Magnetic structure and single crystal studies of UFe_6Ge_6

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Abstract.

An investigation of the magnetic and structural properties of UFe_6Ge_6 using magnetization, neutron and X-ray diffraction measurements, performed on both polycrystalline and single crystal samples, is reported. The Fe sublattice orders at 320 K in a $\kappa = (0\,0\,1/2)$ magnetic structure corresponding to an antiferromagnetic stacking along the c-axis of ferromagnetic (0 0 1) planes of Fe moments pointing along the hexagonal c-axis. An additional anomaly at 220 K is seen on the magnetization data, corresponding to the development of a small ferromagnetic component. This may be due to a small canting of the Fe moments away from the c-axis or, more likely, to a polarization of the actinide sublattice. Neutron and X-ray diffraction data show a doubling of the a and c lattice constants for samples produced by slow cooling from the melt. For these samples a superstructure of YCo_6Ge_6 is formed, due to a partial ordering of the U and Ge atoms at positions $1a$ and $2e$, in such a way that full ordering would result in a crystal structure of the type of $ScNi_6Ge_6$.

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1. Introduction

The intermetallic compounds with the general composition AFe_xM_{12-x} (A = f element; M = d-element, Al, Ga, Si, Ge or Sn), have attracted considerable interest due to their possible application as hard magnets [1]. The presence of two magnetic elements occupying two or three crystallographic positions result in a variety of magnetic properties ranging from simple ferromagnetism [2] to complex modulated antiferromagnetic structures [3], metamagnetism [4], etc.

UFe_6Ge_6 is a magnetic intermetallic compound that crystallises in an hexagonal lattice with cell parameters $a = 5.1268(4)$ Å, $c = 4.0507(5)$ Å, space group $P6/mmm$, in the YCo_6Ge_6-type of structure [6]. An X-ray study showed that the uranium atoms occupy the yttrium site (50% occupancy of the $1a$ crystallographic position) and that 1/3 of the germanium atoms are located in the $2e$ site (also at 50% occupancy) while the remaining germanium and iron atoms occupy the $3g$ and $2c$ positions, respectively. Magnetisation measurements performed on polycrystalline samples show two independent magnetic transitions: an antiferromagnetic transition at 322 K and the onset of weak ferromagnetism at 230 K. The transition at higher temperature was unambiguously associated with the ordering of the iron moments by means of ^{57}Fe Mössbauer spectroscopy. The anomaly at 230 K was not detected on the Mössbauer measurements which, taken together with the low value of the spontaneous magnetisation at 10 K ($\sim 0.05\ \mu_B$/f.u.), may indicate that the second transition is due to the uranium atoms. However, another possibility not excluded from these measurements is a reorientation of the Fe moments, resulting in weak ferromagnetism due to a small canting of the Fe moments as recently reported for one of the polymorphs of $YbFe_6Ge_6$ [5]. Relying on the bulk measurements on polycrystalline samples and in the absence of neutron diffraction data it is difficult to elaborate on details of the magnetic structure. Therefore, it was decided to complement the previous measurements with new magnetisation measurements on a single crystal sample and perform a neutron diffraction study aimed at determining the magnetic structure of UFe_6Ge_6, which are reported in this work.

2. Experimental

UFe_6Ge_6 polycrystalline samples were prepared by induction melting the at least 99.9% purity elements in a cooper cold crucible, under argon atmosphere. Repeated melting was used to ensure a perfect sample homogeneity. Some of the polycrystalline samples, with ~ 15 g, were used as bulk charges for the crystal growth. The single crystals were grown by the Czochralski method in an induction furnace with a levitation crucible, under an argon atmosphere. The previous inexistence of UFe_6Ge_6 single crystals to use as a seed led us to use, instead, a tungsten needle. A rotation rate of 15 rpm and a pulling rate of 1.5 cm/h were employed in order to obtain single crystals of 2 mm diameter and 10 mm height aproximate dimensions.

Magnetization measurements were performed on a SQUID magnetometer (Quantum Design MPMS). Both the longitudinal and transverse magnetization were measured on small single-crystals previously oriented on a X-ray diffractometer. The measurements were made in the $5 - 400$ K temperature range under applied fields up to 5.5 T.

Neutron diffraction experiments were performed on both powder and single-crystalline samples. Powder diffraction measurements were performed at the DN5 diffractometer that was installed at the Siloë reactor (CEN-Grenoble, France) on a finely ground sample of ~ 30 g. This instrument is a two-axis diffractometer equipped with a multidetector counter covering an angular range of 80° and providing an angular resolution of 0.10°. The sample was encapsulated in a vanadium can before being inserted in a ILL orange-type helium-flow cryostat. A series of spectra were collected in the temperature interval ranging from 317 K down to 5 K. In order to better resolve the magnetic peaks at low momentum transfer, a wavelength of 2.48 Å, produced by a focusing PG (0 0 2) monochromator, was used. In addition, one spectrum was collected at room temperature using a shorter wavelength of 1.346 Å from a Cu $(2\ 2 - 0)$ monochromator. Each spectrum was accumulated for 3 hours. The single-crystal neutron diffraction data was collected in the four-circle diffractometer TAS2 at Risø National Laboratory, Denmark. This diffractometer is equipped with a Be monochromator and the sample was mounted inside a closed cycle He cryostat capable of attaining a base temperature of 20 K. A first set of measurements was performed at 310 K on a cylindrical crystal with a volume of ~ 13 mm^3. A total of 413 reflections indexed on a unit cell typical of a YFe_6Co_6-type of structure were measured at $\lambda = 1.027$ Å, which gave, after averaging the equivalents, a set of 71 independent reflections. Then the crystal was cooled and reciprocal-lattice scans were performed along selected high-symmetry directions of the first Brillouin zone around several reciprocal lattice points. A preliminary investigation of the magnetic ordering of the crystal was made following the intensity of some of the magnetic peaks down to 20 K.

The X-ray diffraction data reported in this work were measured in Bragg-Brentano geometry on a Pananalytical X-Pert diffractometer using monochromated Cu $K\alpha$ radiation ($\lambda = 1,5418$ Å). X-ray powder diffraction measurements were performed on two types of samples, one obtained crushing a small piece cut from a large single crystal and the other powdering a piece of the bulk polycrystalline charge from which the single crystals were grown by pulling from the melt. Each of the collected spectra were accumulated for 24 h.

3. Results and discussion

The single-crystal magnetisation measurements confirmed previous results obtained on polycrystalline samples [6]. The temperature dependence of the magnetisation for fields applied along the a and c axes is shown in Figure 1. Two magnetic transitions are

observed: an antiferromagnetic transition, at 320(5) K, more clearly seen when the field is parallel to the c axis; and at 220(10) K a ferromagnetic-like transition with the easy direction parallel to the c axis. There is little difference between the thermomagnetic curves measured while cooling in field and after zero field cooling, even for fields as small as 1 mT. The field dependence of the magnetization for a series of temperatures between 5 and 300 K is shown in Figure 2. The magnetization is pratically linear in field up to the maximum value of the applied field (5.5 T) at all temperatures. There is a strong magnetic anisotropy: at 5 K the magnetization measured for a field parallel to the a-axis is roughly a factor of four times higher than that measured along the c-axis.

The results of a crystallographic least-squares refinement based on the single-crystal neutron diffraction data are shown in Table 1. The Bragg reflections measured where those of a unit cell corresponding to the assumed YCo_6Ge_6 structure, and therefore any extra peaks due to the possible formation of a crystallographic superstructure (see below) were missed at this stage. The atomic coordinates of the previously published single-crystal X-ray diffraction study [6] were used as the starting point for the structure refinement. The uranium and the iron atoms are located in only one crystallographic position, respectively the $1a$ and $3g$ sites, and the germanium atoms in the two remaining positions, the $2c$ and $2e$ sites. The refinement was performed using a locally modified version of the SFLSQ program of the CCSL library [7], which includes the possibility to refine secondary and primary extinction by the Becker-Coppens model [8]. Atomic coordinates not fixed by symmetry, anisotropic temperature factors and site occupancy factors were allowed to refine. The partial occupation of the $1a$ and $2e$ positions gave occupancy values close to 50%, that of the $2c$ site refined to a value close to 100%. These results confirm that, even if a superstructure is formed, the YCo_6Ge_6 structure gives a good description of the *average* crystal structure. A series of reciprocal-lattice scans performed at low temperature show the existence of magnetic peaks of the $(h\ k\ l/2)$ type. The intensity of the (1 0 1/2), (2 0 1/2) magnetic peaks was followed as function of temperature. The evolution of the intensity of the (2 0 1/2) reflection as function of temperature is shown in Figure 3. The magnetic intensity disappears at a temperature close to $T_N = 320$ K, in good agreement with the magnetization and Mössbauer measurements.

During the four-circle neutron diffraction measurements the existence of a number of small extra peaks, not indexed to the YCo_6Ge_6-type structure, was observed. The intensity and position of these peaks are temperature independent, which proves that they are not of magnetic origin. After this experiment, and considering the possibility of formation of a superstructure, powder X-ray diffraction measurements were performed on two types of samples, one obtained crushing a small piece that was removed from the grown single crystal and the other powdering a piece of the bulk charge. The powder X-ray diffraction patterns of the two samples are shown in Figure 4 and Figure 5. They confirm the existence of some extra peaks which are not possible to index in the YCo_6Ge_6-type structure. This is most notorious in the sample prepared from a piece of the large single crystal. The sample prepared from the polycrystalline material

shows only a small number of weak and broad extra peaks in addition to those of the YCo_6Ge_6-type of structure, in contrast with the samples prepared from a piece of the single crystals. In this case, the number of extra peaks is larger and also they are stronger and narrower, indicating that some kind of a superstructure of the YCo_6Ge_6 was formed. This is probably due to the fact that the crystal grows in near equilibrium conditions, leading to a decrease of the disorder observed in the YCo_6Ge_6-type structure with the formation of a crystallographic superstructure.

The neutron powder diffraction spectra for different temperatures are presented in Figure 6. As the temperature was lowered a few peaks significantly increased intensity revealing their magnetic origin. These peaks could be indexed with a propagation vector $\tau = (0\ 0\ 1/2)$, i.e., the magnetic repeat period along c doubles the chemical cell parameter along that direction. Also, it was striking the absence of the (0 0 1/2) and (0 0 3/2) peaks which shows that the magnetic moments are aligned with the *c*-axis. A simple model explaining these observations is that of alternating layers of ferromagnetic Fe moments parallel to the *c*-axis, antiferromagnetically coupled in a sequence along the tetragonal unique-axis (Figure 7). However, the spectra also showed the presence of a few extra peaks that were temperature independent and that could not be indexed neither in the assumed crystallographic cell of the YCo_6Ge_6 structure or in the magnetic cell. After having ruled out the possibility that the extra peaks could be due to impurities in our sample, the most likely explanation was that they originate from some kind of a crystallographic superstructure as observed also in the X-ray diffraction data. In order to verify this point, a second powder diffraction experiment was latter performed in which a new spectrum was collected at a higher resolution on the same diffractometer, using a shorter wavelength of 1.346 Å from a Cu (2 2 0) monochromator. The data was collected at a stabilized temperature of 320 K, which is sufficiently close to the transition temperature to neglect any possible magnetic contribution to the Bragg peaks. Analysis of this spectrum showed the presence of extra lines that could only be indexed in a cell with double *a*- and *c*-axis compared to those of the YCo_6Ge_6 type of structure. A partial ordering of the U and/or Ge atoms both in the (0 0 1) planes and along *c* would result in such a doubling of the cell parameters and for perfect ordering the derived structure is that of $ScNi_6Ge_6$ [9]. Indeed, a Rietveld refinement of the data using the computer program FULLPROF [10] and assuming a partially ordered $ScNi_6Ge_6$ structure could explain all observed unindexed peaks, and gives a good fit of the data. Assuming the crystallographic structure that best fits the data at 320 K remains unchanged at low temperature, we could fit the magnetic peaks using a single parameter, the value of the ordered Fe magnetic moment. A spin-only form factor for the Fe^{2+} moment, internally stored in the FULLPROF program, was used in the calculation of the magnetic intensities. The evolution of the magnetic moments of the Fe atoms with temperature deduced from the Rietveld refinements of the powder data is shown in Figure 8. The value of the ordered moment at low temperature is 1.4 μ_B/(Fe atom). The individual moments of the iron atoms calculated from the intensity of a measured set of magnetic reflections is 1.5(3) μ_B/(Fe atom), assuming a simple antiferromagnetic

coupling of the Fe moments along the c-axis and ferromagnetic coupling in each of the Fe layers extending in the $z = 0$ and $z = 1/2$ planes. Both the value and the temperature dependence of the ordered magnetic moment of the Fe atoms are in good agreement with Mössbauer data [6].

4. Conclusions

On this work we report on the crystallographic and magnetic structure of UCo_6Ge_6 from polycrystalline and single crystalline samples. We have observed both with X-ray and neutron diffraction Bragg peaks on the single-crystal sample that correspond to a crystallographic superstructure of the YCo_6Ge_6, with a doubling of both a and c axis, that could originate from a partial ordering of either U or Ge atoms. For a perfect ordering, the derived structure is that of $ScNi_6Ge_6$. Such crystallographic superstructure are very common in the 1:6:6 germanides and stanides with rare-earths and transition metals [**?**][11]. These superstructures can be ultimately related to different stackings of slabs of the parent $ThMn_{12}$ type of structure that, itself, relates to the $CaCu_5$ type of structure.

A simple collinear, antiferromagnetic, ordering of the Fe moments below 320 K was found from the neutron-scattering experiments. Such type of magnetic ordering is also found in rare-earth compounds with similar compositions [12, 13]. The origin of the magnetic anomaly observed on the magnetization data at $T = 230$ K is not yet clear. One can not rule out the possibility of a spin reorientation of the Fe moments, such as a small canting moving away from the hexagonal axis as observed in the polymorph of the closely related compound $YbFe_6Ge_6$ that cristallises in the $HfFe_6Ge_6$ type of structure. Another possibility, that we find more likely as such canting of the Fe sublattice was not detected by Mössbauer and was also not found in the polymorph of $YbFe_6Ge_6$ that cristallises in the YCo_6Ge_6 structure [5], is that this observed magnetic anomaly originates from the ordering of a small ferromagnetic moment on the U atom but our neutron scattering experiments are inconclusive about the presence of such small magnetic moment on the actinide. A similar situation of weak ferromagnetism on the actinide sublattice was found in the compound UFe_2, a compound which crystallizes in the cubic C15 Laves structure [14]. Polarised neutron diffraction experiments on single crystals have shown that the small value of the U atom (1.4 μ_B) was due to an almost complete cancelation of the spin and orbital components [14][15]. Such cancellation might also apply to the UCo_6Ge_6 compound. This point would deserve future work on a polarised neutron beam.

5. Acknowledgments

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PTDC/QUI/65369/2006."

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Tables and table captions

Table 1. Results of the least-squares refinement of the crystal structure of UFe_6Ge_6 based on single-crystal neutron-diffraction data.

Site	z	Occupancy	U_{11}	U_{22}	U_{33}	U_{12}
U ($1a$)	–	0.50(1)	0.0097(17)	$= U_{11}$	0.091(25)	$= 1/2U_{11}$
Fe ($3g$)	–	1.0[a]	0.0143(6)	0.0103(6)	0.0064(9)	0.0052(3)
Ge ($2e$)	0.3019(9)	0.46(1)	0.013(1)	$= U_{11}$	0.010(19)	0.0066(7)
Ge ($2c$)	–	0.99(1)	0.0120(8)	$= U_{11}$	0.0059(9)	0.0060(4)
$R = 3.62\%$	$R_w = 2.88\%$					

[a] Fixed during refinement.

Figure captions

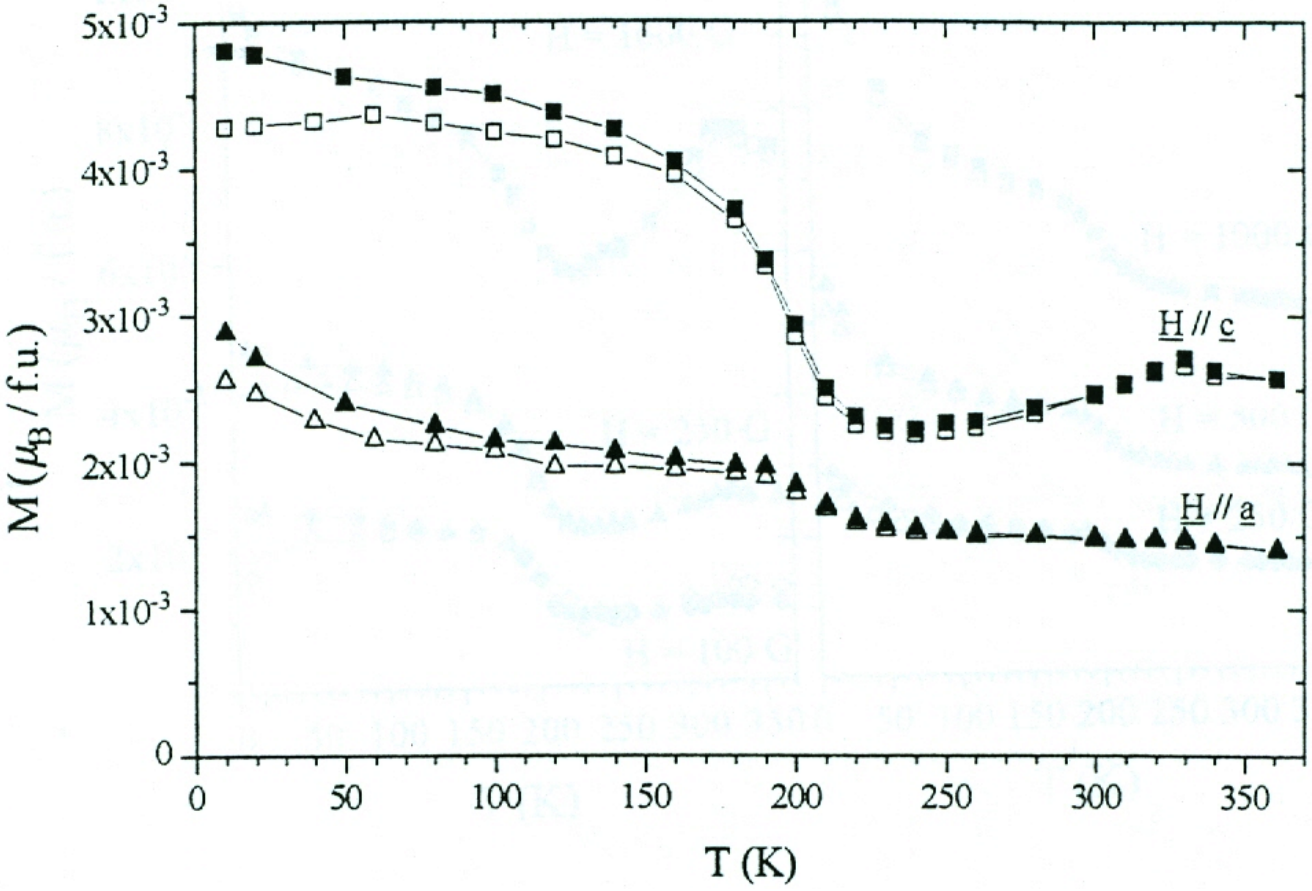

Figure 1. Temperature dependence of the magnetization of a single crystal of UFe_6Ge_6 measured in a field of 25 mT applied parallel to the a (△) and c (□) axis. Open symbols correspond to measurements after zero-field cooling and the solid points to measurements while cooling in field.

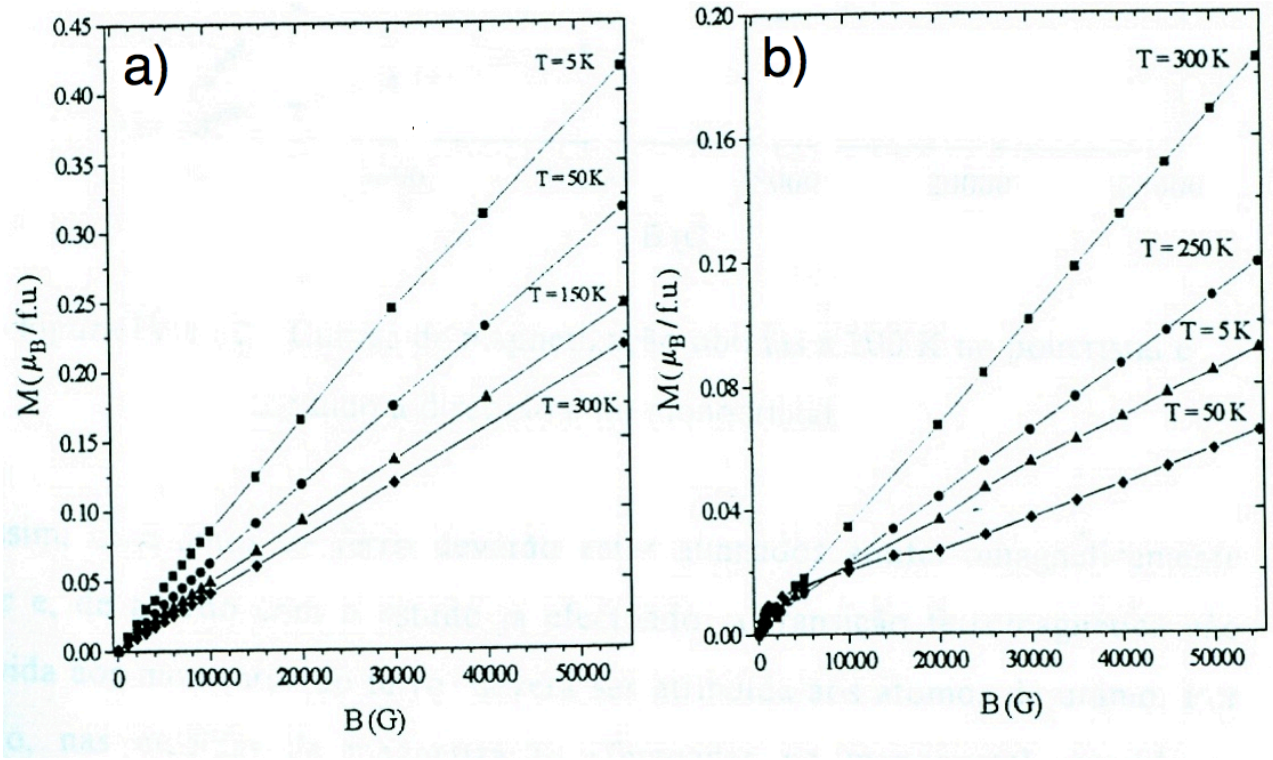

Figure 2. $M(H)$ curves at T = 5 K, 50 K, 150 K and 300 K measured along the a and c axis.

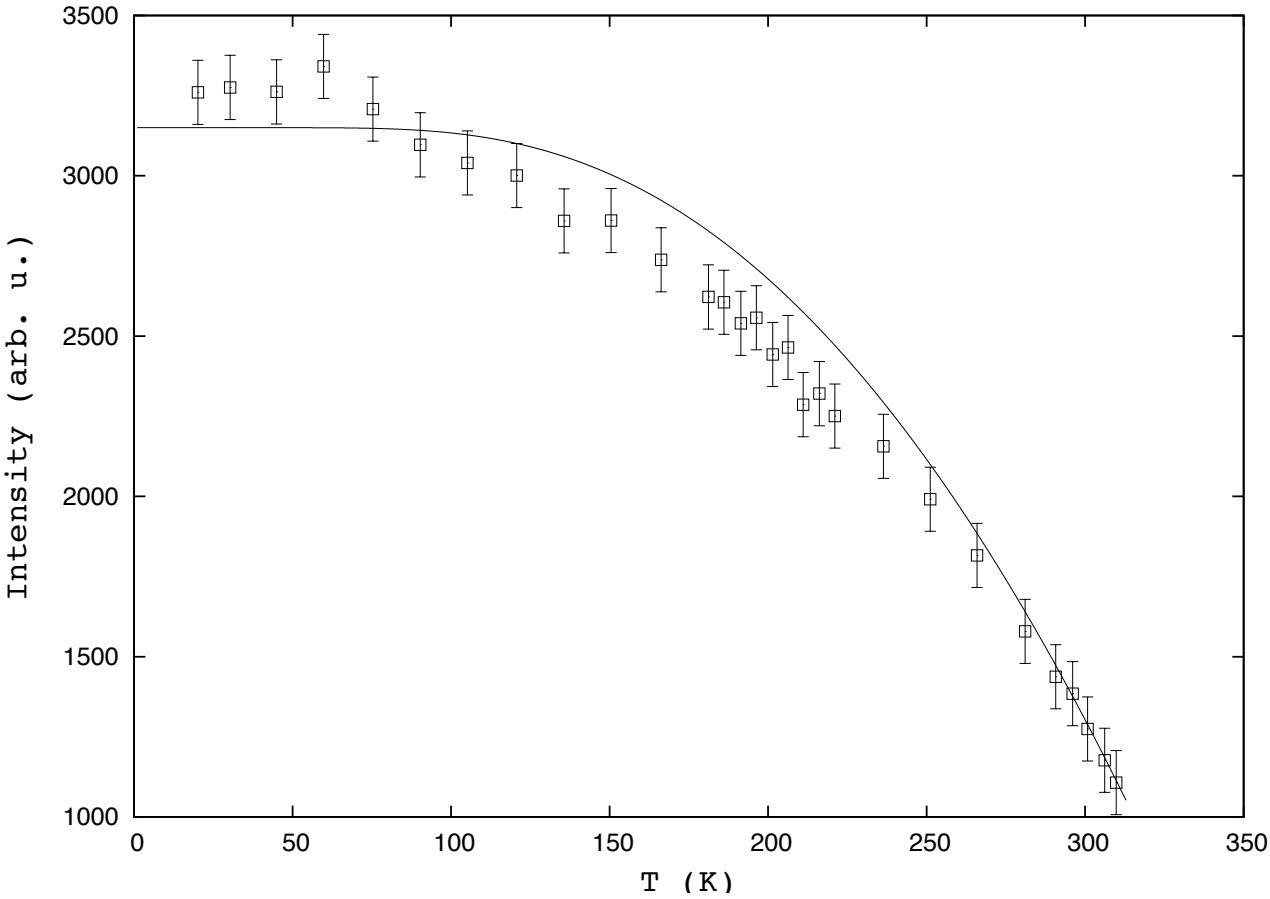

Figure 3. Temperature variation of the intensity of the (2 0 1/2) magnetic reflection.

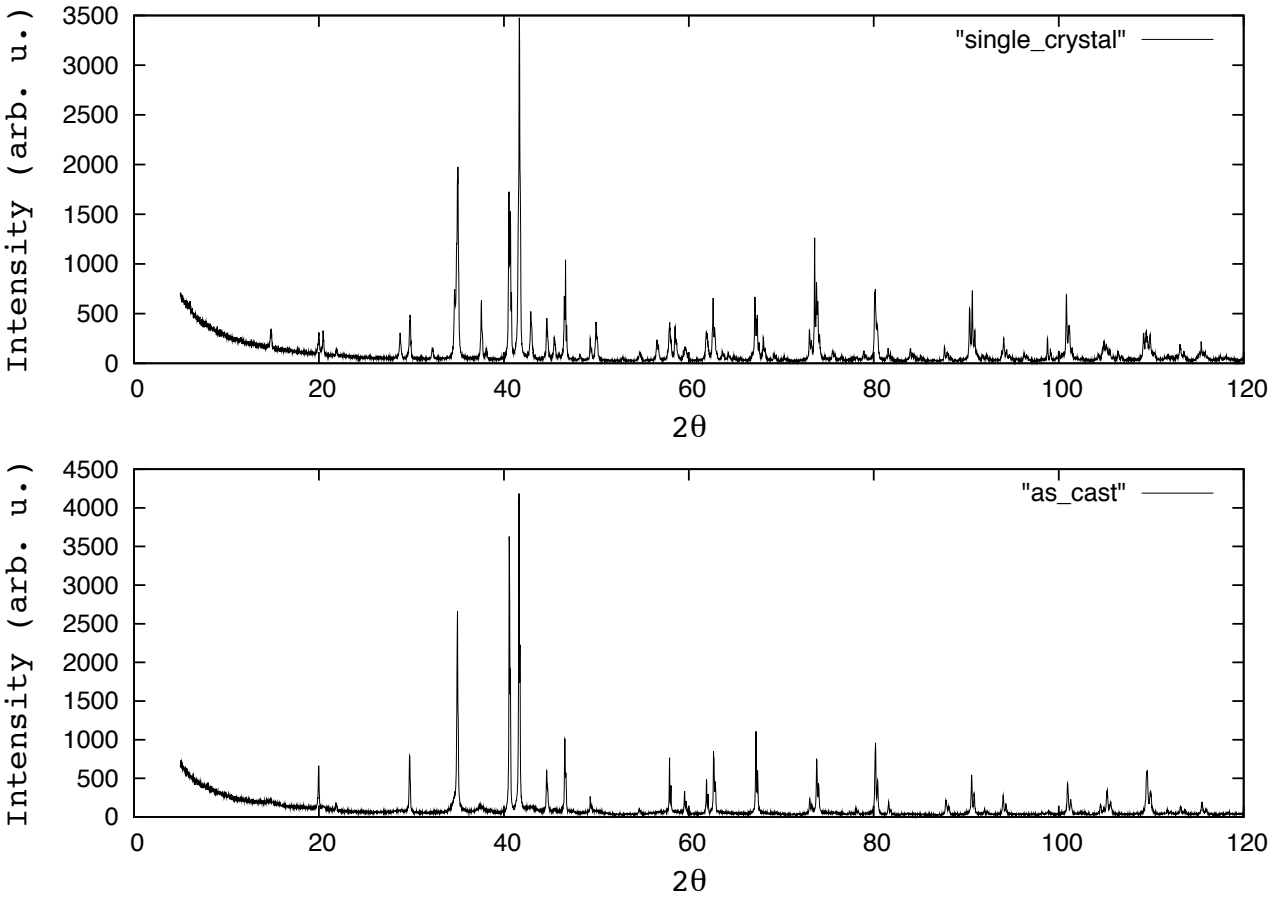

Figure 4. Powder X-ray diffraction spectra of UFe_6Ge_6. a) powder obtained from a piece of a large single-crystal; b) powder obtained from a polycrystalline sample, as cast.

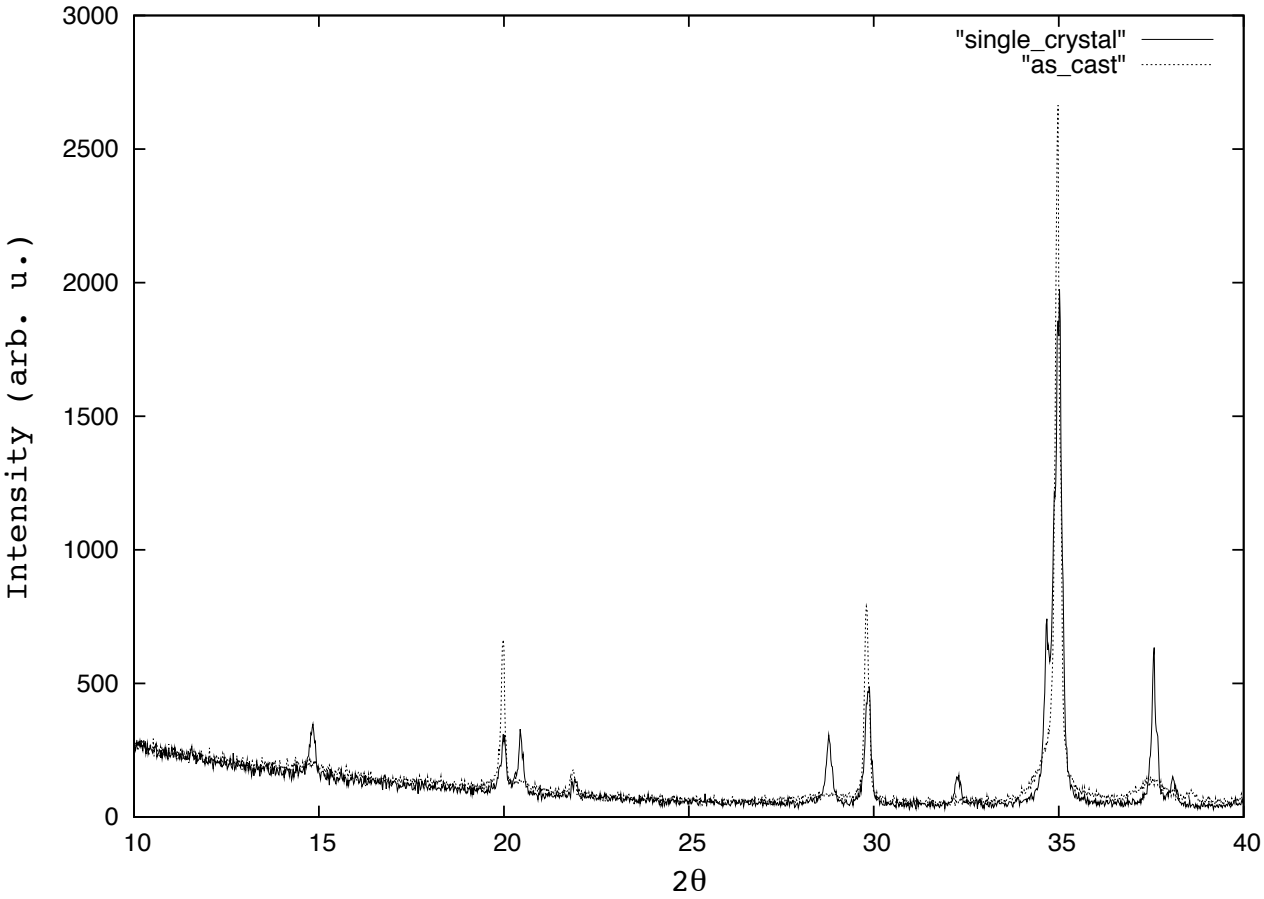

Figure 5. Comparision of the low-angle region of the powder X-ray diffraction spectra of UFe_6Ge_6 for the sample obtained from a piece of a large single-crystal and the polycrystalline sample. The former sample shows peaks not indexed in YCo_6Ge_6 structure, corresponding to a doubling of the a and c-axis as in the $ScNi_6Ge_6$ type of structure.

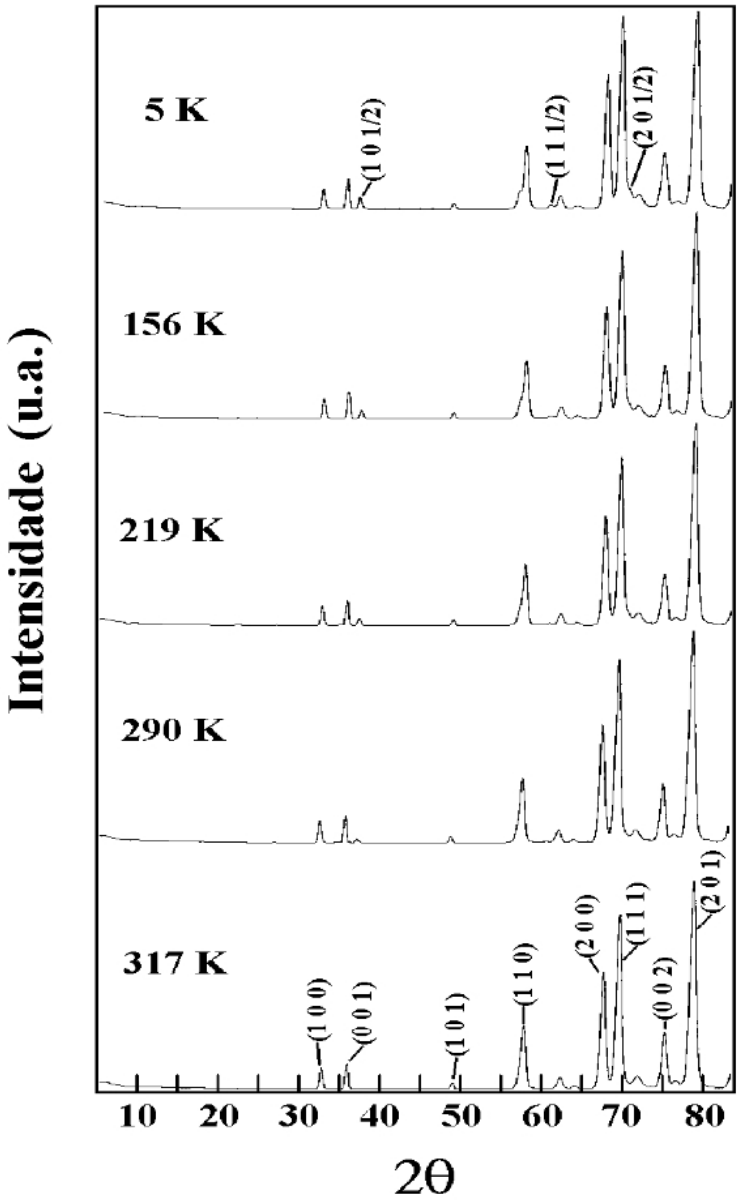

Figure 6. Powder neutron diffraction spectra as function of temperature.

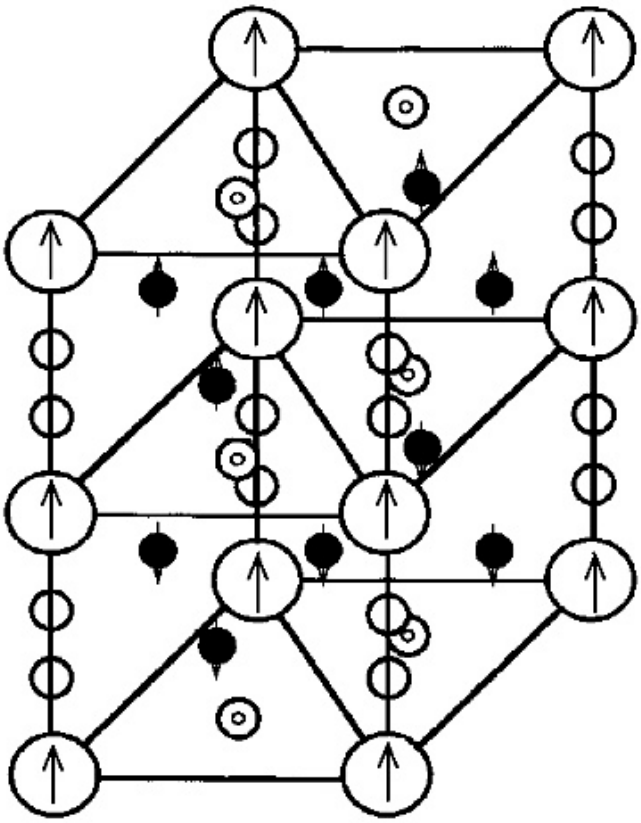

Figure 7. Magnetic structure of UFe_6Ge_6.

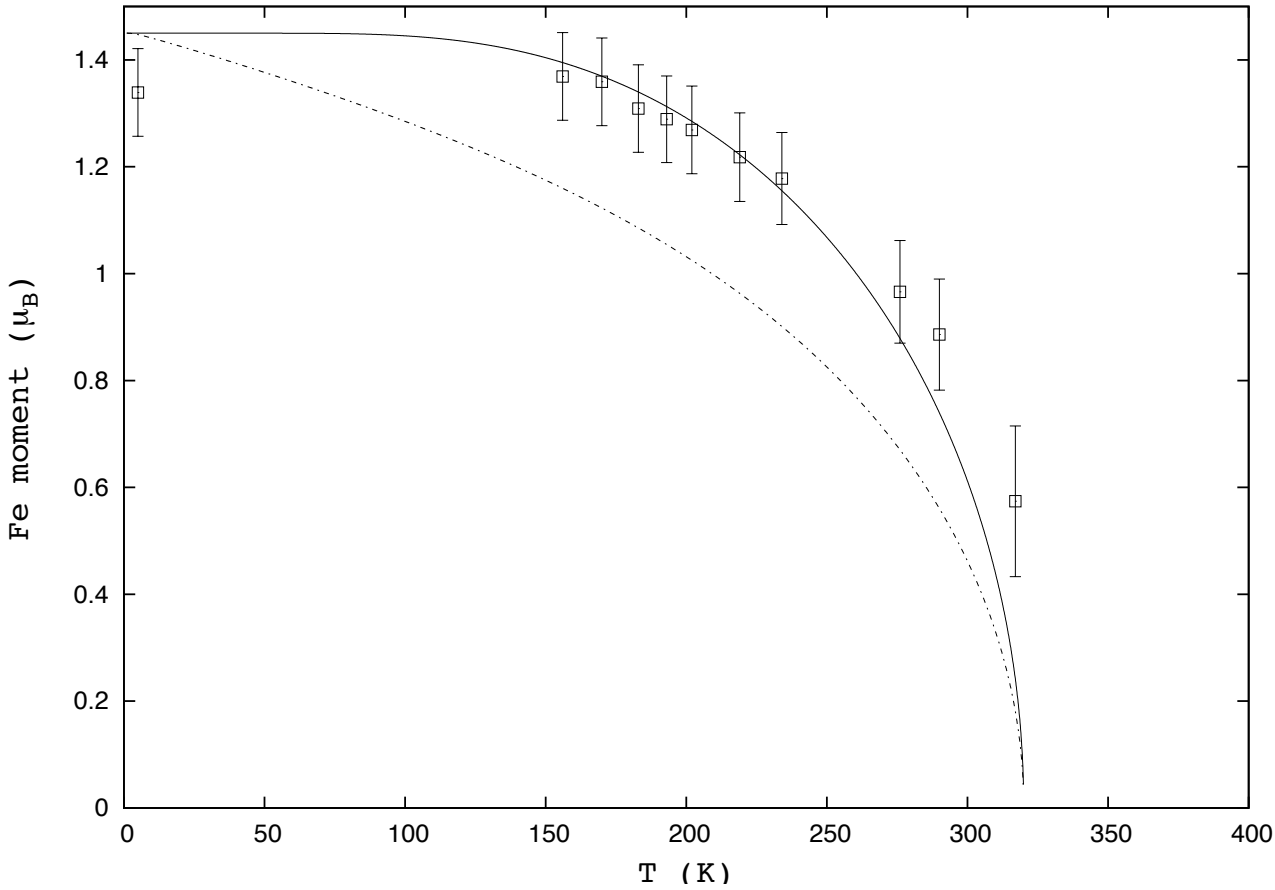

Figure 8. Evolution with temperature of the magnetic moment of the Fe atoms, deduced from the Rietveld refinement of the neutron data. The solid and broken lines show a fit to the square of a Brillouin function with $J = 1/2$ and $J = \infty$