

Influence of Fe on the magnetic properties of h-Yb(Mn_{1-x}Fe_x)O₃

Hazar A. Salama and Glen A. Stewart

*School of Physical, Environmental & Mathematical Sciences, University of New South Wales,
Australian Defence Force Academy, Canberra ACT 2600, Australia.*

⁵⁷Fe-Mössbauer spectroscopy investigations are reported for specimens of hexagonal phase YbMnO₃ with two different concentrations (10 and 25 at.%) of Fe substituted for Mn. When compared with earlier results for more dilute concentrations, it is evident that the Mn sub-lattice Néel temperature increases with increasing Fe concentration. However, the magnetic hyperfine field acting at the ⁵⁷Fe probe nuclei is observed to decrease.

1. Introduction

The hexagonal rare earth manganites, RMnO₃, are currently of interest because of their multiferroic behavior and geometrical frustration, both of which are associated with the Mn sub-lattice. The Mn sub-lattice of YbMnO₃ first orders ferroelectrically at $T_C = 993$ K and then antiferromagnetically at $T_N = 88 - 89$ K (although two lower T_N values have been reported for single crystal specimens) [1, 2]. The Mn spins form a triangular network within each hexagonal c-plane. In a recent investigation [1], we demonstrated that dilute concentrations of ⁵⁷Fe provide a reliable, non-perturbing Mössbauer spectroscopy probe of the Mn sub-lattice magnetisation. Substitution of up to 1 at% ⁵⁷Fe exerts negligible influence on the Néel temperature and point charge model estimates of the electric field gradient agree well with experimental ⁵⁷Fe-Mössbauer results in terms of both sign and magnitude. In this new work, we have extended the Mössbauer investigation of polycrystalline Yb(Mn_{1-x}Fe_x)O₃ to the higher Fe concentrations of $x = 0.1$ and 0.25 . These results will be compared with the complementary magnetisation data of Huang *et al.* [2] for specimens with $x \geq 0.35$.

2. Experimental Details

Specimens with nominal stoichiometries of YbFe_xMn_{1-x}O₃ ($x = 0.1$ and 0.25) were prepared from Yb₂O₃ (99.99%), Fe₂O₃ (99.9%) and MnCO₃ (99.9+%) via the conventional solid state reaction approach. X-ray powder diffraction (XRD) patterns were then recorded at room temperature with Cu K_α radiation and Rietveld analyses were performed using the *Rietica* front end for Windows [3]. The ⁵⁷Fe-Mössbauer spectra were recorded as a function of temperature in transmission geometry with a commercial 10 mCi ⁵⁷Co:Rh source.

3. Results and discussion

3.1. X-ray powder diffraction

Analysis of the room temperature XRD patterns (Fig. 1) is consistent with samples of single hexagonal phase (space group $P6_3cm$). From Fig. 2, it is evident that the substitution of Fe for Mn results in an increase in both the c lattice parameter and the unit cell volume. This is despite the fact that the Mn³⁺ and Fe³⁺ ions are assumed to have the same radius of 0.058 nm for 5-fold oxygen coordination [4]. Huang *et al.* [2] report a similar effect for higher Fe concentrations. They argue that this distortion is brought about because the additional electron in the Fe³⁺ d-shell occupies the $3z^2-r^2$ orbital, which aligns with the c -axis.



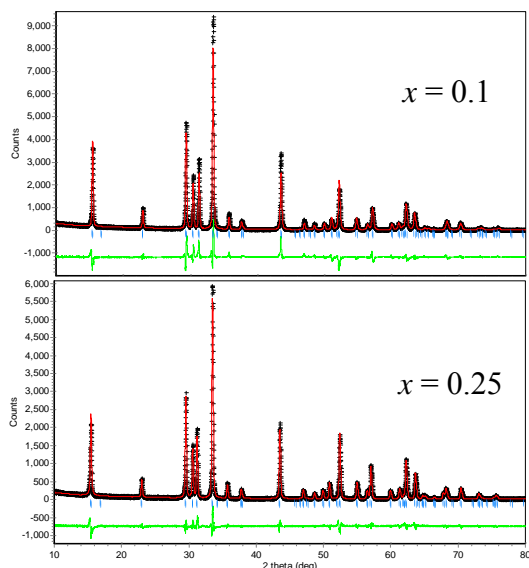


Fig.1. X-ray powder diffraction patterns for $\text{Yb}(\text{Fe}_x\text{Mn}_{1-x})\text{O}_3$ with $x = 0.1$ and 0.25 .

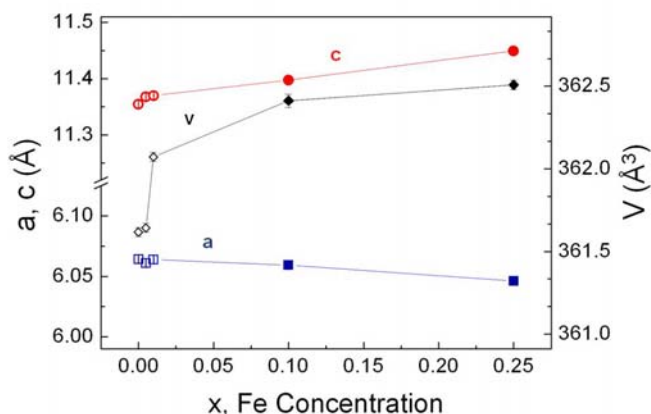


Fig.2. Lattice parameters for $\text{Yb}(\text{Fe}_x\text{Mn}_{1-x})\text{O}_3$ with $x = 0, 0.005, 0.01, 0.1$ and 0.25 (filled symbols, this work; open symbols, Salama *et al.* [1]). Error bars fall within the size of symbols.

3.2. Mössbauer spectroscopy

Representative ^{57}Fe Mössbauer spectra for $x = 0.1$ and 0.25 are presented in Fig. 3. The room temperature Mössbauer spectra are single doublets (green theory lines) corresponding to the paramagnetic phase and the 4.2 K spectra are single magnetically-split sextets (red theory lines) corresponding to the saturated magnetic phase, although an additional single-line, unknown impurity contribution (blue line) is revealed for $x = 0.1$ as the central region of the spectrum becomes less cluttered at low temperatures. The fitted parameters for these key spectra are summarised in Table 1 where they are compared with the previous results for $x = 0.005$ and 0.01 [1]. In all four cases, the orientation of the magnetic hyperfine field B_{hf} is fitted as perpendicular to the principal z -axis of the electric field gradient tensor, which is consistent with the alignment of the Mn moments in the hexagonal c -plane. The quadrupole splitting ($\frac{1}{2}eQV_{\text{zz}}$) increases marginally with Fe concentration and is presumably a consequence of the stretching of the unit cell's c -axis. The saturation values, B_{hf} (4.2 K), are typical of the high spin $S = 5/2$ state of Fe^{3+} and they are observed here to decrease with increasing Fe concentration.

In the intermediate temperature range, the magnetic spectra collapse with increasing temperature (Fig. 3). The temperature dependence of B_{hf} (Fig. 4) has the general appearance of a molecular field theory curve but is more closely represented by an empirical relationship (solid theory curves in Fig. 4) of the form

$$B_{\text{hf}} = B_{\text{hf}}(T = 0) \left(1 - \left(\frac{T}{T_N} \right)^\alpha \right)^\beta$$



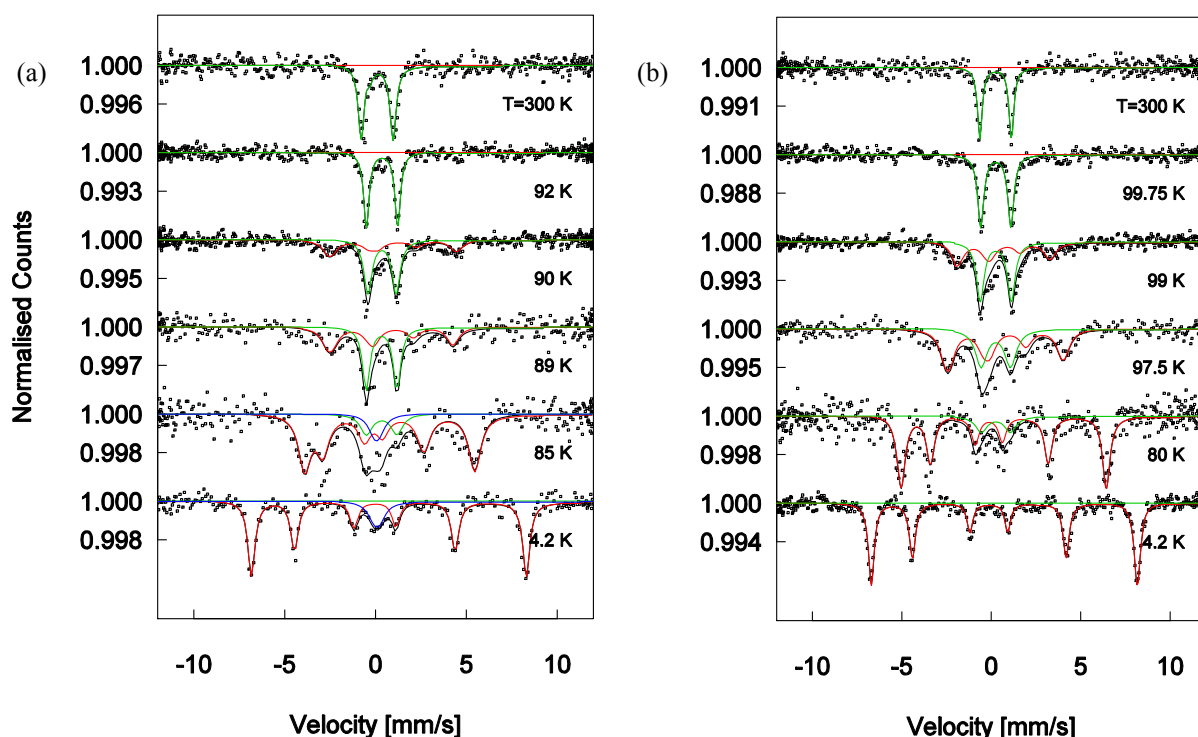


Fig. 3 Representative ^{57}Fe -Mössbauer spectra for $\text{Yb}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ with (a) $x = 0.1$ and (b) $x = 0.25$.

with $\beta = 0.27$ and $\alpha = 2.4/2.2$ for $x = 0.1/0.25$ (compared with $\alpha = 2.6$, $\beta = 0.27$ for $x = 0.005$, 0.01 [1]). The Néel temperatures derived from the temperature dependence of the Mössbauer spectra are shown in Fig. 5 where they are observed to fit well with the results of the earlier Mössbauer investigation [1] as well as the magnetic results of Huang *et al.* [2]. In the concentration range of $0 < x < 0.5$, the value of T_N increases linearly at a rate of 47.4 K per additional Fe atom per formula unit. Immediately below the magnetic transition, the ^{57}Fe -Mössbauer spectra involve both a paramagnetic doublet and a magnetic sextet.

Table 1 ^{57}Fe -Mössbauer spectroscopy results for hexagonal $\text{Yb}(\text{Fe}_x\text{Mn}_{1-x})\text{O}_3$. The isomer shift, δ , is given relative to α -Fe at room temperature.

T (K)	x	$\frac{1}{2}eQV_{zz}$ (mm/s)	δ (mm/s)	B_{hf} (T)	Ref
300	0.005	-1.68(1)	0.292(3)		[1]
	0.01	-1.67(1)	0.296(2)		[1]
	0.1	-1.70(1)	0.300(2)		this work
	0.25	-1.78(1)	0.306(1)		this work
4.2	0.005	-1.60(1)	0.420(7)	47.07(3)	[1]
	0.01	-1.57(1)	0.421(3)	46.67(2)	[1]
	0.1	-1.59(1)	0.419(2)	46.12(1)	this work
	0.25	-1.65(1)	0.421(1)	45.70(1)	this work



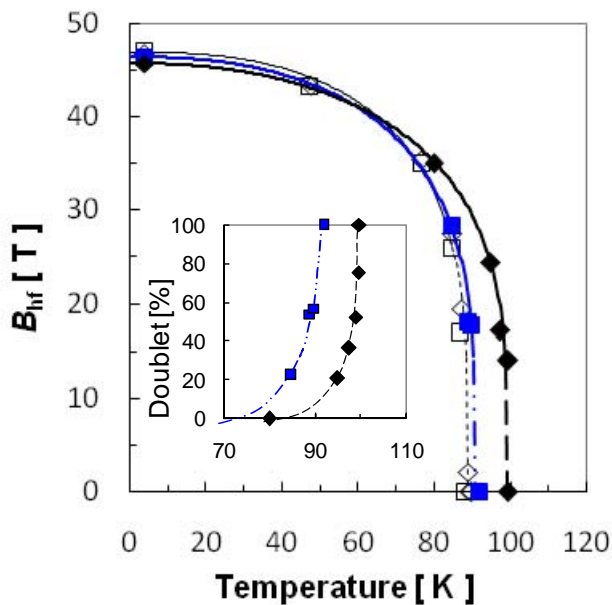


Fig. 4: Temperature dependence of the magnetic hyperfine field, B_{hf} , at ^{57}Fe for $\text{Yb}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ with $x = 0.005, 0.01$ (\square \diamond Salama *et al.* [1]), 0.1 and 0.25 (\blacksquare \blacklozenge this work).

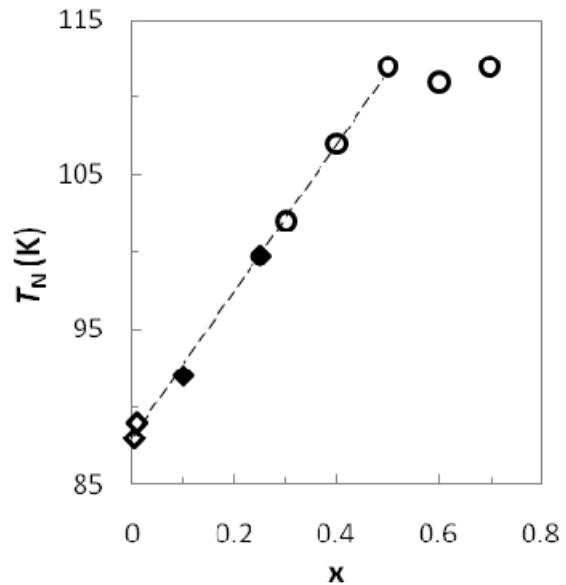


Fig. 5: Néel temperature, T_{N} , versus the Fe doping concentration, x , for $\text{Yb}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ as determined using ^{57}Fe Mössbauer spectroscopy (\blacklozenge this work, \diamond Salama *et al.* [1]) and magnetic susceptibility (\circ Huang *et al.* [2]).

Again, this was observed earlier for the more dilute concentrations [1]. As the transition is approached from below, the proportion of paramagnetic doublet component grows steadily to 100 % over a range of about 15 K (inset in Fig. 4).

4. Conclusion

In conclusion, the temperature dependence of the ^{57}Fe -Mössbauer spectra presented here for $\text{Yb}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ with $x = 0.1$ and 0.25 is very similar to that observed earlier for dilute concentrations of Fe. However, the Néel temperature is now determined to increase linearly with increasing Fe concentration. At the same time, the low temperature saturation value of B_{hf} decreases, suggesting that the local Fe moment is reduced by increased doping. This needs to be investigated further.

Acknowledgments

We thank Roman Kashkarov and Bobin Gorgosky for their assistance with specimen preparation, and Hazar Salama gratefully acknowledges her University International Postgraduate Award and University College Postgraduate Research Scholarship.

References

- [1] Salama H, Stewart G A, Ryan D, Elouneq-Jamroz M and Edge A V J 2008 *J. Phys.: Condens. Matter* **20** 255213
- [2] Huang Y H, Karppinen M, Imamura N, Yamauchi H and Goodenough J B 2007 *Phys. Rev.* **76** 174405
- [3] Howard C J and Hunter B A *Rietica*, available from <http://www.ccp14.ac.uk>
- [4] Shannon R D 1978 *Acta Cryst. A* **32** 751

