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Continuum elasticity analysis of the enhanced modulus effect in metal-alloy superlattice films

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Large enchancements in certain elastic moduli (by more than 100%) of compositionally modulated films of certain metal alloys, in particular copper-nickel, have been reported. Among the explanations proposed for the phenomenon, it has been suggested that the enhancement is due to coherency-induced strains and preliminary calculations based on nonlinear continuum elasticity have been reported in support of this idea. We have explored this mechanism in detail for copper-nickel superlattices. The variation of the elastic constants with strain (including up to fourth-order elastic constants) as well as with alloy composition have been considered. The average elastic moduli have been determined for a sinusoidally modulated film. We have found that the biaxial moduli $Y[001]$ and $Y[111]$ vary as the square of the modulation amplitude (A). The biaxial modulus $Y[001]$ shows a small enhancement, on the order of a few percent, while $Y[111]$ actually *decreases*, by a few percent, from its value for the homogeneous alloy. We have also found a similar decrease of $Y[111]$ for layered copper-nickel superlattices with sharp interfaces. The relative contributions of the strain and composition dependences of the elastic constants to the net change have been investigated. While the strain dependence alone increases the modulus of the modulated film, the composition dependence decreases it. The third- and fourth-order elastic constants (reflecting the strain dependence of the elastic moduli) have to be much larger than their experimentally determined values (even accounting for experimental uncertainty) in order to get even a small enhancement of $Y[111]$. We conclude that the enhancement cannot be explained by a continuum model of the coherency-strained superlattice, but note that an atomic-scale effect cannot be ruled out.

I. INTRODUCTION

Over the last decade, reports[1–5] of great enhancement of the elastic moduli of certain alloy superlattices (formed by a periodic modulation of their composition in one dimension along specific crystallographic directions) have generated much interest,[6–9] as well as some controversy.[10] For sinusoidal modulation, the enhancement arises over a limited range of wavelengths and varies as the square of the amplitude. While this phenomenon has understandably generated a great deal of technological interest, it has also aroused considerable theoretical interest.[6,7,11,12] Although a number of possible explanations have been proposed,[13] a clear theoretical understanding of the phenomenon is not yet available.

The proposed explanations fall largely into two categories. One class invokes changes in the electronic structure due to the compositional modulation in order to explain the enhancement of the elastic moduli. In this approach the effect is most often explained as the consequence of tangential contact between the Fermi surface and the surface of the Brillouin zone perpendicular to the direction of modulation.[1,3–7] (The increased repeat distance in the direction of modulation results in a folding over of the Brillouin zone in this direction.) It has also been suggested that the enhancement might arise from changes in the electronic structure due to the formation of a large number of interfaces, since it is well known that electronic properties of solid interfaces are quite different from those of the bulk.

An alternative approach is to explain the increase in the modulus as arising, at least in part, from the large biaxial strains introduced by the coherency between layers perpendicular to the modulation direction. Jankowski and Tsakalakos[11,12] have taken this approach and have tried to explain the effect on the basis of nonlinear elasticity. They have shown that the biaxial modulus $Y[001]$ of a noble metal (Cu, Ag, or Au) undergoes a large increase when the metal is subjected to biaxial strains of a few percent in the (001) plane.

In this paper we extend their approach and compute $Y[001]$ as well as $Y[111]$ for compositionally modulated films of copper-nickel alloys [modulated perpendicular to the (001) and (111) planes] on the basis of nonlinear continuum elasticity. We have chosen the copper-nickel system simply as a representative test case and the analysis can be trivially extended to other combinations of metals. In addition to accounting for the change of the elastic constants due to strain (which is treated including up to fourth-order elastic constants), we also consider the dependence of the elastic constants on the composition of the alloy. We present the details and the results of our computations as well as a discussion of those results.

II. ELASTIC CONSTANTS OF A MODULATED FILM

A. Effects of strain

The effective elastic constants of a strained crystal can be approximated using the higher-order elastic constants. These higher-order constants are usually defined as the constants involved in a series expansion of the crystal potential energy in terms of the Lagrangian strain tensor and can be determined experimentally.[14] The elastic constants of the strained crystal can be expressed in terms of the higher-order constants as

$$C_{ijkl}=(\rho'/\rho)\alpha_{im}\alpha_{jn}\alpha_{kp}\alpha_{lq}(C^0_{mnpq}+C^0_{mnpqrs}\eta_{rs}+\tfrac{1}{2}C^0_{mnpqrsuv}\eta_{rs}\eta_{uv}+\cdots)\,, \tag{1}$$

where ρ' and ρ are, respectively, the densities of the strained and unstrained crystals, C^0_{mnpq}, C^0_{mnpqrs}, and $C^0_{mnpqrsuv}$ are, respectively, the second-, third-, and fourth-order elastic constants of the unstrained crystal, η_{ij} are components of the Lagrangian strain tensor,

$$\eta_{ij}=(\alpha_{ik}\alpha_{jk}-\delta_{ij})/2\ , \tag{2}$$

and α_{ij} are components of the deformation matrix defined as

$$\alpha_{ij}=\frac{\partial r_i'}{\partial r_j}\ , \tag{3}$$

where $\mathbf{r}'$ and $\mathbf{r}$ are the coordinate vectors in the strained and unstrained crystals, respectively, and δ_{ij} is the Kronecker delta. Unless it is stated otherwise, Latin indices run over the three coordinate directions x, y, and z, and summation over repeated indices is implied.

In the case of a film grown with [001] texture, the biaxial coherency-induced strains in the different layers can be conveniently taken to be along the x and y axes of the unit cell. Then the expression in Eq. (1) can be used directly with

$$\begin{aligned}&\alpha_{11}=\alpha_{22}=1+\epsilon\ ,\\ &\alpha_{33}=1+\epsilon_3\ ,\\ &\alpha_{ij}=0\ \text{ for } i\neq j\ ,\end{aligned} \tag{4}$$

where

$$\epsilon_3=-2(C_{13}/C_{33})\epsilon\ . \tag{5}$$

Here, ϵ is the coherency-induced strain in the plane of the layer. In the state of biaxial strain [in the (001) plane], as Tsakalakos and Jankowski have pointed out,[11] the crystal is no longer cubic but tetragonal. The biaxial modulus is then given by

$$Y[001]=C_{11}+C_{12}-2(C_{13}^2/C_{33})\ . \tag{6}$$

When the modulation direction is normal to the (111) plane, the expressions in Eqs. (4) and (5) can be used to evaluate the deformation matrix and the strain tensor provided the elastic constants are defined in the coordinate system of the film (z axis normal to the film plane, i.e., along the direction of modulation, and x and y axes in the plane of the film). The elastic constants, deformation matrix, and Lagrangian strain tensor in the film coordinate system can be easily related to those defined in the principal coordinate system of the crystal with the help of the coordinate-transformation matrix.[15,16] The uniaxial symmetry of the (111) plane permits the use of Eq. (6) as it stands[16] to compute the biaxial modulus $Y[111]$, which is the same as $Y[001]$ in the film coordinates.

B. Variation of elastic constants with alloy composition

In a composition-modulated film, the elastic constants of different layers differ not only because they are in different states of strain, but also because their compositions differ. In order to account for this, we introduce $C_{ijkl\ldots,cc\ldots}$—the first and higher derivatives of elastic constants of different orders with respect to composition, where c is a variable characterizing the composition of the alloy—typically the proportion of one component of the alloy, or its deviation from some predetermined value. Here, each c in the subscript implies a derivative with respect to c and no summation over c is implied. We can then expand the effective elastic constants of a layer of arbitrary composition, c, which is in a state of strain described by a Lagrangian strain tensor, η_{ij}, in a series about an unstrained layer at some known composition, c_0. This results in a generalization of Eq. (1) to

$$C_{ijkl}=(\rho'/\rho)\alpha_{im}\alpha_{jn}\alpha_{kp}\alpha_{lq}[C^0_{mnpq}+C^0_{mnpqrs}\eta_{rs}+C^0_{mnpq,c}\Delta c+C^0_{mnpqrs,c}\eta_{rs}\Delta c+\tfrac{1}{2}C^0_{mnpqrsuv}\eta_{rs}\eta_{uv}+\tfrac{1}{2}C^0_{mnpq,cc}(\Delta c)^2+\cdots]\ . \tag{7}$$

Here, $\Delta c=c-c_0$ and the elastic constants, $C^0_{mnpq\ldots}$, and their derivatives with respect to the composition variable, $C^0_{mnpq\ldots,c}$ and $C^0_{mnpq\ldots,cc}$ are evaluated at $c=c_0$. For our computations, we have only retained terms up to second order in Δc and η_{ij}.

C. Average elastic moduli of modulated films

As with any composite material, the definition of the effective elastic constants of the modulated film in terms of those of the constituents involves some assumptions. The variation of the composition through the film is taken to be one dimensional, in accordance with the experimental system. The composition is assumed to be homogeneous in a plane perpendicular to the modulation direction (taken to be the z direction) and varies only with z. We then treat the composition-modulated film as a continuum. In order for this continuum approximation to be justifiable, the wavelength of modulation must be much larger than the interplanar spacing along the direction of modulation. Of course, in the films on which the experiments have been performed this criterion is not really satisfied. The typical wavelengths (at which the enhancement of the moduli is reported to occur) is on the order of only a few interplanar spacings. Nonetheless, we use the continuum approximation to address this problem in order that we may apply the theory of nonlinear elasticity to it. In the remainder of the paper, unless otherwise stated, the word "layer" will be used to refer to an infinitesimally thin slice of the continuum perpendicular to the z direction.

In this approach, the actual value of the wavelength is immaterial, since, the solid being approximated by a continuum, there is no other length, such as an interplanar spacing, to which it can be compared. The decrease of the enhanced modulus as the wavelength is changed (away from the value at which the modulus reaches its maximum) must be explained by appealing to mechanisms which reduce the coherency-induced strains. As the wavelength is increased, it is expected that the increasing elastic energy stored in the strained crystal will at some point be released by the formation of misfit dislocations.[17] At this point the strains are largely relieved though not completely removed. Hence, it is easy to see why there is no enhancement in the elastic moduli at large wavelengths. The fall at shorter wavelengths is usually explained by arguing that since the wavelength is of the order of only a few interplanar spacings, the modulation of the composition is not well developed and, hence, large strains are not developed.[11]

In determining the effective elastic constants of the film, we have taken the effective primary elastic stiffness constants of the film to be simple Voigt averages of those of the component layers. It is known[18,19] that this averaging procedure provides a lowest upper bound for the elastic constants of the composite material. Since the structure of the film is periodic in the z direction, it is necessary to average the elastic constants only over one wavelength of modulation. We evaluate the average values of the primary elastic constants, transform these to the film coordinate system, and hence determine the biaxial modulus in the plane of the film. We also evaluate the biaxial modulus of each layer and average this quantity over the repeat length. The difference between the two quantities is on the order of one part in a thousand. It should be noted that the averaging eliminates any variation of the elastic moduli with odd powers of the amplitude, to which both Δc and η_{ij} are proportional. Hence, since dependence on higher (such as fourth) powers of the amplitude is expected to be weak, it is expected that the averaged value of the biaxial modulus will vary as the square of the amplitude. We also point out that even in the absence of the terms bilinear in Δc and η_{ij} the elastic moduli can vary nonlinearly with A because of the nonlinearity introduced by the prefactors in Eq. (7). This is what gives rise to the curvature of Figs. 2—4 in Ref. 12. So, even in the absence of the higher-order terms in Eq. (7), the averaged elastic modulus is expected to vary as the square of the amplitude.

III. RESULTS

We have computed the average values of the elastic stiffnesses for a composition-modulated copper-nickel film using two models for the variation of the composition over the thickness of the film. In the first instance, we have considered the case of a sinusoidally modulated film where the composition of the film (proportion of one component, say copper) varies along the direction of modulation as

$$c(z)=c_0+A\cos(2\pi z/\lambda)\ . \tag{8}$$

Here, c_0 is the average proportion of copper in the film (we have taken $c_0=0.5$), while λ and A are the wavelength and amplitude of modulation, respectively. In this case, since we also have inversion symmetry about $z=\lambda/2$, it is only necessary to average over one half-wavelength. In order that Eq. (8) be physically meaningful, we must have $A\le c_0$, as well as $A\le 1-c_0$. Note that the values of A, as determined in the experiments, do not satisfy these criteria for all the films for which an enhancement has been reported.[20] This indicates deviations from simple sinusoidal modulation.

At the other extreme, we have considered the case in which there is no interdiffusion between the copper and the nickel so that the interfaces between the copper-rich regions and the nickel-rich regions are perfectly sharp. The variation of the composition across one repeat length is then in the form of a square wave:

$$c(z)=\begin{cases} c_1 & \text{for } 0\le z<\mu\lambda\ , \\ c_2 & \text{for } \mu\lambda\le z<\lambda\ , \end{cases} \tag{9}$$

where λ is the repeat length of the modulation and μ is the ratio of the thickness of a copper-rich region to the repeat length; c_1 and c_2 are the proportions of copper in the copper-rich and nickel-rich regions, respectively. The average composition of the film is then given by

$$c_0=\mu c_1+(1-\mu)c_2\ , \tag{10}$$

and the quantities c_1, c_2, and μ can be varied independently within physical limits.

In either case, different layers are strained differently. While some regions are in a state of compression, others are in a state of tension. The strain arises because coherency between layers requires that all the layers have the same lattice constant, $\bar{a}$, and hence the same interatomic distance in the layer, whereas each layer with composition $c(z)$ has a different equilibrium lattice constant, $a(z)$, that depends on its composition. We have taken the equilibrium lattice constant to vary linearly with composition. This is in good agreement with the reported variation of density with alloy composition.[18] The strain in a layer at position z is then represented by

$$\epsilon=[a(z)-\bar{a}]/a(z)\ , \tag{11}$$

where $a(z)$ is the equilibrium lattice constant of the layer in question. Since the elastic constants of copper and nickel are different, it might be suggested that the strains in the copper-rich and the nickel-rich regions are different and that the average lattice constant in the plane of the film is different from that of the corresponding homogeneous alloy. The actual value of $\bar{a}$ must be the one that minimizes the total elastic energy of the system. Hence, we compute the elastic energies of the strained films at different choices of $\bar{a}$, using the elastic constants of the strained layers, and determine the equilibrium value of $\bar{a}$. This procedure will be assumed to have been followed in all cases discussed here unless it is otherwise stated.

We have used experimental values of the primary elastic constants of copper, nickel, and copper-nickel alloys of different compositions.[21] The composition of the homogeneous alloy is taken to be $Cu_{0.5+x}Ni_{0.5-x}$, so that in Eq. (7) we have $c_0=0.5$ and $\Delta c = x$. The second-order elastic constants C_{ijkl} are fitted to a quadratic in x, and the third-order constants C_{ijklmn} to a straight line. These fits are used to determine the constants $C^0_{ijkl,x}$, $C^0_{ijkl,xx}$, and $C^0_{ijklmn,x}$, where the superscript 0 indicates that the quantities are evaluated at $x=0$. The values of the fourth-order elastic constants, $C^0_{ijklmnpq}$, are taken as the averages of the values for pure copper and for pure nickel.

In Fig. 1 we show the variation of the biaxial modulus $Y[001]$ of pure copper with biaxial strain in the [001] plane computed with and without the fourth-order constants. For the purposes of the computations represented here (Figs. 1 and 2), the second- and third-order elastic constants have been taken from the pseudopotential calculations of Jankowski and Tsakalakos[11,12] and of Thomas,[22] respectively. The simplifying relations between the different fourth-order constants given by Hiki and Granato[14] have been assumed to hold and following their arguments we have taken (using abbreviated indices) $C^0_{1111}=10C^0_{111}$. The dashed line in Fig. 1 shows the results of including only up to third-order elastic constants. The rapid variation of the biaxial modulus with changes in the strain and the resulting significant enhancement of the biaxial modulus with a compression of a few percent are clearly seen. These results are in essential agreement with those of Jankowski and Tsakalakos,[12] who included up to third-order elastic constants. The solid line shows the results of including up to fourth-order elastic constants. It can be seen that in either case the curvature, or nonlinearity, which Jankowski and Tsakalakos[12] have claimed is responsible for the enhancement that survives upon averaging over compressed and extended layers, is small. In fact, if the fourth-order elastic constants are neglected, the curvature is very small and negative, which would imply a small *decrease* in $Y[001]$, upon averaging, with increasing magnitude of strain. When the fourth-order constants are included, the sign of the curvature is reversed but its magnitude is still small and a strain of a few percent produces an increase of only a few percent in the averaged value of $Y[001]$. This is illustrated more clearly in Fig. 2, where the even part of the change in the biaxial modulus,

$$Y_e[001]=(Y[001]\,|_{\epsilon=\epsilon_0}+Y[001]\,|_{\epsilon=-\epsilon_0}-2Y[001]\,|_{\epsilon=0})/2\,, \qquad (12)$$

is plotted against ϵ_0, the magnitude of the strain. Figure 3 shows the variation of $Y[111]$ for $Cu_{0.5}Ni_{0.5}$ with biaxial strain. Experimental values[21] have been used for elastic constants of all orders. Note that while there is an enhancement in the value of $Y[111]$, similar to that in the case of $Y[001]$, the curvature in the plot is again small.

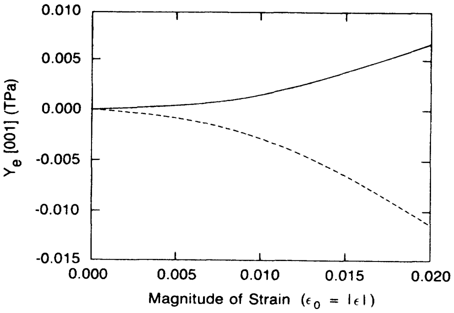

FIG. 2. The even part of the change in $Y[001]$ of pure copper (from Fig. 1) plotted vs the magnitude of the biaxial strain, ϵ_0. The dashed (solid) line shows the results of retaining up to third- (fourth-) order elastic constants.

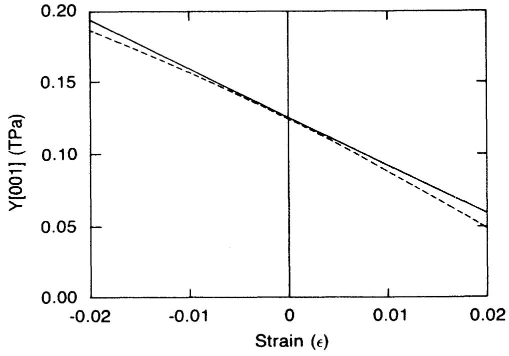

FIG. 1. Variation of the biaxial modulus $Y[001]$ of pure copper with biaxial strain keeping up to third-order (dashed line) and fourth-order (solid line) elastic constants.

Results of our computations for sinusoidally modulated films (with $c_0=0.5$) are shown in Figs. 4–9. Experimental values[21] for elastic constants of all orders have been used as described above. Figure 4 shows, for $A=0.5$, the variation of the elastic energy (in arbitrary units) and the biaxial modulus, $Y[111]$, with $\bar{a}$ for a sinusoidally modulated film of $Cu_{0.5}Ni_{0.5}$. It can be seen that the minimum

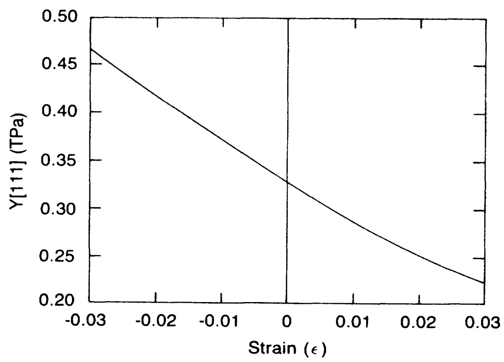

FIG. 3. Variation of $Y[111]$ with biaxial strain in a homogeneous $Cu_{0.5}Ni_{0.5}$ film including up to fourth-order elastic constants.

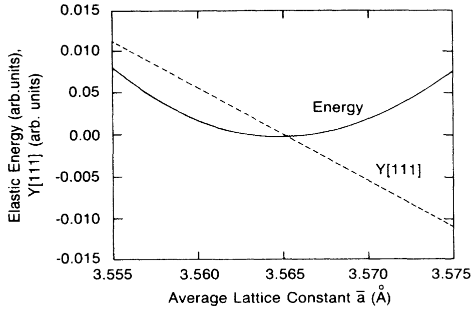

FIG. 4. Variation of elastic energy and $Y[111]$ with average lattice constant $\bar{a}$ for a sinusoidally modulated copper-nickel film with $A=0.5$.

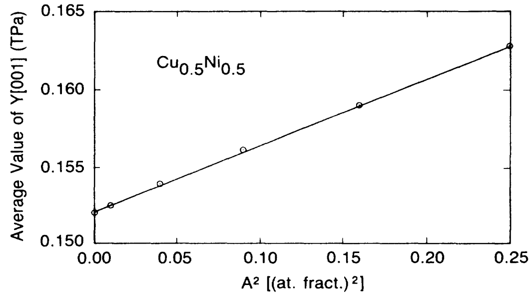

FIG. 6. Plot of $Y[001]$ vs the square of the amplitude of modulation, A^2, for a $Cu_{0.5}Ni_{0.5}$ film.

in the energy occurs when $\bar{a}$ is equal to the lattice constant of the homogeneous alloy $Cu_{0.5}Ni_{0.5}$, i.e., the average of the lattice constants[23] of copper (3.61 Å) and nickel (3.52 Å). This appears to hold in general—the value of $\bar{a}$ which minimizes the elastic energy is the equilibrium lattice constant of the alloy with the same average composition as the modulated film. Closer scrutiny reveals a deviation to a slightly lower value but the difference is insignificant. A significant deviation might have reduced the near-complete cancellation between the changes in elastic constants between the compressed and extended regions and might thus have led to a larger effect.

Figure 5 shows the variation of $Y[001]$ over one half-wavelength of the modulated film. The variation over the remainder of the film can be obtained by reflecting about $z=0$ and $\lambda/2$. The plane richest in copper is on the left, at $z=0$, while the plane at $z=\lambda/2$ is the one richest in nickel. It is interesting to note that the variation is not monotonic. This is caused by a subtle interplay between the dependence of the elastic constants on the strain and on the composition. The average value of $Y[001]$ is plotted against A^2 in Fig. 6. The linear dependence on A^2, in agreement with experiment, is obvious. As we have already stated, such a linear dependence on A^2 is to be expected for the average values of elastic moduli. It is also clear from Fig. 6 that the change in $Y[001]$, even at the maximum possible amplitude, is very small, much smaller than the experimentally reported enhancement.

Results for $Y[111]$ are presented in Figs. 7—10. Figure 7 shows the variation of $Y[111]$ over one half-wavelength of a sinusoidally modulated film of $Cu_{0.5}Ni_{0.5}$ with an amplitude $A=0.5$. Figure 8 shows the variation of the averaged value of $Y[111]$ with the square of the amplitude of modulation. Note that the biaxial moduli of the modulated films are actually *smaller* than that of the homogeneous alloy. However, as in the case of $Y[001]$, the change is small.

In order to estimate the contributions of the various terms in Eq. (7), particularly those that are bilinear in the strain and Δc, we successively omit one or more of the linear or bilinear terms. We do this by introducing artificial prefactors for these terms and rewriting Eq. (7) as

$$C_{ijkl}=(\rho'/\rho)\alpha_{im}\alpha_{jn}\alpha_{kp}\alpha_{lq}[C^0_{mnpq}+t_1C^0_{mnpq,c}\Delta c+t_2C_{mnpqrs}\eta_{rs}$$
$$+f_1C^0_{mnpqrs,c}\eta_{rs}\Delta c+\tfrac{1}{2}f_2C^0_{mnpqrsuv}\eta_{rs}\eta_{uv}+\tfrac{1}{2}f_3C^0_{mnpq,cc}(\Delta c)^2+\cdots] . \tag{13}$$

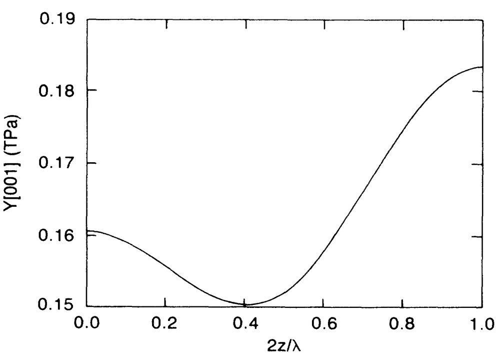

FIG. 5. Variation of $Y[001]$ over one half-wavelength of modulation for a sinusoidally modulated film of $Cu_{0.5}Ni_{0.5}$ with $A=0.5$.

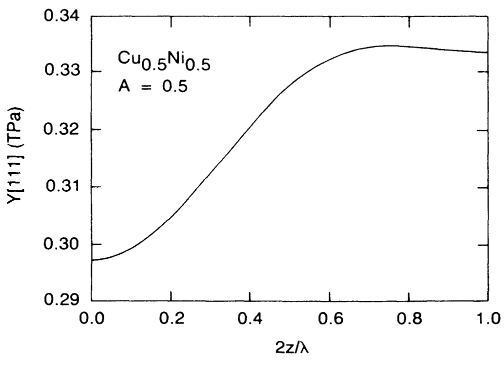

FIG. 7. Variation of $Y[111]$ over one half-wavelength of modulation for a sinusoidally modulated film of $Cu_{0.5}Ni_{0.5}$ with $A=0.5$.

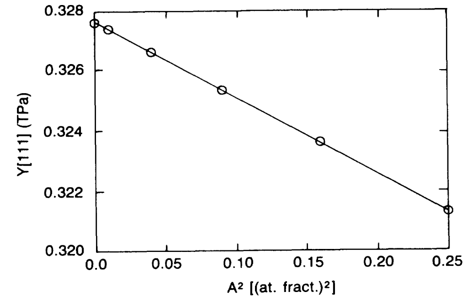

FIG. 8. Plot of $Y[111]$ vs A^2 for $Cu_{0.5}Ni_{0.5}$.

We then set the prefactors t_1, t_2, f_1, f_2, or f_3 to 0 or 1 in order to omit or retain the corresponding term. The results are presented in Figs. 9 and 10. The relative contributions of the two linear terms are shown in Fig. 9, where values of $Y[111]$ are plotted against A^2 for different combinations (t_1,t_2) with $f_1=f_2=f_3=0$. It is clear that the strain-dependent term increases the averaged value of the biaxial modulus, while the composition dependence of the elastic constants decreases it. On the whole, the decrease caused by the composition dependence more than compensates for the strain-induced increase in the biaxial modulus. The net result is a decrease of the biaxial modulus from its value in the homogeneous alloy.

Figure 10 shows the relative contributions of the different bilinear terms. Average values of $Y[111]$ are plotted against A^2 for different combinations (f_1,f_2,f_3) with $t_1=t_2=1$. One can see that the only bilinear term which leads to an enhancement, although still a small one, is the one which involves the fourth-order elastic constants and is proportional to the square of the strain. The other two bilinear terms, which are dependent on the variation of the alloy composition, produce a decrease in the biaxial modulus. Note, also, that the net effect of the two terms which are linear in the strain and composition variation, in the absence of any bilinear terms $(f_1=f_2=f_3=0)$, is a very small decrease in the biaxial modulus.

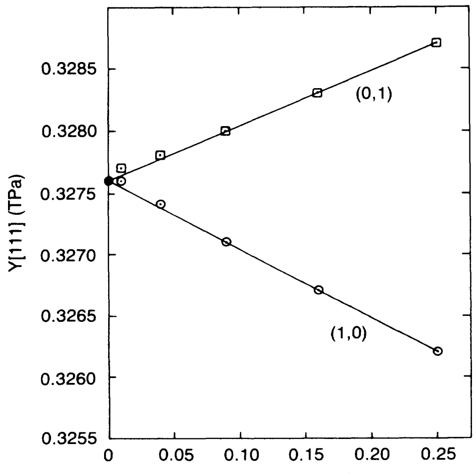

FIG. 9. Plot of $Y[111]$ vs A^2 for $Cu_{0.5}Ni_{0.5}$ excluding all bilinear terms $(f_1=f_2=f_3=0)$ and different linear terms. Curves are identified by the combination of prefactors (t_1,t_2). The quantities t_1, t_2, f_1, f_2, and f_3 are defined in the text.

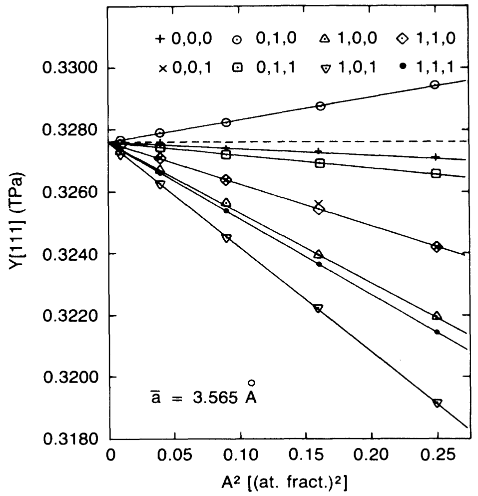

FIG. 10. Plots of $Y[111]$ vs A^2 for $Cu_{0.5}Ni_{0.5}$ with one or more of the bilinear terms omitted (but both linear terms included, i.e., $t_1=t_2=1$). Curves are identified by the combination of prefactors (f_1,f_2,f_3) and the quantities t_1, t_2, f_1, f_2, and f_3 are defined in the text.

In order to get a feeling for the magnitude of the higher-order elastic constants necessary to see a net enhancement, and also because experimental determinations of the higher-order constants tends to have large errors, we have computed the average values of $Y[111]$ using values of the fourth-order constants that were 10 times the reported experimental values. The results of these computations are shown in Fig. 11. The small decrease in the modulus has been changed to a small increase. The important thing to note is that even such a large increase in the fourth-order constants (much larger than the experimental errors) produces only a small in-

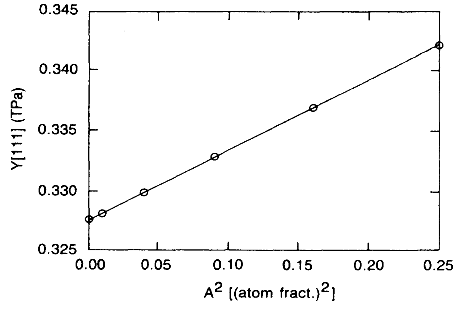

FIG. 11. Plot of $Y[111]$ vs A^2 for $Cu_{0.5}Ni_{0.5}$ computed with the fourth-order elastic constants increased to 10 times their experimentally measured values.

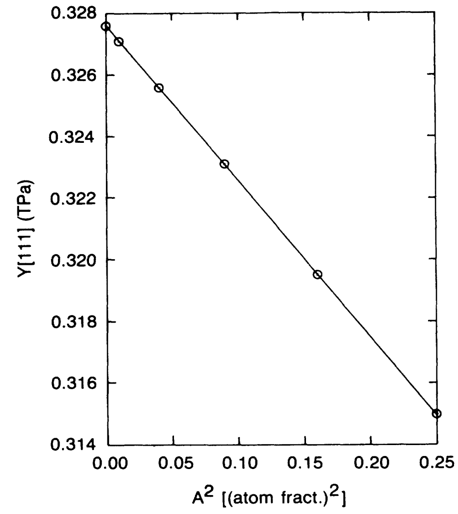

FIG. 12. Plot of $Y[111]$ vs A^2 for a square-wave-modulated copper-nickel film. The average composition is $c_0=0.5$; $\mu=0.5$ and $A=c_1-c_0=c_0-c_2$.

crease in the modulus—much smaller than the observed enhancement.

The case of square-wave modulation which corresponds most clearly to the sinusoidally modulated film has $c_0=0.5$ and $\mu=0.5$. The quantity which then corresponds to the amplitude of modulation is $A=c_1-c_0=c_0-c_2$. Representative results for the case of square-wave modulation are shown in Fig. 12, where $Y[111]$ is plotted against A^2. Again, one can see that the biaxial modulus *decreases* as the amplitude of modulation is increased and that the magnitude of the change, though larger than in the sinusoidally modulated films, is small. Clearly, the decrease in the computed value of the biaxial modulus is not an artifact of the sinusoidal modulation.

IV. DISCUSSION

We have presented results of our computations of the elastic constants, particularly the biaxial moduli $Y[001]$ and $Y[111]$, for compositionally modulated copper-nickel films. As we have said earlier, the treatment outlined here can be extended very easily to other metal pairs, provided their elastic constants (up to fourth order) are known. We have no reason to believe that the results for any other pair of metals will be qualitatively much different from those presented here.

From the results of our computations, it is clear that one cannot explain the great enhancement observed in compositionally modulated alloys on the basis of nonlinear continuum elasticity and coherency-induced strains. While we find, as do Jankowski and Tsakalakos,[12] that a strain alone produces a large change in the elastic moduli of any component material, we find that the averaging over essentially equal amounts of compressed and extended material leaves only a small net change in the moduli of the modulated alloy. We have shown that it is important to take into account the fourth-order elastic constants as well as the variation of the second- and third-order elastic constants with the composition of the alloy. The decrease in the modulus arises primarily because the decrease in modulus in the copper-rich regions (because of the inherently lower modulus of copper-rich alloys) predominates over the increase in modulus due to the fact that the copper-rich regions are in a state of compressive strain. On the other hand, the increase of the modulus in the nickel-rich regions does not adequately compensate for the decrease due to the tensile strain in these regions. The subtle interplay between the strain dependence and the composition dependence of the modulus is shown by the interesting variation (see Figs. 5 and 7) of the modulus over one half-wavelength of modulation. On the whole, the enhancements due to coherency-induced strain are either greatly reduced (as in the case of $Y[001]$) or more than compensated for (e.g., resulting in a decrease in $Y[111]$) by the decrease due to the composition dependence of the elastic constants.

It is possible that the failure to predict an enhancement in the modulus is a problem not with the mechanism, but rather with the particular way in which we have applied it to this situation. It might be suggested that a more physically meaningful averaging procedure for layered structures[24,25] would yield results significantly different from our results obtained by taking the Voigt average. However, it does not, *a priori,* appear likely that the averaging procedure of Refs. 24 and 25 (which is a "hybrid" between Voigt and Reuss averaging) will yield an elastic modulus greater than the one given by Voigt averaging. As has been pointed out, the Voigt average provides an upper limit on the elastic moduli. The Reuss average, on the other hand, gives values of elastic moduli lower than or equal to those given by the Voigt average and, in fact, provides a lower bound[19] for the values of elastic moduli of composite materials. It is more likely that the difficulty lies in the use of continuum elasticity to investigate structures on an atomistic scale. The conceptual difficulties associated with this have already been discussed in Sec. II.

Alternatively, one might just as well conclude that coherency-induced strains are not the cause of the observed enhancement, and that the enhancement has its origin in some other mechanism.[6,7] Among the alternative explanations, the one that is discussed most often invokes a mechanism analogous to that underlying the Kohn anomaly and predicts a rise in the elastic moduli when the edge of the diminished Brillouin zone crosses the Fermi surface.[6] However, it also predicts a *decrease* in the moduli at modulation wavelengths close to the peak wavelength and on either side of it.[6,9] This discrepancy with experiment—such a decrease has not been observed—remains to be explained.

The elastic moduli are measures of the variation of the total energy of the solid with various deformations. It is conceivable that the explanation of the enhancement lies in a fundamental change in the electronic structure of the material which occurs upon modulation of the composition, and which affects the shape of the total-energy surface (in "deformation space") quite strongly. The investigation of this idea involves computing the self-consistent electronic structure of the compositionally modulated material (with variations on an atomistic scale and not treating the solid as a continuum, as we have done) and the total energy as functions of various deformations of the lattice. Some approximations would doubtless have to be made in order to account for the alloying. Such a series of computations, with the large unit cell of the modulated structure, is a tedious, time-consuming, and expensive process, but ought to be undertaken if all other plausible explanations fail.

As has been pointed out in the review by Cammarata,[9] the theoretical approaches to this problem have so far fallen into two broad categories: those that invoke coherency-induced strains and those that invoke a mechanism analogous to the Kohn anomaly. We have sought to provide a definitive answer on the usefulness of one of these and have shown that a combination of continuum elasticity and coherency-induced strains cannot explain the observations. We have also suggested a third approach: an atomic-scale computation of the electronic structure and total energy of the system. This set of computations ought to provide a definitive explanation of the phenomenon.

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[1] W. M. C. Yang, T. Tsakalakos, and J. E. Hilliard, J. Appl. Phys. **48**, 876 (1977).

[2] L. R. Testardi, R. H. Willens, J. T. Krause, D. B. McWhan, and S. Nakahara, J. Appl. Phys. **52**, 510 (1981).

[3] G. E. Hénein and J. E. Hilliard, J. Appl. Phys. **54**, 728 (1983).

[4] T. Tsakalakos and J. E. Hilliard, J. Appl. Phys. **54**, 734 (1983).

[5] A. Jankowski and T. Tsakalakos, J. Appl. Phys. **57**, 1835 (1985).

[6] Tai-Bor Wu, J. Appl. Phys. **53**, 5265 (1982).

[7] W. E. Pickett, J. Phys. F **12**, 2195 (1982).

[8] P. C. Clapp, in *Modulated Structure Materials,* edited by T. Tsakalakos (Nijhoff, Boston, 1984), pp. 455–463.

[9] R. C. Cammarata, Scr. Metall. **20**, 479 (1986).

[10] B. S. Berry and W. C. Pritchet, Thin Solid Films **33**, 19 (1976).

[11] T. Tsakalakos and A. F. Jankowski, in *Modulated Structure Materials,* Ref. 8, pp. 387–407.

[12] A. F. Jankowski and T. Tsakalakos, J. Phys. F **15**, 1279 (1985).

[13] See Refs. 8 and 9 for reviews of the proposed explanations of the enhanced modulus.

[14] See, for example, Y. Hiki and A. V. Granato, Phys. Rev. **144**, 411 (1966); or K. Salama and G. A. Alers, *ibid.* **161**, 673 (1967).

[15] R. F. S. Hearmon, Acta Crystallogr. **10**, 121 (1957).

[16] D. Baral, J. E. Hilliard, J. B. Ketterson, and K. Miyano, J. Appl. Phys. **53**, 3552 (1982).

[17] J. H. van der Merwe, *Single Crystal Films,* edited by M. H. Francombe and H. Sato (MacMillan, New York, 1964), pp. 139–163; J. W. Matthews, *ibid.,* pp. 165–176.

[18] G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook* (MIT Press, Cambridge, 1971).

[19] R. Hill, Proc. Phys. Soc. London, Sect. A **65**, 349 (1952).

[20] See, for example, data in Ref. 4; see also A. F. Jankowski, Ph.D. thesis, Rutgers University, 1984 (unpublished).

[21] R. F. S. Hearmon, *Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology, New Series, Group III: Crystal and Solid State Physics,* edited by K.-H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1979), Vol. 11, Chaps. 1 and 2; Vol. 18, Chaps. 1 and 2 (1984).

[22] J. F. Thomas, Jr., Phys. Rev. B **7**, 2385 (1973).

[23] Charles Kittel, *Introduction to Solid State Physics,* 2nd ed (Wiley, New York, 1956), p. 40.

[24] M. Grimsditch, Phys. Rev. B **31**, 6818 (1985).

[25] M. Grimsditch and F. Nizzoli, Phys. Rev. B **33**, 5891 (1986).