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Electronic structure and elastic properties of Au/Cr(001) superlattices

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We present a first-principles calculation of the electronic structure and elastic properties of a series of Au/Cr(001) superlattices with modulation wavelengths between 30 and 60 Å. The electronic-structure calculations are performed with the linear muffin-tin-orbital method in the atomic-sphere approximation. Results for the density of states and the charge transfer at the interfaces as a function of the modulation wavelength are presented. The force theorem has been used in the investigation of the elastic behavior of the system. We have performed a detailed analysis of the variation of the band contribution to the shear elastic constant c_{44}, with particular reference to the Fermi-surface contribution. This analysis allows us to investigate the role of the electronic-structure variations induced by layering in the elastic anomalies experimentally observed in metallic superlattices. We show that the origin of the enhancement of the c_{44} elastic constant observed in Au/Cr at small modulation wavelengths cannot be ascribed to a Fermi-surface Brillouin-zone interaction mechanism.

I. INTRODUCTION

Metallic multilayers are artificial structures made by sequentially growing thin layers of two different metals, usually noble or transition metals, on an appropriate substrate. The resulting system is characterized by an additional one-dimensional periodicity along the growth direction that has shown to affect all the fundamental physical properties of the system: new superconducting, transport, magnetic, and mechanical properties have all been reported for these structures.[1,2]

The elastic properties of metallic superlattices in particular represent a quite controversial subject. Theoretical investigations of the elastic response of a stratified medium have shown that, in the long-wavelength limit, the elastic moduli of these systems should not depend on the modulation wavelength Λ, but only on the elastic constants of the constituents and their relative thickness.[3,4] The presence of anomalies in the elastic behavior of metallic superlattices was first observed at the end of the 1970s when Yang, Tsakalakos, and Hilliard[5] reported an enormously large increase, up to 300%, of the biaxial modulus in Au/Ni and Cu/Pd multilayers for decreasing modulation wavelengths. Since then a lot of experimental work has been devoted to the investigation of this so-called *supermodulus effect.*[2] Even if the use of more sophisticated investigation techniques has disproven the early reports of enormously large elastic constants variations, the presence of elastic anomalies has been substantially confirmed: the experimental results so far obtained show that in almost all the systems that have been characterized from the elastic point of view, there is a variation (increase or decrease) of the elastic constants up to 50% at small Λ with respect to the values observed in samples of large modulation wavelength.

The supermodulus effect has also been widely investigated from the theoretical point of view. Many different theoretical models have been proposed in order to explain its origin. The main driving mechanisms that have been suggested are electronic effects,[6–10] structural deformations such as lattice expansions along the growth direction,[11,12] coherency strains,[7,13,14] and disorder or alloying at the interfaces.[15,16] Some of these models proved to be reasonable in specific systems, but no satisfactory and general explanation of the origin of the elastic anomalies has been given yet. We want to stress that the complexity of the structures under study has so far discouraged a first-principles approach to the problem: the theoretical work we are referring to is based only on phenomenological models or simulations on model systems.

In this paper we present a first-principles investigation of the electronic structure and elastic properties of the Au/Cr(001) superlattice: for this system the experimental results show an increase of the c_{44} elastic constant up to ~28% for modulation wavelengths between 50 and 90 Å.[17]

The principal aim of this work is to test, from a first-principles point of view, the possibility that the observed anomalies could derive from electronic effects, related to the existence of Fermi-surface Brillouin-zone interactions. It is well known that in superlattices the additional periodicity introduces new zone boundaries: for particular values of the modulation wavelength, these new boundaries could contact the Fermi surface of the system, altering its topology. All the physical properties that depend on the electronic distribution near the Fermi surface will be consequently modified. Under this condition, it is expected that even a small deformation will produce a remarkable variation of the total energy of the system, from which an anomalous elastic behavior could derive. The validity of this mechanism can be tested by analyzing, as a function of the modulation wavelength Λ, the

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electronic contribution to the elastic constants, i.e., the contribution coming from the variation of the electronic band structure with the deformation.

We have therefore performed the calculation of the electronic structure of a series of Au/Cr(001) $n:n$ superlattices with different modulation wavelengths: n represents the number of atomic planes of Au and of Cr in the unit cell and its value has been varied between 3 and 17, in order to cover the range of modulation wavelengths between 30 and 60 Å, which is of interest to the study of the elastic response of the system. The calculations are performed using the linear muffin-tin-orbital (LMTO) method in the atomic-sphere approximation (ASA).[18]

The electronic-structure calculation is a preliminary step in the calculation of the elastic constants, which is realized on the basis of the force theorem.[19] We have computed the electronic contribution to c_{44} as a function of Λ, with special reference to the *Fermi surface contribution,* which is the one deriving from the variations of the electronic states close to the Fermi surface: this is indeed the term that should show an anomalous behavior with Λ if the origin of the elastic anomalies is the one we have previously described.

This work is composed of two main sections. In the first part we describe the electronic-structure calculations. In Sec. II A we present the structure of the system under study and the details of the band-structure calculations; the results of this investigation will be reported in Sec. II B. The second part of the work is devoted to the analysis of the elastic properties. In Sec. III A the method of calculation is described; in Sec. III B we report the details of the calculation, while in Sec. III C the results are presented and discussed.

II. ELECTRONIC STRUCTURE

A. Superlattice structure and details of the calculation

Bulk Au and Cr crystallize in the fcc and bcc structures, respectively. The experimental lattice constants are $a_{\mathrm{Au}}=4.0786$ Å and $a_{\mathrm{Cr}}=2.8846$ Å.[20]

The experimental data relative to the structure of the Au/Cr superlattice show that this system grows preferentially along the [001] direction of the cubic cells of the constituents, with the Au(001) planes rotated by 45° around the growth direction with respect to the Cr(001) planes. The Au/Cr(001) superlattice is characterized by coherent and stress-free interfaces, due to the good lattice matching of the two metals at the interface. The lattice constants of the two-dimensional (2D) unit cell in the (001) planes of Au and Cr are given by $a_{\mathrm{Au}}(001)=a_{\mathrm{Au}}/\sqrt{2}=2.8840$ Å and $a_{\mathrm{Cr}}(001)=a_{\mathrm{Cr}}=2.8846$ Å. Therefore the 2D unit cell of Cr is almost identical to the one of Au, with a mismatch of only 0.02%.

The stacking of the (001) planes is such that atoms in adjacent planes lie in the fourfold hollow site, i.e., at the center of a square made by the atoms in adjacent planes and just above the atoms of the subsequent planes. The resulting lattice exhibits a tetragonal symmetry. We have assumed an interface spacing equal to the average of the bulk interlayer spacing along the [001] direction, $d_{\mathrm{Au}}[001]=2.0393$ Å and $d_{\mathrm{Cr}}[001]=1.4423$ Å, and therefore the lattice constants for a Au/Cr(001) $n:n$ superlattice are given by $a=a_{\mathrm{Cr}}(001)=2.8846$ Å and $c=(nd_{\mathrm{Au}}+nd_{\mathrm{Cr}})$. The primitive unit cell for $n=3$ is represented in Fig. 1.

The electronic-structure calculations have been performed using the LMTO ASA method.[18] We have used the tight-binding LMTO basis set[21] including nine orbitals (spd) per atom. The calculations are scalar-relativistic and include the combined correction term; the core electrons are treated self-consistently. No spin polarization has been taken into account, i.e., Cr is regarded as paramagnetic.

The **k** points mesh in the reciprocal space has been chosen in such a way as to ensure a sampling of the Brillouin zone almost equivalent for superlattices of different dimension. Therefore we have kept the number of subdivisions in the $k_x k_y$ plane fixed to 16×16 within the first Brillouin zone for all the superlattices, while the number of subdivisions along the k_z direction is varied from 10 in the smallest superlattice to 2 in the biggest one: the volume per **k** point is about 10^{-5} Å^{-3}. The Brillouin-zone integrations are performed with the tetrahedral method.[22]

We assumed to have reached self-consistency for charge variations inside the Wigner-Seitz spheres lower than 10^{-4}. Similar to other d or f systems characterized by a high density of states at the Fermi level,[23] the convergence process turned out to be quite unstable due to strong charge oscillations between the Au and Cr layers. Sophisticated mixing schemes, such as Broyden mixing,[24] did not give good results, probably because of the large number of atoms in the unit cell which introduces a further degree of freedom for charge fluctuations. The self-consistent results that we present in the next subsection have been obtained using a simple linear mixing procedure with a mixing parameter lower than 0.01.

B. Results and discussion

In order to better understand the results concerning the superlattices, we first perform calculations for bulk Au and Cr at the experimental lattice constants. The

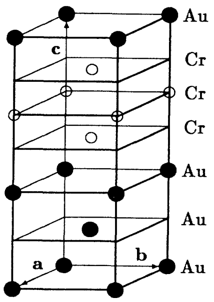

FIG. 1. Schematic representation of the Au/Cr(001) 3:3 unit cell.

corresponding total densities of states (DOS) are shown in Fig. 2. The DOS curves show the typical fcc and bcc profiles: in bulk Au the 5*d* bands give rise to a steplike structure from -7 to about -1.5 eV with respect to the Fermi level, with two characteristic peaks centered at -2 and -4.5 eV, while in bulk Cr the *d* states originate three distinct structures centered at about -3.8, -1.5, and 1.5 eV with the Fermi level lying in the region of low DOS between the bonding and antibonding peaks.

In Figs. 3–6 we show the projected DOS results for the Au/Cr(001) n:n superlattices, with $n=3,5,7,17$. The DOS is projected on the interface atoms (i), on the atoms in the two subsequent layers $(i-1)$ and $(i-2)$ and, in the bigger systems, on the atoms in the central layer, which are in a bulklike configuration (b). The variations of the DOS projected on the interface atoms with respect to the bulk ones are remarkable: the characteristic fcc and bcc profiles for Au and Cr completely disappear. In the case of Au, it may be seen that there is a substantial reduction of the DOS between -3 and -1.7 eV, where the peak centered at -2 eV is absent. The DOS increases around -6 eV and at the Fermi level: these latest structures, resonant with the Cr peaks, are indicative of a Au *d*–Cr *d* hybridization. In the case of Cr, the projected DOS shows a reduction between -4.5 and -3 eV together with the formation of a tail of states at energies lower than -5 eV. The main difference is the closing of the pseudogap at the Fermi level due to the formation of a band of interface states. These states have been already observed on the clean (001) Cr surface:[25] their presence in the DOS of the Au/Cr superlattices indicates that the hybridization between Au *sd* and Cr *d* states at the interfaces is not effective enough to remove these surface states from the Cr pseudogap.

The modifications of the DOS of the interface atoms with respect to the bulk can already be observed in the 3:3 system and remain unchanged in all the other superlattices. The Au-Cr interaction is therefore strictly localized at the interface. This can also be seen by looking at

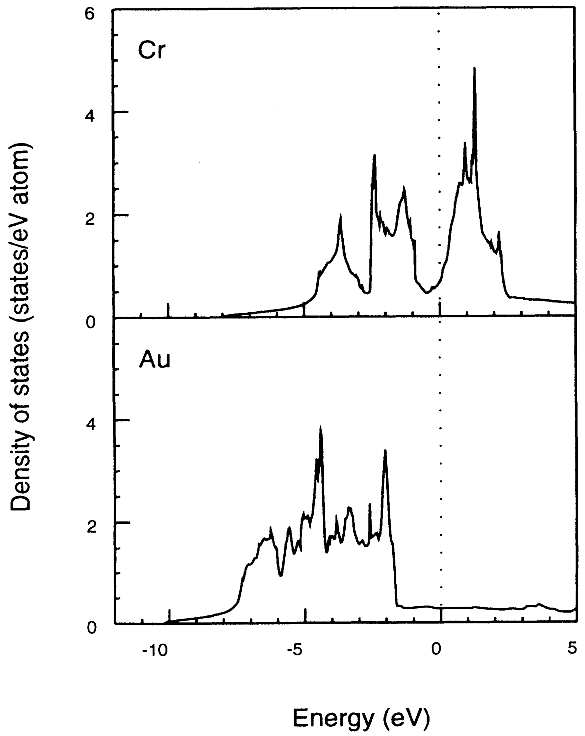

FIG. 2. Total density of states of bulk Au and Cr. Energies are referred to the Fermi level.

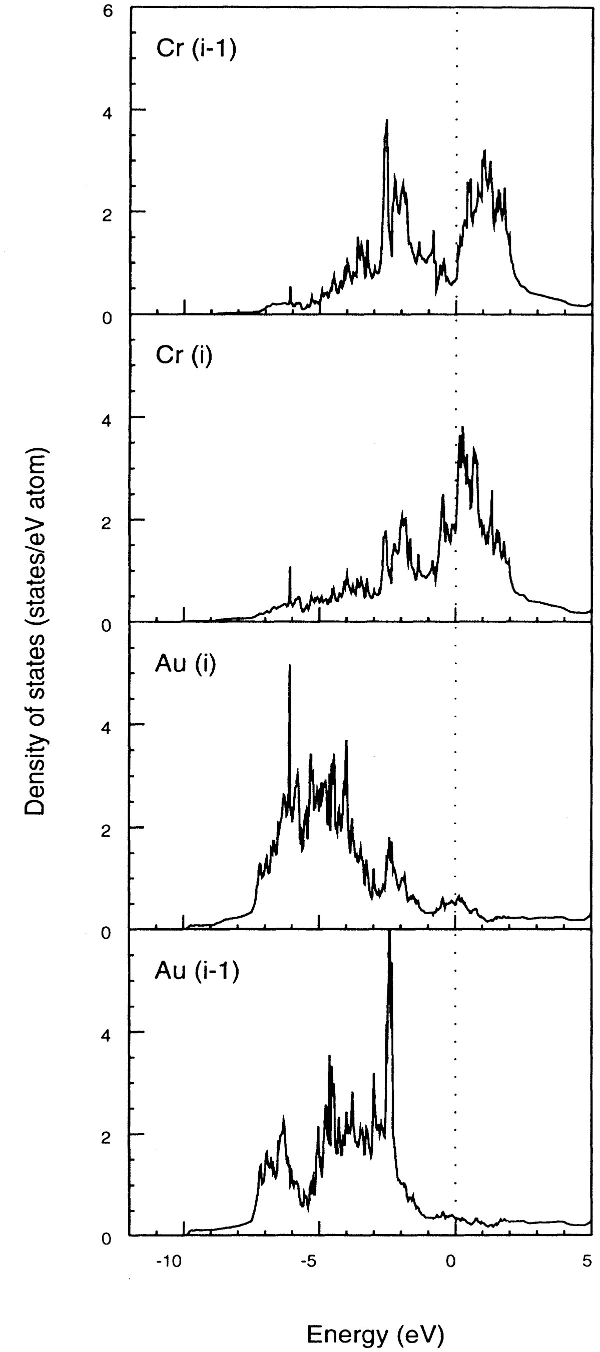

FIG. 3. Au/Cr(001) 3:3 projected density of states. Energies are referred to the Fermi level. The index (i) labels the interface layer, the index $(i-n)$ the nth subsequent layer.

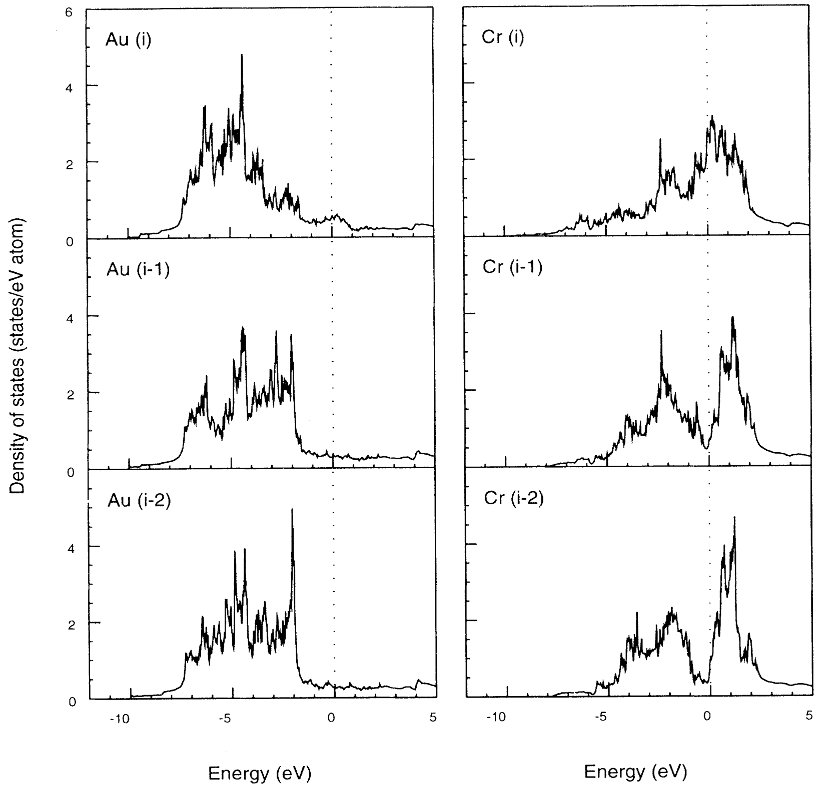

FIG. 4. Same as in Fig. 3, but for the Au/Cr(001) 5:5 superlattice.

the DOS projected on the subinterface atoms where most of the bulk structures already reappear. The Au DOS shows again the structures above -3 eV, including the peak at about -2 eV. In the case of Cr we may observe the reopening of the pseudogap at the Fermi level and the recovery of the states around -3.5 eV. The profile of the bulk DOS is even more recognizable in the DOS projected on the atoms in the second plane from the interface, labeled with $(i-2)$, as it may be seen in the 5:5 superlattice for instance. The bulk characters can be considered completely recovered in the DOS projected on the bulk-like atoms in the 7:7 structure (third plane from the interface), even if in the DOS projected on the Cr atoms we may still notice some spurious peaks close to the Fermi level, due to the tails of the states localized at the interface.

We did not observe any interesting variations in the DOS for bigger systems: the 17:17 projected DOS is not much different from the 7:7 one. Therefore we do not report here the DOS for the $n=9,11,13$ superlattices.

The localization of the Au-Cr interaction at the interface is also supported by the charge-transfer data reported in Table I. We report the values of $\Delta Q = Q_S - Z$, where Q_S is the self-consistent charge density integrated inside the sphere with radius S and Z is the atomic number: a negative (positive) value of ΔQ represents a decrease (increase) of electrons per atom with respect to the neutrality condition, which is the bulk one. A charge transfer from Cr to Au is clearly present at the interface, with a prevalent *sp* character (see Table II); both its numerical value and character remain unchanged in all the superlattices studied. The neutrality condition can already be considered restored in the atoms lying on the second plane from the interface. Moreover, the Au and Cr layers exhibit charge oscillations which decay rapidly from the interface. These Friedel-like oscillations may derive from the screening action of the electron gas with respect to the dipole existing at the interface. We notice that the trends we have observed both in the DOS and charge-transfer profiles have also been reported in previous *ab initio* calculations on metallic superlattices,[26–29] in which systems with no more than six atomic layers per component have been analyzed.

III. ELASTIC PROPERTIES

A. The electronic contribution to the elastic constants

Within elasticity theory, the elastic constants of a system are defined as the second derivatives of the internal energy density with respect to the components of the strain:[30]

$$c_{ij} = \left[\frac{\partial^2 u}{\partial e_i \partial e_j} \right]_S . \qquad (1)$$

Straightforward calculation of the elastic constants requires the calculation of the total energy of the system as a function of the deformation, that is, a series of self-consistent electronic-structure calculations on systems with different degrees of deformation.

Within density-functional theory, the force theorem (FT) provides an alternative approach to the calculation of the elastic constants which does not require the self-consistent determination of the total energy for the distorted systems. The FT states that the first-order change in the total energy of a system due to an infinitesimal variation of the atomic positions can be computed as the sum of the electrostatic force between atomic cells and the change in the band energy $E_B=\sum_n^{\mathrm{occ}}\epsilon_n$, for rigidly shifted potentials:

$$\delta U=\delta\sum_n^{\mathrm{occ}}\epsilon_n+\delta U_e \ . \tag{2}$$

The condition on the potential means that the calculation relative to the distorted system need not be self-consistent: the electronic structure of the deformed system is simply determined through diagonalization of a Hamiltonian in which the potential is the self-consistent potential of the undeformed system. This theorem has already been successfully applied to the calculation of the elastic constant c' in many bulk transition metals,[31,32] even if, in this case, the second-order variation of the total energy is required.

By means of the FT, the elastic constants can be expressed as the sum of a term deriving from the variation of the band energy and of an electrostatic term:

$$c_{ij}=\frac{1}{V}\left[\frac{\partial^2 E_B}{\partial e_i\partial e_j}+\frac{\partial^2 U_e}{\partial e_i\partial e_j}\right]=c_{ij}^b+c_{ij}^e \ . \tag{3}$$

As already explained in Sec. I, we are going to analyze the role of the electronic-structure modifications induced by the artificially imposed modulation in the elastic anomalies experimentally observed. We have therefore calculated the electronic contribution to the elastic constant c_{ij}^b, disregarding the electrostatic contribution c_{ij}^e. It is well known that this contribution has to be taken into account in order to get the correct numerical value of the elastic constant,[31] but it is unlikely that it could be responsible for the elastic anomalies.

Since the main electronic contribution to the variation of the elastic constant should derive from the band structure changes at the Fermi level, we have, further on, decomposed c_{ij}^b in order to evidence these variations.[33]

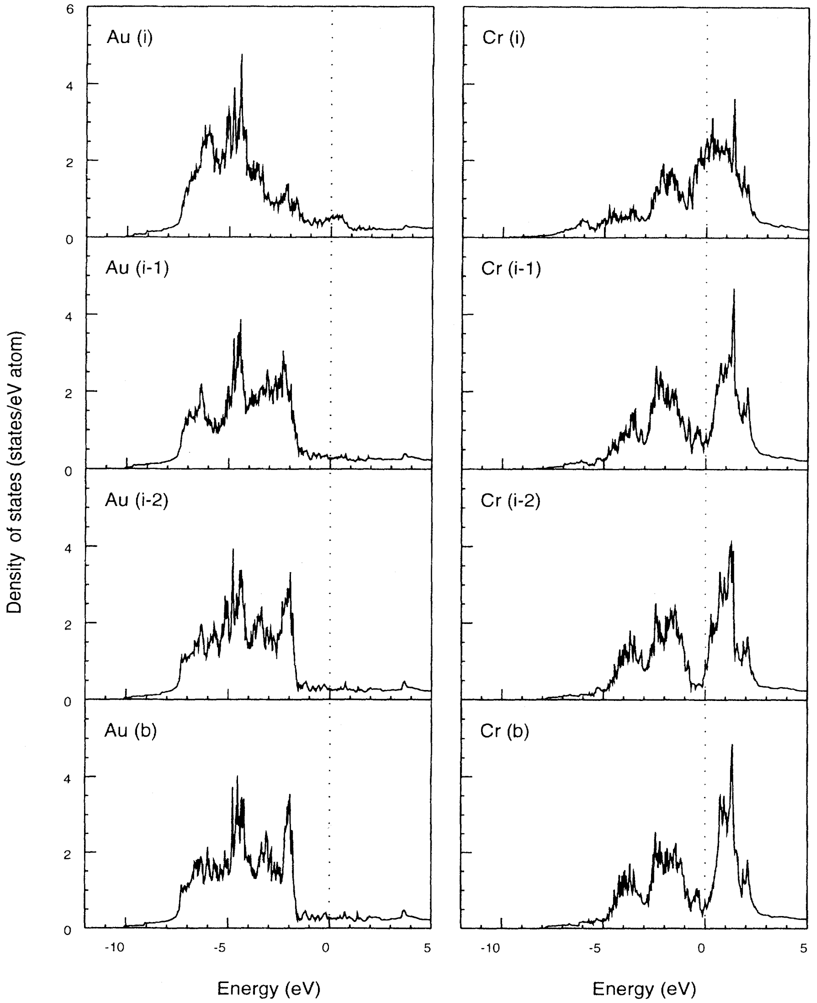

FIG. 5. Same as in Fig. 3, but for the Au/Cr(001) 7:7 superlattice.

Starting from the definition of band energy as the sum of the eigenvalues over the occupied states,

$$E_B=\sum_n \epsilon_n \Theta(E_F-\epsilon_n)\ , \tag{4}$$

where $\Theta(x)=0$ if $x<0$ and $\Theta(x)=1$ if $x>0$, and imposing the number of particles conservation, the band contribution to the elastic constants can be expressed as

$$c_{ij}^{b}=\frac{1}{V}\sum_n \frac{\partial^2\epsilon_n}{\partial e_i \partial e_j}\Theta(E_F-\epsilon_n) - \frac{1}{V}\sum_n \frac{\partial(\epsilon_n-E_F)}{\partial e_i}\frac{\partial(\epsilon_n-E_F)}{\partial e_j}\delta(E_F-\epsilon_n)\ . \tag{5}$$

The first and second terms in this expression can be identified, respectively, as a *volume contribution* c_{ij}^{v}, coming from the variation of the eigenvalues induced by the applied strain inside the undeformed Fermi surface, and a *surface contribution* c_{ij}^{s}, coming from the variation of the eigenvalues *at* the Fermi surface.

B. Details of the calculation

As described in Sec. II A, the Au/Cr system has a tetragonal symmetry; for this symmetry only six independent elastic constants exist: $c_{11}=c_{22}$; c_{12}; $c_{13}=c_{23}$; c_{33}; $c_{44}=c_{55}$, and c_{66}. The expression for the strain energy is therefore given by

$$U=\tfrac{1}{2}V\{c_{11}(e_1^2+e_2^2)+c_{33}e_3^2+c_{44}(e_4^2+e_5^2)+c_{66}e_6^2+2c_{12}e_1e_2+2c_{13}(e_1e_3+e_2e_3)\}\ . \tag{6}$$

To calculate the shear elastic constant c_{44}, which shows an anomalous behavior in the Au/Cr superlattices,[17] we have used a volume-conserving shear deformation in the (100) plane, described by the following strain tensor:

$$[e_{ij}]=\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{\gamma}{2} \\ 0 & \frac{\gamma}{2} & 0 \end{bmatrix}\ , \tag{7}$$

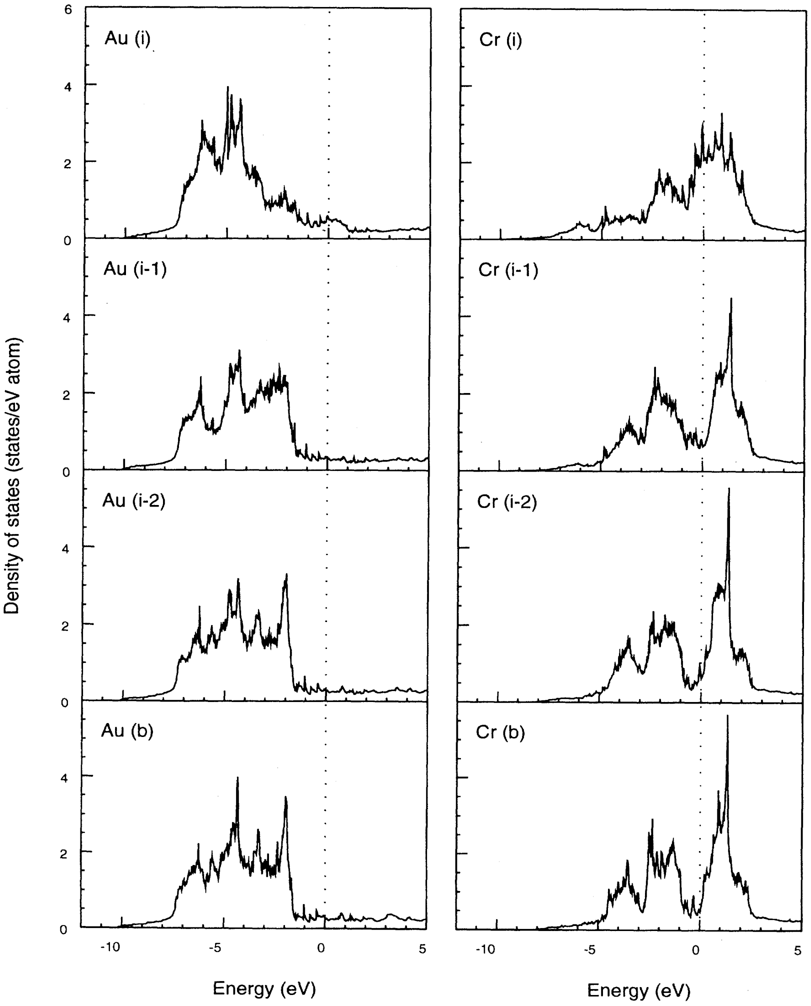

FIG. 6. Same as in Fig. 3, but for the Au/Cr(001) 17:17 superlattice.

TABLE I. Charge transfer (electron/atom) in the superlattices studied. The indices are relative to different layers in the cell, going from the interface layer (a) to the bulklike one.

	3:3	5:5	7:7	9:9	11:11	13:13	17:17
Au_i							+0.0002
Au_h							−0.0005
Au_g						−0.0003	−0.0000
Au_f					−0.0004	−0.0002	−0.0004
Au_e				+0.0004	+0.0001	+0.0003	+0.0001
Au_d			+0.0004	−0.0001	+0.0003	−0.0002	+0.0000
Au_c		+0.0028	+0.0010	+0.0009	+0.0010	+0.0010	+0.0008
Au_b	−0.0530	−0.0271	−0.0263	−0.0259	−0.0260	−0.0261	−0.0260
Au_a	+0.1478	+0.1465	+0.1441	+0.1434	+0.1434	+0.1438	+0.1437
Cr_a	−0.1758	−0.1736	−0.1719	−0.1717	−0.1715	−0.1720	−0.1721
Cr_b	+0.1089	+0.0560	+0.0567	+0.0562	+0.0559	+0.0559	+0.0557
Cr_c		−0.0064	−0.0048	−0.0043	−0.0036	−0.0031	−0.0029
Cr_d			+0.0021	+0.0026	+0.0017	+0.0015	+0.0010
Cr_e				−0.0031	−0.0025	−0.0021	−0.0014
Cr_f					+0.0028	+0.0024	+0.0020
Cr_g						−0.0020	−0.0011
Cr_h							+0.0015
Cr_i							−0.0008

where γ is the strain parameter. This deformation reduces the symmetry of the system: indeed the deformed cell has only a monoclinic symmetry. The shear elastic constant can therefore be calculated as

$$c_{44}=\frac{1}{V}\frac{\partial^2 U}{\partial\gamma^2}\ . \tag{8}$$

By means of Eqs. (5) and (8), the calculation of the electronic contribution to c_{44} requires the calculation of the first and second derivatives of the eigenvalues $\epsilon_{n\mathbf{k}}$ with respect to the deformation parameter γ and then their integration in the Brillouin zone. Both these calculations turned out to be quite demanding, requiring the solution of several numerical problems.

The derivatives have been calculated by numerical differentiation over three points, corresponding to the values $\gamma=0,\pm0.01$. The **k**-point mesh has been shifted from the origin of the Brillouin zone in order to avoid lines and planes of symmetry. The eigenvalues relative to **k** points lying on some of these planes have zero derivative due to the symmetry of the distortion; the contribution of these points are therefore not properly weighed using a finite **k**-point mesh in the Brillouin zone. The shifting procedure solves the problem without resorting to the use of a denser mesh that would make the calculations heavier.

TABLE II. *spd* occupation numbers for bulk Au, bulk Cr, and for the interface layer Au (Au_a) and Cr (Cr_a) in the 7:7 superlattice. No variations have been observed in the other superlattices.

	n_s	n_p	n_d
Au (b)	0.8057	0.7755	9.4188
Au_a	0.9368	0.9006	9.3067
Cr_a	0.5590	0.6967	4.5723
Cr (b)	0.6212	0.8137	4.5653

The Brillouin integrations have been performed using a sampling technique with a Gaussian broadening,[34] i.e., each state has been broadened by a Gaussian whose width σ has been chosen to be equal to the average dispersion of the bands between neighboring states near the Fermi surface. In our calculations we set $\sigma\sim0.2$ eV. We have avoided the use of interpolation techniques due to the errors that they introduce at band crossing: these errors turned out to be non-negligible especially for the superlattices of larger periodicity where the number of band crossings increases because of the band folding, making results for different systems not comparable.

Numerical problems are also introduced by the wrong ordering of the eigenvalues in the deformed systems with respect to the undeformed one. It is well known that the eigenvalues in each **k** point are usually given an index that increases with increasing energy. The ordering of the eigenvalues of the undeformed system is not necessarily preserved in the deformed system. The energy bands are usually shifted because of the strain and it is therefore possible that, if two eigenvalues in the undeformed system are very close to each other, their energies are reversed in the strained system: if this is the case, the standard ordering procedure will assign to the eigenvalues of the deformed system an index that does not agree with that of the original eigenvalues of the undeformed system. Consequently, the corresponding derivatives will be wrong. This kind of error is considerable, especially in the larger superlattices where the multiple-band folding gives rise to a denser energy distribution of the eigenvalues in each **k** point. In order to solve this problem, we have introduced a different ordering procedure for the eigenvalues of the deformed system based on the overlap between the deformed and undeformed wave functions. For a small deformation we can assume that the variation of the wave function relative to a given eigenvalue in the deformed system $\psi^{\gamma}_{n\mathbf{k}}$ with respect to the corresponding wave function in the undeformed system $\psi^0_{n\mathbf{k}}$ is itself small. The overlap integral between the wave functions of the undeformed and deformed system at each $\mathbf{k}$ point can be written as

$$O_{nn',\mathbf{k}} = \langle \psi^0_{n\mathbf{k}} | \psi^\gamma_{n'\mathbf{k}} \rangle = \langle \psi^0_{n\mathbf{k}} | \psi^0_{n'\mathbf{k}} \rangle + \gamma \left\langle \psi^0_{n\mathbf{k}} \middle| \frac{\partial \psi^0_{n'\mathbf{k}}}{\partial \gamma} \right\rangle + O(\gamma^2) \qquad (9)$$

and therefore $O_{nn',\mathbf{k}} \sim 1$ if $n = n'$, while $O_{nn',\mathbf{k}} \sim 0$ if $n \neq n'$. Looking at the value of $O_{nn',\mathbf{k}}$ we can ascertain the correspondence between the eigenvalues of the deformed and undeformed systems and order them consequently. The overlap value is not predictable when degenerate eigenvalues are present; this happens mainly along lines and on planes of high symmetry. The shift of the k-point mesh has therefore been helpful in solving this problem too.

C. Results and discussion

In Table III we report the results for the electronic contribution to c_{44} in bulk Au and Cr and in Au/Cr(001) n:n superlattices, with $n = 3,5,7,9,11,13,17$. Besides the total band contribution c^b_{44}, we also report the values of the surface c^s_{44} and volume c^v_{44} terms, defined in Eq. (5). It may be seen that the absolute value of these contributions is always smaller in the superlattices than in the bulk, especially for the surface term, which is always one order of magnitude smaller than the corresponding bulk values. The band contribution for bulk Au is negative: a negative value of this term has also been found for c' in Au, Pt, and Pd.[31,32] The electrostatic contribution, which we have disregarded, is therefore important in order to obtain the correct numerical value of the elastic constant. The data we have obtained cannot be compared to the experimental values, as we have already explained in Sec. III A. We also note that the effective-medium approximation[3,4] is meaningless in our case because we are not considering the total value of an elastic constant, but the band term only. This argument also justifies the difference between the calculated values of c^b_{44} in superlattices, with respect to the corresponding bulk quantities of Table III and their average. In addition, the band structure of bulk materials and superlattices are quite different both at the Fermi energy and below, so that in a superlattice the band term does not necessarily approach the bulk values.

TABLE III. Numerical values of c^b_{44}, c^v_{44}, and c^s_{44} (Mbar) in bulk Au, bulk Cr, and Au/Cr(001) n:n superlattices, with $n = 3,5,7,9,11,13,17$. Λ is the modulation wavelength (Å).

	Λ	c^s_{44}	c^v_{44}	c^b_{44}
Au (b)		−0.4569	0.1970	−0.2599
Cr (b)		−0.3830	0.7240	0.4180
3:3	10.44	−0.0538	0.1409	0.0871
5:5	17.41	−0.0207	0.0879	0.0672
7:7	24.37	−0.0158	0.0433	0.0275
9:9	31.33	−0.0104	0.0314	0.0211
11:11	38.30	−0.0107	0.0209	0.0102
13:13	45.26	−0.0126	0.0173	0.0047
17:17	59.19	−0.0177	0.0213	0.0035

In Fig. 7 we show the three terms c^b_{44}, c^v_{44}, and c^s_{44} as a function of the modulation wavelength Λ. The band contribution decreases with increasing Λ and becomes almost zero at large periodicity, as already remarked. While the volume contribution shows a monotonic decrease for an increasing value of Λ, the surface term is almost constant on the whole range of modulation wavelength, except in the two smaller superlattices where the interface effects are still considerable.

The available experimental data[17] show an anomalous behavior of c_{44} for Λ between 50 and 90 Å with a variation that on the whole is about 0.067 Mbar. If the origin of this anomaly were related to the existence of a Fermi-surface Brillouin-zone interaction, the surface term c^s_{44} should show a comparable variation in the same periodicity range: our results show that no anomaly exists above 50 Å and that for modulation wavelengths in the range 20–60 Å the variation of c^s_{44} is only 0.007 Mbar, one order of magnitude smaller than the experimental one.

The lack of any considerable variation is a clear proof that the observed elastic anomaly cannot be ascribed to electronic effects, at least in the ideal case we have studied, in which interdiffusion and relaxations have been disregarded.

A recent experimental study of the elastic response of Mo/Ni nonperiodic superlattices[35] has proved that these systems show the same elastic anomalies that have been observed in periodic samples. This analysis indicates that the elastic anomalies cannot be associated with the existence of a Fermi-surface Brillouin-zone interaction, in agreement with our results.

Of course, the origin of the observed anomalies remains an open problem, not only for the Au/Cr system, but for all the other superlattices. It should be noted that the driving mechanism of these anomalies could be different in different superlattices, as can be argued, for example, by comparing the Au/Cr and Ag/Ni systems. The Ag/Ni superlattice has been recently well characterized from the structural and elastic point of view:[36] the

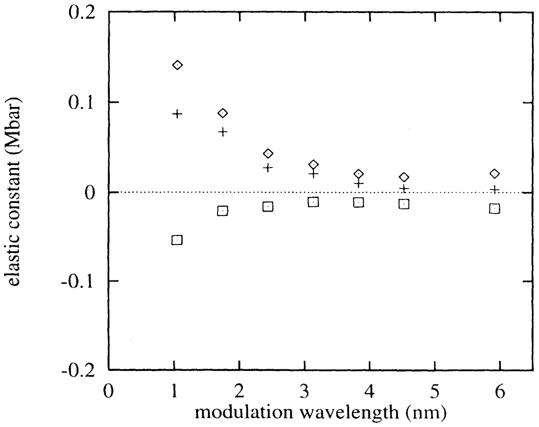

FIG. 7. Total band energy term c^b_{44} (crosses), volume contribution c^v_{44} (diamonds), and Fermi surface contribution c^s_{44} (squares), as a function of Λ.

results of this analysis show that in this system the elastic anomalies may be related to the structural disorder at the interfaces, resulting from the considerable mismatch between the two constituents. This same explanation cannot be used for a well-matched superlattice such as Au/Cr. Due to the miscibility of Au and Cr, it is possible that the elastic anomalies in this system result from the formation of an interface layer deriving from the mixing of the two metals: some experimental evidence of this same driving mechanism has been found in the Ta/Al (Ref. 36) superlattice and suggested for the Ag/Pd multilayer:[15] both of these systems share with Au/Cr the unusual enhancement of the shear elastic constant c_{44} at small modulation wavelengths. However, for the Au/Cr superlattice no detailed structural analysis, including the study of mixing or roughness effects, has been done yet.

IV. CONCLUSIONS

We have investigated the electronic structure and the elastic properties of Au/Cr(001) n:n superlattices for $n=3,5,7,9,11,13,17$. This analysis has been performed within a first-principle approach using the LMTO ASA method and the force theorem.

The DOS projected on the interface atoms is almost the same in all the superlattices studied. Only the two layers closer to the interface for both Au and Cr show remarkable variations with respect to the bulk DOS. This clearly indicates that the Au-Cr interaction is strictly limited at the interface regions. The charge transfer as well is confined to the two layers at the interface; it is mainly *sp* in character and its value remains unchanged for superlattices of different periodicity. Friedel-like charge oscillations are present in both Au and Cr layers.

In the second part of this work we have analyzed the role of the electronic-structure modifications induced by the periodicity in the elastic anomalies that have been observed in this system. We have therefore calculated the electronic contribution to the shear elastic constant c_{44}, as a function of the modulation wavelength, with particular reference to the Fermi-surface contribution. We have found that this term remains almost constant over the relevant modulation wavelength range. This allows us to rule out the Fermi-surface Brillouin-zone interaction as a driving mechanism for the observed anomalies.

Our results are of course not conclusive for the explanation of the supermodulus effect in metallic superlattices. Its origin may not be related to a single driving mechanism, as can be argued from recent experimental results. We stress that a better structural characterization of metallic multilayers is needed as a starting point for a realistic description and modeling of these systems, in particular, for their elastic behavior.

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