Atomistic analysis of the enhanced-modulus effect in metallic superlattices

Brian W. Dodson
Sandia National Laboratories, Albuquerque, New Mexico 87185
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Experimental reports of large enhancements (severalfold) in certain elastic moduli of compositionally modulated transition-metal–noble-metal superlattices have appeared over the last decade. Two general classes of explanations have been proposed for this effect; one depends upon changes in the electronic structure resulting from the superlattice periodicity, whereas the other is based on nonlinear elastic effects driven by the coherency strain of the strained-layer superlattice structures. An atomistic analysis of the elastic properties of a Cu/Ni superlattice has been carried out to differentiate between these ideas. In the case of Cu/Ni superlattices with (100) interfaces and two, four, or six monolayers in each layer, we find roughly a 15% enhancement in the biaxial stretching modulus, compared to the reported severalfold enhancement. The observed enhancement is therefore not due to nonlinear elastic effects driven by coherency strain or interfacial energetics, but probably results from electronic effects associated with the superlattice periodicity.

I. INTRODUCTION

Composition-modulated metallic superlattices with small (10–30 Å) modulation wavelengths composed of certain pairs of noble and transition metals (e.g., Cu/Ni, Cu/Pd, Ag/Pd, etc.) are observed to have greatly enhanced (several hundred percent) elastic moduli relative to the corresponding homogeneous alloy.[1,2] Although this enhanced-modulus, or "supermodulus," effect is by now well established experimentally, general agreement on a mechanism for the phenomenon is still lacking. There are at present two approaches toward understanding the enhanced-modulus effect. In the first, the effect is thought to result from a change in electronic structure owing to interaction of the Fermi surface with the folded Brillouin zone of the superlattice[3] (this class of mechanisms will be abbreviated FSBZI). In this view, the peak in the modulus as a function of compositional wavelength (Fig. 1) appears where this interaction is most effective. The electronic mechanism depends on the periodicity of the superlattice, but not fundamentally upon coherency strain, although it is possible that coherence would play some role in such a mechanism. The second approach seeks to explain the modulus enhancement through nonlinear elastic effects generated by the large biaxial strains appearing in a coherent superlattice.[4] In this model, interfacial coherency is essential to the proposed mechanism, and the peaks in the moduli result from loss of modulation intensity by interdiffusion at short wavelengths and from loss of interfacial coherency by introduction of misfit dislocations at large wavelengths.

It would seem that a tentative choice could be made between these two approaches by experimental studies of the correlation, if any, between interfacial coherency and the presence of the supermodulus effect. Although coherency does seem to be a common feature of those superlattices exhibiting the supermodulus effect, enhanced moduli are also found in systems such as Ni/Au,[5] where the large lattice mismatch (16%) would seem to preclude formation of a coherent structure.[6] Also, there are systems such as Ag/Pd in which the peak in modulus enhancement occurs at a modulation wavelength of 23 Å, whereas x-ray measurements show that the superlattice structures are coherent at least to a

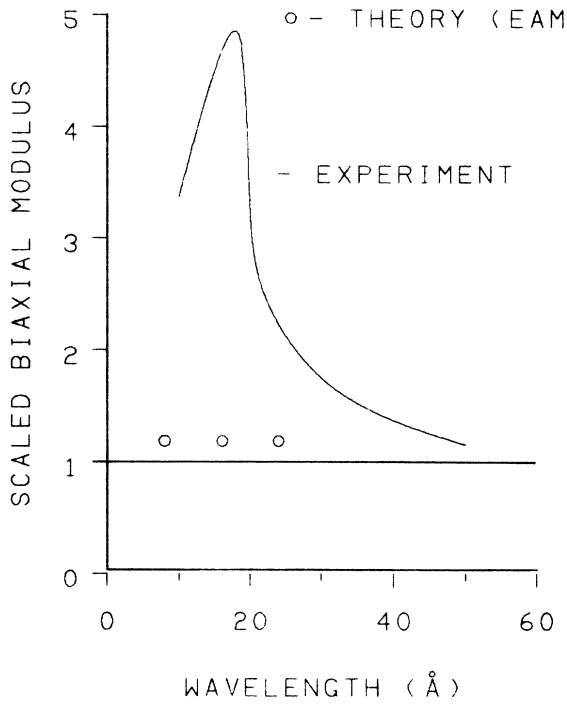

FIG. 1. Scaled biaxial modulus for a Cu/Ni superlattice as a function of superlattice wavelength. The experimental data are taken from Ref. 2, and are scaled to the biaxial modulus for a homogeneous $Cu_{0.5}Ni_{0.5}$ alloy. The theoretical results are obtained in this paper using the embedded-atom method (see text).

wavelength of 33 Å, which argues against the loss of coherence causing the falloff in modulus at a large wavelength.[7] The current experimental picture on a necessary correlation between the supermodulus effect and interfacial coherency seems inconclusive.

Since a choice between the two principal suggested mechanisms for the supermodulus effect cannot, at this time, be made based solely upon the experimental evidence, one possible approach is to resolve this issue through contradiction, i.e., by showing that one theory or the other makes predictions inconsistent with some subset of the experimental results. At present, however, the ideas on which the FSBZI models are based do not seem sufficiently developed to make such an approach tractable.[8] In contrast, models based on the nonlinear elastic properties of coherent layered structures are relatively well characterized, and offer possible fields within which to seek contradictions.

The first major work along these lines was carried out by Jankowski and Tsakalakos,[4] who calculated the elastic constants of the noble metals as a function of biaxial strain, such as would appear in a coherent layered structure, using a pseudopotential approach. They found that the elastic constants, and specifically the biaxial moduli $Y_{(100)}$ and $Y_{(111)}$, are strong functions of applied biaxial stress ϵ, and are nearly linear in ϵ, with compressive biaxial stress producing larger values of $Y_{(100)}$. For example, in the case of Cu undergoing biaxial strain in a plane perpendicular to the [100] direction , $Y_{(100)}$ varies from 0.178 to 0.084 TPa (bulk value is 0.124 TPa) as ϵ varies from -0.015 to 0.015. This increase in $Y_{(100)}$ on compression is of the order of magnitude of the increase observed in a Cu/Ni superlattice having a modulation wavelength around 15–20 Å, which has encouraged the speculation that the nonlinear elastic effects serve a major role in driving the enhanced-modulus effect. However, the pseudopotential methods they used could not easily be applied to other than noble metals, so that the equivalent effect in, for instance, Ni, was not calculated. As the supermodulus effect is not observed in superlattices made up of pairs of noble metals, this treatment of nonlinear elastic properties remained inconclusive on the origin of the enhanced modulus effect.

A continuum-mechanical analysis of the cumulative effect of nonlinear elastic properties on the average elastic moduli of a Cu/Ni superlattice has been carried out by Banerjea and Smith.[9] They model the nonlinear elastic properties of the individual layers by using the bulk elastic constants through fourth order, and then calculate the average elastic response of the composite system with conventional nonlinear continuum-elasticity theory.[10] They agree with Jankowski and Tsakalakos that the coherency strain does cause a major change in the elastic moduli in any given layer. However, in the superlattice structure, alternate layers are strained in compression and tension, resulting in alternate increase and decrease in the biaxial modulus. The result, averaged over the entire superlattice, is that essentially no change in the biaxial modulus is obtained for a Cu/Ni superlattice, whereas a severalfold increase is observed experimentally.

There are (at least) two substantial limitations of this analysis. First, by considering only up to fourth-order elastic constants, Banerjea and Smith do not reproduce all of the nonlinearity found in pseudopotential calculations of Jankowski and Tsakalakos. This may represent a small error in this case (see Fig. 2), but inclusion of nonlinear elastic effects to all orders seems to be needed to rule out safely nonlinear elasticity as a prime cause of the supermodulus effect. Second, the influence of interfacial energetics on the overall elastic properties is not included in the continuum-elasticity analysis of Banerjea and Smith. This is nearly unavoidable, since the nature of such effects in continuum elasticity is not well known. However, neglect of such effects on the elastic response of small-period superlattice structures, in which essentially all atoms are near internal interfaces, seems potentially dangerous. Thus, the analysis of Banerjea and Smith, although serving to discourage the point of view that the enhanced-modulus effect results primarily from nonlinear elasticity driven by coherency strain, cannot be taken as a strong contradiction of this proposed mechanism.

In this paper the average elastic properties of superlattices consisting of alternating slabs of Cu and Ni, having thicknesses of two, four, and six monolayers, are calculated using the embedded-atom method (EAM) of Daw, Baskes, and Foiles[11,12] so as to treat the combined non-

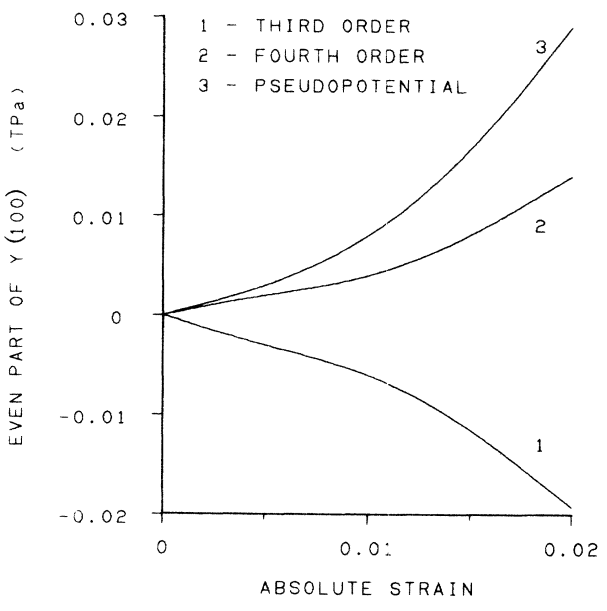

FIG. 2. Effect of biaxial strain on elastic properties of copper. The even part of the change in the biaxial modulus $Y_{(100)}$ $[Y_e(\epsilon)=Y(\epsilon)+Y(-\epsilon)-2Y(0)]$ is plotted as a function of absolute value of biaxial strain for three models of the elastic properties. Curve 1 includes up to third-order elastic constants (Ref. 4), curve 2 includes fourth-order elastic constants (Ref. 9), and curve 3 is the result of a pseudopotential calculation (Ref. 4). Note that even the fourth-order elastic model does not reproduce the nonlinear elastic behavior fully.

linear elastic effects resulting from the coherency strain and the high density of interfaces to all orders. Although the EAM is based on an electronic model for the interatomic interaction, the model is too coarse to include effects related to the proposed FSBZI mechanisms for the supermodulus effect. This calculation will thus provide a clean differentiation between the two classes of proposed mechanisms.

II. ATOMISTIC DESCRIPTION OF A BIMETALLIC SUPERLATTICE

In order to calculate the effective elastic moduli of a Cu/Ni superlattice using an atomistic model, it is necessary to choose an interatomic potential which is capable of describing the energetics of such bimetallic structures. The use of simple pairwise potentials would be tractable, but such potentials do not describe even the simplest elastic properties of metallic structures properly (for example, the Cauchy pressure C_{12}-C_{44} is zero). These inadequacies can be patched up by addition of a volume-dependent energy term, but the ambiguities introduced by applying this procedure to most realistic structures make this approach inappropriate for the current problem. The embedded-atom method (EAM) describes the structural energy of a system of atoms as the sum of a repulsive pairwise interaction and an "embedding" energy, which is the energy released by embedding each atom in the local electron density provided by the other atoms in the structure. This local electron density is always well defined, so that the ambiguities resulting from use of volume-dependent energy terms do not appear.

The EAM is formally derivable from density-functional theory, but development of a practical method requires additional approximations, resulting in a semiempirical procedure. The primary simplifying assumptions are that the local electron density at the atomic site is just the sum of the free-atomic electron densities of the neighboring atoms, and that gradient contributions to the embedding energy are zero. (Note that calculation of the local electron density as the sum of free-atomic densities removes any information concerning the superlattice periodicity from the electron density. This means that the FSBZI mechanisms are not treated in this approximation.) The structural energy of a system of atoms is then

$$E=\sum_i F_i(\rho_i)+\tfrac{1}{2}\sum_i \sum_{j(\neq i)} \Phi_{ij}(R_{ij}) , \tag{1}$$

where ρ_i is the local electron density at site i, $F(\rho)$ is the embedding energy (which is a function of the local electron density), and $\Phi_{ij}(R_{ij})$ is the repulsive pairwise interaction.

This basic form has been applied to description of the alloys of the noble metals Cu, Ag, and Au, and the neighboring transition metals Ni, Pd, and Pt, by Foiles, Baskes, and Daw,[12] who obtain excellent agreement with a wide range of experimental pure-metal and alloy properties. Briefly, a parametrized form for the pairwise potential is chosen. Given this form, the embedding function is determined uniquely by requiring that the structural energy for the homogeneously strained fcc solid agrees with the universal equation of state introduced by Rose *et al.*,[13] which provides a reasonably accurate description of the cohesive energy over a wide range of density. The resulting four-parameter model is fitted to selected pure-metal and alloy properties. The EAM in this form has proven quite accurate over a wide range of bulk, surface, and alloy properties, and thus seems a reasonable choice to treat the current problem.

The EAM must be tested to ensure its accuracy in the case of biaxial strain. The biaxial modulus of bulk Cu was calculated as a function of biaxial strain using the EAM and the parametrization described above, and the results were compared with the equivalent pseudopotential calculations of Jankowski and Tsakalakos. The slope of the modulus is about 10% greater for the pseudopotential calculation, but the overall features of the dependence, including the slight upward curvature, are very similar using both approaches (see Fig. 3). The EAM can thus be used to analyze the current problem with a reasonable level of confidence.

III. ELASTIC BEHAVIOR OF A Cu/Ni SUPERLATTICE

The object is to calculate the effective elastic properties of a bimetallic superlattice, and compare them with experiment. We have chosen a structure composed of alternating slabs of Cu and Ni, having coherent inter-

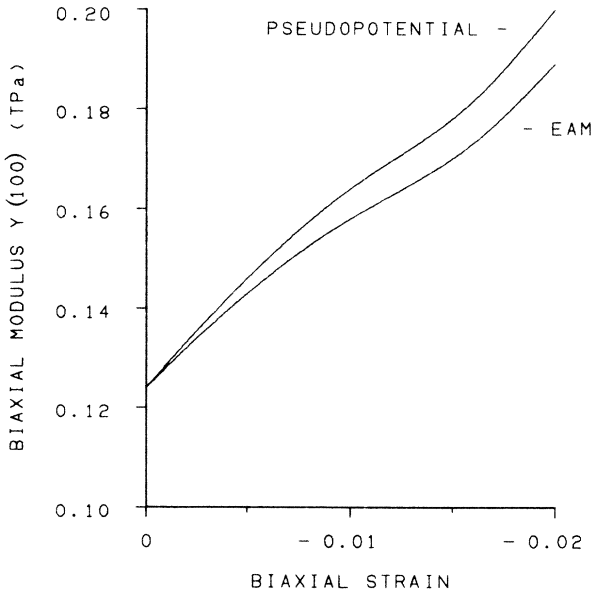

FIG. 3. Comparative calculations of the dependence of the biaxial modulus $Y_{(100)}$ of copper on biaxial strain. The predictions of the embedded-atom method (EAM) obtained here agree well with the more rigorous pseudopotential calculation carried out by Jankowski and Tsakalakos (Ref. 4), which justifies the use of the EAM in the analysis of the supermodulus effect.

faces perpendicular to the (100) layers, partly because this geometry shows a large experimental enhancement, and partly because this enhancement has been seen by a number of independent investigations.[1,2,14] The slab thicknesses are varied from two to six monolayers, with equal thicknesses in both materials. This range of thickness covers the regime of modulation wavelength (8–24 Å) over which the supermodulus effect appears in Cu/Ni superlattices. Each layer is five unit cells square with periodic boundary conditions in both [100] directions perpendicular to the surface. An infinite superlattice is simulated by introducing periodic boundary conditions on the surfaces on the stack parallel to the Cu/Ni interface. Treatment of an infinite superlattice is a reasonable approximation, since the experimental structures are composed of thousands of layers. The structure is large enough that any two atoms in the structure interact directly in only one direction, despite the periodic boundary conditions on the sides. The resulting configuration simulates an infinite-bulk superlattice structure. The energy of the test structure is minimized by varying the atomic positions, and the elastic constants are then calculated by numerical differentiation of the dependence of the structural energy on the applied strain conditions.

Upon carrying out this procedure, the biaxial modulus $Y_{(100)}$ for our test superlattices is found, for all modulation wavelengths calculated, to be 0.17 ± 0.01 TPa, compared to the value of 0.152 TPa expected for a homogeneous $Cu_{0.5}Ni_{0.5}$ alloy.[9] This represents an increase of 10–15 % in this biaxial modulus, compared to the experimental increase of several hundred percent.[1,2,14]

The obvious conclusion to be drawn from the above result is that the enhanced modulus effect does not result from nonlinear elastic effects driven by biaxial coherency strain or interface density, but that some other mechanism must produce the experimental observations. The increase in the contribution to $Y_{(100)}$ from the Cu layers in biaxial compression is almost completely compensated by the reduction in the $Y_{(100)}$ contribution from the Ni layers, which are in biaxial tension. Whatever contributions arise in this system from the interfacial energetics apparently do not upset this compensation.

In summary, attempts to explain the enhanced-modulus effect to date have fallen into two broad categories: those based on nonlinear elastic effects driven by coherency strain, and those based on electronic structure effects driven by the superlattice periodicity. The present work has strengthened the case against the first of these classes. However, it is clear that exclusion of the elasticity models does not prove the accuracy of the FSBZI mechanism. The present state of the models based on electronic superlattice effects is not satisfactory, and must be considerably refined to make a definitive test of such models possible. Although the field of possible explanations is now narrowed considerably, a satisfactory theoretical understanding of the enhanced-modulus effect is not yet available.

ACKNOWLEDGMENTS

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[1]T. Tsakalakos and A. F. Jankowski, Ann. Rev. Mater. Sci. **16**, 293 (1986).
[2]T. Tsakalakos, and J. E. Hilliard, J. Appl. Phys. **54**, 734 (1983).
[3]T. B. Wu, J. Appl. Phys. **53**, 5265 (1982).
[4]A. F. Jankowski and T. Tsakalakos, J. Phys. F **15**, 1279 (1985).
[5]W. M. C. Yang, T. Tsakalakos, and J. E. Hilliard, J. Appl. Phys. **48**, 876 (1977).
[6]B. W. Dodson, Surf. Sci. **184**, 1 (1987).
[7]G. E. Henein and J. E. Hilliard, J. Appl. Phys. **54**, 728 (1983).
[8]R. C. Cammarata, Scr. Metall. **20**, 479 (1986).
[9]A. Banerjea and J. R. Smith, Phys. Rev. B **35**, 5413 (1987).
[10]R. Hill, Proc. Phys. Soc. London, Sect. A **65**, 349 (1952).
[11]M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).
[12]S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).
[13]J. H. Rose, J. R. Smith, F. Guinea, and J. Ferrante, Phys. Rev. B **29**, 2963 (1984).
[14]L. R. Testardi, R. H. Willens, J. T. Krause, D. B. McWhan, and S. Nakahara, J. Appl. Phys. **52**, 510 (1981).