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Magnetic structure of the ternary germanide $U_3Cu_4Ge_4$

S. Pechev[a], B. Chevalier[a,*], D. Laffargue[a,b], B. Darriet[a], J. Etourneau[a]

[a]*Institut de Chimie de la Matière Condensée de Bordeaux, ICMCB-CNRS (UPR 9048), Avenue du Dr A. Schweitzer, 33608 Pessac, France*
[b]*Laboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay, 91191 Gif-sur-Yvette, France*

Abstract

$U_3Cu_4Ge_4$ which crystallizes in the orthorhombic $Gd_3Cu_4Ge_4$-type structure, orders ferromagnetically below $T_C=71(1)$ K. This ternary germanide was investigated by neutron powder diffraction. The ferromagnetic transition is observed by this study at $T_C=69(2)$ K. The magnetic structure is described by U-moments equal to 1.71(1) μ_B and all parallel to the *a*-axis. In other words, the two inequivalent U-atoms (U1 and U2) carry the same moment. This structure is discussed in relation to those previously reported for other germanides as UGe_2, UCu_2Ge_2 and UCuGe which exhibit some structural relationship. © 1998 Elsevier Science S.A.

Keywords: Uranium; Neutron diffraction; Ferromagnetism; Magnetic structure

1. Introduction

Recently the existence of the new ternary germanide $U_3Cu_4Ge_4$ has been reported [1,2]. It was found to crystallize in the orthorhombic $Gd_3Cu_4Ge_4$-type structure, which is closely related to those of other uranium germanides like UGe_2 and UCu_2Ge_2. Thus, one can consider it as an intergrowth of two different kinds of slabs: deformed tetragonal prisms which are characteristic of UCu_2Ge_2 and trigonal prisms similar to those present in UCuGe or UGe_2 [3].

The magnetic structure of the above-mentioned three compounds have already been studied by neutron diffraction. It appeared that UCu_2Ge_2 (tetragonal $ThCr_2Si_2$-type) and UGe_2 (orthorhombic $ZrGa_2$-type) order ferromagnetically below $T_C=107(5)$ K [4,5] and $T_C=52$ K [6], respectively. UCuGe (hexagonal $CeCd_2$-type) was found to adopt, below $T_N=50(5)$ K, a canted antiferromagnetic structure [7].

Previous magnetization measurements performed on $U_3Cu_4Ge_4$ showed that it orders ferromagnetically below $T_C=67$ K [1] and 71(1) K [2]. The structural relationship to other germanides, as well the presence in $U_3Cu_4Ge_4$ of two crystallographically inequivalent sites for the uranium atoms, made the study of its magnetic structure interesting. This was our motivation to undertake a neutron diffraction investigation of the latter. The results are presented in this paper.

*Corresponding author. Tel.: +335 56 846336; fax: +335 56 842761; e-mail: chevalie@icmcb.u-bordeaux.fr

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2. Experimental

The experiments were performed on a polycrystalline sample of $U_3Cu_4Ge_4$. It was prepared by direct melting of stoichiometric amounts of the constituent elements (purity >99.9%) under a purified argon atmosphere in an induction levitation furnace. Then the ingot was annealed in an evacuated quartz tube for 2 weeks at 800°C.

Neutron powder diffraction experiments were carried out at the Orphée reactor (CEA/Saclay, France) on the two-axis diffractometer G4.1 ($\lambda=0.2426$ nm; 800 cells position-sensitive detector). The refinement of both crystal and magnetic structures were made using the Rietveld profile method by FULLPROF program [8], with the U^{3+} magnetic form factor from the International Tables for Crystallography [9].

3. Results

Neutron diffraction measurements were performed in the temperature range 1.5–90 K, i.e. above and below T_C. The pattern at 90 K (Fig. 1(a)) can easily be indexed with the orthorhombic $Gd_3Cu_4Ge_4$-type structure (Immm space group) and it exhibits only nuclear peak contributions. It is in perfect agreement with the crystal structure determined previously by X-ray single-crystal diffraction [1,2]. The lattice parameters at this temperature are: $a=1.3924(1)$ nm, $b=0.6567(6)$ nm and $c=0.4276(4)$ nm.

At $T=1.5$ K the diffractogram does not show any additional reflections. On the other hand, magnetic peak

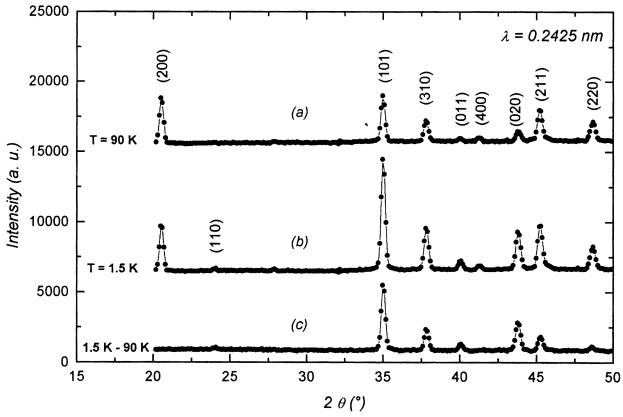

Fig. 1. Neutron powder diffraction patterns of $U_3Cu_4Ge_4$ at 90 K (a), 1.5 K (b) and the difference (c). The patterns are vertically shifted for clearer viewing.

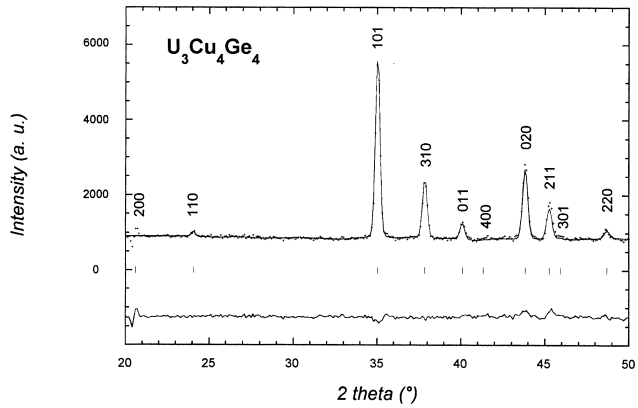

Fig. 2. Observed and calculated neutron powder diffraction pattern for $U_3Cu_4Ge_4$: magnetic Bragg peaks (difference between T=1.5 and 90 K). Symbols: (+) represent the observed points; solid lines, the calculated profile and the difference between observed and calculated patterns; ticks correspond to the Bragg peak positions.

contributions are observed with respect to the 90 K pattern (Fig. 1(b)), which is associated to a ferromagnetic long-range ordering. The absence of additional intensities on (200) and (400) Bragg peaks indicates that the U-magnetic moments are aligned along the *a*-axis. Table 1 presents the best agreement obtained at 1.5 K between observed and calculated nuclear and magnetic intensities. The lattice parameters are: a=1.3918(1) nm, b=0.6567(5) nm, c=0.4273(2) nm, and they present a normal small low temperature contraction.

The final magnetic structure refinement was made using the difference between 1.5 and 90 K neutron diffraction patterns (Fig. 1(c)). All uranium atoms were considered as carrying the same M_U magnetic moment. The best refinement (Fig. 2) corresponds to a collinear magnetic structure with U-moments directed along the *a*-axis with M_U=1.71(1) μ_B at 1.5 K. A schematic representation of the structure is shown in Fig. 3. One should note that magnetic and nuclear unit-cells are equivalent.

Our attempt to differentiate the magnetic moments localized on uranium atoms in the two different crystallographic sites (U1 and U2) did not improve significantly the refinement results. The two values obtained for M_{U1} and M_{U2} were very close and we were unable to choose this magnetic model instead of the single-moment one.

The thermal dependence of the magnetic contribution intensity of the (101) major magnetic peak is displayed in Fig. 4. A huge increase is observed at T_C=69(2) K, which is in good agreement with the transition temperature previously deduced from the magnetic measurements [1,2].

Concerning the direction of the U-magnetic moments, one could notice some similarities between the magnetic structures of $U_3Cu_4Ge_4$ and its crystallographically related compounds: UCuGe, UGe_2 and UCu_2Ge_2. It was found that the U-magnetic moments in UCuGe are aligned normal to the trigonal axis, making an angle of 60° with the *a*-axis [7]. In UGe_2 the moments are along the *a*-orthorhombic axis, normal to the trigonal [U_6] prism [6], while in UCu_2Ge_2 they are along the tetragonal *c*-axis [4,5]. So, with regard to the trigonal prism [U_6], existing in $U_3Cu_4Ge_4$, the U-magnetic moments are in their basalit plane (Fig. 3), as it occurs in UCuGe and UGe_2. At the same time the moments in the deformed tetragonal [U_8] prisms are parallel to their pseudo-tetragonal axis (Fig. 3), which is consistent with the magnetic structure of

Table 1
Nuclear and magnetic intensities contributions for $U_3Cu_4Ge_4$; comparison between observed and calculated values

h k l	2θ (°)	*d* (nm)	Nuclear contribution		Magnetic contribution	
			I_{obs} (barn)	I_{calc} (barn)	I_{obs} (barn)	I_{calc} (barn)
2 0 0	20.07	0.696	7.4	7.4	0	0
1 1 0	23.56	0.594	0.1	0.1	0.2	0.1
1 0 1	34.53	0.409	10.0	9.8	23.1	23.0
3 1 0	37.33	0.379	5.8	6.0	9.4	9.5
0 1 1	39.57	0.358	0.7	0.5	3.0	2.8
4 0 0	40.80	0.348	1.2	1.1	0	0
0 2 0	43.33	0.329	4.2	4.3	9.1	9.3
2 1 1	44.76	0.319	12.6	14.7	18.0	19.1
3 0 1	45.39	0.314	0.1	0.2	0.4	0.7
2 2 0	48.19	0.297	5.5	4.7	2.8	2.0

$R_{mag.}$=4.0%.

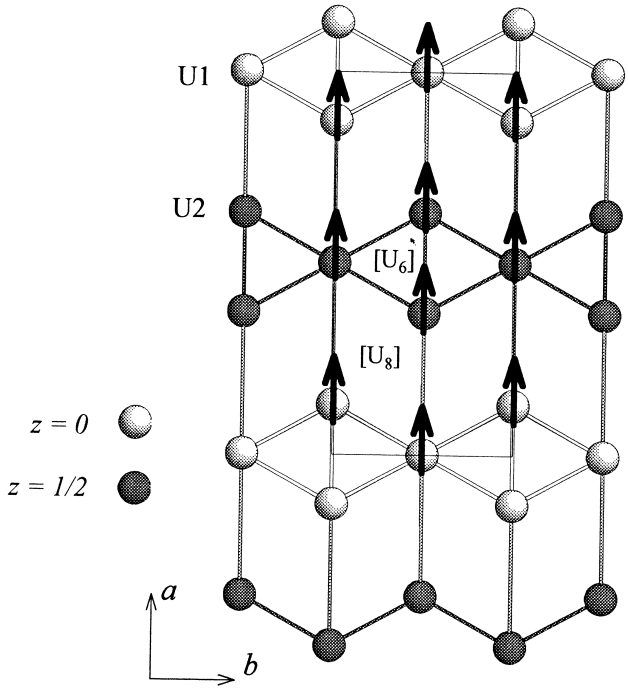

Fig. 3. Projection into the (*a*,*b*)-plane of the magnetic structure of $U_3Cu_4Ge_4$. Only the uranium atoms are represented.

UCu_2Ge_2. It is also worth mentioning that, in $U_3Cu_4Ge_4$, the magnetic moments are directed along the shortest d_{U2-U2} distances.

It is interesting to compare the U-magnetic moment magnitude in $U_3Cu_4Ge_4$ with those of other germanides in the U–Ge or U–Cu–Ge systems. Since the d_{U-U} distances in $U_3Cu_4Ge_4$ are larger than the Hill limit (the shortest is equal to 0.3614 nm [2]), a direct 5f(U)–5f(U) overlap is very improbable. For these compounds the partial delocalization of the 5f(U) electrons may arise from their hybridization with the ligand's electrons. The U-magnetic moment in $U_3Cu_4Ge_4$ (1.71(1) μ_B) is intermediate between those carried by U-atoms in UGe_2 (1.42(4) μ_B) [6] and in UCuGe (2.0(1) μ_B) [7] or UCu_2Ge_2 (1.9(4) μ_B) [4]. The lowest value is obtained for UGe_2 where U-atoms are surrounded by a higher number of Ge-nearest neighbours (NN): 10 NN with d_{U-Ge} between 0.2921 and 0.3232 nm. On the contrary, UCuGe exhibits the higher U-magnetic moment, since there are only six Ge-atoms (at 0.3063 nm) to be around uranium. In that manner, the value of the U-magnetic moment in $U_3Cu_4Ge_4$ appears to be plausible, in-so-far as the two inequivalent uranium atoms have six and eight Ge-nearest neighbours, respectively [2].

We must note that the shortest d_{U-Ge} distance in $U_3Cu_4Ge_4$ is well comparable with the sum of U and Ge atomic radii ($r_U+r_{Ge}=0.2929$ nm [10]). This concerns the less surrounded of the two crystallographically inequivalent uranium atoms and could be at the origin of the strong 5f(U)–3p(Ge) hybridization. This is a possible explanation of the fact that this uranium atom does not have a larger magnetic moment than the uranium, with a more important number of nearest neighbours as was to be expected.

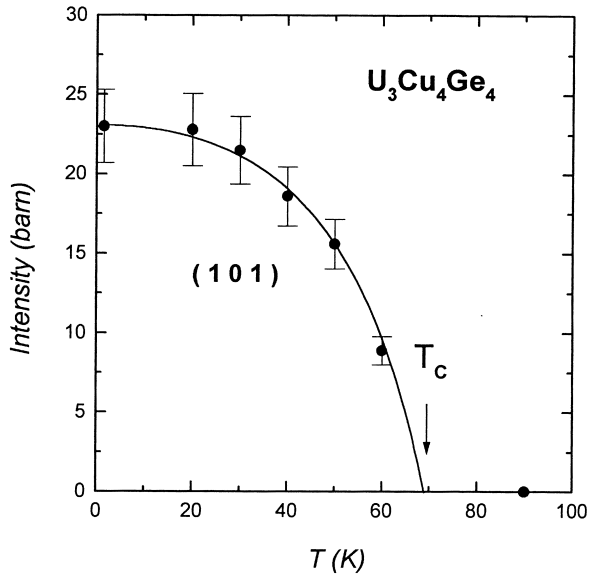

Fig. 4. Thermal variation of the intensity of the (101) magnetic peak for $U_3Cu_4Ge_4$.

4. Conclusions

The powder neutron diffraction investigation of $U_3Cu_4Ge_4$ confirms the ferromagnetic ordering of this compound below $T_C=69(2)$ K. It exhibits a collinear magnetic structure with U-moments aligned along the *a*-axis. The two crystallographically different uranium atoms were found to carry the same magnetic moment.

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