The Origin and Minimization of the Critical-Angle Reflection from a Thin-Film Multilayer Monochromator

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Abstract

A thin-film multilayer device, used as a monochromator for a white beam of neutrons, also reflects the long-wavelength component of the primary beam due to total reflection from the constituent materials of the multilayer and the substrate. This part of the spectrum consists of the primary beam’s flux for all wavelengths above a critical value, which depends on the characteristics of the multilayer and its angular setting. The presence of this component in the neutron beam may interfere with high-resolution structure determinations. Although there is no unique way of eliminating this contamination, the following approaches may be taken to minimize it: (i) using a multilayer with the smallest achievable periodicity; (ii) appropriately selecting the materials of the bilayer, substrate, and the number of layers to minimize total reflection; (iii) coating the multilayer with a 50–100 Å thin layer of gadolinium; and (iv) installing a nickel-coated silicon plate to reflect the undesirable wavelengths away from the main beam.

1. Introduction

Thin-film multilayer devices are used in several reactor installations as monochromators of neutrons. The advantages that such devices offer are: (1) multilayer monochromators have high reflectivities and yield a wide bandwidth of neutrons, which results in a greater flux at the sample than when a crystalline monochromator is used (Saxena & Schoenborn, 1977; Saxena, 1986); (2) unlike natural crystals, multilayers can be used to monochromatize long-wavelength neutrons due to their larger d spacings (Schneider & Schoenborn, 1984); and (3) the small angular deviation of the primary beam upon reflection from a multilayer may allow a spectrometer to be placed in a limited space (Schoenborn, Saxena, Stamm, Dimmler & Radeka, 1985). In addition to the Bragg reflection that is determined by the thicknesses of layers, the complete reflectivity profile of a multilayer also exhibits critical angle reflection for very small values of momentum transfer, \( Q = 4\pi \sin \theta / \lambda \). This region usually appears close to the beam stop and is separated from the Bragg reflection by a large region of negligible reflectivity, making it convenient to ignore its presence. When a white beam of neutrons is incident on a multilayer set to act as a monochromator through Bragg reflection, it also specularly reflects the primary beam’s spectrum of very long wavelengths due to total reflection from the multilayer. The range of this region and its influence on the spectrum of the reflected beam can be investigated using dynamical-theory calculations that take into account the materials of the layers and the substrate.

2. Theory

For a nonabsorbing and nonmagnetic material, the effective refractive index of neutrons is given by the relation (Sears, 1989)

\[
n^2 = 1 - \lambda^2 Nb/\pi, \tag{1}
\]

where \( \lambda \) is the wavelength of the neutrons and \( Nb \) is the average bound coherent scattering-length density. For a monatomic system, \( N \) is the average number of atoms per unit volume and \( b \) is the bound coherent scattering length of an atom. For a homogeneous mixture or a polyatomic system,

\[
Nb = \sum N_j b_j, \tag{2}
\]

where \( j \) labels the contribution of various atomic species. When a neutron beam is incident on a material at a grazing angle \( \theta_0 \), total reflection of neutrons will occur when the neutron wavelength is greater than a critical value \( \lambda_c \) given by the relation (Mäaza, Sella et al., 1993)

\[
\lambda_c = (\pi/Nb)^{1/2} \sin \theta_0. \tag{3}
\]

The maximum momentum transfer that defines the total reflection region may be obtained from (3) as

\[
Q_c = 4(\pi Nb)^{1/2} \tag{4}
\]

and is a characteristic property of the material. For nickel, \( Nb = 9.42 \times 10^{-6} \text{ Å}^{-2} \) and \( Q_c \) is 0.0217 Å\(^{-1}\). The value of \( Nb \) for float glass, calculated from its molecular composition, is approximately 3.14 \( \times 10^{-6} \text{ Å}^{-2} \), which yields \( Q_c = 0.0126 \text{ Å}^{-1} \).

The reflectivity curve for a multilayer monochromator depends on the materials of the layers, number of bilayers, and the composition of the substrate, and can be
obtained from dynamical theory calculations (Ebisawa, Achiwa, Yamada, Akiyoshi & Okamoto, 1979; Hayter & Mook, 1989; Schaerpf, 1989). The values of the real and imaginary parts of the scattering density $f$ for some commonly used materials are listed in Table 1. The real part is simply $\text{Re}(f) = \sum N_b$ and the imaginary part may be calculated from

$$\text{Im}(f) = \frac{(N_0 \rho/A)(\sigma_a + \sigma_{inc})}{\lambda},$$

where $N_0$ is Avogadro’s number, $A$ is the atomic weight of the element, $\lambda$ is the wavelength of the neutrons (assumed to be 2.0 Å in these calculations) and $\sigma_a$ and $\sigma_{inc}$ are absorption and incoherent-scattering cross sections, respectively.

For a multilayer-substrate system, the values of the momentum transfer $Q_m$ defining the upper limit of the total reflection region and $Q_B$ corresponding to the Bragg reflection can be obtained from theoretical calculations. Fig. 1 shows the theoretical reflectivity as a function of $Q$ for an Ni–Ti multilayer consisting of 250 identical bilayers deposited on a glass substrate. The thickness of each layer in the bilayer is 30 Å, resulting in a periodicity of 60 Å. For this multilayer, $Q_m = 0.0139 \, \text{Å}^{-1}$ and $Q_B = 0.1055 \, \text{Å}^{-1}$. The reflectivity between the total reflection region and the first-order Bragg reflection is insignificant except for the presence of weak secondary interference fringes known as Kiessig fringes (Sears, 1983). To select 2 Å neutrons from the incident beam, the multilayer should be set at 0.962° with respect to the beam. However, for this setting of the multilayer, all neutrons with wavelengths greater than $\lambda_m$ given by

$$\lambda_m = 4\pi \sin \theta_B / Q_m$$

Table 1. Real and imaginary parts of the thermal neutron scattering densities of some commonly used materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Re($f$) $(10^{-6} , \text{Å}^{-2})$</th>
<th>Im($f$) $(10^{-9} , \text{Å}^{-2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>9.42</td>
<td>2.07</td>
</tr>
<tr>
<td>Titanium</td>
<td>-1.93</td>
<td>1.15</td>
</tr>
<tr>
<td>Glass</td>
<td>3.14</td>
<td>0.44</td>
</tr>
<tr>
<td>Silicon</td>
<td>2.07</td>
<td>0.02</td>
</tr>
<tr>
<td>Manganese</td>
<td>-3.03</td>
<td>2.62</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>4.52</td>
<td>3510</td>
</tr>
</tbody>
</table>

Fig. 1. Calculated reflectivity profile for an Ni–Ti multilayer deposited on a glass substrate. The number of bilayers was 250 and the thickness of each layer was 30 Å, giving a periodicity of 60 Å.
will also undergo total reflection. If a white neutron beam with a Maxwellian distribution of velocities is monochromatized by multilayers of different $d$ spacings to reflect 2.0 Å neutrons, the reflected beam will consist of the long-wavelength component of the incident distribution, with a short-wavelength cut-off determined by (6), as graphically shown in Fig. 2. As the $d$ spacing of multilayers increases from 50 to 80 Å, $\lambda_m$ decreases due to the decreasing $\theta_B$, and a greater portion of the incident beam's spectrum is reflected along with the main component, thereby increasing the contamination. An analysis of the Maxwellian distribution (Lomer & Low, 1965) shows that the total neutron flux in this part of the neutron beam is about 0.8% of the monochromatized component for a 60 Å multilayer and 1.7% for an 80 Å multilayer. However, the actual flux of long-wavelength neutrons may depart from the Maxwellian distribution because the collisions between the molecules of the moderator and neutrons may not be strictly equivalent to collisions between hard spheres for very low-energy neutrons, as is assumed in thermal-equilibrium calculations.

Thin-film multilayer monochromators are often used in diffractometers designed for work on disordered or partially ordered systems, such as macromolecules in solution and lamellar samples. Such systems make an optimum use of the enhanced neutron flux arising from the use of these devices and can still tolerate the wavelength bandwidth ($\Delta\lambda/\lambda$) in the 3 to 10% range that is usually produced by them. Since the neutron beam reflected by the low-$Q$ region of the reflectivity plot has a continuous distribution of wavelengths, the resulting first-order Bragg reflection from a lamellar sample arising from these wavelengths will appear as a moving reflection. If the lower limit of contamination is 10Å when the multilayer is set to monochromatize 2Å neu-
tron, the moving peak will start at the angular setting of the fifth-order reflection and will traverse the higher-order reflections with decreasing intensity when the angular position of the sample is changed to determine the integrated intensities of higher-order reflections. For partially ordered systems, such as stacked lipid bilayers and smectic compounds, the intensities of higher-order reflections decrease very rapidly so that fifth- and sixth-order Bragg reflections may be three or four orders of magnitude weaker than the first-order reflection (Duff, Gilchrist, Saxena & Bradshaw, 1994). In these cases, the moving peak will interfere with determinations of intensities of higher-order reflections. The moving peak may be ignored for low-resolution studies that are done by analyzing the first few orders.

In theoretical calculations, an attempt was made to reduce or eliminate the low-angle reflection region by considering the effects of an initial layer of titanium between the glass substrate and the multilayer. The thickness of the titanium layer was varied between 200 and 3000 Å. The reflectivity curve was unaffected in the total reflection region by its presence; only the interference fringes near the edge of the total reflection were somewhat different. A multilayer deposited on a titanium substrate has an almost identical low-angle reflectivity. For a hypothetical Ni–Ti multilayer with no substrate, the reflectivity profile is also similar to one deposited on a glass or titanium substrate.

The origin of the low-angle reflection is revealed if theoretical calculations are done for multilayers without a substrate but having nickel and titanium films of unequal thicknesses, while the sum of the two is kept the same as shown in Fig. 3. The nickel–titanium multilayer was assumed to have 250 bilayers. A perfect and symmetric Ni–Ti multilayer of 60 Å d spacing gives 97.8% reflectivity for 100 bilayers and 99.8% reflectivity for 150 bilayers. However, real multilayers have substantial imperfections and the number of bilayers deposited on a useful multilayer is much greater than the theoretical number for a perfect multilayer (Saxena, 1986). The thicknesses of individual layers were changed in increments of 10 Å so that the thickness of the bilayer

![Fig. 3. Calculated reflectivities of 250-bilayer freestanding multilayers with 60 Å d spacing in which the thicknesses of nickel and titanium layers are not equal. From left, the reflectivity curves are plotted for (1) d(Ni) = 5.0 Å, d(Ti) = 55.0 Å; (2) d(Ni) = 15.0 Å, d(Ti) = 45.0 Å; (3) d(Ni) = 25.0 Å, d(Ti) = 35.0 Å; (4) d(Ni) = 35.0 Å, d(Ti) = 25.0 Å; (5) d(Ni) = 45.0 Å, d(Ti) = 15.0 Å; (6) d(Ni) = 55.0 Å, d(Ti) = 5.0 Å. The Bragg reflections for these multilayers are shown after the break in the x axis.](image-url)
Table 2. Theoretical reflectivity calculations for free-standing (no substrate) nickel–titanium multilayers with unequal thicknesses of the layers in each bilayer

\[ \sum N_b \] has been calculated from the atomic composition of a bilayer and has been used to determine \( Q_m = Q_s \) from equation (4).

<table>
<thead>
<tr>
<th>Thickness of Ni layers (Å)</th>
<th>Thickness of Ti layers (Å)</th>
<th>Reflectivity of the Bragg peak</th>
<th>Width of Bragg reflection (°)</th>
<th>( \sum N_b ) (× 10^{-6} Å^{-2})</th>
<th>( Q_m ) (Å^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>55</td>
<td>0.867</td>
<td>0.0058</td>
<td>-0.9825</td>
<td>0.0067</td>
</tr>
<tr>
<td>15</td>
<td>45</td>
<td>0.998</td>
<td>0.0133</td>
<td>0.9065</td>
<td>0.0118</td>
</tr>
<tr>
<td>25</td>
<td>35</td>
<td>0.999</td>
<td>0.0179</td>
<td>2.7955</td>
<td>0.0154</td>
</tr>
<tr>
<td>35</td>
<td>25</td>
<td>0.999</td>
<td>0.0170</td>
<td>4.6847</td>
<td>0.0182</td>
</tr>
<tr>
<td>45</td>
<td>15</td>
<td>0.998</td>
<td>0.0127</td>
<td>6.5735</td>
<td>0.0210</td>
</tr>
<tr>
<td>55</td>
<td>5</td>
<td>0.468</td>
<td>0.004</td>
<td>8.4625</td>
<td>0.0210</td>
</tr>
</tbody>
</table>

remained fixed at 60 Å. Fig. 3 shows that the range of the critical reflection region increases with the proportional thickness of nickel in a bilayer. The values of \( Q_m \), calculated from the atomic composition of the bilayer, are shown in Table 2; they agree perfectly with those obtained from the reflectivity plots. Since the number of bilayers used in these calculations is sufficient to saturate the reflectivity of a symmetric multilayer, the maximum intensity in the first-order reflection is not significantly reduced by the mismatch in the layers' thicknesses. The angle corresponding to the Bragg reflection increases by a small amount with increasing thickness of the nickel layer because the refractive index of the multilayer composite is greater for a greater proportion of nickel in a bilayer.

The extent of the total reflection region of a multilayer is a characteristic property of the materials constituting the bilayer, and the proportional thickness of the two materials in the bilayer. \( Q_m \) will be determined by the \( Q_s \) for the substrate, as obtained by (4), if the

![Graph](image-url)
coherent scattering-length density of the substrate is greater than the corresponding number for the bilayer. In the reverse case when the bilayers have a greater scattering density, the substrate will have a negligible effect on $Q_m$ for the multilayer. Since fabricating a multilayer requires the use of one material with a high scattering density, and float glass has a very smooth surface on the microscopic level, it is not possible to deposit a useful multilayer monochromator with a vanishingly small critical reflection region.

3. Minimization of the long-wavelength component

In a spectrometer that uses a thin-film multilayer to monochromatize the neutron beam, several approaches can be taken to minimize the long-wavelength contamination caused by total reflection from the materials. The first possibility is suggested by (5) and Fig. 2, which show that the contaminant spectrum is truncated from the lower-wavelength end, where the neutron flux is highest, as the Bragg angle of the multilayer is increased. For a multilayer operating at a certain wavelength, $\theta_B$ can be increased by the selection of a multilayer with the smallest $d$ spacing. Since imperfections in layers often decrease the reflectivities of small-$d$-spacing multilayers, a multilayer should be chosen with the smallest $d$ spacing that still has a high reflectivity.

An examination of the scattering densities of materials suggests an approach based on the use of multilayers made of small or negative scattering densities. Some such combinations are Si–Mn, Si–Ti, Ge–Mn and Ge–Ti. Even though the contrast in scattering densities of these materials is not large, theoretical calculations show that high reflectivities can be obtained with a somewhat greater number of bilayers. For perfect multilayers made of these combinations of materials, the numbers of bilayers required to obtain 90% reflectivity from 60 Å multilayers are 151, 190, 120 and 144, respectively. Calculated reflectivity plots for silicon–manganese mul-

![Graph](image_url)

**Fig. 5.** Effect of depositing a thin gadolinium film on top of a multilayer on the critical-angle reflection region. The solid curve is the reflectivity of a 60 Å-$d$-spacing Ni–Ti multilayer with 250 bilayers, and is the same as shown in Fig. 1. The long dashes show the reflectivity in this region when a 50 Å-thick multilayer is deposited on the multilayer. The short dashes indicate the reflectivity for a 100 Å-thick coating of gadolinium film. Owing to its high absorption cross section, the gadolinium film decreases the intensity of the Bragg reflection.
tilayers are shown in Fig. 4. Curve (a) is the low-angle reflectivity of a hypothetical Si–Mn multilayer that does not have a substrate and consists of 250 symmetric bilayers of 60 Å \(d\) spacing. Since \(\sum N b\) for silicon and manganese is \(-0.956 \times 10^{-6} \text{Å}^{-2}\), such a multilayer does not have a total reflection region. The same multilayer deposited on a glass substrate gives curve (b), which has a low-angle reflectivity plateau of about 0.9 and a reflection edge at \(Q_m = 0.0126 \text{Å}^{-1}\), which is the same as \(Q_c\) for glass. Curves (c), (d) and (e) represent similar multilayers deposited on glass substrates consisting of 1000, 2000 and 4000 bilayers, respectively, and show that the reflectivity in the critical-angle region decreases with an increasing number of bilayers. This decrease in reflectivity is caused by absorption in the bilayers. Even though the imaginary part of the scattering density is very small for these materials, it attenuates the total reflection from the glass substrate for a very large number of bilayers. If the same calculations are repeated after neglecting the absorption term, the reflectivity plots will be almost the same for different numbers of bilayers.

Similar calculations for other combinations of materials show that it is possible to minimize the critical reflection region, particularly when the multilayer, made of these low-scattering-density materials, is deposited on a titanium substrate. Although these results are interesting, there are practical problems with making such devices. Roughness in the surface of layers, interdiffusion between layers and other localized imperfections degrade the properties of multilayers in many cases (Saxena, 1988; Maza, Farnoux et al., 1993) and achieving a high reflectivity for an arbitrary combination of materials may require a much greater number of bilayers or may even be impossible. Most of the useful multilayers are made of nickel and titanium or some alloys of these materials.

A somewhat different approach to minimizing the long-wavelength component is suggested by the observation that a thin film of gadolinium, deposited on top of a multilayer, modifies its total reflection region. This effect is shown in Fig. 5 for 50 and a 100 Å-thick films of gadolinium deposited on a 250-bilayer Ni–Ti multilayer with a \(d\) spacing of 60 Å. The low-

![Fig. 6. Theoretical reflectivity plots for nickel films deposited on a silicon substrate. The thickness of the nickel film is assumed to be 300 Å for the solid curve and 2000 Å for the dashed curve.](image)
$Q$ reflectivity changes in shape from a step function to a triangle with continuously decreasing reflectivity from the smallest value of the momentum transfer. Increasing the thickness of the gadolinium film to more than 100 Å results in a negligible change in the low-$Q$ region but reduces the intensity of the Bragg reflection since gadolinium has a very large absorption cross section for neutrons. The reflectivity of the multilayer with the 100 Å gadolinium film is 85.5%, which does not cause an inordinate loss of neutron flux. The modified reflectivity profile shown in Fig. 5 will significantly reduce long-wavelength contamination because the reflectivity is small in the region where the neutron flux is greater. The resultant spectrum of the long-wavelength component of the reflected beam is also shown in Fig. 2, and is considerably reduced when a gadolinium film is present.

Perhaps the easiest way of reducing the long-wavelength contamination from the neutron beam is to use a nickel filter, made by deposition of a nickel film on a silicon substrate, and then set it at an angle such that the mono- chromatic component of the neutron beam is transmitted and the long wavelengths are reflected away from the main beam. Silicon is a good substrate for the nickel film because it has a very low absorption cross section for thermal neutrons. Fig. 6 shows reflectivity plots for 300 and 2000 Å-thick nickel films deposited on silicon substrates. A 300 Å thin film of nickel has greater than 99% reflectivity for $Q$ less than 0.012 Å$^{-1}$ and weak and widely separated Kiessig fringes. For a 3000 Å-thick nickel film, the region of high reflectivity extends up to 0.0217 Å$^{-1}$ but the Kiessig fringes are prominent in the immediate neighborhood of the critical angle. Neutrons with a wavelength of 2.0 Å will be transmitted if their angle of incidence on the nickel film is greater than 0.198°, while neutrons of wavelengths greater than 10 Å will be reflected from the nickel film if the incidence angle is less than 0.989°. Hence, keeping the angular position of the nickel film between these numbers will remove the long wavelengths from the transmitted beam by reflecting them in a different direction. The absorption cross section for silicon is 16 fm$^2$ and it produces negligible incoherent scattering. A 1 mm-thick silicon substrate on which the neutrons are incident at 0.80° will attenuate the transmitted beam by about 5%.

The use of such a nickel filter has two constraints. Firstly, since the angle of incidence on the nickel film is very small, the silicon plate has to be rather long to reflect the entire neutron beam. For filtering a 1 mm-wide beam, the plate should be 7.5 cm long, while for reflecting a 1 cm-wide beam, several nickel-coated silicon plates may have to be installed in a parallel geometry. Secondly, since the angle of incidence is very small, any surface roughness in the nickel film will degrade its filtering action. Any component of long-wavelength neutrons that is incident on the nickel film for $Q$ greater than 0.025 Å$^{-1}$ due to local surface roughness in the nickel film or the silicon substrate will not be reflected away from the main beam and will appear as a residual contamination.

4. Discussion

A thin-film multilayer device, used to monochromatize a white beam of neutrons, will have an undesirable long-wavelength component that will follow the same path as the monochromatic component and cannot be separated from it by geometrical means. This component may interfere with high-resolution structural studies. For such investigations, a multilayer with the minimum $d$ spacing that still has a sufficiently high reflectivity should be used to monochromatize the beam. Multilayers made from a combination of low-scattering-density materials are preferable to ones containing nickel. In these cases, increasing the number of bilayers will shield the effect of the glass substrate. A 100 Å thin coating of gadolinium on top of the multilayer will significantly decrease long-wavelength contamination. However, since gadolinium oxidizes rapidly, this layer must be protected by a layer of titanium. The reflectivity of an Ni–Ti multilayer, with a 100 Å film of gadolinium, is basically unaffected by the presence of a 100 Å-thick outer layer of titanium. The easiest approach, however, is to keep a thin nickel film deposited on a silicon substrate at a small angle to reflect the undesirable wavelengths away from the main beam. For reflecting a wide beam of neutrons, a number of such nickel-coated silicon plates may be kept in parallel geometry.

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References