Effect of strain on the elastic properties of superlattices

Ivan K. Schuller and M. Grimsditch
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 4 June 1986; accepted 7 August 1986)

The elastic properties of superlattices are strongly affected by strains in these materials. Elastic anomalies have been found in Nb/Cu, Mo/Ni, V/Ni, and Au/Cr superlattices. The strains measured with x rays explain quantitatively the elastic softening in Mo/Ni. An extension of these arguments explains not only the softening of Nb/Cu but the hardening *and* softening observed in Au/Cr. The origin of the strains is not known at the present time.

The elastic properties of stratified media was first investigated theoretically by Bruggeman[1] in 1937. Since then there have been a number of theoretical treatments of the subject.[2–6] A general conclusion which can be drawn from all these investigations is that the elastic properties ought to be independent of Λ and depend only on the elastic constants of the constituents and their relative fraction, provided the wavelength of the deformation is larger than the stratification or modulation wavelength (Λ) of the material.

In sharp contrast with the above-mentioned expectation, the elastic properties of a number of superlattices have been found to be strongly dependent on the modulation wavelength (a review is given in Ref. 7). Following from the statement in the preceding paragraph, it can be concluded that since the relative fractions of the constituents are held constant in the experiments, the elastic properties of at least one of the constituents must be different from their values in the bulk.

The investigation of elastic properties of superlattices is a nontrivial problem since these materials are usually prepared in the form of thin films ($\lesssim 1\ \mu$m) in which conventional ultrasonic techniques are not applicable. For this reason unconventional techniques must be used to measure the elastic properties and in most cases these require that the superlattice film be removed from the substrate on which it was deposited.[7] An exception to this rule is Brillouin scattering which can be performed on samples without removal from the substrate. As with all other techniques used to study superlattices, Brillouin scattering from opaque samples yields information on only one elastic modulus; a shear elastic constant which is related to the velocity of a surface wave on the film. It is fortunate, on the other hand, that the surface waves probed in Brillouin experiments have appreciable amplitudes only to a depth of ~ 3000 Å. This greatly simplifies the interpretation of the results since the measured sound velocity is not affected by the mechanical properties of the substrate provided the films are thicker than $\sim 0.5\ \mu$m.

Using Brillouin scattering, we have observed anomalous elastic behavior in all the metallic superlattices we have studied to date: Nb/Cu,[8] Mo/Ni,[9] V/Ni,[10] and Au/Cr.[11] In order to confirm that the observed effects are not technique dependent, very sophisticated ultrasonic methods were used to study the V/Ni system.[10] This study found essentially the same results as those yielded by the Brillouin scattering experiments. We point out[10] that this ultrasonic technique, although considerably more cumbersome than Brillouin scattering, offers some advantages: Like Brillouin scattering, it is a nondestructive technique, and furthermore does not require a very high surface quality, phonon attenuations can be determined, and temperature dependent measurements add no serious difficulty.

In the cases of Mo/Ni,[9] Nb/Cu,[8] and Au/Cr[11] the anomalies in the elastic constants were shown to be concomitant with changes in the lattice spacing perpendicular to the layers as determined by x rays.[12] For the case of Mo/Ni,[9] where a very complete study as a function of Λ and relative fraction of Mo to Ni was performed, the elastic constant measurements indicated that the anomalous constituent in this system is Ni. In Ref. 13 the elastic softening was then explained in terms of the lattice strain in the following manner: Since Ni is known to be responsible for the elastic softening in Mo/Ni it was assumed that all the lattice strain (i.e., expansion) also occurs in the Ni; a molecular dynamics calculation was then performed for a Ni crystal which was strained to reproduce the experimentally measured strain and the sound velocities in such a system evaluated. Figure 1 shows the experimentally measured (circles) and theoretically calculated (triangle) velocity of the acoustic phonons as a function of Ni interplanar spacing. The theoretical calculations were performed with *no* adjustable parameters. However, since the theoretical calculation is for a shear *bulk* wave, whereas the experiment measures a surface wave, these two velocities differ by a factor which lies in the range[14] 0.87–1.00; the agreement between the experiment and the molecu-

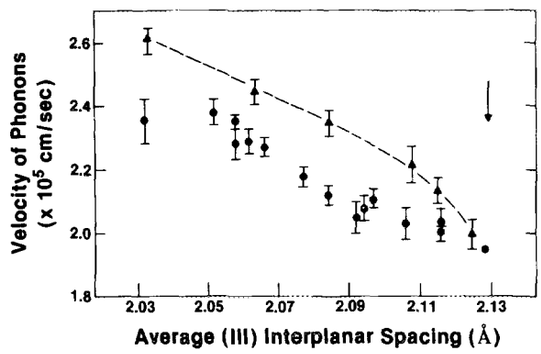

FIG. 1. Velocity of phonons vs average nickel [111] interplanar spacing. Dots are measured values by Brillouin scattering and triangles are values from molecular dynamics calculations. The arrow indicates the value at which the structure becomes highly disordered in the Mo/Ni superlattices and where the molecular dynamics crystal fails.

 0734-211X/86/061444-03$01.00

lar dynamics calculation is excellent. Moreover, the arrow in the graph indicates the point at which the strain becomes so large that the "computer" crystal becomes unstable and breaks apart. This point corresponds to the maximum expansion observed in the laboratory beyond which the superlattice becomes disordered. Since the break up point is obtained with no adjustable parameters it is clear that the central idea of the calculation, i.e., "that the strain causes the anomalous elastic behavior," is correct. We believe this was the first time where a quantitative relationship was established between a physical property and strain in a superlattice.

A simpler but far less rigorous approach is to consider that the elastic moduli of a material will behave in a manner determined by simple analogy with the Murnaghan equation of state[15]

$$B = B_o\left(\frac{a_o}{a}\right)^{3B'}, \tag{1}$$

where B is the bulk modulus, a the lattice constant, B' is a number which lies between 4 and 7 for almost all materials and a subscript o indicates a reference point. This equation has been generalized successfully to describe the longitudinal elastic constants in a layered material.[16] Generalizing it ad hoc for shear waves we can write

$$v \cong v_o\left(\frac{a_o}{a}\right)^{3B'/2}. \tag{2}$$

Choosing B' as 6 reproduces the softening observed in Mo/Ni to within 5%!

In Fig. 2 we present the measured changes in the average lattice constant for Nb/Cu superlattices.[8,12] Using Eq. (2), the results of Fig. 2, and keeping $B' = 6$, we calculate the velocity as a function of Λ. In Fig. 3 we present these results and also the experimental results of Ref. 8. It can be seen that the simple assumption of a strain dependent elastic constant explains the results extremely well. The deviations observed below $\Lambda \sim 20$ are due to the fact that at small thicknesses the Cu superlattice becomes disordered and it no longer can be thought of as layered with strained crystalline constituents.

The other case where extensive x-ray data are available is Au/Cr.[11] This system is different from the two systems mentioned above in that the sound velocity is found to *increase* with decreasing Λ to a maximum at $\Lambda \sim 70$ Å below which it decreases again. Furthermore, contrary to Mo/Ni and Nb/Cu where the superlattice x-ray peaks disappeared at the minimum in velocity, in Au/Cr well defined superlattice peaks are observed throughout the anomalous elastic range. The x-ray investigation of Au/Cr was also able to separate the contributions arising from the Au and Cr, and found that Au contracts monotonically while Cr expands monotonically as Λ is decreased. Using the expression for a shear elastic constant (C) of a superlattice[6]

$$\frac{\Lambda}{C} = \frac{d_{Au}}{C_{Au}} + \frac{d_{Cr}}{C_{Cr}}, \tag{3}$$

and assuming that the elastic constants of Au and Cr behave as described in Eq. (1), a velocity dependence in qualitative agreement with the experimental results is obtained.[11]

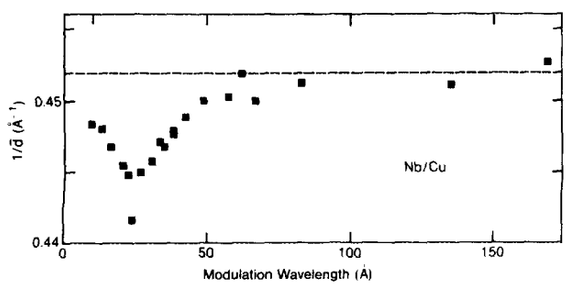

FIG. 2. Reciprocal of the average lattice spacing $\bar{d}$ vs modulation wavelength for Nb/Cu superlattices.

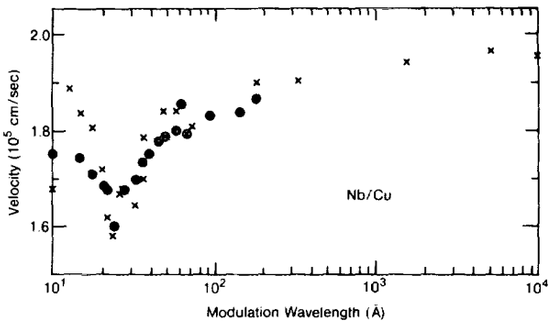

FIG. 3. Surface wave velocity of N/Cu superlattices as a function of modulation wavelength. Crosses are experimental results from Ref. 8 and dots are the values calculated as described in the text.

We feel that the evidence given above, even though the analysis is extremely simple, indicates that the strain produced in fabricating superlattices is responsible for the anomalous elastic properties observed in these systems. The origin of these strains is not yet clear; however, since the measured strains *in* the plane are much smaller than those perpendicular to it, we do not believe that the latter arise from lattice mismatch in the plane which through the Poisson ratio expands or contracts the lattice perpendicular to the layering. The origin most likely lies in an electronic effect, perhaps electron transfer due to the different electronegativities of the constituents. Total energy band structure calculations as a function of lattice spacing might clarify the origin of this expansion.

In conclusion, we have shown that strains in superlattices play a fundamental role in determining the elastic properties of the system.

Acknowledgments: This work was supported by the Office of Naval Research Contract No. N00014-83-F-0031 and the U.S. Department of Energy, BES-Materials Sciences, under Contract No. W-31-109-ENG-38.

[1] D. Bruggeman, Ann. Phys. (Leipzig) **29**, 160 (1937).
[2] S. M. Rytov, Akust. Zh. **2**, 71 (1956) [Sov. Phys. Acoust. **2**, 68 (1956)].
[3] T. J. Delph, G. Herrmann, and R. K. Kaul, J. Appl. Mech. **45**, 343 (1978).
[4] J. Sapriel, B. Djafari-Rouhani, and L. Dobrzynski, Surf. Sci. **126**, 197 (1983).

[5]F. Nizzoli, in *Proceedings of the 17th International Conference on the Physics of Semiconductors,* edited by J. D. Chadi and W. A. Harrison (Springer, New York, 1985), p. 1145.
[6]M. Grimsditch, Phys. Rev. B **31**, 6818 (1985); M. Grimsditch and F. Nizzoli, *ibid.* **33**, 5891 (1986).
[7]I. K. Schuller, in *IEEE 1985 Ultrasonics Symposium,* edited by B. R. McAvoy (IEEE, New York, 1986), p. 1093.
[8]A. Kueny, M. Grimsditch, K. Miyano, I. Banerjee, C. Falco, and I. Schuller, Phys. Rev. Lett. **48**, 166 (1982).
[9]M. R. Khan, C. S. L. Chun, G. P. Felcher, M. Grimsditch, A. Kueny, C. M. Falco, and I. K. Schuller, Phys. Rev. B **27**, 7186 (1983).
[10]R. Danner, R. P. Huebener, C. S. L. Chun, M. Grimsditch, and I. K. Schuller, Phys. Rev. B **33**, 3696 (1986).
[11]P. Bisanti, M. Brodsky, G. Felcher, M. Grimsditch, and L. Sill (in preparation).
[12]I. K. Schuller, Phys. Rev. Lett. **44**, 1597 (1980).
[13]I. K. Schuller and A. Rahman, Phys. Rev. Lett. **50**, 1377 (1983).
[14]G. W. Farnell, in *Physical Acoustics,* edited by W. P. Mason (Academic, New York, 1969), Vol. 6, p. 109.
[15]F. D. Murnaghan, Proc. Natl. Acad. Sci. **30**, 244 (1944).
[16]A. Polian, J. M. Besson, M. Grimsditch, and H. Vogt, Phys. Rev. B **25**, 2767 (1982).