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Neutron diffraction and Mössbauer study of the magnetic structure of YFe_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 over the temperature range 2–600 K to determine the magnetic ordering mode of the Fe sublattice in YFe_6Sn_6. The crystal structure is orthorhombic (space group *Immm*). The Fe sublattice orders antiferromagnetically with a Néel temperature of 558(5) K. The TOF neutron diffraction patterns obtained at 4 and 293 K show that the antiferromagnetic ordering of the Fe sublattice is along [100] with a propagation vector $\mathbf{q}=[010]$. The magnetic space group is $I_Pm'm'm'$. This magnetic structure is confirmed by our ^{119}Sn Mössbauer spectra. © *2000 American Institute of Physics.* [S0021-8979(00)18408-7]

I. INTRODUCTION

Recent studies of rare-earth (R)-iron intermetallics of the form RFe_6X_6 (R=Y, Gd–Lu:X=Ge and Sn) show that the R and Fe sublattices behave quite independently of one another.[1–4] The magnetic ordering temperatures of the Fe and R sublattices differ by nearly 2 orders of magnitude. The Fe sublattice orders antiferromagnetically at ~480 (X=Ge) and ~550 K (X=Sn) and its Néel temperature remains essentially constant across a series. The magnetic ordering of the R sublattice occurs below ~30 K and is dominantly ferromagnetic with an antiferromagnetic component which is perpendicular to the ordering direction of the Fe and R(ferro) directions, which are along [100].[5]

In this article we present the results of a high-resolution neutron powder diffraction study carried out on YFe_6Sn_6 as a first step towards determining the magnetic behavior of the entire RFe_6Sn_6 series.

II. EXPERIMENTAL METHODS

YFe_6Sn_6 samples were prepared by arc-melting stoichiometric amounts of the pure elements under Ti-gettered argon. Samples were then sealed under vacuum in quartz tubes and annealed at 800 °C for one week. 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 ferrimagnetic ordering in either the YFe_6Sn_6 compound or in any impurity phases which might be present. The Néel temperature (T_N) 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 both the ^{57}Fe and ^{119}Sn resonances were collected in constant-acceleration mode using a conventional spectrometer.

Time-of-flight (TOF) neutron powder diffraction was done 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, 293, and 593 K. All neutron diffraction patterns were analyzed using the Rietveld method with the GSAS program.[6]

III. RESULTS AND DISCUSSION

The annealed YFe_6Sn_6 was virtually single-phase with only ~2% YSn_3 impurity detected, which was included in all data refinements. The Néel temperature of the Fe sublattice is 558(5) K. The crystal structure is orthorhombic *Immm* (No. 71) $HoFe_6Sn_6$ type[7] in which there are two Y sites, four Fe sites, and eight Sn sites. Chafik El Idrissi *et al.*[7] previously reported that YFe_6Sn_6 formed a *C*-centered orthorhombic structure *Cmcm* rather than the *I*-centered orthorhombic structure we find. All RFe_6Sn_6 structures are very closely related, being derived from the common FeSn (hexagonal *B*35 structure) building block and there is some evidence to suggest that the crystal structure formed by a particular RFe_6X_6 compound depends on its thermal history.[8]

The lattice parameters of YFe_6Sn_6 (at 293 K) determined by neutron diffraction are $a=8.9021(2)$, $b=27.9891(12)$, and $c=5.3932(2)$ Å. The refinement ''*R* factors (%)'' for the forward and backward data sets, at 293 K, are: $R(wp)=6.6$ and 7.8, $R(p)=5.8$ and 5.9, respectively. In Fig. 1 we

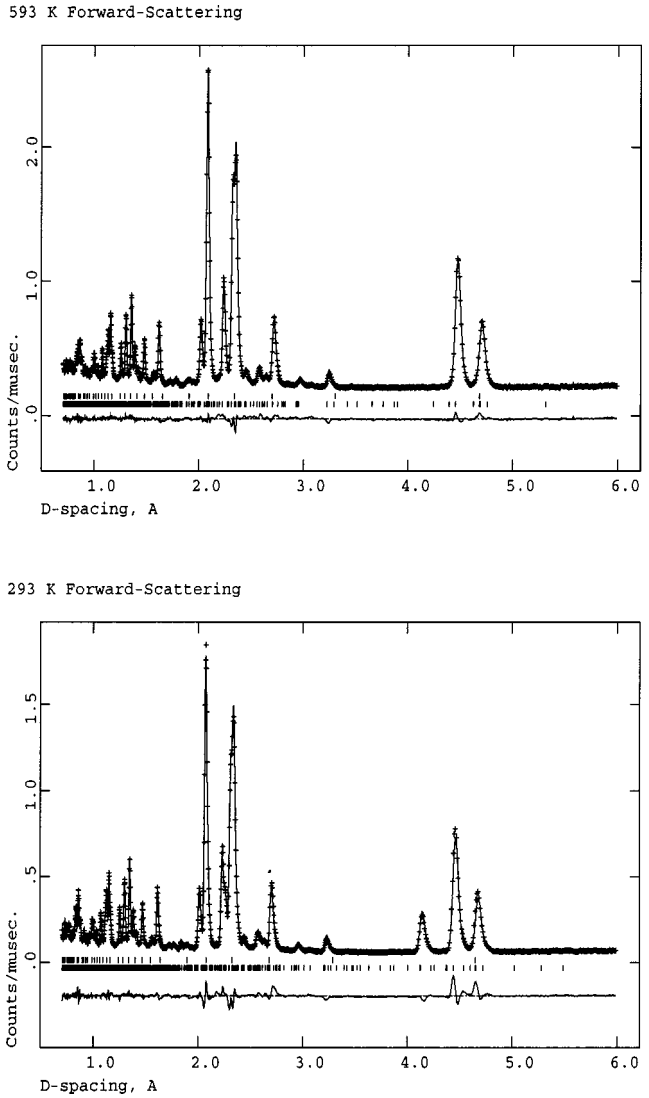

FIG. 1. Neutron powder diffraction patterns of YFe_6Sn_6, obtained at (*top*) 593 and (*bottom*) 293 K in forward scattering mode.

TABLE I. Refined atomic positions (at 593 K) in YFe_5Sn_6 determined by neutron powder diffraction.

Atom	Site	*x*	*y*	*z*
Y	2*a*	0	0	0
Y	4*h*	0	0.1674(7)	$\frac{1}{2}$
Fe	4*f*	0.2458(7)	0	$\frac{1}{2}$
Fe	8*k*	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
Fe	8*n*	0.2535(7)	0.3345(4)	$\frac{1}{2}$
Fe	16*o*	0.2483(3)	0.0837(3)	0.2447(15)
Sn (1)	4*e*	0.3150(14)	0	0
Sn (2)	4*g*	$\frac{1}{2}$	0.0554(8)	$\frac{1}{2}$
Sn (3)	4*g*	0	0.1128(7)	0
Sn (4)	4*g*	0	0.2245(8)	0
Sn (5)	4*h*	0	0.0564(5)	$\frac{1}{2}$
Sn (6)	4*h*	$\frac{1}{2}$	0.1100(6)	0
Sn (7)	4*h*	$\frac{1}{2}$	0.2221(7)	0
Sn (8)	8*n*	0.3399(6)	0.1681(4)	$\frac{1}{2}$

show the neutron diffraction patterns of YFe_6Sn_6 obtained at 593 and 293 K in the forward scattering mode. The 593 K pattern, being above T_N of the Fe sublattice, comprises only nuclear scattering. The refined atomic position parameters are given in Table I.

Comparison of the neutron diffraction patterns taken above and below T_N indicates 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 illustrated by the appearance of the strong (131) magnetic peak at a *d* spacing of ~4.14 Å in the 293 K forward pattern. Thus, the Fe order may be described as *anti-I*, i.e., Fe moments related by the body-centering *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[9] 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 $\overline{1}$. The groups I_Pmmm and $I_Pm'm'm$ are excluded since they would result in an inadmissible magnetic point symmetry at the 8*k* site of $\overline{1}'$.

Finally, the Fe 4*f* site (whose crystal point group is $2_xm_ym_z$) allows us to rule out the $I_Pm'mm$ magnetic space group as 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 $I_Pm'm'm'$. Furthermore, the 4*f* site's magnetic point group of $2m'm'$ is only admissible with the Fe magnetic moment parallel to the 2 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, which is reasonable 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 $I_Pm'mm$ 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, inconsistent with the assumption of collinearity of the Fe sublattice moments. The selected group $I_Pm'm'm'$ gives an 8*n* magnetic point group of m_z' with magnetic order parallel to the mirror plane, i.e., with the Fe moment in the *a*-*b* plane, consistent with the Fe 4*f* site moment. A similar magnetic group determination procedure has been carried out on $ErFe_6Ge_6$ by Oleksyn *et al.*[10]

The fits to the 293 K neutron diffraction patterns with the Fe moments placed along [100] with a propagation vector of [010], yield a refined Fe magnetic moment of $2.03(7)\mu_B$. The neutron diffraction patterns obtained at 4 K (not shown here) are virtually identical to those obtained at 293 K which allows us to rule out any changes in the magnetic ordering mode of the Fe sublattice. The refined Fe magnetic moment at 4 K is $2.14(6)\mu_B$. The ^{57}Fe Mössbauer spectra of the RFe_6Sn_6 compounds have already been published by Rao and Coey.[4] Our measured ^{57}Fe average hyperfine field is 20.6(2) T at 295 K. The YFe_6Sn_6 structure con-

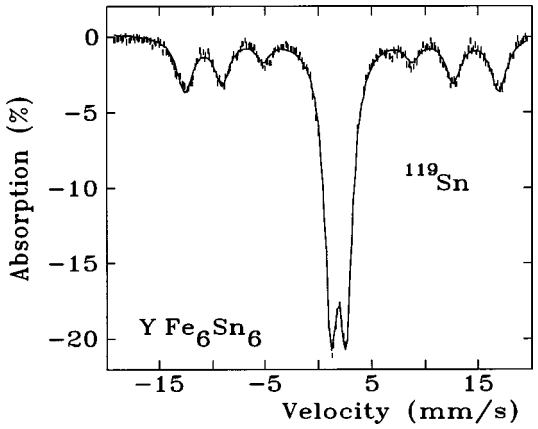

FIG. 2. ^{119}Sn Mössbauer spectrum of YFe_6Sn_6 obtained at 295 K.

tains four crystallographically inequivalent Fe sites but from a Mössbauer viewpoint we may treat them as effectively magnetically equivalent, given the similarity of their magnetic environments. It is generally accepted that the Wigner–Seitz (WS) cell volumes are correlated with the hyperfine field at the Fe sites[11] and we have calculated the WS cell volumes at the four Fe sites using the BLOKJE program.[12] We find the four Fe site volumes to be 11.16, 11.25, 11.34, and 11.34 Å,^{3} respectively, which supports the observed effective magnetic equivalence of the four Fe sites in YFe_6Sn_6. These experimental and theoretical findings are in agreement with band calculations carried out on YFe_6Sn_6 by Rao *et al.*[13]

To confirm our suggested magnetic structure of YFe_6Sn_6, deduced from the neutron diffraction data, we now consider the results of our ^{119}Sn Mössbauer experiments. Sn is nonmagnetic and so any hyperfine magnetic field observed at the ^{119}Sn nucleus is due to surrounding magnetic moments, i.e., a transferred hyperfine field. In YFe_6Sn_6 only the Fe atoms carry a magnetic moment and our WS calculations show that all Sn sites have six Fe nearest neighbors. However, our proposed magnetic structure of the Fe sublattice in YFe_6Sn_6 shows that Sn sites 2–7 have three Fe moments along [100] and three Fe moments antiparallel along [−100], resulting in a zero transferred hyperfine field. Sn sites 1 and 8 have all six Fe moments parallel which should result in a substantial transferred hyperfine field at the Sn site. Sn sites 1 and 8 account for exactly $\frac{1}{3}$ of the Sn sites.

In Fig. 2 we show the ^{119}Sn Mössbauer spectrum of YFe_6Sn_6 obtained at 295 K. The spectrum comprises both magnetically split and nonmagnetic components and the fit to the spectrum indicates that 35(1)% of the Sn sites in YFe_6Sn_6 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 magnetic structure of YFe_6Sn_6, determined from the TOF neutron diffraction.

In conclusion, the Fe sublattice in YFe_6Sn_6 is antiferromagnetic with a Néel temperature of 558(5) K. The direction of Fe magnetic order is [100] with a propagation vector of [010]. The Fe magnetic moment (at 293 K) is $2.03(7)\mu_B$. The magnetic space group is $I_Pm'm'm'$. ^{119}Sn Mössbauer spectroscopy shows that $\frac{1}{3}$ of the Sn sites experience a transferred hyperfine magnetic field from the neighboring Fe moments of 24.6(3) T at 295 K which confirms the Fe sublattice magnetic structure determined from the TOF neutron diffraction patterns.

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