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Site susceptibility tensors and magnetic structure of $U_3Al_2Si_3$: a polarized neutron diffraction study

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Abstract

The nuclear and magnetic structures of $U_3Al_2Si_3$ have been investigated by means of polarized and unpolarized neutron diffraction for single crystals. Measurements were made in the temperature range from 7 to 250 K and in external magnetic fields up to 6 T parallel to [100], [$\bar{1}$10] and [001]. Above the magnetic ordering temperature ($T_C = 36$ K) the crystals have the fully ordered $U_3Ga_2Ge_3$ structure (space group $I4/m$). Below 35 K both polarized and unpolarized neutron measurements show that the magnetic moments on the U3 atoms, which occupy general positions in the space group, order in the ***ab***-plane in a non-collinear arrangement with a net ferromagnetic component. The moments of the U1 and U2 atoms are found to be small. A polarized neutron study of the magnetization induced by applied fields above T_C shows marked anisotropy and makes it likely that it is this strong local anisotropy of the U3 ions which leads to the non-collinearity of the magnetic structure.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A reinvestigation of phase equilibria in the ternary systems U–(Al, Ga)–(Si, Ge) has led to the discovery of some new ferromagnetic compounds with the formula $U_3M_2M'_3$, where M is a group III and M′a group IV metal [2, 3]. All the compounds were found to crystallize in a new structure type ($U_3Ga_2Ge_3$), with space group $I4$, which is a low-symmetry derivative of the Cr_5B_3 anti-type structure (space group $I4/mcm$) [1]. The compounds show ferromagnetic properties with ordering temperatures from 36 to 90 K [1–3]. First attempts to solve the magnetic structure of $U_3M_2M'_3$ from neutron powder data were reported recently [1, 4]. A simple magnetic structure model was suggested involving ferromagnetic ordering of the U3 sublattice and antiferromagnetic ordering of U1 and U2. Although the model of magnetic structure led to attractively low residual values ($R_{F^2} \approx 0.070$), some features of the model were unsatisfactory: for instance, the fact that uranium atoms U1 and U2 in chemically identical atomic environments carried significantly different moments. The first aim of the present paper is therefore to verify the low-temperature magnetic structure of one of these compounds: $U_3Al_2Si_3$, by carrying out neutron diffraction experiments on a single crystal.

$U_3Al_2Si_3$ is a compound with strong planar anisotropy containing several independent magnetic atoms in the primitive unit cell with very different local environments: the U1 and U2 atoms lie on sites with tetragonal symmetry whereas the symmetry of the fourfold U3 sites is triclinic. In the previous paper [5], a new method of modelling the magnetic response of a crystal to an external magnetic field has been put forward based on the concept of site susceptibility tensors χ. This formalism can properly (and easily) describe the local anisotropy in crystals containing several magnetic atoms in the unit cell. The site susceptibility is a second-order tensor and hence its symmetry properties are very similar to those of the tensor u_{ij} describing the thermal motion of atoms. By analogy with the atomic displacement parameters (ADPs), atomic susceptibility parameters (ASPs) have been introduced. These ASPs determine the magnetization distribution in the crystal and their components can therefore be derived from polarized neutron flipping ratio measurements. They can be visualized as magnetic ellipsoids whose diameters in any given direction are proportional to the magnetization which can be induced in that direction by a unit field (1 T) applied in any direction; see [5] for more detail. If the local anisotropy is small, the magnetic ellipsoids approximate to spheres with diameters proportional to the induced magnetization. In other cases, anomalous (elongated or flattened) ellipsoids will occur. It was suggested that anomalous ASPs may mediate a magnetic phase transition [5] in much the same way as anomalous ADPs mediate structural transitions.

In the case of $U_3Al_2Si_3$, the site susceptibility approach, which allows the ASPs to be determined for each type of magnetic atom, shows clearly that, in the paramagnetic region, there is an anomalous elongation of the magnetic ellipsoids of U3 along one of the $\langle 110 \rangle$-type axes. This elongation, which is due to strong enhancement of some of the local susceptibility tensor components χ_{ij}, increases markedly at low temperatures. The non-collinear magnetic ordering, which occurs at low temperatures with magnetic moments along the same $\langle 110 \rangle$-type axes, can be regarded as a freezing of the anomalous site magnetizations induced by the molecular field.

2. Crystal structure of $U_3Al_2Si_3$

The crystal structure of $U_3Al_2Si_3$ is illustrated in figure 1. The tetragonal body-centred unit cell contains three types of uranium atom, U1, U2 and U3. The major building blocks of the structure are bi-capped tetragonal Archimedean antiprisms surrounding the U1 and U2 atoms. The antiprisms consist of four Si and four Al atoms and the bi-caps are Si atoms.

As can be seen from the figure, there is no direct exchange path between the U1 and U2 sublattices, since they are separated by a layer of non-magnetic atoms. Thus any exchange coupling between U1 and U2 must take place by indirect exchange via conduction electrons, via a non-magnetic atom or by coupling to their nearest U3 neighbours which are at a distance of 0.393 nm. On the other hand, each U3 atom has one close U3 neighbour at a distance of 0.346 nm and four next-nearest U3 neighbours at a distance of 0.407 nm. Thus the dominant exchange interactions driving the magnetic ordering phase transition are those within the U3 sublattices. It should also be noted that the symmetry of the 2a sites which the U1 and U2 atoms occupy is tetragonal, whereas the 8c position of U3 is triclinic. As will be shown below, these facts have a major influence on the magnetic phase transition.

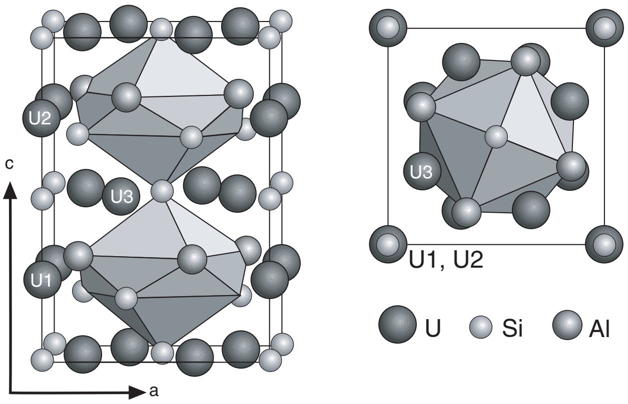


Figure 1. A schematic representation of the structure of $U_3Al_2Si_3$, seen in perspective (LHS), and in projection down [001] (RHS). In both diagrams the bi-capped antiprisms surrounding the U1 and U2 atoms at $(1/2, 1/2, z)$ are depicted as solids.

3. Experimental details

A large single crystal of $U_3Al_2Si_3$ was grown under an argon atmosphere from a pre-melted master alloy of the nominal composition in a Tri-arc Czochralski furnace. The part of the crystal used in the neutron measurements was a cylinder of diameter 3 mm and height 8 mm. The crystal quality was verified by electron microprobe analysis (EMPA) and by a Laue diffraction study, which showed that the crystal growth axis was $\langle 110 \rangle$.

Neutron diffraction studies were performed at the ORPHÉE 14 MW reactor of the Laboratory Léon Brillouin, CEA Saclay. Integrated intensities of Bragg reflections were collected on the four-circle diffractometer 6T2, with the crystal in a DISPLEX refrigerator, using neutrons of wavelength $\lambda_n = 0.090$ nm. Polarized neutron flipping ratios were measured on the lifting-counter diffractometer 5C1 using neutrons with $\lambda_n = 0.084$ nm obtained with a Heusler alloy monochromator. Data were collected on the field-cooled sample in an external field of 6 T both at 7 K, below the ordering temperature, and at 50, 100, 150 and 250 K, above it. For each temperature, three sets of flipping ratios were measured, with the field applied consecutively parallel to one of the main crystal symmetry directions [100], $[1\bar{1}0]$ and [001]. On both instruments, the incident beam collimation was $50'$, and higher-order contamination was suppressed by means of erbium filters to a level of less than 0.01%. The programs MAGLSQ and CHILSQ of the Cambridge Crystallography Subroutine Library [6, 7] were used for least-squares refinements on the measured structure factors and the flipping ratios, respectively. For the magnetic calculations the series expansion of the form factor of U^{3+} as an analytical approximation was used [8].

4. Refinement of the crystal structure

Prior to low-temperature studies the crystal was characterized at 70 K, well above the magnetic ordering temperature. A total of 238 reflections with $\sin\theta/\lambda < 6$ nm^{-1} were measured. In accordance with [4], only reflections permitted in the space group $I4$ were detected. The structure factors of 125 unique reflections were obtained by averaging equivalents. These were used to refine all positional parameters, the occupation factors, the isotropic temperature factors and the extinction parameters. The latter were found to be insignificant. The results

Table 1. Results of refinement of the crystal structure of $U_3Al_2Si_3$ at 70 K in space group $I4$. ($R_{F^2} = 0.054$ for 122 unique reflections $>3\sigma$; $\chi^2 = 3.78$.)

Atom	Site	x	y	z	B (10^2 nm^2)
U1	2a	0	0	0.25 (fixed)	0.82(6)
U2	2a	0	0	0.7488(7)	0.82(6)
U3	8c	0.1593(3)	0.3407(3)	0.0225(7)	0.75(6)
Si1	2a	0	0	0	1.0(1)
Si2	2a	0	0	0.5	1.0(1)
Si3	8c	0.3536(11)	0.1480(10)	0.2089(8)	0.89(5)
Al1	8c	0.1410(11)	0.3613(11)	0.3295(8)	0.89(5)

of refinement using the space group $I4$ are given in table 1. The refinement shows that (within experimental precision of a few per cent) the Al and Si atoms are fully ordered in their respective 8c positions. This confirms the results obtained with powder samples. All other structure parameters derived from single-crystal data for $U_3Al_2Si_3$ were also in an excellent agreement with x-ray and neutron powder diffraction results [1, 4].

5. Magnetic structure of $U_3Al_2Si_3$

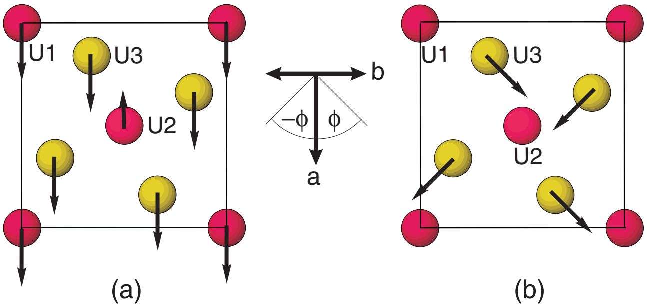
In the magnetically ordered state at 6 K, only reflections permitted in the space group $I4$ were detected, thus indicating that the magnetic unit cell is described by the propagation vector $k = 0$.

5.1. Symmetry analysis of the magnetic structure of $U_3Al_2Si_3$

The symmetry analysis of possible magnetic structures for $U_3Al_2Si_3$ has been carried out by [4] following the methods outlined by Bertaut [9] and Izyumov [10]. For $k = 0$ there are four irreducible representations, Γ_1–Γ_4. The basis vectors (τ_1–τ_4) describing magnetic moments on the 2a sites (U1 and U2) which transform according to the irreducible representations Γ_1–Γ_4 respectively are given in table 2 and those for the general 8c sites in table 3. The structures corresponding to both of the real representations Γ_1 and Γ_3 can be ruled out on the basis of magnetization measurements. From table 3 it can be seen that structures transforming as Γ_3 are pure antiferromagnetic whereas the magnetization measurements show a net ferromagnetic component in the $\boldsymbol{ab}$-plane. Those transforming as Γ_1 are disallowed as they have a net ferromagnetic moment parallel to the c-axis. The basis vectors τ_2 and τ_4 are complex, and so cannot describe real magnetic moments. They can be combined to give two sets of real basis vectors as shown in the final rows of tables 2 and 3 where the combinations have been chosen to retain the same magnitude of moment on all 8c sites. Both combinations have net ferromagnetic moment in the basal plane and are compatible with the magnetization measurements. Rogl *et al* [4] put forward a model for the magnetic structure, illustrated in figure 2(a), which is a simple collinear arrangement of U1, U2 and U3 atoms, with a [100] easy axis. This structure was accepted by [4] as it gave a rather good fit to the powder diffraction data. It was noted, however, that other solutions gave very similar agreement factors.

5.2. Unpolarized neutron diffraction

The temperature dependence of the intensity of the 002 reflection was used to determine the transition temperature, which was found to be 36 K in agreement with the powder results.



(a) (b)

Figure 2. The magnetic structure of $U_3Al_2Si_3$. (a) The collinear structure proposed by [4]. (b) The canted arrangement of spins determined in the present experiment.

Table 2. Basis vectors projected from a general vector $\boldsymbol{M}$ with components M_x, M_y, M_z at the 2a sites of $U_3Al_2Si_3$ (space group $I4$).

Atom		U1	U2
Position		$(0, 0, \frac{1}{4})$	$(0, 0, \frac{3}{4})$
Components	x	y	z
τ_1	0	0	M_z
τ_2	$M_x(1-\mathrm{i})/2$	$M_x(1+\mathrm{i})/2$	0
τ_3	0	0	0
τ_4	$M_x(1+\mathrm{i})/2$	$M_x(1-\mathrm{i})/2$	0
ν_1[a]	M_x	0	0
ν_2[b]	0	M_y	0

[a] $\nu_1 = (1/2)(\tau_2(1+\mathrm{i}) + \tau_4(1-\mathrm{i}))$.
[b] $\nu_2 = (1/2)(\tau_2(1+\mathrm{i}) - \tau_4(1-\mathrm{i}))$.

Table 3. Basis vectors for the 8c sites of $U_3Al_2Si_3$ (space group $I4$).

Atom	U31			U32			U33			U34		
Position	(0.16, 0.34, 0.02)			(0.66, 0.16, 0.02)			(0.34, 0.84, 0.02)			(0.84, 0.66, 0.02)		
$3\tau_1$	M_x	M_y	M_z	$-M_y$	M_x	M_z	M_y	$-M_x$	M_z	$-M_x$	$-M_y$	M_z
$3\tau_2$	M_x	M_y	M_z	$-\mathrm{i}M_y$	$-\mathrm{i}M_x$	$\mathrm{i}M_z$	$\mathrm{i}M_y$	$-\mathrm{i}M_x$	$\mathrm{i}M_z$	M_x	M_y	$-M_z$
$3\tau_3$	M_x	M_y	M_z	M_y	$-M_x$	$-M_z$	$-M_y$	M_x	$-M_z$	$-M_x$	$-M_y$	M_z
$3\tau_4$	M_x	M_y	M_z	$-\mathrm{i}M_y$	$\mathrm{i}M_x$	$\mathrm{i}M_z$	$-\mathrm{i}M_y$	$\mathrm{i}M_x$	$-\mathrm{i}M_z$	M_x	M_y	$-M_z$
$3\nu_1$[a]	M_x	M_y	M_z	M_y	$-M_x$	M_z	M_y	$-M_x$	$-M_z$	$-M_x$	$-M_y$	$-M_z$
$3\nu_2$[b]	M_x	M_y	M_z	$-M_y$	M_x	$-M_z$	$-M_y$	M_x	M_z	M_x	M_y	$-M_z$

[a] $3\nu_1 = 3/2(\tau_2(1+\mathrm{i}) + \tau_4(1-\mathrm{i}))$.
[b] $3\nu_2 = 3/2(\tau_2(1+\mathrm{i}) - \tau_4(1-\mathrm{i}))$.

A total of 160 reflections with $\sin\theta/\lambda < 3\ \mathrm{nm}^{-1}$ were measured at 6 K and again at 70 K and the differences in the measured intensities were used to refine the model of magnetic structure. First the collinear model obtained from powder diffraction was refined. The fit was consistent with an arrangement of the moments within ±5° of the ***ab***-plane and gave the magnetic moment values $\mu_{U1} = 0.89(9)\ \mu_B$, $\mu_{U2} = -0.68(9)\ \mu_B$ and $\mu_{U3} = 1.05(6)\ \mu_B$ (see figure 2(a) with $R_{F^2} = 0.27$.

A considerably better fit was obtained for the structures corresponding to the real combinations ν_1 and ν_2 of τ_2 and τ_4 given in table 3. These correspond to non-collinear arrangements of U3 atoms with net ferromagnetic components in the x- and y-directions respectively. Pairs of U3 atoms related by the diad axes are coupled ferromagnetically;

their moments are parallel to $\langle 110 \rangle$ directions, with those on atoms related by a tetrad being perpendicular to one another (see figure 2(b)). In fact only the mutual orientation of the magnetic moments in the unit cell can be determined from unpolarized neutron diffraction in the absence of a magnetic field because of the presence of both ν_1- and ν_2-type domains. In the structure factor calculations a model containing four equally populated configuration domains (S-domains) obtained by rotation about the fourfold axis was used. The refinement of the non-collinear model gives $\mu_{U1} = \mu_{U2} = 0.09(10)\ \mu_B$, and $\mu_{U3} = 1.26(6)\ \mu_B$ with $R_{F^2} = 0.16$. Thus, the moments of U1 and U2 atoms are found to be very small, suggesting that no ordering occurs in the U1 and U2 sublattices.

5.3. Polarized neutron diffraction

Polarized neutron flipping ratio measurements were made with three different orientations of the crystal. It was mounted in a cryomagnet giving a vertical magnetic field of 6 T. Initially the [100] axis was vertical and in subsequent experiments the $[1\bar{1}0]$ and [001] axes were vertical. A total of 193 Bragg reflection flipping ratios were measured at 7 K with $\sin\theta/\lambda \leqslant 7.0\ \mathrm{nm}^{-1}$. These yielded 163 independent reflections. Since the crystal structure of $U_3Al_2Si_3$ is non-centrosymmetric, neither the calculation of the magnetic structure factors from the measured flipping ratios nor the averaging of symmetry-equivalent (hkl) was performed. The measured values were used directly in the refinement using the MAGLSQ program. This program works from a very general expression for the flipping ratio in terms of the magnetic and nuclear structure factors. It adjusts the parameters of the magnetic model to obtain a least-squares fit to the observations. No assumptions are made about the relative phases of the nuclear and magnetic scattering. The results of the refinement for 90 flipping ratios measured at 7 K in a magnetic field of 6 T parallel to [100] are summarized in table 4. As can be seen from the table, the collinear model proposed by [4] does not account well for the measured flipping ratios ($\chi^2 = 58$). Much better agreement ($\chi^2 = 5.6$) is obtained with the non-collinear arrangement of U3 atoms of figure 2(b), with the pair of atoms (U31, U34) oriented parallel to the [110] direction ($\phi = 45°$) and the other pair (U32, U33) parallel to the $[\bar{1}10]$ direction ($\phi = -45°$). Finally, when the angles ϕ were allowed to vary, a small rotation of the moments towards the direction of the applied magnetic field gave a slightly better fit. This shows that there is a surprisingly strong local anisotropy field which prevents full ferromagnetic alignment of the U3 moments in magnetic fields up to 6 T. Thus the results of the refinements on flipping ratios give unambiguous evidence for the non-collinear arrangement of U3 atom spins and show that the moments are oriented perpendicular to the direction of the nearest-neighbour U3 atom. It should be noted also that the planar anisotropy is very high, since a magnetic field of 6 T applied parallel to the c-axis did not induce any significant moment along the c-axis. The moments on the U1 and U2 atoms are found to be very small, in accordance with the unpolarized neutron results, and seem to align parallel to the external field. The final arrangement is in perfect agreement with the group theoretical analysis.

6. Magnetization and site susceptibilities in the paramagnetic region

In order to investigate the origin of the non-collinear magnetic structure of $U_3Al_2Si_3$, a study of the magnetization induced by a magnetic field above T_C has been carried out. For this purpose, flipping ratio measurements were made at 50, 100, 150 and 250 K with a magnetic field of 6 T applied consecutively parallel to the principal symmetry directions [100], $[\bar{1}10]$ and [001]. The results were interpreted in terms of the model discussed in the introduction which assigns a site susceptibility tensor χ to each crystallographically independent site [5]. In $U_3Al_2Si_3$ the

Table 4. Refinement of different models of the magnetic structure of $U_3Al_2Si_3$ from polarized neutron flipping ratio measurements.

	Collinear (powder model)		Non-collinear (ϕ is fixed)		Non-collinear (ϕ is varied)	
Atom	ϕ (deg)	Moment (μ_B)	ϕ (deg)	Moment (μ_B)	ϕ (deg)	Moment (μ_B)
U1	0	0.49(20)	0	0.18(1)	0	0.16(1)
U2	0	0.45(20)	0	0.18(1)	0	0.16(1)
U31, U34	0	0.97(20)	45	1.39(1)	37(1)	1.29(1)
U32, U33	0	0.97(20)	−45	1.39(1)	−42(3)	1.29(1)
χ^2		58		5.6		3.4

U1 and U2 atoms occupy sites with tetragonal local symmetry and need be characterized by only two parameters $\chi_{11} = \chi_{22}$ and χ_{33}. The U3 atoms, on the other hand, occupy a general position and are therefore subject to no symmetry constraints; all six independent components of χ need to be determined individually. At each temperature, the flipping ratios measured for all three field directions were used simultaneously to refine the independent components of the site susceptibility tensors with the CHILSQ program. This program takes into account the proper orientation of the field for each individual flipping ratio and imposes the necessary symmetry constraints [5].

The results of these refinements are summarized in table 5. Note that for convenience the site susceptibilities are given in units of μ_B T^{-1}; this allows easy comparison with the results of conventional refinement based on a localized magnetic moment model. It can be seen that the susceptibility tensor components of U1 and U2 remain smaller than those of U3 at all temperatures. This confirms that the U1 and U2 sublattices do not play a significant role in the magnetic phase transition. The same is true for the out-of-plane components (χ_{33}, χ_{32} and χ_{31}) of U3. On the other hand, the in-plane components χ_{11}, χ_{22} and χ_{12} of U3 are much larger and increase strongly as the temperature approaches T_C. This is in agreement with the bulk magnetization measurements which also indicate large anisotropy with the easy direction in the ***ab***-plane.

It can be seen in the table that at low temperature one of the non-diagonal elements, χ_{12}, becomes rather large, showing that the principal axes of the representative ellipsoid do not coincide with the crystal axes. (We recall that any second-rank tensor can be written in a diagonal form using an unitary transformation and the non-diagonal terms of the tensor disappear only if the principal axes of the ellipsoid coincide with the crystal axes.) The situation is illustrated in figure 3 in which the magnetic ellipsoids calculated from the refined susceptibilities are shown and compared with the ordered magnetic structure at 7 K. It is evident that the shape and the mutual orientation of the ellipsoids reflect the tetragonal symmetry of the structure. This result confirms that the program has imposed the symmetry correctly. Within these constraints the principal axes of the ellipsoids are found to be oriented along [110] and [$\bar{1}$10] directions, i.e. parallel to the directions of the magnetic moments in the magnetically ordered state. It should be stressed that this orientation is not a consequence of any symmetry imposed on the susceptibilities, but is given naturally by the refinement. The diameters of the ellipsoids along the two principal axes in the basal plane are very different and very temperature dependent. For example, at 50 K the magnetization along the easy and hard local axes differ by a factor of 7, but at 250 K the factor is only about 2. This shows that whilst the local anisotropy is rather small at high temperatures, it is very strongly enhanced when approaching the ordering temperature. The non-collinear magnetic structure can be seen to be the direct consequence of

Table 5. Site susceptibilities in $U_3Al_2Si_3$ obtained from the refinement on polarized neutron flipping ratios.

Atom	Site susceptibilities (μ_B T^{-1})[a]					
	χ_{11}	χ_{22}	χ_{33}	χ_{12}	χ_{13}	χ_{23}
$T = 50$ K, 196 reflections, $\chi^2 = 2.1$						
U1, U2[b]	0.013(1)	0.013(1)	0.0167(8)	0	0	0
U3	0.080(3)	0.084(3)	0.0088(8)	0.056(2)	−0.001(3)	0.001(3)
$T = 100$ K, 412 reflections, $\chi^2 = 1.05$						
U1, U2[b]	0.0052(3)	0.0052(3)	0.0088(2)	0	0	0
U3	0.0227(7)	0.0248(7)	0.0043(2)	0.0123(3)	−0.006(2)	0.0015(13)
$T = 150$ K, 171 reflections, $\chi^2 = 0.95$						
U1, U2[a]	0.0030(3)	0.0030(3)	0.0070(2)	0	0	0
U3	0.0142(7)	0.0147(7)	0.0042(2)	0.0060(3)	0.002(3)	−0.007(4)
$T = 250$ K, 112 reflections, $\chi^2 = 0.93$						
U1, U2[a]	0.0043(3)	0.0043(3)	[c]	0	0	0
U3	0.0073(7)	0.0077(7)	[c]	0.0012(3)	[c]	[c]

[a] 1 μ_B $T^{-1} = 5.58$ J T^{-2} mol^{-1}. The field applied was in all cases 6 T.
[b] The additional constraint $\chi_{ii}(U1) = \chi_{ii}(U2)$ was applied.
[c] Susceptibility components, which could not be obtained from the refinement.

this high anisotropy; the molecular field leading to magnetic order can only orient the moments along the elongated axes of the ellipsoids, so it is along these directions that the moments finally order. The long axes of the ellipsoids are the easy axes of magnetization of individual atoms and it is clear that they do not coincide with the easy magnetization axis of the crystal as a whole.

7. Discussion

It has been shown that the ordered magnetic structure of $U_3Al_2Si_3$ is a non-collinear arrangement with a net ferromagnetic moment parallel to one of the a-axes of the tetragonal cell. The non-collinearity emerges naturally from a strong local anisotropy of the U3 atoms which is present in the paramagnetic phase. The exchange paths between the U atoms of the structure are indicated in figure 4. Within the U3 sublattice each U3 atom has a single nearest neighbour at 0.346 nm. At such a distance the neighbouring 5f shells are sufficiently far apart for direct exchange, which would favour antiferromagnetic alignment, to be neglected. On the other hand, the spin of the incomplete 5f shell is strongly coupled (antiferromagnetically) to the conduction electrons. This results in indirect exchange, through the conduction band, leading to ferromagnetic coupling. The coupling of this pair of nearest neighbours (J_1) is rather strong and certainly dominates all other interactions. The exchange coupling with the four next-nearest (nn) neighbours of U3 (at 0.407 nm) (J_2) is indirect; it could both be via conduction electrons and involve superexchange via a Si atom. However, the anisotropy makes these U3 atoms have their moments (ellipsoids) perpendicular to those of the first pair (see figure 3) and as a result the molecular field due to nn-neighbour U3 atoms vanishes in the magnetically ordered state. The two third-nearest U3 neighbours are situated at a distance 0.575 nm and have their moments parallel to the moment of the first atom. The coupling (J_3) can also be attributed to superexchange via a Si atom. In spite of a much larger U3–U3 distance (0.575 nm) as compared to the nn one (0.407 nm), the U3–Si–U3 exchange path has the same U3–Si distances 0.288 nm, giving the same effective length for the superexchange path. An

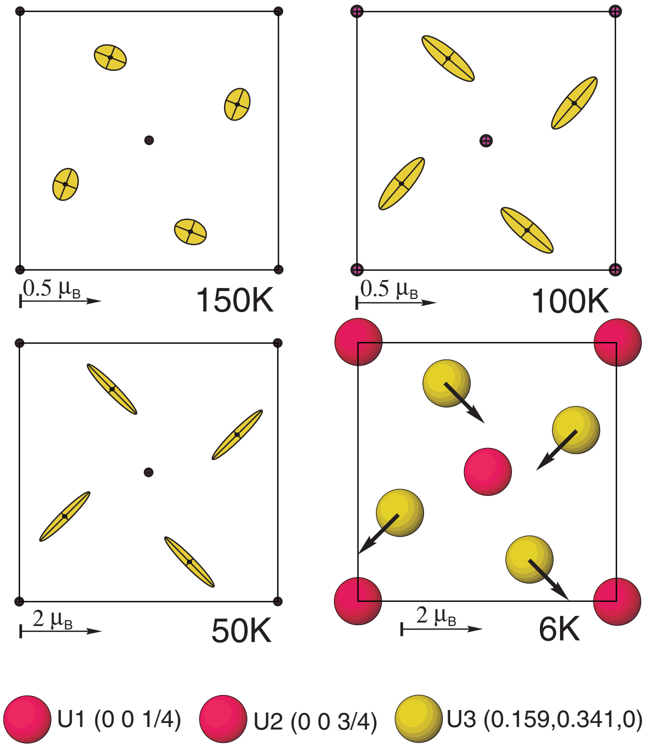


Figure 3. Evolution with temperature of the magnetic anisotropy in $U_3Al_2Si_3$. At high temperature (150 K) the susceptibility is nearly isotropic, as indicated by nearly spherical magnetic ellipsoids. On cooling, the anisotropy increases and the magnetic ellipsoids are elongated along the directions in which the ordered moments point in the magnetic structure stable at 6 K. The structure is shown in projection down [001]. The sizes of the ellipsoids indicated by the scale in μ_B correspond to the magnetization induced by 6 T.

important difference is that the U3–Si–U3 bond angle (171.40°) is close to 180° while that for the nn neighbours is close to 90°. This can be the origin of the ferromagnetic alignment of the third-neighbour U3 atoms.

In contrast with the U3 atoms, the U1 and U2 atoms exhibit a very low local susceptibility (see table 5), and are characterized by nearly spherical magnetic ellipsoids, indicating low local anisotropy. The smallness of the local susceptibility suggests that these atoms have small or zero local moments. The absence of ordering in the U1, U2 lattices at low temperatures must be attributed partly to this low moment, and partly to the fact that there are no magnetic atoms in the first coordination spheres of either U1 or U2, so inter-sublattice exchange is practically absent. Coupling of the U1 and U2 magnetic sublattices could take place either through indirect exchange via conduction electrons or by superexchange coupling via non-magnetic atoms. Both of these interactions are expected to be considerably smaller than the nearest-neighbour U3 interaction; hence, it is not surprising that ordering occurs only in the U3 sublattices.

Thus the magnetic structure of $U_3Al_2Si_3$ can be described as dominated by single-atom anisotropy which constrains the moments on U3 atoms to lie in the ***ab***-plane at right angles to the line joining them to their nearest U3 neighbour. These pairs of U3 atoms are strongly coupled ferromagnetically by indirect exchange through the conduction electrons, and the

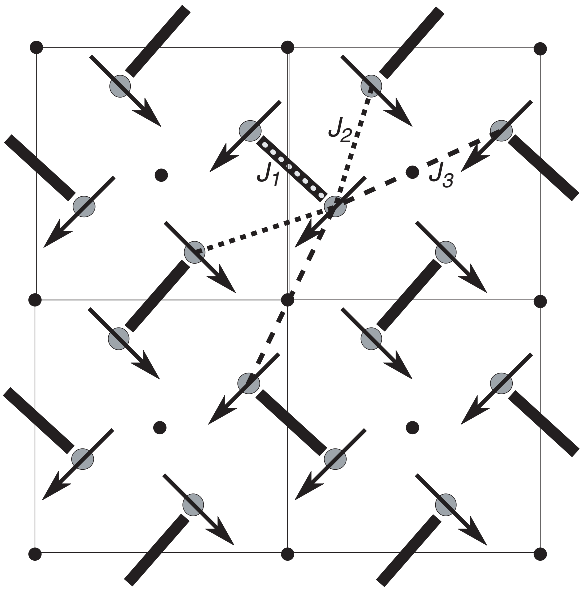


Figure 4. A projection down [001] showing the different exchange paths between the U atoms in $U_3Al_2Si_3$. There is strong ferromagnetic coupling via the shortest exchange path J_1; the coupling via J_2 and J_3 is indirect and weaker with the former being antiferromagnetic and the latter ferromagnetic.

three-dimensional continuity of the structure is ensured by superexchange interactions between the pairs.

The relationship between the site and bulk susceptibility tensors is quite straightforward:

$$\chi^b = \sum_m \sum_q \boldsymbol{R}_q \chi^{mq} \tag{1}$$

where the summations are over the independent magnetic atoms m and the subgroup of symmetry operators q whose rotational part is $\boldsymbol{R}_q$ and which generate distinct positions for the atoms j. The symmetry properties of the tensors ensure that the bulk susceptibility tensor transforms with the full symmetry of the crystallographic class. For tetragonal $U_3Al_2Si_3$ the bulk susceptibility tensor contains only two independent elements. Using the symmetry properties of the local susceptibility tensors of the four U3 atoms in the primitive unit cell, the above equation reduces to

$$\begin{aligned} \chi_{11}^b &= \chi_{22}^b = 2(\chi_{11} + \chi_{22}) \\ \chi_{33}^b &= 4\chi_{33}. \end{aligned} \tag{2}$$

This expression gives the full bulk susceptibility as long as the contribution from the U1, U2 atoms and the conduction electrons can be neglected. The results given in table 5 confirm that the U1, U2 contribution does not exceed a few per cent. On the other hand, the conduction electron contribution cannot be determined from the neutron experiment.

8. Conclusions

The structure of $U_3Al_2Si_3$ determined has been refined from single-crystal neutron diffraction and is in complete agreement with earlier x-ray and neutron powder diffraction results [4]. It confirms that there is complete order of the Al and Si atoms in their respective 8c positions.

Polarized and unpolarized neutron diffraction shows that the ordered magnetic structure is a non-collinear arrangement of U3 atoms. It contains ferromagnetically coupled pairs of near-neighbour U3 atoms with moments oriented parallel to the $\langle 110\rangle$ direction which is perpendicular to the line joining them. This arrangement results in a net ferromagnetic moment in the $\boldsymbol{ab}$-plane in agreement with magnetization measurements. In contrast to the U3 atoms, the U1 and U2 atoms do not show any magnetic ordering.

Polarized neutron flipping ratio measurements made at several temperatures and with several different field directions have been interpreted using the local susceptibility approach [5]. The site susceptibility tensors have been determined and used to construct the magnetic ellipsoids at different temperatures. The U3 atoms are found to have extremely anisotropic magnetic ellipsoids particularly at the lower temperatures, and the longest axis of the ellipsoid may be considered as a local easy axis of magnetization. In the vicinity of the magnetic ordering transition the susceptibility along the easy axes of the U3 atoms is nearly an order of magnitude higher than that along any other direction. The easy axis of each U3 was found to be the same $\langle 110\rangle$ direction as its moment orders along at low temperature. The anomalous elongation of the magnetic ellipsoids in the paramagnetic region can therefore be considered as a precursor of the low-temperature magnetic order.

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