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1989 J. Phys.: Condens. Matter 1 3655

(http://iopscience.iop.org/0953-8984/1/23/009)

J. Phys.: Condens. Matter 1 (1989) 3655–3662. Printed in the UK

A direct measurement of the surface magnetisation of a ferromagnetic metallic glass

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Received 23 January 1989

Abstract. The first-ever measurements of the surface magnetisation of a metallic glass specimen using neutron reflectivity are presented. These have been made on commercial METGLAS 2605S2 metallic glass ribbon using the CRISP neutron reflectometer on the ISIS Spallation Neutron Source at the SERC Rutherford Appleton Laboratory. The reflectivity data were analysed by fitting a model to the data which has enabled an estimate of the magnetisation profile near to the ribbon surface to be made. Long-range variations (with a length scale $\sim$ 80 Å) at the surface of the ribbon have been observed, in which the apparent magnetic moment value at the surface is approximately half that in the bulk. These results can be interpreted in terms of non-collinear moment arrangements which follow the irregularities at the surface.

1. Introduction

Metallic alloy glasses have been intensively studied for nearly two decades. They show interesting scientific properties as well as having many applications in actual devices. Rapidly quenched alloy ribbons based on the transition metals Fe, Co, Ni have been developed as transformer laminates because of the inherently magnetically 'soft' qualities of these alloys. Nevertheless, this does not mean that details of the ferromagnetic state in metallic glasses are completely understood. The development of metallic glass transducers for example often requires a knowledge of the magnetisation near to the surface because of the large surface-to-volume ratio for a ribbon sample. However, the application of conventional techniques for the measurement of surface magnetisation (magnetic colloids, magneto-optical effects) is difficult with these materials because the domain wall dimensions can sometimes approach the ribbon thickness. The neutron reflectometry technique described here takes advantage of the surface sensitivity of long-wavelength neutrons at grazing angles and the interaction of these neutrons with the magnetic atoms in the material investigated.

2. Neutron reflectometry

Neutron reflectometry is a relatively new technique (see Felcher 1981) which relies on the fact that for a beam of long-wavelength neutrons incident at a grazing angle on

0953-8984/89/233655+08$02.50

a surface, the material below appears as a continuous solid having refractive index n given by:

$$n = 1 - \lambda^2 b/2\pi V. \tag{1}$$

Here, λ is the neutron wavelength , V is the atomic volume and b the nuclear scattering amplitude (Bacon 1975). This refractive index is generally less than unity and leads to total external reflection at the material boundary for neutrons incident at grazing angles less than the critical angle given by

$$\theta_c = \lambda(b/\pi V)^{1/2}. \tag{2}$$

Alternatively, for a fixed angle of incidence, there is a critical wavelength λ_c above which total external reflection occurs (the 'critical edge'). Near to this critical edge the intensity of reflection of neutrons (the 'reflectivity') becomes very sensitive to the neutron scattering vector:

$$k = 4\pi \sin\theta/\lambda. \tag{3}$$

A measurement of the reflectivity as a function of neutron wavelength (and hence k) near to the critical edge produces a curve whose shape is characteristic of the refractive index and hence the nuclear scattering length density b/V through equation (1) close to the specimen surface. This is the basis of neutron reflectometry. This behaviour is directly comparable with the refraction and reflection of optical radiation under similar conditions, which has been thoroughly discussed (see, for example, Heavens 1966) and equations derived for reflectivities and other quantities may be used just as well in the case of neutrons (Penfold 1988).

To extend the technique to polarised neutrons incident on a magnetic material, the magnetic part of the scattering amplitude and the direction of the neutron spin with respect to the magnetisation must be taken into account. Thus for an aligned ferromagnet the refractive index may be written as the sum of terms arising from nuclear and magnetic scattering, n_n and n_m:

$$n_p = n_n + n_m = 1 - (\lambda^2/2\pi V)(b + C\mu(z)) \tag{4}$$

$$n_a = n_n - n_m = 1 - (\lambda^2/2\pi V)(b - C\mu(z)) \tag{5}$$

Here, μ is the magnetic moment per atom which is converted to a magnetic scattering amplitude by the constant $C = 0.2695 \times 10^{-12}$ cm μ_B^{-1} (Bacon 1975). It is clear that the total refractive index presented to the neutrons depends on their initial polarisation with respect to the direction of magnetisation; either parallel as in the case of equation (4) denoted by n_p or antiparallel as in the case of equation (5) denoted by n_a . If it is assumed as a first approximation that the magnetic moment μ is the only parameter that is dependent on the distance z from the surface, then a variation in magnetic moment near to the surface of a material will lead to a corresponding variation in the spin-dependent neutron refractive index and a spin-dependent reflectivity.

3. Experimental method and data analysis

METGLAS 2605S2 alloy ribbon produced by Allied Chemicals Corporation and having the composition $Fe_{78}B_{13}Si_9$ was used as the sample material. The ribbon width was 25

mm and the thickness approximately 40 μm. The as-received ribbon had the normal form with a shiny free or upper side and duller lower side which was in contact with the melt spinning wheel and which showed pitting from entrained gas bubbles. The ribbon was cut to a length of 40 mm and bonded flat onto a glass microscope slide. In order to produce the degree of flatness required for this type of experiment, the ribbon was polished with a series of diamond compounds down to a surface of optical quality. Despite the slight pitting it was found easier to polish the duller lower surface to the required quality because of its better long-range flatness. The lower side was examined in all the neutron measurements. The spin-dependent neutron reflectivities were measured using the CRISP neutron reflectometer (Penfold *et al* 1987, Felici *et al* 1987) on the ISIS Spallation Neutron Source at the SERC Rutherford Appleton Laboratory. The CRISP reflectometer views the 20 K liquid-hydrogen moderator of the ISIS source in order to maximise long-wavelength neutrons. The beam line is inclined at 1.5° to the horizontal and collimation gives typical beam dimensions of 40 mm width and 0.5 to 6 mm height. The incident beam is reflected from a series of frame overlap mirrors to prevent long-wavelength neutron contamination from previous pulses and then polarised by reflection at glancing angles from a cobalt–titanium polarising supermirror. The beam then passes through a spin flipper that enables the direction of polarisation (parallel or antiparallel) to be controlled with respect to the sample magnetisation, and through a guide field to fall on the sample at a glancing angle, in this case, 0.5°. A transverse field of 1.2 kG was applied to the sample perpendicularly to the neutron flight direction. A ^{3}He detector was aligned so as to receive only specularly reflected neutrons. For this experiment, neutron reflectivity was measured for both polarisation states as a function of wavelength λ, determined by time-of-flight methods. Polarisation states were alternated after every 20 000 pulses of ISIS (approximately every five minutes). Results for the METGLAS sample are shown in figure 1. The reflectivity for the parallel case has been normalised to unit reflectivity at the critical edge and the same normalisation factor applied to the antiparallel data. These data have been corrected for instrumental effects and for polarisation and flipper efficiencies. The large difference between the two polarisation states indicates a relatively high magnetisation in the sample.

There are two possible choices for the analysis of the reflectivity data, either an inversion process by which a surface profile may be deduced directly or a model fitting procedure. The first is attractive in those cases where the ordering parameter at the surface can be described by a simple power law, say az^{-p}, since a and p can then be obtained uniquely (see Dietrich and Schack 1987). However, in this analysis it is helpful to have a clear picture of the reflectivity profile close to the critical edge—this region is probably influenced by the instrumental resolution and surface quality of the present samples. We believe therefore it is better to adopt a model fitting procedure in these preliminary studies so the data have therefore been fitted using standard optical programs which have been developed at the Rutherford Appleton Laboratory and which use least-squares fitting (Penfold 1988). Equations (4) and (5) show how the refractive index is related to the total scattering amplitudes (nuclear plus magnetic), $(b + C\mu(z))$ and $(b - C\mu(z))$. The main experimental parameter chosen to be fitted was the total scattering amplitude for each layer. The non-magnetic part, b, of the total scattering amplitude was calculated from individual values for the constituent elements (Bacon 1975) and the known densities and were held constant during the fitting process. The magnetic part, $C\mu(z)$, was allowed to vary to simulate any change in magnetisation near to the surface. The program required the initial model to be a

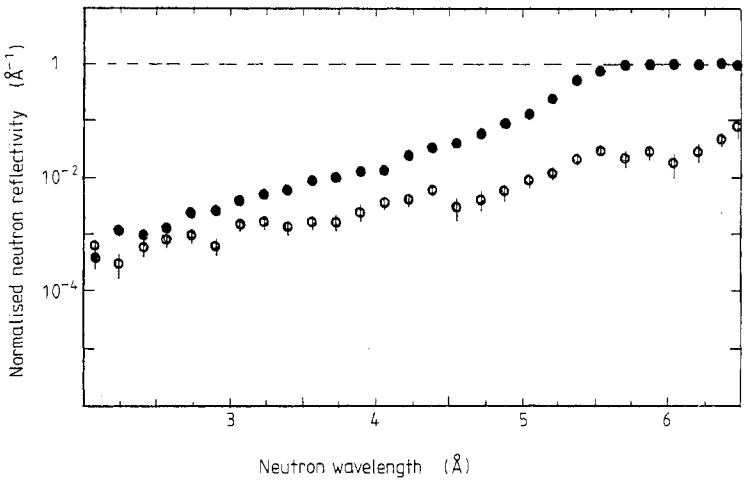

Figure 1. The normalised neutron reflectivity for a sample of METGLAS 2605S2 is plotted on a logarithmic scale as a function of neutron wavelength. Full circles represent spin parallel to the applied field and open circles represent spin antiparallel to the applied field. The error bars relate to the actual neutron counts and for spin-up neutrons they are smaller than the full circles.

fairly good representation of the specimen before a close fit to the experimental data could be produced. Therefore, it was necessary to try a significant number of initial models to decide on the best starting point. Once a promising initial model had been found, the fitting procedure was repeated several times with minor variations in the initial parameters to ensure the best possible fit. From the outset, the data could not be fitted without involving some gradient of magnetic moment at the surface. The final model simulated the region near to the surface with five layers, each of 50 Å thickness. The fitted total scattering amplitude parameters for both polarisation states are shown in table 1. Values of angular resolution and surface roughness were also determined from the fitting procedure. Resolution is dependent both on instrumental parameters and on long-range surface quality (waviness), and was found to be 5% and the RMS surface roughness approximately 15 Å. The quality of the fit suffered noticeably if either of these values were changed significantly. Figure 2 shows the fits (continuous curves) to the experimental points, using the parameters in table 1. The antiparallel reflectivities are approximately an order of magnitude lower than those for the parallel case (logarithmic scale). This brings the accumulated counts closer to the instrumental background level and may account for the poorer quality of fitting in the antiparallel case.

4. Surface magnetism

The only difference in the scattering process between the two polarisation states is the sign of the magnetic part of the total scattering amplitude so the magnetic part of the scattering can be extracted from the values in table 1 without the need for any independent measurement of the nuclear part. Once the magnetic part of the scattering for each layer was obtained from the fitting parameters, it was converted to a magnetic

Table 1. Model parameters produced by fitting the reflectivity from five discrete layers to the experimental data are shown in the form of the scattering length density b/V. The average scattering length per atom $< b >= 8.51 \times 10^{-15}$ m.

Depth from ribbon surface (Å)	$(b + C\mu(z))/V$ (10^{-6} Å^{-2})	$(b - C\mu(z))/V$ (10^{-6} Å^{-2})	Magnetic moment per atom (μ_B) (± 0.1)
0–50	9.92	5.04	1.03
50–100	10.65	4.31	1.34
100–150	11.04	3.92	1.51
150–200	11.26	3.70	1.60
200–250	11.37	3.59	1.65
'Bulk'	11.51	3.45	1.70

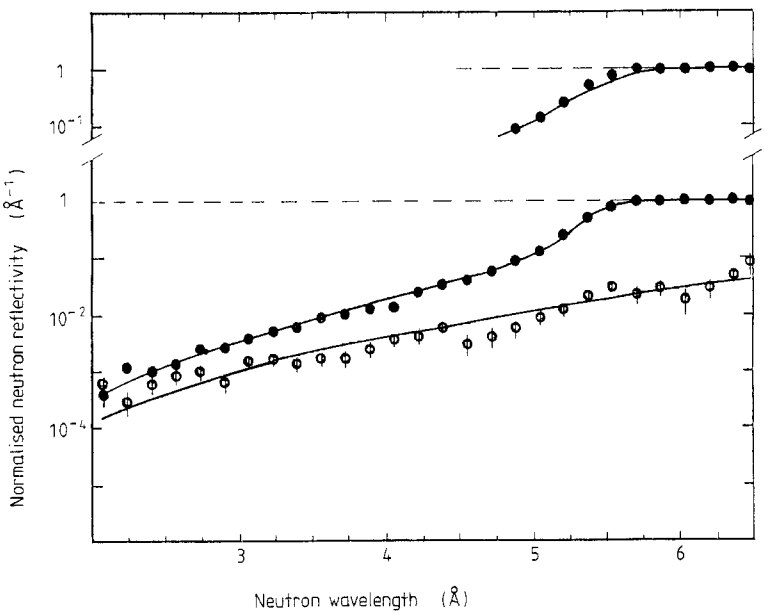

Figure 2. The data points of normalised neutron reflectivity for the METGLAS 2605 sample are fitted with a curve obtained using the model parameters given in table 1. The inset shows the fit near to the critical edge, obtained using a magnetic moment value from bulk magnetisation measurements and a relaxed instrumental resolution.

moment using the constant C in equations (4) and (5) which gives a bulk value of $1.7\mu_B$ per atom. This is slightly larger than may be expected for this type of alloy on the basis of bulk magnetisation measurements (see Mizoguchi 1978, his figure 1 for example). A value of approximately $1.5\mu_B$ per atom may be expected taking into account the composition of the METGLAS sample and its Curie Temperature (Mizoguchi 1978). The fitting process was repeated holding the magnetic moment at this value. In order to achieve a reasonable fit to the data at the critical edge it was necessary to assume a significantly worse experimental resolution. However, the fit achieved which is shown as an inset to figure 2 was not as good as that for the original fitting parameters. In view of this and of the current uncertainty surrounding the expected moment size in metallic glasses (Melamud *et al* 1987, Cowley *et al* 1988) it was decided to retain the

original higher moment value (table 1). This value corresponds to $2.2\mu_B$ per *iron atom* in this $Fe_{78}B_{13}Si_9$ alloy, that is, some 13% larger than expected from bulk magnetisation experiments (Mizoguchi 1978). Figure 3 presents the results as magnetic moment as a function of depth z into the ribbon, which is found to be consistent with an exponential variation of the form

$$\delta\mu(z) = \delta\mu_s \exp(-z/\xi). \tag{6}$$

Here, $\delta\mu(z)$ is the difference between the moment between the moment value at a depth z and that in the bulk, $\delta\mu_s$ is the difference between the moment value in the bulk and at the surface, and ξ is a magnetic coherence length. The values obtained from the smooth curve in figure 3 are $\delta\mu_s = 1.03\mu_B$ and $\xi = 81$ Å, so the apparent moment value reduces from about $1.70\mu_B$ to approximately half that, at the surface. In assessing the accuracy of this magnetisation profile as a whole it is necessary to consider the parameters in the fitting procedure and their possible interdependence. Full investigations of this are in hand. In the present case, there are no adjustable parameters in the fitting of the spin-up and spin-down curves so that the magnetic part of the scattering can be extracted with a high confidence. An estimate of the error in the layer magnetisations can be obtained by altering their values and monitoring the effect on the fittings. It was found that changes of $\pm 0.1\mu_B$ create significantly worse fits to the data and these values are shown as the errors in table 1 and figure 3.

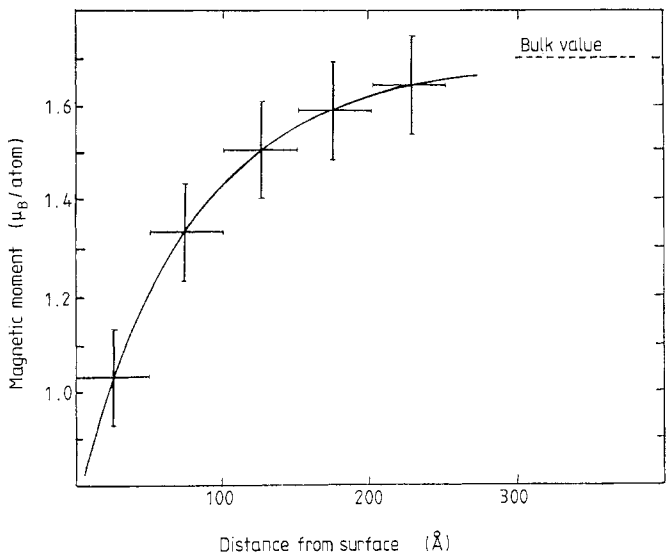

Figure 3. The magnetisation profile derived from the reflectivity measurement for the METGLAS 2605S2 sample is shown.

An exponential variation of moment of the type given in equation (6) has been predicted theoretically (see, for example, Binder and Hohenberg 1974), except that the coherence length is typically of atomic dimensions, $\xi \sim 2$ Å, (Alvarado 1979). However, the present results cannot be consistent with such a value for ξ since, as figure 2 shows, the fitting procedure is sensitive to changes in the parameters used. Two possible explanations of this disagreement can be offered. The first is that the present results illustrate a sensitivity of the surface to chemical and physical effects on a macroscopic

rather than an atomic scale—in the way that Gradman (1977) distinguished between 'size effects' and 'surface effects'. A gross variation of chemical composition near the ribbon surface, for example, is one such macroscopic mechanism. This could be caused by selective diffusion of the alloy constituents either during the melt-spinning process or during subsequent storage of the ribbon before preparation of the specimen. An extreme example of this behaviour is incidentally shown by the Cu–Zr metallic glass system for which the changes in ribbon surfaces are well documented (Gallagher *et al* 1983). In this way the low moment value at the surface of the present sample would correspond to metalloid-rich layers and the (relatively) high value in the bulk with iron-rich material. However, preliminary measurements by EDAX at the Electron Optics Facility at the University of Bath appear to rule out this possibility. A second possibility is the effect of strain at the surface of the ribbon which has resulted from the rapid vitrification of the ribbon specimen; indeed the whole interest in structural relaxation in metalic glasses has developed from the need to remove quenched-in strain. However, both of the above effects are unlikely to account for the variations observed because the preparation and polishing of the samples is certain to have removed surface material on a micrometre rather than an angstrom scale.

An alternative explanation is that the neutron reflectivity technique measures a different quantity from the other experimental techniques. The important feature of magnetic neutron scattering is that it is a vector interaction, in which the component of the magnetic spin resolved perpendicular to the neutron scattering vector determines the magnitude of the scattering cross section (Halpern and Johnson 1939). The geometry of CRISP (Felici *et al* 1987) is such that the magnetic field is applied across the sample so that aligned magnetic moments are normal to the scattering vector in order to maximise the magnetic interaction. Any agency that causes the moment direction to move out of the field direction therefore reduces the resolved component and the apparent moment size in the scattering process.

The present results can be explained qualitatively in terms of a surface having overall optical flatness (say $\lambda/10 \sim 500$ Å) on extended length scales *within the surface plane*, but local variations in surface roughness on a smaller length scale—in this case dimensions of order 15 Åwould be in agreement with values of surface roughness obtained in the data analysis. If the directions of the magnetic moments in the surface then follow these smaller scale variations in surface geometry, the resolved moments will be smaller than the fully aligned moments in the bulk, in agreement with observation. These effects may be expected to reduce as the distance from the surface irregularities increases. Such a model is also consistent with two recent Mössbauer investigations of the magnetic structures of ferromagnetic metallic glass ribbons. Ogale *et al* (1986) have shown using conversion electron Mössbauer spectroscopy that there are significant differences in the hyperfine field distributions between the bottom surface in contact with the melt spinning wheel and the bulk (and also for the top surface) of METGLAS 2605CO samples. Melamud *et al* (1987) have established that significant non-collinear moment strctures exist in METGLAS 2605S2, the material used in the present study. They found angular spreads of moment direction of up to $\pm 50°$ within the plane and $\pm 20°$ out of the plane. By comparison the apparent reduction of moment value from $1.7\mu_B$ to $1.03\mu_B$ given in table 1 corresponds to a misalignment of $\sim 53°$.

5. Conclusion

The new technique of polarised neutron reflectometry has demonstrated that the

variation in the magnetisation near to the surface of a ribbon sample of metallic alloy glass can be measured. The extended length scales of this variation point to it being due to geometrical effects rather than any fundamental effect of surface physics. Nevertheless, the result is important in the context of device applications where the magnetic profile of the surface of commercial ribbons needs to be known. This investigation also provides independent support for recent studies of ferromagnetic metallic glasses which have indicated the presence of non-collinear arrangements of magnetic moments. Work is continuing on the analysis of these and other results, to obtain a more accurate representation of the shape of the magnetisation profile, as well as on glasses based on other transition metals. It is also hoped to develop the technique of data inversion proposed by Dietrich and Schack (1987) initially by measurements on high-quality non-magnetic surfaces.

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