Lattice Expansions and Contractions in Metallic Superlattices

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An electronically driven lattice deformation which explains qualitatively the supermodulus effect in metallic superlattices is derived. It is shown in the Thomas-Fermi approximation that the total energy of a metallic superlattice is lowered by uniform deformations of the constituent materials. The theory gives the correct order of magnitude for changes in lattice constants, explains why the supermodulus effect is not observed in systems in which at least one constituent is nonmetallic, and predicts the absence of an effect when the bulk Fermi energies of the constituent metals are equal.

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According to the predictions of continuum elasticity theory, the elastic moduli (in the long-wavelength limit) of a stratified medium are expected to be independent of modulation wavelength.[1-3] Contrary to these predictions, the elastic constants of metallic superlattices are found to depend dramatically upon modulation wavelength, in some cases being enhanced severalfold (supermodulus effect). Such large changes are even more remarkable, because elastic constants otherwise are quite structure insensitive. Since the first observation of this effect,[4] it has been investigated in many systems by different techniques.[5] Its origin, however, is still controversial, even to the extent as to whether the explanation is structural or electronic.[6]

The effect of coherency strains at an interface has been proposed as a structural explanation,[7,8] but it falls short by at least an order of magnitude.[9,10] Moreover, it does not explain the elastic-constant changes observed in the lattice-matched system Au/Cr,[11] for which coherency strains are small. A recent theory[12] in which an interface is modeled by a (large-angle) grain boundary attributes the modulus enhancement to structural disorder at the interfaces. Although this theory does yield significant changes in elastic constants, it does not explain the observations in Au/Cr.[11]

Several electronic theories based on the effect of energy gaps created at the Fermi surface by the periodic potential of the superlattice have been proposed.[13-15] Although these theories explain the existence of a critical wavelength at which the modulus enhancement is a maximum, it has not yet been demonstrated that the magnitude of the elastic-constant changes is large enough to explain the observed anomalies. Recently another electronic theory, based on charge transfer between layers, was proposed by one of us.[16] Arguments were made that the transferred charge was delocalized. This conclusion, however, is now known to be incorrect as shown by a full calculation of the dielectric response of a thin film.[17]

An important step towards understanding the supermodulus effect was the discovery of changes in the average lattice spacing perpendicular to the superlattice layer planes.[8,11,18-21] The changes of the average lattice spacing becomes larger as the modulation wavelength Λ decreases, being of the order of several percent for $\Lambda=2$ nm. These changes cannot be blamed on coherency strains, since a change is also found for the lattice-matched system Au/Cr.[11] Moreover, changes of the average lattice constant are found to be much larger normal to the plane than in the plane,[18] contrary to what would be expected if the cause were coherency strain. For most systems only the average lattice constant was measured, but for Au/Cr the average lattice constant of *each* constituent was measured, showing that Au contracts and Cr expands.

The interpretation of the average lattice-constant changes is not agreed upon at present and could be due to either localized strains at each interface, uniform strains in each layer, or some combination. The assumption of localized interfacial strains has been shown to explain the observed elastic-constant changes.[21] On the other hand, the assumption of uniform strains has also been shown to explain the observed elastic-constant changes,[19,22] even so far as to explain the maximum in Au/Cr.[11] The origin of the uniform strain was, however, not explained.

In this Letter, we propose an explanation for *uniform* strains in metallic superlattices. For this purpose, it is sufficient to consider a thin layer of one metal M sandwiched between thick layers of another metal M'. We let E_F and E_F' be the Fermi energies of infinite crystals of the two metals, and $\Delta E_F = E_F - E_F'$ be the difference between the Fermi energies of the two metals.[23] When two metals having different Fermi energies are brought into contact, electric charge is transferred from one to the other. According to the conventional model, a dipole layer forms at the interface, giving rise to a potential difference $V=\Delta E_F/e$, which equalizes the Fermi energies in both metals.

The electrostatic energy of the dipole layer for a unit area of the sandwich (which has two interfaces) is

$$U_1=2(\tfrac{1}{2}cV^2), \tag{1}$$

where c is the capacitance per unit area of an interface. In the Thomas-Fermi approximation, the induced charge densities on each side of an interface (at $x=0$) have the form

$$\rho(x)=\begin{cases}(+q/\lambda_{\mathrm{TF}})\exp(-x/\lambda_{\mathrm{TF}}), & x>0,\\ (-q/\lambda'_{\mathrm{TF}})\exp(x/\lambda'_{\mathrm{TF}}), & x<0,\end{cases} \tag{2}$$

where λ_{TF} and λ'_{TF} are the Thomas-Fermi screening lengths in the metals M and M', and q is the charge per unit area. Solving Poisson's equation yields the electrostatic potential,

$$\phi(x)=\begin{cases}4\pi q\lambda_{\mathrm{TF}}[1-\exp(-x/\lambda_{\mathrm{TF}})], & x>0,\\ -4\pi q\lambda'_{\mathrm{TF}}[1-\exp(x/\lambda'_{\mathrm{TF}})], & x<0.\end{cases} \tag{3}$$

Consequently the capacitance per unit area for this charge distribution is

$$c=[4\pi(\lambda_{\mathrm{TF}}+\lambda'_{\mathrm{TF}})]^{-1}, \tag{4}$$

which is the same as the capacitance of a parallel-plate capacitor with plate separation $\lambda_{\mathrm{TF}}+\lambda'_{\mathrm{TF}}$. Since the Thomas-Fermi screening length in a metal is small, typically about 0.05 nm, the capacitance c is large, implying the same for the stored electrostatic energy U_1 [Eq. (1)]. Taking $\lambda_{\mathrm{TF}}=\lambda'_{\mathrm{TF}}=0.05$ nm and $\Delta E_F=2$ eV and substituting in (1) and (4) yields the electrostatic energy $U_1=2\times10^{14}$ eV/cm^2.

The crucial insight of this theory is to recognize that there is another way by which the Fermi energies of the two metals can be made equal, namely, by an appropriate expansion or contraction of the thin layer of metal M. We let the change of the Fermi energy of metal M be

$$\delta E_F=-\alpha v \tag{5}$$

when a uniform volume strain v is applied. (Since the volume strain v is related to the electron-density change δn by $v=-\delta n/n$, $\alpha=n\,dE_F/dn$.) The potential difference $V=\Delta E_F/e$ at the interface needed to equalize the Fermi energies is then reduced by $\delta V=\delta E_F/e$, so that the electrostatic energy per unit area of the sandwich is lowered by

$$\delta U_1=-2c(\Delta E_F)\alpha v/e^2. \tag{6}$$

On the other hand, the elastic energy (per unit area) associated with a uniform strain v in a layer of thickness d is

$$\delta U_2=\tfrac{1}{2}Bv^2d, \tag{7}$$

where B is the bulk modulus of metal M. Since Eq. (6) is linear in v whereas (7) is quadratic in v, the total energy can always be lowered by a uniform deformation of the thin layer. The optimum strain is found by minimizing $\delta U=\delta U_1+\delta U_2$, yielding

$$v=2c(\Delta E_F)\alpha/Bde^2. \tag{8}$$

Equation (8) implies a *uniform* strain throughout the layer which is proportional to $1/d$; this provides an alternative explanation for the observed $1/d$ dependence of the average lattice-constant changes which in Ref. 21 was taken as proof of a constant expansion at the interfaces. Although an isotropic strain was assumed, in practice the strain could be anisotropic because of coherency effects at the interface. The change of the Fermi energy with strain Eq. (5) and the strain energy Eq. (7) should then be evaluated for an anisotropic strain.

We illustrate this theory for a metal having a uniform positive background. The average energy per electron (in Rydbergs) is then approximately

$$E=\frac{2.210}{r_s^2}-\frac{0.916}{r_s}-\frac{0.88}{r_s+6.8}, \tag{9}$$

where r_s (in Bohr radii) is defined by $\frac{4}{3}\pi(r_sa_B)^3=1/n$ and n is the electron density.[24] In (9), the first term is the average kinetic energy, the second is the average exchange energy, and the third is an interpolation formula for the average correlation energy. In Fig. 1, the Fermi energy $E_F=d(nE)/dn$ and $\alpha=n\,dE_F/dn$ are plotted. For a typical electron density $r_s=3$ (which corresponds to $n=6\times10^{22}$ cm^{-3}), $\alpha\cong2$ eV. Taking $\Delta E_F=2$ eV, $B=10^{12}$ dyn/cm^2, and $\lambda_{\mathrm{TF}}=\lambda'_{\mathrm{TF}}=0.05$ nm, and substituting in (4) and (8) yields for the volume strain in a 1-nm-thick film

$$v\cong7\times10^{-3}, \tag{10}$$

which agrees approximately with experimentally ob-

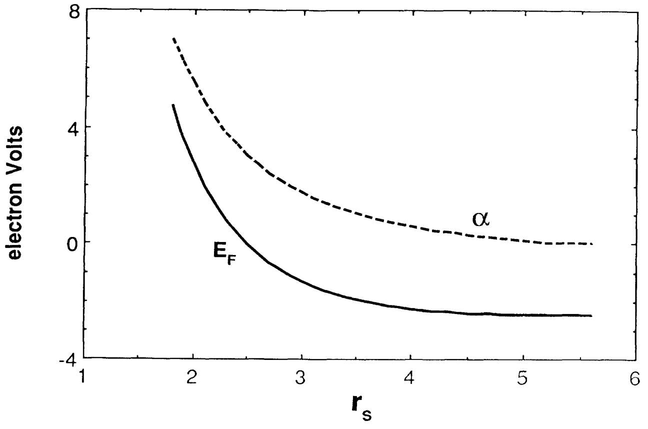

FIG. 1. Fermi energy $E_F=d(nE)/dn$ and $\alpha=n\,dE_F/dn$ vs r_s.

served values of a few percent. The fractional change of the potential difference at the interface is then $\delta V/V \cong -7\times10^{-3}$, and the lowering of the energy of the sandwich is $\delta U \cong -2\times10^{12}$ eV/cm^2.

It is straightforward to extend this theory to a superlattice in which the composition modulation is smooth rather than abrupt. We let $E_F(x)$ be the Fermi energy of an infinite crystal having a uniform composition equal to the composition at position x in the superlattice. Instead of a stepwise variation of $E_F(x)$, we suppose a sinusoidal variation,

$$E_F(x) = \bar{E}_F + \tfrac{1}{2}\Delta E_F \sin(2\pi x/\Lambda)\,, \tag{11}$$

about an average value $\bar{E}_F$ with amplitude $\frac{1}{2}\Delta E_F$ and wavelength Λ. In the Thomas-Fermi approximation, the local Fermi energy is constant across the superlattice. The electric potential which equalizes the Fermi energy is

$$\phi(x) = (\tfrac{1}{2}\Delta E_F/e)\sin(2\pi x/\Lambda)\,, \tag{12}$$

which gives rise to an electric field

$$E(x) = -(\pi\Delta E_F/e\Lambda)\cos(2\pi x/\Lambda)\,. \tag{13}$$

The average electrostatic energy per unit volume is then

$$u_1 = \bar{E}^2/8\pi = (\pi\Delta E_F/e\Lambda)^2/16\pi\,. \tag{14}$$

A sinusoidal strain

$$v(x) = v_0\sin(2\pi x/\Lambda)\,, \tag{15}$$

produces a change

$$\delta E_F(x) = -\alpha v_0 \sin(2\pi x/\Lambda) \tag{16}$$

in the Fermi energy $E_F(x)$. (For simplicity we assume that α varies little with composition.) The change in E_F reduces the amplitude of the original sinusoidal variation of $E_F(x)$. Consequently the average electrostatic energy per volume Eq. (14) decreases by

$$\delta u_1 = -\pi(\Delta E_F)\alpha v_0/4\Lambda^2 e^2\,. \tag{17}$$

On the other hand, the average elastic energy per unit volume increases by

$$\delta u_2 = \tfrac{1}{2}B\bar{v}^2 = \tfrac{1}{4}Bv_0^2\,. \tag{18}$$

(For simplicity we also assume B to be independent of composition.) Minimizing the total energy yields for the amplitude of the induced strain

$$v_0 = \pi(\Delta E_F)\alpha/2B\Lambda^2 e^2\,. \tag{19}$$

Upon substituting $\alpha = 2$ eV, $\Delta E_F = 2$ eV, and $B = 10^{12}$ dyn/cm^2 we find $v_0 = 2\times10^{-3}$ for a film having modulation wavelength $\Lambda = 2$ nm.

A key prediction of the theory presented here is that, since the sum of screening lengths in (4) is larger if at least one constituent is nonmetallic, the induced strain in such a multilayer film is much smaller. This explains the absence of an elastic anomaly in SnTe/Sb (semiconductor/semimetal),[25] NbN/AlN (metal/insulator),[26] and GaAs/AlAs (semiconductor/semiconductor)[27] superlattices.

The preceding theory is based on the Thomas-Fermi approximation, which equates the Fermi energies on both sides of an interface. (The Thomas-Fermi approximation is also used for the dielectric response within each metal layer, but this is secondary.) The more rigorous approach, of course, is to solve the Schrödinger equation for the electron states which are coherent across the interface. Although a previous calculation[28] of this type for a metal sandwich does not confirm the effect predicted here, a systematic investigation has not yet been carried out.

We conclude by noting that a major difference between the models proposed to explain the supermodulus effect lies in the associated changes in lattice constants. Many models claim that the lattice-constant changes are localized at the interfaces while our model predicts that they occur throughout each layer. Therefore one way of testing the validity of the models may be detailed analyses of x-ray data.

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