Elastic-Constant Anomalies in Metallic Superlattices: A Molecular-Dynamics Study

Ivan K. Schuller and Aneesur Rahman
Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

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The elastic constants of Ni are calculated with use of molecular dynamics; at ~ 5% [111] axial strain there is a large (~ 35%) softening of the C_{44} shear modulus and a stiffening of the in-plane Young's (~9.5%) and biaxial (~8%) moduli. These calculations are in remarkable agreement with experimental C_{44} for Mo/Ni superlattices. The experimentally observed transition to a highly disordered state occurs at the same strain value at which in the calculation the crystal becomes unstable.

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The question of the elastic-constant anomalies in metallic superlattices has been the subject of controversy recently. Several reports claim the existence of large enhancements (factors of 1.5–8) of the biaxial,[1,2] Young's, and flexural moduli[3] while others claim total absence[4,5] of such effects in similarly prepared materials, all of which form continuous sets of solid solutions in their equilibrium binary phase diagram. Recently there has also been a report[6,7] of a softening of the shear modulus which coincides with a transition in the structural and electronic properties of Mo/Ni and Cu/Nb metallic superlattices. For the latter case, the constituents are not lattice matched and do not form solid solutions in their equilibrium binary phase diagram. Several theoretical explanations[8-10] based on the electronic structure of such materials have been advanced. However, these explanations are based on a number of crucial assumptions and at best give a qualitative reason for the existence of an enhancement in the elastic constants. The quantitative explanation of these effects using band-structure calculations is extremely difficult because of the high accuracy needed in the calculation of the second derivatives of the total energy.

We propose a theoretical model based on molecular-dynamics calculations which for the first time explains *quantitatively* the softening of the shear modulus, as due to the observed structural changes in Mo/Ni superlattices. In addition, we find a simultaneous small [~(8–10)%] enhancement of both Young's and biaxial moduli. Conversely, these calculations suggest that systems that show anomalies in their elastic constants probably will show structural anomalies. These structural anomalies are possibly due to electron transfer effects (as in intercalated graphite compounds)[11] which might be addressed by total electronic energy calculations.

The novel molecular-dynamics (MD) technique[12] we have used makes it possible to study crystalline systems under constant external anisotropic stress. We shall refer to it as the new molecular dynamics (NMD) to differentiate it from the more traditional procedure of keeping the MD cell fixed in shape and volume. Andersen[13] was the first to show how, by making volume a dynamical variable, MD calculations can be made at constant isotropic pressure. A brief outline of NMD is as follows: N particles with coordinates $\vec{r}_i$ and mass m_i, $i=1,\ldots,N$, and interacting via a pairwise potential $\varphi(|\vec{r}_i-\vec{r}_j|)$ are placed in a parallelepiped cell generated by vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$ emanating from the origin. Thus $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$, $\vec{a}$, $\vec{b}$, and $\vec{c}$ are vectors with respect to some *fixed* frame of reference. In the usual way the cell is repeated periodically to fill all space. The fractional coordinates $\vec{s}_i$, $i=1,\ldots,N$, in the unit cell generated by $\vec{a}$, $\vec{b}$, $\vec{c}$ are given by $\vec{r}_i=\overleftrightarrow{h}\cdot\vec{s}_i$, where column vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ form the 3×3 matrix $\overleftrightarrow{h}$. Later, for $\overleftrightarrow{h}\cdot\vec{s}_i$ we shall use the symbol $\vec{v}_i$. The dynamical variables are the $3N$ components of the $\vec{s}_i$'s and the nine elements of $\overleftrightarrow{h}$. The product $\overleftrightarrow{h}'\cdot\overleftrightarrow{h}=\overleftrightarrow{G}$ and the determinant $\|h\|=\Omega$, the volume of the cell, are then used in the Lagrangian

$$L=\frac{1}{2}\sum_{i=1}^{N}m_i\dot{\vec{s}}_i{}'\cdot\overleftrightarrow{G}\cdot\dot{\vec{s}}_i-\sum_{i=1}^{N}\sum_{j>i}^{N}\varphi(|\vec{r}_{ij}|)+\tfrac{1}{2}W\,\mathrm{Tr}\dot{\overleftrightarrow{h}}{}'\cdot\dot{\overleftrightarrow{h}}-\tfrac{1}{2}\mathrm{Tr}\overleftrightarrow{\Sigma}\cdot\overleftrightarrow{G}-p\Omega, \tag{1}$$

with

$$\overleftrightarrow{\Sigma}=\overleftrightarrow{h}_0{}^{-1}\cdot(\overleftrightarrow{S}-p\overleftrightarrow{I})\cdot\overleftrightarrow{h}_0{}'^{-1}\Omega_0, \tag{2}$$

where $\overleftrightarrow{S}$ and p are respectively the externally applied anisotropic stress tensor and hydrostatic pressure. $\overleftrightarrow{h}_0$ is the reference frame for the definition of the strain tensor and W is a parameter with dimensions of mass.

This Lagrangian gives the equation of motion

$$\ddot{\vec{s}}_i = -\sum_{j\neq i} m_i^{-1}(\varphi'/r_{ij})(\vec{s}_i - \vec{s}_j) - \overleftrightarrow{G}^{-1}\cdot\dot{\overleftrightarrow{G}}\cdot\dot{\vec{s}}_i, \quad i=1,\ldots N, \tag{3}$$

and

$$W\ddot{\overleftrightarrow{h}} = (\overleftrightarrow{\pi} - p)\cdot\overleftrightarrow{\sigma} - \overleftrightarrow{h}\cdot\overleftrightarrow{\Sigma}, \tag{4}$$

with

$$\Omega\overleftrightarrow{\pi} \equiv \sum_i m_i \vec{v}_i\vec{v}_i - \sum_i\sum_{j>i}(\varphi'/r_{ij})\vec{r}_{ij}\vec{r}_{ij}, \tag{5}$$

and

$$\overleftrightarrow{\sigma} \equiv \Omega\overleftrightarrow{h}'^{-1}. \tag{6}$$

As is usual in all molecular-dynamics calculations a system is said to be in equilibrium when all relevant dynamical variables show no secular variation. The degree of fluctuation around the mean is of course specific to each variable and contains useful statistical information.

To apply the NMD to the question of Ni/Mo superlattices we notice that the following has been shown experimentally[6]: (a) the anomalous behavior of the elastic, structural, and transport properties is mostly due to the nickel with the molybdenum playing a passive role, and (b) the (~35%) softening of C_{44} coincides with a slight (4.7%) expansion of the average Ni lattice parameters. The calculation presented here is for a Ni fcc lattice of 1440 particles. $\vec{a}$, $\vec{b}$, and $\vec{c}$ are initially taken to be mutually orthogonal, $\vec{c}$ being the cubic [111] axis (this direction is perpendicular to the substrate in the experiment). The potential $\varphi(|\vec{r}_{ij}|)$ used here is the Morse function

$$\varphi(r) = D\{\exp[-2\alpha(r-r_0)] - 2\exp[-\alpha(r-r_0)]\}. \tag{7}$$

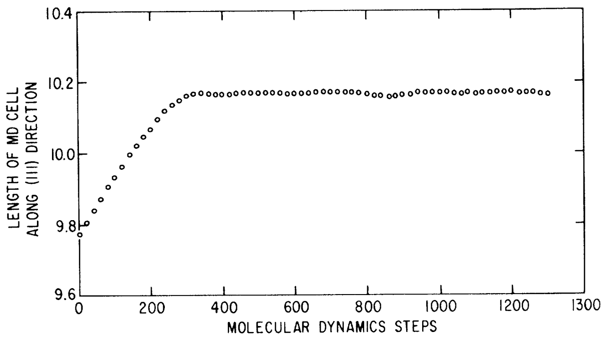

FIG. 1. Time evolution of the length in units of r_0 of the molecular-dynamics cell along the cubic [111] direction for a crystal under tensile [111] load of 8.76 $\times 10^{10}$ dyn/cm^2. The final value shows a strain of ~4.0%.

The constants $D = 0.35059 \times 10^{-12}$ erg, $\alpha = 2.4877$ Å^{-1}, and $r_0 = 2.5275$ Å have been determined by Milstein[14] to fit to the elastic constants C_{11}, C_{12} and the lattice constant $a_0 = 3.5238$ Å of fcc nickel at 0 K. Units used in MD were D, the mass of Ni, and r_0. The unit of time was taken as $\tau = (M_{\text{Ni}} r_0^2/D)^{1/2}$; the integration step for MD was $\Delta t = 0.01\tau$. All calculations were made at 400 K. When the crystal is subjected to an axial stress along the cubic [111] direction, the system responds by adopting new equilibrium values of the vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$.

Figure 1 shows the time evolution of the length h_{33} when the tensile load is increased from 0 to 8.76×10^{10} dyn/cm^2 in a system already in equilibrium at $T = 400$ K and under zero load. Simultaneously with the increase shown in Fig. 1, h_{11} and h_{22} decrease. All h_{ij}, $i \neq j$, fluctuate around zero value, i.e., $\vec{a}$, $\vec{b}$, and $\vec{c}$ remain mutually orthogonal. It took only ~300 molecular-dynamics steps for the length to fluctuate around the new equilibrium value. Ordinarily, the calculations were run for ~1500 MD steps and for checking purposes some runs were made for 5000 steps.

Figure 2 shows the phonon velocities experimentally measured using Brillouin scattering, versus average lattice parameters of nickel determined from x-ray measurements. To com-

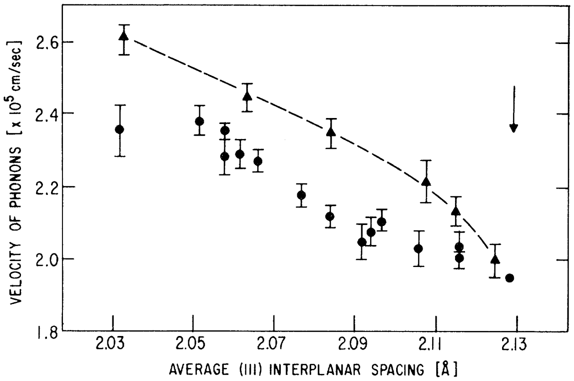

FIG. 2. Velocity of phonons vs average nickel [111] interplanar spacing (Ref. 6a). Dots are values measured by Brillouin scattering (Ref. 7) and triangles are values from the present MD calculations. The arrow indicates the value at which the structure becomes highly disordered in the Mo/Ni superlattices and where the molecular-dynamics crystal fails.

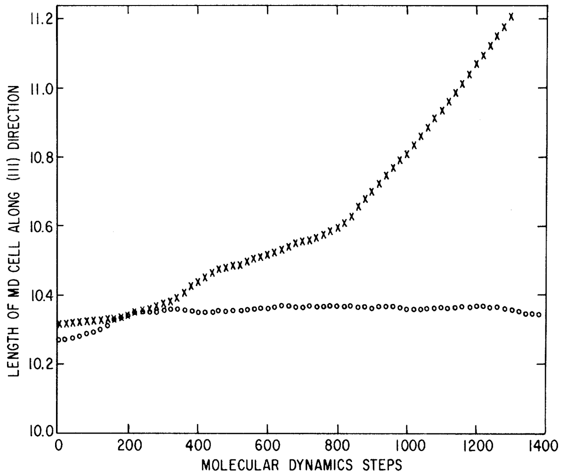

FIG. 3. Time evolution of the MD cell length along the cubic [111] direction: circles, for a stress below failure threshold, and crosses, above this value. The strain at failure threshold is ~5.0%.

pare experiment and theory we note that

$$v_R = \beta (C_{44}/\rho)^{1/2}, \tag{8}$$

with ρ the density and $0.86 \leq \beta \leq 0.98$ a constant.[7] Figure 2 also shows the velocity v_R determined by use of NMD to calculate C_{44} and with $\beta = 1$. The agreement is seen to be excellent especially since we have used no adjustable parameters in this comparison. The deviation from a straight line at large strains in the theoretical calculation shows a further softening at that point. In fact, beyond this strain the crystal fails irreversibly, as shown in Fig. 3, where the length of the MD box along the [111] direction is plotted as a function of MD steps for two strains: just before and just after failure. It is interesting that the failure point in the calculation coincides with an experimentally observed structural transition (indicated in Fig. 2 by the arrow) from a crystalline to a highly disordered state in the Mo/Ni superlattice.[6]

TABLE I. Calculated values for Young's (Y) and biaxial moduli (Y_B) (1 Pa = 1 N m^{-2} = 10 dyn cm^{-2}).

Axial [111] strain	Y_B (Pa)	Y (Pa)
0	3.14×10^{11}	1.86×10^{11}
5.0%	3.40×10^{11}	2.04×10^{11}

The possibility of a simultaneous softening in C_{44} with a hardening in Young's and biaxial moduli has been raised earlier.[7] To address this question, we have also calculated the in-plane Young's (Y) and biaxial (Y_B) moduli for two values of the strain in the length h_{33}, i.e., the cubic [111] direction; these are shown in Table I. We see that in effect there is a simultaneous hardening in Y and Y_B. However, this hardening is much smaller than what has been claimed by some experimenters[1-3] and we feel that the magnitude of this effect cannot be drastically modified by changes in the potential. We have observed qualitatively similar results using a Lennard-Jones potential; however, a quantitative comparison was not pursued. It is relevant to recall that similar calculations for Ni stressed along the cubic [100] direction have shown no anomalous softening either in NMD[12] or in static calculations.[15]

To summarize, we have performed molecular-dynamics calculations for the elastic constants of a single crystal of nickel under [111] axial stress. The results indicate an anomalous softening of the shear modulus and a slight hardening for the Young and biaxial moduli due to this axial stress. The softening is in quantitative agreement with earlier results obtained with use of Brillouin-scattering measurements in Mo/Ni superlattices. The experimentally observed structural transition from crystalline to the highly disordered state coincides with the failure of the crystal in the molecular-dynamics calculations. We hope that the present results will motivate further high-precision x-ray measurements on systems which show anomalous elastic behavior. We suggest that the anomalous expansion of the lattice is probably due to electron transfer as found in intercalated graphite compounds and should be the subject of total electronic energy calculations.

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