Journal of Magnetism and Magnetic Materials 126 (1993) 65–70
North-Holland

journal of magnetism and magnetic materials

Quantitative X-ray diffraction from superlattices

Ivan K. Schuller [a] and Y. Bruynseraede

[a] *Physics Department-0319, University of California-San Diego, La Jolla, CA 92093-0319, USA*
[b] *Solid State Physics, Katholieke Universiteit-Leuven, Leuven 30001, Belgium*

We have developed a structural refinement method which allows the quantitative determination of structural disorder in superlattices. We present first a number of model calculations which give counterintuitive results. One such model calculation implies that structural disorder broadens diffraction line widths contrary to naive expectation. This then forms the basis for structural refinement in which the detailed line shapes are fit to obtain a quantitative determination of a variety of disorder parameters. The parameters obtained from the refinement were found to be in good quantitative agreement with other independent determinations.

1. Introduction

Natural and artificial superlattices have been the subject of studies for many years in a variety of fields including semiconductors physics, magnetism, superconductivity, transport and mechanical properties. In many cases, artificially grown superlattices [1,2], using vapor deposition methods, have been used to check ideas related to the physics of lower dimensionality, the effect of interfaces on the physical properties or the coupling of some physical property across an unlike material. Many of the effects under study depend in a very delicate way on the details of the structure and are intimately related to the arrangement of atoms in the superlattice. Examples of these types of effects include changes in the elastic properties, decrease of the superconducting transition temperature in high and low T_c materials, and changes in the magnetic properties of magnetic superlattices. Because of this it is of utmost importance to develop techniques which allow a quantitative determination of the structure at the atomic level.

A variety of techniques have been used for structural and chemical determination of thin films, including surface techniques at various stages of growth, such as High and Low Energy Electron Diffraction (HEED and LEED), Auger Electron and X-ray Photoelectron Spectroscopy (AES and XPS), Scanning Tunneling Microscopy (STM) and post growth quantitative electron microscopy, neutron and X-ray diffraction [2]. All these techniques have in common the need for detailed structural simulations, since in most cases the experimental data do not give a direct real space image of the structure, but some type of an average which varies from technique to technique. Because of this it is important to perform a comprehensive study using and comparing various techniques if the structure at the atomic level (with length scale of a few angstrom) is needed.

X-ray diffraction is a well established, non-destructive, easy to use technique for the determination of the structure of solids [3] and is one of the most extensively used techniques in the field of superlattices. We have dedicated a considerable amount of effort in the last decennium [4] towards extracting the maximum amount of quantitative structural information from ordinary X-ray diffraction from superlattices. The use of this technique is very attractive because it is easily available in most laboratories, it is non-destructive, and it avoids complicated sample preparation methods which may modify the material under study. Our main motivation behind this work was the observation that although X-ray diffraction spectra from superlattices are in qualitative agreement with simple models, detailed comparisons show quantitative disagreements [5]. For instance, fig. 1 shows the experimentally measured X-ray diffraction from a Mo/Ni superlattice together with a simulation assuming a perfect structure as given by the preparation parameters [6]. Although there is qualitative agreement between data and simulation, the experimentally measured lines are broader, have different relative intensities and are shifted with respect to the model calculation. Clearly disorder or deviation from a perfect structure must be taken into account.

We have devoted initially considerable effort in attempting to understand the effect of different types of disorder on the X-ray diffraction spectra. In many cases, we found results which were unexpected and contrary to the accepted 'wisdom in the field'. After gaining a qualitative understanding of the influence of various disorder parameters on the final diffraction

Correspondence to: Dr. I.K. Schuller, Physics Department-0319, University of California-San Diego, La Jolla, CA 92093-0319, USA.

0304-8853/93/$06.00

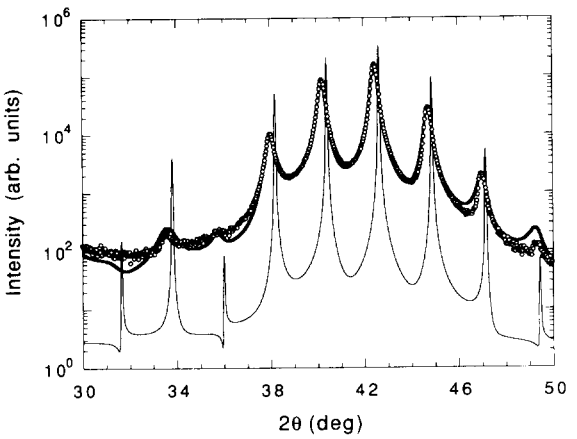

Fig. 1. Measured X-ray diffraction profile of a [Mo(20 Å)/Ni(22 Å)]$_{130}$ superlattice (○) and calculated spectra (thin line) using a model of a perfect superlattice. The thick line is the result of refinement procedure described in text. (See ref. [6]).

spectra, we developed a method which allows structural refinement of the disorder parameters using experimentally obtained X-ray diffraction. The results were then compared with independently measured parameters in order to determine the reliability of the method developed.

We will describe here briefly the different model calculations, emphasizing particularly those which give counterintuitive results and/or which form the basis for the refinement technique. Then we will briefly describe the refinement method and its application in a few representative cases in which the method has been successfully tested. For the sake of brevity we will only address diffraction with the scattering vector perpendicular to the layers (θ–2θ diffraction), although many of the considerations outlined here also apply when the scattering vector is in other directions. In addition, we will also give some ideas of future developments and directions in which this type of research should move.

2. Model calculations

Model calculations are very useful in providing conceptual ideas regarding the effects different parameters have on the X-ray diffraction spectra. Here we will present three examples of model calculations which give counter intuitive results. Therefore their incorrect incorporation into scattering models may not fit quantitatively the data and may give erroneous values for the roughness parameters. Moreover, as it will be shown in the next chapter, even those models which presumably are conceptually correct produce roughness parameters which are only in 10–25% agreement with independent measurements.

The first, most obvious approach towards understanding diffraction from disordered superlattices is to assume that the presence of uncorrelated layer thickness fluctuation is similar to thermal fluctuations. The main idea is that the interfaces fluctuate around the mean value given by the average layer thickness obtained from preparation parameters. Although this type of disorder maybe engineered into the samples, in general there is a fundamental conceptual difference between thermal and layer thickness fluctuations [7]. In classical treatments, thermal fluctuations are assumed to be noncumulative. As a consequence, diffraction line widths remain sharp with increasing temperature, and only their intensity decreases as given by a Debye–Waller formula. On the other hand, layer thickness fluctuations are intrinsically cumulative which affects the diffraction line widths and broadens them. This implies that a Debye–Waller formulation can only be applied to layer thickness fluctuation in very special cases. We showed sometime ago [7] that very slight amounts (of the order of 7%) of layer thickness fluctuations can completely wash out superlattice peaks in crystalline(Pb)–amorphous(Ge) superlattices. The simulated spectra (fig. 2) are in good agreement with the experimental results. This fact has important consequences for a quantitative understanding of the X-ray diffraction from superlattices. In general, the assumption of noncumulative layer thickness fluctuation underestimates the amount of disorder when compared to independent measurements.

The broadening described above has some important consequences which are perhaps counterintuitive to what one may expect from naive considerations. As an example, fig. 3 shows a model calculation for a lattice mismatched superlattice with layer thickness fluctuations included only in one of the constituents [8]. As the layer thickness fluctuations increase in layer b, the diffraction lines close to the q vector corresponding to layer a are broadened. The reason for this is that the superlattice peaks are a consequence of the coherent, constructive interference between layers; the interference between layers of type a is destroyed by the phase shifts introduced by thickness variations in layer b.

A third important consequence of layer thickness fluctuation induced broadening is the variation with lattice mismatch [8]. This is especially important for the field of metallic superlattices where in many cases superlattices are formed from lattice mismatched constituents. Fig. 4 shows the variation of the X-ray diffraction spectra with increasing lattice mismatch, but fixed amount of layer thickness fluctuation. It is

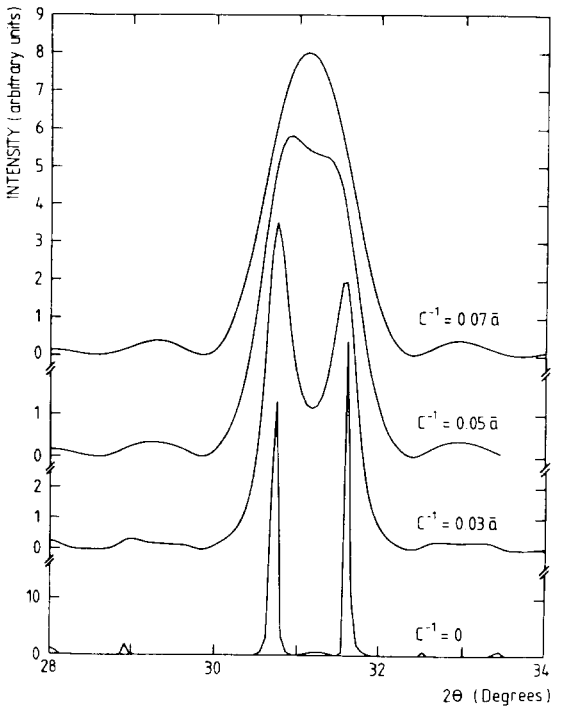

Fig. 2. Simulated high-angle $\theta-2\theta$ X-ray spectra for different values of layer thickness fluctuation. The parameter c^{-1} characterizes the layer thickness fluctuation. [7].

quite interesting that the linewidths broaden with increasing lattice mismatch. Therefore simple considerations, related to coherence lengths calculated from linewidths, are not sufficient when comparing superlattices prepared from constituents with different lattice parameters.

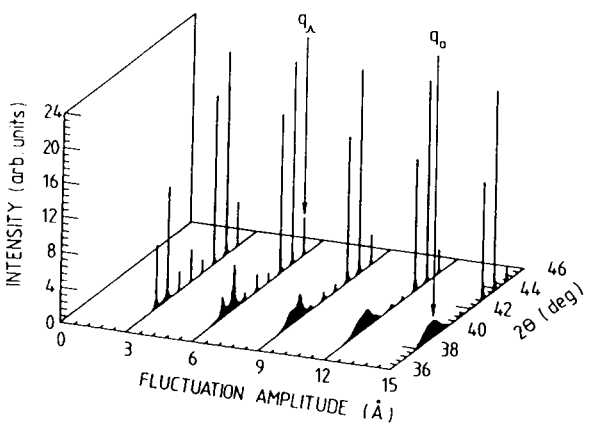

Fig. 3. Evolution of calculated high-angle spectra, as a function of layer thickness fluctuation added only on layer b. Note that the effect of roughness in one of the superlattice constituents (layer b) is to broaden the diffraction peaks corresponding to the other (layer a). [8].

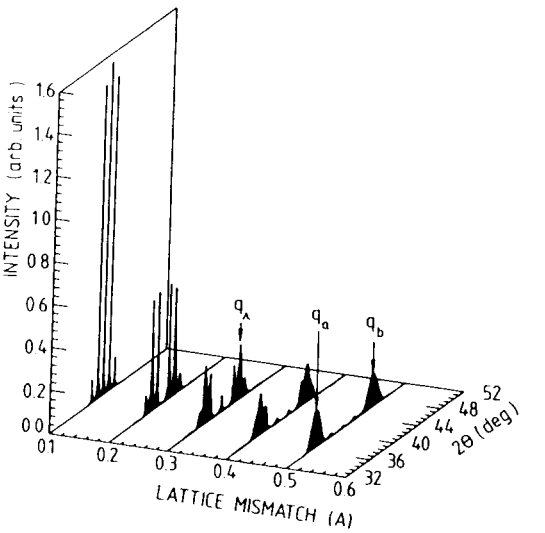

Fig. 4. Evolution of calculated high-angle spectra with increasing lattice mismatch but fixed layer thickness fluctuations. [8].

In addition to the issues discussed above, other types of disorder must be taken into account, including: lateral thickness variations, interdiffusion, formation of interfacial chemical compounds, changes in the interatomic distances due to epitaxial constraints ('strains') and so on. It is also important to stress that these effects are perhaps more important in the field of metallic superlattices than for semiconductors, because in this field lattice mismatched constituents have been studied more intensely. Moreover slight changes in the structural parameters are known to have drastic effects on the transport, magnetic, superconducting and mechanical properties. All this points to the fact that a quantitative analysis of the X-ray diffraction spectra is very important at this stage of the field where qualitative analysis is no longer sufficient.

3. Refinement

'Refinement of the structure' using diffraction data is a well known technique used for many years for the structural determination of complex materials. The general idea is that the structure can be determined quantitatively, with reasonably high accuracy, by performing a comparison between the experimentally measured diffraction data and model calculation. First the expected diffraction from a model, which is close to the expected structure is calculated. This then is compared to the actual data and agreement is defined if the two spectra agree within a predetermined statisti-

cal criterion. If there is a disagreement, the original model is modified, the diffraction spectra from the new structure is calculated and the comparison is performed again. This process is repeated until agreement in the sense described above is obtained. Well defined strategies and checks are presently available for structural refinement of bulk materials. The best known method of this kind is the so called Rietveld refinement [9] method which has been very successfully applied recently for the determination of structure of high temperature oxide superconductors.

The refinement method utilized for the determination of structure in superlattices [6] and thin films is similar in spirit to the one used to refine the structure of bulk materials; i.e. a comparison is made between experimental data and spectra obtained from model calculations. However a major difference exists between the two methods. In the ordinary refinement technique used for complex bulk materials, the basic assumption is that a unit cell exists which is repeated in space. The refined variables in this case are therefore the arrangement of atoms within this unit cell. The diffraction line broadenings are a consequence of the superposition of instrumentally broadened linewidths. On the other hand, for superlattices some of the important refined parameters, such as the layer thickness fluctuations, broaden diffraction linewidths even in the absence of line overlap or instrumental broadening. As a consequence, the mathematical treatment of structural refinement in superlattices as well as the attendant strategies and checks, are considerably different from the bulk.

The model used for structural refinement of superlattices consists of stacks of M bilayers of two materials. The layers are characterized by their structure factors, individual layer thicknesses and lattice parameters, and interfacial distances. In general, no assumptions are made about the crystal structure of the layers. In the most thoroughly studied cases the layers are assumed to be statistically independent, so correlated effects are not included. This simplifies considerably the mathematical treatment, although it is not a strictly necessary assumption. Two types of averages are taken into account; coherent averages of the scattering function and incoherent averages of the intensities. A somewhat subtle point results from these averages. The type of scattering geometry described here (i.e. θ–2θ diffraction), is such that the scattering vector $\Delta \boldsymbol{q} = \boldsymbol{q}_{\text{incident}} - \boldsymbol{q}_{\text{scattered}}$ is perpendicular to the layers. Because of this it is commonly believed that only structure perpendicular to the layers is contained in this data. However, since the models are constructed from randomly stacked columns and since both coherent and incoherent averages are taken, the inplane roughness is taken into account for length scales larger than the lateral coherent averaging distance (typically a few hundred angstrom). It is important to stress at this point that as with all nonlinear multivariate optimization techniques, it is crucial to test for the stability of the solution. The reason for this is that, in these kinds of techniques, it is possible to fall into a local minimum in parameter space and thus obtain false physical results.

In order to check whether this methodology can in fact be applied and to ascertain whether the results that are obtained are meaningful, we have performed a number of tests [6]. The stability of the solutions were checked by performing refinements using a variety of different initial conditions or by fixing some of the parameters and comparing the results obtained by fixing different parameters. The results from the refinement were checked for internal consistency by comparing with out of plane diffraction or by comparing high and low angle diffraction. Artificially disordered samples were prepared with known layer thickness variations. Layer thickness fluctuations obtained from growth parameters were then compared to the ones obtained from the refinement method. In some cases where independent data on structural variations could be obtained these were compared with results obtained from the refinement. Finally, in those cases where indirect evidence (for instance, magnetization) is available this was compared to the implications for the structure as obtained from the refinement. In all cases studied, to some accuracy, which varies from parameter to parameter, satisfactory agreement was found.

For the sake of brevity we will present here an example of one such a check. Fig. 5 shows the X-ray diffraction spectra from two Ag/Mn superlattices prepared by Molecular Beam Epitaxy (MBE). An excellent fit can be obtained between the experimental data and the refined spectrum using the technique outlined above over more than four orders of magnitude in intensity. The parameters obtained from the refinement of the high angle data shown in fig. 5a) were used in the low angle dynamical calculation shown in fig. 5c). Notice that the parameters are capable of describing not only the positions and widths but the whole spectrum with reasonably high accuracy. The parameters refined in these studies include layer thickness fluctuations as well as changes in the interfacial lattice parameters. These interfacial lattice parameters were determined independently by Extended X-ray Fine Structure Spectroscopy (EXAFS) [10] study and in two different X-ray Photoelectron Diffraction (XPD) [11,12] studies. In all cases the lattice parameters obtained in this fashion were within the experimental error and were determined with an accuracy better than 3%. Of

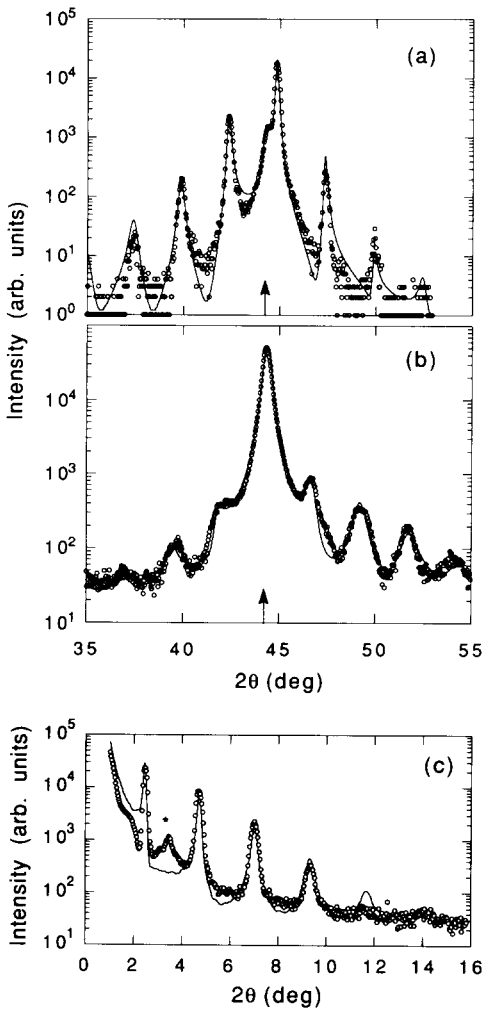

Fig. 5. Experimental (○) and calculated (solid line) high-angle X-ray-diffraction profiles for (a) [Ag(33 Å)/Mn(6 Å)]$_{10}$ and (b) [Ag(31 Å)/mn(8 Å)]$_{20}$ superlattices using the refinement technique described in the text. (c) Experimental (○) and calculated (solid line) low-angle X-ray-diffraction profile for the [Ag(33 Å)/Mn(6 Å)]$_{60}$ superlattice using the refined parameters determined from the high-angle profile in (a). * indicates the peak resulting from capping layers. [6].

course, in addition to the independently determined lattice parameters this study also provided data on the layer thickness fluctuations and average thicknesses of the layers.

4. Conclusions and future studies

X-ray diffraction from superlattices is at a stage at which quantitative information can be obtained regarding disorder parameters and structural details from the experimental data. In all cases studied, the parameters obtained using the refinement technique satisfactorily described both high and low angle data and were in excellent agreement with independent measurements.

Ongoing studies include the development of an integrated dynamical refinement method which can help optimize disorder parameters using small angle diffraction data. Diffuse X-ray diffraction data contain detailed information regarding disorder and should be studied in detail using more sensitive probes such as are available at synchrotron radiation sources. Out of plane scattering studies are also developed which should be incorporated into similar refinement programs. Similar refinement studies are underway for incorporation into structural studies using electron diffraction (High and Low Energy) techniques.

The refinement program together with a detailed instruction manual, for a variety of computers is available by writing directly to the authors of this article.

We thank our collaborators of many years in this work. Their names are mentioned in the reference section. We also thank B.T. Jonker, G. Prinz, R. Oberle and R. Cammarata for allowing the use of their X-ray data and S. Sinha, C. Falco, R. Dynes, J. Jorgensen, M. Grimsditch, D. McWhan, B. Clemens, and G. Felcher for helpful discussion. This work was supported by DOE Grant No. DE-FG03-87ER45332 at UCSD and the Belgian Inter University Institute for Nuclear Science, the Inter University Atraction Poles and Concerted Action Programs at KUL. Special thanks should go to the NATO for funding and stimulating this international collaboration.

References

[1] See for instance: Physics, Fabrication and Applications of Multilayered Structures, ed. by P. Dhez and C. Weisbuch (Plenum Press, New York, 1988): Metallic Superlattices, Artificially Structured Materials, ed. T. Shinjo and T. Takada (Elsevier, Amsterdam, 1987).

[2] For a recent review see for instance: MRS Bulletin Volume XVII, No. 12 (1992) and Volume XVIII, No. 1 (1993).

[3] See for instance: A. Guinier, X-ray Diffraction in Crystals, Imperfect Crystals and Amorphous Materials (Freeman, San Francisco, CA, 1963).

[4] For an early report see: I.K. Schuller, Phys. Rev. Lett. 44 (1980) 1597.

[5] See for instance: T.W. Barbee, MRS Bulletin, Volume XV, No. 2, 37 (1990); for a recent review see J.M. Slaughter and C.M. Falco, J. Magn. Magn. Mater. 126 (1993) 3.

[6] E.E. Fullerton, I.K. Schuller, H. Vanderstraeten and Y. Bruynseraede, Phys. Rev. B 45 (1992) 9292.

[7] W. Sevenhans, M. Gijs, Y. Bruynseraede, H. Homma and I.K. Schuller, Phys. Rev. B. 34 (1986) 5955.
[8] J.-R. Locquet, D. Neerinck, L. Stockman, Y. Bruynseraede and I.K. Schuller, Phys. Rev. B. 39 (1989) 13338.
[9] For a recent review see: Advances in the Rietveld Method, ed. R.A. Young (Oxford University Press, Oxford, 1992).
[10] Y.U. Idzerda, B.T. Jonker, W.T. Elam and G.A. Prinz, J. Appl. Phys. 67, (1989) 5385.
[11] B.T. Jonker, J.J. Krebs and G.A. Prinz, Phys. Rev. B. 39 (1989) 1399.
[12] W.F. Egelhoff, Jr., I. Jacob, J.M. Rudd, J.F. Cochran and B. Heinrich, J. Vac. Sci. Technol. A-8 (1990) 1582.