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$LFe_6Sn_4Ge_2$ (L = Dy, Ho, Er) studied by neutron diffraction and Mössbauer spectroscopy

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ABSTRACT

The compounds $LFe_6Sn_4Ge_2$ (L = Dy, Ho, Er) have been studied by neutron diffraction and ^{119}Sn Mössbauer spectroscopy. At room temperature the magnetic structure consists of ferromagnetic Fe (0 0 1) planes which are coupled antiferromagnetically along the stacking direction, with the moments aligned along the hexagonal *c* axis. The lanthanoid sublattice orders around T_t = 21 and 11 K for the Dy and Ho compounds respectively. The erbium moment is not ordered at 1.7 K. Below T_t, $LFe_6Sn_4Ge_2$ (L = Dy, Ho) display a helimagnetic structure with propagation vectors of (0, 0, 0.1262) and (0, 0, 0.1559) respectively. Ordering of the Dy and Ho moments causes a small distorsion of the high temperature AF structure of the iron sublattice and the development of a weak helimagnetic component (0.33 and 0.27 μ_B respectively). The orientation of the iron component with respect to the L moments suggests that the main magnetic interaction between the two sublattice takes place between the L plane and the next nearest Fe planes.

1. Introduction

Although the orthorhombic LFe_6X_6 compounds (L = lanthanoid, X = Ge, Sn) display unique behaviour among the intermetallic compounds: the independent ordering of the Fe and lanthanoid sublattices [1–4], a recent study of hexagonal $TbFe_6Sn_4Ge_2$ pseudo-ternary compound has shown that a slight modification of the iron magnetic order occurs at the ordering point of the lanthanoid sublattice [5]. This transition is characterized by a helimagnetic ordering of the terbium moments and the concomitant development of a helimagnetic component on the iron sublattice. In order to better understand this phenomenon, an investigation of the magnetic properties of other Ge-stabilized hexagonal $LFe_6Sn_4Ge_2$ (L = Dy–Er) has been undertaken by neutron diffraction and Mössbauer spectroscopy.

2. Experimental methods

The samples were prepared in an induction furnace starting from stoichiometric amounts of the elements. The resulting ingots were annealed at 1123 K for 1 week, ground compacted again and annealed for one more week. The samples were checked by conventional X-ray powder analysis (Guinier Co Kα). The main systematic impurity lines detected were those of elemental tin, L_2O_3 and hexagonal Fe_3Ge. The erbium compound seemed to contain additional weak amounts of impurities indexed as a Ni_2In-type $Fe_{2-x}Ge$ alloy and a $CeNiSi_2$-type $ErFe_xSn_2$ compound [6].

The neutron diffraction patterns were recorded on the D1B diffractometer at the Institut Laue Langevin (Grenoble) using the wavelength (λ = 2.520 Å). Two long duration patterns were recorded at 300 and 2 K and short duration patterns in the 2–50 K temperature range to check the variation of the Bragg angles and intensity. Refinements were done using the FULLPROF software [7].

^{119}Sn Mössbauer spectra were collected in transmission mode on a constant acceleration spectrometer using a 0.4 GBq ^{119m}Sn CaSnO3 source with the sample in a helium flow cryostat. A 25 μm Pd filter was used to absorb the Sn Kα X-rays also emitted by the source. The spectrometer was calibrated using a ^{57}CoRh source and a α-Fe foil. Typical line widths were 0.85 mm/s full width at half maximum (FWHM), somewhat broader than the 0.6 mm/s obtained using a $CaSnO_3$ standard. Isomer shifts were measured relative to the same $CaSnO_3$ standard. The spectra were fitted using a conventional non-linear least-squares minimisation routine to a sum of Lorentzian line shapes. As the magnetic hyperfine fields (B_{hf}) at the Sn(2d) sites were quite small, and thus comparable to the quadrupole interaction, line positions and intensities were calculated using a full solution to the nuclear Hamiltonian [8]. Each spectrum was fitted with three components: a well-split magnetic sextet ($B_{hf} \approx 20$ T at 5 K), corresponding to tin atoms in the Sn(2e) site, and a quadrupole-split doublet attributed to tin in the Sn(2d) site accounted for over 90% of the observed area, with a singlet associated with a metallic tin impurity completing the fit. The area of this last component was strongly temperature dependent, becoming much larger at low temperatures as expected from the low Debye temperature of metallic tin. The contribution of minority tin in the Sn(2c) sites was not included as these sites are known to be occupied almost entirely by germanium and no additional feature was apparent in the spectra.

3. Results

3.1. Crystal structure

The neutron diffraction patterns of the $LFe_6Sn_4Ge_2$ samples clearly display the typical lines of the $HfFe_6Ge_6$ type structure

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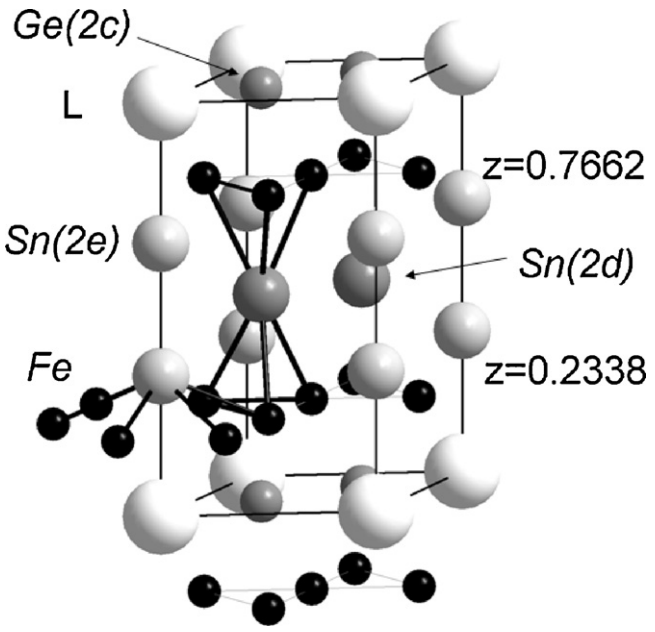

Fig. 1. Crystal structure of the $LFe_6Sn_4Ge_2$ compounds (the iron coordination of the Sn atoms is outlined).

[*P*6/*mmm*; Hf in 1(a) (0, 0, 0); Fe in 6(i) (1/2, 0, *z*); Ge in 2(c) (1/3, 2/3, 0), 2(d) (1/3, 2/3, 1/2) and 2(e) (0, 0, *z*)] (Fig. 1). Previous studies indicated that the Ge atoms were mainly located in the 2(c) site [9]. This distribution was confirmed for the room temperature data. A preliminary refinement was done starting with the Sn atoms in the 2(d) and 2(e) sites and the Ge atoms in the 2(c) site and then refining the occupancy factors. In each case, we found that the occupation of the 2(c) site decreases slightly. According to the relative Fermi lengths of tin (6.225 fm) and germanium (8.185 fm), this means that the 2(c) site is partly occupied by tin atoms. The occupation of the 2(e) site is always close to the ideal value or slightly weaker, indicating that a full occupation of this site by tin could be assumed. This occupation was fixed in the final refinements. In the case of the Dy and Ho compounds, the occupancy factor of Sn in site 2(d) exhibited a weak increase indicating a possible substitution by germanium while it decreases slightly in the Er compound. The final refinements with the relative occupation by tin and germanium atoms are given in Table 1. In all cases, we observed a strong shift of the z_{Fe} coordinate from the idealized 1/4 value. This means that the Fe planes move towards the 2(c) site (1/3, 2/3, 0) occupied by the small Ge atoms yielding Fe–2(c) distances that are much shorter than the Fe–2(d) distances. As a result, the Fe–Fe interplane distances are shorter in the Fe–2(c)–Fe slab than in the Fe–2(d)–Fe slab.

Table 1
Crystallographic and magnetic parameters of $LFe_6Sn_4Ge_2$ refined at 300 K.

L	Dy	Ho	Er
a (Å)	5.2746(6)	5.2797(5)	5.2787(7)
c (Å)	8.635(1)	8.644(1)	8.667(1)
z_{Sn}	0.339(1)	0.337(1)	0.335(1)
z_{Fe}	0.2338(6)	0.2328(5)	0.2339(5)
$\%_{Sn1}[\%_{Ge1}]$	96[4](4)	92[8](4)	100[0]
$\%_{Ge2}[\%_{Sn2}]$	89[11](4)	84[16](3)	89[11](5)
$\%_{Sn3}[\%_{Ge3}]$	100[0]	100[0]	100[0]
μ_{Fe} (μ_B)	2.06(6)	1.96(4)	2.03(5)
R_{Bragg}, R_f, R_{magn}	2.6, 2.1, 1.7	2.2, 1.9, 5.9	2.0, 2.1, 5.8
χ^2	6.80	9.44	9.34

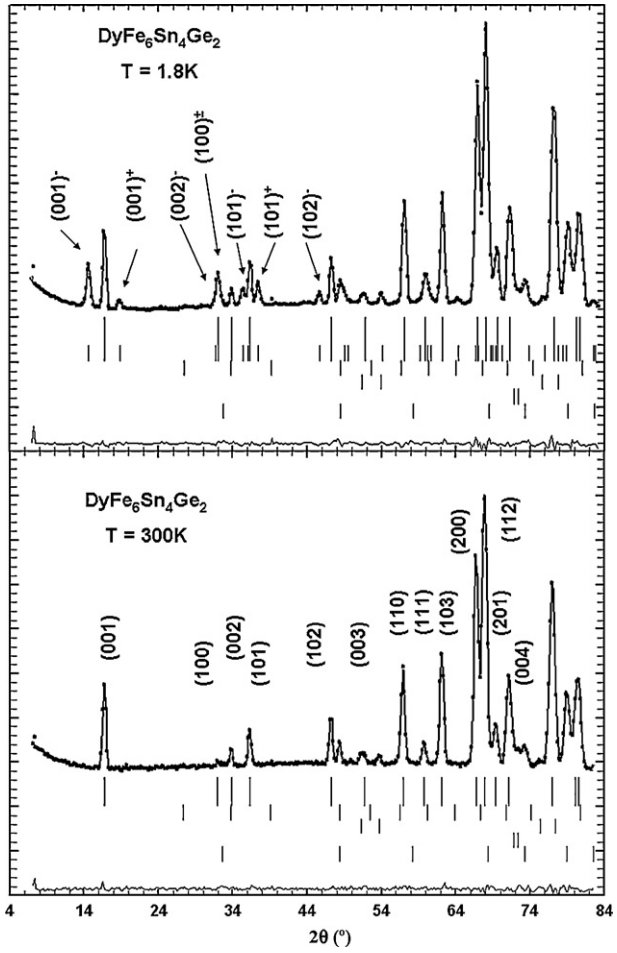

Fig. 2. Observed and calculated neutron diffraction spectra of $DyFe_6Sn_4Ge_2$ at room temperature and at 1.8 K (ticks of extra phases from bottom to top: Fe_3Ge, sample holder, Sn, Dy_2O_3).

3.2. Magnetic structures

The room temperature patterns do not exhibit any extra peaks of magnetic origin thus indicating that all of the magnetic contributions coincide with the nuclear peaks (Figs. 2–4). The refinements of the nuclear structure only show magnetic contributions on the ($h\,k\,l$) peaks with l odd giving evidence of the usual magnetic structures of LFe_6X_6 compounds (X = Ge, Sn) characterized by ferromagnetic Fe Kagomé planes, antiferromagnetically coupled along the stacking direction [1–5,10–17] (Fig. 5). In the present compounds, the absence of a magnetic contribution at the (0 0 l) peaks indicates that the Fe moments are aligned along the hexagonal c axis (Fig. 5). The results of the refinements are gathered in Table 1. At 300 K, the Fe moments are close to 2 μ_B for all three compounds.

At lower temperatures, additional lines appear in the neutron diffraction patterns (Figs. 2–4). In the case of the Dy and Ho compounds, these magnetic lines can be indexed as satellites of the nuclear ones using a propagation vector $Q = (0, 0, q_z)$ as previously reported for $TbFe_6Sn_4Ge_2$ [5]. Preliminary refinements including only the contribution of the lanthanoid sublattice do not account for the very asymmetric intensities of the $(0\,0\,1)^-$ and $(0\,0\,1)^+$ satellites. Therefore, refinements carried out including both a helimagnetic structure for the Ho or Dy moments and, as already observed in $TbFe_6Sn_4Ge_2$, a helimagnetic contribution from of the Fe sublattice. The refined parameters are the lanthanoid moment, the iron helimagnetic component and the phase angle of the Fe sublattice defined as ϕ_{Fe} and $-\phi_{Fe}$ for the Fe moments lying in $z \approx 1/4$ and