The magnetic moment at the yttrium site in Y-Fe compounds: pressure dependence of the magnetisation and hyperfine field

The magnetic moment at the yttrium site in Y–Fe compounds: pressure dependence of the magnetisation and hyperfine field

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Abstract. The pressure dependence of the magnetisation of Y_2Fe_{17}, Y_6Fe_{23} and YFe_2 at 4.2 K has been deduced from forced volume magnetostriction measurements in fields up to 12 T. The pressure dependence of the ^{89}Y hyperfine field in the above compounds and YFe_3 has been measured using NMR. The results are consistent with a model in which a moment of $\simeq -0.4\,\mu_B$ exists at the Y site of all four compounds as found in computer calculations for YFe_2.

1. Introduction

The Y–Fe compounds (Y_2Fe_{17}, Y_6Fe_{23}, YFe_3, YFe_2) have always been considered to be the simplest members of the large class of compounds of the type R_mFe_n, where R is a rare earth and m and n integers, because it was assumed that the magnetic moment at the Y site (μ_Y) was zero. First-principles computer calculations (Mohn and Schwarz 1985) and measurements of the pressure dependence of the magnetisation per unit mass (σ) and hyperfine field (HFF) at the Y site (H_Y) of YFe_2, however, showed conclusively that $\mu_Y \simeq -0.4\,\mu_B$, i.e. antiparallel to $\mu_{Fe} = 1.66\,\mu_B$ (Armitage *et al* 1986, Dumelow *et al* 1986).

In the present paper we present values for $\partial \ln H_Y/\partial P$, the pressure derivative of the Y HFF, and forced magnetostriction data, from which $\partial \ln \sigma/\partial P$ may be deduced, for the Y–Fe compounds and show that all the results are consistent with $\mu_Y \simeq -0.4\,\mu_B$. It is not therefore correct to assume that μ_Y is zero in the analysis of the magnetisation of compounds of the type $R_{m-c}Y_cFe_n$ as has commonly been the practice in the past (see for example the review article by Buschow 1977).

Similarly the earlier treatment of the Y HFF as arising purely from conduction electron polarisation (Oppelt and Buschow 1973, Riedi and Webber 1983, Riedi *et al* 1985) has already been shown to be incorrect for YFe_2 (Dumelow *et al* 1986) because the localised μ_Y makes a positive contribution to the HFF via core polarisation (H_c) which partially cancels the negative term induced by the iron moments. H_c will now be shown to make a similar contribution to H_Y in the other Y–Fe compounds.

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2. Crystal structures

The compounds YFe_2 and Y_6Fe_{23} are cubic while YFe_3 is rhombohedral and Y_2Fe_{17} either hexagonal or rhombohedral. A review is given by Buschow (1977). There is only one Y site in YFe_2, Y_6Fe_{23} and rhombohedral Y_2Fe_{17} but two sites in YFe_3 and hexagonal Y_2Fe_{17}. There are two inequivalent Fe sites in YFe_2, three in YFe_3 and four in Y_6Fe_{23} and Y_2Fe_{17}. The various Fe sites have different magnetic moments leading to a broad distribution of HFF so ^{57}Fe NMR has only been reported in YFe_2 although Mössbauer spectra have been analysed for all compounds (Gubbens *et al* 1974).

3. Magnetisation

The average moment per iron atom in the Y–Fe compounds, deduced from bulk magnetisation measurements by assuming that the Y moment is zero, is shown in table 1. The increase in the average Fe moment if it is assumed that the Y site carries a moment of -0.4 μ_B in all of the compounds is also shown. The computational evidence for such a moment, and the only neutron scattering data available, will now be reviewed for each of the Y–Fe compounds.

The earliest calculation for YFe_2 (Cyrot and Lavagna 1979) assumed that the Y moment was zero and used the tight-binding approximation (TBA) and the Stoner model to calculate $\mu_{Fe} = 1.48$ μ_B. Yamada *et al* (1984) also used the TBA but, allowing both species to carry a moment, found $\mu_Y = -0.29$ μ_B and $\mu_{Fe} = 1.58$ μ_B. Mohn and Schwarz (1985) made a first-principles calculation using the local-spin-density (LSD) method from which they deduced the lattice constant and bulk modulus and showed that the ground state was magnetic with $\mu_Y = -0.45$ μ_B and $\mu_{Fe} = 1.66$ μ_B giving a net moment of 2.87 μ_B per formula unit in agreement with the experimental value of 2.90 μ_B.

The calculation for YFe_2 by Mohn and Schwarz (1985) remains the only true first-principles calculation for the Y–Fe compounds but Malozemoff *et al* (1983) applied the LSD method to YFe_3 on a Cu_3Au cubic lattice rather than the actual rhombohedral structure. The calculated moment per formula unit was 1.65 μ_B, in rather poor agreement with the experimental value of 1.2 μ_B, but again showed a Y moment of $\mu_Y = -0.23$ μ_B with $\mu_{Fe} = 2.27$ μ_B. Inoue and Shimizu (1985) calculated values for each Fe site in YFe_3 using the TBA and obtained iron moments in the range $(1.59–1.67)\mu_B$ assuming that $\mu_Y = 0$.

With the same assumption Inoue and Shimizu (1985) calculated that μ_{Fe} was in the range $(1.68–2.19)\mu_B$ for the four Fe sites in Y_6Fe_{23} in good agreement with the neutron scattering data of Hardman *et al* (1981). However, the neutron scattering data also gave μ_Y approximately equal to -0.4 μ_B.

Inoue and Shimizu (1985) found Fe moments in the range $(1.55–2.31)\mu_B$ for Y_2Fe_{17} while Szpunar *et al* (1987) found rather larger moments $((2.09–2.45)\mu_B)$ from a TBA calculation not involving μ_Y. However, a similar calculation for Y_2Co_{17} (Szpunar 1985) showed the two Y sites in the hexagonal phase to have values of μ_Y of -0.22 μ_B and -0.17 μ_B.

In summary then, all calculations for Y–Fe compounds that have not arbitrarily set $\mu_Y = 0$ give $\mu_Y \simeq -0.4$ μ_B, a conclusion that is also supported by the neutron scattering data on Y_6F_{23} (Hardman *et al* 1981). Furthermore the moment of dilute Y in Fe was found to be $\simeq -0.2$ μ_B in a first-principles calculation by Akai *et al* (1985) so it appears that μ_Y is never equal to zero in an iron host. We therefore propose to model the Y–Fe

Table 1. The magnetisation per unit volume and forced magnetostriction of Y–Fe compounds at 4.2 K. The calculated value of the average Fe moment assuming that the Y moment is (*a*) zero or (*b*) $-0.4\,\mu_B$ is also shown.

| | $\mu_0 I\,(\mathrm{T\,m^{-3}})$ | $\mu_{Fe}\,(\mu_B)$ | | $\partial \ln V/\partial B\,(10^{-6}\,\mathrm{T^{-1}})$ |
		(*a*)	(*b*)	
Y_2Fe_{17}	1.29	1.935	1.98	43 ± 4
Y_6Fe_{23}	1.14	1.87	1.97	16.7 ± 0.8
YFe_2	0.677	1.45	1.65	4.48 ± 0.22

Table 2. The value of the ^{89}Y hyperfine frequency ν_Y and hyperfine field (H_Y) and their pressure dependence and the pressure dependence of the magnetisation per unit mass, calculated from table 1, for Y–Fe compounds. The computed value of $\partial \ln H_Y/\partial P$ for YFe_2 and that derived for the other compounds using equation (5) is also indicated.

| | | ν_Y (MHz) | H_Y (kG) | $\partial \ln \sigma_0/\partial P$ $(10^{-4}\,\mathrm{kbar^{-1}})$ | $(\partial \ln H_Y/\partial P)\,(10^{-4}\,\mathrm{kbar^{-1}})$ | |
					Experiment	Calculated
Y_2Fe_{17}		42.60†	−204§	—	-17.4 ± 1.0§	—
		42.59‡	−204	−41.6	-13.8 ± 0.2	−26
Y_6Fe_{23}		39.05	−187	−18.5	-11.6 ± 0.6	−2.2
YFe_3	I	38.665	−185		2.1 ± 0.3	2.4
				−14‖		
	II	48.150	−231		1.5 ± 0.3	0.8
YFe_2		45.945	−220	−8.4	6.7 ± 0.3	6.63¶

† First sample: rhombohedral and hexagonal phases.
‡ Second sample: rhombohedral phase.
§ Main line.
‖ Interpolated from measurements on Y_6Fe_{23} and YFe_2.
¶ Dumelow *et al* (1986).

series with $\mu_Y \simeq -0.4\,\mu_B$ when we consider the HFF in § 5.2, since calculations of the HFF exist only for YFe_2 (Dumelow *et al* 1986).

4. Experimental details

4.1. Forced volume magnetostriction

The pressure dependence of the magnetisation per unit mass (σ) of a ferromagnet may be calculated from the forced magnetostriction using the thermodynamic relation

$$\partial \ln \sigma/\partial P = (-40\pi/\mu_0 I)\partial \ln V/\partial B \tag{1}$$

where P is in kbar and $\mu_0 I$ the magnetisation per unit volume (note that $\partial \ln I/\partial P = \partial \ln \sigma/\partial P + \kappa_T$ where κ_T is the isothermal compressibility).

The change of volume ΔV of a polycrystalline sample may be found from measurements of the length l parallel and perpendicular to the field,

$$\Delta V/V = 2(\Delta l_\perp /l) + \Delta l_\parallel /l$$

provided the crystallites of the material are randomised. This does not seem to be a problem with cubic materials (YFe_2, Y_6Fe_{23}) but it is a source of uncertainty in the result for Y_2Fe_{17}.

Polycrystalline discs of diameter 5 mm and thickness 1 mm were spark machined from ingots of YFe_2 and Y_6Fe_{23}. The ingot of Y_2Fe_{17} was smaller and the disc had dimensions 3×0.8 mm^2. The magnetic field was applied in the plane of the disc and the change in length parallel and perpendicular to the field measured using a capacitance cell and a transformer ratio bridge. All experiments were made at 4.2 K in fields up to 12 T. The change in length of YFe_2 and Y_6Fe_{23} was linear in the field between 2 T and 12 T and showed no hysteresis. The Y_2Fe_{17} sample, however, showed some hysteresis even at 12 T due to its higher magnetocrystalline anisotropy—the value of $\partial \ln V/\partial B$ therefore has a larger error than for the other two compounds. The values of $\partial \ln V/\partial B$, from measurements in the range 2–12 T, are shown in table 1 and derived values of $\partial \ln \sigma/\partial P$ in table 2.

4.2. Hyperfine fields

The ^{89}Y NMR spectra of the Y–Fe compounds were measured at 4.2 K using an automated spin-echo spectrometer (Dumelow and Riedi 1987a). The ^{57}Fe NMR has already been reported for YFe_2 (Dumelow *et al* 1986). The high-pressure measurements were made in a Be–Cu cell that was pressurised at room temperature and then locked. The pressure at 4.2 K was measured using a semiconductor transducer provided by Unipress (Warsaw).

The distributions of ^{89}Y HFF are shown in figure 1, the pressure dependence of the HFF in figure 2 and the values of H_Y and $\partial \ln H_Y/\partial P$ in table 2. Two results are shown for Y_2Fe_{17}. The first sample, Y_2Fe_{17} (I), showed a broad distribution of HFF, whose shape changed under pressure (figure 3), and x-ray analysis showed both hexagonal and rhombohedral lines. The second sample, Y_2Fe_{17} (II), was cut from the same ingot as the disc used for the forced magnetostriction measurements.

Other than for YFe_2 the NMR lines in the Y–Fe compounds are asymmetric (see figure 1). The lines are, however, sufficiently sharp for the small shifts of frequency with pressure up to 7 kbar to be resolved. The origin of the asymmetry is presumably related to defect sites or a second phase because it is observed even in the cubic compound Y_6Fe_{23}. In Y_2Fe_{17} (II) a single peak is observed in agreement with the single Y site in the rhombohedral phase. In Y_2 Fe_{17} (I) the partially resolved double peak may arise from the hexagonal phase. The main line in Y_2Fe_{17} (I) has almost the same pressure dependence (table 2) as that of Y_2Fe_{17} (II) but if the broad peak near 44 MHz at atmospheric pressure corresponds to that near 41.5 MHz at 6.8 kbar (figure 3) then for this line $\partial \ln H/\partial P \simeq -8 \times 10^{-3}$ kbar^{-1}, i.e. is some five times greater than the main line. It has been proposed that the large pressure dependence of the Curie point in Y_2Fe_{17} arises because the moments on the Fe atoms in the dumb-bell sites decrease rapidly with decreasing separation so it is quite plausible that the HFF at the two Y sites in hexagonal Y_2Fe_{17} should have quite different values of $\partial \ln H_Y/\partial P$; the value $\simeq -8 \times 10^{-3}$ kbar^{-1} is still a factor of four smaller than the value for $\partial \ln T_c/\partial P$ (Givord *et al* 1971, Riedi *et al* 1985).
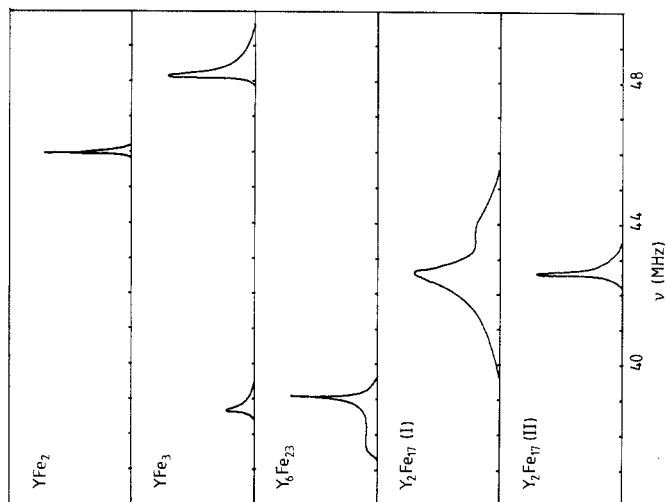
Figure 3. The pressure dependence of the distribution of ^{89}Y hyperfine fields in the Y_2Fe_{17} (I) sample.

Figure 2. The pressure dependence of the ^{89}Y hyperfine field of Y–Fe compounds at 4.2 K. The value for Y_2Fe_{17} is for sample II with the rhombohedral structure.

Figure 1. The normalised distribution of ^{89}Y hyperfine fields in Y–Fe compounds at 4.2 K. The sample Y_2Fe_{17} (I) contained both hexagonal and rhombohedral phases. Y_2Fe_{17} (II) had the rhombohedral structure.
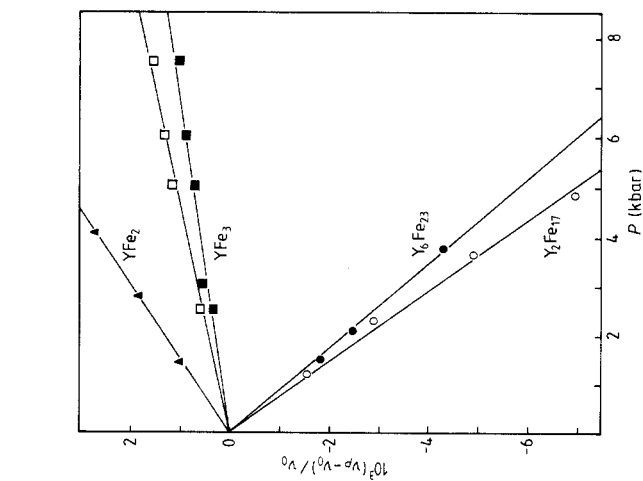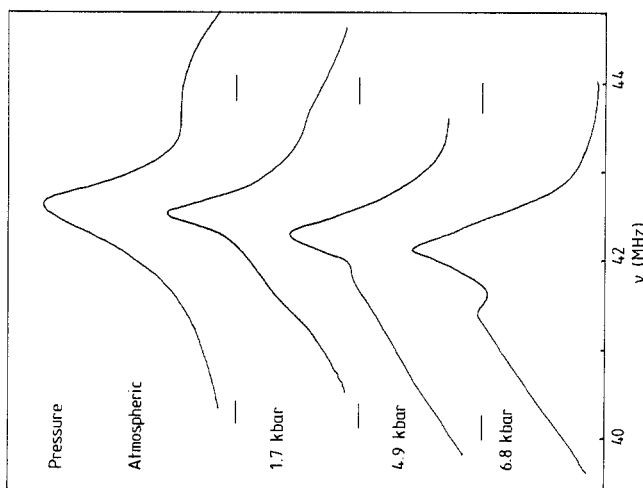
5. Discussion

5.1. Magnetisation

The pressure dependence of the magnetisation per unit mass of YFe_2, Y_6Fe_{23} and Y_2Fe_{17} is shown in table 2. The computed value (Armitage *et al* 1986) of $\partial \ln \sigma/\partial P$ for YFe_2 (-13.2×10^{-4} kbar^{-1}) is in reasonable agreement with the experimental value when it is considered that it represents the small difference between two values of the magnetisation computed from first principles at different volumes. The agreement for $\partial \ln \sigma/\partial P$ is in fact as good for YFe_2 as it is for iron and nickel (Armitage *et al* 1986). According to the computer calculations the magnitudes of both μ_Y and μ_{Fe} decrease under pressure in YFe_2. The contribution of μ_Y is not very important in the evaluation of the magnetisation, because $2\mu_{Fe} \simeq -7 \mu_Y$, but will be seen in § 5.2 to be crucial to the understanding of the Y HFF.

Thge magnetisation of all three compounds is seen in table 2 to decrease under pressure as expected for band ferromagnetism and the magnitude of $\partial \ln \sigma/\partial P$ increases with the Fe content of the compound. The increasing volume sensitivity of the magnetisation of the Y–Fe compounds with Fe content is in agreement with earlier work on the pressure dependence of the Curie point T_c: $\partial \ln T_c/\partial P$ changes from small and positive to large and negative as the Fe content increases (Givord *et al* 1971). The surprisingly low Curie point of Y_2Fe_{17} ($\simeq$311 K) and the large value of $\partial \ln T_c/\partial P$ ($\simeq -3.4 \times 10^{-2}$ kbar^{-1}) have been attributed by Gubbens *et al* (1974) to pairs of Fe atoms that are so close together that their interaction is almost antiferromagnetic. Mohn and Wohlforth (1987), however, used a band model to calculate T_c for all the Y–Fe compounds, yielding values in good agreement with experiment in all cases. It is not clear at present, therefore, if local interactions need to be included for a full understanding of the magnetisation of the Y–Fe compounds.

5.2. Hyperfine fields

The values of the ^{89}Y HFF for the Y–Fe compounds, and the pressure dependence of the HFF, are shown in table 2. It will be seen that there is no simple relationship between the HFF and the mean iron moment of a given compound (table 1). Indeed the value of the Y HFF changes remarkably little from its value (-250 kG) as a dilute impurity in iron (Akai *et al* 1985). The pressure coefficient of the Y HFF, however, is strongly dependent on the composition of the compound. The values of $\partial \ln \sigma/\partial P$ for the Y–Fe compounds are all negative (table 1) and $\partial \ln H_{Fe}/\partial P$ is also negative in YFe_2, the only Y–Fe compound for which a value has been published (Dumelow *et al* 1986). The value of $\partial \ln H_Y/\partial P$, however, is positive for YFe_2 and YFe_3 but decreases with increasing Fe content so that it is negative for Y_6Fe_{23} and Y_2Fe_{17}.

Riedi and Webber (1983) pointed out that if H_Y arises from a Rudermann–Kittel polarisation of the conduction electrons then $\partial \ln H_Y/\partial P \sim \partial \ln \sigma/\partial P$. At that time it was thought, from indirect measurements, that $\partial \ln \sigma/\partial P$ was positive for YFe_2 and zero for Y_2Fe_{17} (Buschow *et al* 1977) so conduction electron polarisation appeared to be a reasonable mechanism for the Y HFF in YFe_2 but not Y_2Fe_{17} (Riedi *et al* 1985). Now that $\partial \ln \sigma/\partial P$ is known to be negative for all the Y–Fe compounds, it is clear that the Rudermann–Kittel interaction cannot be applied to any of these compounds.

The computer calculations of the HFF of YFe_2 (Dumelow *et al* 1986) show that H_{Fe} arises from core polarisation via the contact interaction and that $\partial \ln H_{Fe}/\partial P$ is negative in agreement with experiment. At the Y site there are two important contributions,

$$H_Y = H_c + H_v = A_c \mu_Y + A_v \sigma \tag{2}$$

where H_c is due to core polarisation from μ_Y, H_v is the contribution of valence electrons and A_c and A_v are hyperfine coupling constants. In YFe_2 the values of H_c and H_v are $+60$ and $-280\,kG$ respectively, so H_v is the dominant term in H_Y. Hoewever, using the primed notation H'_Y to represent values of YFe_2, the computer calculations show that

$$\partial H'_Y/\partial P \simeq \partial H'_c/\partial P \qquad \partial H'_v/\partial P \simeq 0. \tag{3}$$

Increasing the pressure lowers the magnitude of both μ_Y and μ_{Fe} in YFe_2. The values of H'_c therefore becomes less positive, but the decrease in σ with pressure is balanced in YFe_2 by the volume dependence of A'_v leaving H'_v unchanged.

It is difficult to perform first-principles calculations of the Y HFF for Y–Fe compounds apart from YFe_2 because of the greater complexity of their unit cells. A simple model will, however, demonstrate that all the results shown in table 2 are in agreement with a moment on the Y site which induces a positive HFF at the nucleus. We assume that μ_Y may be written in the form $f(r)\sigma$ and that $\partial \ln f/\partial P$ and the pressure dependence of the hyperfine coupling constants may be taken as constant across the series, i.e.

$$\partial \ln A_c/\partial P = \partial \ln A'_c/\partial P \qquad \partial \ln A_v/\partial P = \partial \ln A'_v/\partial P \tag{4}$$

Then using equations (2)–(4) an expression for $\partial \ln H_Y/\partial P$, with no adjustable parameters, may be written:

$$\partial \ln H_Y/\partial P = (H_c/H'_c)(H'_Y/H_Y)\,\partial \ln H'_Y/\partial P + \partial \ln \sigma/\partial P - \partial \ln \sigma'/\partial P. \tag{5}$$

The value of H_c has been calculated to be $+60\,kG$ for Y in YFe_2 and $+50\,kG$ as a dilute impurity in Fe (Akai *et al* 1985). It will therefore be assumed that H_c remains constant across the series of Y–Fe compounds.

The values of $\partial \ln H_Y/\partial P$ found from equation (5) are shown in table 2. It will be seen that the equation correctly predicts the trend from positive to negative values for $\partial \ln H_Y/\partial P$ on going from YFe_2 to Y_2Fe_{17} and even gives the pressure dependence at the two sites in YFe_3 correctly. Equation (5) must of course be an oversimplification. For example, no allowance has been made for the variation of the iron moment with lattice site or the fact that $\partial \ln \mu_{Fe}/\partial P$ is expected to depend on the site. Nonetheless the above analysis demonstrates that a model that includes a pressure sensitive contribution to the HFF arising from a moment on the Y site may be applied to all the Y–Fe compounds.

6. Conclusion

Computer calculations for dilute impurities in iron (Akai *et al* 1985) have shown that a magnetic moment exists for many impurities (e.g. Y and Nb) that have traditionally been considered as non-magnetic. Similarly, first-principles calculations for YFe_2 (Mohn and Schwarz 1985) show a moment of $\simeq -0.4\,\mu_B$ at the Y site. Hyperfine-field measurements as a function of pressure have been shown to provide evidence for a moment at the Y site of more complicated iron-based intermetallics for which a full computational treatment is not possible. Very similar results have been obtained for the hyperfine field of Nb in $ZrFe_2$ where a moment of $\simeq -0.7\,\mu_B$ has been estimated to exist at the Nb site

(Dumelow and Riedi 1987b). It is therefore not permissible to consider yttrium to be a simple magnetic dilutant in $R_{m-c}Y_cFe_n$ compounds.

Acknowledgments

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