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The magnetic structure of YFe_6Ge_6

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Abstract. We have determined the magnetic structure of the Fe sublattice in YFe_6Ge_6 by high-resolution neutron powder diffraction. The crystal space group is $Cmcm$ and the magnetic space group is $C_P m'c'm'$. The Fe modes are G_X^-, G_X^- and G_X^- at the 8d, 8e and 8g sites, respectively. The easy direction of magnetization is [100] and the propagation vector is [010].

1. Introduction

In recent work we identified a series of rare-earth–iron-rich intermetallics which show independent magnetic behaviour of the rare-earth (R) and Fe sublattices [1, 2]. We prepared RFe_6Ge_6 compounds with R = Y, Gd, Tb, Dy, Er, Tm, Lu and Yb and studied their magnetic behaviour by means of Mössbauer spectroscopy (^{57}Fe), ac susceptibility and magnetometry and we demonstrated that the magnetic ordering temperatures of the Fe and R sublattices differ by nearly two orders of magnitude. The Fe sublattice orders antiferromagnetically and its Néel temperature T_N remains essentially constant across the series at ~480 K with no evidence of a net magnetization in any of the alloys. Furthermore, the hyperfine field B_{hf} at the ^{57}Fe nuclei is virtually independent of the rare earth present. Apart from a gradual decline in B_{hf} (5%) and T_N (2%) there appears to be no significant change in the magnetic properties on going from Gd to Lu. For R = Gd–Er, the rare-earth sublattice orders ferromagnetically with T_C-values that drop from a high of 30 K at Gd to 3 K at Er.

One possible explanation for this independent behaviour lies in the magnetic structure of the Fe sublattice. The ordered state of the binary FeGe compound, from which the RFe_6Ge_6 alloys are derived, consists of ferromagnetic Fe planes coupled antiferromagnetically to each other [3]. The RFe_6Ge_6 structures are formed by placing rare-earth atoms between these Fe planes, and if the basic magnetic structure of the parent FeGe compound is retained, one can obtain a net cancellation of the Fe–R exchange at the rare-earth sites, effectively isolating them from the ordering of the iron moments. Given that the rare-earth moments do order in RFe_2Ge_2 where the iron atoms carry no moment [4], one would expect order to develop on the rare-earth sublattice at low enough temperatures, as we observed. Our work on $ErFe_6Ge_6$ has recently been confirmed by Oleksyn *et al* [5] using neutron diffraction.

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In this paper we determine the magnetic modes and the magnetic space group of the Fe sublattice in YFe_6Ge_6 using high-resolution neutron powder diffraction, carried out at 2 K, 295 K and 520 K (i.e. above T_N), as a first step towards understanding the magnetic behaviour of the entire RFe_6Ge_6 series.

2. Experimental procedure

The YFe_6Ge_6 samples were prepared by arc melting stoichiometric amounts of the pure elements under Ti-gettered argon. Samples were annealed at 900 °C for two weeks, sealed under vacuum in quartz tubes. Powder x-ray diffraction patterns were obtained using Cu Kα radiation on an automated Nicolet–Stoe diffractometer. Thermogravimetric analysis was carried out on a Perkin–Elmer TGA-7 in a small field gradient to look for evidence of ferromagnetic or ferrimagnetic ordering in either the YFe_6Ge_6 compound or in any impurity phases which might be present. The Néel temperature was measured on a Perkin–Elmer DSC-7, using the heat capacity peak at T_N as the signature of magnetic ordering.

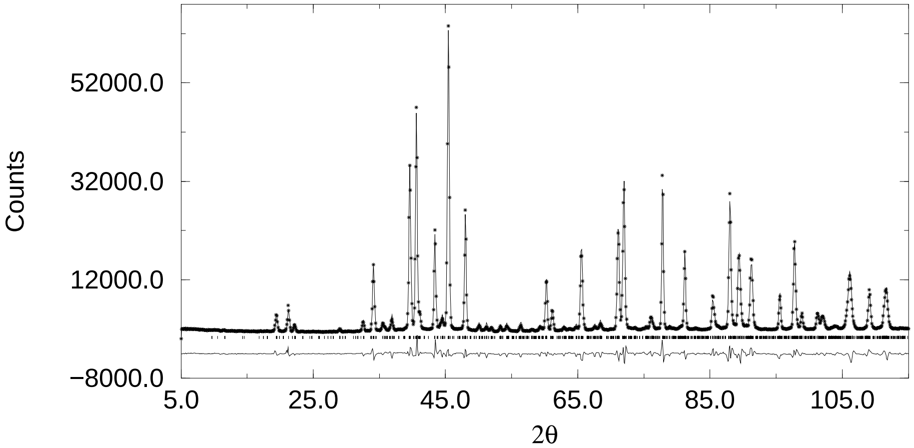

Figure 1. The neutron powder diffraction pattern of YFe_6Ge_6 at 295 K.

Neutron powder diffraction experiments were carried out at 2 K, 295 K and 520 K (i.e. above T_N) on ~4 g samples on the DUALSPEC C2 high-resolution powder diffractometer located at the NRU reactor, Chalk River Laboratories, operated by Atomic Energy Canada Limited. The neutron wavelength was 1.5049(1) Å. A detailed review of the neutron scattering facilities at Chalk River, including a description of C2, can be found in [6]. All of the diffraction patterns were analysed using the Rietveld method with the FULLPROF program [7].

3. Results and discussion

The annealed sample of YFe_6Ge_6 was single phase with no impurities detected by x-ray diffraction or TGA. The Néel temperature of the Fe sublattice is 486(1)K. The crystal structure is orthorhombic *Cmcm* (No 63) $TbFe_6Sn_6$-type [8, 9] in which there is one Y site, three Fe sites and five Ge sites. The lattice parameters determined from the neutron diffraction pattern (at 295 K) are: $a = 8.1245(3)$ Å, $b = 17.7051(7)$ Å and $c = 5.1261(3)$ Å.

The refinement R-factors are: R(Bragg) $= 4.32$, R(F-structure) $= 4.62$, R(wp) $= 7.58$, R(exp) $= 2.05$ and R(mag) $= 13.4$.

In figure 1 we show the neutron diffraction pattern of YFe_6Ge_6 obtained at 295 K. The refined atomic position parameters are given in table 1. We note that we have not employed any site disorder in fitting these patterns, unlike in the recent report by Oleksyn *et al* [5].

Table 1. Atomic positions and isotropic thermal parameters for YFe_6Ge_6.

Atom	Site	x	y	z	B_{iso} (Å^2)
Y	4a	0	0	0	1.34(12)
Fe	8d	$\frac{1}{4}$	$\frac{1}{4}$	0	0.30(3)
Fe	8e	0.251(2)	0	0	0.44(3)
Fe	8g	0.251(2)	$\frac{1}{8}$	$\frac{1}{4}$	0.49(4)
Ge	4c	0	0.043(2)	$\frac{3}{4}$	0.60(5)
Ge	4c	$\frac{1}{2}$	0.043(2)	$\frac{3}{4}$	0.58(4)
Ge	4c	0	0.211(2)	$\frac{3}{4}$	0.41(4)
Ge	4c	$\frac{1}{2}$	0.211(2)	$\frac{3}{4}$	0.36(5)
Ge	8g	0.348(1)	$\frac{1}{8}$	$\frac{1}{4}$	0.77(4)

Comparison of the neutron diffraction patterns taken above and below T_N indicated that the magnetic ordering of the Fe results in the appearance of extra peaks which may be indexed as $h + k =$ odd (nuclear scattering peaks obey $h + k =$ even for the $Cmcm$ space group). Thus, the Fe order may be described as *anti-C*, i.e. Fe moments related by the C-translation $+(\frac{1}{2}\frac{1}{2}0)$ are antiparallel.

Table 2. Magnetic groups and allowed ordering directions.

Magnetic group	Fe 8d		Fe 8e		Fe 8g		Ordering direction
C_Pmcm	$\bar{1}'$	—	2	x	m	z	None
$C_Pm'cm$	$\bar{1}$	—	2	x	m	z	None
$C_Pmc'm$	$\bar{1}$	—	$2'$	yz	m	z	z
C_Pmcm'	$\bar{1}$	—	$2'$	yz	m'	xy	y
$C_Pm'c'm$	$\bar{1}'$	—	$2'$	yz	m	z	None
$C_Pmc'm'$	$\bar{1}'$	—	2	x	m'	xy	None
$C_Pm'cm'$	$\bar{1}'$	—	$2'$	yz	m'	xy	None
$C_Pm'c'm'$	$\bar{1}$	—	2	x	m'	xy	x

There are sixteen possible magnetic space groups associated with the $Cmcm$ crystal space group [10, 11] and we may rule out eight of these immediately on the basis of the observed *anti-C* order. The remaining eight magnetic groups are those of the form C_P of which four may be excluded by considering the special position of the Fe 8d site which has the crystal point group $\bar{1}$. The groups C_Pmcm, $C_Pm'c'm$, $C_Pmc'm'$ and $C_Pm'cm'$ may be excluded since they would result in a magnetic point symmetry at the 8d site of $\bar{1}'$ which is an *inadmissible* magnetic point group [10]. Thus, we are left with $C_Pm'cm$, $C_Pmc'm$, C_Pmcm' and $C_Pm'c'm'$ as possible magnetic space groups. Of these, $C_Pm'cm$

may be excluded since it only supports orthogonal magnetic ordering directions on the Fe 8e and 8g sites: we assume that the Fe sublattice is collinear (the strength of the Fe–Fe exchange ($T_N \sim 480$ K) makes non-collinearity of the Fe sublattices unlikely). In table 2 we show the *anti-C* magnetic space groups, magnetic point symmetries and admissible ordering directions at the three Fe sites. For each site we show the point group and the possible ordering direction supported by the group. For the admissible 8d groups there are no restrictions on the ordering direction (indicated by —). An excellent summary of the various magnetic modes supported by the $Cmcm$ space group may be found in the article by Prandl [11].

In table 3 we show the magnetic modes of the three Fe sites corresponding to the remaining three magnetic space groups. A G mode corresponds to $\{+ - +-\}$ moment orientations. The $-$ superscript indicates the anti-C relation (so, a G^- mode corresponds to $\{+ - + - - + - +\}$ for the eight Fe moments; four $+(000)$ and four $+(\frac{1}{2}\frac{1}{2}0)$ of a particular site). The order of the sites used for this mode description is given in the table.

Table 3. Magnetic sites, modes and ordering directions for $\mathrm{YFe_6Ge_6}$.

Magnetic group	Fe 8d	Fe 8e	Fe 8g	Ordering direction
	$\frac{1}{4}\frac{1}{4}0$	$x\ 0\ 0$	$x\ y\ \frac{1}{4}$	
	$\frac{3}{4}\frac{1}{4}0$	$-x\ 0\ 0$	$-x\ -y\ \frac{3}{4}$	
	$\frac{1}{4}\frac{1}{4}\frac{1}{2}$	$x\ 0\ \frac{1}{2}$	$x\ -y\ \frac{3}{4}$	
	$\frac{3}{4}\frac{1}{4}\frac{1}{2}$	$-x\ 0\ \frac{1}{2}$	$-x\ y\ \frac{1}{4}$	
$C_P mc'm$	G_Z^-	G_Z^-	G_Z^-	[001]
$C_P mcm'$	G_Y^-	G_Y^-	G_Y^-	[010]
$C_P m'c'm'$	G_X^-	G_X^-	G_X^-	[100]

We obtained the best fits to the 2 K and 295 K neutron diffraction patterns with the Fe moments placed along the [100] direction with a propagation vector of [010]. The refined Fe magnetic moment at 295 K is 1.42(8) μ_B which is in very good agreement with the value determined by Mössbauer spectroscopy (*vide infra*). Thus, the Fe antiferromagnetic ordering modes are G_X^-, G_X^- and G_X^- for the 8d, 8e and 8g sites, respectively. The magnetic space group of $\mathrm{YFe_6Ge_6}$ is $C_P m'c'm'$. The neutron diffraction pattern obtained at 2 K shows the same features as that obtained at 295 K, with a corresponding increase in the Fe moment to 1.88(6) μ_B.

We have previously published the ^{57}Fe Mössbauer spectra of the $\mathrm{RFe_6Ge_6}$ series [1, 2]. Despite the fact that there are three crystallographically inequivalent Fe sites in the $\mathrm{YFe_6Ge_6}$ structure, the Mössbauer spectrum is well fitted with a single magnetically split sextet with a hyperfine field at 295 K of 14.8(1) T. It is instructive to consider the Fe sites from the point of view of their Wigner–Seitz (WS) cells which are correlated with the hyperfine field [12]. We have determined the WS cells and nearest-neighbour environments of the Fe sites using the BLOKJE program [13]. Each of the three Fe WS cells has 12 faces, corresponding to the same nearest-neighbour environment of two Y, four Fe and six Ge neighbours. The respective WS-cell volumes for the Fe 8d, 8e and 8g sites are 11.39 Å^3, 11.33 Å^3 and 11.31 Å^3, showing that the Fe sites are effectively magnetically equivalent, at least from the Mössbauer viewpoint.

The ^{57}Fe B_{hf}-value of 14.8 T (at 295 K) can be translated into an Fe atomic magnetic moment if one knows the conversion factor. A direct measurement of the magnetization of $\mathrm{YFe_6Ge_6}$ is ruled out by the antiferromagnetic order. However, Häggström *et al* [14] have tabulated field–moment conversion factors for a number of Fe–Ge binary compounds, taken from the literature, and they found a conversion factor of 11.2 ± 2.5 T/μ_B. Adopting this value, our Mössbauer spectrum of YFe_6Ge_6 corresponds to an Fe moment of 1.3 ± 0.3 μ_B at 295 K, in agreement with the neutron result.

The ordering of the Fe moments along the orthorhombic a-axis is fully consistent with the magnetic order found in the parent FeGe compound. Above about 10 K, the Fe moments in FeGe order along the c-axis of this hexagonal cell. The orthorhombic $Cmcm$ structure of YFe_6Ge_6 is formed by stacking FeGe units such that the a-direction of YFe_6Ge_6 corresponds to the c-axis of FeGe. The planar ordering of the Fe moments is also consistent with our previous arguments based on consideration of the ^{57}Fe quadrupole splitting measured by Mössbauer spectroscopy. Below about 10 K there is some evidence that the Fe moments in FeGe cant away from the hexagonal c-axis by a few degrees. We have seen no evidence of a similar magnetic reorientation behaviour in YFe_6Ge_6 in either the 2 K neutron diffraction pattern or in ac susceptibility carried out to 2 K.

4. Conclusion

The Fe sublattice in YFe_6Ge_6 is antiferromagnetic with a Néel temperature of 486(1) K. The direction of magnetic order is [100] and the Fe magnetic moment (at 295 K) is 1.42(8) μ_B. Using high-resolution neutron powder diffraction we have determined the magnetic space group to be $C_P m'c'm'$. The Fe ordering modes are G_X^-, G_X^- and G_X^- at the 8d, 8e and 8g sites, respectively.

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Note added in proof. After this article was submitted, Schobinger-Papamantellos *et al* [15] published the results of their neutron diffraction study of YFe_6Ge_6, which confirm our findings.

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