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# Independent magnetic ordering of the rare-earth (R) and Fe sublattices in the $RFe_6Ge_6$ and $RFe_6Sn_6$ series

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**Abstract**

Magnetic ordering of the rare-earth (R) and Fe sublattices in R–Fe based intermetallic compounds is normally a cooperative phenomenon with the R and Fe sublattices ordering together — at the same temperature. We have recently studied the $RFe_6Ge_6$ and $RFe_6Sn_6$ compounds using a combination of neutron powder diffraction and Mössbauer spectroscopy (both $^{57}Fe$ and $^{119}Sn$). These series show independent magnetic behaviour of the R and Fe sublattices. The Fe sublattice orders antiferromagnetically below a Néel temperature of ~485 K in $RFe_6Ge_6$ and ~555 K in $RFe_6Sn_6$. The R sublattice orders predominantly ferromagnetically at much lower temperatures, ranging from 45 K for $GdFe_6Sn_6$ to 3 K for $ErFe_6Ge_6$, without affecting the Fe order. Here, we review neutron diffraction and Mössbauer work carried out in the study of this magnetic independence.

*Keywords:* Intermetallics; Magnetically ordered materials; Neutron diffraction; Magnetic measurements; Nuclear resonances

## 1. Introduction

Intermetallic compounds which contain both rare-earth (R) and transition metal (T) elements provide an environment in which to study the complex magnetic interactions of localized and delocalized electrons, not only with each other but also with their environment. As a result of the exchange coupling between the R and T sublattices the respective magnetic moments generally order magnetically in a cooperative fashion with a common ordering temperature and a collinear magnetic structure. Non-collinear magnetic structures can arise in situations, for example, where the crystal-field acting on the 4f electrons of the $R^{3+}$ ions contains competing contributions from terms of different order, which have quite different temperature dependences, as in the case of $Nd_2Fe_{14}B$ [1].

Not so common in metallic systems is the phenomenon of independent magnetic order whereby the R and T sublattices order at different temperatures and/or in orthogonal directions. Such independent magnetic behaviour has recently been observed in the $RFe_6X_6$ intermetallic compounds which form with R=Y and Gd–Lu and X=Ge and Sn. It is well established that in those $RFe_6Ge_6$ and $RFe_6Sn_6$ compounds where the $R^{3+}$ ion has a magnetic moment, the magnetic ordering processes of the R and Fe sublattices take place quite independently of one another [2–5]. The Fe sublattice orders antiferromagnetically and its Néel temperature ($T_N$) remains essentially constant across the series at ~485 K for $RFe_6Ge_6$ or ~555 K for $RFe_6Sn_6$, with no evidence of a net magnetization in any of the alloys. Furthermore, the hyperfine field $B_{hf}$ at the $^{57}Fe$ nuclei, as measured by Mössbauer spectroscopy, is virtually independent of the rare-earth present [3,4].

The $RFe_6X_6$ structures are naturally layered and are formed by placing rare-earth atoms between the hexagonal Fe planes of the parent FeGe or FeSn (B35) structure [6]. Neutron powder diffraction has been used to show that the easy direction of magnetic order of the Fe sublattice is along the [100] direction in the orthorhombic setting [7–10].

For R=Gd–Er, the rare-earth sublattice orders ferromagnetically with Curie temperatures ($T_C$) ranging from a high of 45 K at Gd in $GdFe_6Sn_6$ to 3 K at Er in $ErFe_6Ge_6$ [3]. In $TbFe_6Ge_6$ the Tb magnetic order comprises a ferromagnetic mode along [100] and an antiferromagnetic mode along [001] [11,12]. $ErFe_6Ge_6$ orders ferromagnetically along [100] [7] and $DyFe_6Ge_6$ orders ferromagnetically along [001] [13]. The case of $HoFe_6Ge_6$ is more complex and the magnetic ordering has been

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described in terms of microdomains, 75% of which are ordered in the (100) plane with the remaining 25% aligned along [100], i.e. perpendicular to the former microdomains [14]. The Ho sublattice in $HoFe_6Sn_6$ orders ferromagnetically along [001] [15].

The magnetic independence of the R and Fe sublattices is related to the layered structure of these compounds. Binary FeGe (FeSn) consists of ferromagnetic Fe planes coupled antiferromagnetically to each other [16] and the local environment of the R atoms in the $RFe_6Ge_6$ and $RFe_6Sn_6$ structures leads to a net cancellation of the Fe–R exchange at the rare-earth sites, effectively isolating them from the ordering of the Fe moments. The magnetic ordering of the R sublattice, two orders of magnitude lower in temperature than the Fe ordering, is most likely the result of an RKKY-type coupling between R moments, which seems to take place without upsetting the magnetic order of the intervening Fe layers. This is supported by the fact that the ordering temperatures of the R sublattice scale linearly with the de Gennes factor of the $R^{3+}$ ion. This situation is reminiscent of the R magnetic ordering observed in the tetragonal $RFe_2Ge_2$ and $RFe_2Si_2$ compounds, where the R sublattice is the only magnetically ordered species [17].

In this paper we review our neutron diffraction and Mössbauer results on the $RFe_6Ge_6$ and $RFe_6Sn_6$ series with particular emphasis on the determination of the magnetic structures by neutron diffraction. We will also consider the symmetry aspects of the magnetic ordering modes.

## 2. Experimental methods

The $RFe_6X_6$ ($X$=Ge, Sn) samples were prepared by arc-melting stoichiometric amounts of the pure elements under Ti-gettered argon. All samples were subsequently annealed at 900°C for 2 weeks, sealed under vacuum in quartz tubes. All attempts to prepare $RFe_6Si_6$ compounds (Si being in the same periodic group as Ge and Sn) failed, with tetragonal $RFe_2Si_2$ and cubic FeSi being the main products.

Powder X-ray diffraction patterns were obtained using Cu K$\alpha$ radiation on an automated Nicolet-Stoe diffractometer. Thermogravimetric analysis was carried out on a Perkin-Elmer TGA-7 in a small magnetic field gradient to look for evidence of ferro- or ferri-magnetic ordering in either the $RFe_6X_6$ compound or in any impurity phases which might be present. The Néel temperatures of the Fe sublattice in $RFe_6X_6$ were measured by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-7, using the heat capacity peak at $T_N$ as the signature of magnetic ordering. The ordering temperatures of the R sublattices were determined by magnetometry and ac-susceptometry measurements made on a Quantum Design PPMS system. $^{57}$Fe Mössbauer spectroscopy was carried out in constant-acceleration, transmission mode with a $^{57}$CoRh source to determine the local Fe magnetic moment and also to check the sample purity. The results of our $^{57}$Fe Mössbauer study of the entire $RFe_6Ge_6$ series have been reported previously [3,4]. We also carried out $^{119}$Sn Mössbauer work on the $RFe_6Sn_6$ series to investigate the transferred hyperfine field at the Sn nuclei due to the surrounding Fe and R moments.

Neutron powder diffraction experiments were carried out on ~4-g samples on: (i) the DUALSPEC C2 high-resolution powder diffractometer located at the NRU reactor, Chalk River Laboratories, operated by Atomic Energy Canada Ltd., and (ii) the E9 fine-resolution powder diffractometer (FIREPOD) at the Hahn-Meitner Institute, Berlin, Germany.

Time-of-Flight (ToF) neutron powder diffraction patterns were collected on the ROTAX diffractometer at the ISIS spallation neutron source, Didcot, UK. Data were collected from two separate scattering detector banks, a low-angle 'forward' bank located at $2\theta=28.1°$ and a high-angle 'backward' bank located at $2\theta=125.5°$. Data were collected at 4, 295 and 593 K. All diffraction patterns were analysed using the Rietveld method with either the FULLPROF [18] or GSAS programs [19].

## 3. Results and discussion

In Table 1 we summarise the crystal structures, space groups and magnetic ordering temperatures of the $RFe_6Ge_6$ and $RFe_6Sn_6$ compounds.

### 3.1. Magnetic structure of the Fe sublattice

#### 3.1.1. $YFe_6Sn_6$ [10]

We will illustrate the magnetic structure determination procedure from neutron diffraction measurements for the Fe sublattice by considering the case of $YFe_6Sn_6$ [10].

The annealed sample of $YFe_6Sn_6$ was single-phase with no impurities detected by either X-ray powder diffraction or TGA. The Néel temperature of the Fe sublattice is 558(5) K. The crystal structure is orthorhombic *Immm* (#71) $HoFe_6Sn_6$-type [6,10] in which there are two Y sites, four Fe sites and eight Sn sites.

In Fig. 1 we show the neutron diffraction patterns of $YFe_6Sn_6$ obtained at 593 K, 295 K and 4 K. The 593 K pattern, being above $T_N$ of the Fe sublattice, comprises only nuclear scattering.

Comparison of the neutron diffraction patterns taken above and below $T_N$ indicate that the magnetic ordering of the Fe results in the appearance of extra peaks which may be indexed as $h+k+l$=odd (nuclear scattering peaks obey $h+k+l$=even for the *Immm* space group). This is most clearly seen at a $d$-spacing of 4.14 Å which corresponds to the (131) magnetic peak. Thus, the Fe order may be described as *anti-I* meaning that Fe moments which are

Table 1
Crystal space groups, lattice parameters, Fe sublattice Néel temperatures and R sublattice Curie temperatures in $RFe_6X_6$

| Compound | Space group | $a$ (Å) | $b$ (Å) | $c$ (Å) | Structural type [6] | $T_N$ (Fe) (K) | $T_C$ (R) (K) |
|---|---|---|---|---|---|---|---|
| $YFe_6Ge_6$ | *Cmcm* | 8.1245 | 17.7051 | 5.1261 | $TbFe_6Sn_6$ | 486 | – |
| $GdFe_6Ge_6$ | *P6/mmm* | 5.120 | 5.120 | 4.075 | $YCo_6Ge_6$ | 489 | 29.3 |
| $TbFe_6Ge_6$ | *Cmcm* | 8.127 | 17.67 | 5.138 | $TbFe_6Sn_6$ | 490 | 7.8 |
| $DyFe_6Ge_6$ | *Cmcm* | 8.1223 | 17.7111 | 5.1209 | $TbFe_6Sn_6$ | 489 | 7.5 |
| $HoFe_6Ge_6$ | *Cmcm* [14] | 8.1141 | 17.7107 | 5.1126 | $TbFe_6Sn_6$ | 484 | 8.0 |
| $ErFe_6Ge_6$ | *Immm* [7] | 8.1008 | 26.5318 | 5.1077 | $HoFe_6Sn_6$ | 484 | 3.1 |
| $TmFe_6Ge_6$ | *Immm* [2] | 8.095 | 26.53 | 5.107 | $HoFe_6Sn_6$ | 482 | – |
| $YbFe_6Ge_6$ | *P6/mmm* [2] | 5.097 | 5.097 | 8.092 | $HfFe_6Ge_6$ | 481 | – |
| $LuFe_6Ge_6$ | *P6/mmm* [8] | 5.09843 | 5.09843 | 8.08066 | $HfFe_6Ge_6$ | 485 | – |
| $YFe_6Sn_6$ | *Immm* | 8.896 | 27.966 | 5.389 | $HoFe_6Sn_6$ | 558 | – |
| $GdFe_6Sn_6$ | *Cmcm* | 8.925 | 18.722 | 5.393 | $TbFe_6Sn_6$ | 554 | 45 |
| $TbFe_6Sn_6$ | *Cmcm* | 8.916 | 18.718 | 5.388 | $TbFe_6Sn_6$ | 553 | 19 |
| $DyFe_6Sn_6$ | *Cmcm* | 8.914 | 18.733 | 5.386 | $TbFe_6Sn_6$ | 559 | 14 |
| $HoFe_6Sn_6$ | *Immm* | 8.907 | 28.121 | 5.386 | $TbFe_6Sn_6$ | 559 | 8 |
| $ErFe_6Sn_6$ | *Cmcm* | 8.901 | 37.414 | 5.386 | $ErFe_6Sn_6$ | 560 | 4 |
| $TmFe_6Sn_6$ | *P6/mmm* | 5.479 | 5.479 | 8.921 | $HfFe_6Ge_6$ | 562 | – |
| $LuFe_6Sn_6$ | *P6/mmm* | 5.381 | 5.381 | 8.885 | $HfFe_6Ge_6$ | 540 | – |

related by the body-centring $I$-translation $+(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ are antiparallel.

There are eight possible magnetic space groups associated with the *Immm* crystal space group [20] and we may rule out four of these ($Immm$, $Im'mm$, $Im'm'm$ and $Im'm'm'$) immediately on the basis of the *anti-I* magnetic order.

The remaining four magnetic groups are those of the form $I_P$ of which two may be excluded by considering the special position of the Fe 8$k$ site which has the crystal point group $\bar{1}$. The groups $I_P mmm$ and $I_P m'm'm$ may be excluded since they would result in an inadmissible magnetic point symmetry at the 8$k$ site of $\bar{1}'$.

Finally, the Fe 4$f$ site (whose crystal point group is $2_x m_y m_z$) allows us to rule out the $I_P m'mm$ magnetic space group since it would result in the inadmissible *2mm* magnetic point group. Thus, by the process of elimination we are left with the only possible magnetic space group being $I_P m'm'm'$. Furthermore, the 4$f$ site's magnetic point group of $2m'm'$ is only admissible with the Fe magnetic moment parallel to the two-fold axis which shows that the magnetic ordering direction of the Fe sublattices in $YFe_6Sn_6$ is the [100] '$a$' axis. We assume that the magnetic moments of the four Fe sites are collinear, a reasonable assumption given the strength of the Fe–Fe exchange interaction (we recall that $T_N = 558$ K).

As a final check of these arguments we can consider the Fe 8$n$ site whose crystal point group is $m_z$. The magnetic space group $I_P m'mm$ would result in a magnetic point group at the 8$n$ site of $m_z$ which requires the Fe magnetic moment to be perpendicular to the mirror plane, i.e. along [001] and thus perpendicular to the Fe 4$f$ site's moment. However, the selected group $I_P m'm'm'$ gives an 8$n$ magnetic point group of $m_z'$ with magnetic order parallel to the mirror plane, i.e. the Fe moment in the $a$–$b$ plane, consistent with the Fe 4$f$ site moment.

The fit to the 295 K 'forward-scattering' neutron diffraction pattern with the Fe moments placed along the [100] direction and a propagation vector of [010] is shown in Fig. 1. The refined Fe magnetic moment at 295 K is 2.03(7) $\mu_B$. The neutron diffraction patterns obtained at 4 K are virtually identical with those obtained at 295 K, which allows us to rule out any changes in the magnetic ordering mode of the Fe sublattice at low temperatures. The refined Fe magnetic moment at 4 K is 2.14(6) $\mu_B$. The magnetic space group is $I_P m'm'm'$.

The $^{57}$Fe Mössbauer spectra of the $RFe_6Sn_6$ compounds have already been published by Rao and Coey [5]. Our measured $^{57}$Fe average hyperfine field is 20.6(2) T at 295 K. The $YFe_6Sn_6$ structure contains four crystallographically inequivalent Fe sites but from a Mössbauer point of view we may treat them as effectively magnetically equivalent, given the similarity of the magnetic environments. It is generally accepted that the Wigner–Seitz (WS) cell volumes are correlated with the hyperfine field at the Fe sites [21] and we have calculated the WS volumes at the four Fe sites using the BLOKJE program of Gelato [22]. We find that the Fe site volumes in $YFe_6Sn_6$ lie in the narrow range 11.4–11.6 Å$^3$, which supports the observed effective magnetic equivalence mentioned. These experimental and theoretical findings are in agreement with band calculations carried out on $YFe_6Sn_6$ by Rao et al. [23].

The ordering of the Fe moments along the orthorhombic $a$-axis in $YFe_6Sn_6$ and $YFe_6Ge_6$ (see below) is also fully consistent with the magnetic order found in the parent FeSn and FeGe compounds [16,24]. The Fe moments in FeGe and FeSn order along the $c$-axis of this hexagonal cell. The orthorhombic *Immm* and *Cmcm* structures of $YFe_6Sn_6$ and $YFe_6Ge_6$, respectively, are formed by stacking Fe$X$ ($X$ = Ge or Sn) units such that the $a$-direction of $YFe_6X_6$ corresponds to the $c$-axis of Fe$X$. The planar

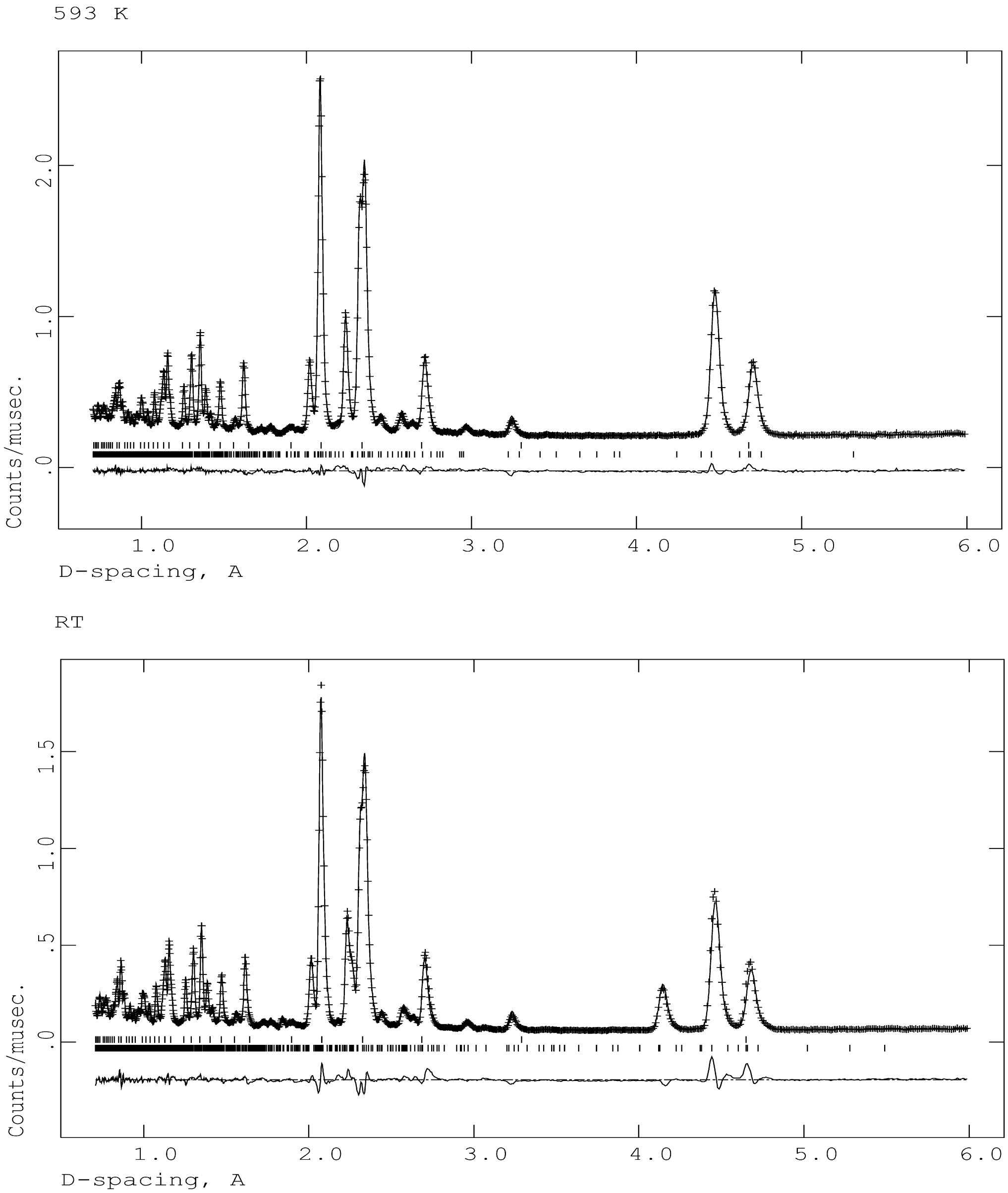

Fig. 1. Neutron ToF powder diffraction patterns of $YFe_6Sn_6$ obtained at 593 K (top) and 295 K (bottom) in forward-scattering mode.

ordering of the Fe moments is also consistent with our previous arguments based on a consideration of the $^{57}$Fe quadrupole splitting measured by Mössbauer spectroscopy [3]. Below about 50 K there is some evidence that the Fe moments in FeGe cant away from the hexagonal *c*-axis by a few degrees [16,25,26]. We have seen no evidence of similar behaviour in $YFe_6Ge_6$ in either the 4 K neutron diffraction pattern or magnetometry carried out to 2 K.

To confirm our suggested magnetic structure for the Fe sublattice in $YFe_6Sn_6$, deduced from the neutron diffraction data, we now consider the results of our $^{119}$Sn Mössbauer experiments. Sn is non-magnetic and so any hyperfine magnetic field observed at the $^{119}$Sn nucleus is due to surrounding magnetic moments, i.e. a transferred hyperfine field. We determined the nearest-neighbour environments of the eight Sn sites in $YFe_6Sn_6$ by calculating their Wigner–Seitz cells using BLOKJE [22]. In $YFe_6Sn_6$ only the Fe atoms carry a magnetic moment and the Wigner–Seitz calculations show that all Sn sites have six Fe nearest-neighbours with WS cell volumes in the range 19.9–22.5 $Å^3$. However, the magnetic structure of the Fe sublattice in $YFe_6Sn_6$, determined from our neutron diffraction data, indicates that Sn sites 1–6 have three Fe moments along [100] and three Fe moments antiparallel along $[\bar{1}00]$, resulting in a zero transferred hyperfine field. Sn sites 7 and 8 have all six neighbouring Fe moments parallel which should result in a substantial transferred hyperfine field at the Sn site. Sn sites 7 and 8 account for exactly $\frac{1}{3}$ of the Sn sites.

In Fig. 2 we show the $^{119}$Sn Mössbauer spectrum of

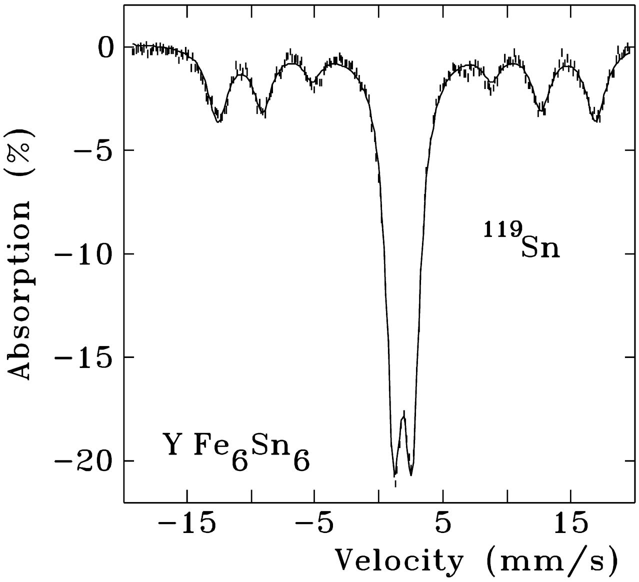

Fig. 2. $^{119}$Sn Mössbauer spectrum of YFe$_6$Sn$_6$ obtained at 295 K.

YFe$_6$Sn$_6$ obtained at 295 K. The spectrum comprises both magnetically-split and non-magnetic components and the fit to the spectrum shows that 35(1)% of the Sn sites have a transferred hyperfine field of 24.6(3) T whereas the remaining 65(1)% of the Sn sites experience no net transferred hyperfine field. These results are in full agreement with our suggested magnetic structure of YFe$_6$Sn$_6$, determined from the ToF neutron diffraction.

### 3.1.2. *YFe$_6$Ge$_6$ [9]*

In a similar manner to the procedure outlined above for YFe$_6$Sn$_6$, a comparison of the neutron diffraction patterns taken above and below $T_N$ of YFe$_6$Ge$_6$ (space group *Cmcm*) shows that the magnetic ordering of the Fe results in the appearance of extra peaks which are 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* meaning that Fe moments which are related by the *C*-translation $+(\frac{1}{2}\frac{1}{2}0)$ are antiparallel and the magnetic space group is of the type $C_P$.

To illustrate the use of symmetry arguments in determining the magnetic ordering mode of the Fe sublattice we list, in Table 2 the possible magnetic space groups of YFe$_6$Ge$_6$ derived from the crystal group *Cmcm* and we give the magnetic point groups of the three Fe sites and the possible magnetic ordering directions of the Fe moments for each magnetic space group.

The refined Fe magnetic moment at 295 K is 1.42(8) $\mu_B$ and at 2 K is 1.88(6) $\mu_B$. The patterns obtained at 295 and 2 K are virtually identical, apart from the increased Fe magnetic moment at 2 K, and this allows us to rule out any spin reorientations in YFe$_6$Ge$_6$, such as was previously reported to occur in FeGe by Häggström et al. [25]. Our fitting of the YFe$_6$Ge$_6$ neutron diffraction patterns shows that the magnetic space group of the Fe sublattice in YFe$_6$Ge$_6$ is $C_Pm'c'm'$ (along [100])

An excellent summary of the various magnetic modes supported by the *Cmcm* space group as well as an discussion of magnetic symmetry can be found in the article by Prandl [27].

Finally, our average $^{57}$Fe hyperfine field in YFe$_6$Ge$_6$ at 295 K is 14.8(1) T which, when combined with the neutron-refined Fe moment of 1.42(8) $\mu_B$, yields a field-moment conversion factor of 10.4(7) T/$\mu_B$, in very good agreement with the value of 11.2(25) T/$\mu_B$ deduced by Häggström et al. [28] from a literature survey of data obtained in a number of Fe–Ge binaries.

It is therefore a common feature of the RFe$_6$Ge$_6$ and RFe$_6$Sn$_6$ compounds that the Fe moments form ferromagnetic planes with an easy [100] direction and an antiferromagnetic coupling between adjacent planes.

## 3.2. *R sublattice ordering*

### 3.2.1. *HoFe$_6$Sn$_6$ [15]*

The annealed sample of HoFe$_6$Sn$_6$ was virtually single-phase, with a small amount of cubic HoSn$_3$ present as an impurity in the amount of 3 wt%, as determined from the fits to the neutron diffraction patterns. The impurity was included in all data refinements. The Néel temperature of the Fe sublattice in HoFe$_6$Sn$_6$ is 559(5) K. The crystal structure of HoFe$_6$Sn$_6$ is orthorhombic *Immm* (#71) [6,10] in which there are two Ho sites, four Fe sites and eight Sn sites.

In Fig. 3 we show the neutron diffraction patterns of HoFe$_6$Sn$_6$ obtained at 593, 30 and 4 K, obtained in forward-scattering mode. The 593 K pattern, being above

Table 2
Magnetic space and point groups and corresponding allowed magnetic ordering directions for the Fe sites in YFe$_6$Ge$_6$ [9][a]

| Magnetic group | Fe(8*d*) | Fe(8*e*) | Fe(8*g*) | Ordering direction |
|---|---|---|---|---|
| $C_Pmcm$ | $\bar{1}'$ None | 2 *x* | *m z* | None (inadmissible point group at 8*d* site) |
| $C_Pm'cm$ | $\bar{1}$ *xyz* | 2 *x* | *m z* | None (orthogonal moments) |
| $C_Pmc'm$ | $\bar{1}$ *xyz* | 2′ *yz* | *m z* | *z* |
| $C_Pmcm'$ | $\bar{1}$ *xyz* | 2′ *yz* | *m*′ *xy* | *y* |
| $C_Pm'c'm$ | $\bar{1}'$ None | 2′ *yz* | *m z* | None (8*d* site) |
| $C_Pmc'm'$ | $\bar{1}'$ None | 2 *x* | *m*′ *xy* | None (8*d* site) |
| $C_Pm'cm'$ | $\bar{1}'$ None | 2′ *yz* | *m*′ *xy* | None (8*d* site) |
| $C_Pm'c'm'$ | 1 *xyz* | 2 *x* | *m*′ *xy* | *x* |

[a] The individual site columns show the magnetic point group followed by the allowed ordering direction (*xyz* means no restriction on ordering direction).

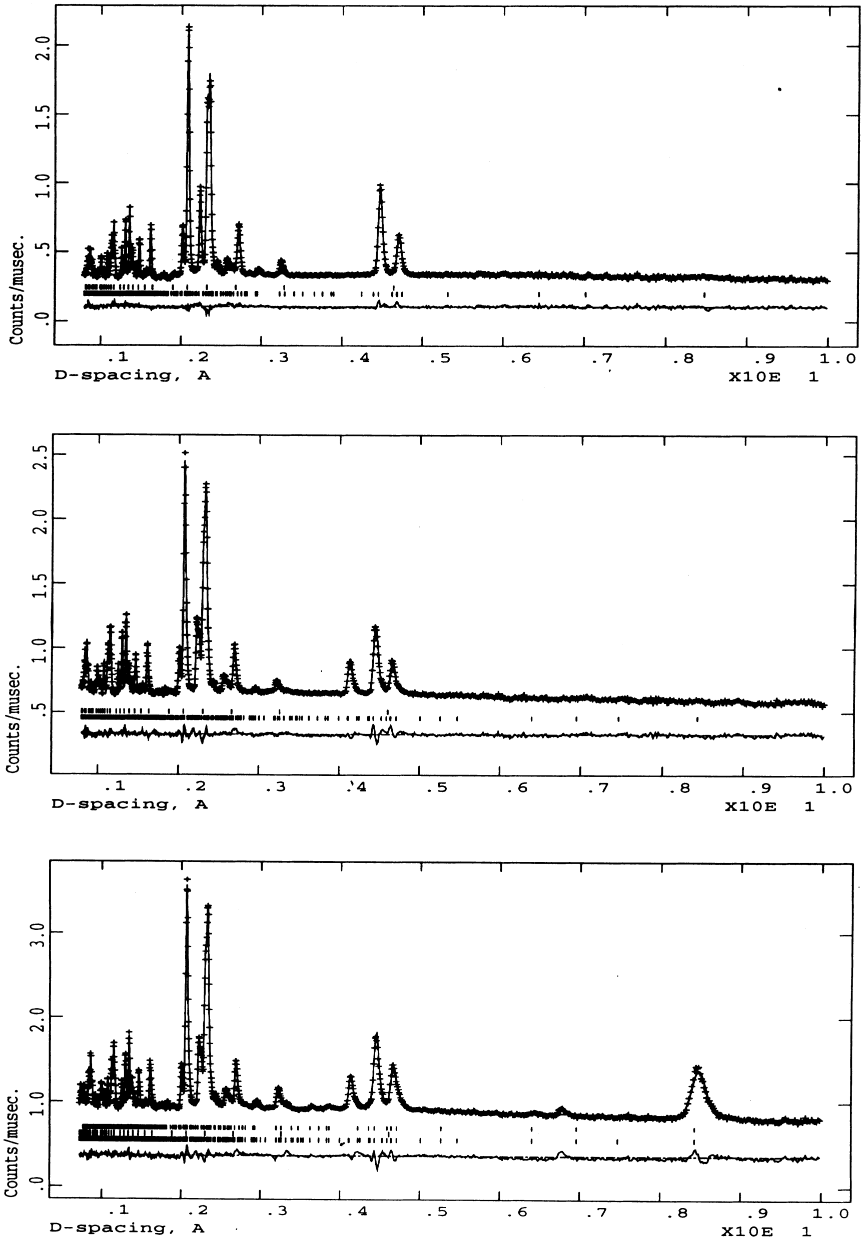

Fig. 3. Neutron powder diffraction patterns of $HoFe_6Sn_6$ at 593 K (top), 30 K (middle) and 4 K (bottom).

$T_N$ of the Fe sublattice, comprises only nuclear scattering. The 295 K pattern is omitted since it is virtually identical with the 30 K pattern.

As with $YFe_6Sn_6$, the neutron diffraction patterns of $HoFe_6Sn_6$ obtained at 295 and 30 K, which are below $T_N$ of the Fe sublattice but above the $T_C$ of the Ho sublattice, show that the magnetic ordering of the Fe results in the appearance of extra peaks which may be indexed as $h+k+l=$odd (nuclear scattering peaks obey $h+k+l=$even for the *Immm* space group). This is most clearly seen at $d=4.11$ Å, the extra peak being indexed as (131),(160). Thus, the Fe order may be described as *anti-I*.

$YFe_6Sn_6$ has the same crystal space group as $HoFe_6Sn_6$, namely *Immm*, and the derivation of the Fe magnetic ordering mode follows the same procedure discussed in the previous section on $YFe_6Sn_6$. Thus, we deduce that the magnetic space group for the Fe sublattice in $HoFe_6Sn_6$ is $I_P m'm'm'$.

The fit to the 30 K neutron diffraction pattern with the Fe moments placed along the [100] direction and a propagation vector of [010] is shown in Fig. 3. The refined Fe magnetic moments at 295 and 30 K are 2.04(5) and 2.32(5) $\mu_B$, respectively.

As in our previous study of the Fe sublattice order in $YFe_6Sn_6$ [10], we have used $^{119}Sn$ Mössbauer spectroscopy to confirm the Fe sublattice magnetic ordering mode deduced from our neutron scattering experiments.

The neutron diffraction patterns of $HoFe_6Sn_6$, shown in Fig. 1, clearly indicate that the Ho sublattice magnetically orders between 4 and 30 K. The strong magnetic peak appearing at $d = 8.46$ Å in the 4 K pattern is indexed as (110), i.e. $h + k + l =$ even, and is due to the Ho sublattice ferromagnetic order. The fitting of the 4 K pattern shows that the Ho ordering direction is perpendicular to that of the Fe sublattice (*a*-axis). We find the best fit is with the Ho moments along the *c*-axis. The refined Ho magnetic moments at 4 K are 4.4(2) and 5.2(2) $\mu_B$ at the 2*a* and 4*h* sites, respectively. The magnetic space group of the Ho sublattice in $HoFe_6Sn_6$ is $Im'm'm$.

### 3.2.2. $DyFe_6Ge_6$ [13]

$DyFe_6Ge_6$ has the orthorhombic *Cmcm* space group, as does $YFe_6Ge_6$, and the analysis of the neutron diffraction patterns of $DyFe_6Ge_6$ obtained at 295 and 30 K, which are below $T_N$ of the Fe sublattice but above the $T_C$ of the Dy sublattice, follows the same procedure as that in $YFe_6Ge_6$. Thus, the magnetic ordering of the Fe sublattice in $DyFe_6Ge_6$ is along the *a*-axis [100] with a propagation vector of [010] and a refined Fe moment at 295 K of 1.40(9) $\mu_B$. The refined Fe moment at 15 K is 1.66(8) $\mu_B$.

In our previous Mössbauer and magnetometry study of the $RFe_6Ge_6$ series [3,4] we showed that the Dy sublattice in $DyFe_6Ge_6$ orders magnetically at 7.5(1) K, which we deduced by magnetometry. Interestingly, besides a magnetic contribution to the nuclear peaks in the 2 K neutron diffraction pattern of $DyFe_6Ge_6$, which indicates a ferromagnetic component to the Dy magnetic order, we also observed extra peaks in this pattern corresponding to $h + k =$ odd, i.e. an antiferromagnetic component. Of the 16 possible magnetic space groups derived from the *Cmcm* crystal group, only three allow ferromagnetic order at the Dy site. These groups and their ordering directions are $Cmc'm'$ (along [100]), $Cm'cm'$ (along [010]) and $Cm'c'm$ (along [001]). Now, for a given ferromagnetic group there are only four options for the corresponding anti-*C* antiferromagnetic group, given that the ferromagnetic and antiferromagnetic modes are orthogonal. We find that the best fit to the 2 K pattern is obtained with the Dy ferromagnetic component along [001] and the antiferromagnetic component along [010], leading to the magnetic space groups F-$Cm'c'm$ and AF-$C_Pm'cm'$, respectively.

The ferromagnetic Dy moment at 2 K is 6.64(14) $\mu_B$ and the antiferromagnetic component is 2.20(22) $\mu_B$, yielding a net moment of 6.99(15) $\mu_B$, which is 70% of the free-ion value, appropriate to $T/T_C = 0.27$. The magnetic ordering of the Dy sublattice has no discernible effect on the Fe order and we note here that the ferromagnetic Dy magnetic ordering mode is perpendicular to the antiferromagnetic order of the Fe sublattice.

As mentioned earlier, Schobinger-Papamantellos et al. [11] showed that $TbFe_6Ge_6$ has a ferromagnetic ordering mode along [100] and an antiferromagnetic mode along [001]. We have shown that isostructural $DyFe_6Ge_6$ has its Dy ferromagnetic order along [001], i.e. perpendicular to that of the Tb sublattice in $TbFe_6Ge_6$. This difference illustrates the effect of the crystal-field acting on the $R^{3+}$ ions in $RFe_6Ge_6$. Both ions have negative second-order Stevens crystal-field constants [29] but their fourth- and sixth-order terms have opposite signs. Clearly, the magnetic ordering direction of the R sublattice in $RFe_6Ge_6$ cannot be determined solely by the second-order crystal-field terms. and are determined by the fourth- and sixth-order crystal-field terms.

## 4. Conclusions

The $RFe_6Ge_6$ and $RFe_6Sn_6$ intermetallic compounds are formed by the introduction of R atoms into the hexagonal B35 structure of FeGe and FeSn, respectively. The Fe sublattice in $RFe_6Ge_6$ and $RFe_6Sn_6$ is antiferromagnetic with Néel temperatures of ~485 and ~ 555 K, respectively. The Fe ordering is uninfluenced by the R atom present. We have used high-resolution neutron powder diffraction to show that the direction of Fe magnetic order is [100] with a propagation vector [010].

The R sublattices order at much lower temperatures (<45 K) and are either ferromagnetic or mixed ferro-/antiferromagnetic. The Ho sublattice in $HoFe_6Sn_6$ orders ferromagnetically along [001] at 8 K, i.e. perpendicular to the Fe order, and has no discernible effect on the magnetic order of the intervening Fe layers. The Dy sublattice in $DyFe_6Ge_6$ shows both ferromagnetic and antiferromagnetic ordering modes below 7.5(1) K. The ferromagnetic component is along [001] and the antiferromagnetic component is along [010].

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