Surface Charge Densities and Atom Diffraction

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First-principles surface charge densities are calculated and used to form He-surface interaction potentials which can account for atom-beam diffraction intensities from GaAs(110) and Ni(110)-H 2×1 surfaces.

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The diffraction of monoenergetic atomic beams from single-crystal surfaces is an old phenomenon which until recently has been observable for only a small group of ionic crystals.¹ In the past several years, modern experimental techniques have opened up this field, showing that sharp and accurate diffraction data can be obtained from semiconductor,^{2,3} metal, and adsorbate covered surfaces.⁴ This raises the possibility that atom diffraction can become an important tool for surface structural analysis.

Two steps are necessary to relate a measured set of diffraction intensities to surface structure. First, the surface-atom interaction potential must be calculated as a function of the surface atomic geometry. Then a series of sets of diffraction intensities must be calculated and compared with the data. Considerable success has been achieved in the second problem with use of empirically fit corrugated hard-wall potentials,¹ and recently with use of realistic empirical potentials.⁵ The first step has received much less attention. Recent calculations suggest that the repulsive He-surface interaction potential may be approximated as a universal local function of the surface charge density, a result which is potentially extremely important.^{5, 6} These calculations find the energy of embedding He in a uniform electron gas, and neglect the variation of the actual surface charge density across the very small volume of the He atom.^{5,6} This Letter reports a very encouraging test of this relation by comparing potentials from self-consistently computed surface charge densities for several structures of GaAs and H chemisorbed on Ni(110) with those empirically inferred from He diffraction.^{3,4}

For the beam energies typically employed, 10-100 meV, the He atoms are reflected at charge densities of order $10^{-5}-10^{-4}$ a.u. (electrons per cubic Bohr radius).^{5,6} These densities occur in the distant tail of the surface charge, typically from 6 to 7 a.u. beyond the plane of surface atoms. (Unless noted otherwise, atomic units are implied hereafter.) The only calculational tech-

niques which stand a chance of treating the charge accurately at these distances and low densities are those which use the Laue representation for the wave function in the surface region. These include the pseudopotential scattering method⁷ and the surface linear augmented-plane-wave (SLAPW) method.⁸ The Laue representation consists of parallel plane waves times numerical normal functions, and can treat exponential decay accurately. The SLAPW technique used here divides space into three regions: muffin tin, interstitial, and surface, with the wave function expanded in numerical radial, plane wave, and Laue functions in the respective regions. The present implementation of this method uses fully general (and similar) expansions for the potential and charge density in these regions. The only approximations made in the self-consistency are those inherent in the truncation of the wave function basis set itself, and the widely used local approximation for the electron exchange and correlation potential.⁹ The Wigner form is used.¹⁰

The GaAs(110) He diffraction data³ was taken for two energies (0.063 and 0.021 eV), with inplane diffraction measured for several incident polar and azimuthal angles. The specular intensity was also measured as a function of polar angle for several azimuthal angles. The scattering was found to be consistent with a corrugated hardwall potential of height

$$h(x, y) = \sum_{mn} d_{mn} \exp[(2\pi i m x/L_x) + (2\pi i n y/L_y)], \qquad (1)$$

where d_{mn} are corrugation parameters, L_x and L_y are surface unit-cell dimensions, x is in the (001) direction (across the ridges and troughs of the surface), and y is in the (110) direction (along the troughs). The parameters were fit approximately in four ways, analyzing the classical "rainbow" envelope and the eikonal approximations for the diffracted beams, and analyzing semiclassical interference and the eikonal approximation for the specular intensity.¹ They

found for an average best fit $d_{10} = 0.52$, and $d_{01} = 0.14$. (Symmetry related *d*'s are, of course, included in the sum.) A detailed soft-wall scattering calculation⁵ (based on an improvement of the coupled differential equation method¹) gave an approximate fit with $d_{10} = 0.43$ and $d_{01} = 0.09$.⁵ The Van der Waals attractive well was found to have a depth of ~ 0.007 eV.^{5, 11}

The present results for the GaAs surface charge density are shown in Fig. 1 as contours of constant charge density on two planes. The relaxed surface geometry indicated by low-energyelectron-diffraction (LEED) analysis¹² is used, with the bulk bond length and the plane of the surface Ga-As bonds rotated 27° below the surface plane.

With use of the Ejsberg-Nørskov relation⁶ for the He potential in the relevant energy range,

$$V_{\rm He}(\mathbf{\hat{x}}) = 750\rho(\mathbf{\hat{x}}),\tag{2}$$

where ρ is in atomic units and V in eV, we see that the classical turning points of the He occur on contours at 2.8×10^{-5} and 8.4×10^{-5} for 0.020 and 0.063 eV. The even spacing of the logarithmic contours shows that the potential can be written analytically as

$$V(x) = V_0 \exp\{[z - h(x, y)]/l\},$$
(3)

where *h* is expanded as in Eq. (1), *l* is a decay length, and V_0 is an energy which depends on the absolute *z* origin and is hence irrelevant. The parameters for *h*, which are fit to the surface of classical turning points at an average He energy, 0.045 eV, are $d_{10} = 0.44$ (- 162°), $d_{01} = 0.15$ (180°), $d_{11} = 0.03 (76^{\circ}), d_{20} = 0.09 (-152^{\circ}), d_{21} = 0.018 (-89^{\circ}), d_{02} = 0.016 (180^{\circ}), d_{30} = 0.028 (-141^{\circ}),$ where the complex coefficients are given in the form amplitude (phase), and the unit cell origin is above the (unrelaxed) second layer As. The decay length is l = 0.79. It is clear that these first-principles theoretical numbers are in excellent agreement with the fitted results for the principal corrugations.

The exponential form of Eq. (3) is not strictly obeyed, and we find some energy dependence for h, typified by $d_{10} = 0.39$ at 0.015 eV. The quality of the presently available fits to the diffraction data does not yet warrant a test of this dependence.

The geometry dependence was examined by calculating the charge for unrelaxed GaAs(110). The principal corrugation amplitudes decreased markedly, to d_{10} =0.29 and d_{01} =0.06. Even within the present scattering calculations, the relaxed and unrelaxed surfaces are clearly distinguished.

The second group of systems studied was Ni(110), clean and with chemisorbed H. Diffraction intensities both in and out of the scattering plane were studied for these systems for several incident angles and a He energy of 0.06 eV. Results were analyzed by fitting a corrugated hardwall potential with use of the eikonal approximation.⁴ Corrugations were much larger for the several H structures studied than for the clean surface (but still small compared to GaAs). The present comparisons concentrated on the lowtemperature 2×1 structure, which is barely evident in LEED and thus presumably does not involve Ni displacements. The corrugated-wall potential had peaks consistent with the H arrangement shown as the "buckled bridge" geometry in Fig. 2 (assuming the H to be responsible for the



FIG. 1. GaAs(110) surface charge density contours. Surface and second layer atoms are shown. Contour progression is 1, 2.2, and 4.6.



FIG. 2. Positions in surface plane of surface Ni (open circles) and H (filled circles) for two Ni-H structures considered. Radii are proportional to metallic or covalent radii.



FIG. 3. Ni(110) and Ni(110)-H charge density contours. Surface bonded H and second layer Ni lie in plane of plots.

peaks).4

Surface charge densities were calculated for (paramagnetic) Ni(110) and Ni(110)-H in a number of structures. Results for three of these are shown in Fig. 3. For clean Ni, the corrugations are weak, but are nonetheless nearly three times as large as those inferred from the hard-wall fit (see Table I). For corrugations whose maximum height Δh is large compared to the decay length l, it is physically reasonable that a hard and a soft wall should scatter similarly. This is indeed the case for GaAs ($\Delta h = 1.8$, l = 0.79). For $\Delta h \ll l$, however, model calculations show soft-wall diffraction intensities substantially reduced from hard-wall values.¹³ For the present clean Ni results, l = 0.77 and $\Delta h = 0.30$. While the soft-wall calculations¹² did not include the relevant parameter range, it is plausible that the hard-wall fit could underestimate the soft-wall corrugations. Greater inelastic scattering from a metallic surface could also play a role.

Rieder and Engel, Ref. 4, suggest that the Ni-H 2×1 geometry may have the H in the threefold site formed by two surface atoms and one secondlayer atom. This geometry was tried in a 1×1 structure, and it was found that this well-buried H reduced the corrugations. To try another extreme, the 1×1 bridge geometry shown in Fig. 2 was used, with a Ni-H bond length based on the usual H radius of 0.6 a.u. The corrugations in this case, shown in Fig. 3, were much larger than the experimental 2×1 fit (see Table I). "Rolling" the H's alternately off the bridge site to a 45° angle produced too little corrugation and too little 2×1 character, measured by the ratio of $d_{11/2}$ to d_{10} . A greater angle for more 2×1 character would give even less corrugation.

Structures of transition-metal-cluster molecules suggest that an H radius of 0.9 a.u. is more appropriate for bridge-bonded sites.¹⁴ With use of the resulting bond length of 3.2 a.u. and the xy position of Fig. 2, which minimizes H-H Coulomb repulsion, the results shown in the center of Fig. 3 were obtained. The two principal corrugation coefficients given in Table I are seen to be in reasonable agreement with the experimental fit allowing for some soft-wall effect (l = 0.70and $\Delta h = 0.42$ in this case). Their ratio is in very good agreement. Compared to clean Ni, inelastic effects should be smaller for this stiffer and more covalent surface. The significance of the discrepancies in the smaller terms cannot yet be assessed. Note that the contour peak position indicated by the dashed line in Fig. 3 is seen to depend on density and thus He energy, so direct interpretation of corrugated-wall structure is in fact only suggestive of atom positions.

I have demonstrated here that first-principles charge calculations, combined with a recent proposal for extracting the He-surface potential from them,^{5,6} and a theoretical calculation of atom dif-

mn	Clean	Clean	Bridge H	2×1 H	$2 \times 1 \text{ H}$
	expt. ^a	theory	theory	theory	expt. ^a
10	-0.023±0.005	- 0.075	- 0.193	-0.062	$\begin{array}{c} -\ 0.047 \pm 0.009 \\ -\ 0.033 \pm 0.005 \\ 0.00 \\ 0.00 \end{array}$
11/2				-0.041	
01	0.00	0.000	- 0.032	-0.015	
11	0.00	0.003	0.008	0.000	
20 21/2	0.00	-0.006	-0.025	- 0.002 - 0.005	$-0.014 \pm 0.005 \\ -0.009 \pm 0.005$

TABLE I. Ni(110) corrugation parameters d_{mn} in atomic units.

^aRef. 4.

fraction, can give nontrivial geometric information. Examples are the (known) relaxation of the GaAs(110) surface, and a detailed geometry of 2×1 H on Ni(110). Further tests of the potential, of soft-wall effects, and of other effects in diffraction are necessary to move towards more quantitative accuracy.

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Observation of Superlattice Effects on the Electronic Bands of Multilayer Heterostructures

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Electroreflectance measurements have been performed on the GaAs-Ga_{1-x} Al_x As superlattice, and the observed structure has been related to interband transitions at different points of the Brillouin zone. For increasing x the energies of these transitions shift progressively to higher values with respect to those of bulk GaAs, indicating the effect of the superlattice potential on the band structure beyond the zone center. In contrast, similar shifts observed in In_{1-x} Ga_x As-GaSb_{1-y} As_y only occur for x, y > 0.2, an anomaly arising from its unusual periodic potential.

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Recently, semiconductor superlattices of both GaAs-Ga_{1-x}Al_xAs and In_{1-x}Ga_xAs-GaSb_{1-y}As_y have been extensively studied. The formation of quantum states or subbands and their influence on electronic properties have been explored successfully by a variety of experiments.¹⁻⁸ These in-vestigations, however, were confined to the subband structure in the vicinity of the fundamental gaps (Γ_{15v} - Γ_{1c}) of the host semiconductors. The basic question as to the general effect of the peri-

odic potential on the band structure remains unanswered.

In this Letter we report electrolyte electroreflectance (EER) measurements on GaAs-Ga_{1-x}Al_xAs (type-I) superlattices⁹ that provide the first observation of the superlattice effect on the band structure away from the Brillouin zone center. Of special significance is the observation of transitions associated with both E_1 and E_1 $+ \Delta_1 (L_{3v}-L_{1c})$, and E_0 and $E_0 + \Delta_0$ (the lowest