Neutron diffraction and Mössbauer study of the magnetic structure of $HoFe_6Sn_6$

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We have used Time-of-Flight (ToF) neutron powder diffraction, and both ^{57}Fe and ^{119}Sn Mössbauer spectroscopy, to study the independent magnetic ordering behaviour of the Fe and Ho sublattices in $HoFe_6Sn_6$. The crystal structure of $HoFe_6Sn_6$ is orthorhombic (space group *Immm*). The Fe sublattice orders antiferromagnetically with a Néel temperature of 559(5) K, determined by differential scanning calorimetry. The ToF neutron diffraction patterns obtained at 30 K and 295 K show that the antiferromagnetic ordering of the Fe sublattice is along [100] with a propagation vector $\mathbf{q}$ = [010]. The magnetic space group of the Fe sublattice is $I_P m'm'm'$ and the Fe magnetic moment at 30 K is 2.3(2) μ_B. This magnetic structure is confirmed by our ^{119}Sn Mössbauer spectra in which 37% of the Sn nuclei experience a substantial transferred hyperfine field from the Fe sublattice while the remaining 63% of the Sn sites show no magnetic splitting, due to the cancellation of transferred hyperfine fields from the Fe neighbours, in full agreement with our Wigner-Seitz cell calculations for each of the eight Sn sites in the $HoFe_6Sn_6$ structure. The Ho sublattice orders ferromagnetically at 9(1) K. ToF data obtained at 4 K show that the Ho moments are aligned along [001] i.e. perpendicular to the Fe ordering. The magnetic space group of the Ho sublattice is $Im'm'm$. The refined Ho magnetic moments at 4 K are 4.4(3) μ_B and

5.2(3) μ_B at the 2a and 4h sites, respectively.

Introduction

It is well established that the Fe and R sublattices in the RFe_6Ge_6 and RFe_6Sn_6 intermetallic compounds (R=Gd–Lu, Y) exhibit independent magnetic behaviour with roughly two orders of magnitude difference between the antiferromagnetic ordering temperature of the Fe sublattice (450–550 K) and the ordering temperature of the R sublattice ($<$ 30 K) [1–4]. The R order is predominantly ferromagnetic with some R atoms showing additional antiferromagnetic components [5–8]. This magnetic independence seems to be a consequence of the special position of the R sites whereby there is a net cancellation of the exchange fields from the surrounding Fe planes. The R ordering is then due to an RKKY-type of indirect exchange.

In this paper we present the results of a high-resolution, Time-of-Flight (ToF) neutron diffraction study of $HoFe_6Sn_6$ from which we determine the magnetic ordering modes of both the Fe and Ho sublattices.

Experimental Methods

The $HoFe_6Sn_6$ samples were prepared by arc-melting stoichiometric amounts of the pure elements under Ti-gettered argon. Samples were subsequently annealed at 900 ^{o}C for two weeks, sealed under vacuum in quartz tubes. 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 $HoFe_6Sn_6$ compound or in any impurity phases which might be present. The Néel temperature of the Fe sublattice in $HoFe_6Sn_6$ was measured on a Perkin-Elmer DSC-7, using the heat capacity peak at T_N as the signature of magnetic ordering. Mössbauer spectra using the ^{57}Fe and ^{119}Sn resonances were collected in constant-acceleration mode using a conventional transmission spectrometer. Magnetization measurements were made at 2 K on a Quantum Design SQUID magnetometer in applied magnetic fields up to 9 T.

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 2θ=28.1° and a high-angle 'backward' bank located at 2θ=125.5°. Data were collected at 4 K, 30 K, 295 K and 593 K. All neutron diffraction patterns were analysed using the Rietveld method with the GSAS program [9].

Results and Discussion

The annealed sample of $HoFe_6Sn_6$ 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 $HoFe_6Sn_6$ is 559(5) K. The crystal structure of $HoFe_6Sn_6$ is orthorhombic *Immm* (#71) [10] in which there are two Ho sites, four Fe sites and eight Sn sites. The lattice parameters (at 295 K) determined by neutron diffraction are a=8.9017(3)Å, b=27.9899(21)Å and c=5.3927(4)Å. The refinement 'R-factors (%)' are: R(Bragg)=5.32, R(wp)=8.41 and R(mag)=13.5.

In figure 1 we show the neutron diffraction patterns of $HoFe_6Sn_6$ obtained at 593 K, 30 K and 4 K, obtained in forward-scattering mode. The 593 K pattern, being above 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. The refined atomic position parameters are given

Table 1: Refined atomic positions and isotropic thermal parameters in $HoFe_6Sn_6$ at 593 K

Atom	Site	x	y	z	B_{iso}($Å^2$)
Ho	2a	0	0	0	3.06(7)
Ho	4h	0	0.1671(9)	$\frac{1}{2}$	3.73(7)
Fe	4f	0.7445(6)	$\frac{1}{2}$	0	2.18(7)
Fe	8k	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	3.43(8)
Fe	8n	0.7519(7)	0.8344(4)	0	2.30(7)
Fe	16o	0.2463(4)	0.0838(4)	0.2513(2)	2.71(7)
Sn	4e	0.3255(2)	0	0	2.45(7)
Sn	4g	0	0.5562(8)	0	2.07(8)
Sn	4g	0	0.1129(7)	0	3.44(6)
Sn	4g	0	0.2218(8)	0	3.58(5)
Sn	4h	0	0.0572(5)	$\frac{1}{2}$	0.69(8)
Sn	4h	0	0.6102(8)	$\frac{1}{2}$	1.76(5)
Sn	4h	0	0.7204(7)	$\frac{1}{2}$	1.47(5)
Sn	8n	0.8387(8)	0.6667(5)	0	2.23(7)

in Table 1.

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 d=4.11 Å , the extra peak being indexed as (131),(160). Thus, the Fe order may be described as *anti-I* i.e. Fe moments 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 [11] and we have previously discussed in detail the derivation of the magnetic space

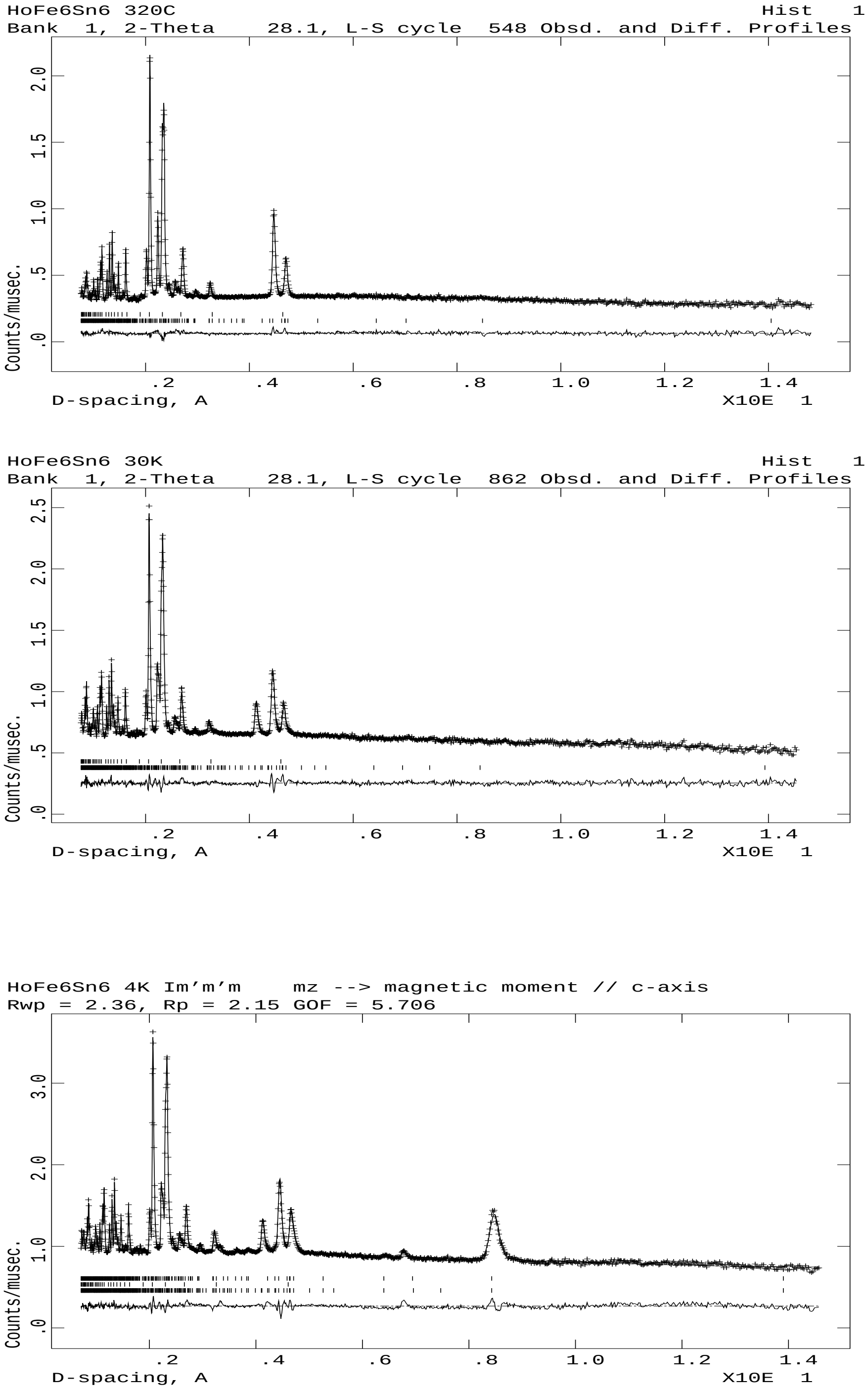

Figure 1: Neutron powder diffraction pattern of $HoFe_6Sn_6$ at 593 K (top), 30 K (middle) and 4 K (bottom)

group for the Fe sublattice in our paper on the isostructural YFe_6Sn_6 compound [12], which has the same crystal space group as $HoFe_6Sn_6$, namely *Immm*. This derivation is based on a consideration of the point symmetries of the four Fe sites in the $HoFe_6Sn_6$ structure and we refer the reader to our previous paper for this discussion. Thus, we deduce that $I_P m'm'm'$ is the magnetic space group for the Fe sublattice in $HoFe_6Sn_6$. Furthermore, the Fe 4f site's magnetic point group of $2m'm'$ is only admissible with the Fe magnetic moment parallel to the 2 axis which shows that the magnetic ordering direction of the Fe sublattices in $HoFe_6Sn_6$ is the [100] 'a' axis. We assume that the magnetic moments of the four Fe sites are collinear which is reasonable given the strength of the Fe-Fe exchange interaction (we recall that $T_N = 559$ K).

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 figure 1. The refined Fe magnetic moments at 295 K and 30 K are 2.04(5) μ_B and 2.32(5) μ_B, respectively.

The ordering of the Fe moments along the orthorhombic a-axis is fully consistent with the magnetic order found in the parent FeSn compound, as explained in our previous paper on YFe_6Ge_6 [13].

As in our previous study of the Fe sublattice order in YFe_6Sn_6 [12], we have used ^{119}Sn Mössbauer spectroscopy to confirm the Fe sublattice magnetic ordering mode deduced from our neutron scattering 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 have determined the nearest-neighbour environments of the eight Sn sites in $HoFe_6Sn_6$ by calculating their Wigner-Seitz cells using the BLOKJE program [14]. In $HoFe_6Sn_6$ above ~10 K only the Fe atoms carry a magnetic moment and the Wigner-Seitz calculations show that all Sn sites have six Fe nearest-neighbours. However, the magnetic structure of the Fe sublattice in $HoFe_6Sn_6$, determined from our neutron diffraction data, indicates that Sn sites 1–6 have three Fe moments along [100] and three Fe moments an-

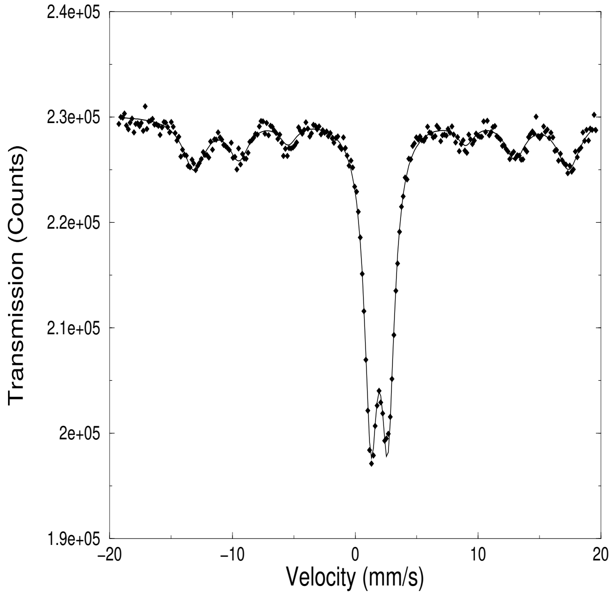

Figure 2: ^{119}Sn Mössbauer spectrum of $HoFe_6Sn_6$ obtained at 295 K

tiparallel along [-100], resulting in a zero transferred hyperfine field. Sn sites 7 and 8 have all six 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 figure 2 we show the ^{119}Sn Mössbauer spectrum of YFe_6Sn_6 obtained at 295 K. The spectrum comprises both magnetically-split and non-magnetic components and the fit to the spectrum shows that 37(1)% of the Sn sites have a transferred hyperfine field of 22.3(1)T whereas the remaining 63(1)% of the Sn sites experience no net transferred hyperfine field. These results are in excellent agreement with our suggested magnetic structure of the Fe sublattice in $HoFe_6Sn_6$, determined from the ToF neutron diffraction.

Ho sublattice ordering

The neutron diffraction patterns of $HoFe_6Sn_6$, shown in figure 1, clearly indicate that the Ho sublattice magnetically orders between 4 K and 30 K. The strong magnetic peak appearing at d=8.46Å 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) μ_B and 5.2(2) μ_B at the 2a and 4h sites, respectively. The magnetic space group of the Ho sublattice in $HoFe_6Sn_6$ is $Im'm'm$.

Conclusion

The Fe sublattice in $HoFe_6Sn_6$ is antiferromagnetic with a Néel temperature of 559(5) K. The direction of magnetic order is [100] with a propagation vector of [010]. The Fe magnetic moment (at 295 K) is 2.04 μ_B. The magnetic space group of the Fe sublattice is $I_P m'm'm'$. ^{119}Sn Mössbauer spectroscopy confirms the Fe sublattice magnetic structure determined from the ToF neutron diffraction patterns. The Ho sublattice orders ferromagnetically at 9(1) K along the [001] c-axis, i.e. perpendicular to the Fe order. The refined Ho magnetic moments at 4 K are 4.4(2) μ_B and 5.2(2) μ_B at the 2a and 4h sites, respectively. The magnetic space group of the Ho sublattice is $Im'm'm$.

Acknowledgements

This work was supported by grants from the Australian Research Council, the Australian Nuclear Science and Technology Organisation, the Natural Sciences and Engineering Research Council of Canada, Fonds pour la formation de chercheurs et l'aide à la recherche, Québec, and Istituto Nazionale per la Fisica della Materia, Italy.

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