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Helium diffraction from adsorbate-covered surfaces: A study of the O-Ni(001) system

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Elastic helium-atom—surface scattering is currently being used to obtain important structural information from adsorbate-covered surfaces. Since our earlier work on helium diffraction from $p(2\times2)$ and $c(2\times2)$ phases of oxygen on Ni(001) there have been three new developments. These are (i) the suggestion by Rieder of a prolate charge distribution on oxygen, (ii) the pseudobridge site proposal of Demuth *et al.*, and (iii) the self-consistent calculation of the helium-surface interaction potential due to Lang and Nørskov. In this paper we present results for a wide range of calculational parameters for the $c(2\times2)$ phase of oxygen on Ni(001) and comment on the above developments. Specifically, based on the results in (iii), we are able to explore the implications of the use of the Esbjerg-Nørskov-Lang relation with and without helium averaged surface-charge density. We conclude that the prolate charge distribution produces a shape function in better agreement with experiment. Changes in corrugation coefficients introduced by shifting to the pseudobridge site from the centered site are noted to be small.

I. INTRODUCTION

The chemisorption of oxygen on Ni(001) is among the most thoroughly investigated[1-23] adsorption systems. It appears from a number of recent publications[15-23] that the controversy about the vertical position of chemisorbed oxygen on Ni(001) is nearly resolved in favor of a single height of about 0.9 Å for both the $p(2\times2)$ and $c(2\times2)$ phases. Most of the experimental investigations have projected a single vertical height of oxygen above the nickel surface for the two phases. The cause of reduction[6,11] in the frequency of the oxygen symmetric stretch as one goes from $p(2\times2)$ to $c(2\times2)$ is still not fully established. A possible explanation[12,13] that oxygen atoms in the $c(2\times2)$ case are drawn closer to the nickel surface is not consistent with low-energy electron diffraction,[2,23] extended x-ray-absorption fine structure,[15] surface extended energy-loss fine structure,[19] and helium diffraction.[20] Our previous work[21] as well as this contribution clearly favors the height, $z_0=0.9$ Å as opposed to 0.26 Å, for both $p(2\times2)$ and $c(2\times2)$ phases. But the issues we particularly wish to address in this publication are threefold. We briefly describe those below and then discuss them in detail subsequently.

The first issue we address has to do with the helium scattering[24-29] in general. In the energy range of interest the repulsive part of the helium-surface interaction potential is proportional to the surface-charge density.[26,27,29] The value of the proportionality constant (α) is not fully settled. In particular, Lang and Norskov[29] have shown that the value of α changes almost by a factor of 2 depending upon whether or not one performs electrostatic potential averaging of the surface-charge density. In this connection we shall provide explicit analytical expressions for the electrostatic potential averaged charge density and change in the value of α if unaveraged charge density is replaced by an averaged one. Despite this uncertainty in the value of α, a number of adsorption systems have been successfully investigated[30-32] using the diffraction technique in combination with a nearly first-principles calculation.

The second development which forms the bulk of this paper has to do with the shape of the corrugation function for the $p(2\times2)$ and $c(2\times2)$ phases of oxygen on Ni(001). Rieder[20] has presented helium diffraction data and has found that for both the phases the oxygen adatoms form individual (Gaussian) corrugation hills of height 0.55 ± 0.05 Å and full width at half maximum (FWHM) 2.05 ± 0.05 Å. From this and more thorough analysis he has concluded that the geometric position of the oxygen adatoms in both phases is $z_0\simeq0.9$ Å above the plane of the nickel atoms. Charge-density calculations[20,21] using an O^- wave function gave a value for the corrugation height in reasonable agreement with the experimental data but too large a value (~2.6 Å) for the FWHM. Rieder[20] has noted that if one used neutral oxygen charge density the FWHM is more in line with the experimental data but then the height is also considerably reduced. These observations led Rieder[20] to propose a prolate charge distribution around each adsorbed oxygen atom. We have carried out a large number of calculations assuming spherical and prolate charge distribution on oxygen atom using neutral, ionic, and mixed basis sets. Our conclusion is that whereas the prolate distribution does in fact lead to different classical turning points, the height and FWHM of corrugations is barely affected. However, we do find an improvement in the shape function. We shall provide our quantitative findings in Sec. III.

Finally, the third issue we address has to do with the more recently proposed[23] pseudo-bridge-bonding site for $c(2\times2)$O-Ni(001). According to Demuth *et al.*[23] new LEED analysis indicates that oxygen in a $c(2\times2)$ overlayer resides at $z_0=0.80\pm0.025$ Å but is displaced by 0.3 ± 0.1 Å along the [110] direction. We calculate the corrugation coefficients for the displaced structure. It is difficult for us to assess if these new corrugation coefficients would have measurable effects on the helium diffracted intensities. However, Rieder's[20] model calculations have indicated that they would be able to detect lateral displacements as small as 0.15 Å.

II. HELIUM-SURFACE INTERACTION POTENTIAL

The effective-medium theory has given a linear[26,27,29] relationship between the helium-surface repulsive potential and the surface-electron density. This potential has the form

$$V(\vec{r}) = \alpha\rho(\vec{r}) \ . \tag{1}$$

These calculations are based on the energy of embedding He in a uniform electron gas. The value of the uniform electron density is taken to be equal to the surface electron density $\rho(\vec{r})$ at the He atom position $\vec{r}$. Lang and Nørskov[29] have also provided another justification for Eq. (1) based on self-consistent helium-jellium model calculations. A slightly refined form of the relation (1) is obtained[29] by treating the deviations of the electron density from homogeneity in the first-order perturbation theory. The result is

$$V(\vec{r}) = \alpha_{\text{eff}}\bar{\rho}(\vec{r}) + \Delta E \ , \tag{2}$$

where $\bar{\rho}$ is the charge density averaged over the electrostatic potential, ϕ_a,

$$\bar{\rho}(\vec{r}) = \frac{\int \rho(\vec{r}\,')\phi_a(|\vec{r}\,'-\vec{r}|)d\vec{r}\,'}{\int \phi_a(\vec{r}\,')d\vec{r}\,'} \ , \tag{3}$$

and in atomic Rydberg units

$$\phi_a(\vec{r}) = 2\int \frac{\rho_a(\vec{r}\,') - z\delta(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}d\vec{r}\,' \ . \tag{4}$$

Here $z\,(=2)$ is the helium atomic number, $\alpha_{\text{eff}} = \alpha - \alpha_a$,

$$\alpha_a = -\int_{\Omega_a} \phi_a(\vec{r})d\vec{r} \ , \tag{5}$$

and the integration is over the atomic region only. We note that the negative sign in Eq. (5) was inadvertantly missed in Ref. 29. There have been several values of α proposed in the literature[25–27,29] (ranging from 275 to 750 eV bohr^3).

Let us now calculate α_{eff} and $\bar{\rho}$ for an assumed spherical charge distribution for the helium atom given[26] by

$$\rho_a(\vec{r}) = \frac{2\beta^3}{\pi}e^{-2\beta|\vec{r}|} \quad (\beta = 1.68 \text{ bohr}^{-1}) \ . \tag{6}$$

From Eqs. (4)–(6) we readily obtain

$$\phi_a(\vec{r}) = -\frac{4}{|\vec{r}|}(1 + \beta|\vec{r}|)e^{-2\beta|\vec{r}|} \tag{7}$$

and

$$\alpha_a = \frac{8\pi}{\beta^2}[1 - (1 + \beta R_{\text{cut}})^2 e^{-2\beta R_{\text{cut}}}] \ . \tag{8}$$

The value of α_a does depend[29] on the choice of R_{cut} of the atomic region. However, it is a rather weak dependence for any reasonable value of R_{cut} ($\gtrsim 2$ bohr). For $R_{\text{cut}} = \infty$, $\alpha_a = 8.90$ Ry bohr^3 $= 121.1$ eV bohr^3. Therefore, if $\alpha \simeq 300$ eV bohr^3, then $\alpha_{\text{eff}} \simeq 180$ eV bohr^3, a reduction of nearly 40%.

For an exponentially decaying surface-charge density of the form

$$\rho(\vec{r}) = Ae^{-2kz} \ , \tag{9}$$

the electrostatic potential averaged charge density ($R_{\text{cut}} \to \infty$) is

$$\bar{\rho}(\vec{r}_a) = -\frac{\beta^2}{8\pi}\int \rho(\vec{r})\phi_a(|\vec{r} - \vec{r}_a|)d\vec{r} \ . \tag{10}$$

Using Eq. (9) it becomes

$$\frac{\bar{\rho}(\vec{r}_a)}{\rho(\vec{r}_a)} = -\frac{\beta^2}{8\pi}\int e^{-2kz'}\phi_a(\vec{r}\,')d\vec{r}\,' \ .$$

Substituting Eq. (7) and carrying out integrations in spherical coordinates assuming $\beta > k$ we get

$$\bar{\rho}(\vec{r}_a) = \frac{\rho(\vec{r}_a)}{2}\left[\frac{\beta^2(2\beta^2 - k^2)}{(\beta^2 - k^2)^2}\right] \ . \tag{11}$$

For $\beta = 1.68$ bohr^{-1} and $k = 0.5$ bohr^{-1}, $\bar{\rho}(\vec{r}_a)/\rho(\vec{r}_a) \simeq 1.15$. Thus for typical metals the averaging only changes the charge density by about 15%. For such cases the major effect is the change in the value of α. Since ΔE is usually ignored in corrugation calculations, one gets substantially different results depending on whether one uses $\alpha\rho$ or $\alpha_{\text{eff}}\bar{\rho}$. The reason, however, is not that ρ and $\bar{\rho}$ are all that different from each other but the multiplying factors α and α_{eff} differ from each other by nearly 40%. If α is treated as a semiempirical parameter, the results are quite similar whether or not any averaging is performed. For most of our work we shall make use of Eq. (1). However, Eqs. (8) and (11) permit one to readily calculate how much difference the averaging should make.

III. HELIUM DIFFRACTION ANALYSIS FROM O-Ni(001)

The atomic arrangement of the (001) surface of Ni covered with oxygen in the $c(2\times2)$ configuration is shown in Fig. 1. The location of oxygen atoms along the [110] direction is identical for the $p(2\times2)$ and $c(2\times2)$ phases, the separation being $\sqrt{2}a$, where $a = 3.52$ Å is the lattice constant of bulk nickel. However, along the x ([100]) direction the oxygen atoms are spaced a apart in the $c(2\times2)$ and $2a$ apart in the $p(2\times2)$ structure. For calculating surface-charge density which enters Eq. (1) we used superposition of atomic charge densities (to be discussed more fully below) arising from the two-dimensional periodic system. Three layers of nickel were included along the [001] direction. For oxygen we assumed an

$$\text{O}^-(1s^2 2s^2 2p_x^q 2p_y^t 2p_z^u, \ q + t + u = 5)$$

charge distribution. The choice of O$^-$ is guided by cluster model calculations[3,4,8,16,17] which have indicated $\sim$1–1.3 excess negative charge on the oxygen atom. Since our calculation is not self-consistent, we have explored the effect of various basis functions to set limits on

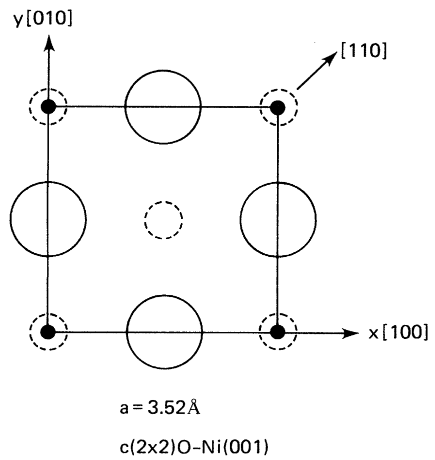

FIG. 1. Oxygen in the $c(2\times2)$ structure on Ni(001). The solid circles are oxygen atoms in the four fold hollow sites. Large open circles are Ni atoms in the top layer, dashed circles are Ni atoms in the layer $(a/2)$ below. The third layer lies below the top Ni layer displaced by a along the [001] direction. The surface unit cell is $(a\times a)$ in area.

our calculated results. These include the neutral $[N]$ quadruple basis functions[33] for the outer shells corresponding to the ^3P state and the ionic $[I]$ basis set consisting of three exponential functions for $2s$, and five functions for $2p$ corresponding[33] to the ^2P state. In addition we also used a mixed basis set (where different magnetic quantum numbers used N or I) to generate prolate charge distribution on oxygen. We shall use the notation $X^q[N]$ ($[I]$) to denote orbital occupancy q of the O($2p_x$) orbital described by neutral (ionic) basis functions. Similar definitions apply to $Y(2p_y)$ and $Z(2p_z)$ orbitals of oxygen. The top layer of nickel (Ni$^{+0.5}$) and the two remaining neutral nickel layers were described by quadruple zeta functions (^3D).[33]

A summary of the calculated corrugation results for the $c(2\times2)$ phase of oxygen on Ni(001) along the [110] direction is given in Table I. The results for the $p(2\times2)$ phase are quite similar. It is clear that for $z_0=0.9$ Å the corrugation height ζ_0 varies from 0.37–0.64 Å and FWHM (W) has the range 2.36–2.65 Å. At $z_0=0.26$ Å, ζ_0 drops to less than 0.23 Å (see the last two lines in Table I) causing us to clearly rule out the shorter vertical height for the $c(2\times2)$ phase because the experiment does indicate $\zeta_0\sim0.55\pm0.05$ Å. For a fixed value of α, averaging the charge density with the electrostatic potential of He produced only minor effects (see second row in Table I).

We note that the value of W is larger than the experimental value ($\sim$2 Å).[20] It is interesting that the usage of neutral basis sets does reduce W as well as ζ_0. This has been found by Rieder[20] earlier and he therefore proposed a prolate charge distribution on oxygen. Our results for the prolate distribution, say given by table entry $X^{1.5}[I]Y^{1.5}[I]Z^2[I]$ at $z_0=0.90$ Å, indicate a slight positive change from the corresponding spherical case. However, the shape function is improved as discussed below.

According to Rieder,[20] putting a Gaussian with the same height and width [as found for the $p(2\times2)$ case] in the middle of the $p(2\times2)$ cell to model the $c(2\times2)$ yields a good description of the experimental spectra. However, he gets[20] a somewhat better fit by using a Fourier representation of the corrugation:

$$D(x,y)=\tfrac{1}{2}D_{1,0}\left[\cos\left[\frac{2\pi}{a}x\right]+\cos\left[\frac{2\pi}{a}y\right]\right]+D_{1,1}\cos\left[\frac{2\pi}{a}x\right]\cos\left[\frac{2\pi}{a}y\right]$$

$$+\tfrac{1}{2}D_{2,0}\left[\cos\left[\frac{4\pi}{a}x\right]+\cos\left[\frac{4\pi}{a}y\right]\right]+D_{2,1}\left[\cos\left[\frac{4\pi}{a}x\right]\cos\left[\frac{2\pi}{a}y\right]+\cos\left[\frac{2\pi}{a}x\right]\cos\left[\frac{4\pi}{a}y\right]\right]. \quad (12)$$

TABLE I. Corrugation height ζ_0 (Å) and full width at half maximum W (Å) along the [110] direction of the $c(2\times2)$O-Ni(001) phase for $E_z=80$ MeV and $\alpha=375$ eV a_0^3. The results are shown as a function of assuming different charge density (prolate and spherical) described by neutral or ionic oxygen basis functions. The notation $X^q[I,N]$ specifies that the O($2p_x$) orbital had an occupancy of q electrons and was described by neutral $[N]$ or ionic $[I]$ basis functions. A similar explanation holds for Y and Z. Also given are the classical turning points Z_A and Z_M for the on top and the midpoint along the [110] direction.

Description	z_0 (Å)	Z_A (Å)	Z_M (Å)	ζ_0 (Å)	W (Å)
$X^{1.67}[I]Y^{1.67}[I]Z^{1.67}[I]$	0.90	3.48	3.02	0.46	2.64
Average with He potential	0.90	3.58	3.13	0.45	2.64
$X^{1.67}[N]Y^{1.67}[N]Z^{1.67}[N]$	0.90	3.11	2.74	0.37	2.37
$X^{1.67}[N]Y^{1.67}[N]Z^{1.67}[I]$	0.90	3.47	2.86	0.61	2.62
$X^{1.5}[I]Y^{1.5}[I]Z^2[I]$	0.90	3.53	3.03	0.50	2.65
$X^{1.5}[N]Y^{1.5}[N]Z^2[N]$	0.90	3.14	2.74	0.40	2.36
$X^{1.5}[N]Y^{1.5}[N]Z^2[I]$	0.90	3.52	2.88	0.64	2.65
$X^{1.67}[I]Y^{1.67}[I]Z^{1.67}[I]$	0.26	3.03	2.83	0.20	2.64
$X^{1.5}[I]Y^{1.5}[I]Z^2[I]$	0.26	3.06	2.83	0.23	2.60

TABLE II. Corrugation coefficients (in Å) of the $c(2\times2)$O-Ni(001) phase for the spherical O^- charge density using the ionic basis set corresponding to the configuration $X^{1.67}[I]Y^{1.67}[I]Z^{1.67}[I]$ at $z_0=0.9$ Å. Results are given for several values of the normal energy E_Z and α. No averaging with the helium potential was performed. The experimental values are due to Rieder (Ref. 20).

	E_Z (meV)	D_{10}	D_{11}	D_{20}	D_{21}
$\alpha=175$	40	0.238	0.011	−0.018	−0.002
	60	0.274	0.012	−0.023	−0.003
	80	0.304	0.014	−0.028	−0.004
$\alpha=275$	40	0.204	0.009	−0.018	−0.002
	60	0.235	0.011	−0.017	−0.002
	80	0.259	0.012	−0.021	−0.003
$\alpha=375$	40	0.184	0.008	−0.012	−0.001
	60	0.209	0.009	−0.015	−0.002
	80	0.233	0.011	−0.017	−0.002
Expt.		0.32±0.02	0.06±0.01	0.02±0.01	−0.02±0.01

The values of the corrugation coefficients are given in Table II in the row labeled "Expt." The other entries give our calculated values for an assumed spherical charge distribution (ionic basis) at $z_0=0.9$ Å. Table III gives corresponding results for a prolate charge distribution. We make the important observation that everything else being equal, prolate charge distribution does in fact produce the shape function in better accord with the experimental data (see Fig. 2). Tables IV and V give results for $z_0=0.26$ Å for spherical and prolate charge distributions, respectively. The displacement with the experimental values is sufficiently gross to rule out this vertical height.

We also calculated the corrugation coefficients using neutral basis functions. Once again the prolate charge distribution was closer to the experimental values but results were inferior than the corresponding values obtained using ionic basis functions. Finally the corrugation coefficients were generated using mixed basis sets to describe spherical, $X^{1.67}[N]Y^{1.67}[N]Z^{1.67}[I]$, and prolate, $X^{1.5}[N]Y^{1.5}[N]Z^{2}[I]$, charge distribution on oxygen atoms. The O($2p_x$) and O($2p_y$) orbitals were constructed with neutral basis functions and O($2p_z$) was described by the ionic set. We noted that the $D_{1,0}$ corrugation coefficient was in better agreement with the experimental value. The maximum corrugation height for these sets is ~0.6 Å and is within the acceptable experimental range. However, the FWHM did not improve at all. Thus we conclude that the ionic basis functions and prolate charge distribution give a somewhat better description of the experimental observations than any other combination of basis sets. It also suggests that while performing non-self-consistent calculations the physical realism can be improved somewhat by choosing appropriate basis sets to reflect ionicity. The issue of FWHM is still unresolved; the calculated value being always larger than the experimental value. Since we have tried various combinations of basis sets without success the issue is not likely to be resolved by going to self-consistency within the local density formalism. It might require a configuration-interaction type of calculation which properly takes into account the self-

TABLE III. Corrugation coefficients (in Å) of the $c(2\times2)$O-Ni(001) phase for the prolate O^- charge density using the ionic basis set corresponding to the configuration $X^{1.50}[I]Y^{1.50}[I]Z^{2.00}[I]$ at $z_0=0.9$ Å. Results are given for several values of the normal energy E_Z and α. No averaging with the helium potential was performed. The experimental values are due to Rieder (Ref. 20).

	E_Z (meV)	D_{10}	D_{11}	D_{20}	D_{21}
$\alpha=175$	40	0.263	0.013	−0.022	−0.003
	60	0.301	0.015	−0.027	−0.004
	80	0.333	0.017	−0.032	−0.005
$\alpha=275$	40	0.227	0.011	−0.016	−0.002
	60	0.259	0.013	−0.021	−0.003
	80	0.285	0.014	−0.025	−0.004
$\alpha=375$	40	0.205	0.010	−0.014	−0.002
	60	0.234	0.012	−0.018	−0.002
	80	0.257	0.013	−0.021	−0.003
Expt.		0.32±0.02	0.06±0.01	0.02±0.01	−0.02±0.01

TABLE IV. Corrugation coefficients (in Å) of the $c(2\times2)$O-Ni(001) phase for the spherical O^- charge density using the ionic basis set corresponding to the configuration $X^{1.67}[I]Y^{1.67}[I]Z^{1.67}[I]$ at $z_0=0.26$ Å. Results are given for several values of the normal energy E_Z and α. No averaging with the helium potential was performed. The experimental values are due to Rieder (Ref. 20).

	E_Z (meV)	D_{10}	D_{11}	D_{20}	D_{21}
$\alpha=175$	40	0.102	−0.009	−0.001	0.001
	60	0.121	−0.009	−0.001	0.002
	80	0.137	−0.011	−0.001	0.002
$\alpha=275$	40	0.084	−0.008	−0.001	0.000
	60	0.100	−0.008	−0.001	0.001
	80	0.113	−0.009	−0.001	0.001
$\alpha=375$	40	0.075	−0.006	−0.001	0.002
	60	0.088	−0.006	−0.001	0.001
	80	0.099	−0.008	−0.001	0.002
Expt.		0.32±0.02	0.06±0.01	0.02±0.01	−0.02±0.01

interaction correction.

In Fig. 2 we have shown some typical results for the corrugation function along the [100] direction. Since the results are symmetrical about the oxygen atom, we have only shown the range $x=0$ to $a/2$. Prolate charge distribution constructed from $X^{1.5}[I]Y^{1.5}[I]Z^{2}[I]$ gives a somewhat better fit of the experimental data in the least-squares sense. The shorter distance $z_0=0.26$ Å is clearly ruled out.

We also investigated the pseudo bridge site proposed by Demuth *et al.*[23] This was obtained by shifting oxygens along the [110] direction by 0.3 Å but we kept $z_0=0.9$ Å. Keeping the origin at one of the oxygen atoms, the Fourier representation (12) needs an additional term, $-\frac{1}{2}D'_{1,0}[\sin(2\pi x/a)+\sin(2\pi y/a)]$ with $D'_{1,0}\approx0.002$. This appears to be a minor change to us and therefore we want to conclude that the pseudo bridge structure cannot be ruled out by our theoretical analysis. Rieder,[20] from a more thorough analysis, has suggested that the shift along the [110] direction by an amount as small as 0.15 Å should be detectable.

Before closing this section we would like to comment on some of the approximations made in our calculations. The major one involves the usage of superposition of atomic charge densities to generate the surface-charge density. A more accurate surface charge would obviously be obtained by performing a high-precision self-consistent field (SCF) calculation. Such calculations are extremely demanding[30] especially since the charge densities are required near the classical turning points of thermal helium particles. These classical turning points typically occur 5—7 a.u. above the atomic nuclear positions of the topmost surface layer of atoms. In general, an SCF calculation would give lower corrugation values than those obtained using the atomic superposition. However, we have made another approximation which at least partly offsets this effect. We have only considered the repulsive part of the potential whereas the helium particles sample corrugation in the total potential. The total helium potential is more strongly corrugated[31,32] than the repulsive potential. The difference is proportional[32] to the slope of the attractive potential in the region of classical turning points of

TABLE V. Corrugation coefficients (in Å) of the $c(2\times2)$O-Ni(001) phase for the prolate O^- charge density using the ionic basis set corresponding to the configuration $X^{1.50}[I]Y^{1.50}[I]Z^{2.00}[I]$ at $z_0=0.26$ Å. Results are given for several values of the normal energy E_Z and α. No averaging with the helium potential was performed. The experimental values are due to Rieder (Ref. 20).

	E_Z (meV)	D_{10}	D_{11}	D_{20}	D_{21}
$\alpha=175$	40	0.118	−0.004	−0.002	0.001
	60	0.138	−0.005	−0.003	0.001
	80	0.156	−0.006	−0.003	0.002
$\alpha=275$	40	0.099	−0.004	−0.001	0.001
	60	0.116	−0.004	−0.002	0.001
	80	0.130	−0.005	−0.002	0.001
$\alpha=375$	40	0.088	−0.002	−0.002	0.001
	60	0.102	−0.004	−0.002	0.000
	80	0.115	−0.004	−0.003	0.001
Expt.		0.32±0.02	0.06±0.01	0.02±0.01	−0.02±0.01

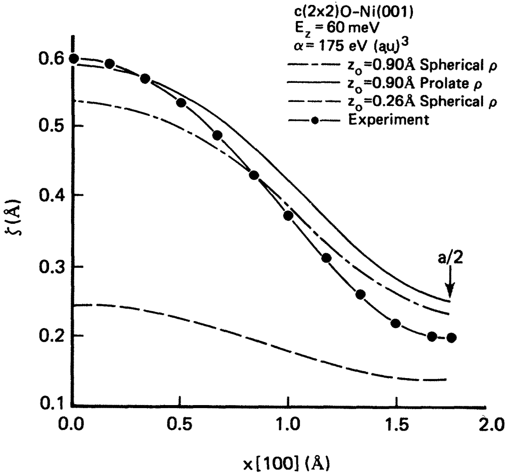

FIG. 2. Corrugation for the $c(2\times2)$ phase of oxygen on Ni(001) along the [100] direction. The results are symmetrical about the origin taken at one of the oxygen atoms.

the He in the total potential. Thus the two approximations (the lack of self-consistency and repulsive as opposed to total He potential corrugation) tend to compensate each other but the extent of cancellation is uncertain. Thus one expects to get reasonable values of corrugations using atomic superposition. Furthermore, by choosing different basis sets we have demonstrated that one can unambiguously rule out the shorter distance for oxygen chemisorption. No combination of basis sets gives the corrugation height for the shorter distance which can be considered in agreement with the experimental data. Finally, we might mention that we have explicitly included only d type ($l=2$) of nonspherical term in the prolate oxygen atomic density. The total charge density is, however, nonspherical and contains other l components due to atomic superposition.

In conclusion, we have put in perspective the effect of helium-potential averaging of the surface-charge density by an analytical example. Keeping α fixed at some empirical value this produced a small change ($<15\%$) in the averaged charge density. The calculated FWHM of the corrugation function is found to be larger than the experimental value. The calculated value can be improved by using neutral basis functions but it leads to an unacceptable value of the corrugation height. The usage of neutral basis functions to describe O^- by simply altering the orbital occupancy is not recommended. The prolate charge distribution on oxygen with an ionic basis set improves the corrugation shape function. The short O-Ni bond length can be easily ruled out. From an examination of a variety of basis functions we have reached the conclusion that the FWHM is not likely to be improved by going to self-consistency within the local density framework. Finally, the pseudo bridge site for the $c(2\times2)$ phase may lie within the theoretical uncertainties of our calculations.

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