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Metallic Superlattices: Structural and Elastic Properties

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Abstract. The fabrication and structural characterization of metallic superlattices is discussed. Methods to determine the elastic properties of these materials (which can only be prepared as thin films) are reviewed and the results obtained using various techniques are summarized. Contrary to theoretical expectation, the elastic properties are found to depend on the modulation wavelength.

From the vast literature that exists on thin film growth [1] it may be argued on energy grounds that if (in thermodynamic equilibrium) material A grows as a smooth layer on material B, then B will grow as islands on material A. This conclusion would preclude the possibility of preparing thinly layered superlattices. Experimentally however, it has been found that with modern technologies, like MBE and sputtering, it is indeed possible to fabricate such structures [2] and it must therefore be argued that kinetic effects are also important in determining thin film growth.

That layered structures can be produced is clearly shown in Fig. 1 which shows θ-2θ x-ray scans for Mo/Ni superlattices [3]. In samples with large modulation wavelengths (Λ) peaks are observed at the Mo[110] and Ni[111] positions: this is expected since materials usually grow normally to the densest planes; (110) for bcc, (111) for fcc and (001) for hcp. As Λ is reduced additional peaks appear indicating the existence of a superstructure. It can be easily shown that peaks are expected at

$$\frac{1}{\bar{a}} \pm \frac{n}{\Lambda} \qquad (1)$$

where $\bar{a}$ is the average lattice constant and n an integer. The intensity of the peaks depends on many factors including the lattice parameters of the constituents, scattering factors, roughness, etc. We shall return to this point later; for the moment it is sufficient to note that from the x-ray spectra and Eq. 1, Λ and $\bar{a}$ may be obtained without resorting to any specific model.

Having produced these novel materials there is of course interest in determining their physical properties. Many of them have been discussed extensively in the literature [2,4], here we will concentrate only on the elastic properties of superlattices. In the continuum limit it is straightforward to calculate the elastic constants (C_{ij}) of a layered system [5-7]. Two main features arise from these calculations: the C_{ij} of the superlattice are an average of those of its constituents, i.e.,

$$C_{ij}(B) < C_{ij} < C_{ij}(A)\,, \qquad (2)$$

and they are also independent of Λ. Figure 2 shows the results obtained for the biaxial modulus (Y_B) of Cu/Ni superlattices [8] in clear contradiction with theory. What is even more spectacular (and controversial) is that Y_B for Cu/Ni (Λ = 20 Å) is larger than Y_B for diamond! The reason for the controversy lies in the severe difficulties encountered in measuring elastic constants of materials which can only be prepared as thin films. There have been a number of techniques developed to deal with this problem [9-16] but most of them require the removal of thin film from the substrate and are consequently open to criticism. Brillouin scattering [11] is one of the few techniques which does not require the removal of the film from the substrate and it has played an important role in the study of metallic superlattices.

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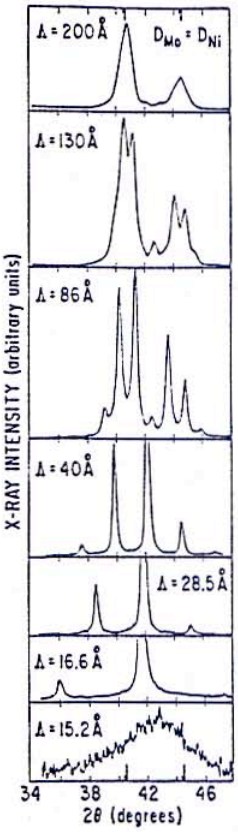

Fig. 1. X-ray spectra of Mo/Ni superlattices (Ref. 3).

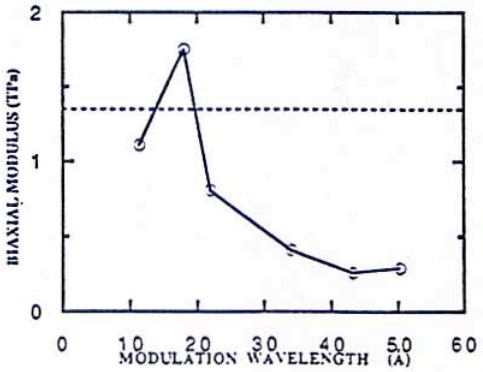

Fig. 2. Biaxial modulus of Cu/Ni supoerlattices (Ref. 8). The dashed line is the biaxial modulus of diamond.

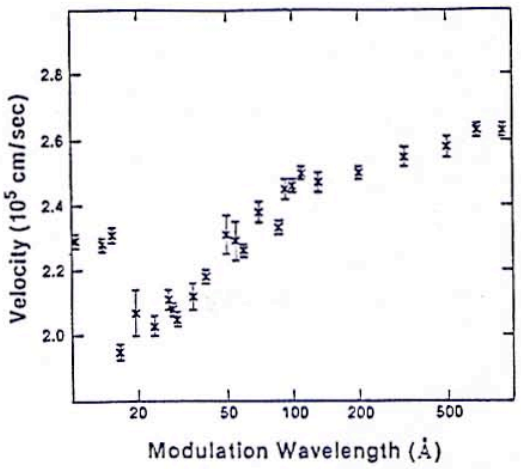

Fig. 3. Surface wave velocity in Mo/Ni superlattices (Ref. 3).

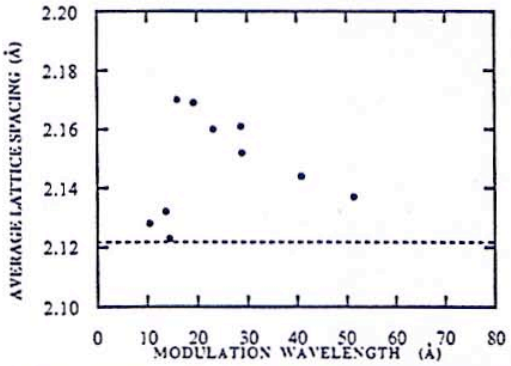

Fig. 4. Average lattice spacing perpendicular to the layering of Mo/Ni superlattices (Ref. 3).

Figure 3 shows the surface wave velocity in Mo/Ni superlattices determined by Brillouin scattering [3]. Since the velocity is related to the elastic constants its Λ dependence is also in contradiction with continuum theory [5-7]. Table I contains a summary of all the experimental determinations of elastic constants of superlattices performed to date: it contains the system studied, C_{ij} measured, existence of an anomaly, correlation with a structural change (to be discussed below) and the reference. Although there are some contradictions for some systems (notably Cu/Ni), the inescapable conclusion that can be drawn from Table I is that the elastic constants of superlattices are anomalous in the sense that they do not behave as expected from continuum theory.

Before diving into the possible origins of the effect it is interesting to note that the results given in Table I show no evident correlation with the crystal structure of the constituents (viz., bcc, fcc, hcp, etc.) nor with the fabrication method (viz., sputtering or evaporation). From the experimental standpoint however, it has been found that in all cases where the average lattice constant has been determined from x-rays, there is a strong correlation between changes in $\bar{a}$ with respect to the average of the bulk materials and anomalies in the elastic properties.

Table I. Superlattices in which elastic constants have been determined

System	Elastic Constant	Anomaly	Correl. Struc.	Ref.
Cu/Ni	Y_B	Yes		8
	Y,F	Yes		17
	Y_B, T, F, C_{66}	No		18
	C_{44}	No		19
Cu/Pd	Y_B	Yes		9
	Y_B, Y, F, C_{66}	No		13
	C_{44}	Yes		20
Mo/Ni	C_{44}	Yes	Yes	3
	C_{33}	Yes	Yes	12
Pt/Ni	C_{33}	Yes	Yes	12
Ti/Ni	C_{33}	Yes	Yes	12
Cu/Nb	C_{44}	Yes	Yes	21, 22
	C_{44}, C_{33}	Yes		23
	Y_B	Yes	Yes	24
	C_{12}	?	?	25
NbN/AlN	C_{44}	No	Yes	26
GaAs/AlAs	C_{33}, C_{44}	Yes	Yes	27
Nb/Si	C_{44}	Yes	Yes	28
Au/Cr	C_{44}	Yes	Yes	29
Ag/Pd	Y_B	Yes		30
Au/Ni	Y_B	Yes		9
Cu/Au	Y_B	No		30
Cu/Al	?	Yes		31
V/Ni	C_{44}	Yes	Yes	15
Fe/Pd	C_{44}, C_{11}?	Yes		32
Co/Ag	C_{44}	Yes	Yes	33,34
Mo/Ta	C_{44}	Yes	Yes	35
	C_{33}	No	No	35
Co/Cu	C_{44}	Yes	Yes	36

System	Elastic Constant	Anomaly	Correl. Struc.	Ref.
Fe/Cu	C_{44}	Yes	Yes	37
ZrN/AlN	C_{33}	Yes		38

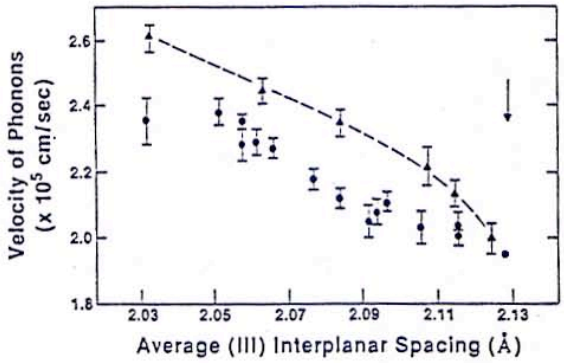

Fig. 5. Molecular dynamics calculations (Ref. 39) of a shear sound velocity as a function of strain in a Ni crystal.

This correlation is indicated in the fourth column of Table I: In all cases but one, whenever changes in $\bar{a}$ were detected by x-rays, anomalies were also observed in some elastic constant. The exception is a Λ independent C_{33} in Mo/Ta where changes in $\bar{a}$ were present; note however that C_{44} does indeed change in this superlattice. Figure 4 shows the experimentally determined $\bar{a}$ for Mo/Ni obtained from the spectra in Fig. 1; it clearly has very similar behavior to the velocity shown in Fig. 3. The correlation between $\bar{a}$ and C_{ij} was explained in Ref. 39, using Molecular Dynamics techniques where it was shown that the elastic softening is a direct consequence of the lattice expansion. These calculations are shown in Fig. 5 together with the experimental results of Fig. 3 plotted as a function of measured lattice expansion. The origin of the expansion remains however unexplained by these calculations.

There have been a number of models proposed to explain the observed behavior [40-51]. At present it has not been possible to determine which one of the models is correct. This is due to the fact that none of the models are capable of predicting *a priori* the behavior expected for a given system. Furthermore, for those models that have some predictive capabilities there is at least one experimental piece of evidence which contradicts the prediction. Notwithstanding the above comments, the model described in Refs. 44-47 is at present the most likely candidate.

In order to understand at a microscopic level the elastic anomalies in superlattices two avenues of research appear to be necessary: the theoretical models must be enhanced so that they acquire predictive capabilities and, more experimental work is required to determine the detailed atomic structure at interfaces. The latter should be aimed at obtaining structural information parallel to the layers as well as roughness, interdiffusion, etc. Figure 6 shows an x-ray spectrum from a Mo/Ni superlattice and two model fits: the upper fit was obtained using the bulk properties of Mo and Ni and "perfect" interfaces, the lower portion is a fit containing 7 fitting parameters (individual lattice constants of the constituents, nonuniform lattice expansion, roughness, etc. etc.) [52]. Although excellent fits can be obtained enormous care must be taken before the fit parameters can be assigned a reliable physical meaning.

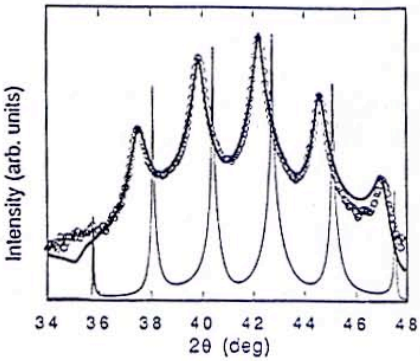

Fig. 6. Experimental x-ray spectrum from a Mo/Ni superlattice (dots) and fits to the data (full line). The light line is obtained using bulk values for the relevant parameters, the heavy line is a fit with 7 fitting parameters.

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