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To cite this version:

HAL Id: jpa-00229693
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Submitted on 1 Jan 1989

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GRAZING-ANGLE NEUTRON DIFFRACTION

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Résumé - Nous décrivons les principes de la diffraction en incidence rasante et y apportons notre propre contribution. En s'affranchissant des collimations non nécessaires, nous pouvons augmenter l'intensité limitée utilisable provenant des sources conventionnelles de neutrons, tout en préservant la sensibilité en profondeur de la méthode de diffusion en incidence rasante. Nous avons étudié un film de 3200 Å de Cr, déposé par épitaxie en jet moléculaire. Nous présentons et discutons les résultats obtenus.

Abstract - We describe the principles of grazing-angle neutron diffraction and our implementation of it. By relaxing non-essential collimations, we can make optimal use of the limited intensity available from conventional neutron sources, yet still preserve the depth-sensitivity of the grazing-angle method. We have studied a 3200Å Cr film, grown by molecular beam epitaxy and discuss the results of this measurement in the context of current experimental conditions and future improvements.

1 - INTRODUCTION

Grazing-angle diffraction is a powerful tool in the study of surfaces and interfaces. The development of synchrotron x-ray sources in the decade since the first demonstration /1/ of grazing-angle diffraction has led to a broad application of the method to problems of surface and interface structure (for a recent review, see /2/). Grazing-angle diffraction methods possess two unique advantages. For one, the interaction of x-rays(neutrons) with matter is weak, so that, unlike electron and atom scattering, the diffracted intensity can be described by a simple structure factor. Secondly, grazing-angle x-ray(neutron) diffraction is the only probe that provides subsurface as well as surface information within the same experimental setting: the depth of penetration of the x-rays(neutrons) into the surface can be controlled by varying the incident glancing angle $\phi$ below the critical angle for total external reflection $\theta_{c}$ /3,4/. It is then possible to probe beyond the first several layers of the surface, yet still have the scattered beam produced in the near-surface region. The low flux of conventional neutron sources relative to synchrotron x-ray fluxes has, until recently, resulted in the neglect of the development of grazing-angle neutron diffraction techniques. We will outline the principles involved and describe our implementation of these ideas and our initial experiments in this field.

There are several fields in which grazing-angle neutron diffraction can provide information which is, at

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(1)Supported by U.S. Department of Energy (Division of Materials Sciences) under grant number DE-AC02-76-ER01198.
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present, unobtainable using other methods. The first and most obvious of these fields is the study of surfaces
and thin films of magnetic materials. The ability of neutrons to probe to varying depths beneath the surface
allows one to study the depth dependence of in-plane magnetic order and to observe “buried” magnetic
layers (e.g. rare earth films with non-magnetic anti-oxidant overlayers). In addition to magnetic studies,
the ability of neutrons to distinguish between hydrogen and deuterium makes possible experiments on films
of hydrogen-rich materials. Chemical substitution of deuterium for hydrogen in a particular section of a
molecule and comparison with unsubstituted data is a well-developed technique in neutron crystallography
and reflectometry and can be readily applied to grazing-angle experiments. The contrast achieved by such
substitutions allows a more precise determination of the crystal structure of hydrogen-rich polymers and
biomaterials (e.g. Langmuir-Blodgett films). In experiments involving magnetic materials, polymers, and
biomaterials, the sensitivity and depth tunability of grazing-angle neutron diffraction can provide unique
information on surface, subsurface, and interface in-plane structure.

2 – NEUTRON REFLECTIVITY

Neutron reflectivity forms the physical basis of grazing-angle diffraction. Neutron reflectometry studies the
layer-averaged nuclear and magnetic scattering density as a function of depth. The refractive index of a
material for thermal neutrons can be written /5,6/:

\[ n^\pm(z) = 1 - \frac{\lambda^2}{2\pi v} \left[ b(z) \pm C \mu(z) \right] - i\beta, \]  

(1)

where \( \lambda \) is the wavelength of the incident neutrons, \( v \) the molecular volume of the material being studied,
\( C = 0.2695 \times 10^{-12} \text{cm/} \mu_B, \mu_B \) the Bohr magneton, and \( \beta = a_0/4\pi \), with \( a_0 \) the length absorption coefficient.
The layer-averaged, depth-dependent quantities measured in a neutron reflectivity experiment are the
scattering amplitude \( b(z) \) and the magnetic moment \( \mu(z) \). Neutrons polarized parallel to the magnetic
moment have refractive index \( n^+ \) and those anti-parallel \( n^- \); for unpolarized neutrons, a ferromagnetic
material is therefore bi-refrangent. If we assume that the quantities \( b \) and \( \mu \) are homogeneous within the
material, we can derive expressions for the critical angle for total external reflection \( \phi_c \) and the reflectivity
\( R \):

\[ \phi_c^\pm \approx \text{Re} \left( \sqrt{2[1 - \text{Re}(n^\pm)]} \right) = \text{Re} \left( \lambda \left[ \frac{1}{\pi v} (b \pm C\mu) \right]^{1/2} \right), \]  

(2)

\[ R^\pm(\phi) \approx \frac{\phi - \sqrt{\phi^2 - (\phi_c^\pm)^2 - 2i\beta^2}}{\phi + \sqrt{\phi^2 - (\phi_c^\pm)^2 - 2i\beta^2}}. \]  

(3)

The quantity \( \phi \) is the angle between the incident neutron beam and the surface of the sample. There are several important differences between neutron and x-ray reflectivity: 1) neutron critical angles are
generally several times smaller than those for x-rays, 2) the interaction of x-rays with sample magnetic
moment is negligible, and 3) the absorption \( \beta \) is typically several orders of magnitude greater for x-rays
than for neutrons. The relevant parameters for cobalt are listed in table 1; figure 1 shows the reflectivities
\( R \) generated with these parameters. The x-ray reflectivity (dotted line) has a larger critical angle and is somewhat more rounded near \( \phi_c \) than the neutron curves because of absorption. The dashed line shows the reflectivity of un-magnetized cobalt (above \( T_C \)); the solid lines are the two possible reflectivities of a fully magnetized sample, (+) when the incident neutrons are polarized parallel to the sample moment,
(−) anti-parallel. As can be seen from figure 1, the reflectivity curve and in particular the ratio \( R^+/R^- \)
is a very sensitive measure of net magnetic moment. Neutron reflectometry has been used to study the magnetization of thin films /7/ as well as the magnetic field penetration depth of superconductors /8/.
The neutron (−) curve exhibits another unique feature of the interaction of neutrons with matter. From
table 1, we observe that the (−) branch of fully-magnetized Co has a negative scattering amplitude, which appears in figure 1 as a curve which has unit reflectivity only at \( \phi = 0 \). For instance, hydrogen has a negative scattering amplitude \( (b_H = -0.374 \times 10^{-4} \text{Å}) \), while chemically identical deuterium possesses a positive one \( (b_D = 0.667 \times 10^{-4} \text{Å}) \). One can therefore selectively alter the scattering density (through \( b(z) \)) of materials containing hydrogen. The isotopic substitution of D for H is a widely-used technique in the study of hydrogen-rich biological and polymer /9/ films and membranes. Grazing-angle diffraction extends the capabilities of reflectometry in these areas to the determination of in-plane structure.
Table 1. - Cobalt reflectivity parameters.

<table>
<thead>
<tr>
<th></th>
<th>$b$</th>
<th>$C_\mu$</th>
<th>$a_\Gamma$</th>
<th>$v$</th>
<th>$\phi_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutron (−)</td>
<td>0.25</td>
<td>−0.47</td>
<td>2.85</td>
<td>11.0</td>
<td>0</td>
</tr>
<tr>
<td>neutron (0)</td>
<td>0.25</td>
<td>0</td>
<td>2.85</td>
<td>11.0</td>
<td>1.38</td>
</tr>
<tr>
<td>neutron (+)</td>
<td>0.25</td>
<td>+0.47</td>
<td>2.85</td>
<td>11.0</td>
<td>2.34</td>
</tr>
<tr>
<td>x-ray (x)</td>
<td>7.6</td>
<td>−</td>
<td>408</td>
<td>11.0</td>
<td>7.80</td>
</tr>
</tbody>
</table>

Figure 1 - Reflectivity of cobalt at $\lambda = 1.62\text{Å}$: (x) x-ray, (+) neutron polarized parallel to sample magnetic moment, (0) neutron from unmagnetized sample, and (−) neutron polarized anti-parallel to sample magnetic moment.

3 - PRINCIPLES OF GRAZING-ANGLE DIFFRACTION

The essence of the grazing-angle method is the excitation of a diffracted beam under conditions of total external reflection. Figure 2 shows the diffraction geometry. A neutron beam ($\vec{k}$) is incident onto the surface of a crystal at glancing angle $\phi \approx \phi_s$ and is specularly reflected ($\vec{k}'$); the sample is oriented such that the in-plane component of $\vec{k}'$ satisfies the diffraction condition with reciprocal lattice vector $\vec{G}$ and produces a grazing-angle diffracted beam ($\vec{k}_G$, $\phi_G$). The theory of grazing-angle diffraction was worked out by Vineyard /3/ and the depth-dependence clarified by Dosch, Batterman, and Wack /4/. The surface-sensitivity of the method arises because, for $\phi, \phi_G < \phi_s$, the momentum transfer normal to the surface $Q_z$ becomes complex and waves cannot propagate into the bulk:

$$Q_z = k_Gz - k_z = \left(\frac{2\pi}{\lambda}\right) \left[\left(\phi^2 - \phi_s^2 - 2i\beta\right)^{1/2} + \left(\phi_G^2 - \phi_s^2 - 2i\beta\right)^{1/2}\right].$$ (4)

The scattering depth $\Lambda$ is defined simply as $|\text{Im}(Q_z)|^{-1}$. In figure 3 we have plotted, for fixed incident angle $\phi$, the scattering depth $\Lambda$ as a function diffracted exit angle $\phi_G$ for Cr with $\lambda = 1.66\text{Å}$. The neutrons have a minimum penetration depth of 82.6Å, which represents the thinnest observable layer and is characteristic of the material being studied (in this case bcc Cr). The scattering depth increases slowly until $\phi_G \approx \phi_s$, at which point it jumps to a value determined by $\phi$—only when both $\phi$ and $\phi_G$ exceed $\phi_s$ does bulk transmission occur. The diffracted intensity is given by:

$$I \propto \delta(Q_x - G_x)\delta(Q_y - G_y)S(Q_z).$$ (5)
The expression consists of delta functions for the in-plane diffraction condition and a $Q_z$-dependent part that describes the intensity distribution normal to the surface,

$$S(Q_z) \approx \frac{(\lambda/a_z)^2}{1 + [(2\lambda/a_z) \sin(\text{Re}(Q_z)a_z/2)]^2},$$

where $a_z$ is the lattice spacing in the $z$-direction (in our case Cr(110) has $a_z = 2.04\,\text{Å}$). Figure 4 shows a family of $S$-curves plotted as a function of $\phi_G$ for fixed incident angle $\phi$. For any given $\phi$, these curves peak at $\phi_G = \phi_c$ as the penetration depth increases and fall off as the reflectivity declines above $\phi_c$; as $\phi$ increases, the peak becomes sharper and higher, more layers are probed, and the scattering becomes more characteristically three dimensional (delta-function in $Q_z$) than the lower angles of incidence, which exhibit a more “rod-like” character due to the thin layer in which the scattering occurs. For $\phi > \phi_c$, the intensity falls off due to the increasingly large $\text{Re}(Q_z)$ that no longer satisfies the in-plane diffraction condition.

Figure 2 - Grazing-angle diffraction geometry.

Figure 3 - Neutron scattering depth in Cr for $\lambda = 1.66\,\text{Å}$. 

$\phi = 0.9\phi_c$

$0.7\phi_c$

$0.5\phi_c$

$0.3\phi_c$

$\phi = 0.1\phi_c$
The primary obstacle to be overcome in the implementation of grazing-angle neutron diffraction is the comparatively low intensity of neutron sources. In our prototype instrument, we have attempted to maximize the intensity while retaining the surface-sensitivity of the grazing-angle technique by relaxing all non-essential collimations. Figure 5 is a schematic representation of our instrument. We have modified a triple-axis diffractometer (instrument BT4) at the Neutron Beam Science Reactor (NBSR) at the National Institute of Standards and Technology (NIST) for use as a grazing-angle diffractometer. A “white” neutron beam passes out of the reactor, through either a Be or graphite filter to remove λ/2 and is Bragg-monochromated (Δλ/λ=0.008) by a highly-oriented pyrolitic graphite crystal, as in a conventional instrument. Cadmium collimating masks with single slits reduce the angular divergence of the incident glancing angle to 0.3 mradian (1 arcmin). This beam passes at glancing incidence onto the surface of the sample, the angle φ being controlled by the diffractometer’s sample table motor; a Huber single-axis goniometer, mounted with its axis vertical to that of the sample table, provides the θ motion for the sample (see figure 2). The sample is oriented and the wavelength selected such that 2θ_B = 90° and the diffracted beam goes straight up into detector #2, which is mounted in a tower atop the sample table. Detector #1, in the conventional double-axis position, records the specularly reflected intensity. The most important feature of this instrument is the collimation scheme. Of the three angles shown in figure 2, only φ is collimated. The diffraction angle θ is collimated solely by the dimensions of the beam tube and φ_C is left wide open. This configuration allows us to achieve the maximum intensity beam that still retains the surface sensitivity of the grazing-angle method, as will be demonstrated in the next section.
Using the instrument described above, we have performed the first grazing-angle neutron diffraction measurements. Measurements of this type were proposed a number of years ago \cite{10, 12, 13}, and in an earlier work \cite{13}, we demonstrated the feasibility of grazing-angle neutron diffraction using a large, perfect silicon crystal, which we treated within the framework of dynamical diffraction theory. We have now extended the method to a model kinematical scatterer: an MBE-grown (by J.A. Dura and C.P. Flynn) 3200Å Cr(110) film atop a 400Å Nb(110) buffer layer on a (1120) sapphire substrate. We have studied the Cr(110) in-plane Bragg reflection from this film—these data are plotted in figure 6. The incident angle $\phi$ is scanned up through the critical angle $\phi_c$ as we record simultaneously the specularly reflected (detector #1, dotted line) and reflected-diffracted (detector #2, solid line and data points) intensities. The specularly reflected beam exhibits the critical angle of the sapphire substrate (2.17 mradians at $\lambda = 1.66\text{Å}$) since this is larger than that of either Cr (1.60 mradians) or Nb (1.76 mradians); the specularly reflected data has been scaled so that both data sets may appear on the same plot—its peak intensity is actually 420 times that of the diffracted beam. The change in background level on the diffracted curve above and below $\phi_c$ is a result of incoherent scattering from the tape used to mount the sample. The reflected-diffracted beam has a peak intensity at $\phi = \phi_{G}^{Cr} = 1.60$ mradians and its shape may be explained by reference to figure 4. Since $\phi_{G}$ is not collimated, each reflected-diffracted data point in figure 6 represents the integrated intensity of the corresponding $\phi_{G}$ intensity curve in figure 4. How depth-sensitive are these “integrated” peaks? Figure 3 shows that the neutron beam remains confined to a depth on the order of 150Å over the whole range of $\phi_{G}$ for small $\phi$ values. So, at the cost of a relatively modest increase in scattering depth, we can, by opening up $\phi_{G}$, greatly increase the available intensity. By executing $\theta$ rocking scans at fixed $\phi < \phi_c$ (our instrument has $\Delta \theta = 1.8^\circ$ fwhm), one can, for example, study antiferromagnetic ordering as a function of temperature for a specified depth beneath the surface. In addition, the collimation scheme outlined above can be used with conventional x-ray tube sources in those applications where high resolution and intensity are not required or used as a characterization step prior to a synchrotron run. We believe that, by performing experiments in the manner described above, one can best utilize the limited intensity available for grazing-angle neutron diffraction at this time.
Figure 6 – Data from measurement of Cr(112) in-plane reflection from Cr(110) surface under grazing-angle conditions: dotted curve is specularly reflected intensity (scaled down by a factor of 420), solid line and data points are reflected-diffracted intensity.

6 – FUTURE DEVELOPMENTS

We have described how grazing-angle neutron diffraction might be carried out, constructed a prototype instrument, and performed the first measurements on it. The application of this technique to studies of magnetic and hydrogen-rich materials promises to enhance our understanding of these systems by providing depth-dependent structural information which can be interpreted in terms of a simple structure factor. We are adding polarization analysis to and reducing the background of the instrument and will study thin-film magnetic systems in the near future. Within the next several years, dedicated instruments at NIST and at the Institut Laue-Langevin will greatly extend our capabilities in these experiments and should establish grazing-angle neutron diffraction as a very useful new probe in surface and interface science.

REFERENCES