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## Coherency strain effects in metallic bilayers

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**Abstract.** Since its discovery, the so-called 'supermodulus effect' has attracted considerable attention, both in view of possible applications and because of its intrinsic fundamental scientific interest. Recent experimental investigations have, however, cast doubts on the very existence of the effect, or at least on its magnitude. From a theoretical point of view, several models have been proposed to explain the effect, but none is fully convincing. In the present paper we investigate the coherency strain model, which we believe may yield the most plausible quantitative explanation of the supermodulus effect. We follow the approach first proposed by Jankowski and Tsakalakos, but, in addition to other modifications, we evaluate the biaxial modulus for a deformation in the [111] direction, as observed experimentally, rather than the [100] direction, as chosen by Jankowski and Tsakalakos (probably because it was easier to determine the biaxial modulus in this rather than in the [111] direction).

### 1. Introduction

Two-component multilayer metal films consist of alternating layers of two different metals deposited on a suitable substrate. These films are commonly known as composition-modulated multilayers, and the bilayer thickness,  $\lambda$ , is referred to either as the composition-modulated wavelength or as the repeat distance. The development of multilayer films, initially produced to study diffusional effects in metal films, led to the discovery of the 'supermodulus effect' by Hilliard and co-workers in Au/Ni and Cu/Pd multilayers [1-3]. They observed that in these multilayers, and for a repeat distance in the range of 15-20 Å, the measured biaxial modulus was two to three times larger than the value predicted by the simple rule of mixture. Following the original study on Au/Ni and Cu/Pd films, Baral (another student of Hilliard) investigated the changes in the primary elastic properties of Cu/Ni multilayers [4]. Baral showed the existence of a supermodulus effect not only in the biaxial modulus but also in other moduli, such as the flexural and torsional moduli, for a repeat distance of about 20 Å. Therefore, the supermodulus effect is understood to mean a significant increase in the elastic moduli of multilayer systems in general and, specifically, in the biaxial modulus.

Multilayer films represent a new class of materials with novel electronic, magnetic, and mechanical properties. Consequently, the discovery of the supermodulus effect has given rise to the hope that, in the future, it would be possible to develop multilayered materials with specifically engineered mechanical and physical properties.

As a consequence of the pioneering work of Hilliard and co-workers, extensive investigations have been conducted in order to study possible anomalies in the elastic behaviour of multilayer metal films. Since its discovery, different models have been proposed to explain, on an atomic scale, the origin of the supermodulus effect. All the proposed models start with the implicit assumption that the effect must be associated with the fact that, for repeat distances of around 20 Å (corresponding to a few atomic layers), a large volume fraction of the two different metal atoms lie at or near an interface. Below, the three prevalent models proposed to explain the supermodulus effect are briefly summarized.

(i) In the first model, as proposed by Wu [5] and later also by Pickett [6, 7], the increase in the biaxial modulus is assumed to be the result of the interaction of the Fermi surface with the Brillouin zone, arising from the layered structure of the materials. In this model the important parameter is the valence difference between the two metal constituents.

(ii) The second model, originally proposed by Grimsditch and co-workers [8], tries to explain the effect with electronic-structure considerations. According to this model, the supermodulus effect is the result of the charge transfer that takes place when two metals with different work functions come into intimate contact.

(iii) The third model relies on the coherency strains that may be present at the multilayer interfaces due to the lattice mismatch of the two component metals. At a coherent interface, the component with the larger lattice constant is compressed laterally, whereas the component with the smaller lattice constant is expanded. This state of affairs produces coherence strains at the interface and the multilayer system minimizes its total energy by adjusting its interlayer spacing perpendicular to the interface plane. The main proponents of the coherency strain model are Jankowski and Tsakalakos [9–11].

In the last few years the whole issue of the supermodulus effect has been carefully re-examined both experimentally and theoretically. To date, no one has been able to duplicate the original results reported by Hilliard and co-workers. These recent results cast doubt upon the existence of a supermodulus effect in metallic multilayers or its relative magnitude. A brief summary of the recent experimental and theoretical results relating to the question of the existence and relative magnitude of the supermodulus effect is given below.

Studies by Ketterson and co-workers on the mechanical properties of Cu/Ni multilayers did not show any enhancement in either the biaxial or the Young's modulus of self-supporting film specimens [12]. Their mechanical test results were consistent with Rayleigh acoustic wave measurements on the same films. These were conducted by Mattson and co-workers who did not observe any anomaly in the Rayleigh wave velocity [13]. On the other hand, Falco and co-workers, who also used Brillouin scattering to study the elastic properties of Mo/Ta, Cu/Nb, and Cu/Co and Ag/Pd multilayers, observed that the values of some elastic constants (such as  $C_{11}$ ,  $C_{13}$ ,  $C_{44}$  and  $C_{55}$ ) depend on the repeat distance  $\lambda$ . Changes of up to 20% in the Rayleigh acoustic wave velocity were observed in Ag/Pd multilayers as the repeat distance was varied between 5 and 100 Å [14]. Cammarata and co-workers, who measured the elastic properties of Cu/Ni multilayers by a nano-indentation technique, did not observe the elastic property anomalies which are characteristic of the supermodulus effect [15]. Finally, atomistic model studies by Gilmore and Provenzano [16], by Chen *et al* [17], and by Jaszczak *et al* [18] on Cu/Pd and Cu/Ni multilayers showed increases of from

20–35% in some of the elastic moduli.

To reiterate, the results of the above experimental and theoretical studies lead one to conclude that, if the supermodulus effect really exists, its magnitude is significantly smaller than originally reported by Hilliard and co-workers, with a 40% increase above the value predicted by the rule of mixture representing the upper limit of the effect.

Among the three aforementioned models for the explanation of the supermodulus effect, the coherency strain approach appears to be the most plausible. In fact, it is the only one that is consistent with the observations reported by Gleiter [19] in connection with his fundamental studies on the properties of materials with nanosize grain dimensions. Gleiter observed a significant modulus enhancement in nanocrystalline pure metals, such as Cu and Pd, but not in ionic materials with nanocrystalline grain size. Other difficulties with the first two models are discussed in references [20, 21].

Besides being more promising, the coherency strain model is particularly appealing for its intrinsic simplicity, since it connects, via a pseudopotential energy approach, the elastic properties to the local atomic structure. Jankowski and Tsakalacos' calculations [9–11], however, were performed in the [100] direction, in order to simplify the analysis. Since most measurements have been performed on metal film samples grown with the interface parallel to the [111] direction, it has been difficult to make a direct comparison between the theoretical results obtained by Jankowski and Tsakalacos and experimental results (Hilliard and co-workers [1–3]). Furthermore, as will be shown in the next section, their calculations contain an element of inaccuracy which, although relatively small, we believe should be corrected.

The purpose of the present paper is to establish the formalism for the calculations of the elastic constants (and therefore of the biaxial modulus and other elastic moduli) for a single metallic layer strained in an arbitrary direction. Following assumptions of Jankowski and Tsakalacos concerning the total energy of multilayer systems, as detailed in the next section, we then apply our formalism to predict the amount of 'supermodulus effect' (variation of the biaxial modulus) which can be expected for a given strain of the same metallic layer in the [111] direction. In a subsequent paper we will first verify Jankowski and Tsakalacos' assumptions by the use of a more general model, and then calculate the amount of strain which can be predicted for various combinations of two different metals (such as Cu/Ni, Au/Ni, Cu/Pd, Ag/Pd, etc). This should yield a quantitative answer as to the amount of supermodulus effect that can be expected on the basis of the coherency strain model.

## 2. The elastic constants

As stated in the introduction, we first derive general formulae for the calculation of the elastic constants for a single metallic layer, subject to an arbitrary (but small) initial deformation. We adopt Jankowski and Tsakalacos' model [9–11], which is based on the pseudopotential energy approach [22, 23]. According to this model, the total crystal energy for a noble metal may be written as

$$E = E_{es} + E_{fe} + E_{be} + E_r \quad (2.1)$$

where  $E_{es}$  represents the electrostatic Coulomb energy of positive point charges in the uniform negative-charge background (the so-called Madelung energy);  $E_{fe}$  is the

free-electron energy, which depends on the crystal volume;  $E_{be}$  is the band-structure energy; and  $E_r$  the ion-core (Born–Mayer) repulsive energy term.

From their calculations, Jankowski and Tsakalakos conclude that  $E_r$  is the predominant term for calculations of the elastic constants. Following Soma [24], the energy term,  $E_r$ , can be expressed as:

$$E_r = 0.5\alpha \sum_n \exp(-\beta R^{(n)}) \quad (2.2)$$

where  $\alpha$  is the repulsive energy parameter and  $\beta$  is the repulsive range parameter. The sum is extended to all the nearest neighbours which are located at distances  $R^{(n)}$ , as will be explained later. The values of  $\alpha$  and  $\beta$  for Cu, Au and Ag are given in [9].

In the present paper we also write  $E_r$  as in (2.2) and neglect all other terms in (2.1). (In a subsequent paper, we will, however, generalize the present treatment to include the other three energy terms and also consider other functional forms for  $E_r$ .) We then write the second-order elastic constants (stiffness constants) as

$$C_{ijkl} = \frac{\partial^2 \bar{V}}{\partial \eta_{ij} \partial \eta_{kl}} \quad (2.3)$$

where

$$\bar{V} = E/\Omega \quad (2.4)$$

is the potential energy of deformation per unit volume (or elastic potential),  $\Omega$  is the cell volume and  $\eta_{ij}$  is the Lagrangian strain tensor.

Starting with equations (2.1–2.4), Jankowski and Tsakalakos [9–11] proceeded to determine the elastic constants by considering a number of *ad hoc* crystalline deformations. While this approach is convenient and quite straightforward in some cases (e.g. the deformation in the direction [100] which they consider), it becomes very tedious and complicated for a general treatment. Also, it is important to make sure that the deformations that are chosen correspond either to dilatations or to pure strains without a rotation (see [25] for a pictorial representation of a general deformation split into a pure strain plus a rotation). It appears that this was not the case in the analysis by Jankowski and Tsakalakos (e.g. equations (13) and (14) of [9] and table 1 of [11]), thus leading to formulae for some of the elastic constants which are not symmetric, as they should be. For these reasons we prefer to rely on a more systematic approach to compute the elastic constants, based on the formula

$$\frac{\partial}{\partial \eta_{ij}} = \frac{1}{2} \left( X_i \frac{\partial}{\partial x_j} + X_j \frac{\partial}{\partial x_i} \right). \quad (2.5)$$

The above formula is derived in appendix A (where we also discuss the separation of pure strains from pure rotations for the case of a general deformation). In (2.5)  $X_i$  are the Lagrangian coordinates corresponding to an initial state which may be subject to an (initial) finite deformation,  $x_i$  are the final (Eulerian) coordinates, differing from  $X_i$  by an infinitesimal deformation. It is important to note that, in applying (2.5), the Lagrangian coordinates  $X_i$  must be considered as constants (since they refer to a predefined initial state).

Table I. Values of the elastic constants and biaxial modulus in the (X, Y, Z) reference system as a function of strain. Units are 10<sup>12</sup> dyn cm<sup>-2</sup>.

	Epsilon	C <sub>11</sub>	C <sub>22</sub>	C <sub>44</sub>	C <sub>55</sub>	C <sub>12</sub>	C <sub>23</sub>	C <sub>25</sub>	Y <sub>b</sub>
1	-0.040	2.508	3.935	1.256	0.4667	0.6012	1.423	0.200200	5.070
2	-0.038	2.496	3.815	1.217	0.4701	0.6019	1.380	0.201030	4.905
3	-0.036	2.485	3.699	1.180	0.4733	0.6026	1.338	0.201870	4.745
4	-0.034	2.473	3.587	1.144	0.4766	0.6035	1.298	0.202740	4.590
5	-0.032	2.462	3.478	1.110	0.4798	0.6043	1.259	0.203630	4.440
6	-0.030	2.451	3.373	1.076	0.4829	0.6052	1.221	0.204540	4.295
7	-0.028	2.440	3.271	1.043	0.4861	0.6062	1.184	0.205470	4.155
8	-0.026	2.429	3.173	1.012	0.4892	0.6072	1.149	0.206420	4.019
9	-0.024	2.419	3.078	0.9816	0.4923	0.6083	1.115	0.207410	3.887
10	-0.022	2.408	2.986	0.9522	0.4954	0.6094	1.082	0.208410	3.759
11	-0.020	2.398	2.897	0.9237	0.4984	0.6106	1.050	0.209440	3.636
12	-0.018	2.389	2.811	0.8961	0.5015	0.6119	1.019	0.210500	3.516
13	-0.016	2.379	2.728	0.8695	0.5045	0.6132	0.9887	0.211580	3.400
14	-0.014	2.370	2.647	0.8437	0.5076	0.6145	0.9598	0.212690	3.288
15	-0.012	2.360	2.569	0.8188	0.5106	0.6160	0.9318	0.213830	3.180
16	-0.010	2.352	2.494	0.7946	0.5137	0.6175	0.9047	0.215000	3.074
17	-0.008	2.343	2.421	0.7713	0.5167	0.6190	0.8786	0.216190	2.973
18	-0.006	2.334	2.351	0.7488	0.5198	0.6206	0.8533	0.217420	2.874
19	-0.004	2.326	2.283	0.7270	0.5228	0.6223	0.8288	0.218680	2.779
20	-0.002	2.318	2.217	0.7059	0.5259	0.6241	0.8052	0.219970	2.686
21	0.000	2.310	2.153	0.6855	0.5290	0.6259	0.7824	0.221290	2.597
22	0.002	2.302	2.092	0.6658	0.5322	0.6278	0.7603	0.222650	2.510
23	0.004	2.295	2.033	0.6468	0.5353	0.6298	0.7390	0.224040	2.426
24	0.006	2.288	1.975	0.6284	0.5385	0.6318	0.7185	0.225470	2.345
25	0.008	2.281	1.919	0.6106	0.5417	0.6340	0.6986	0.226940	2.266
26	0.010	2.274	1.866	0.5935	0.5450	0.6362	0.6794	0.228440	2.190
27	0.012	2.267	1.815	0.5769	0.5482	0.6385	0.6609	0.229990	2.116
28	0.014	2.261	1.765	0.5609	0.5516	0.6408	0.6430	0.231570	2.044
29	0.016	2.255	1.717	0.5454	0.5549	0.6433	0.6257	0.233200	1.975
30	0.018	2.249	1.670	0.5305	0.5583	0.6458	0.6091	0.234870	1.908
31	0.020	2.243	1.625	0.5160	0.5618	0.6485	0.5930	0.236590	1.843
32	0.022	2.238	1.582	0.5021	0.5653	0.6512	0.5775	0.238350	1.780
33	0.024	2.232	1.540	0.4887	0.5689	0.6540	0.5626	0.240150	1.719
34	0.026	2.227	1.500	0.4757	0.5725	0.6569	0.5481	0.242010	1.660
35	0.028	2.223	1.461	0.4633	0.5762	0.6600	0.5343	0.243920	1.603
36	0.030	2.218	1.423	0.4512	0.5800	0.6631	0.5209	0.245880	1.548
37	0.032	2.214	1.387	0.4396	0.5838	0.6663	0.5080	0.247900	1.494
38	0.034	2.210	1.352	0.4284	0.5877	0.6697	0.4956	0.249970	1.442
39	0.036	2.206	1.319	0.4176	0.5917	0.6731	0.4836	0.252100	1.392
40	0.038	2.202	1.287	0.4072	0.5958	0.6767	0.4721	0.254290	1.343
41	0.040	2.199	1.256	0.3972	0.6000	0.6804	0.4611	0.256540	1.296

Using (2.5), it is straightforward to prove that, for a differentiable function  $f(r)$ , the following relation holds:

$$\left( \frac{\partial^2 f(r)}{\partial \eta_{kl} \partial \eta_{ij}} \right)_{r=R} = \frac{1}{R^3} [Rf''(R) - f'(R)] Y_{ijkl} + \frac{1}{4R} f'(R) Z_{ijkl} \tag{2.6}$$

where

$$Y_{ijkl} = X_i X_j X_k X_l \tag{2.7}$$

$$Z_{ijkl} = X_i X_k \delta_{jl} + X_i X_l \delta_{jk} + X_j X_l \delta_{ik} + X_j X_k \delta_{il} \tag{2.8}$$

and

$$R = \sqrt{X_1^2 + X_2^2 + X_3^2}. \quad (2.9)$$

From (2) and (3), it then follows that

$$C_{ijkl} = A_{ijkl} - B_{ijkl} \quad (2.10)$$

where

$$A_{ijkl} = \sum_n f^{(n)} Y_{ijkl}^{(n)} \quad (2.11)$$

$$B_{ijkl} = \sum_n g^{(n)} Z_{ijkl}^{(n)} \quad (2.12)$$

$$f^{(n)} = f(R^{(n)}) = 4g^{(n)}[(1 + \beta R^{(n)})/(R^{(n)})^2] \quad (2.13)$$

$$g^{(n)} = g(R^{(n)}) = (K/R^{(n)}) \exp(-\beta R^{(n)}) \quad (2.14)$$

where  $K$  is defined as

$$K = \alpha\beta/8\Omega \quad (2.15)$$

and  $Y^{(n)}$ ,  $Z^{(n)}$ , and  $R^{(n)}$  refer to the corresponding quantities defined in (11), (9), and (12) respectively, as calculated for the  $n$ th nearest neighbour.

In order to simplify the calculation of the elastic constants, it is useful to observe that the number of terms to be evaluated explicitly may be greatly reduced due to some special symmetries, in addition to the usual symmetries of  $C_{ijkl}$ . These special symmetries, which are due to the special structure of  $Y_{ijkl}$  and  $Z_{ijkl}$ , are listed in appendix B.

It is straightforward to apply (2.13) to the case of deformations in the [100] direction, which transform an FCC crystal into one with only tetragonal symmetry. One then obtains formulae for the elastic constants and moduli which agree with those reported in [11], except for some corrections due to the incorrect inclusion of rotational components in some of the deformations considered in [9-11].

### 3. Biaxial deformation in the direction [111]

Let us assume that an FCC crystal cell is deformed in the [111] direction, which is represented, in figure 1, by an axis  $X$  parallel to OD (diagonal of the cube) and normal to ABC. The deformation can be analysed easily by considering the three sets of axes, all centred in O:

- (i) a set of axes  $(x, y, z)$  parallel to three sides of the cube (see figure 1)
- (ii) an auxiliary set of axes  $(x', y', z')$  obtained from  $(x, y, z)$  with a  $45^\circ$  rotation around  $z \equiv z'$
- (iii) a third set of axes  $(X, Y, Z)$ , obtained from  $(x', y', z')$  with a rotation around  $y' \equiv Y$  of an angle

$$\theta = \arcsin(1/\sqrt{3}). \quad (3.1)$$

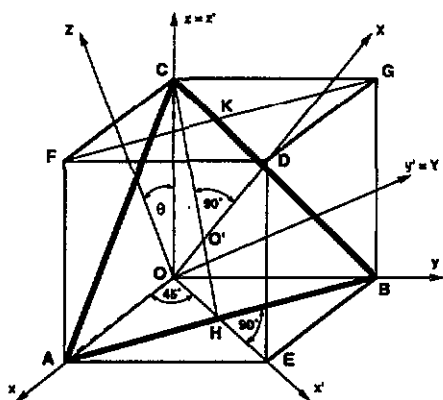


Figure 1. Representation of the sets of axes  $(x, y, z)$  and  $(X, Y, Z)$ . The latter is used to study the crystal in a biaxially deformed state. The angle  $\theta$  is defined in (3.1).

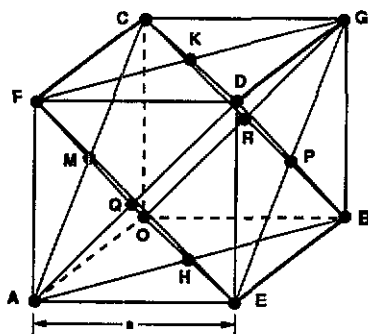


Figure 2. The FCC unit crystal cell.

It can be easily shown that the transformation equations from  $(x, y, z)$  to  $(X, Y, Z)$  are:

$$X = (x + y + z)/\sqrt{3} \quad Y = (-x + y)/\sqrt{2} \quad Z = (-x - y + 2z)/\sqrt{6} \quad (3.2)$$

Now all the allowed positions for atoms in an undeformed FCC crystal (figure 2) may be specified by three coordinates  $x, y, z$  which are integer or half-integer multiples of the lattice constant  $a$ , the only restriction being that  $x + y + z$  must be an integer multiple of  $a$ . Applying (3.2) we find that the corresponding coordinates in the  $(X, Y, Z)$  reference system are given by:

$$X = la/\sqrt{3} \quad Y = ma/\sqrt{8} \quad Z = na/\sqrt{24} \quad (3.3)$$

where  $l, m, n$ , are integers, the only restriction being that  $m$  and  $n$  must have the same parity. Figure 3 shows the lattice arrangement, as obtained from (3.3), for the plane ABC ( $X = a/\sqrt{3}$ ) and the two neighbouring planes  $X = 0$  and  $X = 2a/\sqrt{3}$ . Figure 3 shows, in addition to others, all the lattice positions shown in figure 2, except for the lattice point D, which lies in the plane  $X = 3a/\sqrt{3}$ .

Using (3.3) or, equivalently, figure 3, it is now easy to represent the eight 'nearest neighbours' to any atom (say the atom at O). In figure 4 we show them schematically both in the  $(x, y, z)$  and  $(X, Y, Z)$  systems of axes. In the undeformed crystal they are located at a distance  $a/\sqrt{2}$  from O.

In the  $(X, Y, Z)$  system a biaxial deformation in the  $[111]$  direction can be described by the transformation equations

$$X_1 = X(1 + \epsilon') \quad X_2 = Y(1 + \epsilon) \quad X_3 = Z(1 + \epsilon) \quad (3.4)$$

i.e. consistent with section 2 we call  $X_i$  the coordinates of the lattice positions in the (initial) deformed state, after the biaxial deformation, but before the infinitesimal deformation which we have used to derive (2.10).



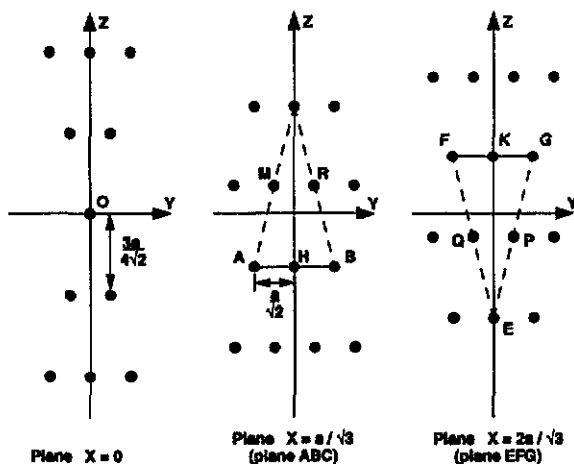


Figure 3. Lattice representation in the  $(X, Y, Z)$  reference system.

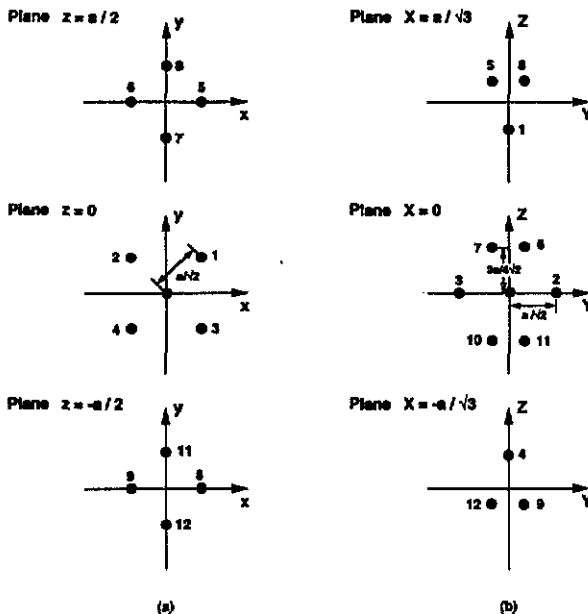


Figure 4. Representation of the twelve nearest neighbours (a) in the  $(x, y, z)$  system and (b) in the  $(X, Y, Z)$  system.

Equation (3.4), above, can be used to obtain the coordinates, after the biaxial deformation, of the twelve nearest neighbours shown in figure 4. Alternatively, figure 4(b) may be used directly to read their coordinates, with the proviso that, in the equations of the planes,  $a$  becomes  $a(1 + \epsilon')$  and, in the planes themselves,  $a$  becomes  $a(1 + \epsilon)$ .

It then becomes straightforward, albeit rather lengthy, to calculate all the sums over the nearest neighbours in (2.11) and (2.12) and obtain explicit expressions for the elastic constants. Although one might assume *a priori* that in the deformed state the crystal loses all its symmetries (i.e. it becomes triclinic), it can be proved,

either by crystallographic arguments or directly through our calculations, that the crystal retains trigonal symmetry. The independent non-zero elastic constants after the biaxial deformation are then given by

$$\begin{aligned} C_{11} &= A_{11} - B_{11} & C_{22} &= C_{33} = A_{22} - B_{22} & C_{44} &= \frac{1}{2}(C_{22} - C_{23}) \\ C_{55} &= C_{66} = A_{13} - B_{55} & C_{12} &= C_{13} = A_{13} & C_{23} &= \frac{1}{3}A_{22} \\ C_{25} &= C_{46} = A_{25} & C_{35} &= -A_{25} \end{aligned} \quad (3.5)$$

where

$$\begin{aligned} A_{11} &= \frac{2}{3}f_c\eta'^4 & A_{22} &= \frac{1}{16}(9f_a + f_c)\eta^4 & A_{13} &= \frac{1}{6}f_c\eta^2\eta'^2 \\ A_{25} &= 1/(12\sqrt{2})f_c\eta^3\eta' \end{aligned} \quad (3.6)$$

$$B_{11} = 8g_c\eta'^2 \quad B_{22} = (6g_a + 2g_c)\eta^2 \quad (3.7)$$

$$\begin{aligned} B_{55} &= \frac{1}{2}[3g_a\eta^2 + g_c(\eta^2 + 4\eta'^2)] & f_a &= f(R_a) & f_c &= f(R_c) \\ g_a &= g(R_a) & g_c &= g(R_c) \end{aligned} \quad (3.8)$$

$$R_a = (1/\sqrt{2})\eta a \quad R_c = a\sqrt{\frac{1}{3}\eta'^2 + \frac{1}{6}\eta^2} \quad (3.9)$$

and, finally

$$\eta = 1 + \epsilon \quad \eta' = 1 + \epsilon. \quad (3.10)$$

In (3.9), the functions  $f$  and  $g$  are explicitly defined by (2.13) and (2.14), respectively.

#### 4. The biaxial modulus

We define the biaxial modulus as the stress-strain ratio [26]

$$Y_b = \sigma/\epsilon \quad (4.1)$$

where, assuming symmetry in the  $X_2$ - $X_3$  plane, we have (in the compact notation)

$$\sigma_2 = \sigma_3 = \sigma \quad \sigma_1 = \sigma_4 = \sigma_5 = \sigma_6 = 0 \quad (4.2)$$

and

$$\epsilon_2 = \epsilon_3 = \epsilon \quad (4.3)$$

$Y_b$  can be measured with a bulge test in a thin film: it represents the stress over strain ratio for a stretching of the film without shear ( $\sigma_4 = 0$ ). The equations  $\sigma_1 = \sigma_5 = \sigma_6 = 0$  give the natural boundary conditions, since there cannot be any stress component outside the  $X_2$ - $X_3$  plane.

Due to the assumed symmetry in the  $X_2$ - $X_3$  plane

$$\epsilon_2 = \epsilon_3 = (S_{22} + S_{23})\sigma \quad (4.4)$$

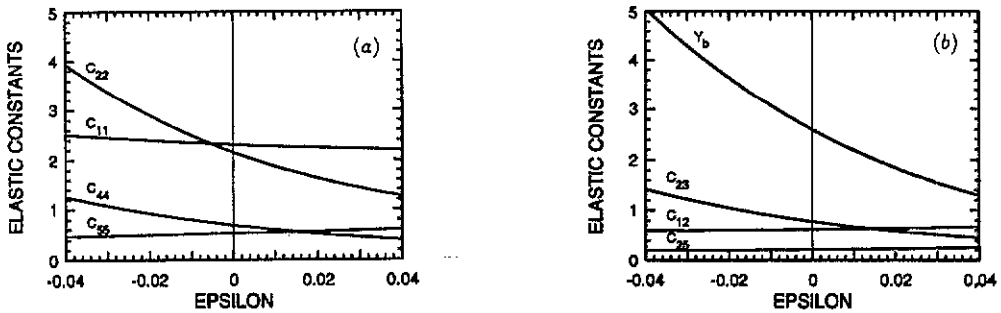


Figure 5. Plots of the elastic constants and biaxial modulus in the  $(X, Y, Z)$  system as a function of the strain: (a)  $C_{11}, C_{22}, C_{44}, C_{55}$ ; (b)  $C_{12}, C_{23}, C_{25}$ , and  $Y_b$ . Units are  $10^{12}$  dyn  $\text{cm}^{-2}$ .

and

$$Y_b = 1/(S_{22} + S_{23}) \quad (4.5)$$

In (4.4) and (4.5) above,  $S_{ij}$  is the elastic compliance tensor, which is the inverse of the stiffness tensor; in compact notation it may be written as

$$S_{ij}C_{jk} = \delta_{ik} \quad (4.6)$$

For special symmetries (e.g. trigonal, as in our case), it is possible to find simple relationships between the components of the stiffness and compliance tensors [26]. Applying these relationships to (4.4) and (4.5) we obtain

$$\epsilon' \equiv \epsilon_1 = -2(C_{12}/C_{11})\epsilon \quad (4.7)$$

$$Y_b = C_{22} + C_{23} - 2(C_{12})^2/C_{11} \quad (4.8)$$

In a similar fashion, it is also possible to calculate other elastic moduli.

## 5. Numerical results

In sections 3 and 4 we have derived the explicit expressions for the elastic constants and biaxial modulus of an FCC crystal that is subjected to a biaxial deformation in the  $[111]$  direction. We now proceed to a numerical evaluation of the pertinent elastic constants. There are two parameters in our formulae that need to be specified:  $\alpha$  and  $\beta$  (2.2). The choice of  $\alpha$  is irrelevant, from our point of view, since it affects only the absolute values of the elastic constants and the moduli as a multiplicative constant, whereas we are interested in their relative change. To give it a value, we have used it as a 'free' parameter to fit the experimental value of  $C_{11}$  in the case of zero deformation in the  $(x, y, z)$  reference system (see figure 1). We have obtained  $\beta$  values from [9] in units of  $a^{-1}$  (where  $a$  is the lattice constant):  $\beta = 26.46$  for Cu, 25.9 for Au and 25.46 for Ag. We have chosen  $\beta = 26$  as the representative value for all three metals.

By applying (3.5) and (4.8), we have evaluated all the independent elastic constants and the corresponding biaxial modulus for strains between  $-4\%$  and  $+4\%$ ; the numerical results are given in table 1 and are plotted in figure 5. It is important to note that the reported values refer to the system of axes  $(X, Y, Z)$  that is shown in figure 1 and defined in section 3 of this paper.

Figure 5 shows that a relatively small deformation may lead to a large change in  $Y_b$  due mainly to the contribution of  $C_{22}$ . The other two terms  $C_{23}$  and  $-2C_{12}^2/C_{11}$  are, however, also important. The latter term is almost constant but, nevertheless, helps to increase the effect in relative terms by decreasing the absolute value of the biaxial modulus. The effect is more pronounced for negative deformations; for example, a variation of +65% in  $Y_b$  results for  $\epsilon = -0.03$ , compared to a change of about -40% for  $\epsilon = +0.03$ .

## 6. Conclusions

As mentioned in the introduction, the purpose of the present study was to investigate (theoretically) the so-called 'supermodulus effect' in very thin films made of metal layers such as Cu, Au, and Ag. In our analysis we have adopted the coherency strain model, as proposed by Jankowski and Tsakalakos. However, since in multilayer systems the interfaces are usually parallel to the [111] direction, in order to have a meaningful comparison with experimental results we have derived the general formulae both for elastic constants and the biaxial modulus in any deformed state. We have then applied our formulae to calculate the relative variations in the elastic constants and the biaxial modulus when the crystal is subject to a small biaxial deformation.

Our numerical results show that even relatively small strains can greatly affect the biaxial modulus, thus providing a plausible qualitative explanation for the supermodulus effect, albeit not to the extent reported in the first experimental papers on the subject. In order to obtain a quantitative answer as to the magnitude of the supermodulus effect for different metallic multilayer systems, we need to model the atom matching between different metal layers, so that we can evaluate the resulting coherency strains. Afterwards, a plot similar to figure 5 can be used to predict quantitatively the actual variation of the biaxial modulus on the basis of the coherency strain model. This will be done in a subsequent paper.

Our calculations are based on a pseudopotential energy approach similar to the one employed by Jankowski and Tsakalakos with some additional assumptions, as explained in section 2. The assumptions were incorporated in our analysis in order to simplify the calculations by retaining only the predominant terms in the evaluation of the elastic constants. In order for our model to be fully reliable, however, we need to compare it with other pseudopotential energy models which have been used to predict other atomic properties [27, 28]. This may require some modification in the ion-core repulsive energy term (2.2) and the retention of other relevant energy terms. As mentioned earlier, this will also be done in a subsequent paper by following closely the approach described in sections 2 and 3 of this work.

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## Appendix A. Proof of equation (2.5)

Let us consider an arbitrary infinitesimal deformation

$$u_i = x_i - X_i = e_{ij} X_j \quad (i = 1, \dots, 3) \quad (\text{A1})$$

where  $X_i$  are the initial coordinates (material or Lagrangian description),  $x_i$  are the final coordinates (Eulerian description) and

$$e_{ij} = \partial u_i / \partial X_j \simeq \partial u_i / \partial X_j. \quad (\text{A2})$$

By neglecting second-order terms it is easy to prove that the Lagrangian strain tensor

$$\eta_{ij} \equiv \frac{1}{2} \left( \frac{\partial x_k}{\partial X_i} \frac{\partial x_k}{\partial X_j} \right) - \delta_{ij} \quad (\text{A3})$$

coincides with the Eulerian strain tensor

$$\epsilon_{ij} = \frac{1}{2} (e_{ij} + e_{ji}) \quad (\text{A4})$$

so that

$$\partial / \partial \eta_{ij} = \partial / \partial \epsilon_{ij}. \quad (\text{A5})$$

The deformation described by (A1) is, in general, a linear combination of dilatations (terms with  $j = i$ ), pure strains (given by  $\epsilon_{ij}$ ), and rotations which correspond to the antisymmetric tensor

$$w_{ij} = \frac{1}{2} (e_{ij} - e_{ji}). \quad (\text{A6})$$

It follows that

$$e_{ij} = \epsilon_{ij} + w_{ij} \quad e_{ji} = \epsilon_{ij} - w_{ij} \quad (\text{A7})$$

and therefore, if  $i \neq j$ , then

$$\partial / \partial e_{ij} = \partial / \partial \epsilon_{ij} + \partial / \partial w_{ij} \quad \partial / \partial e_{ji} = \partial / \partial \epsilon_{ij} - \partial / \partial w_{ij} \quad (\text{A8})$$

Equation (A8) allows us to separate, in the derivatives, the contributions of the pure strains from those of pure rotations. If the last term is ignored, then (A8) is also valid for dilatations.

It then follows that

$$\begin{aligned} \frac{\partial}{\partial \epsilon_{ij}} &= \frac{1}{2} \left( \frac{\partial}{\partial e_{ij}} + \frac{\partial}{\partial e_{ji}} \right) = \frac{1}{2} \left( \frac{\partial}{\partial x_k} \frac{\partial x_k}{\partial e_{ij}} + \frac{\partial}{\partial x_k} \frac{\partial x_k}{\partial e_{ji}} \right) \\ &= \frac{1}{2} \left( X_j \frac{\partial}{\partial x_i} + X_i \frac{\partial}{\partial x_j} \right). \end{aligned} \quad (\text{A9})$$

Equation (A9) is also valid when  $i = j$ , in which case

$$\partial / \partial \epsilon_{ij} = X_i \partial / \partial x_i \quad (\text{A10})$$

with no implied summation over the index  $i$ .

Appendix B. Special symmetries in the tensors  $A_{ijkl}$  and  $B_{ijkl}$ 

As is well known, the number of independent  $C_{ijkl}$  is reduced from 81 to 21 (in the most general case), by applying the symmetries

$$C_{ijkl} = C_{jikl} = C_{ijlk} = C_{klij}. \quad (\text{B1})$$

This can be automatically achieved by using the compact notation in which a single index, running from 1 to 6, replaces each pair of indices

$$i, j \longrightarrow n = i\delta_{ij} + (1 - \delta_{ij})(g - i - j) \quad (n = 1, \dots, 6). \quad (\text{B2})$$

In addition, there are, however, some special symmetries of  $A_{ijkl}$  and  $B_{ijkl}$  which are due to the structure of the definitions of  $Y_{ijkl}$  and  $Z_{ijkl}$ . They are listed as follows

(i) Since the order of the indices in  $Y_{ijkl}$  is irrelevant, it is easy to see that (using compact notation)

$$A_{12} = A_{66} \quad A_{13} = A_{55} \quad A_{23} = A_{44} \quad (\text{B3})$$

$$A_{14} = A_{56} \quad A_{25} = A_{46} \quad A_{36} = A_{45}$$

(ii) From the definition of  $Z_{ijkl}$  it follows that

$$B_{12} = B_{13} = B_{23} = B_{14} = B_{25} = B_{36} = 0 \quad (\text{B4})$$

$$B_{16} = B_{26} = 2B_{45} \quad (\text{B5})$$

$$B_{15} = B_{35} = 2B_{46} \quad (\text{B6})$$

$$B_{24} = B_{34} = 2B_{56} \quad (\text{B7})$$

(iii) If there is cell symmetry with respect to a certain coordinate  $X_i$  and the index  $i$  occurs an odd number of times, then the corresponding elastic constant vanishes.

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