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Magnetic properties of $Nb_{1-x}Hf_xFe_2$

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Abstract ^{57}Fe-Mössbauer spectroscopy for the $Nb_{1-x}Hf_xFe_2$ intermetallic series reveals the presence of local Fe 6h-site moments well above the magnetic transition temperatures determined from bulk magnetisation measurements. The techniques combine to demonstrate that the system orders antiferromagnetically at $x = 0.4$ with a remarkable change to strong ferromagnetic character between $x = 0.7$ and 0.8. Low temperature spin glass behaviour is observed for $x = 0.45$ to 0.79.

Keywords Mössbauer spectroscopy · Intermetallics · Spin glass · Laves phase

1 Introduction

The intermetallic series $Nb_{1-x}Hf_xFe_2$ ($0 < x < 0.8$) forms with the hexagonal C14 Laves phase structure with space group $P6_3/mmc$ and exhibits an unusual range of magnetic properties. Stoichiometric $NbFe_2$ is a weak itinerant antiferromagnet with a spin-density-wave transition at $T_{sdw} \approx 10$ K [1]. More recently, considerable interest has been directed at the existence of ferromagnetic quantum criticality for a small excess of Nb ([2] and references therein). In its unannealed form, $HfFe_2$ exhibits a minor C14 phase component (the preferred phase is cubic C15) that orders ferromagnetically at $T_C \approx 427$ K [3, 4]. With increasing Hf concentration, the magnetic ordering temperature is expected to increase fairly smoothly between these

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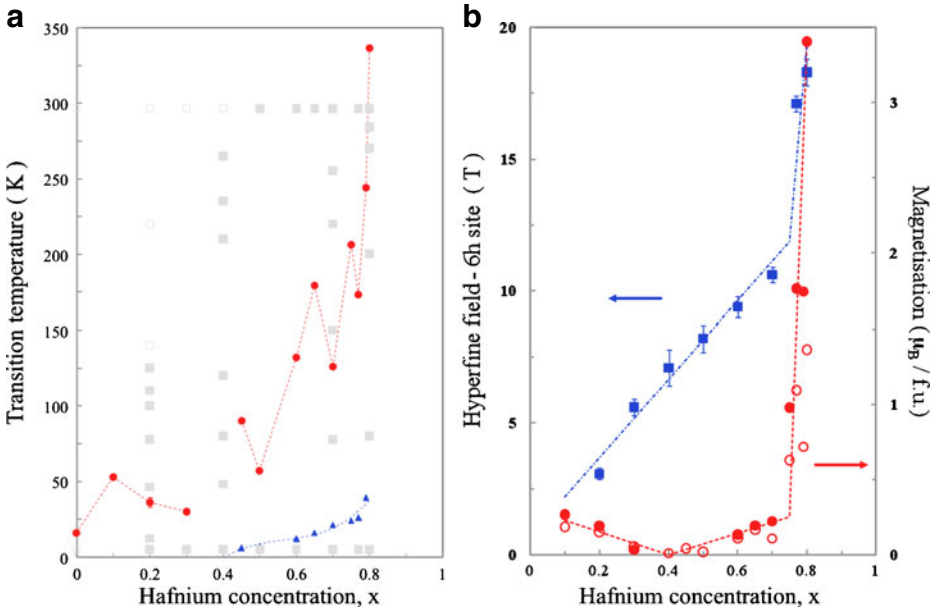

Fig. 1 **a** Bulk magnetic phase transition temperatures (*circles*) and spin glass transitions (*triangles*) for $Nb_{1-x}Hf_xFe_2$ are compared with ordered (*solid squares*) and paramagnetic (*open squares*) magnetic behaviour as indicated by ^{57}Fe-Mössbauer spectroscopy. **b** The low temperature (T = 5 K) magnetic behaviour of $Nb_{1-x}Hf_xFe_2$ is represented by the magnetisation observed for an applied field of 0.1 T (*open circles*), the saturation magnetisation (*solid circles*), and the magnetic hyperfine field (B_{hf}) at the Fe 6h-site. *Broken lines* are a guide to the eye

two end values. However, it is difficult to be precise about ordering temperatures and magnetic structure from the magnetisation measurements alone. The m ain thrust of this work is the use of ^{57}Fe-Mössbauer spectroscopy to monitor the magnetism at the atomic level via the magnetic hyperfine fields (B_{hf}) acting at the 2a- and 6h-Fe sites. To this end, Mössbauer spectra have been recorded as a function of temperature and hafnium concentration ($0 < x < 0.8$), and our analysis is presented in conjunction with new bulk magnetisation data.

2 Experimental details

Single-phase, polycrystalline samples of $Nb_{1-x}Hf_xFe_2$ were synthesised from high purity elemental constituents via argon arc melting. Ingots were then wrapped in Ta foil and sealed in evacuated quartz tubes for annealing at 1000°C for one week. Bulk magnetisation measurements were performed on a Quantum Design MPMS magnetometer capable of measuring down to 2 K in applied fields up to 7 T. The ^{57}Fe-Mössbauer spectra were recorded using a liquid helium bath cryostat and a 20 mCi ^{57}Co:Rh source mounted externally on a sinusoidal motion drive. They were analysed using a full Hamiltonian model [5]. However, the parameters eta, theta and phi were fixed to zero, thus amounting to coaxial magnetic and electric quadrupole hyperfine interactions. The 6h and 2a component sub-spectra intensities were

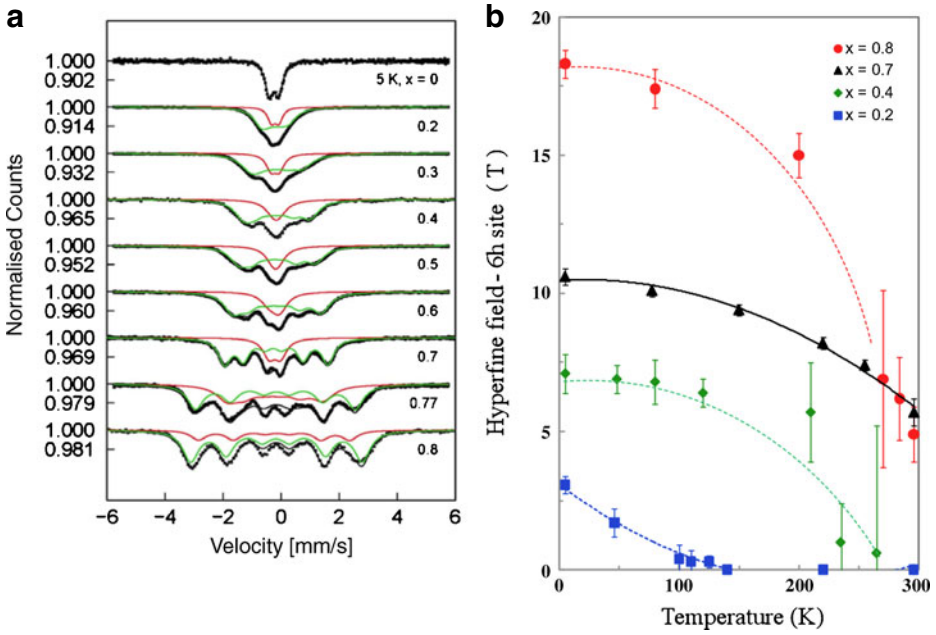

Fig. 2 **a** ^{57}Fe-Mössbauer spectra recorded at 5 K for $Nb_{1-x}Hf_xFe_2$ with the indicated hafnium concentrations, x. The sub-spectra correspond to the 6h- and 2a-sites (*green* and *red*, respectively). **b** Magnetic hyperfine field (B_{hf}) fitted to the 6h-site sub-spectrum as a function of temperature for $x = 0.2$, 0.4, 0.7 and 0.8

maintained at the expected ratio of 3:1 for the two Fe sites in this structure. The B_{hf} value was fixed to zero for spectra above the magnetic transition temperature and allowed to vary for temperatures below the transition. In some spectra overlapping peaks made it necessary to carefully choose starting parameters to achieve consistent fits.

3 Results

Low field (0.1 T) bulk magnetisation data for the $Nb_{1-x}Hf_xFe_2$ intermetallics generally indicate a single magnetic phase transition. The transition temperatures estimated, via extrapolation of M^2 *v's* T plots to the temperature axis, are plotted in Fig. 1a as a function of x (solid circles). Based on Arrott plots, the nature of the magnetic order was determined as being ferrimagnetic with decreasing saturation magnetisation in the range $x = 0.2$ to 0.3, antiferromagnetic for $x = 0.4$, and ferrimagnetic with increasing magnetisation for $x = 0.45$ to 0.7. There is a remarkable change to strong ferromagnetic character between $x = 0.7$ and 0.8. Estimated values of the saturation magnetisation are shown in Fig. 1b (solid circles). In addition, a comparison of field cooled and zero field cooled M data indicates an additional low temperature spin glass-like phase for $0.45 < x < 0.8$. These latter transition temperatures are indicated by triangles in Fig. 1a.

The ^{57}Fe-Mössbauer spectra were recorded for 5 K and 296 K, and also as a function of temperature for selected hafnium concentrations. Except for the strongly

ferromagnetic compounds ($0.7 < x < 0.8$) B_{hf} is zero at the higher symmetry 2a-site, so that the 6h-site B_{hf} is the more useful probe of local Fe magnetism. The full set of 5 K spectra is shown in Fig. 2a and the corresponding fitted 6h-site B_{hf} (solid squares in Fig. 1b) are observed to increase almost linearly over $0.2 < x < 0.7$. This supports the argument for antiferromagnetic order at $x = 0.4$ (as opposed to an array of negligible local moments). The temperature dependence of B_{hf} is fitted for $x = 0.2$, 0.4, 0.7 and 0.8 (Fig. 2b) and the distribution of non-zero B_{hf} values (solid squares in Fig. 1a) indicates that the magnetic transition temperatures derived from Mössbauer spectroscopy are generally higher than those derived from bulk magnetisation measurements. This is puzzling, given that the bulk magnetic data offer no indication for higher temperature antiferromagnetic behaviour.

4 Discussion

In apparent contradiction of the bulk magnetic data, the low temperature 6h-site B_{hf} for the $Nb_{1-x}Hf_xFe_2$ series increases monotonically while the saturation magnetisation exhibits a minimum at $x = 0.4$. Furthermore the Mössbauer data indicate generally higher transition temperatures. The former is consistent with the existence of an antiferromagnetic phase while the latter needs to be explored further. In addition, the magnetisation data reveal spin glass behaviour at low temperatures in the region $x = 0.45$ to 0.79, which may be partly responsible for the suppression of the bulk moment through this region.

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