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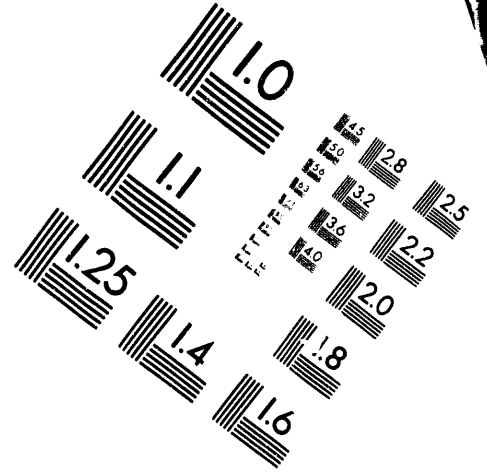
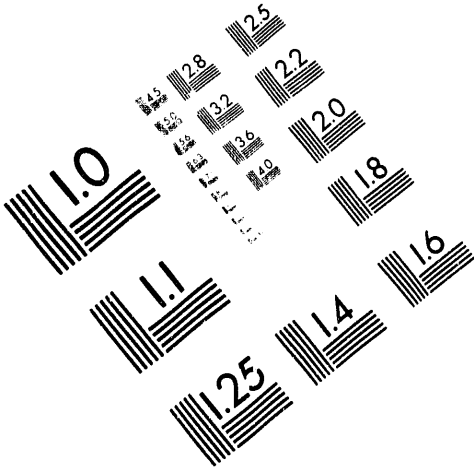**Association for Information and Image Management**
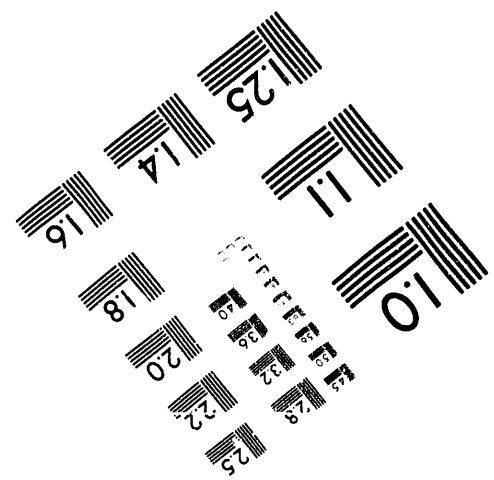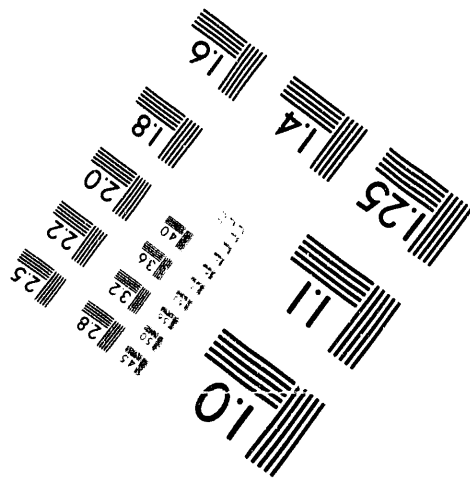
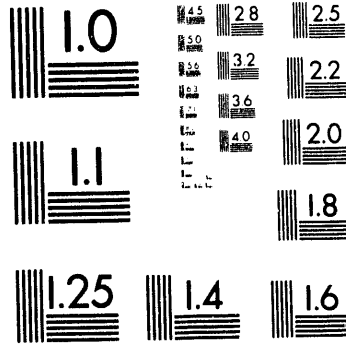1100 Wayne Avenue, Suite 1100
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Centimeter

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Inches

1.0

1.1

1.25   1.4   1.6

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O S T I

Phenomenological Explanation of Elastic Anomalies in Superlatices*

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PHENOMENOLOGICAL EXPLANATION
OF ELASTIC ANOMALIES IN SUPERLATTICES

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ABSTRACT

The experimental fact that measured elastic and structural properties of superlattices are strongly correlated can be understood on the basis of a simple model based on the packing of hard spheres. The model is consistent with features of many models that have been proposed to explain the supermodulus effect, but contrary to previous explanations, it allows predictions for a given pair of constituents to be made. For an arbitrary pair of elements, it predicts the existence or non-existence of an elastic anomaly, and a rough estimate of its magnitude.

INTRODUCTION

Most of the original claims of huge enhancements of the biaxial modulus known as the supermodulus effect [1] are now generally believed to be erroneous [2]. There is, however, overwhelming evidence that the elastic properties of superlattices are anomalous in the sense that they are different from those expected from simple continuum elasticity [3]. Usually the observed changes are a decrease in the elastic constants. There have been many models proposed to explain the anomalous elastic properties of superlattices [4-8]. To date however none of the proposed mechanisms have been capable of predicting the elastic behavior expected for a given arbitrary combination of constituents. Guided by two recent investigations [9,10] which show that the anomalous elastic properties are closely tied to structural phase transitions in at least one of the constituents, we present a simple model based on a 'hard sphere' concept which is quite successful in predicting the existence of an elastic anomaly as well as a rough estimate of its magnitude. The model addresses the issue of the alternative structures available to the constituents to lower interface energies and only indirectly addresses the changes in elastic constants caused by structural changes.

The structure of a superlattice is determined, in general, by the competing energies from the bulk crystal structure of the constituent layers and interface energies resulting from the differences of lattice spacings or crystal symmetry of the two materials. For thick layers, each layer will relax towards its bulk structure and the interface will be incommensurate or the strain will be relieved by misfit dislocations. For very thin layers, the interface energies may dominate and the layers will arrange to minimize this energy which often results in the growth of metastable phases. In most superlattice systems, there should be a transition thickness in which the structure goes from being

dominated by the bulk structures to being dominated by interface energies.

A number of different structural transitions for thin layer thicknesses have been experimentally observed. Layers with the same crystal symmetry can strain ᴜᴏ form coherent interfaces (e.g. Mo/V [11]). In systems with different crystal symmetries, one layer can change symmetry (e.g. Fe/Cu [3,9]). Systems with large lattice mismatches can go through a crystal-to-amorphous transition (e.g Fe/Nb [12], W/Ni [10]). The basic assumption of the model is that the lowest interface energy state is achieved when the atoms are in registry on either side. To achieve this registry, it is necessary (but not sufficient) that the surface atomic density on either side of the interface be equal. To estimate atomic surface densities, we use the classical hard sphere structures viz. fcc, bcc and rcp (random close packed). These structures have volume packing fractions of 0.74, 0.68 and 0.63 respectively, and it is straight forward to calculate that the surface packing fractions are 0.907, 0.833 and 0.735 for fcc (111), bcc (110) and rcp respectively. These particular surfaces of the fcc and bcc structures are the close packed faces and are the orientations that most often grow. Using relative in-plane densities, we predict the structure for very thin layers and relate the final structure to the expected elastic anomalies.

MODEL AND STRUCTURAL RESULTS

The arrows in figure 1 show the area per atom which hypothetical fcc, bcc and rcp hard sphere Cu (radius 2.56Å) would have. These structures are incompressible so that their energy is infinite for smaller areas per atom and zero for any larger area since there is no attractive force. For visualization purposes it is helpful to replace this energy curve by a more realistic potential: in Fig. 1 we have arbitrarily drawn Lennard-Jones potentials so that their minima correspond to the hard sphere packing. We make no attempt to estimate the difference in energy of the corresponding minima. It should be clear that this simple model will not be valid in cases where the constituents react to from a different chemical compound or if they form solid solutions and alloy at the interface.

In Fig. 2 we show the corresponding curves for Ni (dashed) and W (solid); the thicker lines indicate the stable structure, viz. bcc (110) for W and fcc (111) for Ni. It is clear from this figure that the most obvious possibility of matching the number of atoms per unit area of Ni and W is to transform Ni into the rcp phase. Fig. 3 shows the in-plane x-ray spectra of W/Ni superlattices [10]; below 30Å the sample looses the diffraction spectra characteristic of a bcc(110)/fcc(111) structure. In Fig. 4 we compare the last spectrum in Fig. 3 (L=19Å) with that of amorphous $Fe_{80}P_{13}C_7$ which is known to be well described by an rcp structure [13]. This comparison allows the new structure of the superlattice to also be classified as rcp. To avoid the possibility of the model being over interpreted we must point out that the model only 'predicts' that Ni should become rcp; experimentally it is clear that W has also become disordered. A posteriori this can be understood since when W no longer has a crystalline base on which to grow it also reverts to a disordered phase.
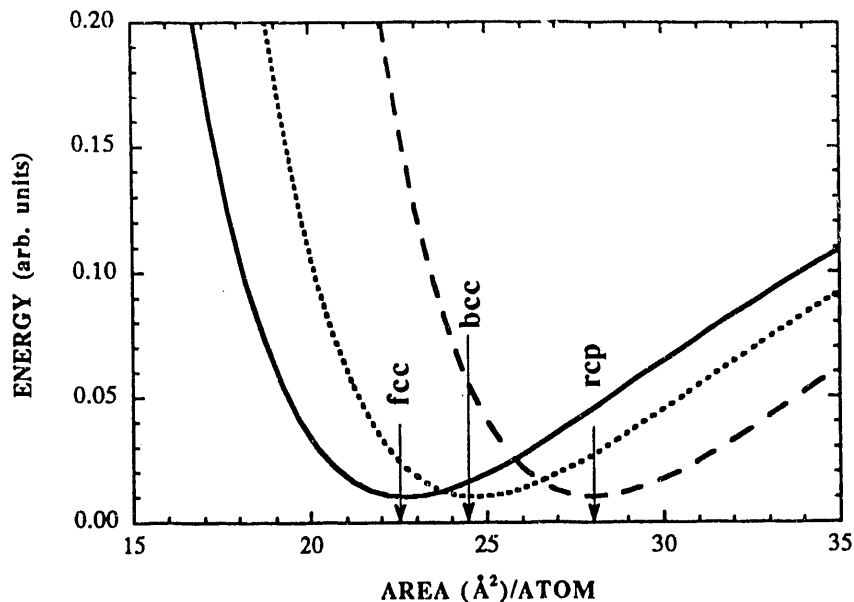
Figure 1:   Surface atomic density of atoms on fcc (111) (full) bcc(110) (dotted) and rcp (dashed) surfaces. The arrows indicate the packing expected from a hard sphere (R=2.56Å) model, the curves represent arbitrary Lennard-Jones potentials chosen with their minima to coincide with the hard sphere model.

Figure 2:   Same as Fig. 1 for Ni (dashed lines) and W (full lines) atoms. The thick lines indicate the stable structure. For each material fcc (rcp) has the highest (lowest) surface density.

Similar arguments can be made for other bcc/fcc superlattices Nb/Cu, Mo/Ni and V/Ni, all of which disorder at small modulation wavelengths [14,15]. A more interesting bcc/fcc case is Fe/Cu where the number of atoms per unit area are similar from the outset; the energy curves for these two materials are shown in Fig. 5. To achieve registry the remaining requirement is to: either change the Cu structure to bcc and then contract it to fit the bcc Fe, or transform Fe
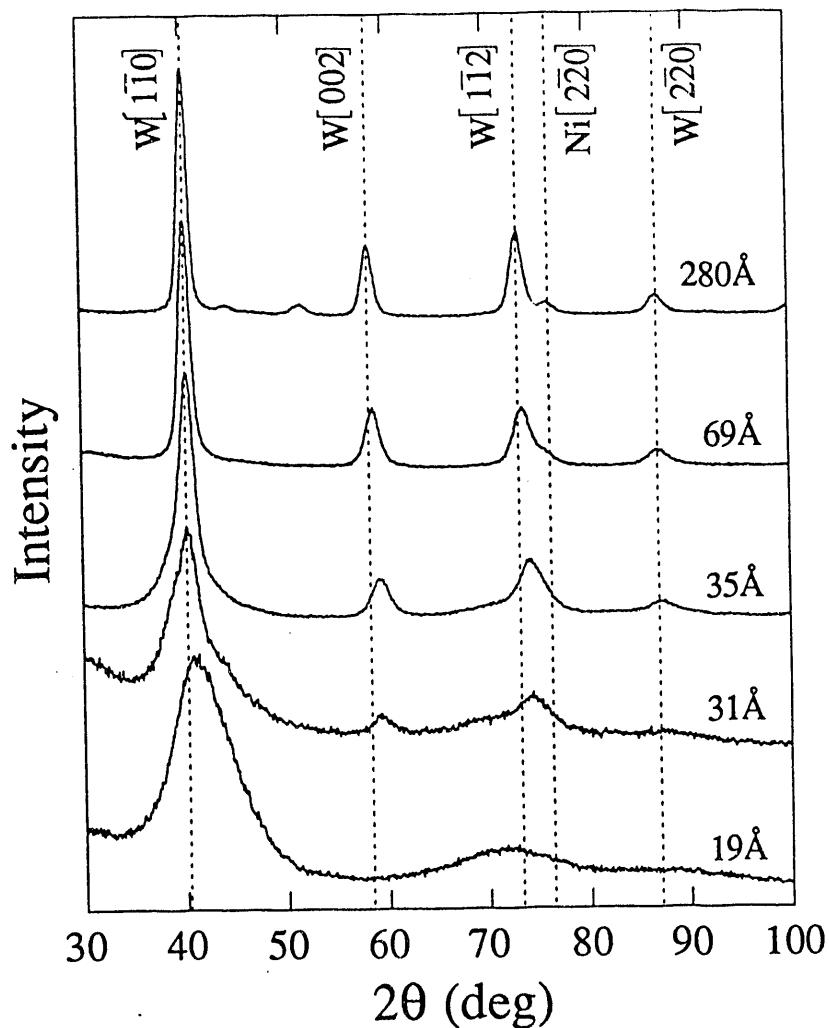
Figure 3: Transmission X-ray diffraction spectra for equal layer thickness W/Ni superlattices for various modulation wavelengths. Vertical lines indicate expected bulk positions.

to fcc and expand it to fit the Cu. Experimentally the latter is found to occur [9, 16].

Structural data is only available for a few bcc/bcc superlattices: Mo/Ta [17], Mo/V [11], V/Nb [12], and Fe/Nb [12]. In the case of Mo/Ta and Mo/V our model predicts that since Mo or V can be expanded to match the Ta or the Mo without reaching the rcp instability, the structure should become coherent. Experimentally this is observed. Energy curves for Fe/Nb shown in Fig. 6 predict that Fe will transform to rcp in a similar way as shown earlier for W/Ni. This is also observed experimentally [12]. The case of V/Nb, which is incorrectly predicted by the model, will be discussed in the conclusion section.

Predictions for fcc/fcc superlattices are similar to those for bcc/bcc. Cu/Ni and Cu/Pd are expected to be transform to a coherent structure, while Ag/Ni is expected to disorder; all these expectations are observed experimentally [2, 18].

Figure 4: X-ray spectra for L=19Å W/Ni superlattice shown in Fig. 3 and amorphous (rcp) $Fe_{80}P_{13}C_7$ from Ref. 13.
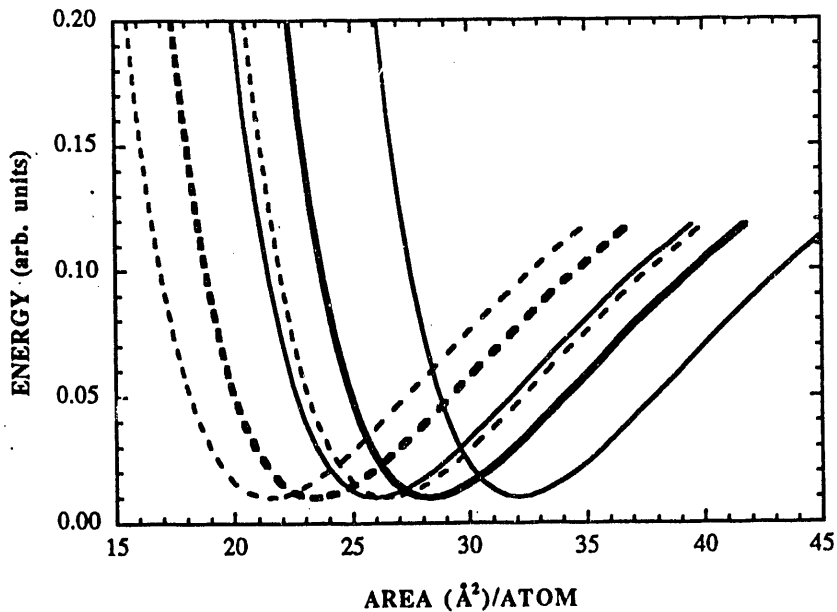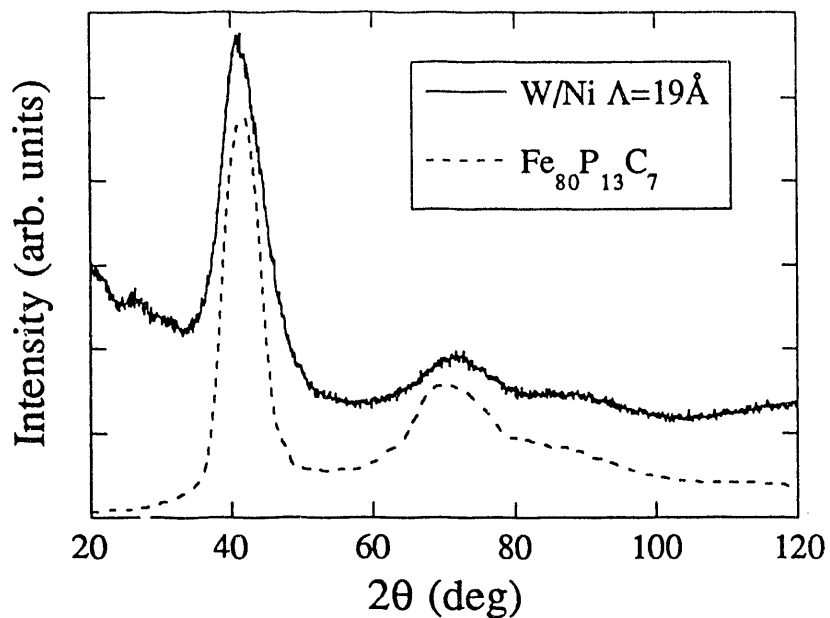

Figure 5: Same as Fig. 1 for Fe (dashed lines) and Cu (full lines) atoms. The thick lines indicate the stable structure. For each material fcc (rcp) has the highest (lowest) surface density.
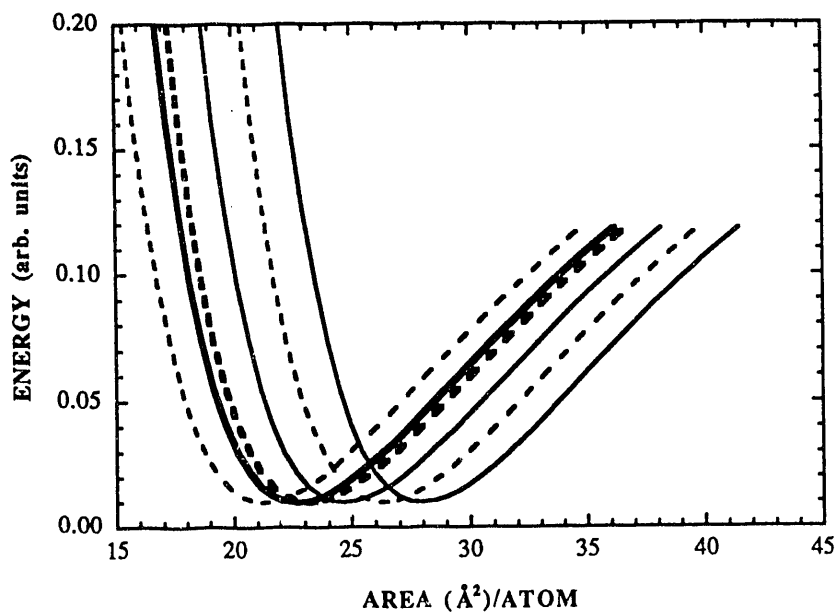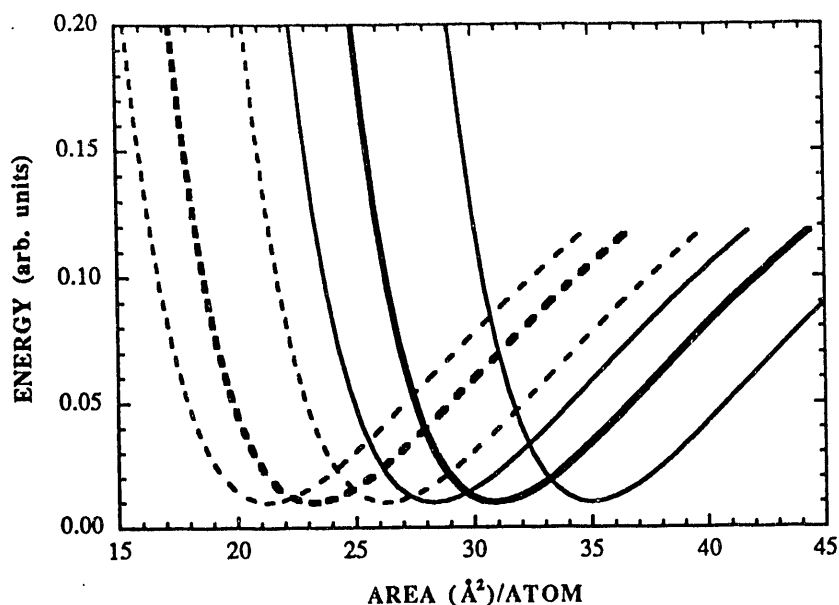
Figure 6: Same as Fig. 1 for Fe (dashed lines) and Nb (full lines) atoms. The thick lines indicate the stable structure. For each material fcc (rcp) has the highest (lowest) surface density.

ELASTIC PROPERTIES

In order to relate the above arguments to the expected elastic behavior of the superlattices, we draw on the results of Refs. 2 and 19 where it has been shown that the introduction of disorder has a strong influence on the elastic properties. This interpretation is in agreement with the results of ion irradiation of single crystals where the introduction of defects has a significant effect on the elastic properties [20]. For superlattices above the critical thickness, the interfaces will be incoherent leading to locaı disorder at the interfaces. If we view this disorder as the driving force behind the structural and elastic changes, then it is clear from Fig. 1 or from an equivalent picture in three dimensions, that the larger barrier between the fcc and rcp phases will require larger amounts of disorder to drive the transition. Consequently, larger elastic anomalies would be expected. Concentrating on the shear surface velocity (related to the modulus C_{44}) which is the most commonly measured elastic property of superlattices, the above expectations are confirmed. All fcc to rcp transformations are accompanied by a 18-26% softening in shear velocity (e.g. W/Ni, Mo/Ni, V/Ni, Ag/Ni, Nb/Cu), bcc to either rcp or fcc should be smaller and are 4% for Fe/Nb and 10% for Fe/Cu. In incoherent to coherent transformations the softening should depend on the size of the mismatch: in Cu/Ni, Mo/Ta, and Cu/Pd with lattice mismatches of 2.5, 4.8, and 7.8%, the velocity changes are 0, 6, and 7% respectively.

Another experimental feature which is accounted for by the present approach is the variation of the elastic anomalies as the ratio of the constituents is changed. Although for a fixed ratio results can be interpreted as being directly proportional to the density of interfaces [21], work on Mo/Ni superlattices with different ratios of $d_{Ni}:d_{Mo}$ produced results which were inconsistent with an effect that depended only on the number of interfaces per unit length [22]. It was

argued in Ref. 22, purely on the basis of the elastic results, that only the Ni layers were responsible for the anomalies: a fact consistent with our prediction that Ni is driven to the rcp phase.

Finally our model is the first to explain the existence of an extremum in the elastic constant data. Because in this model the anomaly is associated with an instability of a phase transition, once the transition has occurred the elastic constants revert to normal values of a stable structure.

DISCUSION AND CONCLUSIONS

In order to put the present simple model in perspective it is necessary to illustrate its shortcomings. So far we have found two counter examples: Ag/Al (fcc/fcc) is very close to being lattice matched and therefore our model predicts no structural change and consequently no elastic anomaly. However, since the observed large changes in velocity [23] can be accounted for by the (observed) formation of the compound γ-Ag_2Al, it is clearly a system in which the initial assumptions of the model are not valid. A second exception is Nb/V which the model predicts should disorder; experimentally it is found to form a coherent structure [12]. Here again the discrepancy may result from the fact that V-Nb form solid solutions which also invalidates one of the assumptions of the model.

The most obvious improvement of the model would be to include the relative energy minima for the potentials shown in Fig. 1. For Cu, the fcc potential will have the lowest energy minimum since this corresponds to the bulk structure. This will result in some modifications of the final structures predicted and may also explain the discrepancy with V/Nb. The model presented also ignores thermodynamic quantities such as the surface free energy and the heat of mixing which will affect the superlattice structure [24]. However, this simple model is able to predict the interface dominated structure for a wide range of superlattices.

In conclusion, with a simple model we are able to account for the elastic anomalies in superlattices which have been experimentally measured. Although at a microscopic level our approach does not add any further insight into the physical process involved, it does allow *predictions* to be made regarding the existence of an anomaly for a given combination of metals and also provides an estimate of its magnitude. Although the model predicts the likely structures to which a given system may revert, it requires the microscopic insight of the grain boundary model [2,19] to explain how these transformations occur.

In a general sense the assumptions of our model are not conceptually different from the 'coherency strain' model proposed by Jankowski [6] nor with the surface tension model of Cammarata and Sieradzki [5] since our premise of balancing the atomic surface densities can be viewed as an explanation of the proposed surface tension. The electron transfer model [7], and the electronic folding model[8], appear to be inconsistent with the present rationalization of the experimental results.

ACKNOWLEDGMENTS

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