Information on Adsorbate Positions from Low-Energy Recoil Scattering: Adsorption of Hydrogen on Pt

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Low-energy (10-keV) recoil scattering is proposed as a tool for measurement of adsorbate positions on monocrystalline surfaces. This technique, which makes use of high-energy–recoil adsorbate atoms (energy $\geqslant 1$ keV), supplies real-space structure information. Its potentialities are illustrated in a study of the adsorption system H on (111) sites of Pt. By exploiting surface channeling of incident 10-keV Ne ions on vicinal Pt surfaces we show unambiguously that H occupies fcc-type adsorption sites on Pt(111) terraces.

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The determination of adsorbate-substrate structures is a topic of continuing interest in surface science. Up to now most information is taken from diffraction-type measurements. By their nature such experiments provide images of the surface in the *reciprocal space.* Information with respect to the symmetry or to the size of the unit cell is readily obtained. However, derivation of the structure within the unit cell is less straightforward. Essentially one needs additional information; e.g., in low-energy electron diffraction (LEED) such information is extracted from multiple-scattering effects. In the case of adsorbed hydrogen this does not work well because the scattering cross section of H is small.[1] Thermal-energy atom diffraction has the advantage of being very sensitive to adsorbed hydrogen. However, in this case the corrugation profile is related to the electron density rather than to the atomic positions.[2,3]

In contrast, low-energy ion scattering (LEIS), supplying *real-space* images, probes directly the positions of the nuclei (e.g., see the works of Begemann and Boers,[4] Poelsema, Verheij, and Boers,[5] Verheij, van den Berg, and Armour,[6] and Niehus and Comsa[7]). In addition it provides mass-specific information; i.e., the collision partners can be distinguished in energy or time-of-flight distributions of the backscattered projectiles. For low adsorbate masses (like, for instance, H) the backscattering mode (LEIS) obviously cannot be applied. Low-energy recoil scattering (LERS) is a way out of this difficulty, maintaining the advantages of LEIS described above. In a recoil process the target atom is kicked out of the surface upon ion impact in a binary encounter with a relatively high energy (typically ca. 5%–20% of the energy of the incident ions).[8,9]

We propose here LERS as a method to determine the positions of (light) adsorbates. The probability for a recoil event is given by the product of three factors: the probability to "illuminate" the (H) target atom (the involved impact parameters are small, ca. 0.05 Å), the cross section for the considered recoil process, and the probability of the recoil atom to reach the detector. We have chosen to work with stepped surfaces because this allows us to exploit the surface-channeling mechanism in a simple way. We select a geometry in which the incident beam is directed parallel to the (111) terraces ($\Psi = 0°$; see Fig. 1). The detector is situated at a fixed scattering angle of $\theta = 30°$. Thus the polar exit angle is constant and sufficiently large to avoid blocking effects on the recoil's way to the detector (on terraces hydrogen is bound approximately 1 Å above the plane through the Pt atoms[10]). Since the ions are directed parallel to the terraces they can approach the surface only at a stepup ledge. There they are scattered by the step atoms or they may penetrate into the surface channels. Only these latter ions can reach the H terrace sites closely enough to give rise to a recoil event. The intensity of the recoils is then measured as a function of the azimuthal angle of incidence δ. For these conditions the (relative) recoil intensity is determined exclusively by the first factor above, i.e., the probability to illuminate the adsorption sites with incident ions.

Surface channels are present in the low-index directions $\delta = 0°$, 30°, and 60°. Obviously, $\delta = 30°$ represents the most open channel ($\langle 110 \rangle$) and consequently, the primary particles can penetrate more deeply into the (111) terraces along this direction. This penetration may result in the recoil of hydrogen adsorbed on those terraces. Hydrogen is also adsorbed at step sites, but these atoms can be reached by incoming ions for every azimuthal angle and contribute to a structureless background (see for details the work of Koeleman *et al.*[11]). Thus the feature of surface channeling implies the illumination of a varying number of

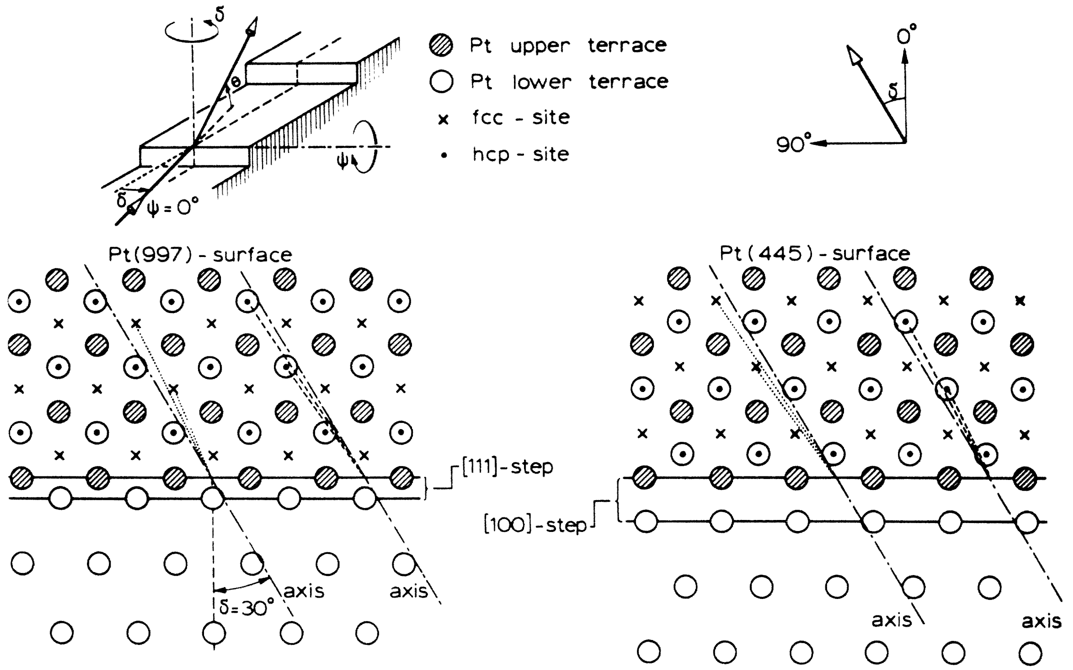

FIG. 1. Model of the two configurations used: Pt(997) [(111)-step orientation] and Pt (445) [(100)-step orientation]. The hcp and fcc threefold hollow adsorption sites are indicated for both surfaces in the terrace plane (the shaded Pt atoms). Inset: The scattering geometry used, with conventional indications for the incident and scattering angles (respectively, ψ and θ), as well as the angle δ which is defined with respect to the stepup direction; $\delta = 30°$ is the direction of the most open surface channel.

terrace adsorption sites upon changing the azimuthal angle of incidence. Consequently, an azimuthal scan should produce clear structure in the measured recoil yield, depending on the position of hydrogen adsorbed on the (111) terraces.

The trajectories of the incident ions are calculated with a Monte Carlo type of program,[12] which includes the influence of the terrace in front of the step edge. Figure 2 shows simulated azimuthal scans (in fact, illumination probabilities) for 10-keV Ne primary ions, assuming a Molière potential, for a vibrating Pt(997) surface {or, in Somorjai's notation, Pt(*S*)-[9(111) × (111)]}. The Debye temperature is taken as 259 K parallel and 174 K perpendicular to the surface.[13]

$I(\delta)$ curves have been calculated for hydrogen at different heights above the (111) terraces and the result for a height of 0.75 Å is shown in the figure. Since H is known to occupy threefold hollow sites,[3,10] the calculations have been performed for two types of sites: hcp and fcc sites, denoted in Fig. 2 with circles and crosses, respectively. Because hydrogen adsorbed at step sites only contributes to a nonstructured background, they have been neglected in this consideration. The main peak is indeed located near $\delta = 30°$ for both types of sites, as expected because of channeling effects along the ⟨110⟩ direction. However, the maximum intensity is shifted towards larger δ values for the hcp site and smaller δ values for the fcc site. The origin of this shift may be deduced from purely geometrical considerations. The threefold sites are shifted away from the channel axis (see Fig. 1). Thus the maximum and minimum azimuthal angles at which a site is "seen" through the channel entrance are located asymmetrically to the ⟨110⟩ axis and are just reversed for the two sites. The influence of the step atoms at the ion trajectories does not alter the essence of this picture, and so the direction of the shift allows us to distinguish between fcc and hcp sites. Since the magnitude of the shift depends on the position of the H atoms, an estimate of the height of the adatoms above the surface can also be obtained. Inspection of Fig. 1 shows that for a (100)-oriented step the situation would be exactly reversed: The maximum illumination should occur at smaller δ values in the case of hcp sites and at larger δ values for fcc sites. In order to check this presumption we have simulated δ scans for H adsorbed on a Pt(445) surface {or Pt(*S*)-[9(111) × (100)]} as well. The results (see Fig. 2) for hcp-H on Pt(445) coincide within the statistical limits with those for fcc-H on Pt(997) and vice versa. Possible steering effects by the lower terraces can thus be neglected (see for details Ref. 11).

In a simplified way one may understand the data in terms of a shadow-cone model. The shadow cone is only well defined at short distances behind ledge atoms. A maximum recoil intensity is obtained if the

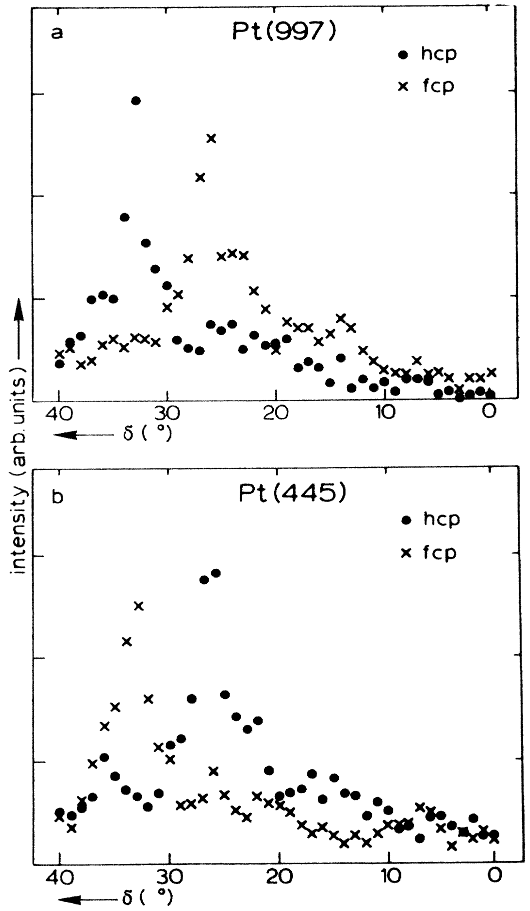

FIG. 2. Calculated "illumination" probability for hcp and fcc adsorption sites at the terrace plane of both Pt(997) and Pt(445) stepped surfaces. The height of H above the surface is taken as 0.75 Å, corresponding to a bond length of 1.78 Å. As a projectile we used 10-keV Ne ions with a Molière potential (reduced screening length of 0.85). The impact points are averaged over 0.05 Å. Note that all adsorption sites (of the same type) at the terrace are occupied, H adsorbed at the step edge has been neglected.

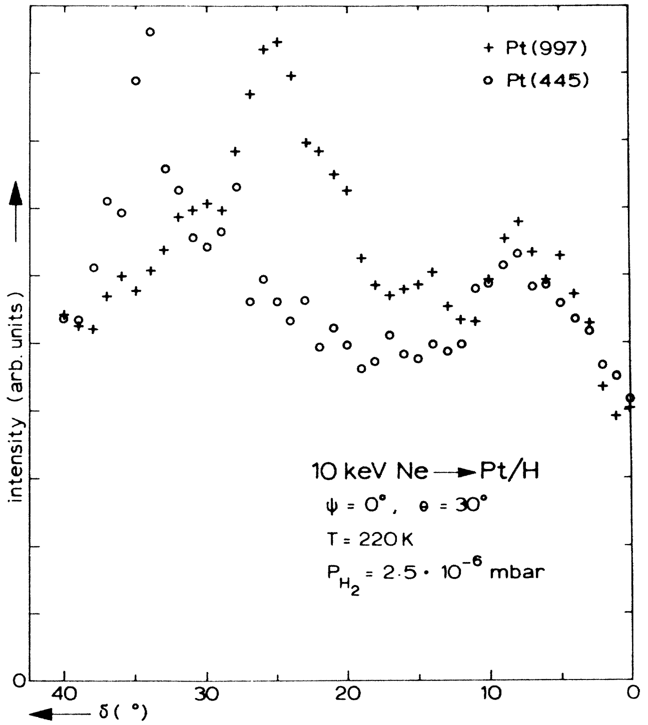

FIG. 3. Measured azimuthal scans of the recoil-H yield for Pt(997) and Pt(445). The measured peak positions show the same trend as the calculated illumination probabilities for the fcc site in Fig. 2.

shadow-cone edge hits an adsorption site. In order to achieve this situation for second-row H atoms the crystal has to be rotated away from the ⟨110⟩ ($\delta = 30°$) direction: towards smaller or larger δ values for fcc or hcp sites, respectively. For hitting H sites deeper on the terraces the required rotation away from $\delta = 30°$ becomes progressively smaller because of a combination of geometric effects and more pronounced ⟨110⟩ channeling.

The reported measurements are performed in a UHV system described previously.[9] The energy of the primary Ne beam was 10 keV. The samples were cleaned by means of ion bombardment. In our experiments the target was kept at a constant temperature of 220 K. The equilibrium hydrogen pressure amounted to 2.5×10^{-6} mbar. Under these conditions the step sites are saturated and the coverage on the (111) terraces is about 0.35.[14] The H-recoil spectra are dominated by the (quasi-)single collision peak (for details see Ref. 11). For the sake of simplicity we take therefore the integrated yield of the spectra for the H-recoil intensity. It is noted that the total ion dose required for acquisition of a time-of-flight spectrum corresponds to about 1×10^{-4} Ne ions per Pt surface atom. Therefore, beam-induced damage effects can be neglected.

We have used the two vicinal Pt(111) surfaces for which the calculations in Fig. 2 are performed: Pt(997) and Pt(445). These surfaces have been oriented carefully during preparation by the Laue technique. Note that their orientation has been checked also *in situ* by channeling experiments with 10-keV H ions.[15]

Figure 3 shows the experimental results. The main intensity is concentrated around the ⟨110⟩ surface channel direction ($\delta = 30°$). For the Pt(997) surface the peak is shifted towards smaller δ values. This implies that H is occupying fcc sites on the (111) terraces as is evident upon comparison with Fig. 2. The results obtained for the Pt(445) surface showing a shift of the peak in the opposite direction provide independent support for this assignment. Combining these results for Pt(997) and Pt(445) we conclude that H adsorbed on (111) terraces of these surfaces occupies fcc sites regardless of the step orientation. The steps do not influence the type of adsorption site on the terraces. Simulations show that both the magnitude of the shift of the main peak and the shape of the smaller features around $\delta \simeq 8°$ depend on the height h of the H atom above the first Pt layer. A first estimate of h leads to a value of $h = 0.7 \pm 0.2$ Å, corresponding to a bond length of 1.78 ± 0.08 Å.

The present result, i.e., occupation of fcc positions, differs from recent findings of H/Pt(111) obtained by Batra and co-workers[16,17] based on the He diffraction results of Lee, Cowin, and Wharton.[3] The latter authors conclude that *if* the larger bump in their corrugation profile is assigned to hydrogen rather than to platinum, H occupies hcp sites on Pt(111). On the basis of electron-density calculations, Batra assigned the larger bumps to H atoms. Their final conclusion, H on hcp sites, is in obvious contrast to the present results. This discrepancy might be caused by the fact[18] that it is hardly possible to distinguish between mountains and valleys in the measured corrugation function.

In this paper we have shown the potentialities of LERS for determining the position of light adsorbates on monocrystalline surfaces. For H adsorbed on (111) terraces we have shown unambiguously that the adsorbates occupy threefold hollow sites of the fcc type. The H—Pt bond length could be estimated to be 1.78 ± 0.08 Å. With this example we have illustrated that LERS has the same capabilities for light adsorbates as LEIS has for heavier adsorbates: to provide real-space and site-specific information about the position of atoms on the surface. This property of the LERS technique is of special importance for those systems where more adsorption sites are possible which are not too different with respect to the symmetry of the unit cell. Measurement of the bond length (surface-extended x-ray absorption fine structure, electron-energy-loss spectroscopy) is in these cases not sufficient for characterizing the structure, whereas also diffraction measurements are often difficult to interpret in these cases. Secondly it must be stressed that, in contrast to most other techniques for structural analysis, LERS is sensitive to hydrogen. In summary we conclude that LERS is a powerful real-space technique for determining adsorbate positions on monocrystalline surfaces which may become a useful addition to the already large scope of techniques for analyzing surface structures.

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