Energy Dependence and Softness of the Potential for He Scattering from Ni(110)

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Studies of He diffraction from Ni(110) with energies between 17 and 270 meV and different scattering geometries yield for the first time quantitative data on the energy dependence of both corrugation and softness. The results are discussed in connection with recent surface electron-density calculations for Ni(110).

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Recent diffraction experiments have established the power of He scattering as a surface structural tool.[1-3] Analyses of diffraction intensities using the hard corrugated wall (HCW) model allowed deduction of corrugation functions $\zeta(x,y)$, which correspond to the periodic modulation of the repulsive part of the He-surface potential and often yield direct pictures of the geometrical arrangement of the surface atoms.[3] According to Esbjerg and Norskov[4] the repulsive potential reflects directly the electronic surface charge density; He atoms with higher effective energies $E_{iz}=E_i\cos^2\theta_i$ (E_i is He energy, θ_i angle of incidence with respect to surface normal z) penetrate more deeply into the sea of valence electrons (their classical turning points being closer to the ion cores) and the corresponding corrugations represent contours of higher electron density. An almost linear relation should connect energy with surface charge density,[4] the charge densities "seen" with E_{iz} between 10 and 300 meV being of the order of 10^{-5} to 10^{-3} a.u.[4-6] Calculations of surface-charge distributions became possible recently, even for such small densities.[5,6]

The present work shows that on the basis of experimental diffraction data a stepwise reconstruction of the He-surface repulsive potential is possible for a large range of He energies: Analyses of diffraction spectra for different E_{iz} can yield the corrugations $\zeta(x,y;E_{iz})$ together with the softness parameters $\kappa(E_{iz})$; the latter measure the steepness of the repulsive potential, so that the relative distances along z of the corrugations for different E_{iz} can be determined. Both functions can, for example, be derived for fixed E_{iz} by measurements at different azimuthal orientations of the sample. In our investigation of clean Ni(110), corrugations were derived for E_{iz} between 13 and 249 meV. Quantitative data on softness parameters were obtained for E_{iz} between 13 and 105 meV with a soft exponential potential (SEP).

Our improved He beam[7] gave sufficient resolution ($\Delta v/v \lesssim 9\%$, beam width 1.3°) for E_i up to 270 meV. Thus even for the smallest wavelengths all diffraction peaks were well resolved. Extensive in-plane as well as out-of-plane diffraction data were taken at various θ_i with the beam incident both parallel ($\alpha = 0°$) and perpendicular ($\alpha = 90°$) to the close-packed Ni rows. The specular and the first-order diffraction beams were always the most intense and, at low E_{iz},[7] the only ones observed. For large E_{iz}, 25 beams $G=(m,n)$ (up to $m, n = \pm 2$) were measured, whereby the signal-to-noise ratio was 1 : 1 for the smallest diffraction beam, the (2, 2), and 1000 : 1 for the specular. To extract diffraction intensities accurately the diffraction peaks were fitted with Gaussians taking into account the proper broadening due to the beam velocity spread. The remaining smooth background of mainly inelastic contributions was appreciable at medium and large E_{iz} (possible structure in the inelastic background being smeared out because of the beam velocity spread). At the largest E_{iz} for in-plane scans, the background was typically about 30% of the total scattering intensity for a sample temperature T_s of 100 K. From the number of inelastic contributions, we estimate the uncertainty of diffraction intensities to be 5% in the worst case of the largest E_i. Note that the corrugation amplitudes are practically not affected by such uncertainties as they go with the square root of the intensities. To elaborate further on the accurate intensity determination, we measured the decrease of elastic intensities with increasing T_s, and found an effective Debye temperature close to that of bulk Ni. The same intensity ratios $I(m,n)/I(0,0)$ were obtained for T_s at 100 and 200 K within reproducibility limits, showing that the inelastic background had been correctly subtracted, and confirming the negligible influence of thermal effects on the intensity ratios expected from the high effective Debye temperature. Figure 1(a) shows

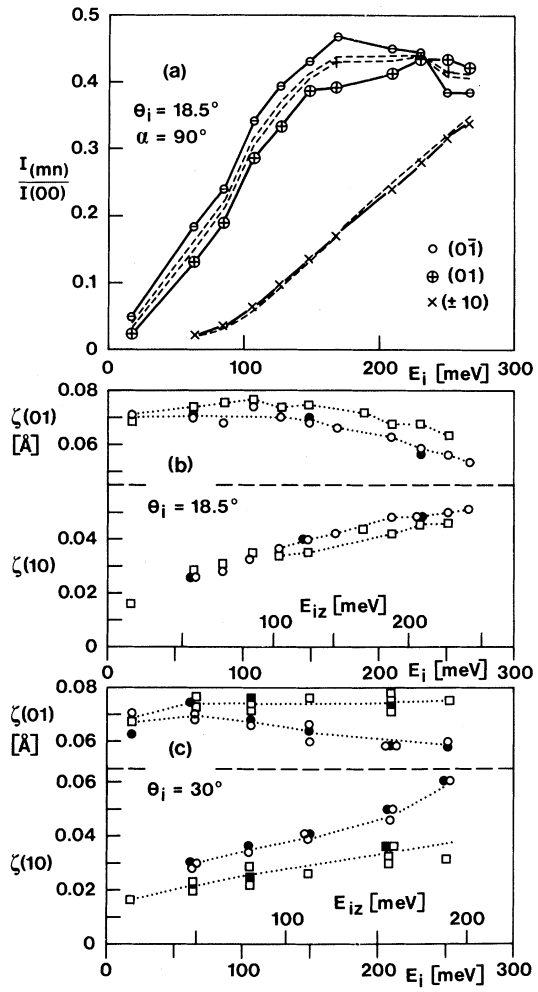

FIG. 1. (a) A typical set of intensity ratios $I(mn)/I(00)$ for first-order beams as a function of incoming energy E_i obtained for He diffraction from Ni(110); the angle of incidence θ_i is 18.5° and the beam impinges perpendicular to the close-packed rows (α = 90°). The solid and dashed lines connect experimental and hard-wall best-fit values, respectively. The plus symbols identify the calculated (01) branch. (b) Energy dependence of the hard-wall parameters $\zeta(10)$ and $\zeta(01)$ describing the corrugation of Ni(110); various data for θ_i = 18.5° corresponding to α = 0° (squares) and 90° (circles) and sample temperatures of 100 (open symbols) and 200 K (full symbols) are exhibited to demonstrate the reproducibility of the diffraction data. (c) Same as (b) for θ_i = 30°. Dotted lines in (b) and (c) are merely guides to the eye. Fits with the soft exponential potential give results practically identical to the experimental results in (a), and remove the α dependence of the corrugation parameters in (b) and (c).

typical results for the first-order beams relative to the specular as a function of E_i for $\theta_i = 18.5°$. Also shown are intensity ratios obtained by fitting all measured intensities with the HCW model with a corrugation described by the Fourier coefficients $\zeta(10)$, $\zeta(01)$, and $\zeta(11)$. Both the eikonal formula[7,8] and the exact Rayleigh solution[8] gave the same results. The best-fit HCW values for $\zeta(10)$ and $\zeta(01)$ for $\theta_i = 18.5°$ for both $\alpha = 90°$ and 0° are shown in Fig. 1(b). There is a clear increase of $\zeta(10)$, the corrugation amplitude parallel to the close-packed Ni rows, from a value <0.02 Å to a value of >0.05 Å with increasing energy. $\zeta(01)$ increases slightly at low E_i to ~ 0.07 Å at medium E_i and decreases slightly at the highest energies. $\zeta(11)$ is always much smaller than $\zeta(10)$ and $\zeta(01)$ [$\zeta(11) \approx 0.015$ Å at the highest E_{iz}]. It is important to note that at low E_{iz}, only the close-packed rows are visible in the corrugation,[7] whereas at high E_{iz} every Ni atom shows up as an individual hill, so that the arrangement of surface atoms becomes fully visible.

We now present evidence for the softness of the potential. Figure 1(c) shows that at $\theta_i = 30°$ the HCW values for $\zeta(10)$ and $\zeta(01)$ obtained with $\alpha = 0°$ and 90° are clearly separated. The same trend is actually also present at 18.5°, Fig. 1(b), and is even stronger at 45°. Figure 1(a) shows that the HCW best fits of the (01) and (0$\bar{1}$) intensities lie always between the measured values, so that the HCW tends to equalize the intensities of beams G and $-G$, if they are in plane. This was also established with $\alpha = 0°$ for the (10) and ($\bar{1}$0) beams despite their very small intensities at low E_i. This observation is in accordance with recent SEP calculations, which showed that beams for which $e = E_{Gz}/E_{iz} < 1$ are more reduced relative to the corresponding hard-wall intensities than such for which $e > 1$ (Ref. 9); thus, beams emerging near the surface normal feel less of the potential softness than beams emerging at grazing angles. Note that the Debye-Waller factor does just the reverse! The discrepancies in the HCW results for different azimuths shown in Fig. 1(c) can be understood on this basis: The HCW tends to average the intensities of the in-plane beams (01) and (0$\bar{1}$) for $\alpha = 90°$, so that the $\zeta(01)$ values become systematically too small when compared to the values of $\zeta(01)$ obtained with $\alpha = 0°$, in which case the beams (01) and (0$\bar{1}$) are symmetric with $e \approx 1$ out of plane. The reverse is obviously the case for $\zeta(10)$ in connection with the beams (10) and ($\bar{1}$0). Another striking example of the influence of softness is exhibited in Fig. 2. There the dependence of $\zeta(01)$ and $\zeta(10)$ is shown for $E_i = 64$ meV and $\alpha = 90°$ as a function of θ_i: Whereas $\zeta(10)$ (determined by out-of-plane beams) de-

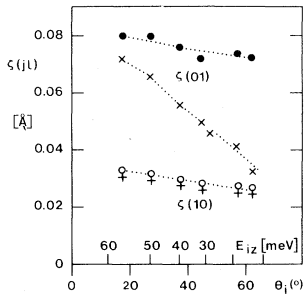

FIG. 2. Angular dependence of the hard-wall (crosses) and soft-wall (circles) Fourier coefficients $\zeta(10)$ and $\zeta(01)$ obtained from diffraction data with $E_i = 63$ meV and $\alpha = 90°$, proving another influence of the softness of the He-metal potential.

creases with decreasing E_{iz} in accordance with the data of Fig. 1(b), $\zeta(01)$ exhibits a drastic decrease not consistent with Fig. 1(b). Again the reverse is found for $\alpha = 0°$. This means that for the true potential the specular increases more rapidly as a function of θ_i than for a HCW. Obviously, the HCW is too crude to describe the He/Ni(110) potential properly. However, it yields reasonable corrugation parameters for small θ_i.

Our experimental data allowed the first quantitative analyses of the softness of a He/surface potential. An exact method to calculate diffraction intensities from a SEP $V(x,y,z) = C\exp\{-\kappa \times [z - \zeta(x,y)]\}$ has been developed by Armand and Manson.[9,10] We used a method based on the distorted-wave Born approximation (DWBA),[11,12] which works well for small corrugation amplitudes and small κ (large softness) and is restricted to not too large E_{iz} (< 100 meV)[13]; numerical results compare well with those of Ref. 9. With use of the SEP, a better overall agreement with the measured intensities was obtained. The discrepancies concerning (a) the α and (b) the θ_i dependence of the corrugation parameters are removed: (a) The proper separation of the (01) and $(0\bar{1})$ intensities is reproduced [Fig. 1(a)] and the $\zeta(01)$ and $\zeta(10)$ values are only slightly larger than the upper HCW ones at $\theta_i = 18.5°$ [Fig. 1(b)]; this establishes our conclusion that corrugation parameters can be derived reliably from HCW intensity fits at small θ_i (except maybe for very small κ) and provides confidence in the HCW results for higher E_{iz}. (b) As demonstrated in Fig. 2, the SEP properly gives the slight decrease of $\zeta(10)$ and $\zeta(01)$ with $\kappa = 3.6$ Å^{-1} for the whole range of θ_i in accordance with the results of Fig. 1(b). Representative values for $\zeta(10)$, $\zeta(01)$, and κ for $12 < E_{iz} < 105$ meV ($\alpha = 90°$) for different θ_i are given in Table I. In this range of E_{iz}, $\zeta(01)$ is 0.075 ± 0.005 Å and $\zeta(10)$ increases from 0.025 to 0.04 Å in good agreement with the HCW results at small θ_i. Very similar values for the corrugation parameters were also derived with SEP fits of data for $\alpha = 0°$. The softness parameter κ decreases smoothly from 3.6 ± 0.2 Å^{-1} to 2.8 ± 0.2 Å^{-1} with increasing E_{iz} for $\alpha = 90°$; for $\alpha = 0°$, κ is 3 Å^{-1} for all E_{iz}. This indicates that the SEP is still a simplification as it takes into account only one softness parameter κ, whereas in reality $\kappa = \kappa(x,y)$. Our SEP analyses yield different spatial averages for different scattering geometries: The κ's obtained for $\alpha = 90°$ may be representative for $\kappa(01)$ and those for $\alpha = 0°$ for $\kappa(10)$.

TABLE I. Typical results for corrugation and softness parameters obtained by intensity fits for $\alpha = 90°$ with a soft exponential potential.

E_{iz} (meV)	E_i (meV)	Θ_i (°)	$\zeta(01)$ (Å)	$\zeta(10)$ (Å)	κ (Å^{-1})
12.8	17	30	0.074	0.025	3.6
13.4	63	62.5	0.072	0.025	3.8
15.3	17	18.5	0.070	0.027	3.6
18.2	63	57.5	0.074	0.027	3.6
31.5	63	45	0.072	0.027	3.6
39.6	63	37.5	0.076	0.030	3.4
47.2	63	30	0.080	0.032	3.6
49.6	63	27.5	0.080	0.032	3.4
57.3	63	17.5	0.080	0.032	3.6
48.5	168	57.5	0.072	0.030	3.0
53	106	45	0.072	0.028	3.0
74	148	45	0.070	0.035	3.0
76.7	168	47.5	0.074	0.035	2.8
104.5	209	45	0.070	0.043	2.7
105.7	168	37.5	0.074	0.038	2.6

We compare our results on the He/Ni(110) potential with those of recent theoretical density calculations of Hamann[5] and Manninen, Norskov, and Umrigar[6] which are consistent with each other. Necessary for this comparison is the knowledge of the Esbjerg-Norskov parameter[4] connecting He energies with surface electron densities, whose value seems to be uncertain within a factor of ~3 at present.[6] With use of the original value of Ref. 4, the experimental $\zeta(01)$ ≈ 0.075 Å is about 2.5 times smaller than the theoretical one for $E_{iz} \approx 50$ meV[5,6]; with the new smaller value[6] this discrepancy becomes even larger. The experimental $\kappa(01) = 2.8$ Å^{-1} for 60

$< E_{iz} < 100$ meV agrees reasonably well with the theoretical value of 2.6 $Å^{-1}$ (Ref. 5); the increase of the experimental $\kappa(01)$ to 3.6 $Å^{-1}$ at lower E_{iz} as well as the fact that the corrugation does not go to zero at low E_{iz} demonstrate the influence of polarization forces,[13] which have not been taken into account in the density calculations. $\kappa(10)$ is 3.0 $Å^{-1}$ in the whole energy range, in agreement with the trend in Ref. 5. The most important discrepancy concerns the change in shape of the corrugation as a function of E_{iz}: $\zeta(01)$ increases strongly in the calculations with increasing E_{iz}, but remains almost constant in the experiment; $\zeta(10)$ is vanishingly small in the calculations in the whole energy range, but becomes almost as large as $\zeta(01)$ at the highest E_{iz} in the experiment. Thus, every Ni atom becomes distinquishable at high E_{iz} in the experiment, whereas according to the calculations only the close-packed rows should be visible in the whole energy range investigated. The reason for this serious qualitative difference may be twofold: (1) The electron densities "seen" with He may be sensitively influenced by specific surface bonds. These bonds are certainly not properly described by simply superimposing atomic charge densities[6]; therefore the extent of agreement of these results with those of the *ab initio* calculations of Hamann[5] is surprising. Note, however, that Ni is ferromagnetic, but that the calculations in Refs. 5 and 6 refer to a paramagnet. (2) The relation between the repulsive He potential and the electron density may be more complex[14] than stated in Ref. 4.

We finally remark that according to very recent work[15] diffraction intensities can be obtained with general $\kappa(x,y)$ in the expression cited above for the SEP with the DWBA. Application to Ni(110) showed that for E_{iz} between 12 and 100 meV all data can be well reproduced by use of two corrugation parameters $\zeta(10)$ and $\zeta(01)$ and three softness parameters $\kappa(00)$, $\kappa(10)$, and $\kappa(01)$. The good agreement with the present results proves that a stepwise reconstruction of the potential by use of neighboring E_{iz} as proposed here represents a useful and reliable procedure. Further development of the theory of diffraction from soft potentials is desirable, especially extension to high He energies and large corrugation amplitudes.

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