The spin-reorientation transition in H-type YbFe$_6$Ge$_6$

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Abstract. The two crystallographic forms of YbFe$_6$Ge$_6$ have been studied using neutron powder diffraction, and both $^{57}$Fe and $^{170}$Yb Mössbauer spectroscopy. Only the H-type (HfFe$_6$Ge$_6$–type) form undergoes a spin reorientation, and $^{57}$Fe Mössbauer data taken on a single crystal mosaic confirm that the Fe moments go from parallel to the c-axis to making an angle of 69(2)$^\circ$ with the crystal c-axis. $^{170}$Yb Mössbauer spectra show that the Yb ions are trivalent in both forms, the Yb moments do not order above 5 K and that there is no transferred field from the Fe moments in either form.

1. Introduction
The rare-earth (R) and Fe sublattices in the RF$_6$Ge$_6$ and RF$_6$Sn$_6$ intermetallic compounds exhibit independent magnetic behaviour ([1] and references therein). The Fe sublattice orders antiferromagnetically with a Néel temperature which remains essentially constant across a series at $\sim$485 K for RF$_6$Ge$_6$ or $\sim$555 K for RF$_6$Sn$_6$. For R = Gd – Er, the R sublattice orders with Curie temperatures ranging from a high of 45 K in GdFe$_6$Sn$_6$ to 3 K in ErFe$_6$Ge$_6$.

YbFe$_6$Ge$_6$ has been shown to occur in two closely related forms within the hexagonal $P6/mmm$ (#191) space group. The first to be identified was the ordered hexagonal HfFe$_6$Ge$_6$–type (hereafter “H-type”) structure in which the crystal cell is doubled along the hexagonal c-axis relative to the underlying FeGe basis, with full site-occupancies [2]. Later, a hexagonal YCo$_6$Ge$_6$–type (“Y-type”) form was described in which the Yb ions have a 50% occupancy of the 1a site and the cell size is almost the same as that of the parent FeGe compound [3]. For a general discussion of RF$_6$X$_6$ crystallography, see Venturini’s review [4].

Remarkably, the two structural forms exhibit distinct magnetic behaviours: the Fe sublattice in the H-type form undergoes a spin reorientation starting just below 80 K as the Fe moments tilt away from the c-axis [5], while in the Y-type form, the Fe order remains unchanged. The co-existence of the two structural forms in many samples of YbFe$_6$Ge$_6$ initially led to more complex descriptions of the ordering [6] in terms of mixed ordering, however we now believe that almost all Y-type samples of YbFe$_6$Ge$_6$ contain small amounts of the H-type form.

As the magnetic structures of both forms have been presented in some detail elsewhere [5], we concentrate here on using $^{170}$Yb Mössbauer spectroscopy to determine the Yb valence in the two forms, and $^{57}$Fe Mössbauer spectroscopy of a single crystal mosaic of the H-type form of YbFe$_6$Ge$_6$ to obtain an independent estimate of the Fe moment canting angle for comparison with that derived from neutron diffraction.
2. Experimental Methods

Several samples of YbFe₆Ge₆ were prepared by arc-melting stoichiometric amounts of the pure elements (Yb: 99.9%, Fe: 99.95%, Ge: 99.999%) under Ti-gettered argon, allowing an excess of 20 wt% Yb to compensate for the inevitable Yb boil-off in the arc-furnace. The arc-melted ingots were sealed under vacuum in quartz tubes and annealed at temperatures from 750 K to 900 K for two weeks. This approach generally yields samples in the Y-type form with varying levels of H-type as an ‘impurity’, however we did obtain one pure H-type sample by this means. The Y-type sample used here was obtained by annealing at 750 K.

The only method that consistently yields YbFe₆Ge₆ in the HfFe₆Ge₆ H-type form involves growth from a tin flux [7]. About 25 grams of an iron-deficient starting mixture (Yb:Fe:Ge:Sn atomic proportions of 1:1:3:20; Sn: 99.99%) was loaded into a 11 mm i.d. quartz tube sealed under vacuum. The tube was stood vertically in a furnace and heated rapidly to 1220 °C and held there for 10 hours, before cooling to 500°C at 5°C/hr. The tube was then inverted to drain off the majority of the tin flux and furnace-cooled to RT. The crystals were removed from the tube and the excess tin metal was removed by dissolving it in concentrated HCl for two days. Many millimetre-sized hexagonal plates and several hexagonal rods were recovered from each batch, along with about 0.5 g of finer powder. Approximately twenty of the plates from several batches were assembled to form a mosaic for the ⁵⁷Fe Mössbauer spectroscopy work, and about 2 g of smaller crystals and powder was hand-ground and used for both ⁵⁷Fe and ¹⁷⁰Yb Mössbauer spectroscopy and then neutron diffraction.

⁵⁷Fe Mössbauer spectroscopy was carried out in transmission mode using a 25 mCi ⁵⁷CoRh source with the sample in a vibration-isolated closed-cycle fridge. Transmission mode ¹⁷⁰Yb Mössbauer spectra were obtained at 5 K with both the source and sample located in a helium flow cryostat. The 20 mCi ¹⁷⁰Tm source was prepared by neutron activation of ∼25 mg of Tm as a 10 wt% alloy in aluminium. The ⁵⁷Fe spectra were fitted to a sum of Lorentzian lines with positions and intensities determined from first-order perturbation, while the line positions and intensities for the ¹⁷⁰Yb spectra were obtained from diagonalization of the full nuclear hyperfine Hamiltonian [8].

3. Results and Discussion

The clearest indication of the spin-reorientation in H-type YbFe₆Ge₆ comes from neutron diffraction measurements [5]. A full Rietveld analysis of the diffraction patterns yielded Fe moments of 1.62(30) μB lying at an angle of 69(12)° from the c-axis [5]. The reorientation starts just above 80 K and is essentially complete by ∼40 K.

The ⁵⁷Fe Mössbauer spectra of the two forms of YbFe₆Ge₆ at 12 K (Fig. 1) clearly show the impact of the spin-reorientation that leads to the single crystallographic Fe site in the H-type form being sub-split into three, equal-area, magnetically inequivalent sites as the Fe moments cant away from the c-axis below ∼80 K. No contribution from the un-canted Y-type pattern was detected in the spectrum of the H-type sample, consistent with this sample being a pure H-type YbFe₆Ge₆. Similarly, there are no apparent mis-fits that could be associated with an H-type ‘impurity’ in the Y-type pattern, however, given the estimate of 5% from the neutron diffraction data [5], and the three-way splitting that this component undergoes, this is not a strong test of the phase purity of the sample. The temperature dependences of the hyperfine parameters shown in Fig. 2 clearly illustrate the differences between the two forms. Bhf values at the three sub-split sites in the H-type form are all reduced from that seen in the Y-type form (that does not re-orient) as a result of anisotropic contributions to the hyperfine field [5, 9].

The mosaic of H-type YbFe₆Ge₆ crystals was constructed so that the c-axes of the platelets were all parallel to the direction of the Mössbauer γ−beam. Spectra were obtained at 100 K (above the re-orientation) and 13 K (well below the re-orientation) and are shown in Fig. 3. The hyperfine parameters used in the fits (Bhf, δ, Δ) were all taken from spectra measured
using powdered samples at the corresponding temperature, and only the baseline, total spectral intensity and the relative intensities of the two $\Delta m_I = 0$ transitions (lines #2 and #5 in the 6-line magnetic patterns) were refined. A small (~5%) paramagnetic impurity was included to account for the slight asymmetry in the centre of both spectra.

The six lines in a magnetically split $^{57}$Fe Mössbauer spectrum have, to first order, relative intensities of $3:R:1:1:R:3$, where $R$ is given by: $R = \frac{4 \sin^2 \theta}{1 + \cos^2 \theta}$ ($\theta$ is the angle between the direction of the $\gamma$-beam and the hyperfine field). Analysis of the 100 K pattern in Fig. 3 yields $R=0.04(8)$, fully consistent with zero, and confirming that the moments are indeed oriented parallel to the $c$-axis as derived from the neutron diffraction data [5]. It is clear from a visual inspection of the 13 K spectrum in Fig. 3 that the two $\Delta m_I = 0$ lines are at least as strong as the outer lines, suggesting that $R$ is now of order 3, and indicating that the Fe moments are now lying somewhere close to the ab-plane. Fitting the pattern with the constraints on the hyperfine parameters identified above, yields $R=3.07(15)$, giving an angle $\theta = 69(2)^\circ$ between the moments and the $\gamma$-beam (which is in turn parallel to the crystal c-axes in the mosaic). This value is in full agreement with the 69(12)$^\circ$ derived from the neutron diffraction pattern at 3.9 K [5], has slightly better precision, and provides a completely independent confirmation of the canting angle.

One possible source of the differences in magnetic behaviour between the H-type and Y-type forms of YbFe$_6$Ge$_6$ might be the valence of the Yb ions in the two compounds. Analysis of both the lattice parameters [6] and single-crystal XANES data [7] for the H-type form of YbFe$_6$Ge$_6$ suggests that the Yb is trivalent in this form, while a comparison of the lattice parameters for the two forms of YbFe$_6$Ge$_6$ shows no anomaly that could be attributed to a valence change [5] between the two forms. We therefore expect that the Yb ions are trivalent in both forms of YbFe$_6$Ge$_6$.

The striking similarity between the 5 K $^{170}$Yb Mössbauer spectra of both forms of YbFe$_6$Ge$_6$ shown in Fig. 4 clearly confirms this expectation. Analysis of the two spectra yields quadrupole splittings ($eQV_{zz}$) of 9.58(10) mm/s for the Y-type form and 9.52(13) mm/s for the H-type form implying that the Yb environments in the two forms are effectively indistinguishable. The observed quadrupole splittings indicate that the Yb ions are definitely trivalent as the diamagnetic Yb$^{2+}$ ion has a closed $4f$ shell which is necessarily spherically symmetric, yielding...
Figure 3. $^{57}$Fe Mössbauer spectra of the H-type YbFe$_6$Ge$_6$ crystal mosaic at 100 K (top) and 13 K (bottom).

Figure 4. $^{170}$Yb Mössbauer spectra of the Y-type (top) and H-type (bottom) forms of YbFe$_6$Ge$_6$ at 5 K.

no 4f contribution to the quadrupole splitting. We also note that there is no evidence for a magnetic field at the Yb site in either form, indicating that the Yb ions do not order above 5 K. Furthermore, there is no evidence for a transferred field from the ordered Fe sub-lattice, in either the c-axis (Y-type) or canted (H-type) ordered states. An observation that is consistent with the neutron diffraction derived magnetic structures of both forms at this temperature [5]. In both the collinear (Y-type) and canted (H-type) magnetic structures, the contributions from the Fe moments at the Yb site are expected to cancel.

4. Conclusions

$^{57}$Fe Mössbauer measurements of the HfFe$_6$Ge$_6$-type (“H-type”) and YCo$_6$Ge$_6$-type (“Y-type”) forms of YbFe$_6$Ge$_6$ show that only the H-type form undergoes a spin re-orientation below $\sim$80 K. Working with flux-grown single crystals of H-type YbFe$_6$Ge$_6$ we showed that below the re-orientation temperature, the Fe moments make an angle of 69(2)$^\circ$ with the crystal c-axis, in full agreement with earlier neutron diffraction results. $^{170}$Yb Mössbauer spectra of the two forms show that in both cases the Yb ions are trivalent.

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