

## QUANTITATIVE X-RAY DIFFRACTION FROM THIN FILMS

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**Abstract**—We have developed a general procedure for quantitative structural refinement of superlattices and thin films. To analyze a wide variety of thin films, we developed the mathematical formalism necessary to include all types of randomness and changes in structural parameters. This formalism was used to implement a non-linear-fitting algorithm which is able to fit quantitatively the entire X-ray diffraction profile. The results from the structural refinement were compared to results obtained independently from other methods such as: Extended X-ray Absorption Fine Structure (EXAFS), X-ray Photoelectron Diffraction (XPD), chemical analysis, artificially roughened superlattices, etc. We also describe the application of this method to the refinement of thin film structures of high temperature superconductors where no independent information is available.

### INTRODUCTION

Thin films are at the frontiers of material science and condensed matter physics research, and are the basis for the microelectronics industry. The physical properties of thin films are strongly affected by their structural properties, and therefore it is of utmost importance to characterize their structure with high precision. In many cases slight changes in the structural properties at the atomic level have large effects on the physical properties and consequently not only affect the physics of these materials but also their performance as devices (1). Examples of these type of effects include changes in the elastic properties of metallic superlattices (2), increases in the giant magnetoresistance of magnetic multilayers (3), changes in the superconducting (4) and transport properties (5) of ultrathin films and multilayers, and changes in the quantum well properties of semiconducting superlattices (6).

The structural determination of thin films using X-ray diffraction has been slowly evolving over the last ten years, and is now at a stage at which detailed, quantitative, structural information at the atomic level may be obtained. Although quantitative structural information, including refinement techniques have been available for many years for bulk materials (7,8), they have only recently been applied to thin films. The reason for this is that thin film materials usually are only available in very limited quantity, and therefore the X-ray intensity available for refinement studies

is substantially reduced. Moreover, although philosophically the refinement procedure is similar for the case of thin films and bulk material, in practice the application of refinement techniques to thin films is quite different. For bulk materials the assumption is made that the constituent unit cell is periodically repeated in space and therefore line shapes are controlled mostly by peak overlap from the various reflections. In the case of multilayers or thin films, and especially for the case of superlattices, deviations from perfect periodicity adds additional line shape changes, which can be used as important input into structural refinement models.

Two important developments have recently occurred that allow the application of refinement techniques to thin films: the development of a general kinematic formalism which makes the application of numerical methods computationally feasible, and the application of these methods to a variety of situations showing that the method gives reliable results for the cases for which the answer is known from independent measurements (9,10). Here we will give a brief description of the methodology involved in the refinement procedure, give a few examples of the checks that have been performed, and refer the interested reader to the published literature for further information (9,10).

### FORMALISM

The general model for a superlattice consists of a stack of  $M$  bi-layers of material A and B, characterized by the structure factors  $F_{Aj}$  and  $F_{Bj}$ , thicknesses  $t_{Aj}$  and  $t_{Bj}$ , and interface distances  $a_{Aj}$  and  $a_{Bj}$ , as shown in Figure 1. Two types of roughness are included in this model; a discrete change in the film thicknesses to include atomic steps and a continuous variation of the interface

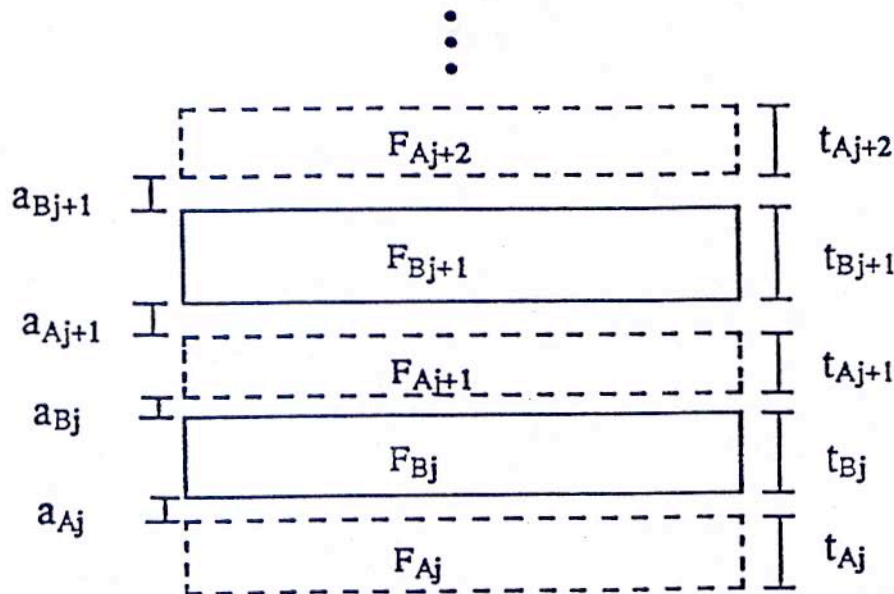


Figure 1. Representation of a superlattice consisting of layers of materials A and B, with thicknesses  $t_{Aj}$ ,  $t_{Bj}$  and structure factors  $F_{Aj}$ ,  $F_{Bj}$ . The layers are separated by interface distances  $a_{Aj}$  and  $a_{Bj}$ .



distance, which simulates the situation for lattice mismatched incoherent interfaces. The exact distribution for the disorder can be varied, although most of our studies have been performed assuming a statistically independent Gaussian distribution. In this fashion the scattering intensity can be written in terms of the averaged parameters of material A and B independent of the number of layers in the superlattice. We would like to stress that all the disorder in this formalism is cumulative, which leads to broadening of the diffraction peaks and is not equivalent to an effective Debye-Waller coefficient. Moreover, two types of averages in the scattering function and the diffracted intensities must be included: i.e. coherent and incoherent averaging. The way in which these averages are included is somewhat delicate and is related to the issue of the lateral length scale of the roughness. This discussion is quite lengthy, is presented in some detail in the references mentioned and is the subject of further research.

The calculation of the intensity requires the construction of a specific model that includes all types of disorder relevant to the particular case under study. For instance, interfacial strains are included assuming a particular variation of the interatomic spacing close to the interface, a low Z number amorphous layer is simulated by assuming the scattering power of one of the layers to be zero, intra-layer disorder may be simulated by allowing the positions of the atomic planes of one of the crystalline layers to vary randomly, etc.

### FITTING PROCEDURE

The refined parameters are fit using a standard refinement procedure, as shown in Figure 2. The structural parameters of the averaged unit cell, including statistical fluctuations, are adjusted to minimize the difference between the calculated and measured intensities. In order to assure that the numerical methodology employed was correct, two independent computer programs were written, in two languages (TURBOPASCAL and FORTRAN) and the results were compared. In all cases good, quantitative agreement was obtained from both calculations.

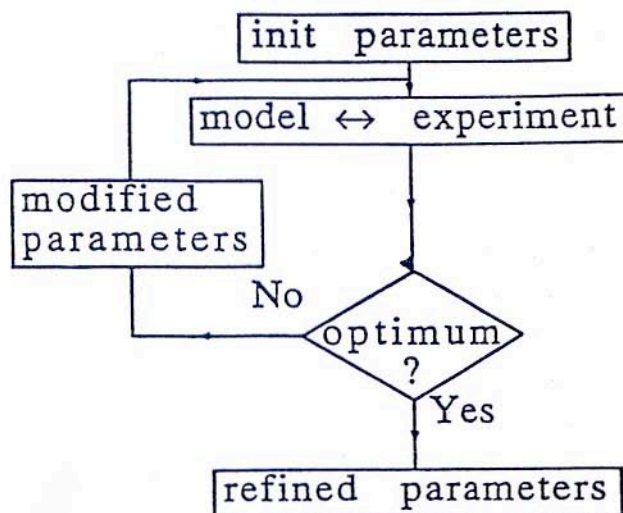


Figure 2. Standard refinement procedure.

As in all multiparameter fits, extreme care must be taken to avoid false minima and detailed studies must be performed on the effects of different parameters, their interconnection and convergence to the solution. This methodology is mostly dictated by the physics and chemistry of the material and is quite similar to the methodology used in the more conventional refinement methods used for bulk material, such as the Rietveld refinement. Here is where art and science come together!

### EXAMPLES

The method described above was applied to a large number of systems for which the answers were known *a-priori* from other measurements. These systems include normal, magnetic, superconducting, ceramic and semiconducting materials. In all cases tested, the agreement between the structural refinement described above and the independent measurements were quite good. This gives us the confidence that application of this method to other systems, where no independent data is available, is quite reliable. The checks that were performed against other measurements include; self consistency between low and high angle data, chemical composition, profilometry, evaporation rates, Extended X-Ray Fine Structure Spectroscopy (EXAFS), X-Ray Photoelectron Diffraction (XPD), artificial roughness, bulk lattice spacings, etc. All these checks are described in detail in references 9 and 10.

A good example of a crystalline-amorphous superlattice is Pb-Ge layers prepared by Molecular Beam Epitaxy (MBE) on a liquid nitrogen cooled sapphire or silicon oxide substrate. The low angle data for Pb(50Å)/Ge(50Å), shown in Figure 3, exhibits a number of peaks, with the even order satellites suppressed, as expected for equal layer thickness superlattice with a square modulation. Although this figure shows clearly the presence of the layers, further analysis is

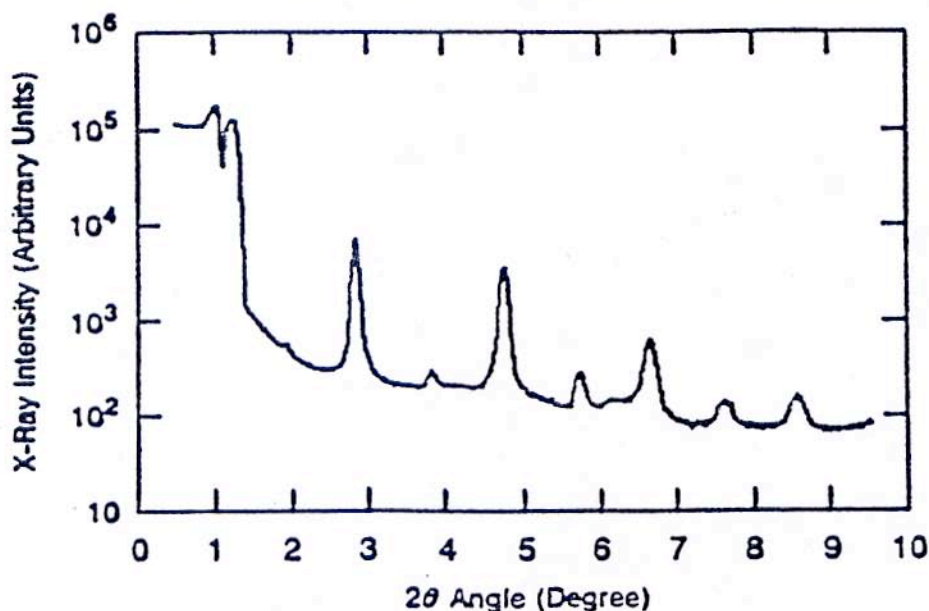


Figure 3. Small angle diffraction spectrum of a Pb/Ge (50Å/50Å) multilayer.



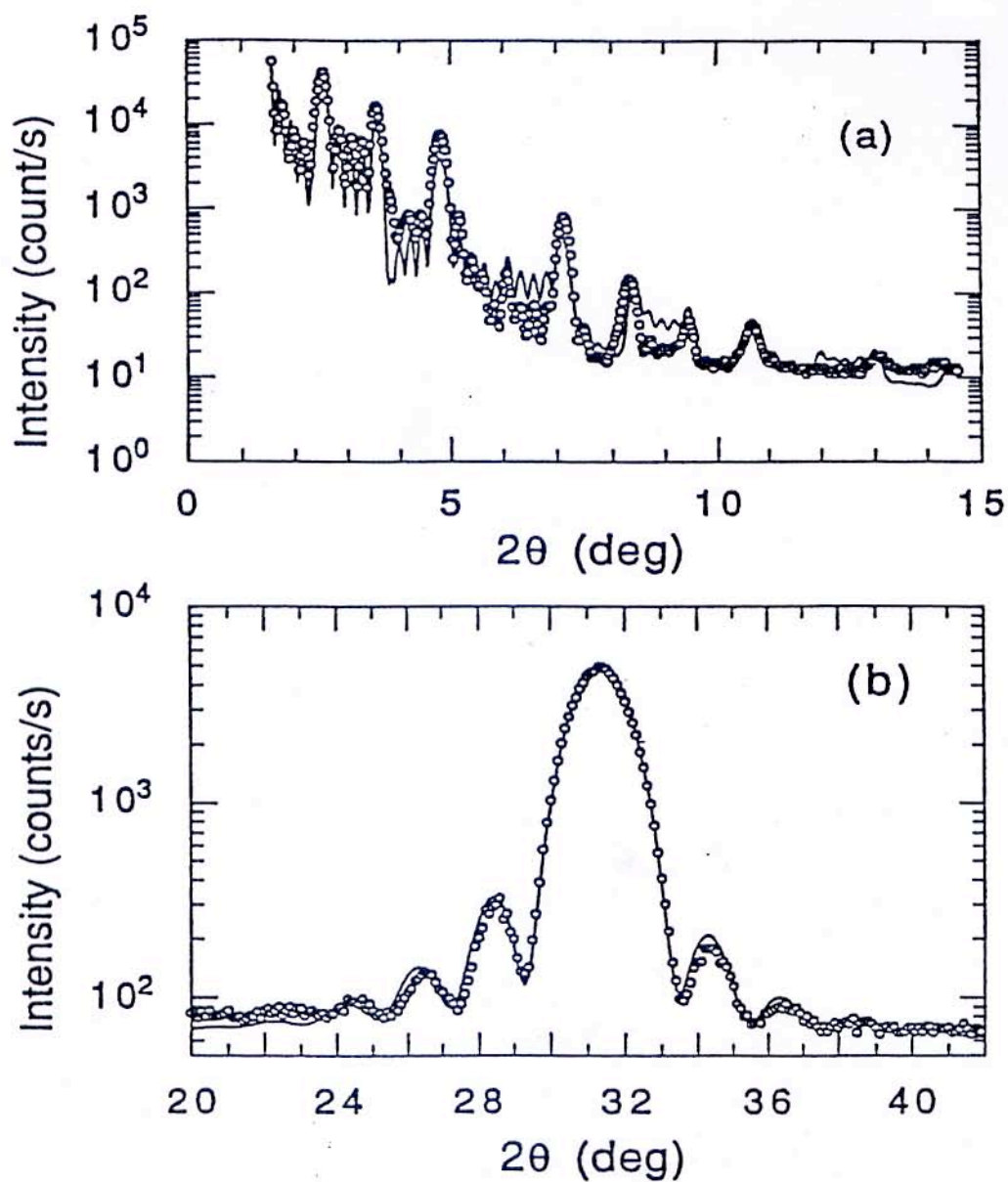


Figure 4. (a) Low angle x-ray diffraction profile of a  $[\text{Pb}(45.4\text{\AA})/\text{Ge}(29.5\text{\AA})]_5$  superlattice where the open circles are the measured intensity and the solid line is a simulation, assuming  $1\text{\AA}$  of layer thickness fluctuation of both layers. (b) High angle profile of the same superlattice where the open circles are the measured intensity and the solid line is the refined profile.

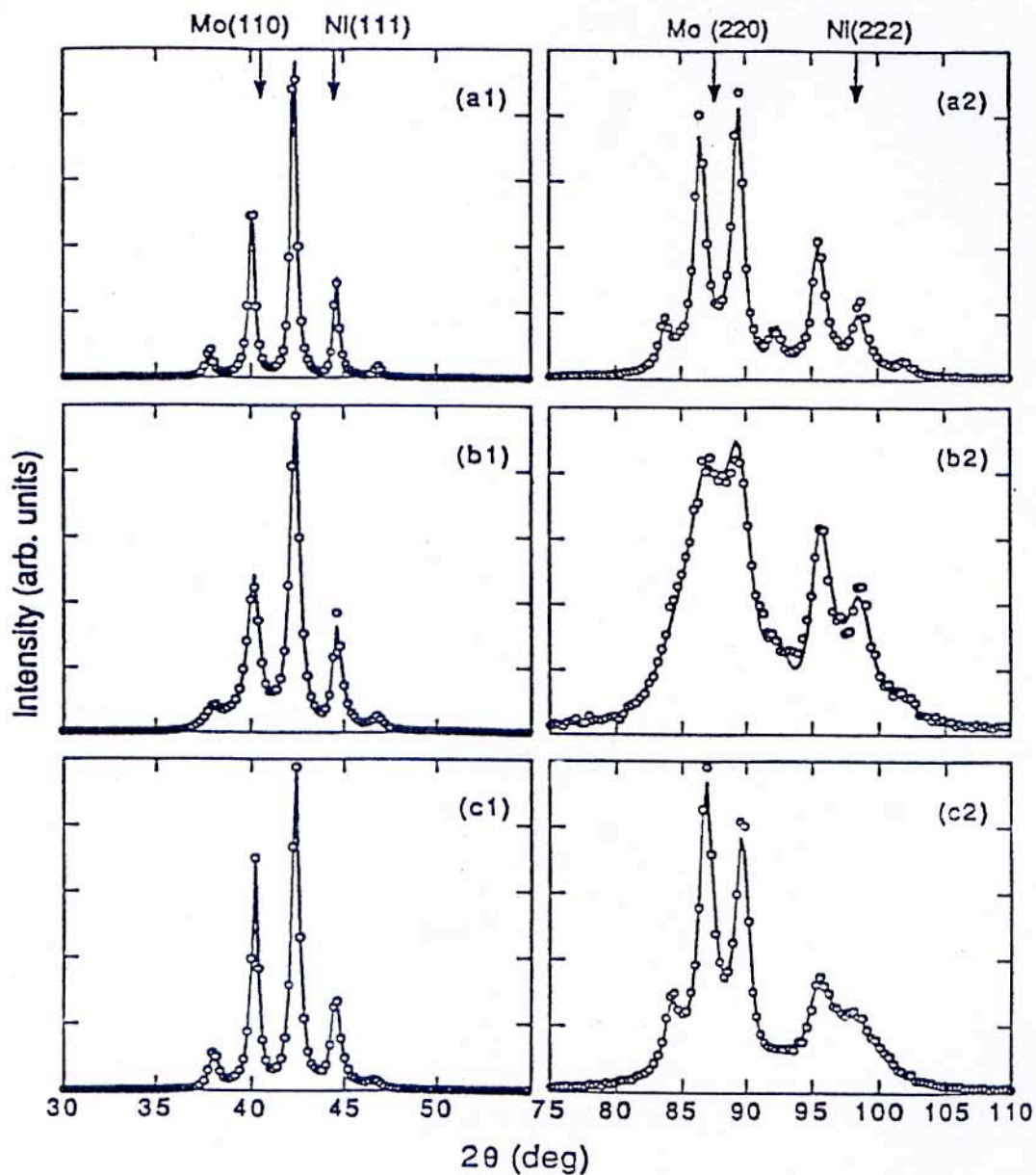


Figure 5. Experimental profiles (o) and refined calculations (full lines) of three  $[\text{Mo}(20\text{\AA})/\text{Ni}(22\text{\AA})]_{130}$  superlattices: (a) without artificial roughness, (b) with  $2.7\text{ \AA}$  artificial roughness on Ni and (c)  $2.7\text{ \AA}$  on Mo. The profiles on the left are taken around the first order main Bragg reflections, the profiles on the right around the second order.



needed in order to extract quantitative information. Since the Ge layers are amorphous (i.e. continuous roughness on the Ge) the high angle diffraction data looks like the superposition of the intensity diffracted from a single finite sized Pb layer. This is shown quite beautifully in Figure 4. A fit of this diffraction data using the methodology described above is shown by the solid line in Figure 4. This data is the same as obtained from the superposition of  $M$  independent Pb layers and therefore the method described above can be applied also to single layers (Pb in this case). The best fit of this data indicates that it is necessary to include *intra*-layer disorder in addition to the interfacial disorder. The various parameters obtained from these fits are: Pb(111) lattice spacing  $d_{\text{Pb}} = 2.846 \text{ \AA}$  compared to  $2.858 \text{ \AA}$  in bulk, a slight lattice expansion of  $0.03 \text{ \AA}$  close to the interface, *intra*-layer disorder of  $0.06 \text{ \AA}$  and discrete disorder ("steps") of one monolayer ( $\sim 3 \text{ \AA}$ ). Consistent results were obtained from similar refinements in a large number of Pb/Ge multilayers.

An example of the type of cross checks performed on the methodology used is illustrated for the case of Mo(110)/Ni(111) superlattices in which layer fluctuations were introduced artificially during the growth. The samples were made by DC magnetron sputtering onto ambient temperature silicon substrates. The substrates were rotated over the targets and held for predetermined amounts of time by a computer controlled substrate holder to achieve the desired thickness. To introduce disorder into the layer thicknesses, the deposition time of the materials was varied randomly for each layer so that the layer thicknesses approximated a Gaussian distribution about the average layer thickness. Samples were made with thickness variations of only one of the constituent materials or with variations in both layers.

Examples of the diffraction profiles are shown in Figure 5 for  $[\text{Mo}(20\text{\AA})/\text{Ni}(22\text{\AA})]_{130}$  superlattices, where the values in parentheses refer to the average layer thickness and the subscript gives the total number of bi-layers. Figure 5a shows the diffraction profiles for a sample without artificial roughness, and Figure 5b and 5c for samples with  $2.7 \text{ \AA}$  artificial roughness added to Ni and Mo respectively. The circles are the measured x-ray intensity and the solid line the structural refinement. The arrows indicate the expected peak positions for Mo and Ni. The effect of the additional disorder can be seen in both the relative intensity and line width of the profiles; increased disorder of the Mo (Ni) layers leads to a broadening of the superlattice peaks associated with Ni (Mo). The second order superlattice peaks are much more sensitive to discrete disorder. An artificial disorder of  $2.7 \text{ \AA}$  is enough to almost completely suppress the second order high angle superlattice peaks.

The parameters used in the refinement were; the interface distance  $a$  and continuous fluctuation width  $c$ , the average number of atomic planes  $\bar{N}_{\text{Mo}}$  and  $\bar{N}_{\text{Ni}}$ , the standard deviation in layer thickness resulting from discrete disorder  $S_{\text{Mo}}$  and  $S_{\text{Ni}}$ , the lattice parameters  $t_{\text{Mo}1}$ ,  $\Delta t_{\text{Mo}2}$ ,  $t_{\text{Ni}}$ ,  $\Delta t_{\text{Ni}1}$ , and  $\Delta t_{\text{Ni}2}$ . The exponential  $\alpha$  that defines the decay distance of the lattice deviation away from the interface was set at  $\alpha = 0.5$ .

The results of the structural refinement values of  $S_{\text{Mo}}$  and  $S_{\text{Ni}}$  can be directly compared to the amount of additional artificial disorder introduced during growth. The samples without additional disorder have typical discrete disorder values of  $1.0 \text{ \AA}$  indicating the layer thicknesses vary on average less than one monolayer. The value of the continuous disorder was  $0.18 \text{ \AA}$  and is close to the difference in the lattice spacing of Mo and Ni of  $0.2 \text{ \AA}$ . The amount of additional structure disorder, determined from the fits shown in Figure 5 from the first (second) order peaks, is for Ni  $2.0(3.3) \text{ \AA}$  and for Mo  $1.0(2.6) \text{ \AA}$ , which is in good agreement with the values added during growth. There is a discrepancy between the values determined from the first and second order portions of the profiles, with the second order values in better agreement with the growth value.



A possible explanation for the difference is that the second order peaks are much more sensitive to discrete disorder and should give a more accurate measure of the disorder for a small amount of additional disorder. When the amount of disorder increases, this is no longer true. In samples with an additional 3.3 Å of additional roughness, the second order superlattice peaks are no longer resolved. The refinement procedure can then only give a lower limit of the disorder ( $\approx 3.5$  Å). The first order satellite peaks are still clearly resolved and give a more accurate measure of the roughness.

This methodology was also applied to solve several problems for which there was no other quantitative solution available (11). An interesting case is the issue of interdiffusion in high temperature ceramic superlattices. The so called "1:2:3" materials have a complicated structure which can be thought off as a superlattice with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  being the prototype material (12). In order to check whether the superlattice refinement method is applicable to these types of complicated structure, we have applied it to refine the structure of 1:2:3 thin films with several substitutions on the Y site. In all cases the refined lattice spacings were within 0.02 Å of the bulk values. An unsolved issue so far in this field has been the interdiffusion on the Y site in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}/\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  superlattices. Figure 6a shows the result of a calculation assuming a perfect superlattice without any disorder. Although the calculated spectra (Figure 6a) have the same qualitative features as the measured ones (Figure 6b), it is clear that there are a number of discrepancies in both the line widths and relative intensities of the satellite peaks. The results of the refinement procedure in Figure 6c show that both the relative intensities and line

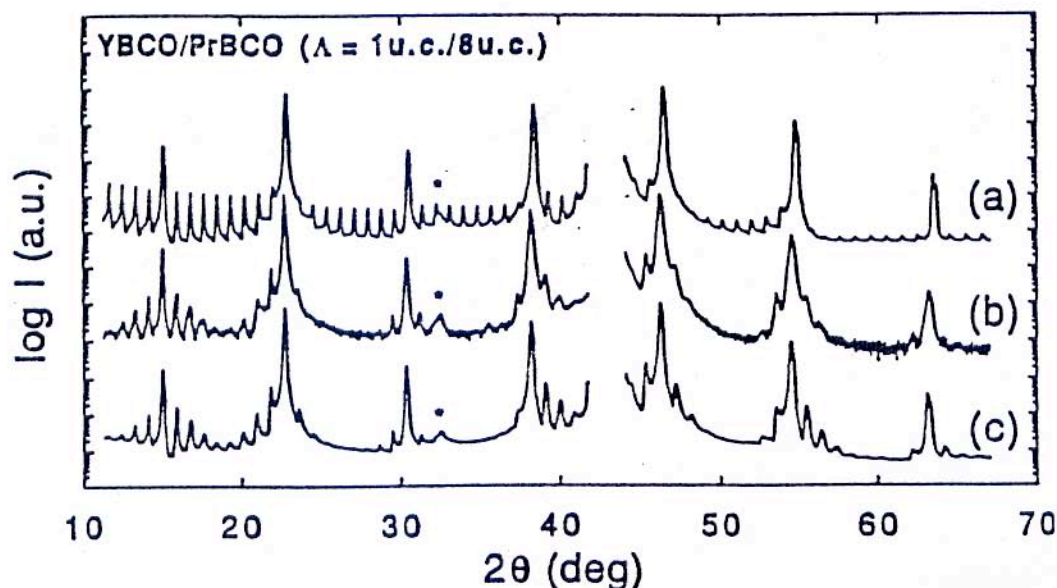


Figure 6.  $\theta$ - $2\theta$  x-ray spectra for a 2000 Å thick YBCO (1 unit cell)/PrBCO (8 unit cells) superlattice. (a) perfect superlattice simulation, (b) experimental data, (c) refined spectrum including layer thickness fluctuations and interdiffusion. The spectra were offset by three decades and the MgO substrate peak was deleted for clarity. The asterisk indicates a small peak corresponding to the (110) diffraction.



widths of all peaks are quantitatively reproduced. The refinement shows that the discrete disorder is 1 unit cell; that is, for a 1 unit cell layer, there is a finite probability of having 0 or 2 unit cells. For the superlattice containing a single unit cell  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  layer, the interdiffusion of Pr in the Y site is approximately 30%. This interdiffusion has important implications for the physics of these materials, which is beyond the scope of this article.

## CONCLUSIONS AND AVAILABILITY OF THE PROGRAM

In conclusion, we have developed a refinement method that allows the determination of quantitative structural information from X-ray diffraction on thin films and especially superlattices. The computer programs for a number of different computers, instruction manuals and relevant references can be obtained by writing directly to the authors of this article. A typical refinement takes approximately 10 minutes on a personal computer equipped with a 80486 processor. All diffraction spectra shown in this work were acquired using a Rigaku Rotating Anode Diffractometer.

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