

Elastic Anomalies in Superlattices

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The presence and origin of elastic anomalies in superlattices, interfaces, composites, and nanocrystalline materials has been a subject of much interest and controversy in recent years.^{1,2} In particular, superlattices are being used as model systems to study the effect of interfaces on the mechanical properties of novel materials. Early claims³⁻⁵ of anomalously large enhancements of the biaxial and flexural moduli of Au/Ni and Cu/Ni superlattices ("supermodulus effect") created considerable controversy and contradictory reports in the experimental and theoretical literature. To understand the mechanical properties of superlattices and their implication for other types of nanofabricated materials, it is important to look critically at the field.

Superlattices have been fabricated in different laboratories by a variety of preparation methods and have been characterized structurally and elastically to various degrees. Because of this, before addressing any sophisticated theoretical issues regarding elastic anomalies, it is important to understand in detail the experimental techniques and the possible pitfalls in the experimental determination of mechanical properties of thin films. Once the presence or absence of the effect is ascertained, the need arises to understand any possible experimental correlations with other structural and/or physical properties. These correlations can be used to address issues regarding the possible origins of the effect and their theoretical basis. It will be apparent from this article that slight changes in structural properties are correlated with relatively large elastic anomalies. Consequently, this points to the importance of precise, comprehensive, and detailed structural characterization. With our present understanding of the physics of superlattices, qualitative studies are no longer sufficient!

Mechanical Measurements

Many experimental techniques have been used to study the mechanical properties of metallic superlattices. These techniques can be divided into two categories, depending on whether the technique requires the film to be removed from the substrate or not: (1) techniques that require removal from the substrate include bulge test,⁵ vibrating reed,⁶ vibrating membrane,⁷ and continuous ultrasonic wave measurements;⁸ (2) techniques that do not require removal from the substrate include Brillouin scattering,⁹ pico-reflectance,¹⁰ surface acoustic wave,¹¹ and nano-indenter.¹²

The obvious question arises — does removal from the substrate alter the mechanical properties of the films? We believe that most results to date imply that removal from the substrate does not alter substantially the mechanical properties of the films. However, it should be recognized that many of the measurements on self-supporting films are subject to experimental artifacts caused by the removal from the substrate. Tables I and II list the various experimental techniques used to study the mechanical properties of metallic superlattices, the elastic properties that they can determine, and possible experimental difficulties.

Examining Tables I and II clearly shows that the *complete* characterization of the mechanical properties of thin films requires the application of a wide battery of tests, on the *same samples*, together with simultaneous structural characterization. Since no single laboratory can apply all these techniques, it is desirable to exchange samples between the various research laboratories.

Structural Properties

The number of systems that have been studied is very large and includes com-

binations of elements, compounds, and alloys. Although correlations between physical properties and the binary thermodynamic phase diagram of the constituents have been pointed out,¹ we believe that this only affects the mechanical properties through changes in the structure, which are known to cause drastic effects on their transport properties.¹³ Moreover, small changes in the structure of thin films are theoretically expected to have drastic effects on the mechanical properties. For instance, an early theoretical model¹⁴ has shown that small changes (about a few percent) in the lattice parameters may drastically affect the elastic properties. It is therefore important to perform precise, detailed structural studies¹⁵⁻¹⁶ to ascertain whether the origin of the elastic anomalies is correlated and/or caused by structural or electronic effects.

X-ray diffraction has been one of the most successful, precise techniques for determining the structure of thin films and superlattices. Although x-ray diffraction has been used for many years for precise, quantitative determinations of the structure of *bulk* materials, to date its application to superlattices has only been semiquantitative. The reason is that many of the properties of interest, such as magnitude and type of interfacial roughness, interdiffusion, and lattice parameter changes, can only be obtained by modeling and fitting to x-ray diffraction spectra. The methodology for these fits is only recently emerging and has not yet been applied and compared with mechanical measurements.

Although detailed information on the interface structure of a superlattice requires some degree of modeling, we note that the average lattice spacing *perpendicular* to the growth direction is independent of the model used. This average as a function of modulation wavelength (Λ) has been determined for a number of systems, and in many cases elastic anomalies have been correlated with these lattice constant changes. The *in-plane* lattice parameters are seldom measured and have usually been inferred by using the Poisson's ratios of the materials. Unfortunately, using Poisson's ratios to determine lattice parameters may be incorrect. Several investigations in the epitaxial literature¹⁷⁻¹⁸ have shown that it is possible to have a simultaneous expansion in both the perpendicular and parallel directions to the substrate, clearly indicating a breakdown of the Poisson ratio argument.

This again shows that it is important to determine structural parameters *experimentally* without relying on theoretical considerations.

Figure 1 shows the average perpendicular lattice parameter in Cu/Nb superlattices; the lattice expands as Λ decreases to ~ 20 Å, and then returns to the average value.¹⁹ In addition, below $\Lambda = 20$ Å, the x-ray line widths broaden considerably, indicating that a substantial amount of disorder has set in. Note that although the lattice expansions are quite small (a few percent), they correspond to large internal strains. These types of expansions have now been observed in several superlattices; caution should be used in comparing different systems that may have varying degrees of interfacial imperfections, such as roughness, interdiffusion, etc.

Mechanical Properties

A large number of superlattice systems have been investigated in search of anomalies in their elastic properties. Many of the measurements have been questioned, either based on a reanalysis of the original data or on independent measurements. Cu/Ni is a classical example. After the original report of an enormous hardening of the biaxial modulus,⁴ one report found no anomaly.²⁰ Later experiments confirmed the presence of an anomaly in the flexural modulus,²² but recent measurements of the flexural²³ and shear moduli²³⁻²⁴ have again claimed the absence of an effect. From the latter measurements,²³ the biaxial (Y_B) and Young's (Y) moduli were inferred, which also showed no evidence for the large original effects. Similar conflicting results arise for Cu/Pd. The first measurements⁵ showed anomalous behavior in Y_B at $\Lambda \sim 20$ Å. However, re-analysis of the original data²¹ claimed that the anomaly is an experimental artifact. Recent results⁸ on F, Y, Y_B , and C_{66} (Figure 2a) show no anomalies in the 13–40 Å range, but Brillouin scattering²⁵ (Figure 2b) results over the $\Lambda = 15$ –100 Å range exhibit anomalous behavior in C_{44} .

Despite these controversies, the presence of elastic anomalies is well established in some systems. Figure 3 shows the shear elastic constants in Cu/Nb superlattices measured using Brillouin scattering on two sets of samples prepared and measured in different experimental setups by two independent groups.²⁶⁻²⁷ Unquestionably, the anomaly is present and reproducible. Note, however, that the softening is at most 35%. A comparison of the elastic anomalies

Table I: Techniques for Mechanical Property Measurements on Self-Supporting Thin Films.

(Y = Young's, Y_B = Biaxial, F = Flexural, C_{ij} = elastic constant)

Technique	Elastic Constant Determined	Affected by Warping	Affected by Brittleness	Other
Bulge Tester ⁵	Y_B	x	?	Clamping
Vibrating Reed ⁶	Y, F	x		
Vibrating Drum ⁷	Y_B	x		Large area needed
Continuous Ultrasonic Wave ⁸	Y, Y_B, F, C_{66}	x	x	Extra tension applied

Table II: Techniques for Mechanical Property Measurements on Supported Thin Films. (C_{ij} = elastic constant)

Technique	Elastic Constant Determined	Problem
Brillouin Scattering ⁹	$C_{11}, C_{12}, C_{13}, C_{33}, C_{44}$	Needs excellent quality surfaces. No coupling of light in some cases.
Pico-reflectance ¹⁰	C_{33}	Depends on smoothness of film-substrate interface.
Surface Acoustic Wave ¹¹	C_{44}	Film must be deposited on piezoelectric substrate. Complicated deconvolution of the substrate contribution.
Nano-indenter ¹²	?	Complicated combination of elastic constants. Contribution of substrate not clear. Plastic deformations are induced.

lies in V/Ni superlattices¹¹ using Brillouin scattering from samples on deposited Al_2O_3 substrates and using surface acoustic waves on samples deposited on $LiNbO_3$ substrates shows they are in good quantitative agreement (Figure 4). The reproducibility of these measurements indicates that the substrate does not play a major role in determining the elastic properties of the superlattice. Figure 5 shows the shear elastic constant of Mo/Ni superlattices measured using Brillouin scattering²⁸ and of the C_{33} elastic stiffness constant using pico-reflectance.¹⁰ Again, two sets of data from independent groups on independently prepared samples show the presence of a strong anomaly around $\Lambda \sim 20$ Å. Clearly, careful measurements from different groups give reproducible results that, in some cases, exhibit elastic anomalies.

Examining the experiments done to date indicates that recent measurements that claim the observation of elas-

tic anomalies are all correlated with structural anomalies, more specifically with expansions or contractions of the lattice parameter perpendicular to the layers. Differences in electronic properties do not seem to play a major role. This seems to imply that theories that invoke electronic effects to explain elastic anomalies are possibly not valid. They may, however, play an indirect role through the structural changes that they cause.

Having established the presence of elastic anomalies, an immediate question arises—Is the effect localized at the interfaces, or is it a bulk effect? The answer is somewhat controversial since two different groups arrived at opposite conclusions in the same system. Khan et al.¹⁹ compared three series of Mo/Ni samples with individual layer thicknesses in the ratios 3:1, 1:1 and 1:3. They concluded that it is impossible to explain the observed changes in the shear elastic constant by assuming the

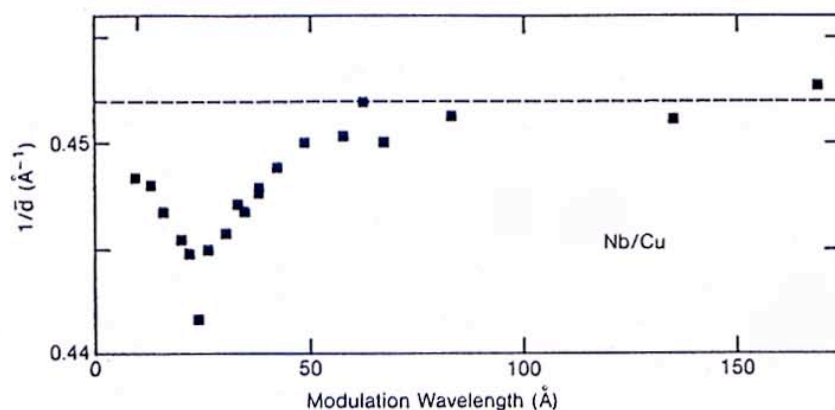


Figure 1. Inverse of average lattice parameter \bar{d} vs. multilayer modulation (Λ) for Cu/Nb superlattices.¹⁹ Note, that to a Λ of 20 Å, the lattice expands and then it contracts toward its original value. The broken line is the average calculated from bulk values. The widths of the x-ray peaks below $\Lambda \sim 20$ Å are substantially broader, indicating that these samples are considerably disordered.

effect to be concentrated at the interface. On the other hand, Clemens and Eesley¹⁰ compared the behavior of Mo/Ni, Pt/Ni, and Ti/Ni superlattices and claimed that the Λ dependence of the lattice constant and elastic anomaly is proof that the elastic anomaly is an interfacial effect. Further work is necessary to clarify this point.

The effect of heavy ion irradiation on the elastic anomalies may address this issue and has been studied in Ag/Co²⁹ and Nb/Si³⁰ superlattices. The effect of irradiation was found to restore the elastic constant toward the mean average value expected from a continuum theory and found in thick layers. The structural effect of ion bombardment is, however, controversial: it may relieve the interfacial strains, it may even smooth the interfaces, or it may mix the constituents in different layers. Detailed structural measurements and calculations are under way in the ion irradiated samples to address these points.

Theoretical Explanations

A surprisingly large number of different models have been proposed to explain the observed anomalies. It was first suggested that additional periodicity introduced by the layering could modify the electronic band structure which would, in turn, lead to modifications in elastic properties.³¹⁻³² "Coherency" strains (i.e., the interfacial strain caused by the in-plane mismatch of the constituents) have also been sug-

gested as the source of elastic anomalies.³³ Recent approaches have ascribed the effects to electron transfer between adjacent metallic layers³⁴ or to "surface tension" at each interface.³⁵ The model for which the most complete calculations have been performed is one based on the idea of "grain boundary" interfaces.³⁶ An example³⁶ of these theoretical results is shown in Figure 6; the shear constant behavior is similar to that observed by Brillouin scattering in many systems and the biaxial modulus hardenings are qualitatively similar to that observed by mechanical techniques in other systems.

In assessing the above explanations, it should be borne in mind that some of the models may be very closely related. For example, grain boundary type calculations show that the atomic rearrangement at a surface leads to a term that can be viewed as a surface tension.³⁵ It is also possible that different explanations are needed for different types of superlattices. The most serious drawback encountered experimentally in trying to determine which (if any) model is the correct one is that all models rely on a structural or electronic effect that has not been verified independently.

The following two examples illustrate the difficulties encountered in evaluating a particular model. Calculations of the effects of coherency strains in systems where the strain is shared by both constituents³⁷ lead to very small effects; however, it can still be argued that far

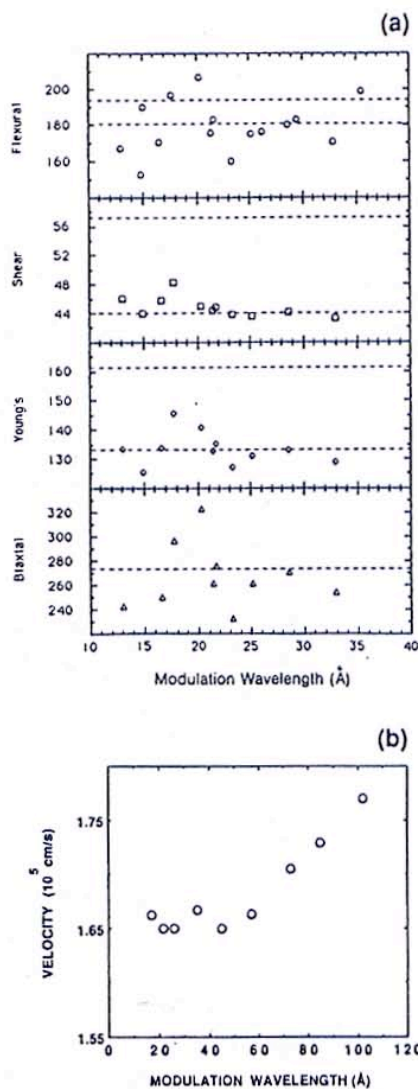


Figure 2. Elastic moduli of Cu/Pd superlattices: (a) various moduli reported in Reference 8 showing no anomaly in the range $\Lambda = 13$ to 35 Å; (b) velocity of surface waves reported in Reference 25 showing a change in velocity at $\sim \Lambda = 90$ Å.

from the interface, the strains relax so that effects need not have opposite signs in each constituent. The electron transfer model³⁴ predicts no effect in superlattices in which one of the constituents is a nonmetal; since an effect is observed in Nb/Si, it would appear that the model is incorrect. Proponents of the model, however,³⁴ argue that the experimental

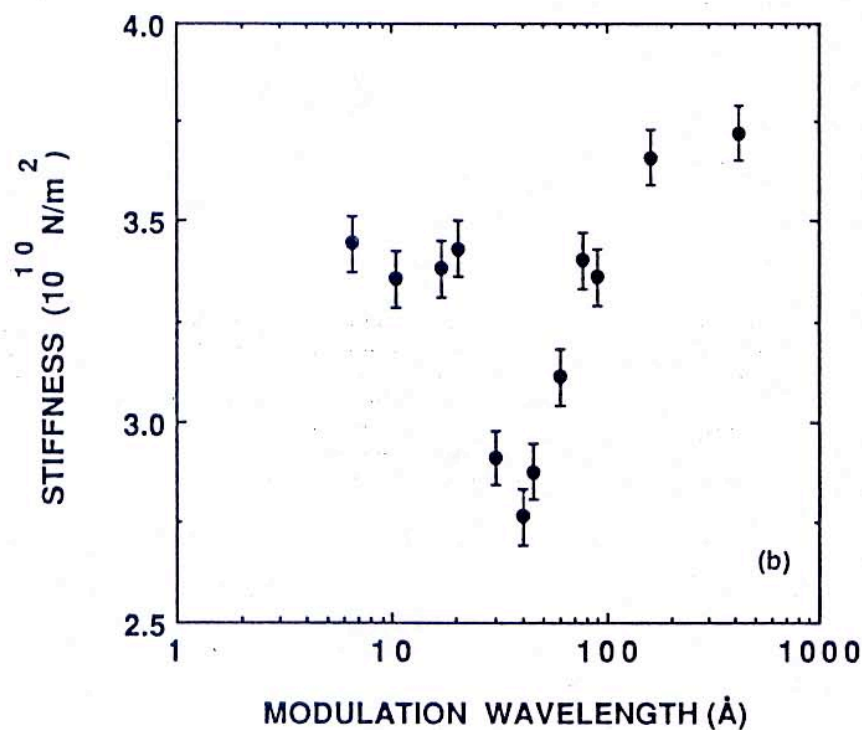
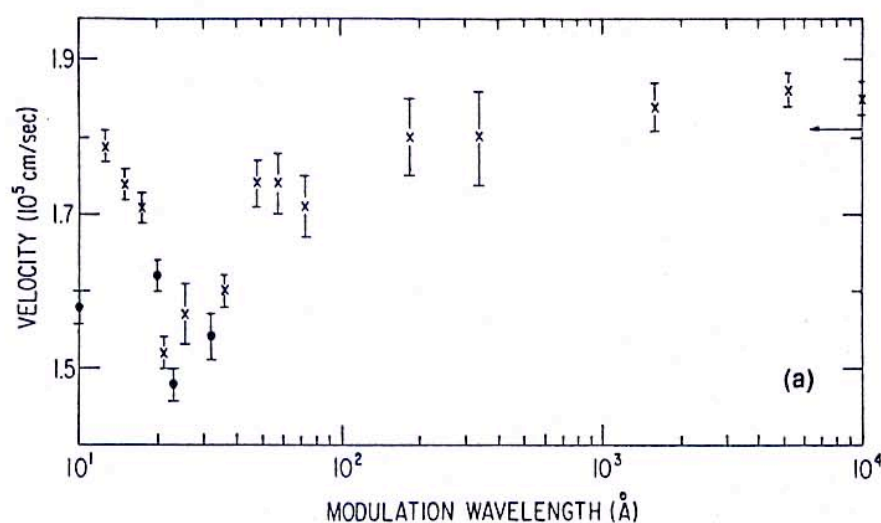


Figure 3. Shear elastic constant C_{44} measured in Cu/Nb superlattices using Brillouin Scattering. The two independent sets of measurements (a) Reference 26 and (b) Reference 27 are in good agreement.

evidence for the formation of interface layers of Si_2Nb invalidates the assumptions of a constant ratio of constituent materials. Similar contradictions and counterarguments can be found for all proposed models. To conclude, it seems that the grain boundary model is pres-

ently the one on firmest footing, but even this model is unable to explain all experimental results; in its present form it does not explain the hardening observed in a shear constant in Au/Cr³⁸ nor does it straightforwardly account for anomalies in compositionally modu-

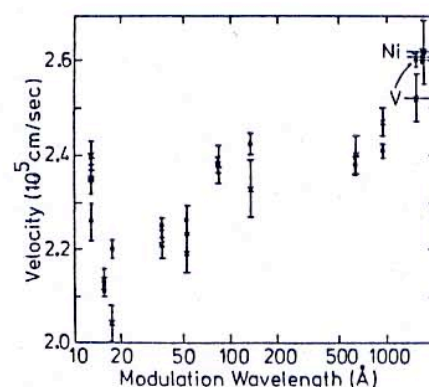


Figure 4. Shear elastic constant anomalies in V/Ni superlattices using Brillouin Scattering (crosses) and surface acoustic waves (dots).¹¹

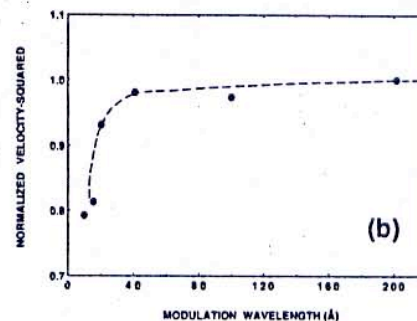
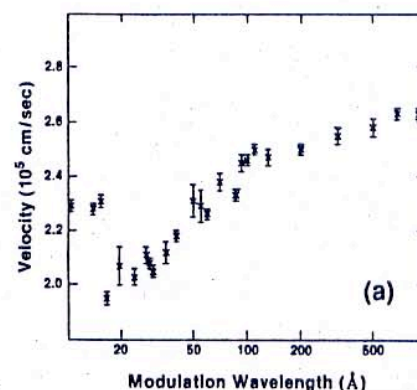


Figure 5. (a) Shear elastic constant²⁸ and (b) perpendicular elastic stiffness (C_{33}) vs. superlattice wavelength¹⁰ for Mo/Ni superlattices.

lated systems where grain boundaries are unlikely.

Clearly, more theoretical work and detailed comparisons with experiments are needed.

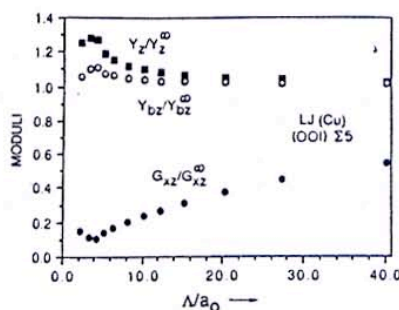


Figure 6. Calculated moduli (G : shear, Y_1 : Young's, Y_2 : biaxial) vs. modulation wavelength (λ) normalized by the lattice spacing (a_0) in a grain boundary superlattice.³⁶

Conclusions

Elastic anomalies have been observed in superlattices with small modulation wavelengths. The anomalies are peculiar to some systems and absent in others, but no clear-cut correlations are found with the electronic structure of the constituents. This seems to rule out theoretical explanations based on electronic effects. A strong correlation has been found, however, between the elastic anomalies and changes in the average lattice constant of the superlattice.

Many questions remain controversial or unanswered: Is the original report of the large anomaly on the biaxial modulus of Cu/Ni correct? Whenever present, is the effect restricted to the interface? Is ion bombardment relaxing the strains and consequently restoring the elastic constants to their mean value? Are the different elastic constants always correlated in the same fashion? For instance, is a softening in the shear modulus always correlated with a hardening in the biaxial modulus? What is the relationship to the elastic anomalies observed in nanophase materials and to the large strengths observed in composite materials? Could more than one effect be operational? With so many questions to be answered, we believe that from the experimental standpoint the most serious problem to be addressed is that of the microscopic structure of the interfaces. Until such information becomes available it appears unlikely that it will be possible to irrefutably dis-

criminate between the proposed mechanisms. Much quantitative structural work is required using x-rays and electron diffraction, transmission electron microscopy, and EXAFS — together with simultaneous elastic constant measurements. Theoretical predictions regarding structure as well as elastic constants, together with detailed predictions for specific systems are a must.

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