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S. T. Ceyer, R. J. Gale, S. L. Bernasek, and
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Scattering of Thermal Helium Beams from High-Miller Index
(Stepped) Platinum Crystal Surfaces

by

S. T. Ceyer, R. J. Gale, S. L. Bernasek, and G. A. Somorjai

ABSTRACT

Helium beams generated by a 300 K source were scattered from single crystal platinum surfaces. The angular distribution of the scattered beam was monitored as a function of azimuthal angle ϕ and incident angle θ . The effect of the presence of atomic steps on the angular distribution of scattered helium atoms was studied on a crystal surface composed of terraces on the average five atoms in width separated by steps of monatomic height. Rainbow scattering is observed when the steps are oriented perpendicular to the incident beam direction indicating strong modulation of the angular distribution by the periodic step potential. Only specular scattering is observed when the incident beam impinges on the crystal along the step edges which indicates minimal effects of the presence of steps on the scattering distribution. These results as well as the absence of diffraction are in good agreement with the calculations of Miller et al.

0 0 0 0 4 0 0 8 2 7

Introduction

The scattering of thermal energy (~ 0.02 eV) helium beams from solid surfaces is a probe of the atomic surface structure and of the gas-surface interaction potential. Due to the weak interaction of the helium atom with the surface (potential well of adsorbed helium is about 2 kcal) and its small deBroglie wavelength (< 1 Å), the angular distribution of the scattered helium atoms is sensitive to the atomic structure¹ and, thus, can readily detect atomic disorder on the surface.²

We have explored the scattering of helium atomic beams from high Miller index platinum surfaces that exhibit ordered, periodic steps on the atomic scale to probe the effect of atomic steps on the helium atom scattering distribution. These studies examine how the periodic surface structure, i.e., monatomic steps, ~ 2.3 Å in height, separated by ordered atomic terraces of five atoms wide (~ 11 Å) on the average, is seen by an atomic beam incident on such a surface from various directions.

Previous atomic scattering experiments have yielded several types of angular scattering distributions that are schematically shown in Fig. 1. Intense, narrow, specularly-directed scattering distributions have been observed from high density low Miller index surfaces.³ Such scattering distributions indicate a surface that is well-ordered and whose surface potential is smooth. These distributions also indicate very poor energy exchange between the incident gas atom and the surface. A second type of angular distribution of scattered helium atoms that has been observed from a solid surface exhibits a double-peaked intensity profile.⁴ The angular separation and the relative intensity of the two peaks are determined by the surface periodic potential. This type of scattering has been termed

rainbow scattering by McClure⁵ and is the result of atomic periodicity on the surface. Such an angular distribution can be calculated by classical mechanics. Diffraction, which is a quantum mechanical consequence of the surface periodicity, is a third type of scattering distribution seen from a certain low Miller index metal surface.⁶

The helium atomic scattering distributions seen from a stepped platinum surface in our work are dependent on the orientation of the incident beam with respect to the atomic rows or step edges. Specular scattering is observed as the incident beam impinges along the step edges. Rainbow scattering as well as a shift in the scattering distribution maximum is observed when the step edges are perpendicular to the incident helium atoms. The rainbow scattering distribution confirms the ordered periodic step structure of the surface indicated by LEED and gives qualitative information concerning the periodic surface potential as a function of the orientation of the steps to the incident helium atoms. Diffraction is not observed in our experiments for reasons well understood and described below. Comparison of the specular scattering distribution from the stepped surface to the distribution from a smooth platinum(111) surface and to that of a completely disordered surface also yields valuable insight regarding the energy transfer between a gas and the solid.

Experimental

The ultra-high vacuum molecular beam surface scattering apparatus in which these experiments were carried out as well as the surface preparation and characterization has been described previously in detail.⁸ The procedure for these experiments has also been described.^{7,8}

A diagram of the experimental arrangement is shown in Fig. 2. Briefly, the room temperature helium beam is formed by effusion from a multichannel capillary array. The beam is modulated at 160 Hz by a mechanical chopper. The pressure of the beam at the surface is about 10^{-7} torr. AC detection of the scattered beam by a quadrupole mass spectrometer in the plane defined by the incident beam and the surface normal is employed. The surface temperature in these experiments is ~1100 K.

The three platinum single crystal surfaces used in this study are designated by their Miller indices at Pt(111), Pt(553), and Pt(997). A more descriptive nomenclature for the stepped surface designates the Pt(553) as Pt(S)-[5(111)×(111)] and the Pt(997) as Pt(S)-[9(111)×(111)]. The (111) surface is the hexagonal close-packed plane in which each atom has six nearest neighbors. The (553) and (997) surfaces are cut 6.2° and 12.5° , respectively, from the (111) plane in the $\langle 111 \rangle$ direction resulting in a surface characterized by ordered monatomic steps of (111) orientation. These steps are separated by terraces of (111) orientation which are on the average five atoms wide in the (553) and nine atoms wide in the (997). They are shown schematically in Fig. 3.

The crystal is mounted on a manipulator which extends from the top of the main scattering chamber and provides several degrees of freedom of motion for the crystal. To measure the incident beam intensity and thus

normalize all the measurements, the crystal can be translated upward out of the beam line. The angle of incidence, θ_i , can be varied by rotating the crystal around its diameter perpendicular to the plane defined by the incident beam and the macroscopic surface normal as seen in Fig. 4. Further, it is possible to vary the azimuthal angle ϕ (the orientation of the step edges with respect to the plane defined by the incident atomic beam and the macroscopic surface normal), by rotating the crystal around its center in its own plane as shown in Fig. 4. The azimuthal orientation is determined by LEED patterns to an accuracy of $\pm 5^\circ$.

Before each run, the platinum single crystal is heated in an ambient pressure of oxygen of 5×10^{-6} torr for one and one-half hours to provide an uncontaminated surface as established by Auger Electron Spectroscopy. Low-Energy Electron Diffraction shows the presence of well-ordered atomic domains of the stepped platinum surface.

It should be noted that while the macroscopic surface is always 45° (or some other constant angle of incidence) from the incident beam at any azimuthal angle of rotation, the microscopic stepped surface is not. Since the helium atom "sees" the surface on the atomic scale, a variable fraction of the helium beam scatters outside the plane of the detector which is lined up with respect to the macroscopic surface normal. In these experiments we have only measured the scattering distribution in the plane defined by the incident beam and the macroscopic surface normal.

Results

Figures 5a-e show the scattering distributions from the platinum(553) surface for various azimuthal orientations. Each distribution except for azimuthal angle $\phi = 24^\circ$ (where $\phi = 0^\circ$ when the step edges are perpendicular to the incident beam and $\phi = 90^\circ$ when the beam impinges on the crystal along the step edges) is an average of at least two different runs with error bars indicative of the scatter in the points at each angle sampled. Each point is an average of at least twelve values. The intensity scattered into the solid angle subtended by the detector at a given scattering angle is normalized to the incident beam. The angle of incidence in each case is indicated by the arrow on the horizontal axis of the distribution as 45° .

The effect of varying the azimuthal orientation of the crystal step edges to the incident molecular beam, while the angle of incidence is held constant, is dramatic. Note that as the incident beam comes in along the step edges, the total scattering distribution becomes less intense due to out-of-plane scattering. Since the detector is mounted in the plane of incidence defined by the macroscopic surface normal and the incident beam, it does not sample molecules scattered out-of-plane. The peak intensity of the cone-shaped distribution also shifts in space as the azimuthal orientation of the crystal is changed. Only when the step edges are perpendicular to the incident beam does the detector sample directly along the axis of the cone as indicated in Fig. 6. At any other azimuthal orientation, the detector "sees" only slices of the scattering distribution, since the axis of the scattered cone lies out of the plane defined by the macroscopic surface normal and the detector.

Two further observations can be made. There is a definite shift toward the surface normal of the more intense peak and the appearance of a second peak or shoulder near the specular as the steps are oriented in a more perpendicular direction to the incoming beam.

This shift toward the macroscopic surface normal reaches a maximum of 25° from the specular when the step edges are perpendicular to the incident beam. Whether this shift is observed toward the macroscopic surface normal or away from it depends on whether the open edge of the step is away from the incident beam or into it. In the case of the (553) surface, the molecular beam was oriented away from the open step edge.

Figures 7a-d show the effect of varying the angle of incidence on the double-peaked scattering distribution for a fixed azimuthal angle of $\phi = 5^\circ$. Each of these distributions is an average of at least two runs. Again, the arrow on the abscissa indicates the angle of incidence. The two peaks in the scattering distribution coalesce as the angle of incidence is increased. The intensity of these two peaks also increases as the angle of incidence is increased.

Figure 8 compares the specular scattering distribution seen from the platinum stepped surfaces (553) and (997) when the beam comes in along the step edges to the specular scattering distribution seen from a platinum(111) surface and to a scattering distribution previously seen in our laboratory from a totally disordered platinum(100) surface after ion bombardment.

Discussion

Particles that scatter from the overall macroscopic surface appear at the specular angle in the scattering distribution. However, the helium atoms scatter with reference to the microscopic surface normal, rather than the macroscopic surface normal. A diagram of this effect is shown in Fig. 9, indicating the microscopic specularity when the step edges are perpendicular to the beam. The helium atom intensity scattered from the terrace normal should be shifted twice the angle of cut from the (111) plane or 25° away from the specular angle when the step edges of the Pt(553) crystal are perpendicular to the beam. This is precisely what is observed indicating that the helium atoms do indeed probe the atomic surface structure. Increasing the azimuthal angle ϕ from 0° to 90° decreases the shift as shown in Fig. 10. Cosine dependence of the shift on the azimuthal angle for small angles of cut from the (111) plane would be expected for specular scattering from the terrace. It would be valuable to have a theoretical calculation which predicts the azimuthal dependence of the rainbow peaks from a stepped surface. When the azimuthal angle ϕ is equal to 90° , the normal to the terrace and the macroscopic normal now point in the same direction. Since the periodic potential now appears smooth to the incident atom no shift and only specular scattering is observed.

The two maxima which are apparent in the scattering distribution from the platinum(553) surface when the step edges are perpendicular to the incoming beam are indicative of rainbow scattering. It has been shown that both the distance between the two rainbow peaks and the relative intensities are greatly dependent upon the dynamical interaction between the

gas and the solid and the nature of the periodic potential.⁵ In our case, rainbow scattering is only observed when the step edges are oriented almost perpendicular to the incident beam. The periodicity as seen by the gas-atom is very much reduced when the beam comes in along the step edges, i.e., the surface appears smooth to the incoming helium atom. These results are in agreement with the diffractive studies of helium scattering from W(112).⁶ In that case, diffraction is only observed as the rows of troughs and ridges are oriented in a perpendicular direction to the incoming beam.

The maximum peak intensity near the macroscopic specular angle is much less than the intensity of the peak in the scattering distribution that is shifted toward the surface normal. This is most likely due to a shadowing effect of the step edge on the step inflection point of the potential. The maximum shifted toward the surface normal is of course due to the scattering from the inflection point of the potential on the terrace. Figure 11 illustrates the maximum and minimum scattering angles from the step and terrace inflection points, respectively.

The variation of the angle of incidence, θ_i , for a fixed orientation of the steps of the (553) surface to the incoming beam, i.e., fixed azimuthal angle ϕ , also indicates the double peaked scattering distribution as the result of rainbow scattering. For greater angles of incidence as measured from the surface normal the surface appears smoother and less periodic to the incoming helium atom, and, thus, the two rainbow peaks coalesce. At smaller angles of incidence (beam impinging closer to the macroscopic surface normal), the helium atom samples the full strength of the surface periodicity and the two rainbow peaks separate.

The increase in intensities of the surface rainbows for an increase in the angle of incidence qualitatively follows the trend predicted in calculations by McClure⁹ for classical scattering of helium atoms. At grazing angles of incidence the surface appears less spatially rough and, thus, allows a more intense elastic scattering distribution. At more normal angles of incidence the elastic scattering distribution is less intense due to an increase in spatial roughening of the surface as seen by the helium atom.

A platinum(111) surface exhibits only specular scattering.³ The fact that rainbow scattering has been observed from a platinum stepped surface is indicative of a strong periodic potential introduced by the steps which is seen clearly only when this periodicity lies in a perpendicular direction to the incoming particle.

Quantum diffraction features as a result of the step periodicity were not observed. In our experiments the deBroglie wavelength of the helium atom ($\lambda \approx .62 \text{ \AA}$) was too small compared to the periodicity ($a \approx 11 \text{ \AA}$) to allow for well-resolved diffracted intensities. In model semiclassical calculations by Miller et al.,¹⁰ diffracted intensities are evident within the classical rainbow angles when the deBroglie wavelength of the incident beam is large compared to the length of the surface periodicity (in his case $\lambda/a = .125$). When the wavelength becomes small compared to the periodicity ($\lambda/a = .075$), the diffracted intensities merge. Thus, under our experimental conditions with $\lambda/a \approx .06$, diffracted beams are not observable. Only rainbow envelopes are observed. There is excellent qualitative agreement between the calculations of Miller et al. and our experimental observations. A cooled monoenergetic beam with its longer wavelength may yield diffracted

intensities in between the two rainbow angles.

There is additional information to be gained from the specular scattering distributions when the beam impinges along the step edges. The specular scattering seen from a smooth (111) surface of platinum is very different from the specular scattering seen from the platinum stepped surfaces. The broader, less intense scattering distribution from the stepped surfaces when the beam comes in along the step edges indicates increased energy exchange between the gas and the surface. The extent of energy transfer is greatly determined by the extent of microscopic disorder due to the steps. The specular scattering distributions is less intense and broader for the (553) surface where approximately 20% of the surface atoms are in step sites than it is from the (997) surface which has only approximately 10% of the surface atoms in the step sites. For scattering from a disordered surface, a small specular peak is observed on top of a broad cosine scattering distribution. The degree of energy transfer between the gas and the surface appears to be directly related to the microscopic disorder or roughness of the surface.

Conclusion

Rainbow scattering has been observed from a platinum stepped surface. This observation indicates the presence of a strong periodic potential introduced by the steps. The subspecular shift of the rainbow peak originating from the terrace inflection point confirms the presence of ordered step domains as indicated by LEED. Specular scattering distributions from the stepped surfaces observed when the beam comes in along the step edges show greater energy accommodation between the gas and the surface as the step density of the surface increases. These results confirm the sensitivity of helium beam scattering to atomic surface structure. The absence of well-resolved diffraction peaks is in agreement with the calculations of Miller et al.

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Figure Captions

- Fig. 1. Diagram schematically indicating three types of scattering distributions previously observed from metal surfaces;
(a) specular scattering, (b) rainbow scattering, and (c) diffraction.
- Fig. 2. Schematic diagram of ultra-high vacuum molecular beam scattering apparatus.
- Fig. 3. Schematic diagram of the platinum surface studied in this work:
(a) Pt(111), (b) Pt(553) or Pt(S)-[5(111)×(111)], and
(c) Pt(997) or Pt(S)-[9(111)×(111)].
- Fig. 4. Diagram defining:
(a) θ_i , angle of incidence and (b) ϕ , azimuthal angle.
- Fig. 5. Normalized scattered intensity vs. angle from surface normal for several azimuthal angles:
(a) $\phi = 79^\circ$, (b) $\phi = 51^\circ$, (c) $\phi = 39^\circ$, (d) $\phi = 24^\circ$, and (e) $\phi = 5^\circ$,
with a fixed angle of incidence of 45° for a Pt(553) surface.
- Fig. 6. Schematic diagram defining the macroscopic surface normal and the terrace normal:
(a) The steps are oriented so that they are perpendicular to the incident beam. Note that the incident beam, the normal to the terrace N_t , the macroscopic normal N_m , the scattered distribution and the detector are all situated in one plane, the plane of the paper. In this case, the incident beam is oriented away from the open edge of the step.
(b) The incident beam (not shown) impinges on the filled circle at a 45° angle of incidence to the paper, but in the plane of the macroscopic normal or along the step edges. The normal to the
contd.

Fig. Cap., contd.

Fig. 6. contd.

terrace and to the macroscopic surface are now normal to a plane which is perpendicular to the plane of the paper. Note that the incident beam, the macroscopic normal and the detector are in one plane while the scattering distribution is out of the plane sampled by the detector.

Fig. 7. Normalized scattered intensity vs. angle from surface normal for a fixed azimuthal angle $\phi = 5^\circ$ with various angles of incidence from a Pt(553) surface. (a) $\theta_i = 25^\circ$, (b) $\theta_i = 35^\circ$, (c) $\theta_i = 45^\circ$, (d) $\theta_i = 65^\circ$.

Fig. 8. Comparison of specular scattering distributions from a Pt(111), Pt(997), Pt(553), and a Pt(100) which was a disordered surface by ion bombardment.

Fig. 9. Diagram indicating microscopic specularity for step edges perpendicular to the incident beam.

Fig. 11. Diagram qualitatively showing the origin of the two rainbow peaks. Scattering from the step inflection point leads to a scattered intensity at a maximum angle from macroscopic surface normal. Scattering from terrace inflection point leads to a scattered intensity at a minimum angle from the macroscopic surface normal.

Fig. 10. Shift away from the specular of the maximum intensity peak vs. azimuthal angle. Solid line indicates cosine distribution.

XBL 759-7 309

Figure 1

MOLECULAR BEAM SURFACE SCATTERING APPARATUS

XBL 732-5744A

Figure 2

5 2 8 0 0 4 4 0 0 0 0

XBL 759-7310

Figure 3

XBL 759-7311

Figure 4

XBL 759-7312

Figure 5a

0000400837

-21-

XBL 759-7313

Figure 5b

XBL 759-7314

Figure 5c

XBL 759-7315

Figure 5d

8 2 8 0 0 7 7 0 0 0 0

XBL 759-7316

Figure 7c
and 5e

N_t - Terrace normal

N_m - Macroscopic normal

ms - Mass spectrometer detector

———— In the plane of the paper

----- Below the plane of the paper

XBL 759-7317

Figure 6

6 2 8 0 0 7 7 0 0 0 0

XBL 759-7318

Figure 7a

XBL 759-7 319

Figure 7b

0 0 8 0 0 7 0 0 0 0

XBL 759-7320

Figure 7d

XBL 759-7321

Figure 8

1 7 8 0 0 4 0 0 0 0

$\gamma = 12.5$ Angle of cut from
(111) surface

$$\alpha + 2\gamma = \beta$$

N_m = Macroscopic normal

N_t = Terrace normal

XBL 759-7323

Figure 9

XBL 75 9-7 353

Figure 10

0 0 0 0 4 0 0 8 4 2

XBL759-7322

Figure 11

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