Observation of Interference Oscillations in Helium Scattering from Single Surface Defects

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Large-angle-diffraction oscillations in the intensity of helium atoms elastically scattered from randomly stepped Pt(111) are reported. A formalism based on the concept of reflection-symmetry interference explains the observed features and the data analysis yields a value of 4.4–4.6 Å for the hard-core repulsive cross section of a single step. The observed oscillations are sensitive to the presence of adsorbates at step sites.

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There is now considerable evidence that surface defects (steps, kinks, and point defects) provide the active sites for chemical reactions on single-crystal surfaces.[1] LEED provides the present standard technique for determining defect geometries and densities,[2] but to date its sensitivity has only been sufficient to study the statistical distribution of defects and not their individual details. The angle or energy dependence of the specular scattering of He atoms has been shown to provide quantitative information on step heights and average densities,[3] and more recently the attenuation of the specular beam in He atom scattering by steps has been demonstrated.[4] Since the integral total cross sections derived in the latter type of measurement are dominated by long-range attractive forces, they are rather large (≈ 12 Å) (Ref. 4) and consequently do not provide direct details on the physical size or orientation of the steps, nor on changes in the immediate environment of the single steps as may occur during gas adsorption. In this Letter, we report on the first observation of large-angle hard-core diffraction from single randomly spaced monatomic steps on a single crystal surface, in this case Pt(111). Since the observed diffraction patterns are determined by the interference of atom trajectories probing the repulsive potential of the step and the adjacent undisturbed smooth mirrorlike regions, the actual size and orientation of the single steps could be determined. We also see striking changes in the step diffraction as CO is adsorbed at the steps, demonstrating that valuable chemical information on active sites in heterogeneous catalysis can be obtained by this new technique.

The observation of diffraction from single steps has been made possible by the introduction of high-resolution He nozzle beams and sensitive time-of-flight detection techniques used to study surface phonons.[5] The apparatus is essentially identical to that used in the phonon studies; however, in the present experiment only the elastic peak is of interest. The helium beam energy can be varied between 8 and 80 MeV ($k_i = 4$–12.7 Å^{-1}) with a velocity resolution $\Delta v/v$ of 1%. The polished Pt (111) crystal was cleaned in vacuum (base pressure 10^{-10} Torr) by cycles of sputtering, annealing at 1000 K, and heating in oxygen until no impurities were detected in the Auger trace. In most of the experiments the sum of incident θ_i and final angles θ_f is 90°. The parallel momentum transfer, $\Delta K = k_i(\sin\theta_f - \sin\theta_i)$, is varied by rotation of the crystal in the scattering plane while $\theta_i + \theta_f$ is kept constant. Nearly identical results were obtained in scans of θ_f with θ_i fixed. The helium atoms are detected at the end of a 1.2-m flight tube with an angular resolution of 0.1°. The clean defect-free surface showed no oscillations in specular beam intensity as a function of incident energy,[3] and on the basis of the transfer width of the experiment, this would indicate a mean step separation in excess of 500 Å.

The bottom histogram in Fig. 1 shows a typical helium diffraction scan without time-of-flight resolution from the defect-free surface. In addition to a small first-order diffraction peak, a weak second-order diffraction peak is also observed for the first time on a close-packed (111) metal surface. Between diffraction peaks the helium signal does not fall to zero but is very small and falls rapidly with increasing parallel momentum transfer. The time-of-flight spectra reveal that most of this intensity is due to single-phonon and multiphonon annihilation and creation processes (single-phonon interactions are very improbable beyond the first Brillouin-zone boundary at $\Delta K = 1.3$ Å^{-1}) and the remaining small elastic part is due to imperfections such as steps, vacancies, and dislocations. Since the energy spread of this elastic peak is identical to that of the incident beam, even at large momentum transfers, contributions from slightly inelastic effects such as multiphonon exchange or electron-hole pair creation can be ruled out with considerable confidence.

To investigate diffraction from single steps, these were created in a reproducible manner by sputtering the surface for 10 min with 1-keV neon ions at a dosage of 1.5 μA/cm^2, while maintaining the crystal at a temperature of 600 K. In this way single vacancies formed by the neon ions can diffuse fast and far enough to form new terraces bounded by monatomic steps.[6] The observed oscillations of the specular beam

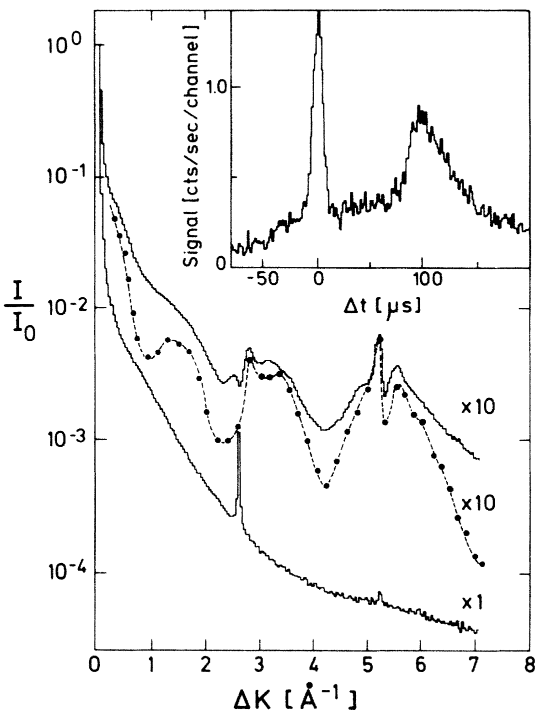

FIG. 1. Lower curve: Angular distribution of intensity from smooth surface in ⟨112⟩ direction. Upper curve: Equivalent distribution for randomly stepped surface. Circles: elastic peak only. Inset: A typical time-of-flight spectrum (channel width 1.5 μs) at small ΔK. The experimental intensity distributions without time-of-flight analysis were recorded in 0.2° steps at 1 s per angle giving a total measuring time of less than 5 min per scan. With time-of-flight analysis a measurement takes between 1 and 5 min per angle. All measurements are at a crystal temperature of 300 K at which temperature there was no evidence for H_2 adsorption.

with incident energy indicate that the steps are monatomic, and the angular broadening at the antiphase condition for scattering from adjacent terraces allows us to estimate an average terrace width of 30–70 Å for the sputtered surface.[7] The upper histogram in Fig. 1 shows the resulting angular distribution after sputtering. The intensity at large ΔK is enhanced and several shoulders and maxima are observed. In addition, both diffraction peaks are split and the second-order peak is greatly enhanced. To get better resolution of the elastic structures, time-of-flight spectra, of which a typical example is shown in the inset, were measured. The points in Fig. 1 show that the angular distributions of this elastic component have more pronounced structures. The oscillations could only be observed along the ⟨112⟩ direction. At an azimuth 10° to one side and also in the ⟨110⟩ direction, no oscillations were present and the angular distributions for the sputtered surface were similar to those for the pristine surface. This indicates that the steps are preferentially oriented along the close-packed and energetically most favorable ⟨110⟩ directions (normal to the ⟨112⟩ directions).

Since the only previous theoretical treatment of scattering from single steps by Blatter[8] has neglected their finite width, we draw from available knowledge and experience in gas-phase scattering to explain these structures. In atom-molecule scattering at energies comparable to those used in the present experiment there is a large differential cross section for scattering at small forward angles due to the long-range attractive potential.[9] The cross section falls off rapidly by several orders of magnitude over an angular range of a very few degrees, after which it flattens out and becomes marked by oscillations, which have been attributed to Fraunhofer shadow diffraction from the hard core of the potential.[10] Fraunhofer diffraction has been observed for many systems in He-molecule scattering and has been shown to provide a sensitive measure of the distance at which the repulsive and attractive forces just cancel each other.[11] At even larger angles molecular scattering is dominated by the hard-core repulsive potential.

Thus, in order to explain the large-momentum-transfer scattering observed here, we can to a good approximation use a hard-wall model. In contrast to point defects, which are three dimensional, steps can be well described by a two-dimensional profile. Since a step connects two terraces at different heights we must consider a statistical distribution of terrace heights and widths. The effect of averaging over such a distribution is essentially to convolute the scattering intensity with a strongly peaked function.[3] For the worst case, i.e., antiphase scattering from adjacent terraces, the measured broadening of the specular and diffraction beams was less than 2° (FWHM) corresponding to a K-space width of $\Delta K \leq 0.15$ Å^{-1}. We note that, as pointed out by Blatter,[8] any interference in the scattering from different step faces can only affect the intensity distribution in the immediate vicinity of the diffraction peaks (see also discussion below). Thus, in treating the broad oscillations between diffraction peaks we can characterize the scattering from a random distribution of different steps as the sum of contributions from single steps. For essentially the same reason we can approximate the scattering from a randomly stepped surface by the scattering from a hard mirror surface with a localized line disturbance. For simplicity we represent the disturbance by a hard boss. The exact scattering wave function can then be written asymptotically ($r \rightarrow \infty$) as

$$\Psi_{\mathbf{k}_i}(r) = e^{i\mathbf{K}_i\cdot\mathbf{R}} e^{-ik_{iz}z} - e^{i\mathbf{K}_i\cdot\mathbf{R}} e^{ik_{iz}z} + f_T(\mathbf{K},k_z) e^{ikr}/\sqrt{r}, \quad (1)$$

where the first term represents the incoming beam, the second term is due to the mirror reflection, and the third term, the scattering from the hard boss. To ensure that the surface boundary condition of vanishing wave function is also satisfied, f_T must consist of two contributions:

$$f_T(\mathbf{K},k_z)=f(\mathbf{K},-k_z)-f(\mathbf{K},k_z), \tag{2}$$

where the terms $f(\mathbf{K},k_z)$ are the scattering amplitudes from a single line source of arbitrary shape which, however, is symmetric with respect to the surface plane. If the incident beam is normal to the axis of the boss then Eq. (2) can be reexpressed as

$$f_T(\theta_f)=f(|\theta_f-\theta_i|)-f(\pi-|\theta_f+\theta_i|), \tag{3}$$

where θ_i and θ_f are the incident and final angles measured with respect to the surface normal. The first term is due to trajectories which have been scattered first from the boss and then from the mirror, and the second term is due to direct scattering. The interference implied by Eq. (3) is similar to that observed in identical-particle scattering, which can be seen by setting $\theta_i=0$ in Eq. (3). We then have

$$f_T(\theta_f)=f(\theta_f)-f(\pi-\theta_f), \tag{4}$$

which has the form of the properly symmetrized spatial wave function for the scattering of two spin-$\frac{1}{2}$ fermions in the triplet state.[12]

In this preliminary analysis we approximate the boss by a half cylinder. In the short-wavelength limit ($ka\rightarrow\infty$) the scattering from a full cylinder has been calculated and gives

$$f(\theta)=-\left[\frac{a\sin\theta/2}{2}\right]^{1/2}e^{-i2ka\sin\theta/2}+\frac{e^{-i\pi/4}}{(2k\pi)^{1/2}}\frac{(\cos\theta+1)}{\sin\theta}\sin(ka\sin\theta), \tag{5}$$

where a is the radius of the cylinder.[13] The first term is the illuminated-face contribution while the second is the Fraunhofer diffraction term. The symmetrization of Eq. (5) according to Eqs. (2) and (3) assures that f_T then gives the correct solution for a half cylinder on a mirror. For small parallel momentum transfer the Fraunhofer term dominates but since its average contribution is expected to decrease with $(\Delta K)^{-2}$, at larger momentum transfer the dominant contribution comes from the first term and its mirror interference. Hence we shall refer to these structures as reflection-symmetry-interference oscillations. Finally we note that for comparison with experiment the elastic differential reflection coefficient is given by

$$dR/d\theta=nA(\theta_i,\theta_f)|f_T|^2, \tag{6}$$

where n is the density of the steps and A is a slowly and monotonically varying function which depends on the apparatus geometry.

Figure 2 shows a comparison of calculated best-fit differential reflection coefficients with the experimental data at two energies. The slight decrease in a from 2.3 to 2.2 Å with increasing energy is consistent with the expected increase in penetration of the helium atoms. As can be seen from Fig. 2 the fit is remarkably good considering the crude and somewhat unrealistic way in which we have modeled the step profile. The success of such a simple model provides support for our interpretation in terms of reflection-symmetry oscillations comprising scattering from the step faces together with back reflection from the terraces. The only major disagreement with theory is the absence in the experiment of the last major peak predicted by the theory. This can be explained by considering the true shape of the steps in more detail, and in particular by noting that, unlike the cylinder in our model, the real

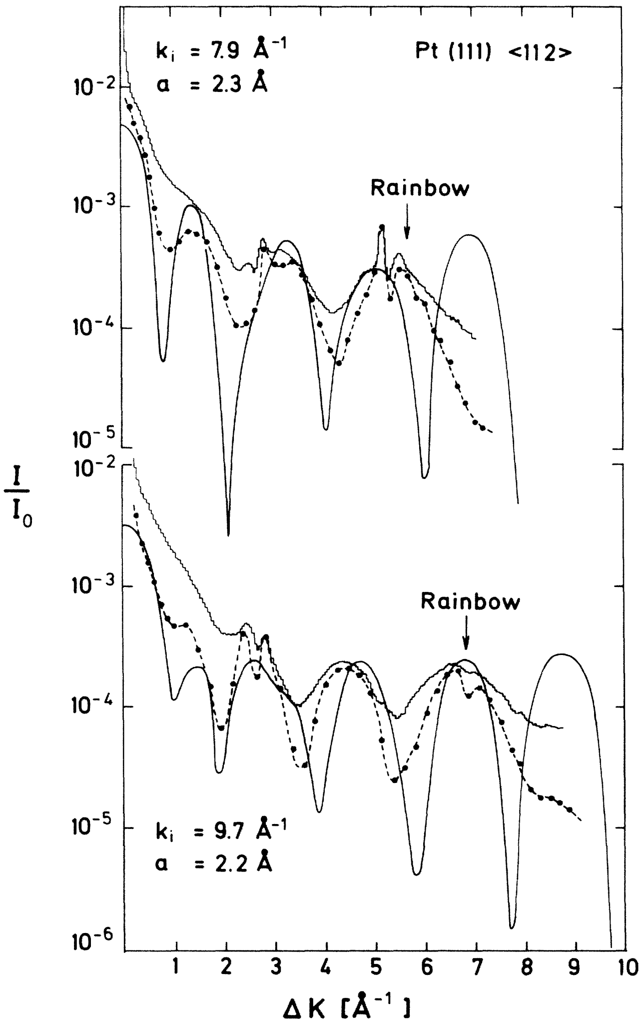

FIG. 2. Comparison of theoretical angular distribution (continuous curve) and experiment (circles are elastic contribution only) for He atoms scattering from randomly stepped Pt(111). Incident energies are 32 MeV ($k_i=7.9$) and 50 MeV ($k_i=9.7$).

step profile will have an associated classical rainbow angle corresponding to scattering from the point of maximum slope. At angles larger than this, a rapid fall off in intensity is expected. Extensive helium diffraction studies by Lapujoulade and Lejay[14] of the periodically stepped copper (113), (115), and (117) surfaces have shown that steps on these surfaces can be described by a hard-core profile with an inclination of 30° to the terraces. This value predicts a classical rainbow[15] at the ΔK values marked in Fig. 2, in excellent agreement with the observed falloff in intensity. This indirect observation of a rainbow suggests that scattering at positive ΔK $(\theta_f > \theta_i)$ is largely sensitive to steps sloped away from the incident beam direction. However, at negative ΔK values $(\theta_f < \theta_i)$ we observe oscillations at identical values of $|\Delta K|$ indicating that oppositely facing steps have a similar effective cross section despite the two types' not being strictly identical for this threefold symmetric system.

In the present model we have ignored the weak periodic corrugation of the terraces which is the source of the sharp diffraction features. The splitting and enhancement of these peaks observed at certain energies we attribute to interference between the single-step diffraction and the coherent diffraction from the periodic corrugation. These features may also be affected by the fact that the steps are constrained by the crystal structure to lie at lattice positions thus forming a dilute one-dimensional lattice gas. For ΔK equal to a reciprocal lattice vector, i.e., at the diffraction positions, this can produce interference between waves scattered from different steps.[16] Finally, we point out that the deduced step width of $2a = 4.4$–4.6 Å compares well with the value of 3.9 Å which is a lower bound obtained by assuming a profile consisting of a straight line inclined at 30° connecting two terraces of height difference 2.27 Å as appropriate for Pt(111).

Further experiments have been performed in which the intensity distribution from the stepped surface was measured after exposure to various amounts of CO, which is known to absorb preferentially at step sites.[17] At very low exposures $\{< 0.2$ L [1 L (Langmuir) $= 10^{-6}$ Torr sec]$\}$ corresponding to a relative site coverage of about 2% the oscillations become weaker and finally they disappear at ~ 0.5 L. We attribute this to the production by the CO molecules of a strong corrugation in the previously smooth profile parallel to the step edge, which then scatters the helium atoms predominantly out of the incident plane, causing the strong oscillations to disappear. We have also recently observed oscillations in the diffuse scattering from low-coverage random distributions of adsorbed molecules on a smooth surface. The present concept of reflection-symmetry-interference oscillations can easily be extended to this case of a three-dimensional isolated perturbatiuon and can give important information on the hard-core profile of single adsorbed molecules.[18]

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