

Surface Structure Investigations Using Helium Diffraction

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The first observation of He diffraction from LiF cleavage surfaces was reported by J. Estermann and O. Stern in 1929, only two years after C.J. Davisson and L.H. Germer announced the discovery of low-energy electron diffraction (LEED). Whereas LEED has already been used for more than two decades in surface science and has yielded most of the presently available information on the crystallography of clean and adsorbate-covered surfaces, it is only in the past few years that the technique of He diffraction could be developed into an experimental method for surface structural investigations. Recent studies have demonstrated the applicability of He diffraction to systems which are difficult to study with LEED, such as light adsorbates on heavy substrates. Moreover, new insights have been gained into atomic configurations on reconstructed surfaces and adsorbate systems - sometimes challenging well-accepted LEED results.

He diffraction is unique in the sense that it yields a replica of the electron density contours of the outermost atoms, which contain information on both the configuration and the bonding characteristics of the surface atoms. Further virtues of He-diffraction lie in its non-destructive nature as well as the comparatively easy data analysis involved, which does not require any *a priori* model structure and which nevertheless, allows a transparent and often straightforward interpretation.

Surface structure investigations are motivated by two main reasons: First, many processes of technological importance occur at the topmost layers of solids, and are not only sensitive to the chemical composition of the surfaces, but also to their geometry. Second, there is often a subtle balancing of interatomic forces in the bulk, which can be disrupted as soon as such a strong perturbation as the creation of a surface takes place. The system then tries to find a new minimum of potential energy, often realized via a rearrangement of the atoms at and near the surface, so that the atomic configuration no longer resembles that of the bulk (surface reconstruction). Thus, a lot can be learned about atomic interactions through detailed studies of surface structures.

He-Surface Interaction Potential

Diffraction experiments give information on both the dimensions of the unit cell via the angular location of Bragg peaks, and the distribution of scattering centres within

the unit cell via the intensities of diffracted beams. As He atoms with thermal energies cannot penetrate into the solid, they pick up the periodicity of the outermost atoms.

At not too large distances from the surface, each impinging atom feels an attraction due to Van der Waals forces. The corresponding attractive potential is always small in depth for He atoms ($D < 10$ meV) compared to the incoming He energy ($E = 25-100$ meV), so that we can neglect it for the purpose of the present discussion. Closer to the surface, the particle is repelled due to the overlap of its electronic density with that of the solid surface. This causes the steeply rising repulsive part of the potential. In general, the classical turning points are farther away, just on top of the surface ions rather than between them. This gives rise to a periodic modulation of the repulsive part of the potential parallel to the surface, which follows a contour of constant electron density, as recently shown in theoretical work by N. Esbjerg and J. Norskov.

Each point of the density contour constitutes a scattering centre, and the resulting scattering surface is called the corrugation function. With higher energies, the He atoms penetrate more deeply into the sea of valence electrons and the corrugation function corresponds to a contour of larger electron density. Thus, the corrugation function is energy dependent and not only reflects the geometrical arrangement of the surface atoms, but also contains information on their bonding.

Experimental

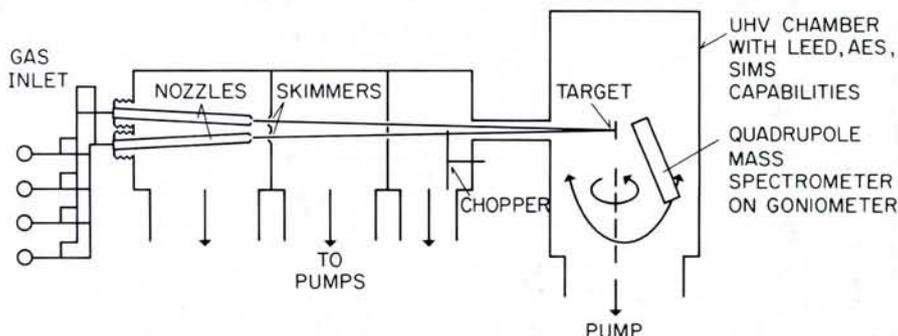
To extract the maximum possible information from a diffraction experiment, both the angular locations and the intensities of the Bragg peaks must be measured. In their experiments, Stern and Estermann used

low-pressure effusion sources which gave beams with low intensity and a broad Maxwellian velocity distribution, so that only first-order diffraction peaks could be well resolved. It took almost forty years of research in gas dynamics until sources delivering thermal beams with high intensity and narrow velocity distribution became available. In modern high-pressure nozzle sources, a complicated interplay of adiabatic cooling and hydrodynamic flow, leads to a narrowing of the velocity distribution and to an enhancement of the mean velocity of the He atoms by a factor of 5/3 relative to the most probable velocity of an effusion source at the same temperature. Such sources are now commonly in use in gas surface scattering experiments.

Figure 1 shows a schematic drawing of the system used in the author's laboratory and developed in collaboration with T. Engel. The gas load due to the high pressure behind the nozzle is handled by three differential pumping stages using high-speed oil-diffusion pumps in the first two stages and a turbomolecular pump in the third. With this arrangement, a pressure of 5×10^{-10} Torr can be maintained in the scattering chamber with the beam on. A well-designed nozzle-skimmer geometry is essential for good beam-system performance. Typical He-beam parameters for a nozzle at room temperature are: $E = 63$ meV or $\lambda = 0.57$ Å. With a pressure behind the nozzle of 1 atm, a velocity spread (FWHM) of about 12% of the mean velocity can be readily achieved. The mean energy of the beam can be varied easily by heating and cooling the nozzle.

The particles scattered from the target are analyzed with a quadrupole mass spectrometer mounted on a goniometer, which allows in-plane as well as out-of-plane detection. Modulation of the beam with a

Fig. 1 - Schematic drawing of a modern system for He-surface diffraction studies.



mechanical chopper in the third pumping stage and phase-sensitive detection results in an improved signal-to-noise ratio. Surface cleaning, using ion bombardment and heating cycles, and surface characterization, using standard methods like Auger electron spectroscopy, secondary ion mass spectroscopy and LEED, are carried out in the scattering chamber.

With a similar experimental setup, G. Boato and co-workers (Genoa) in 1976 obtained He-diffraction spectra with well-resolved peaks up to sixth and seventh order from the (100) surface of LiF.

Calculation of Diffraction Intensities

At about the same time, A. Levi and co-workers (Genoa) and N. Garcia and N. Cabrera (Madrid) started to develop theories for calculating the diffraction intensities corresponding to a given corrugation function $\zeta(\mathbf{R})$. They used the hard corrugated-wall model in which the steeply rising repulsive part of the He-surface potential is approximated by a sharp infinitely high wall. Assuming that the total particle wavefunction can be written as

$$\psi(\mathbf{r}) = \exp(i\mathbf{k}_i \cdot \mathbf{r}) + \sum_{\mathbf{G}} A_{\mathbf{G}} \exp(-i\mathbf{k}_{\mathbf{G}} \cdot \mathbf{r}) \quad (1)$$

where $\mathbf{r} = (\mathbf{R}, z)$ denotes the space coordinates with the z -direction chosen perpendicular to the surface; $\mathbf{k}_i = (\mathbf{K}, k_z)$ is the wavevector of the incoming and $\mathbf{k}_{\mathbf{G}} = (\mathbf{K} + \mathbf{G}, k_z)$ that of the outgoing beam corresponding to the surface reciprocal lattice vector \mathbf{G} .

In principle, the sum extends over all \mathbf{G} s, i.e., over propagating ($k_z^2 > 0$), as well as over evanescent ($k_z^2 < 0$) waves. The intensities of the former, given by

$$P_{\mathbf{G}} = A_{\mathbf{G}} \cdot k_z / k_i$$

must obey the unitarity condition $\sum P_{\mathbf{G}} = 1$ (particle flux conservation).

The Ansatz Eq. (1) was already put forward a century ago by Lord Rayleigh, who used it in his investigations of sound scattering from solid walls. With the boundary condition $\psi(\mathbf{R}, \zeta(\mathbf{R})) = 0$, which simply states that no particles can penetrate the hard wall, we arrive at the equation

$$\sum_{\mathbf{G}} A_{\mathbf{G}} \exp(i(\mathbf{G}\mathbf{R} + k_z \zeta(\mathbf{R}))) = -\exp(i(k_z \zeta(\mathbf{R}))) \quad (2)$$

which must be fulfilled for any \mathbf{R} within the unit cell.

Multiplying Eq. (2) with $\exp(-i(\mathbf{G}'\mathbf{R} + k_{z'} \zeta(\mathbf{R})))$ and integrating over the surface unit cell of area S yields the matrix equation

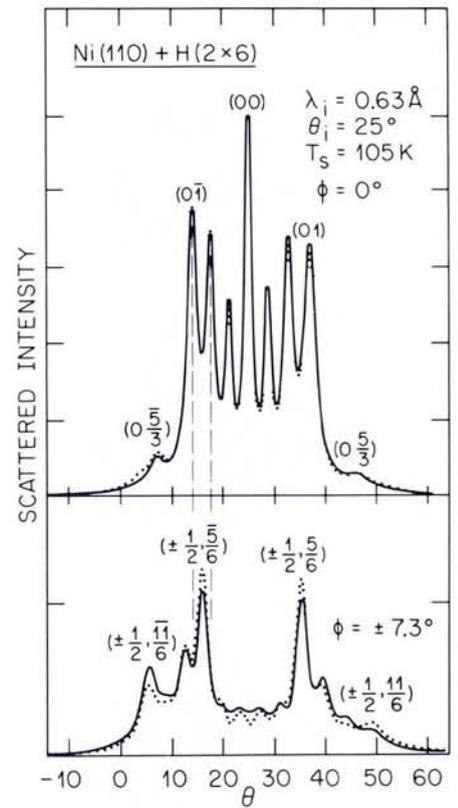
$$\sum_{\mathbf{G}} M_{\mathbf{G}\mathbf{G}'} A_{\mathbf{G}} = A_{\mathbf{G}'} \quad (3)$$

$$M_{\mathbf{G}\mathbf{G}'} = (1/S) \int \exp(i(\mathbf{G}-\mathbf{G}')\mathbf{R} + i(k_{z'} - k_z) \zeta(\mathbf{R})) d\mathbf{R} \quad (4)$$

$$A_{\mathbf{G}}^0 = (1/S) \int \exp(i\mathbf{G}\mathbf{R} + i(k_{z'} - k_z) \zeta(\mathbf{R})) d\mathbf{R} \quad (5)$$

which can be solved numerically for the $A_{\mathbf{G}}$ s.

Fig. 2 — In-plane ($\phi = 0^\circ$) and out-of-plane ($\phi = \pm 7.3^\circ$) He-diffraction spectra for the adsorbate phase $H(2 \times 6)$ on Ni(110). The solid curves correspond to experimental traces and the broken ones to the best-fit calculations. [After Phys. Rev. Lett. 45 (1980) 825.]



Although at first sight, the Rayleigh Ansatz seems plausible, convergent solutions are obtained only for corrugation amplitudes that are not too large. For example, the maximum corrugation amplitude for a one-dimensional sinusoidal corrugation is 14% of the lattice constant. Neglect of off-diagonal terms in Eq. (3), which corresponds to the neglect of multiple scattering and implies the neglect of evanescent waves, yields $A_{\mathbf{G}} = A_{\mathbf{G}}^0$. This so-called eikonal approximation works reliably for small wavelengths, shallow corrugations and small angles of incidence, and has the important advantage of being computationally fast.

More general methods have also been developed, but most real surfaces investigated up to now have corrugation amplitudes below the Rayleigh limit. Furthermore, by relaxing the hard-wall assumption, G. Armand and J. R. Manson (Saclay) found an enhanced intensity for the specularly reflected beam, so that application of the hard-wall model tends to underestimate the corrugation amplitude.

Examples of Surface Structures Studied with He Diffraction

The first determination of a corrugation function was performed by Garcia for the experimental data obtained in Genoa for He diffraction from LiF(100). He used a Fourier representation of the corrugation function

$$\zeta(\mathbf{R}) = \sum_{\mathbf{G}} \zeta(\mathbf{G}) \exp(i\mathbf{G}\mathbf{R})$$

and varied the amplitudes of the $\zeta(\mathbf{G})$ until optimum agreement between measured and calculated intensities was obtained. Only $\zeta(10)$ and $\zeta(11)$ were significant and the maximum corrugation amplitude obtained was 0.61 Å. This is slightly smaller than the difference of the bulk ionic radii $r(\text{F}^-) - r(\text{Li}^+) = 0.65$ Å, and led Garcia to the conjecture that the Li^+ ions relax outwards in the topmost layer. However, since the coordination number of the ions at the surface is reduced, modified ionic radii have to be taken into account. Using the smaller radius for F^- and the larger for Li^+ in five-fold coordinated bonds, as estimated by F. G. Fumi and M. P. Tosi, the large corrugation amplitude observed means that the F^- ions relax outwards, in agreement with theoretical predictions.

Today, only three years after Garcia published his result for LiF, surface structural investigations using He diffraction have become so numerous, that the author is forced to select a few characteristic and striking examples. Naturally, such a selec-

tion is subjective and emphasizes his own work. However, the author has attempted to choose the examples in such a way, that contributions of most other groups working in the field are also represented.

Whereas He diffraction from ionic and covalent crystals yields appreciable diffraction intensities, diffraction from close-packed metal surfaces was long searched for until Boato et al. and J. M. Horne and D. R. Miller at UC in La Jolla managed to detect extremely weak first-order diffraction peaks (0.2% of the specular beam). This indicates a corrugation amplitude smaller than 0.01 Å, and clearly demonstrates the smoothing effect of the free electron charge at metal surfaces. More open metal surfaces such as the Ni(110) and W(112) show for small He energies (20-60 meV) larger corrugation amplitudes (0.06 and 0.15 Å, respectively) in the direction perpendicular to the close-packed rows, where the smoothing effect is less pronounced.

The first He-diffraction studies on adsorbate-covered metal surfaces were performed in 1979 by T. Engel and the author. Several ordered phases of hydrogen on Ni(110) could be observed and analyzed. Here, the discussion is restricted to the two phases for which the most striking and complete information could be obtained: The (2×6) phase corresponding to a coverage of $\theta_H = 0.8$ monolayers (ML) and the (2×1) phase for $\theta_H = 1.0$ ML. Only the last of these phases had been previously seen with LEED. The nomenclature $(m \times n)$ means that the surface unit cell has the dimensions ma_1 and na_2 , with a_1 being the shorter unit-cell vector of the

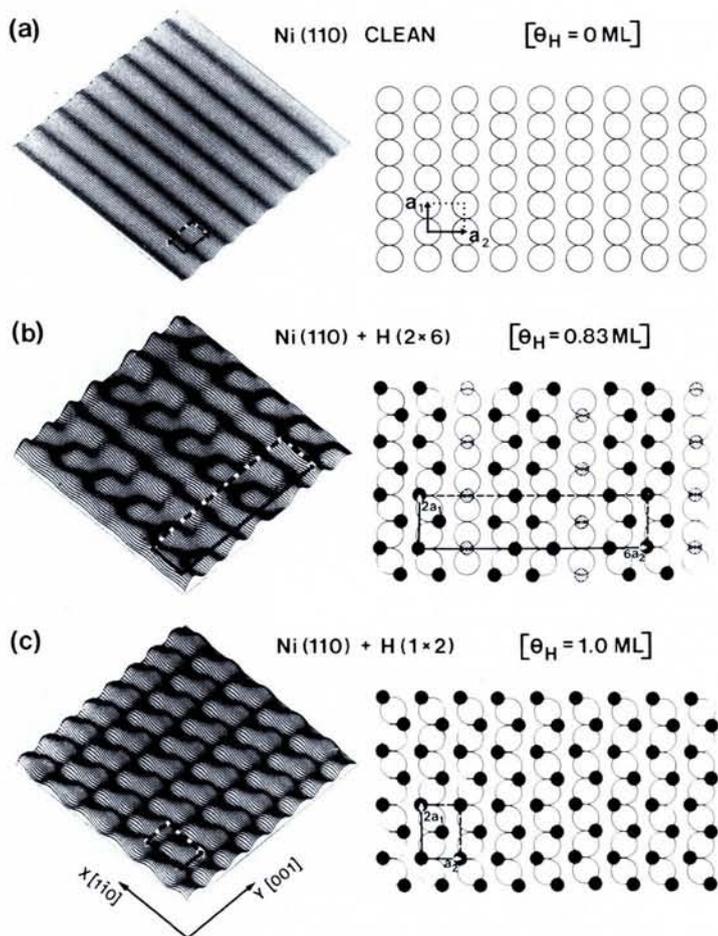


Fig. 3 — Corrugation functions and hard-sphere models for: (a) the clean Ni(110) surface, (b) the (2×6) and (c) the (2×1) adsorbate phases of hydrogen on Ni(110). The surface unit cells are indicated. The corrugations are expanded by a factor of six in the vertical direction. [Fig. 3(a) after Proc. Erice Summer School on "Dynamics of Gas-Surface Interactions" (Springer-Verlag, Heidelberg), 1981. Figs. 3(b) + (c) after Phys. Rev. Lett. **45**, (1980) 826.]

substrate. A coverage $\theta_H = 0.5$ ML means that there are half as many adsorbed atoms as there are atoms in the topmost substrate layer.

Typical in-plane ($\phi = 0^\circ$) and out-of-plane ($\phi = \pm 7.3^\circ$) diffraction spectra for the $H(2 \times 6)$ phase are shown in Fig. 2. The incident He beam is perpendicular to the close-packed Ni rows. The solid lines correspond to the experimental traces and the dashed lines to the best-fit eikonal calculations. Besides the data shown in Fig. 2, several other spectra obtained for different angles of incidence and different wavelengths corresponding to a total of about 120 intensities were analyzed, so that best-fit values of the Fourier coefficients describing the corrugation function could be determined to a high degree of reliability. This corrugation is displayed in Fig. 3b together with the corrugation of the clean Ni(110) surface (Fig. 3a) and that of the $H(2 \times 1)$ structure (Fig. 3c). For the H-adsorbate phases the maximum corrugation amplitude is 0.27 Å and the corrugation is appreciable in both directions.

As every maximum in these corrugations can be attributed to an underlying H-atom,

the adatom configuration can be inferred directly from these pictures. Hard-sphere models of the clean surface and the $H(2 \times 6)$ and $H(2 \times 1)$ structures are shown on the right-hand side of Figs. 3a-c. Registry of the H-atoms relative to the substrate atoms was chosen such, that the number of equivalent adsorption sites was maximized. It can be seen from Fig. 3c, that for $\theta_H = 1.0$ ML all adatoms sit in nearly a three-fold coordinated sites, but that for $\theta_H = 0.8$ ML, the lateral repulsion of the hydrogens forces some of them to occupy the energetically less favourable two-fold coordinated sites. Coverage of both adsorption phases can be determined simply by counting adatoms per unit cell, and is consistent with flash desorption measurements

Oxygen adsorption on Ni(110) leads to a one-dimensional corrugation for the (2×1) -phase, which occurs at a coverage of about 0.5 ML. The corrugation is orthogonal to that of the clean surface, i.e., it occurs in the X-direction (compare Fig. 3). This observation rules out the model put forward on the basis of a LEED analysis, in which the oxygens are adsorbed in two-

fold coordinated sites on top of the Ni rows. However it supports a model based on low-energy ion-scattering data by L.K. Verheij et al. (University of Salford) which requires a massive reconstruction of the topmost Ni layer upon adsorption of oxygen: every second row of Ni atoms perpendicular to the close-packed rows is missing. The oxygens are incorporated into the remaining rows, and the resulting dense packing causes the apparent one-dimensional corrugation in the Y-direction. The corrugation of the $O(2 \times 1)$ -Ni(110) system is very similar to that found by Lapujoulade et al. in Saclay for $O(2 \times 1)$ on Cu(110).

Most semiconductor and many metal surfaces tend to reconstruct even without the influence of adsorbed reactive gases. The most famous and probably most investigated surface of this kind is Si(111) with its (7×7) -periodicity. This surface was investigated with He diffraction by M. Cardillo and G. Becker (Bell Laboratories), and their results recently led to a very interesting proposal concerning its structure: The observed angular dependence of the specular beam, points to the existence of terraces separated by a double layer spacing. Cardillo suggested a regular arrangement of two terraces, so that in every unit cell each terrace occupies half of the cell area; this suggestion was supported by intensity analyses of diffracted beams performed by Garcia, and may constitute the clue to final solution of this difficult puzzle, if the many findings obtained with other methods can be reconciled with this model.

Conclusions and Outlook

These few examples illustrate the power of He diffraction as a surface structural tool. Not only can it decide between models proposed on the basis of other techniques, but it very often gives direct pictures of the surface atom configurations. Due to the low He energies used, it is absolutely nondestructive and can therefore be applied to systems influenced or even destroyed by electron or other high-energy beams. Furthermore, as the corrugation function measured is a replica of the electron density, He diffraction does not encounter such difficulties as LEED, where it is extremely hard to observe light elements in the presence of heavy ones.

Finally, it has to be emphasized that the potential of He diffraction is far from being exhausted. Measurements up to rather high He energies (~ 500 meV) should be possible with sufficient instrumental resolution. Intensity analyses with soft-wall models can yield not only the form of the corrugation for different energies, but also the separation between the different electron-density contours. Thus, a mapping of the surface charge density, containing important information on surface bonds, should be possible.