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Sensitivity of helium diffraction to surface geometry

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In order to examine the sensitivity of He diffraction to surface structure, we develop explicit expressions for the principal features of the He scattering potential in terms of simple atomic and lattice parameters. A measure of structural sensitivity evolves naturally out of these relationships. In particular, the surface lattice constant emerges as the most crucial factor in determining when He diffraction will provide useful structural information. For surface lattice constants less than ~5–6 Å, the potential is often well approximated by a simple universal form, and has little sensitivity to the precise structure. The conclusions are illustrated with recent experimental results for selected metal, semiconductor, and adsorbate-covered surfaces.

I. INTRODUCTION

There has been considerable recent progress in understanding the diffraction of He atoms from single-crystal surfaces. As a result, He diffraction is emerging as an important technique in the study of surface structures. In a number of recent studies information on an adatom binding site[1–6] or a surface atomic configuration[6–8] has been obtained. However, with few exceptions,[6,8] it has not been clear how reliable these He-diffraction assignments are, since no assessment of the *sensitivity* of the technique to surface geometric parameters is made. It is the purpose of this paper to provide some useful guidelines for this assessment.

It is important to distinguish from the outset between sensitivity and related issues, such as accuracy. This paper addresses only the question of when the He-surface interaction potential, as measured by He diffraction, is sensitive to the surface atomic geometry, i.e., when changing the atom positions would be reflected in a measurable change in diffraction intensities. The related issue of how accurately structural information can be extracted from the diffraction data, is beyond the scope of this paper. Sensitivity is a necessary condition for structure determination, but not a sufficient one. In particular, we make use of approximations here, such as an atom-superposition model for surface charge density, which may not be sufficiently accurate for the data analysis required to determine surface structure, but which are quite adequate for addressing the issue of structure sensitivity.

Based on our present understanding of the He-surface potential, we develop approximate but explicit expressions for the principal features of the surface potential corrugation in terms of simple atomic parameters and lattice constants. A measure of structural sensitivity evolves naturally out of these relationships. In particular, the surface lattice constant emerges as the most crucial factor determining whether He diffraction provides useful structural information. When the surface lattice constant is less than 5–6 Å, as for unreconstructed low-Miller-index surfaces, the potential corrugation follows a universal form and is determined almost entirely by the surface lattice constants, and therefore provides little useful information on the atomic coordinates. This is true for adsorbate systems as well as clean surfaces. Explicit criteria are presented for determining when the scattering is sensitive to the surface-adsorbate bond length.

We illustrate these results using recent experimental determinations of the principle Fourier coefficient of the He-surface potential corrugation in the literature. Our intent is that the relationships derived here will prove useful in assessing the structural information content of He diffraction and provide a more widespread appreciation for the capabilities and limitations of He diffraction as a surface structural probe.

Scattering experiments probe the structure of the interaction potential between the projectile and the target. For diffraction of x rays, neutrons, or energetic electrons from solids or surfaces, the scattering potential is probed at or around the nucleus, so that the derived potential directly gives a structure. However, He atoms at the energies of interest (~10–100 meV) approach only within 2–3 Å of the target nuclei. Thus the derivation of structural information is indirect and requires, first, that the scattering potential at these distances be sensitive to nuclear positions and, second, that the potential can be calculated from the structure with sufficient accuracy. Recent progress in understanding the He-surface potential[9–11] permits us to test the first point, albeit approximately, for a variety of systems in a fairly general form.

The organization of this paper is as follows. We briefly discuss the present state of understanding of the He-surface potential, and the relationship recently demonstrated between the dominant repulsive part of the interaction and the target charge density. We cite the calculations of surface charge densities and approximations thereto, and make use of these approximations to derive analytic relationships for the principal features of the scattering potential and their variation with nuclear positions and atomic parameters. A simplified but general graphical description of the structural sensitivity is presented based on these approximate relationships. Specific examples from recent He-diffraction experiments are then cited to exemplify the extent to which structural information is (or is not) contained within the potential inferred from diffraction measurements.

II. THE HELIUM-SURFACE POTENTIAL

A. Charge-density relation

The He-surface potential may be qualitatively characterized by a weak long-range attractive region which attains a depth typically 5–20 meV, and which changes to a repulsive corrugated potential at distances of 2–3 Å measured from the outermost plane of nuclei. The structural information arises predominately from this corrugated repulsion, as it dominates the scattered angular distribution. For the purpose of this paper, and for simplicity, we will ignore the attractive region, with the caveat that the potential parameters derived from fitting a He-diffraction pattern are not generally reliable unless a reasonably accurate form for the attractive region of the potential is included in the analysis.

An important and simple result has now been established for the repulsive component of the He-surface potential. It has been shown[9,11] that the repulsive energy of a He atom immersed in a dilute electron density ρ is linear in ρ. Specifically, $E=\alpha\rho$, where $\alpha\sim 500$ eV a.u.^{3}. This linear term was independently shown[10] to be the dominant term in a more general empirical form of the He-surface potential. The coefficients in the following trial expression were fitted using accurate experimental He—rare-gas potentials and local-density calculations for ρ:

$$E=A\rho-B\rho^{1/3}-\sum\frac{C_6}{r^6}\ . \tag{1}$$

The fitted coefficients are $A=650$ eV a.u.^{3} and $B=25$ eV a.u. For our purposes it is not important whether these two expressions are correct in detail. We require only that, over the interaction region of interest, the repulsive part of the potential can be approximated as linearly proportional to the charge density with an effective coefficient. In a recent assessment[12] it is concluded that in the very low-density limit, scattering theory, electron scattering experiments, and a local-density approximation with a self-interaction correction converge to a coefficient $\bar{\alpha}=200$ eV a.u.^{3}. The appropriate value of α, however, depends on whether and how the attractive terms of the He-surface potential are included.

In general these theoretical considerations indicate that thermal energy He atoms probe the surface potential only up to distances at which the target charge density is of the order of 10^{-4} a.u.$^{-3}$, and that contours of constant charge density are approximately isopotential contours. Therefore, to assess the structural information content of He diffraction, a reliable method of generating charge densities at these low values is required.

B. Calculation of charge densities

Charge profiles believed to be accurate at very low densities were first calculated and compared to He-diffraction experiments[6] using the linear-augmented plane wave (LAPW) approach. These self-consistent, all-electron calculations compared well with the experimentally derived potential parameters; the calculations confirmed the tilt angle of the surface bond in the GaAs(110) surface reconstruction[13] and identified the appropriate binding site and probable bond length of H on the Ni(110) surface.[14] However, a definite discrepancy with the small corrugation of the clean Ni(110) surface was noted. Some of this discrepancy is associated with the appropriate inclusion of the attractive part of the He-surface interaction, and with hardwall approximations used in analyzing the experiment. It has been argued that the LAPW calculations contain small errors in the dilute charge densities due to its approximations in dealing with long-range correlations. Although this problem is a focal point of current theory, it is not strongly related to an assessment of He diffraction as a structural probe. The potentials presently being emphasized theoretically are those of close-packed metal surfaces with small corrugations, for which the discrepancies are also numerically small (but significant). There is essentially no structural information content in the diffraction data because of the small corrugations. For systems with large corrugations in the potential, it is likely that absolute LAPW charge-density errors will not be significantly larger. The shape of the charge density in these cases is predominantly determined by the strong electron potential in the region near the surface atoms, and only weakly affected by the shape of that potential in the low-density region. Indeed we will take LAPW calculations as a standard with which we assess the utility of a simple scheme to estimate the surface charge density, namely the superposition of atomic charge densities.

C. Atomic charge-density superposition

We have tested atom superposition for a variety of surfaces, and compared the results at the charge densities of interest to LAPW calculations. The test cases include close-packed metal surfaces, reconstructed open semiconductors, and ordered chemisorbed arrays. In the atom superposition, we have used numerical atom charge densities. These are calculated semirelativistically, using a local-density approximation for correlation and exchange. In each case where the uppermost atoms are all *equivalent* (including adsorbate systems), we find that the principal Fourier coefficients of the atom-superposition charge contours at the 10^{-4} a.u. level agree well with the full LAPW calculation, often within $\sim 10\%$. We conclude that for a range of qualitatively different bonding and variations in surface atom density, the superposition of atomic charge densities is a reasonable approximation for a first-order evaluation of He-diffraction data. Specifically, it is sufficiently accurate to test the structural sensitivity of the diffraction. The derivation of quantitative structural parameters, however, requires more caution. In the Appendix we analyze the behavior of the true surface charge density, and show that for the homogeneous surfaces it has important similarities to the atom-superposition charge density. In this way we provide a partial justification of the use of atom superposition, in addition to the strictly empirical observation that for the homogeneous surfaces it often works well.

In contrast we note that for the case of GaAs(110), Laughlin[10] showed that atom superposition gives rise to a large error in the He-surface potential corrugation. The isolated Ga atom is larger than As, but in the solid compound this is no longer the case. If the (unrealistically large) Ga is omitted, superposition of As atoms alone gives a rather accurate potential. Similarly, in the buckled dimer model of Si(100), the two uppermost Si atoms are inequivalent, and "subsurface" Si are exposed. Sakai *et al.* found[8] that the charge density could be reproduced by atom superposition only if some nonsphericity and different atomic sizes of the two Si dimer atoms and the subsurface atoms were included semiempirically. A generalization of these results would include any surface which contains proximate chemical heterogeneity, including charge transfer between like surface species. In these cases the effective atomic sizes may be in considerable error, rendering structural conclusions unreliable. For homogeneous surfaces, including fairly open surfaces, one may often utilize the simplification of a free-atom charge-density summation, at least at the level of a qualitative topographical assignment.

We may therefore make use of the linear-potential—charge-density relation and atom superposition, in order to treat the question of structural sensitivity of He diffraction at a qualitative but still fairly general level. An assessment of the *quantitative* capabilities of He diffraction, for regimes where the results are sensitive to structure, must deal with more complex problems.

III. STRUCTURAL SENSITIVITY OF HELIUM DIFFRACTION

In this section we use the simplification of atom superposition to draw general conclusions regarding the relation between surface structure and He-surface potential. We begin by approximating the surface charge density by the superposition of spherical atom charge densities,

$$\rho(\mathbf{r})=\sum_{\mathbf{R}}\phi(\mathbf{r}-\mathbf{R})\ , \tag{2}$$

$$\phi(r)=\phi_0[\exp(-\kappa r)]/\kappa r\ , \tag{3}$$

where $\mathbf{R}$ is a surface lattice vector, and $\phi(r)$ is an analytic approximation which models the atom charge density far from the nucleus. The choice of denominator in (3) is made for convenience as seen below. The behavior of $\phi(r)$ is dominated by the exponential, so (3) is adequate to fit actual atomic results over the entire relevant density range.

Since $\phi(r)$ and hence $\rho(\mathbf{r})$ are by construction solutions of $\nabla^2-\kappa^2=0$, we can expand (2) for $z>0$ as

$$\rho(\mathbf{r})=\sum_{\mathbf{G}}a_G\exp[-(\kappa^2+G^2)^{1/2}z]\cos(\mathbf{G}\cdot\mathbf{r})\ , \tag{4}$$

where $\mathbf{G}$ are the (two-dimensional) surface reciprocal-lattice vectors. A two-dimensional rectangular lattice with one atom per unit cell is assumed for simplicity. Equation (4) is similar to a model potential proposed by Harris and Liebsch,[11] but gives a more accurate description of the variation of corrugation with distance (see the Appendix).

The effect of the second layer can be included approximately by adding its $G=0$ component to (4). This extra contribution is simply

$$\rho_2(\mathbf{r})=n_2a_0\exp[-\kappa(d+z)]\ , \tag{5}$$

d and n_2 being the interlayer distance and the number of atoms per cell in the second layer

The coefficients a_G are easily evaluated:

$$\begin{aligned} a_0&=2\pi\phi_0(\Omega_0\kappa^2)^{-1}\ ,\\ a_G&=2a_0(1+G^2/\kappa^2)^{-1/2}\quad (G\neq 0)\ , \end{aligned} \tag{6}$$

where Ω_0 is the unit cell area. In general, the corrugation is greatest along the direction of the smallest reciprocal-lattice vector $\mathbf{G}_1$. To simplify our presentation we consider only the corrugation in that direction. An extension to two dimensions is more complex but straightforward, and leads to identical conclusions regarding sensitivity.

An accurate treatment of He diffraction requires the full three-dimensional potential. However for the purpose at hand the potential is described adequately by the surface of constant potential (i.e., constant charge density) which gives the classical turning point of the He atoms. This surface $z_c(x,y)$ is implicitly defined by $\rho(\mathbf{r})=\rho_c$. $\rho_c=E_i/A$ is the charge density which, in conjunction with the linear charge-potential relationship, gives the He classical turning point, where E_i is the incident-He kinetic energy (corrected for the finite potential-well depth).

We therefore average the charge perpendicular to G_1, and find the extrema of the surface $\rho(\mathbf{r})=\rho_c$, which occur where $\cos(G_1x)=\pm 1$. Labeling the extremal z as z_+ and z_- and combining (4)—(6),

$$\rho_c=a_0\exp(-\kappa z_\pm)\times\left[1+n_2e^{-\kappa d}+\sum_{n=1}^{\infty}(\pm 1)^n\alpha_n\exp(-q_nz_\pm)\right]\ , \tag{7}$$

$$\begin{aligned} \alpha_n&=2(1+n^2G_1^2/\kappa^2)^{-1/2}\ ,\\ q_n&=(\kappa^2+n^2G_1^2)^{1/2}-\kappa\ . \end{aligned} \tag{8}$$

We denote the peak-to-trough corrugation as $\Delta=z_+-z_-$. We will concentrate on Δ as the most significant indicator of the surface structure, although it is desirable experimentally to determine 3 or 4 Fourier coefficients with an accuracy of $\lesssim 10\%$.

Equation (7) may be solved iteratively, but its peculiar value lies in its amenability to successive levels of approximation. One can often replace $z_\pm$ inside the large parentheses in (7) with

$$z\approx\kappa^{-1}\ln(a_0/\rho_c)\ , \tag{9}$$

the solution of (7) keeping only the first-layer $G=0$ term. If in addition, one keeps only the $G=0$ and G_1 terms of the first layer, one finds

$$\Delta = \kappa^{-1}\ln\left[\frac{1+\alpha_1 e^{-q_1 z}}{1-\alpha_1 e^{-q_1 z}}\right]$$
$$= \kappa^{-1}\ln\left[\frac{1+\alpha_1(\rho_c/a_0)^{q_1/\kappa}}{1-\alpha_1(\rho_c/a_0)^{q_1/\kappa}}\right] . \qquad (10)$$

For weak corrugation (10) simplifies to

$$\Delta \approx 2\kappa^{-1}\alpha_1 e^{-q_1 z} \quad (\Delta \ll \kappa^{-1})$$
$$\approx 4\kappa^{-1}\exp(-\tfrac{1}{2}G^2\kappa^{-1}z) \quad (G^2 \ll \kappa^2) . \qquad (11)$$

Typically $\rho_c/a_0 \sim 10^{-3}$ for He diffraction, so the existence of measurable Δ depends crucially on the smallness of $q_1/\kappa \approx \frac{1}{2}G_1^2/\kappa^2$. Figure 1 shows results of both (7) and (10) for the corrugation of an ideal face-centered-cubic Au(110) surface as the (001) lattice constant is varied. Both curves shown include corrugation in only one dimension (a good approximation in this case), and both neglect the corrugation in the second layer. The solid curve, among other approximations, describes a single layer of atoms, so the corresponding corrugation diverges when He can penetrate the layer.

Results of self-consistent LAPW calculations for various noble-metal surfaces are also shown. The values of $\phi_0 = 2$ a.u.$^{-3}$ and $\kappa = 1.4$ a.u.$^{-1}$, while fitted to the Au atom, reproduce Cu and Ag results fairly well also. We take $\rho_c = 10^{-4}$ a.u.$^{-3}$, corresponding to a typical incident-He kinetic energy, around 20 meV.

These simple results demonstrate several important points. In the region where the two curves of Fig. 1 are nearly the same, the surface is "close-packed," in that the helium atom does not "see" the second layer. [The small difference for $\Delta \leq 0.8$ Å is due mainly to replacing z with its average value in (10), which underestimates Δ slightly.] At larger Δ the neglect of higher Fourier coefficients and of the second layer in (10), which overestimates Δ, becomes the dominant source of error until (10) diverges. In the close-packed regime, the corrugation is determined almost entirely by the lattice constant (and by ρ_c), and the corrugation difference between Cu(110) and Ag(110) is attributable to the slightly different lattice constant. Helium diffraction in this regime is structurally relatively uninformative.

Around $a = 5$ Å there is a crossover to an "open" regime, where Δ is roughly heading towards the interlayer spacing [1.4 Å for Au(110)]. The 2×1 Au(110) surface, with alternate $\langle 1\bar{1}0\rangle$ rows missing, falls in the open regime for He diffraction. Overall agreement of these results with self-consistent calculations (shown in Fig. 1) is excellent.

Figure 1 suggests that a convenient criterion for the surface lattice constant $a = 2\pi/G_1$, at which crossover from open to close-packed occurs, is the divergence of the approximate formula (10). Since κ does not vary drastically among the elements, and results are less sensitive to ϕ_0 and ρ_c, the "critical" value of $a \sim 5$–6 Å found here for Au(110) is qualitatively applicable to many solid surfaces.

Even in the close-packed regime the second layer must have some effect, especially if the interlayer spacing d is small. We define the "sensitivity" to d as $\delta\Delta/\delta d$, the change in corrugation per unit change in interlayer distance. Letting $d \to d + \delta d$ in (7), it is easy to show that

$$\frac{\delta\Delta}{\delta d} \leq \exp[\kappa(\Delta - d)] . \qquad (12)$$

Thus, unless the corrugations Δ is within κ^{-1} (~ 0.4 Å) or so of the interlayer spacing d, the sensitivity to the second layer is quite negligible. This result is illustrated in Fig. 2, which repeats Fig. 1 but for several different values of the interlayer spacing.

Note that the charge density ρ_c and the atom parameter ϕ_0 enter only as the dimensionless ratio ρ_c/ϕ_0, although the equations have not been written so as to make this explicit. Similarly the lattice constant a (or equivalently

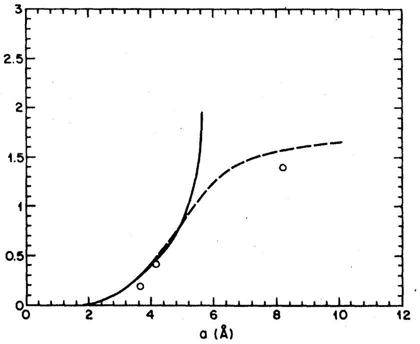

FIG. 1. Peak-to-trough corrugation amplitude Δ of the surface of charge density 10^{-4} a.u. vs (001) surface lattice constant a, for analytic atom superposition model of an fcc (110) surface, with atom parameters as for Au. Solid line: approximate formula (10). Dashed line: more exact formula (7). Circles are results of self-consistent LAPW calculations for, from left to right, Cu(110), Ag(110), and a missing row model of Au(110)(2×1). The full solution is essentially indistinguishable from the simple universal form (10) for lattice constants smaller than about 5 Å, or more generally for $\kappa a < 10$-15.

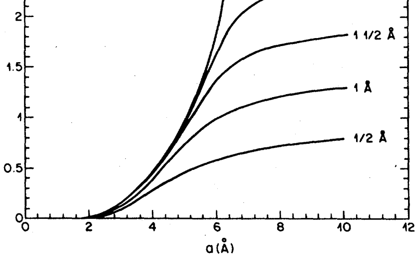

FIG. 2. Peak-to-trough corrugation amplitude Δ vs surface lattice constant, as in Fig. 1. Each line corresponds to a different interlayer spacing d as indicated. As expected from (12), each curve merges with the "universal" $d = \infty$ curve when the corrugation Δ is significantly ($\sim \kappa^{-1} = 0.4$ Å) less than the interlayer spacing d minus the decay length.

G_1) and the interlayer spacing d occur only in dimensionless combinations with the atomic decay length κ^{-1}, e.g., G_1/κ and κd. Thus, within the present model, the "shape" of the surface charge density is completely determined by the geometry, while the atomic species enters only via a scaling of charge density (by ϕ_0) and length (by κ^{-1}).

IV. EXAMPLES

To illustrate our conclusion regarding the relationship between surface atomic spacing and structure sensitivity, we have selected a series of experimental results for metal, semiconductor, and adsorbate-covered surfaces, and compared the values which have been estimated for the principal Fourier coefficient of the corrugation to the curves drawn in Fig. 2. The results are shown in Fig. 3.

These estimates are plotted with somewhat arbitrary error bars, by which we intend to include both the experimental uncertainty, and the uncertainty due to the level of theory used in extracting the scattering potential from the data. This comparison is intended to illustrate the qualitative aspects of the structural sensitivity of He diffraction. The value for the principal Fourier coefficient is taken in the direction of maximum corrugation. Bear in mind that the curves drawn are for Au, and should be compared only qualitatively to experimental results for other systems.

The sequence of metal surfaces, Ni(110),[14] Cu(110),[15] Ag(110),[16] and W(112),[17] follow the correlation with the lattice parameter is predicted by our model. However, the amplitudes of the corrugation are all smaller than expected, a discrepancy which remains for more accurate charge-density calculations and is currently the subject of theoretical investigation. Since the lattice spacings are well known in these surfaces, it is clear that there is little structural information in these experimental results, which serve better as part of the general development of an accurate description of the He-surface potential.

The Au(110) surface reconstructs into a (2×1) periodicity, with a surface atom spacing of 8.12 Å along the corrugated direction. The measured corrugation[7] $\Delta\approx1.6$ Å is appropriate to the missing row model, as has recently been confirmed by x-ray diffraction[18] and transmission electron microscopy.[19] Although there remained significant details to be explained for a final structural assessment, the gross topographical nature of the Au(110) surface was immediately evident from the He-potential corrugation.

The semiconductor surfaces selected are believed to be variations of a "tilted dimer" surface reconstruction, but with different top-layer atomic spacings. They are good examples of the sensitivity of the He potential to changes in the surface atomic spacing. For GaAs(110) the tilting of the surface bond produced a small first-to-second layer spacing, $d=0.6$ Å. If the Ga and As are forced to be coplanar, the corrugation in the scattering potential drops from ~0.9 to ~0.5 Å.[6] This calculation directly demonstrates the structural sensitivity of He diffraction when $d\sim\Delta$. For Si(100) and Ge(100), the dimerization increases the surface atomic spacing, and hence the corrugation. The proposed tilting of the dimer gives a further increase. If adjacent dimers tilt in opposite directions, as in the $c(2\times4)$ periodicity proposed for both the Si(100) (Ref. 8) and Ge(100) (Ref. 20) surfaces, the top-layer spacing and consequent corrugation are increased considerably. The range of top-layer spacings for various dimer models of both surfaces is indicated by the horizontal bar in Fig. 3, where the vertical bar indicates the range of peak-to-trough corrugations. The essential point is that these lattices are sufficiently open to render He diffraction quite sensitive to the differences among various models and periodicities which have been proposed. Of course, atom superposition is inadequate for an accurate description of the He scattering from these reconstructed semiconductor surfaces.[8] Nevertheless, our results allow a useful description of the gross trends in corrugation and structure sensitivity.

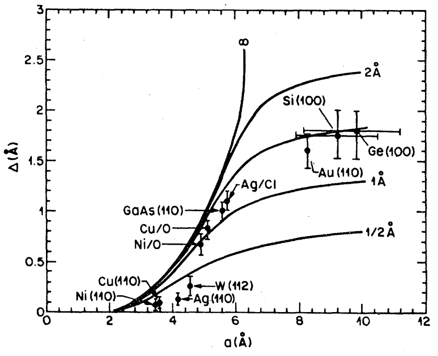

FIG. 3. Same as Fig. 2, but including experimental results for the corrugation amplitude of various systems. Note that the calculation (solid lines) is for Au, and should be slightly rescaled for atoms of different "size" κ before attempting *quantitative* comparisons.

The three adatom systems in Fig. 3 provide instructive examples of the limitations of He-diffraction analysis. The Ag(001)$c(2\times2)$Cl was studied[4] to determine whether the Cl adatom was situated above the fourfold hollow of the Ag(001) surface, or substitutionally within the outer plane of Ag atoms. This choice of topographies corresponds roughly to an interlayer spacing $d\approx1.7$ or 0 Å. The principal corrugation $\Delta\approx1.1\pm0.15$ Å is consistent with the former, i.e., the overlayer site. A direct calculation of the dependence of the corrugation on d for this site was carried out, corresponding to a vertical cut in Fig. 2 at the Cl adatom spacing of 5.7 Å. Little increase of the corrugation with increasing d was found, as expected from the coalescence of the different d curves below $a=6$ Å in Fig. 2. This fact was confirmed by LAPW calculations. From the estimated uncertainty in the principal corrugation parameter, the vertical distance of Cl atom can only be restricted to $d_{12}>1.2$ Å based on He diffraction. This example dramatically demonstrates the lack of sensitivity of the He potential to vertical displacement of adatoms when the charge densities of the adatoms at the 10^{-4} a.u. level overlap, i.e., when they are effectively close packed. A similar conclusion holds for the Cu(110)(2×1)O. We estimate from the published diffraction spectra[5] a value $\Delta\approx0.8$ Å±0.15, leading to the restricted conclusion that $d_{12}\gtrsim0.7$ Å. A study of

Ni(100)$c(2\times2)$O (Ref. 21) is similar to the Ag(100)$c(2\times2)$Cl. The goal of the diffraction study was to distinguish between two previously proposed alternatives for the height of the oxygen above the Ni(100) surface, one close to the surface and the other ~1 Å above the surface. The principal Fourier coefficient clearly indicates the latter, as was concluded in that study. As with Ag/Cl, however, the actual height of the O above the Ni atom plane is subject to a very large uncertainty. Thus for the Ag/Cl, Cu/O, and Ni/O systems, He-diffraction analysis can only reliably estimate a lower limit to the adatom height.

We note that a diffraction study has been carried out for Pt(111)(1×1)H where the interatomic spacing is 2.8 Å.[2] The sensitivity to vertical spacing at this separation, even for H atoms, is probably slight. In addition, the atomic "size" of the H atom depends on the nature of the bonding. An atom superposition analysis[2] of the corrugation ($\Delta\approx0.3$ Å) must be regarded as only suggestive in the absence of careful testing of the sensitivity to bond-length and to the effective atomic size.

V. CONCLUSIONS

Within the approximations described above, we have derived explicit expressions relating the surface structure to the He-interaction potential. The most important result is that for a large class of surfaces which can be described as "close packed," the scattering potential has a universal form and and depends primarily on the surface lattice constant. As a result, helium scattering in this regime gives little or no useful structural information.

In the "close-packed" regime, the surface-atom charge densities overlap sufficiently that, for typical interlayer spacings, the helium atom does not sense the second layer. The position of the first layer relative to the underlying crystal is therefore not reflected in the diffraction data. This regime extends up to surface lattice constants of 5—6 Å, and so includes many apparently "open" structures, such as $c(2\times2)$ adsorbates on transition- and noble-metal surfaces.

The best rule of thumb for whether the experimental data are sensitive to the surface structure is Eq. (12). If the experimental corrugation is much less than the interlayer spacing, then the sensitivity to the second layer is nil. Good structure sensitivity most often occurs because reconstruction or ordered adsorption increases the surface lattice constant, although it may also result from a small interlayer spacing (i.e., two types of atoms which are nearly coplanar).

Unfortunately, the situations in which the diffraction data are sensitive to the surface structure are precisely those where the interpretation is most difficult. Typically these involve surfaces which are highly corrugated, so that the detailed quantitative analysis of experimental diffraction intensities is difficult at best. Also, structural sensitivity implies that the helium interacts with atoms which may be chemically different, at least to the extent that they have different local coordination. In such cases, naive atom superposition cannot be expected to accurately describe the surface charge density, except for systems where bonding effects are small, such as noble metals, condensed rare gases, and alkali halides.

Nevertheless, helium scattering remains a proven and a valuable technique for studying surface structure. It is especially suited for giving a measure of how "rough" a surface is, and for discriminating between models of substantially different topographies. The main danger lies in the overinterpretation of data; it is our hope that the present work will aid in deciding what conclusions can, and cannot, be drawn from diffraction data.

APPENDIX

We now consider the true charge density, and how it relates to the atom superposition results. The wave function far from the surface is a solution of $(\nabla^2-K^2)\psi_\nu=0$, where $K=\hbar^{-1}[-2m(E_\nu-V)]^{1/2}$, V is the potential in the region of interest, and E_ν is the energy of the wave function. For the states which determine the vacuum charge density, $E_\nu-V$ is an electron volt or so greater than the work function on average, so $E_\nu\sim5$—6 eV and $K\approx1.2$ Å^{-1}. The state ψ_ν may then be expanded as

$$\psi_\nu(\mathbf{r})=\sum_{\mathbf{G}} A_G \exp[-(K^2+K_G^2)^{1/2}z]\exp(i\mathbf{K}_\mathbf{G}\cdot\mathbf{x}) \ , \tag{A1}$$

where $\mathbf{K}_G\equiv\mathbf{k}_{\parallel}+\mathbf{G}$, and $\mathbf{k}_{\parallel}$ and $\mathbf{G}$ are the (two-dimensional) Bloch wave vector and reciprocal-lattice vector.

A given wave function ψ_ν contributes a charge density

$$\begin{aligned}|\psi_\nu|^2=\sum_{\mathbf{G},\mathbf{G}'} & A_G A_{G'}^{*}\exp[-(K^2+K_\mathbf{G}^2)^{1/2}z] \\ & \times\exp[-(K^2+K_{\mathbf{G}'}^2)^{1/2}z]\exp[i(\mathbf{K}_\mathbf{G}-\mathbf{K}_{\mathbf{G}'})] \ .\end{aligned} \tag{A2}$$

Since $\mathbf{K}_\mathbf{G}-\mathbf{K}_{\mathbf{G}'}=\mathbf{G}-\mathbf{G}'$, $|\psi_\nu|^2$ has the periodicity of the lattice, and can be Fourier expanded,

$$|\psi_\nu|^2=\sum_{\mathbf{G}} u_{\nu G}(z)e^{i\mathbf{G}\cdot\mathbf{r}} \ . \tag{A3}$$

The total charge may similarly be written

$$\rho(\mathbf{r})=\sum_{\nu}|\psi_\nu|^2 f(E_\nu)=\sum_{\mathbf{G}}\rho_G(z)e^{i\mathbf{G}\cdot\mathbf{r}} \ , \tag{A4}$$

$$\rho_G(z)=\sum_{\nu} u_{\nu G}(z)f(E_\nu) \ ,$$

where $f(E)$ is the Fermi function.

If we restrict ourselves to a single value of $\mathbf{k}_{\parallel}$, the best approximation to the total charge is obtained[23] by taking $\mathbf{k}_{\parallel}=\frac{1}{4}\mathbf{G}_1$, where $\mathbf{G}_1$ is the smallest $\mathbf{G}$. (As before, we neglect corrugation perpendicular to $\mathbf{G}_1$ for simplicity.) It is then easy to show that the longest exponential decay length for $\rho_0(z)$ is

$$\bar{K}\equiv(K^2+\tfrac{1}{16}G_1^2)^{1/2}\approx K \ , \tag{A5}$$

and for $\rho_{G_1}(z)$,

$$\bar{K}_{G_1}=(\bar{K}^2+\tfrac{1}{2}G_1^2)^{1/2}\approx\bar{K}+\tfrac{1}{4}G_1^2/\bar{K} \ . \tag{A6}$$

An inaccurate result for this decay constant was reported previously by Harris and Liebsch, who used $k_{||}=0$ as their sample point.[11]

Comparing this with the atom superposition result (8), we see that the first two Fourier components of the charge have the same exponential z dependence (to first order in G^2/κ^2) in both cases if we make the natural correspondence $\kappa=2\bar{K}$. This corresponds to taking the characteristic atomic and solid-state energies to be equal, a good approximation for many systems. A more detailed analysis shows a similar correspondence in decay lengths for higher Fourier components. Thus if atom superposition gives a good description of the charge near the surface, it will also do well at large distances, since the asymptotic z dependence of the true charge density is well reproduced. An alternative derivation has been presented by Tersoff and Hamann,[24] who have used a similar approach in analyzing the structure sensitivity of the scanning tunneling microscope.

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