (as mentioned above, generally in section 2 and for UCu_2Ge_2 in section 3).

The only ferromagnetic ordering in UCu_2Si_2 (below $T_C = 103$ K) and in adjacent Cu-rich solid solutions in the systems $U(Co_{1-x}Cu_x)_2Si_2$ [8] and $U(Ni_{1-x}Cu_x)_2Si_2$ [8, 34], such as the solid solution $U(Co_{0.25}Cu_{0.75})_2Si_2$ (below $T_C = 115$ K), was confirmed in the NRCN neutron-diffraction studies of annealed polycrystalline samples. As indicated above in section 2, the NRCN studies on the 'Magnetic phase diagrams of the $U(M, M')_2X_2$ systems' were summarized in an article in the Proceedings of the SCES'95 Conference held in Goa, India [8].

McElfresh *et al* [35] investigated an annealed polycrystalline UCu_2Si_2 sample by magnetization measurements in applied fields of 0.01–0.3 T and also found only ferromagnetic ordering below $T_C = 103$ K. They detected a tiny peak in the magnetization measured in applied fields of 0.01–0.1 T in the narrow temperature range 103–107 K but it disappeared completely in an applied field of 0.15 T. They attributed the peak to some AF transition but could not find any AF ordering in their preliminary neutron-diffraction study. Torikachvili *et al* [36] also investigated an annealed polycrystalline sample of UCu_2Si_2, by ac-susceptibility measurements, and found only ferromagnetic ordering below $T_C = 97$ K, and again a tiny peak at 104 K, which could be traced in their resistivity measurements. They mentioned also the inability of neutron diffraction to detect AF ordering in the temperature range 97–104 K.

At this stage the NRCN group attributed [37] the occasional appearance of the above AF feature to minor substoichiometry of the copper sublattice, as inferred from neutron-diffraction study of the $U(Ni_{1-x}Cu_x)_2Si_2$ system [34], with emphasis on the $U(Ni_{0.15}Cu_{0.85})_2Si_2$ solid solution [8, 34].

In later publications on annealed polycrystalline samples of UCu_2Si_2 the previous results were confirmed. Roy *et al* [38] observed from magnetization measurements in several applied fields (shown only for 0.05 T) only ferromagnetic ordering below $T_C = 103$ K. The above tiny peak [35, 36] appeared in their magnetization measurements just as 'a distinct structure around 108 K' and disappeared only under a field of 0.5 T (while the above peak [35] disappeared under 0.15 T). Hiebl [39] deduced from his ac-susceptibility measurements only ferromagnetic ordering below $T_C = 97.3$ K, and again a tiny peak at 106.5 K, which was attributed to 'AF spin alignment'. As in the study of Torikachvili *et al* [36], it could also be traced in his resistivity measurements [39].

These later publications [38, 39] did not change the above NRCN attribution [37] of the additional feature in UCu_2Si_2 around T_C to minor substoichiometry on the copper sublattice. Different temperatures for the appearance of the feature (107 K [35], 104 K [36], 108 K [38] and 106.5 K [39]) are well understood by the NRCN discussion. The absence of the feature in the annealed sample of Hiebl *et al* [33], claimed to be stoichiometric, is also consistent with the NRCN attribution.

5. Comments on misinterpreted recent observations on UCu_2Si_2

The only ferromagnetic ordering in UCu_2Si_2 below T_C seemed to be an agreed feature among all researchers, as it became well accepted in the case of UCu_2Ge_2. But recently Fisk *et al* [40] have claimed in this journal that 'single crystals of UCu_2Si_2, grown from Cu flux, have a 50 K AF transition below the 100 K ferromagnetic transition'. Without referring to any of the numerous studies that finally confirmed the existence of only ferromagnetic ordering below T_C in the sister compound UCu_2Ge_2, namely those coming from NRCN [8–10, 14–16, 24], BARC [25–28] and Pechev *et al* [29], that had to overcome incorrect conclusions on an AF phase at LT of five other groups [2–5, 7, 11–13, 17–23], Fisk *et al* [40] are now setting the study of UCu_2Si_2 back many years.

Fisk *et al* [40] have made SQUID magnetization measurements in the 2–350 K temperature range on Cu-flux-grown single crystals of UCu_2Si_2 and present (in their figure 1) their dc-susceptibility data for an applied magnetic of 0.1 T, both parallel and perpendicular to the *c* axis. The dc-susceptibility curve for the field along the *c* axis rises sharply below around 100 K and then drops sharply around 50 K. The dc-susceptibility curve for the field in the *ab*-basal plane rises moderately around 92 K to a level reduced six-fold with respect to the *c*-axis case and then falls sharply around 50 K. Fisk *et al* [40] report similar behaviour for an applied field of 0.001 T but no 'AF transition' for an applied field of 1.5 T. From the curves, presented for applied fields of 0.001 T and 0.1 T, Fisk *et al* [40] conclude that their Cu-flux-grown single crystals of UCu_2Si_2 order ferromagnetically at 100 K and undergo a first-order-like AF transition at 50 K.

Reading carefully the paper of Fisk *et al* [40], one gets the impression that either the authors are not aware that ferromagnetic domains exist in ferromagnetic materials, such as UCu_2Si_2, or they do not believe that such ferromagnetic domains exist in (Cu-flux-grown) UCu_2Si_2 single crystals. In the published article of Fisk *et al* [40] magnetic domains do not exist and are not referred to. However, these ferromagnetic domains do exist in polycrystalline samples as well as in single crystals of UCu_2Si_2, as they exist in the sister compound UCu_2Ge_2 and other ferromagnetic materials. As indicated above in section 2, the ferromagnetic domains have a minor effect on the neutron-diffraction measurements but a major effect on the magnetization measurements.

The ferromagnetic domains are responsible for the sharp drop in the magnetization measured in an applied field of 0.1 T by Fisk *et al* [40] in a single crystal of UCu_2Si_2 around 50 K (presented in their figure 1), as they are responsible for the drop in the magnetization measured in a similar applied field of 0.1 T by Hiebl *et al* [33] in polycrystalline UCu_2Si_2

around 30 K (presented in their figure 3), and as they are responsible for the drop in the magnetization measured also in an applied field of 0.1 T by Chandrasekhar Rao *et al* [27] in polycrystalline UCu_2Ge_2 around 70 K (presented in their figure 4(c)). The results, showing no drop in the magnetization in an applied field of 5 T that aligns all ferromagnetic domains in both materials [27, 40], are equally the same. As domain walls in the $ThCr_2Si_2$-type materials are narrow and located mostly in basal planes, the effects of the ferromagnetic domains on the magnetization in single crystals are strong for the parallel case and much reduced for the perpendicular case, as shown for UCu_2Si_2 [40]. In polycrystalline samples the effects are rather intermediate, as observed in UCu_2Si_2 [33] and UCu_2Ge_2 [27]. This evidence, and all the background discussions in the present paper, lead to one conclusion, namely: there is only ferromagnetic ordering in UCu_2Si_2 below T_C. Interpretation of the LT magnetization of Fisk *et al* [40] as related to an AF phase is incorrect and unjustified. Neutron-diffraction studies on the Cu-flux-grown single crystals should finally decide it.

Fisk *et al* [40] use their paramagnetic data for UCu_2Si_2 to support their conclusions about the two magnetic transitions. From the straight-line parts of the inverse susceptibility they obtain paramagnetic Curie temperatures, $\theta = 104$ K for the parallel case and $\theta = -55$ K for the perpendicular case, and deduce effective paramagnetic moments $\mu_{eff} = 3.11\ \mu_B$ for the parallel case and $\mu_{eff} = 3.37\ \mu_B$ for the perpendicular case. They claim that the parallel-case $\theta = 104$ K (arising from a 'ferromagnetic intercept') is related to the temperature (around 92–100 K) of the ferromagnetic transition, while the perpendicular-case $\theta = -55$ K (arising from an 'AF intercept') is related to the temperature (around 50 K) of the claimed AF transition.

The conclusions of Fisk *et al* [40] from their paramagnetic-state data of UCu_2Si_2 are rather strange. It is well known that ferromagnetic materials have positive θ values, close to the ordering temperature T_C for simple ferromagnets and somewhat lower when the ferromagnets undergo an AF transition at LT. The NRCN data for the solid-solution systems $U(Ni_{1-x}Cu_x)_2Ge_2$ [15], $U(Ni_{1-x}Cu_x)_2Si_2$ [34] and $U(Co_{1-x}Cu_x)_2Ge_2$ [30] show it clearly. AF materials can have θ values which are either negative or positive, the latter below the ordering temperature T_N, but there is no simple relation between the θ and T_N values in such materials. Examples for AF materials with both signs of θ can be found in the systems $U(M, Cu)_2X_2$ mentioned above [15, 30, 34]. The terms 'ferromagnetic and AF intercepts' used by Fisk *et al* [40] are therefore unjustified. While their 'ferromagnetic intercept' at 104 K is related to T_C, the 'AF intercept' at -55 K cannot be related to any AF transition at 50 K. In any case, if such a relation indeed exists, it should be well referred to.

The values of θ and μ_{eff} published by Fisk *et al* [40] for UCu_2Si_2 are also quite problematic. While in the ordered magnetic state of the $ThCr_2Si_2$-type materials $U(M, M')_2X_2$ the (ordered) magnetic moments are aligned along the *c* axis in ferromagnetic planes [8], in the paramagnetic state the magnetic moments have no exchange interactions among them and interact mainly with an external field, if applied, even in the case of single crystals. Therefore the values of θ and μ_{eff} should not depend so strongly on the direction of the applied field, as does the magnetization in the ordered magnetic state. The values of θ and μ_{eff} published by Fisk *et al* [40] do not obey these known features, and furthermore their μ_{eff} values, 3.11 μ_B and 3.37 μ_B, for the parallel and perpendicular cases, respectively, are quite different from the μ_{eff} values obtained for annealed polycrystalline samples: 2.62 μ_B [31], 2.7 μ_B [33], 2.8 μ_B [35] and 2.5 μ_B [39]. The μ_{eff} values of Fisk *et al* [40] are close to the older value of Chełmicki *et al* [2], 3.58 μ_B, obtained for an as-cast sample that has not been annealed. In fact, this is probably the state of the Cu-flux-grown UCu_2Si_2 single crystals of Fisk *et al* [40].

The absence of clear observations of Fisk *et al* [40] of the above tiny peak, presumably AF, in the magnetization of UCu_2Si_2 above T_C is well understood by the NRCN attribution of such a peak to substoichiometry on the copper sublattice [37], since 'the Cu-flux grown crystals (of Fisk *et al* [40]) are highly stoichiometric' [40]. The fact that Fisk *et al* [40] do not see any trace of it in the resistivity, as seen previously when the tiny peak appeared in the magnetization [36, 39], also supports the above attribution [37]. We have no way of assessing the tiny feature appearing in the specific heat curve of Fisk *et al* [40], less than 1.5% in C (when reconstructed from the published C/T), but anyway it supports any magnetic feature only indirectly.

Fisk *et al* [40] do not find any clear sign of the 'AF transition at 50 K' in their specific-heat and resistivity measurements on the Cu-flux-grown single crystals of UCu_2Si_2 but see a certain feature at 70 K in the resistivity. However, in these measurements, which are not magnetic, one does not necessarily observe all magnetic transitions, especially where they do not really exist.

The major conclusion of this comment, and the detailed comments in section 5, is that UCu_2Si_2, as with its sister compound UCu_2Ge_2, have only ferromagnetic ordering below T_C.

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