Models of diffraction from layered ultrathin coherent structures

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We show how relatively simple diffraction theory can be applied to layered ultrathin coherent structures to yield diffraction patterns with main peaks and satellites. We also discuss how the introduction of lattice strain into the model affects the results, and how this modified model might be applied to a real system.

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I. INTRODUCTION

Layered ultrathin coherent structures (LUCS) are a new type of material which consists of ultrathin layers of metals prepared by sequential vapor deposition of two *dissimilar* materials. A simple model based on the structure of the constituent materials has the same qualitative features as the real material. We further propose a model in which the strain between two adjacent dissimilar atomic planes can be varied, and we examine the results of changing this strain parameter linearly.

The problem of modeling a periodic composition modulation was first approached by Daniel and Lipson.[1] For an early history of the problem the reader is referred to De Fontaine.[2] More recently, a great deal of interest has been shown in artificially produced materials, and specifically in artificially layered materials.[3,4,5] In particular, layered materials show promise of having applications as monochromators of polarized neutrons[6] and x rays. Elongated and aligned particles are of considerable importance in permanent magnet applications.[7] This is due to the fact that the remanent magnetization, magnetic anisotropy, as well as the coercivity can be considerably larger in such materials. Large coercivities have already been found in the layered Cu/Ni system.[8]

In Sec. II we present the basic diffraction theory and the solution in some simple limiting cases, and in Sec. III we present computer calculation results for a specific case for which experiments have been performed.

II. DIFFRACTION THEORY

Ideally a LUCS consists of a large number N of layers stacked to form a macroscopic crystal. Each layer is made of M atomic planes, whose chemical and structural composition is modulated in the preparation process. If $\bar{a}$ is the average separation of the atomic planes, the periodicity of the LUCS is $\lambda = M\bar{a}$.

For diffraction experiments, where the scattering vector is normal to the planes, the ideal sample behaves as a one-dimensional grating giving rise to diffraction peaks obtained in terms of the scattering function:

$$F(q) = \sum_{n=0}^{N} A(q) \exp[iq \cdot n(M\bar{a})]. \tag{1}$$

$F(q)$ is the scattered amplitude, whose square is proportional to the diffracted intensity. The summation contained in Eq. (1) ensures that the intensity peaks for the values of the scattering vector $q = 2\pi p/M\bar{a}$, where p is an integer. For a well-constructed sample composed of an adequate number of layers ($N \sim 10^3$) the width of the peaks is quite negligible compared to the instrumental resolution of a conventional x-ray apparatus.

The square of the scattering amplitude $|A(q)|^2$ is directly related to the experimentally measured intensities of the diffraction peaks. By performing a model calculation, $|A(q)|^2$ can be calculated, then compared to the experimental intensities, and in this fashion the microscopic structure of the material is determined. The amplitude is given by the expression:

$$A(q) = A(2\pi p/M\bar{a}) \equiv A_p$$

$$= \sum_{m=1}^{M} f_m \exp(2\pi ipm/M) \exp(2\pi i \Delta\phi_m p/M), \tag{2}$$

where f_m is the scattering amplitude of the mth layer, and $a\Delta\phi_m$ is the displacement of the mth layer from its average position $m\bar{a}$. The master formula, Eq. (2), shows that $2M$ quantities have to be determined by the experimental measurements, namely the f_m and $\Delta\phi_m$, and thus at least $2M$ different diffraction peaks have to be measured in order to obtain those physical quantities. Before doing that, however, it is worthwhile to see whether physical insight can provide a reduction of the general expression. This can be reduced to simpler analytical form in some simple but relevant cases, and it can provide a way to fit the experimental data to a less formidable number of parameters.

Some of the diffraction peaks given by Eq. (2) assume particular significance, for their intensity is nonzero even if the material contained in the basic period is homogeneous, i.e., $f_m = \bar{f}$, and $\Delta\phi_m = 0$ for all values of m. These peaks, due to the average lattice, occur for $p = rM$, where r is an integer. The other reflections could be reindexed as $p = rM \pm s$, where s is also an integer, to be called "satellites" of the sth order of the average lattice line r. It is important to note that the intensity of the satellites is weak compared to that of the average lattice line only in the limit of a weak perturbation. This means that for large modulation all peaks should be treated on the same footing. Let us consider a particular case, namely that the LUCS is made of two elements in equal portions, so that the basic period is composed of $M_1 = M/2$ layers enriched in one of the constituents, fol-

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lowed by $M/2$ layers enriched in the second constituent. Let us further assume that the fluctuations in composition and strain are identical and symmetric for the two half-periods, namely:

$$\Delta f_m = -\Delta f_{M_1+m}, \quad \Delta\phi_m = -\Delta\phi_{M_1+m},$$
$$\Delta f_m = \Delta f_{M_1-m+1}, \quad \Delta\phi_m = -\Delta\phi_{M_1-m+1}, \tag{3}$$

where $\Delta f_m = f_m - \bar{f}$. With this constraint, only modulations symmetric to the quarter-period (such as those of sinusoidal or square-wave form) are accepted, while others (such as a sawtooth modulation) are excluded. The scattering amplitude takes now the rather simple form:

$$p = rM \text{ (average lattice line) } |A_p| = 4\bar{f}\sum_{m=1}^{M/4}\cos[2\pi r\Delta\phi_m], \tag{4a}$$

$$p = rM \pm (2s+1) \text{ (odd satellites) } |A_p| = 4\bar{f}\sum_{m=1}^{M/4}\cos\left[2\pi\frac{m-1/2}{M}(2s+1)\right]\sin\left[2\pi\left(r\pm\frac{2s+1}{M}\right)\Delta\phi_m\right]$$
$$\pm 4\sum_{m=1}^{M/4}\Delta f_m\sin\left[2\pi\frac{m-1/2}{M}(2s+1)\right]\cos\left[2\pi\left(r\pm\frac{2s+1}{M}\right)\Delta\phi_m\right], \tag{4b}$$

$$p = rM \pm 2s \text{ (even satellites) } |A_p| = 4\bar{f}\sum_{m=1}^{M/4}\cos\left[2\pi\frac{m-1/2}{M}2s\right]\cos\left[2\pi\left(r\pm\frac{2s}{M}\right)\Delta\phi_m\right]$$
$$\mp 4\sum_{m=1}^{M/4}\Delta f_m\sin\left[2\pi\frac{m-1/2}{M}2s\right]\sin\left[2\pi\left(r\pm\frac{2s}{M}\right)\Delta\phi_m\right]. \tag{4c}$$

From Eqs. (4) several important consequences can be drawn. Let us first examine the evolution of the average lattice line ("central peak") as a function of the length of the period M. Its scattering amplitude depends only on the strain, which gives rise to a displacement that can be expanded in the Fourier series:

$$\Delta\phi_m = \Delta_1\frac{M}{2\pi}\cos\left(2\pi\frac{m}{M}\right) + \Delta_3\frac{M}{2\pi}\cos\left(6\pi\frac{m}{M}\right) + \ldots . \tag{5}$$

Retaining only the leading first term of the expansion (which corresponds to a sinusoidal strain) the amplitude of the average lattice line takes the simple form:

$$A_{rM} = \bar{f}M J_0\left(2\pi r\Delta_1\frac{M}{2\pi}\right), \tag{6}$$

where J_0 is the zeroeth-order Bessel function. This equation is only valid in the large M limit, where terms involving higher-order Bessel functions in the expansion of Eq. (4a) can be neglected. Comparing the expression Eq. (6) with real cases, we find that semiconductor superlattices show small changes of the amplitude of the central peak as a function of wavelength. This is precisely because the strain in these materials is small.[3] On the other hand, LUCS formed by dissimilar metals show large changes in the central peak amplitude in qualitative agreement with Eq. (5).

The behavior of the satellites cannot be described in such a straightforward way. However, it is still possible to sort out some of their features. For instance, the interference between the amplitude and lattice perturbation causes asymmetries in the amplitudes of the $+s$ and $-s$ satellites. If no strains are present ($\Delta\phi_m = 0$), the even-order satellites identically vanish. If the scattering amplitudes are the same for all atoms ($\Delta f_m = 0$) the satellites of order s amplitudes essentially proportional to the Bessel functions sth order. Inspection of Eqs. (4b) and (4c) indicates also that in this case symmetrical satellites have equal intensity, because the second term in each equation is identically zero.

III. COMPUTER CALCULATION FOR LAYERED ULTRATHIN COHERENT STRUCTURE

The qualitative features revealed by the analytical expansion of the scattering amplitudes are confirmed by numerical calculations, when the diffracted intensities of a (periodically repeated) set of planes are calculated. For our purposes we have chosen a simple model for the LUCS where the atomic planes of each material have their own spacing (d_1 and d_2), and the separation between the atomic planes of dissimilar metals is given by δ. We assume m layers of material 1, followed by n layers of material 2, and thus the modulation wavelength given by

$$\lambda = (m-1)d_1 + (n-1)d_2 + 2\delta. \tag{7}$$

Equation (2) for $A(q)$ has been evaluated numerically for such a model assuming $d_1 = 2.335$ Å and $d_2 = 2.087$ Å as appropriate for the (110) planes of Nb and the (111) planes of Cu, respectively. The f_m are the form factors of the two atoms,[9] and we have neglected slowly varying functions of θ such as Debye-Waller factors, Lorentz polarization for x rays,[10] etc.

Figure 1 illustrates a sequence of computed diffraction patterns, obtained for increasing values of m,n (but keeping $m = n$). For this calculation we chose $\lambda = md_1 + nd_2$ as if the different nature of the two metals separated by the δ-spacing would not cause a strain. From the patterns it can be noticed that in the low-λ limit a single large peak is present with evenly spaced satellites. This central peak occurs at a position which is halfway between the Bragg peaks corresponding to the pure niobium and pure copper planes. The two satellites are asymmetric in height due to the fact that both an amplitude and a phase modulation is present (in a calculation in which only a phase or amplitude modulation

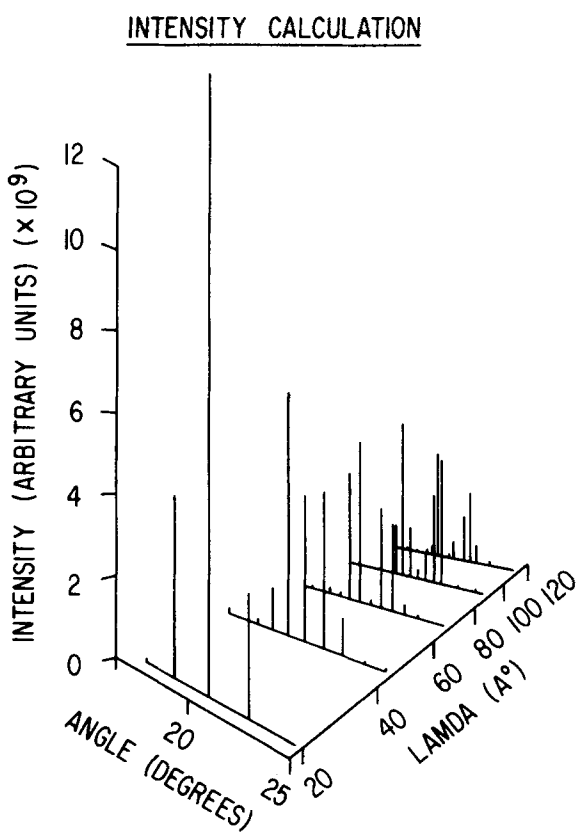

FIG. 1. X-ray vs intensity for various layer thicknesses. The Cu-Nb interface distance is taken to be the Cu (111) plane distance and the Nb-Cu interface distance is taken to be the Nb (110) plane distance.

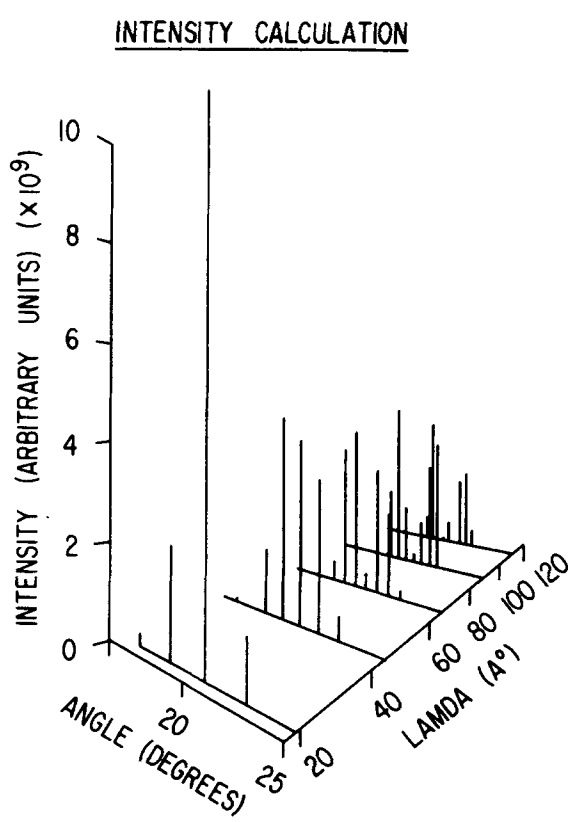

FIG. 2. X-ray diffraction for various layer thicknesses with the Nb-Cu and Cu-Nb distance $\delta = 2.21$.

is present the peaks are symmetric).

The position of two consecutive peaks i and $i+1$ are related to the modulation wavelength through the equation

$$\lambda = \frac{\lambda_x}{2} \frac{1}{\sin\theta_i - \sin\theta_{i+1}}, \tag{8}$$

where λ_x is the wavelength of the x rays. Figure 2 shows a set of intensities calculated for a strained lattice ($\delta = 2.21$ Å). The effect of strain is to change the relative intensities, but no major qualitative changes occur. In a detailed comparison between experiment and theory the relative peak intensities can be fitted to obtain the values of the strain parameter.

From the figures show an unusual evolution of the x-ray patterns as a function of layer thickness. This model behavior does not resemble that observed in semiconductor superlattices (where the modulation is mainly in the scattering amplitude f and not in the spacing), but is in good agreement with that found in Nb/Cu LUCS.[11] In that experimental case, as in this model, the x-ray pattern evolves from central peak with satellites to two distinct peaks with their own satellites. The main conclusions of the calculation can be summarized as follows: (1) The qualitative evolution of the x rays versus layer thickness, observed experimentally, can be obtained from a simple model calculation. In this model, all peaks (central peak and satellites) arise in a natural way, from the new superlattice periodicity; (2) the "central peak" amplitude is only dependent on the strain modulation [see Eq. (4a)]. For a large number of atomic planes the amplitude of the central peak is given by the simple Eq. (6).

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[1] V. Daniel and H. Lipson, Proc. R. Soc. London **A181**, 368 (1943); **A182**, 378 (1944).
[2] D. De Fontaine, in *Local Atomic Arrangement Studies by X-Ray Diffraction* (Gordon and Breach, New York, 1966), pp. 51–94.
[3] A. Segmüller, Appl. Phys. Lett. **28-1**, 39 (1976).
[4] J. Hilliard, in *Modulated Structures-1979*, AIP Conf. Proc. **53**, 407 (1979).
[5] I. K. Schuller and C. Falco, in *Modulated Structures-1979*, AIP Conf. Proc. **53**, 417 (1979), and I. K. Schuller and C. M. Falco in *Inhomogeneous Superconductors-1979*, AIP Conf. Proc. **58**, 197 (1979).
[6] J. W. Lynn, J. K. Kjems, L. Passell, A. M. Saxena, and B. P. Schoenborn, J. Appl. Crystallogr. **9**, 454 (1976).
[7] G. Y. Chin, Science **208**, 888 (1980).
[8] J. Q. Zheng, C. M. Falco, J. B. Ketterson, and I. K. Schuller, Appl. Phys. Lett. **38**, 424 (1981).
[9] *International Tables for X-Ray Crystallography* (Kynach, Birmingham, England, 1967), Vol. III, pp. 223, 210–211.
[10] M. Woolfson, *An Introduction to X-Ray Crystallography* (Cambridge University, Cambridge, 1970), pp. 167–206.
[11] I. K. Schuller, Phys. Rev. Lett. **44**, 1597 (1980).