

Effect of the electronic kinetic energy on the elastic strain in metallic multilayers

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A recent theory of induced strain in metallic multilayers, caused by electron transfer effects, is revised by taking into account the electronic kinetic energy. When this is done, it is found that the predicted sign of the strain is opposite to what was found previously. For a multilayer having abrupt composition changes, the predicted magnitude of the strain is greater by a factor of $\frac{9}{5}$ than what was found previously, whereas for a multilayer having smooth composition changes, it is the same as what was found previously.

I. INTRODUCTION

When two metals having different Fermi energies are brought into contact, electric charge is transferred from one to the other, giving rise to an electric potential which equalizes the Fermi energies in the two metals. In a recent paper,¹ it was shown that the total energy (electrostatic and elastic) associated with this charge transfer could be reduced by a uniform expansion of one metal and contraction of the other. The resulting sign of the strain in each metal was such as to bring the Fermi energies of the two metals closer together, thereby decreasing the transferred charge. In that analysis, however, the electronic kinetic energy was not considered. Here we show that inclusion of the kinetic energy leads to a change in sign of the induced strain but to only a small change in its magnitude.

The driving force behind the transfer of charge from one metal to the other is the reduction of electronic kinetic energy. When charge is transferred, the reduction of kinetic energy more than compensates for the increase of electrostatic energy, the total electrostatic and kinetic energy being less after charge is transferred than before. It is shown here that the total energy (electrostatic, kinetic, and elastic) after charge transfer can be reduced even further by a uniform expansion of one metal and contraction of the other. The predicted sign of the strain, namely, such as to push the Fermi energies of the two metals further apart, thereby increasing the transferred charge, is opposite to what was found previously. Somewhat surprisingly it is thus found that, when the effect of electronic kinetic energy is included, metal layers strain in order to transfer more charge rather than less.

II. THEORY

We consider an interface between two metals, the one on the right ($x > 0$) having Fermi energy E_F and the one on the left ($x < 0$) having Fermi energy E'_F . The Fermi energy before charge transfer is then

$$E_F^{(0)}(x) = \begin{cases} E_F, & x > 0 \\ E'_F, & x < 0. \end{cases} \quad (1)$$

After charge transfer the local Fermi energy is constant (in the Thomas-Fermi approximation). For clarity we first ignore strain and treat only the two usual effects which change the local Fermi energy from its bulk value: electrostatic potential and electron density.

(i) An electrostatic potential $\phi(x)$ changes the Fermi energy by

$$\delta E_F(x) = -e\phi(x). \quad (2)$$

(ii) In a free-electron model the Fermi energy is related to the electron density n through $E_F = \hbar^2 k_F^2 / 2m$ and $k_F^3 = 3\pi^2 n$. To first order, a charge density $\rho = -e\delta n$ therefore changes the Fermi energy by

$$\delta E_F(x) = -4\pi e \lambda_{TF}^2 \rho(x), \quad (3)$$

where $\lambda_{TF} = (\pi \hbar^2 / 4me^2 k_F)^{1/2}$ is the Thomas-Fermi screening length. In lowest order the effect of the transferred charge on the screening length can be neglected. Consequently, in the Thomas-Fermi approximation

$$E_F^{(0)}(x) - e\phi(x) - 4\pi e \lambda_{TF}^2(x) \rho(x) = \text{const}, \quad (4)$$

where the Thomas-Fermi screening length on each side of the interface is

$$\lambda_{TF}(x) = \begin{cases} \lambda_{TF}, & x > 0 \\ \lambda'_{TF}, & x < 0. \end{cases} \quad (5)$$

Far from the interface, the charge density vanishes. Using Eq. (4) to equate the local Fermi energy at $x = +\infty$ to the local Fermi energy for $x > 0$ yields

$$-e[\phi(x) - \phi(\infty)] - 4\pi e \lambda_{TF}^2 \rho(x) = 0 \quad (6a)$$

for $x > 0$. Similarly equating the local Fermi energy at $x = -\infty$ to the local Fermi energy for $x < 0$ yields

$$-e[\phi(x) - \phi(-\infty)] - 4\pi e \lambda_{TF}^{\prime 2} \rho(x) = 0 \quad (6b)$$

for $x < 0$. Finally, by equating the local Fermi energies at $x = \pm\infty$, we obtain the potential change across the interface,

$$\phi(\infty) - \phi(-\infty) = \Delta E_F / e, \quad (7)$$

where $\Delta E_F \equiv E_F - E'_F$ is the Fermi-energy difference.

The electrostatic potential can be chosen arbitrarily at a point; it is convenient to take $\phi(0)=0$. Using Poisson's equation in conjunction with Eq. (6) to solve for $\phi(x)$, matching the solutions for ϕ and $d\phi/dx$ at $x=0$, and using Eq. (7), we find

$$\phi(x) = \begin{cases} \frac{\Delta E_F}{e} \frac{\lambda_{TF}}{\lambda_{TF} + \lambda'_{TF}} [1 - \exp(-x/\lambda_{TF})], & x > 0 \\ -\frac{\Delta E_F}{e} \frac{\lambda'_{TF}}{\lambda_{TF} + \lambda'_{TF}} [1 - \exp(x/\lambda'_{TF})], & x < 0. \end{cases} \quad (8)$$

The electrostatic energy per unit area

$$U_1 = \int_{-\infty}^{\infty} \frac{1}{8\pi} \left(\frac{d\phi}{dx} \right)^2 dx \quad (9)$$

is then²

$$U_1 = \frac{(\Delta E_F/e)^2}{16\pi(\lambda_{TF} + \lambda'_{TF})}. \quad (10)$$

For a free-electron gas having Fermi energy E_F , the average kinetic energy per electron is $\frac{3}{5}E_F$. The electronic kinetic energy per unit area after charge transfer relative to its value before charge transfer is therefore

$$U_2 = \frac{3}{5} \int_{-\infty}^{\infty} [n(x)E_F(x) - n^{(0)}(x)E_F^{(0)}(x)] dx, \quad (11)$$

where $n^{(0)}(x)$ and $n(x)$ are, respectively, the electron density at position x before and after charge transfer, and $E_F^{(0)}(x)$ and $E_F(x)$ are, respectively, the maximum kinetic energy at position x before and after charge transfer. It is shown in the Appendix that

$$U_2 = -\frac{14}{5} \frac{(\Delta E_F/e)^2}{16\pi(\lambda_{TF} + \lambda'_{TF})}. \quad (12)$$

Combining Eqs. (10) and (12) yields the total kinetic and electrostatic energy per unit area after charge transfer relative to its value before charge transfer,

$$U = -\frac{9}{5} \frac{(\Delta E_F/e)^2}{16\pi(\lambda_{TF} + \lambda'_{TF})}, \quad (13)$$

which, compared to the electrostatic energy alone, is greater in magnitude by a factor of $\frac{9}{5}$ but of opposite sign. Since $U < 0$, the total energy is lowered by charge transfer.

We now show that the total energy of a multilayer can be lowered even further if the layers are uniformly strained. We begin by considering a metallic sandwich consisting of a thin layer of one metal, having Fermi energy E_F , between thick (semi-infinite) layers of another metal, having Fermi energy E'_F . Since the elastic energy required to strain a metal includes the change of electronic kinetic energy, care must be taken to count kinetic-energy changes only once. A simple way to ensure this is to apply strain before transferring charge. For simplicity, a hydrostatic strain is assumed. The elastic energy per unit area required for a uniform volume strain v in the inner layer is then

$$U_3 = \frac{1}{2} B v^2 t, \quad (14)$$

where B is the bulk modulus of the metal in the inner layer and t is its thickness. A uniform volume strain v changes the Fermi energy of the metal in the inner layer by

$$\delta E_F = -\alpha v, \quad (15)$$

where α is the rate of change of Fermi energy with strain for the metal in the inner layer. The difference in Fermi energies between the metals in the inner and outer layers is then $\Delta E_F - \alpha v$ instead of ΔE_F . Assuming that the inner layer is thick enough ($t > 2\lambda_{TF}$) that the screening charges at its two interfaces do not overlap, the kinetic and electrostatic energy per unit area in the strained state after charge transfer relative to its value in the strained state before charge transfer is given by twice Eq. (13) with ΔE_F replaced by $\Delta E_F - \alpha v$. (Since the Thomas-Fermi screening length depends weakly on electron density, i.e., $\lambda_{TF} \propto n^{-1/6}$, the effect of strain on the screening length can be neglected.) The total energy per unit area in the strained state after charge transfer relative to its value in the unstrained state before charge transfer is then

$$U = -\frac{18}{5} \frac{[(\Delta E_F - \alpha v)/e]^2}{16\pi(\lambda_{TF} + \lambda'_{TF})} + \frac{1}{2} B v^2 t. \quad (16)$$

For $\alpha = 3$ eV, $\lambda_{TF} = \lambda'_{TF} = 0.05$ nm, $B = 10^{12}$ dyn/cm², and $t = 1$ nm, it can be confirmed that the quadratic strain term proportional to α^2 can be neglected compared to the quadratic term proportional to B . The optimum uniform strain which minimizes the total energy is then found to be

$$v = -\frac{9}{5} \frac{1}{4\pi(\lambda_{TF} + \lambda'_{TF})} \frac{(\Delta E_F)\alpha}{B e^2 t}, \quad (17)$$

which is greater in magnitude by a factor of $\frac{9}{5}$ and opposite in sign compared to what was found previously when the effect of electronic kinetic energy was neglected.^{1,2}

This theory is easily extended to a metallic superlattice, having alternating layers of one metal with Fermi energy E_F and thickness t and another metal with Fermi energy E'_F and thickness t' . Let one metal have a uniform volume strain v and the other a uniform volume strain v' . By the same argument as before, the total energy per unit area (per repeat period) in the strained state after charge transfer relative to its value in the unstrained state before charge transfer is

$$U = -\frac{18}{5} \frac{[(\Delta E_F - \alpha v + \alpha' v')/e]^2}{16\pi(\lambda_{TF} + \lambda'_{TF})} + \frac{1}{2} B v^2 t + \frac{1}{2} B' v'^2 t'. \quad (18)$$

As before, the quadratic terms proportional to α^2 , $\alpha\alpha'$, and α'^2 can be neglected in first approximation. The optimum uniform strains which minimize the total energy of the superlattice are then

$$v = -\frac{9}{5} \frac{1}{4\pi(\lambda_{TF} + \lambda'_{TF})} \frac{(\Delta E_F)\alpha}{B e^2 t} \quad (19a)$$

and

$$v' = + \frac{9}{5} \frac{1}{4\pi(\lambda_{TF} + \lambda'_{TF})} \frac{(\Delta E_F)\alpha'}{B'e^2t'} . \quad (19b)$$

The uniform strain in each layer is inversely proportional to the thickness of that layer but independent of the thickness of other layers.

We next consider a metallic superlattice in which the composition modulation is smooth rather than abrupt. We let $E_F^{(0)}(x)$ be the Fermi energy at position x before charge transfer. Instead of a stepwise variation of $E_F^{(0)}(x)$, we suppose a sinusoidal variation

$$E_F^{(0)}(x) = \langle E_F^{(0)} \rangle + \frac{1}{2} \Delta E_F \sin(2\pi x / \Lambda) , \quad (20)$$

about an average value $\langle E_F^{(0)} \rangle$ with amplitude $\frac{1}{2} \Delta E_F$ and wavelength Λ . By following the preceding analysis, it can be shown that the total energy of a composition-modulated superlattice can be lowered by a sinusoidal uniaxial strain (in the growth direction)

$$\varepsilon(x) = \varepsilon_0 \sin(2\pi x / \Lambda) , \quad (21)$$

with

$$\varepsilon_0 = -\pi(\Delta E_F)\alpha / 2Ce^2\Lambda^2 , \quad (22)$$

where C is the elastic modulus appropriate for a uniaxial strain.³ This result is equal in magnitude but opposite in sign, compared to what was found previously when the effect of electronic kinetic energy was neglected.¹

III. DISCUSSION

Induced strain caused by electron transfer effects has been proposed¹ as a possible explanation of the observed dependence of elastic constants in metallic superlattices on modulation wavelength.⁴ In a recent experiment,⁵ it was found that the elastic response in the metal-insulator superlattice zirconium nitride-aluminum nitride also depended on modulation wavelength. This shows that an electron-transfer mechanism, which only predicts anomalous behavior in metallic systems, cannot be the complete explanation of elastic anomalies in multilayers. In contrast to what is observed in metallic superlattices,⁶⁻¹⁰ however, the changes of the average perpendicular lattice constant in the metal-insulator superlattice zirconium nitride-aluminum nitride are small and uncorrelated with changes of the elastic response. Thus, although an electron-transfer mechanism cannot explain elastic-constant changes in metal-insulator superlattices, it still may play a role in explaining such changes in metallic superlattices.

Two main criticisms have been raised regarding our previous treatment of charge-transfer-induced strains in which electronic kinetic energy was neglected:¹ (i) since both electrostatic and elastic energies are positive, the total energy was greater after charge transfer than before, and (ii) although it was shown that a uniform strain

throughout each layer lowered the total energy, it was not shown that it was the state of lowest energy. Both criticisms are valid. The first objection has been answered here by showing that, when electronic kinetic energy is included, the total energy is reduced by charge transfer. The second objection, which still applies, will be addressed in the future by examining the spatial dependence of the strain field which minimizes the total energy of a metallic multilayer.

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APPENDIX

The change of electronic kinetic energy as a result of charge transfer, Eq. (11), can be expressed as the sum of

$$U_{2a} = \frac{3}{5} \int_{-\infty}^{\infty} [n(x) - n^{(0)}(x)] E_F(x) dx \quad (A1)$$

and

$$U_{2b} = \frac{3}{5} \int_{-\infty}^{\infty} n^{(0)}(x) [E_F(x) - E_F^{(0)}(x)] dx . \quad (A2)$$

Substituting

$$E_F(x) = \text{const} + e\phi(x) \quad (A3)$$

in Eq. (A1) and using conservation of charge gives

$$U_{2a} = \frac{3}{5} \int_{-\infty}^{\infty} e [n(x) - n^{(0)}(x)] \phi(x) dx . \quad (A4)$$

Substituting $\rho = -e(n - n^{(0)})$, using Poisson's equation, integrating by parts, and using Eqs. (9) and (10), we obtain

$$U_{2a} = -\frac{6}{5} \frac{(\Delta E_F/e)^2}{16\pi(\lambda_{TF} + \lambda'_{TF})} . \quad (A5)$$

Substituting

$$E_F(x) - E_F^{(0)}(x) = -4\pi e \lambda_{TF}^2(x) \rho(x) \quad (A6)$$

in Eq. (A2), using Poisson's equation for $\rho(x)$, and substituting for $n^{(0)}(x)$ and $\lambda_{TF}(x)$ gives

$$U_{2b} = \frac{3}{5} \frac{1}{6\pi e} \int_{-\infty}^{\infty} E_F^{(0)}(x) \frac{d^2\phi}{dx^2} dx . \quad (A7)$$

Using Eqs. (1) and (8) for $E_F^{(0)}(x)$ and $\phi(x)$ yields

$$U_{2b} = -\frac{8}{5} \frac{(\Delta E_F/e)^2}{16\pi(\lambda_{TF} + \lambda'_{TF})} . \quad (A8)$$

Combining the results for U_{2a} and U_{2b} , we thus obtain

$$U_2 = -\frac{14}{5} \frac{(\Delta E_F/e)^2}{16\pi(\lambda_{TF} + \lambda'_{TF})} . \quad (A9)$$

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¹M. L. Huberman and M. Grimsditch, *Phys. Rev. Lett.* **62**, 1403 (1989).

²In Ref. 1, the electrostatic energy stored in a double layer at an interface was overestimated by a factor of two, the error being caused by the use of an incorrect analogy with the electrostatic energy of a capacitor. This error led to an overestimate of the induced strain [in Eq. (10) of Ref. 1] likewise by a factor of two.

³If the nonuniform strain in Eq. (21) were to be hydrostatic, every atomic layer would be lattice mismatched with the adjacent atomic layers. It is assumed here that such mismatch is prohibited energetically, and that therefore the induced strain is uniaxial (in the growth direction).

⁴For a review, see I. K. Schuller, in *Ultrasonics Symposium*,

edited by B. R. McAvoy, IEEE Symposium on Ultrasonics, 1985 (IEEE, New York, 1985), p. 1093.

⁵W. J. Meng, G. L. Eesley, and K. A. Svinarich, *Phys. Rev. B* **42**, 4881 (1990).

⁶M. R. Khan, C. S. L. Chun, G. P. Felcher, M. Grimsditch, A. Kueny, C. M. Falco, and I. K. Schuller, *Phys. Rev. B* **27**, 7186 (1983).

⁷I. K. Schuller and M. Grimsditch, *J. Vac. Sci. Technol. B* **4**, 1444 (1986).

⁸P. Bisanti, M. B. Brodsky, G. P. Felcher, M. Grimsditch, and L. R. Sill, *Phys. Rev. B* **35**, 7813 (1987).

⁹B. M. Clemens and G. L. Eesley, *Phys. Rev. Lett.* **61**, 2356 (1988).

¹⁰J. L. Makous and C. M. Falco, *Solid State Commun.* **68**, 375 (1988).