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The spin-reorientation transition in H-type $YbFe_6Ge_6$

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Abstract. The two crystallographic forms of $YbFe_6Ge_6$ have been studied using neutron powder diffraction, and both ^{57}Fe and ^{170}Yb Mössbauer spectroscopy. Only the H-type ($HfFe_6Ge_6$–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)° 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 RFe_6Ge_6 and RFe_6Sn_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 ∼485 K for RFe_6Ge_6 or ∼555 K for RFe_6Sn_6. For R = Gd – Er, the R sublattice orders with Curie temperatures ranging from a high of 45 K in $GdFe_6Sn_6$ to 3 K in $ErFe_6Ge_6$.

$YbFe_6Ge_6$ 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 $HfFe_6Ge_6$–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_6Ge_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 RFe_6X_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 $YbFe_6Ge_6$ 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 $YbFe_6Ge_6$ 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 $YbFe_6Ge_6$ 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 $\mathrm{YbFe_6Ge_6}$ 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 $\mathrm{YbFe_6Ge_6}$ in the $\mathrm{HfFe_6Ge_6}$ 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 ^{57}Fe Mössbauer spectroscopy work, and about 2 g of smaller crystals and powder was hand-ground and used for both ^{57}Fe and ^{170}Yb Mössbauer spectroscopy and then neutron diffraction.

^{57}Fe Mössbauer spectroscopy was carried out in transmission mode using a 25 mCi ^{57}Co**Rh** source with the sample in a vibration-isolated closed-cycle fridge. Transmission mode ^{170}Yb Mössbauer spectra were obtained at 5 K with both the source and sample located in a helium flow cryostat. The 20 mCi ^{170}Tm source was prepared by neutron activation of $\sim$25 mg of Tm as a 10 wt% alloy in aluminium. The ^{57}Fe 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 ^{170}Yb 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 $\mathrm{YbFe_6Ge_6}$ comes from neutron diffraction measurements [5]. A full Rietveld analysis of the diffraction patterns yielded Fe moments of 1.62(30) μ_B lying at an angle of 69(12)° from the c-axis [5]. The reorientation starts just above 80 K and is essentially complete by $\sim$40 K.

The ^{57}Fe Mössbauer spectra of the two forms of $\mathrm{YbFe_6Ge_6}$ 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 $\sim$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 $\mathrm{YbFe_6Ge_6}$. 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. B_{hf} 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 $\mathrm{YbFe_6Ge_6}$ crystals was constructed so that the c-axes of the platelets were all parallel to the direction of the Mössbauer $\gamma-$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 (B_{hf}, δ, Δ) were all taken from spectra measured

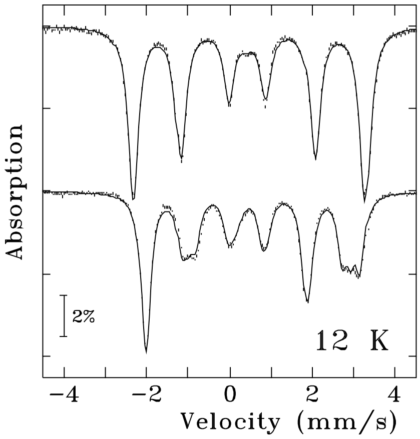

Figure 1. ^{57}Fe Mössbauer spectra of powdered Y-type (top) and H-type (bottom) samples of $YbFe_6Ge_6$ at 12 K.

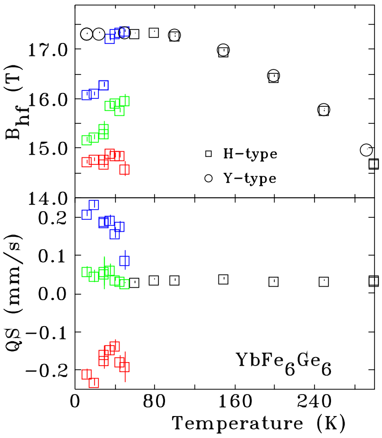

Figure 2. (Top) Temperature dependence of the ^{57}Fe hyperfine field (B_{hf}) and (Bottom) quadrupole splitting for the two forms of $YbFe_6Ge_6$.

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: $R = \frac{4\sin^2\theta}{1+\cos^2\theta}$ (θ 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)° 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 $YbFe_6Ge_6$ 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 $YbFe_6Ge_6$ suggests that the Yb is trivalent in *this* form, while a comparison of the lattice parameters for the two forms of $YbFe_6Ge_6$ 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 $YbFe_6Ge_6$.

The striking similarity between the 5 K ^{170}Yb Mössbauer spectra of both forms of $YbFe_6Ge_6$ 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

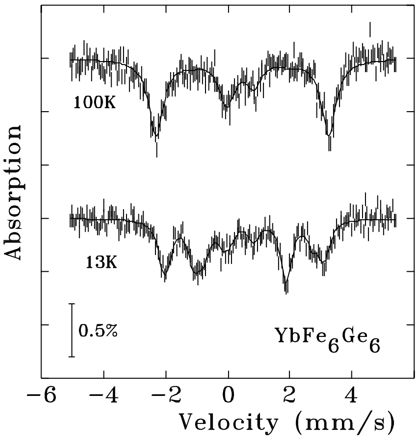

Figure 3. ^{57}Fe Mössbauer spectra of the H-type YbFe$_6$Ge$_6$ crystal mosaic at 100 K (top) and 13 K (bottom).

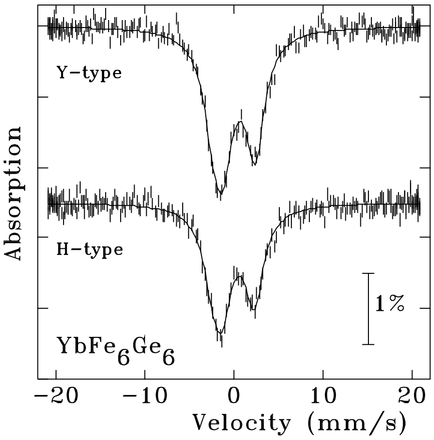

Figure 4. ^{170}Yb Mössbauer spectra of the Y-type (top) and H-type (bottom) forms of YbFe$_6$Ge$_6$ at 5 K.

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 ∼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)° 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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