PROCEEDINGS - 36th ANNUAL CONDENSED MATTER AND MATERIALS MEETING, 31 Jan. -3 Feb. 2012. Wagga Wagga, NSW, Australia

^{89}Y NMR Hyperfine Relaxation Times and Transport in MBE Grown $REFe_2/YFe_2$ Multilayer Films

G.J. Bowden[a], R.C.C. Ward[b], K.N. Martin[a] and P.A.J. de Groot[a]

[a]*School of Physics and Astronomy, University of Southampton, SO17 1BJ, UK,*
[b]*Clarendon Laboratory, Oxford University OX1 3PU, UK*

It is argued that defects introduced during crystal growth of epitaxial molecular beam (110)-$REFe_2$ films are responsible for (i) the broadening of the ^{89}Y NMR line-width, and (ii) very low residual resistance ratios.

1. Introduction

In an earlier communication, ^{89}Y NMR studies of molecular beam epitaxial (MBE) grown YFe_2, a superlattice [300Å$DyFe_2$/300ÅYFe_2]×40, and bulk powdered YFe_2 samples, all at 4.2 K, were reported and discussed [1]. In particular, it was shown that there are significant differences between bulk and MBE-grown films. In the latter, the NMR frequency (45.85 ± 0.2 MHz) is shifted down in frequency by ~0.1 MHz, with respect to bulk (powdered) YFe_2 (45.94 ± 0.09 MHz). This frequency shift can be understood *qualitatively*, in terms of negative pressure, arising from the expanded nature of the MBE-grown $REFe_2$ (RE = rare earth) films [2]. But, rather surprisingly, given the single crystal nature of the MBE-grown films, the NMR line width was found to be broader by about a factor of two. Even more dramatically, the spin-spin lattice relaxation time T_2 was found to be almost ten times longer in the films (T_2 = 5.1 ms), than in bulk YFe_2 (T_2 = 0.6 ms). This was attributed to an increase in inhomogeneous line-width, which inhibits energy-conserving mutual spin-spin-flops, thereby increasing T_2. The increase in inhomogeneous line-width was attributed to strain within the MBE-grown films, and/or differing dipolar fields particularly near the $DyFe_2/YFe_2$ interfaces.

In this communication, we take a closer look at NMR broadening, originating from local dipolar fields induced by both strain and defects. It is argued that while strain-induced changes in local dipolar fields are present, dipolar-field broadening arising from defects offers a much more plausible explanation. In practice, it is difficult to grow $REFe_2$ films with a stoichiometric ratio better than 1%. Concomitantly, defects will also affect the resistivity of the MBE-grown films, via 'impurity scattering'. This interpretation is supported by transport measurements on MBE-grown YFe_2, $ErFe_2$, $DyFe_2$ and superlattice films. Despite their single crystal nature, all films show a very low residual resistance ratio $R_{4.2K}/R_{300K} \approx 3\text{-}6$.

2. Experimental details and transport measurements

Details of the MBE crystal growth of the $REFe_2$ films have been given by [3,4]. For present purposes it is sufficient to know that the films are grown epitaxially on polished sapphire $(11\bar{2}0)$ substrates, coated initially with Nb and Fe seed layers. At 900 °C the Fe alloys with the Nb to form a Nb/Fe alloy which acts as a template for the $REFe_2$ layers. The $ErFe_2$ and YFe_2 layers are subsequently grown a-top the Nb/Fe layer at a temperature of 600 °C. Finally, on cooling down to room temperature, the films become uniformly strained due to substrate clamping. This occurs because the sapphire has a lower thermal expansion coefficient than that of the $REFe_2$ film. The contraction is along the (110) film growth-axis, giving rise to a shear strain $\varepsilon_{xy} = -0.55\%$ [2].

Over the past decade, several transport measurements have been reported on MBE grown $REFe_2$ films, with emphasis on the role played by magnetic exchange springs. In particular, giant magneto-resistance (GMR) in $DyFe_2/YFe_2$ films has been reported by [5]. Here the increase in GMR was ascribed to magnetic exchange springs in the soft YFe_2 layers, which are wound ever more tightly as the magnetic field is increased. More recently, the anomalous Hall effect (AHE) has been measured in $ErFe_2/YFe_2$ films [6]. In this case, the AHE is driven primarily by the Fe sub-lattice. The RE magnetic moments do not affect transport properties, directly, because the occupied $4f$ levels are ~7.0 eV below the Fermi surface

In characterizing the electrical conduction of any metallic compound, it is instructive to measure the residual resistance ratio (RRR), which is the ratio of the resistance at 300 K to that at 4.2 K. In the past, RRR measurements have been used as a guide to the presence of impurities. For example, the RRR of iron lies within the range 35-400, depending on the concentration of impurities [7]. For bulk polycrystalline YFe_2, the RRR is ~30 [8]. By way of contrast the RRR of MBE-grown $REFe_2$ films and super-lattices is found to be much lower. An example, can be seen in Fig. 1

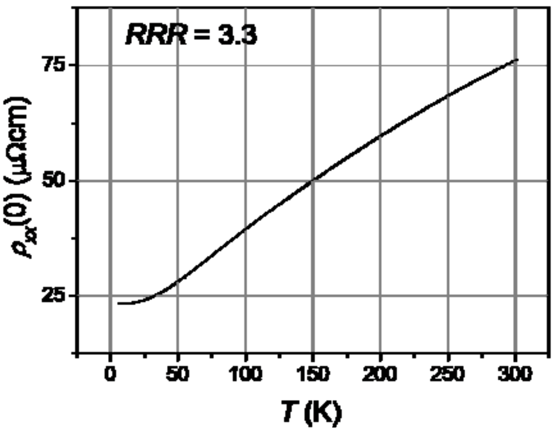

Fig. 1 The resistivity of an $[ErFe_2(50A)/YFe_2(150A)]\times23$ multilayer film. The patterned template was physically machined using a computer controlled mill with a 0.2 mm mill-bit.

At first sight, this low RRR is difficult to believe, given that the films are single crystal in nature with a mosaic spread of just 0.9°, and little in the way of interlayer diffusion [4]. But in Ref. [9] the stated achievable stoichiometry is about 5%. A figure of 1-2% is given by Wang *et al*. [4]. The exact figure is determined by the known accuracy of the deposition rates of the elements in question. Moreover, it is known that YFe_2 can retain its cubic $MgCu_2$-type structure despite small ~1% off-stoichiometry [10]. We believe therefore that the low RRR ratio of the MBE-grown $REFe_2$ films is due to defects, introduced during crystal growth. Such defects will have significant implications for both ^{89}Y NMR and transport studies. In section 3, we take a closer look at the effect of strain, interfaces, and defects at the Y-sites.

3. Strain-induced changes in hyperfine fields

Following [11], the internal magnetic field at a given Y(RE)-site, generated by the dipolar moments $\boldsymbol{\mu}_{Fe}$ *and* $\boldsymbol{\mu}_{RE}$ can be written:

$$\mathbf{B_d}(RE) = \mathbf{B^{Fe}_{loc}}(RE) + \mathbf{B^{RE}_{loc}}(RE) - \tfrac{1}{3}\mu_0 M_{REFe2}\hat{\mathbf{n}} + D\mu_0 M_{REFe2}\hat{\mathbf{n}}.\hat{\mathbf{k}} \qquad (1)$$

Here (i) $\hat{\mathbf{n}}$ is the direction of the net magnetic moment, (ii) the third term is the Lorentz field, and (iii) the fourth term is the demagnetizing term associated with the thin-film. The first term, the local dipolar field arising from the Fe moments, takes the form:

$$\mathbf{B}^{\mathbf{Fe}}_{\mathbf{loc}}(\mathrm{RE}) = \left(\sum_i \sum_j \sum_k \frac{\mu_0 \mu_B}{4\pi\, r^2_{ijk}} \begin{pmatrix} 3x^2_{ijk} - r^2_{ijk} & 3x_{ijk}y_{ijk} & 3x_{ijk}z_{ijk} \\ 3x_{ijk}y_{ijk} & 3y^2_{ijk} - r^2_{ijk} & 3y_{ijk}z_{ijk} \\ 3x_{ijk}z_{ijk} & 3y_{ijk}z_{ijk} & 3x^2_{ijk} - r^2_{ijk} \end{pmatrix} \right) \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix}_{\mathrm{Fe}} = \mathbf{D}_{\mathrm{Fe}} \cdot \boldsymbol{\mu}_{\mathrm{Fe}} \qquad (2)$$

A similar expression exists for the contributions from the RE sites. In both cases, the summation is taken over a Lorentz sphere, large enough to ensure convergence.

In cubic YFe_2, the local dipolar field contributions mutually cancel each other out. However, if the YFe_2 lattice is strained, the Y sites are no-longer at cubic sites. In the presence of strain, the Lorentz and demagnetization terms will be unaffected provided (i) the distortion conserves volume and (ii) the direction of magnetization stays the same. However, the local fields $\mathbf{B}_{\mathbf{loc}}(RE) = \mathbf{D}_{Fe} \cdot \boldsymbol{\mu}_{Fe} + \mathbf{D}_{RE} \cdot \boldsymbol{\mu}_{RE}$ will change. In MBE-grown films the principal magnetostriction term is the shear term $\varepsilon_{xy} = -0.55\%$ [2]. We find:

$$\mathbf{D}_{Fe} = 10^{-4} \begin{pmatrix} 0 & -1.47 & 0 \\ -1.47 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \; ; \; \mathbf{D}_{RE} = 10^{-3} \begin{pmatrix} 0 & 1.44 & 0 \\ 1.44 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \mathrm{T}/\mu_{\mathrm{B}} \qquad (3)$$

There are additional non-zero diagonal elements (not shown). But they are an order of magnitude smaller than off-diagonal terms. So, for clarity, we have set the diagonal terms equal to zero. On the assumption that (i) the magnetisation in YFe_2 lattice lies along a [111] axis, and (ii) the Fe and Y moments are $\mu_{\mathrm{Fe}} = 1.5$, and $\mu_{\mathrm{Y}} = -0.4\,\mu_{\mathrm{B}}$, respectively, the dipolar field contribution at the Y site is given by $\mathbf{B}_{\mathbf{loc}}(Y) = 4.6 \times 10^{-4} (\mathbf{i} + \mathbf{j})$ T. Given that the hyperfine field at the Y site is 22 T, we may conclude from the NMR point of view that the strain-induced dipolar field shift is negligible.

4. Changes in local dipolar fields at the interface between a $DyFe_2$ and YFe_2 film

It is easy to modify the above treatment to calculate local dipolar field contributions at the interface between two differing $REFe_2$ layers. For simplicity, we shall consider a simple bi-layer. In place of Eq. (1), for the local dipolar fields we write:

$$\mathbf{B}_{\mathbf{loc}}(RE) = \left(\mathbf{D}^T_{Fe} + \mathbf{D}^B_{Fe}\right) \cdot \boldsymbol{\mu}_{Fe} + \left(\mathbf{D}^T_{RE} + \mathbf{D}^B_{RE}\right) \cdot \boldsymbol{\mu}_{RE} \qquad (4)$$

Here $\mathbf{D}^{\mathrm{T}}_{\mathrm{Fe}} (\mathbf{D}^{\mathrm{B}}_{\mathrm{Fe}})$ are the contributions from the top (bottom) of the Lorentz sphere. We find:

$$\mathbf{D}^T_{Fe} = 10^{-1} \begin{pmatrix} 0 & -1.081 & 0 \\ -1.081 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \; ; \; \mathbf{D}^B_{Fe} = 10^{-1} \begin{pmatrix} 0 & 1.079 & 0 \\ 1.079 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \mathrm{T}/\mu_{\mathrm{B}}$$
$$\mathbf{D}^T_{RE} = 10^{-2} \begin{pmatrix} 0 & 4.918 & 0 \\ 4.918 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \; ; \; \mathbf{D}^B_{RE} = 10^{-2} \begin{pmatrix} 0 & -4.774 & 0 \\ -4.774 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \mathrm{T}/\mu_{\mathrm{B}} \qquad (5)$$

Note that the dipolar field contributions from the two halves of the Lorentz sphere, taken separately, are two orders of magnitude larger than those of the full sphere. On setting $\mu_{\mathrm{Dy}} = 10\,\mu_{\mathrm{B}}$, we find $\mathbf{B}_{\mathbf{loc}}(Y)_{Fe} = -0.28(\mathbf{i} + \mathbf{j})\,(\mathrm{T})$. It is therefore clear that dipolar fields, either at or near interfaces, have the potential to shift and broaden the ^{89}Y NMR line-width, considerably. However, such Y sites will not contribute much to the NMR signal, because their NMR enhancement factors η will be small [1]. Consequently, we are obliged to seek an explanation involving YFe_2 layers taken in isolation.

5. Changes in NMR-line width due to defects

The precise form of the defects in MBE-grown $REFe_2$ films is unknown. They will depend on whether the film is RE-rich or Fe-rich. It is known that in the RE_2Fe_{17} compounds, one RE-earth is replaced by two Fe-atoms (dumbbell-sites) in the substituted $TmFe_5$ motifs [13]. However, for present purposes, we shall assume that there is an overall Fe-deficiency, and calculate the effect of removing Fe atoms. For the three Fe-atoms in a tetrahedral network closest to the Y site (0,0,0), the dipolar field matrices for the three individual Fe atoms take the form:

$$\mathbf{D}_{Fe}\left(\tfrac{1}{8},\tfrac{1}{8},\tfrac{3}{8}\right)=10^{-2}\begin{pmatrix} -2.408 & 0.903 & 2.709 \\ 0.903 & -2.408 & 2.709 \\ 2.709 & 2.709 & 4.816 \end{pmatrix} \quad \mathrm{T}/\mu_{\mathrm{B}} \tag{6}$$

with similar matrices for $\mathbf{D}_{Fe}\left(\tfrac{1}{8},\tfrac{3}{8},\tfrac{1}{8}\right)$ and $\mathbf{D}_{Fe}\left(\tfrac{3}{8},\tfrac{1}{8},\tfrac{1}{8}\right)$. In practice, these dipolar contributions should be subtracted from that of the Lorentz sphere. However, it is sufficient to examine the individual contributions themselves, given that their absence will give rise to NMR broadening. From an examination of Eq. (7), the dipolar-field gain/loss at a given Y site amounts to 5×10^{-2} (T). This is equivalent to ~0.1 MHz, at the resonance frequency of 45.85 MHz. Thus the extra line broadening witnessed in MBE-grown YFe_2 can be attributed to Fe vacancies. Clearly, it would be useful to grow a series of Fe deficient/rich YFe_2 films with a view to correlating this information with both RRR and NMR measurements.

References

[1] Bowden G J, Riedi P C, Tomka G J, Ward R C C and Wells M R 2001 *Hyp. Interact.* **136/137** 433-437
[2] Mougin A, Dufour C, Dumesnil K and Mangin Ph 2000 *Phys. Rev. B* **62** 9517-9531
[3] Bentall M J, Ward R C C, Grier E J, and Wells M R, 2003 *J. Phys.: Condens. Matt. Phys.* **15** 6493
[4] Wang C, Kohn A, Wang S G and Ward R C C 2011 *J. Phys.: Condens. Matter* **23** 116001
[5] Gordeev S N, Beaujour J-M L, Bowden G J, Rainford B D, de Groot P A J, Ward R C C, Wells M R and Jansen A G M 2001 *Phys. Rev. Lett.* **87** 186808
[6] Martin K N, Morrison C, Bowden G J and de Groot P A J 2008 *Phys. Rev. B* **78** 172401
[7] Fujii T and Morimoto I 1969 *Jpn. J. Appl. Phys.* **8** 1154-1158
[8] Gratz E, Bauer E, Pöllinger S, Nowotny H, Burkov A T and Verdernikov M V 1988 *J. de Physique Colloques* **49** C8-511
[9] Oderno V, Dufiur C, Dumesnil K, Mangin Ph and Marshall G 1996 *J. Cryst. Growth* **165** 175
[10] Okamoto H 2000 *Phase Diagrams for Binary Alloys* (ASM International) p 454
[11] Bowden G J, Bunbury D St P, Guimaraes A P and Snyder ? 1968 *J. Phys. C.* (Proc. Phys. Soc.) **1** 1376-1387
[12] Kittel C 1971 *Introduction to Solid State Physics* (New York: Wiley) 4th ed
[13] Gubbens P C M and Buschow K H J 1974 *Proceedings of the International Conference on Magnetism (Nauka, Moscow 1973)* Vol V p 60