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1993 J. Phys.: Condens. Matter 5 L637

(http://iopscience.iop.org/0953-8984/5/49/001)

J. Phys.: Condens. Matter 5 (1993) L637–L642. Printed in the UK

LETTER TO THE EDITOR

Spin and orbital magnetic x-ray diffraction in $HoFe_2$

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Received 15 September 1993

Abstract. We report the first direct measurements of spin/orbital magnetization ratios in a ferromagnetic material using x-ray diffraction. The simple technique, based on diffraction of elliptically polarized white synchrotron radiation, produces spin/orbital ratios that are independent of the precise photon polarization. Results from $HoFe_2$ are shown to be generally in very close agreement with relativistic spin-polarized band calculations and known moments, but the measured orbital moment at the iron site is anomalously large.

In recent years there has been a great deal of interest in resonant magnetic x-ray diffraction, where scattered beam intensities close to absorption edges are sensitive to magnetic ordering. At photon energies far from resonance, magnetic scattering is usually much weaker, but becomes directly sensitive to magnetization densities. The resulting data are qualitatively similar to those from magnetic neutron scattering, but have a unique advantage: non-resonant x-ray diffraction is sensitive to the spin and orbital magnetization densities separately.

In antiferromagnets, where the weak magnetic diffraction peaks are separated from the dominant charge scattering, spin and orbital components have been successfully isolated using linear polarization analysis [1]. However, the technique has been limited by the combination of weak scattering and inefficient polarization analysers, and only one serious measurement has been reported to date.

The experimental difficulties with ferromagnetic systems are rather different. Magnetic and charge Bragg peaks are coincident, with the magnetic component accounting for typically no more than a millionth of the total intensity. Fortunately, when the incident photon beam is elliptically polarized, the magnetic and charge scattering amplitudes interfere [2, 3]. This interference not only enhances the magnetic sensitivity, but also changes sign upon reversal of the sample magnetization direction, and thus provides a mechanism for isolating the magnetic diffraction.

Radiation from a synchrotron source is naturally elliptically polarized when viewed from a small angle above or below the plane of the radiating electron beam, which makes synchrotron radiation ideal for magnetic diffraction. At the Daresbury SRS, we have developed a very simple method for measuring magnetic x-ray diffraction in ferromagnetic crystals [4]. The technique involves diffracting a white beam of elliptical synchrotron radiation from a magnetized sample, through 90° into an x-ray detector. Magnetic diffraction is then isolated by periodically reversing the sample magnetization direction, and recording the fraction change in diffracted intensity. The merits of this approach are discussed elsewhere [5].

0953-8984/93/490637+06$07.50

In this letter, we report on white beam magnetic x-ray diffraction measurements on $HoFe_2$, and the first direct determination of spin and orbital magnetization densities in a ferromagnet.

The fractional change in diffraction intensity upon reversal of the sample magnetization direction has the following simple form, for the special case of 90° scattering:

$$R(\alpha) = \frac{I_\uparrow - I_\downarrow}{I_\uparrow + I_\downarrow} = g f_p \frac{2S(\boldsymbol{k})\sin\alpha + L(\boldsymbol{k})(\sin\alpha + \cos\alpha)}{n(\boldsymbol{k})} \tag{1}$$

where $g = \hbar\omega/m_e c^2$, $f_p = P_c/(1 - P_l)$, P_c and P_l are the Stokes parameters for circular polarization and linear polarization in the plane of scattering, and α is the angle between the incident beam and the sample magnetization. Fourier components of the charge density are written as $n(\boldsymbol{k})$, and those of projections of the spin and orbital angular momentum densities along the magnetization direction are given by $S(\boldsymbol{k})$ and $L(\boldsymbol{k})$.

The asymmetry ratios are very sensitive to g and f_p (the energy and polarization factors) and ideally these would both be large. For a fixed scattering angle, however, the energy of a given crystal reflection is determined by Bragg's law, and cannot be altered. The polarization factor can be varied by changing the vertical viewing angle, and much effort has gone into determining the viewing angle that produces the largest polarization factor [4].

By choosing appropriate magnetization angles α, the sensitivity of the asymmetry ratio (equation (1)) to the spin or orbital density can be maximized or eliminated. Moreover, a pair of measurements, taken with different magnetization angles can be combined to obtain $S(\boldsymbol{k})$ and $L(\boldsymbol{k})$ separately. Two particularly useful geometries are those with the magnetization parallel to the incident beam ($\alpha = 0$) and to the scattered beam ($\alpha = 90°$), which produce asymmetry ratios of

$$R(0) = g f_p L(\boldsymbol{k})/n(\boldsymbol{k}) \tag{2}$$

$$R(90°) = g f_p (2S(\boldsymbol{k}) + L(\boldsymbol{k}))/n(\boldsymbol{k}) = g f_p \mu(\boldsymbol{k})/n(\boldsymbol{k}). \tag{3}$$

One can therefore obtain either the total magnetization density $\mu(\boldsymbol{k})$, or just the orbital density $L(\boldsymbol{k})$, from a measurement of one of these asymmetry ratios, as long as g, f_p and $n(\boldsymbol{k})$ are known. The *ratio* of spin to orbital components, however, can be obtained from the two asymmetry ratios alone, by writing

$$S(\boldsymbol{k})/L(\boldsymbol{k}) = \tfrac{1}{2}\left(R(90°)/R(0) - 1\right). \tag{4}$$

This is an important result, as it provides spin/orbital ratios that are completely insensitive to uncertainties in the beam polarization.

Magnetic x-ray diffraction measurements have been performed at room temperature on a crystal of the cubic Laves phase compound $HoFe_2$, grown by the Czochralski method [6]. The sample, a 2.5 mm cube, was magnetized by a small electromagnet which produced a field strength of just over one tesla. The crystal was cut and mounted with four vertical {110} faces and two horizontal {100} faces. This enabled the sample to be magnetized along two perpendicular ⟨100⟩ easy directions, which were arranged to lie along the directions of the incident and diffracted beams, as illustrated in figure 1. The scattering vector was therefore along a ⟨110⟩ direction, and this geometry provided access to the series of *hh*0 Bragg reflections. A small hole was drilled through the centre of one of the magnet poles for the x-ray beam.

The illuminated area of the crystal varied from measurement to measurement, but was always a fraction of a square millimetre. The area was adjusted to keep the total diffracted count rate to around 3×10^4 counts s^{-1}. By using a very short (0.1 μs) spectroscopy amplifier shaping time, and a fast ADC, dead-time was kept to a negligible level.

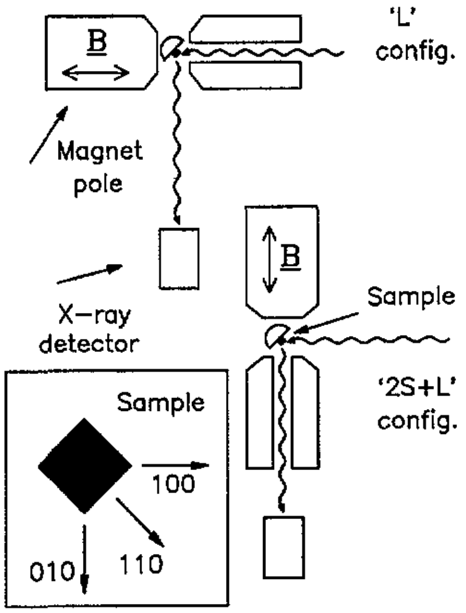

Figure 1. A schematic layout of the two magnet configurations employed in this work. The top diagram shows the sample magnetized along the incident beam direction, where the magnetic scattering is only sensitive to orbital polarization. The second orientation has the magnet rotated through 90° to provide data that are sensitive to the *total* magnetization. The orientation of the cubic crystal is illustrated in the inset.

Measurements of the total magnetization density Fourier components $\mu(\boldsymbol{k})$ were performed with the diffracted beam passing through the hole in the magnet pole (the '$2S+L$' configuration in figure 1). By rotating the magnet through 90° (without moving the sample) to the 'L' configuration, the orbital magnetization was probed.

For each magnet configuration, the intensity asymmetry ratios were measured for at least an hour with a two-second asynchronous field-reversal cycle. The radiation viewing angle was repeatedly checked for movements by re-measuring the central beam position. Data taken above and below the nominal beam height (with opposite photon helicity) were then averaged to eliminate any residual systematic errors. In fact, the asymmetry ratios with opposite helicity were all found to be in good agreement.

These measurements were performed on two beamlines at the SRS: a bending magnet line (station 7.6) which provided the low energies necessary for low-order Bragg reflections, and a high-energy wiggler beamline (station 9.4) for the high-order peaks. Data collection time on the latter was restricted to a few hours, because of the very high demand for the station. The measured asymmetry ratios are shown in table 1.

Armed with the relevant structure factors, it is possible to derive spin and orbital magnetic moments from the x-ray diffraction data. The structure factors for $hh0$ reflections in $HoFe_2$ are of the form

$$\begin{array}{ll} h \neq 2n & S(\boldsymbol{k}) = 0 \\ h = 4n & S(\boldsymbol{k}) = S_{\mathrm{Ho}} f^S_{\mathrm{Ho}}(k) + 2S_{\mathrm{Fe}} f^S_{\mathrm{Fe}}(k) \\ h \neq 4n & S(\boldsymbol{k}) = S_{\mathrm{Ho}} f^S_{\mathrm{Ho}}(k) \end{array} \qquad (5)$$

where S and $f^S(k)$ are the net spin, and the spin form factor. Similar expressions apply to the orbital and charge densities $L(\boldsymbol{k})$ and $n(\boldsymbol{k})$.

Table 1. A list of experimental results and parameters. $R(2S+L)$ and $R(L)$ are the measured asymmetry ratios for the two magnet configurations shown in figure 1. The polarization factors f_p were calculated from the nominal synchrotron beam parameters, and the structure factors $n(k)$ are from reference [9]. Note that the spin/orbital ratios $S(k)/L(k)$ are independent of f_p and $n(k)$.

h, k, l	k ($\mathrm{Å}^{-1}$)	SRS station	Energy (keV)	f_p	R (%) ($2S+L$)	R (%) (L)	$n(k)$	$S(k)$	$L(k)$	$S(k)/L(k)$
4, 4, 0	0.39	7.6	6.8	3.41	0.134 ± 0.006	0.185 ± 0.006	73.8	−0.41 ± 0.07	3.01 ± 0.10	−0.14 ± 0.02
6, 6, 0	0.58	7.6	10.2	3.49	0.382 ± 0.007	0.286 ± 0.007	36.0	0.25 ± 0.03	1.48 ± 0.04	0.17 ± 0.02
8, 8, 0	0.77	7.6	13.6	3.60	0.217 ± 0.008	0.190 ± 0.007	44.9	0.06 ± 0.03	0.89 ± 0.04	0.07 ± 0.03
10, 10, 0	0.97	9.4	17.0	2.77	0.188 ± 0.011	0.187 ± 0.015	23.9	0.00 ± 0.02	0.48 ± 0.04	0.00 ± 0.05
12, 12, 0	1.16	9.4	20.4	2.78	0.103 ± 0.007	0.095 ± 0.009	32.3	0.01 ± 0.02	0.28 ± 0.03	0.04 ± 0.06
14, 14, 0	1.36	9.4	23.8	2.79	0.040 ± 0.013	0.106 ± 0.018	18.0	−0.05 ± 0.02	0.15 ± 0.02	−0.31 ± 0.07
16, 16, 0	1.55	9.4	27.2	2.82	0.026 ± 0.011	0.039 ± 0.015	25.3	−0.01 ± 0.02	0.07 ± 0.02	$-0.17^{+0.17}_{-0.25}$
18, 18, 0	1.74	9.4	30.6	2.85	−0.003 ± 0.026	0.089 ± 0.034	14.8	−0.04 ± 0.02	0.08 ± 0.03	−0.52 ± 0.15
20, 20, 0	1.94	9.4	34.0	2.88	0.040 ± 0.027	−0.032 ± 0.037	20.1	0.04 ± 0.02	−0.03 ± 0.04	

The simplest data to interpret are those with $h \neq 4n$, which are sensitive *only* to the holmium ions. Since the spin to orbital ratio is expected to be very close to the Hund rule value of $S/L = 1/3$, we can write

$$h \neq 4n \qquad S(k)/L(k) = \tfrac{1}{3} f^S_{\mathrm{Ho}}(k)/f^L_{\mathrm{Ho}}(k). \tag{6}$$

In order to interpret the measured spin/orbit ratios, we have performed an electronic band structure calculation for $\mathrm{HoFe_2}$ using the self-consistent, relativistic, spin-polarized muffin-tin orbital method [7, 8]. We then obtained the spin/orbital ratio in the form factor of holmium in $\mathrm{HoFe_2}$ from the calculated spin and orbital magnetization densities.

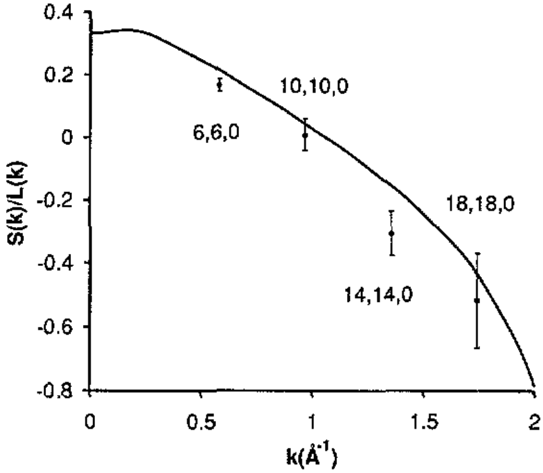

Figure 2. The spin/orbital form factor ratios for holmium in $\mathrm{HoFe_2}$ at room temperature. The solid line represents the results of a relativistic spin-polarized band calculation, which has been normalized to the Hund rule ratio of 1/3 at $k = 0$.

Figure 2 shows the experimental data for the spin to orbital form factor ratio of the holmium ions, along with the band theory results. Agreement is clearly very good, with the experimental data exhibiting the expected sign change (due to the reversal of the spin form factor) at around one reciprocal angström. Despite the larger statistical errors in the high-order reflections arising from the shorter data collection times, these points are still of value because of the rapid increase in the negative slope of spin/orbit ratio toward high momentum transfers.

Reflections with $h = 4n$ are harder to interpret, since $S(k)/L(k)$ depends not only on the spin and orbital composition of the holmium and iron ions, but also the ratio of the holmium to iron moments. We have attempted to fit the spin and orbital moments of holmium and iron to all the experimental asymmetry ratios, using calculated magnetic form factors and polarization factors, along with charge form factors from [9]. The results are

$$\begin{array}{ll}
\mu^S_{\mathrm{Ho}} = 2.00 \pm 0.20\mu_{\mathrm{B}} & \mu_{\mathrm{Ho}} = 5.30 \pm 0.25\mu_{\mathrm{B}} \\
\mu^L_{\mathrm{Ho}} = 3.30 \pm 0.14\mu_{\mathrm{B}} & \mu_{\mathrm{Fe}} = -2.20 \pm 0.33\mu_{\mathrm{B}} \\
\mu^S_{\mathrm{Fe}} = -3.00 \pm 0.26\mu_{\mathrm{B}} & S_{\mathrm{Ho}}/L_{\mathrm{Ho}} = 0.30 \pm 0.03 \\
\mu^L_{\mathrm{Fe}} = 0.80 \pm 0.19\mu_{\mathrm{B}} & L_{\mathrm{Fe}}/S_{\mathrm{Fe}} = -0.53 \pm 0.14.
\end{array}$$

The holmium and iron moments are in quite good agreement with the values $\mu_{\mathrm{Ho}} = 6.3\mu_{\mathrm{B}}$ and $\mu_{\mathrm{Fe}} = -1.85\mu_{\mathrm{B}}$ obtained from polarized neutron diffraction at room temperature [10] (remember that unlike the $h \neq 4n$ spin/orbital ratios, these results are sensitive to errors in the x-ray polarization factor, which we have taken to be ±10%). The measured holmium spin/orbital ratio agrees very well with the Hund rule value. The iron orbit/spin ratio, however, shows a surprising large negative value.

The orbital moment from the relatively delocalized iron 3d band is usually expected to be highly quenched, leading to very small orbit/spin ratios. Iron metal has, for example, $L/S = +0.088$ [11]. The origin of the large negative value obtained for iron in $HoFe_2$ (at room temperature) is not at all clear. The measured total moments, and the holmium spin/orbital ratio, do give some confidence in the validity of the data. Moreover, none of the x-ray results are significantly at variance with neutron diffraction data, which are not directly sensitive to spin/orbital ratios. However, the large negative iron orbit/spin ratio is rather hard to understand, and we cannot rule out the possibility of a small systematic error in these very sensitive measurements.

In summary, we have demonstrated that it is possible to extract spin/orbital ratios, as well as magnetic moments, from magnetic x-ray diffraction using the simple white-beam technique. This method is limited to systems that can be magnetized with conventional electromagnets, providing rapid field-reversal cycles. The particular magnet geometry outlined here is further restricted to cubic crystals with ⟨100⟩ or ⟨110⟩ magnetic easy axes. Despite these limitations, the technique is very straightforward, and has provided some interesting data.

Reversing the sample magnetization is not ideal. It can lead to number of systematic errors, from sample movements to unavoidable magnetostriction effects. Equivalent asymmetry ratios can be obtained by reversing the photon helicity rather than sample magnetization. Future work will concentrate on developing a new technique that will allow polarization flipping by passing the incident synchrotron beam through a dichroic polarizing filter. It is envisaged that this approach, which will be described in detail elsewhere, will provide very high polarization factors, enabling statistical and systematic errors in the data to be vastly reduced.

The authors are indebted to J S Abell, Y J Bi and J Sutton of the School of Metallurgy and Materials, University of Birmingham, for growing the $HoFe_2$ crystal.

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