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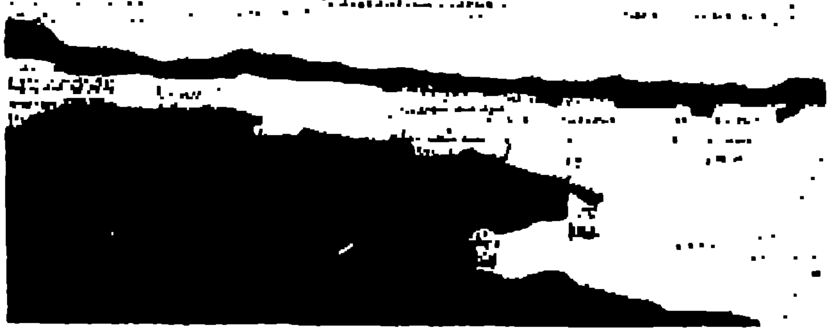

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Low-energy $^4He^+$ scattering from deuterium adsorbed on stepped Pd(331)

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We have taken angle resolved data for the scattering of low-energy (< 1 keV) $^4He^+$ from deuterium adsorbed on a stepped Pd(331) surface. The impact geometry was "up the staircase," that is, the $^4He^+$ beam was perpendicular to and directly incident onto the unshadowed <011> Pd ledge atoms. A strong quasi-elastic scattering signal of $^4He^+$ from D ($^4He^+$/D) was observed at a forward scattering angle of $\theta = 25°$ and an incidence angle of $\alpha = 76°$ from the (331) normal. The results agree with shadow cone calculations of scattering first from Pd ledge atoms followed by a second event, $^4He^+$/D. The resultant adsorption geometry shows D to reside in the quasi threefold ledge site on the surface directly above the bulk fcc octahedral void. These results are consistent with the previous $^4He^+$ scattering study of the geometrically related Pd(110)-D(ads) system.

Angle resolved scattering of low-energy ions provides a sensitive method to detect, identify, and locate adatoms on surfaces of single crystals. By using forward scattered $^4He^+$ ions in a previous study,[1] we located deuterium in the valley channels of Pd(110) on quasi threefold or on "long-bridge" sites in agreement with LEED studies[2] and theoretical predictions.[3,4] The present study extends the substrate system to a structurally related but more complex Pd(331) terrace ledge (TL) surface. The objective of this study was to locate deuterium adsorption sites on the TL Pd(331) surface by $^4He^+$/D(ads) low-energy ion scattering (LEIS).

The classical expression for a projectile scattered elastically (i.e., translational energy and momentum are conserved) in a binary collision with an initially stationary target can be stated as[1,5]

$$2\cos\theta = (1 + A)v + (1 - A)/v, \qquad (1)$$

where θ is the laboratory scattering angle, A is the target to projectile mass ratio, and v is the relative velocity of the scattered particle defined as $v = (E/E_0)^{1/2}$ where E/E_0 is the ratio of final to initial translational energy of the scattered ion. For A < 1, there is a maximum cutoff angle for scattering at $\theta(max) = \sin^{-1}A$. Two scattered ion velocities are derived from Eq. (1) at $\theta < \theta(max)$ for A < 1, which is a consequence of two center-of-mass scattering angles (from collisions with slightly different impact parameters) mapping onto the same θ.[5] Two peaks are observed, e.g., for $^4He^+$/D(ads)[1] and the present study, for Ne^+ scattering from C impurity on gold,[6] and for Kr^+ from Cu.[7] For $^4He^+$ scattering by D, A = 0.5 and $\theta(max) = 30°$.

Full experimental details are given in Ref. 1. Briefly, angle-resolved scattering data were taken using a gas-discharge ion source and a differentially pumped high vacuum scattering chamber equipped with a 5-cm-diam hemispherical electrostatic energy analyzer. The incident beam produced mass filtered, neutral free 1 keV $^4He^+$ with ΔE (FWHM) < 3 eV. The analyzer angle was positioned to ±1°; the channel multiplier detector was operated in the pulse counting mode. The palladium single crystal was oriented by x rays, cleaned by repeated ion bombardment and annealed in vacuum at 1000K[1] to remove surface impurities. LEED measurements confirmed that an ordered (331) surface resulted from this procedure. The $D_2(g)$ gas-doser was positioned 2 cm from the sample.

Figure 1 shows the scattering geometry. An ordered fcc(331) surface consists of repeating terraces in a terrace ledge (TL) array with the (331) surface at 22.0° from the (111) atomic terraces. The incident $^4He^+$ beam and detector both are in the {110} plane of incidence which is perpendicular to the (111) terraces, the (331) and the ledges. The beam is perpendicular to the close packed row of Pd ledge atoms at an angle α from the (331) surface normal. We refer to this configuration as going "up the staircase." The incident beam is parallel to the (111) terraces at α = 90° - 22° = 68°. At α = 76° where our most significant data were taken, the incident ions are actually 8° below the (111) terraces and impinge upon the Pd ledge atoms. The optimum laboratory scattering angle, θ of Eq. (1), was nominally θ = 25°, which yielded well resolved, strong scattering signals.

Atomic geometry is illustrated in the hard sphere photograph of Fig. 2. In the (n,n,n-2) sequence of (111) vicinal surfaces, n = 3 for the (331). The repeat sequence is three <110> rows of atoms then a step of single atomic height in the {111} plane, three rows and a step, and so forth. Deuterium adsorption sites labeled 1, 2 and 3 are identified in Fig. 2. Site 3 is co-linear with the <110> Pd ledge atoms, and Site 2 is of special interest not only because it is consistent with our data, but also because it along with Site 1 is a surface location directly above the bulk octahedral void at the lattice position (1/2, 1/2, 1/2). Further, Sites 2 and 1 correspond to the quasi threefold positions found to be occupied by D(ads) in Ref. 1.

The presence of surface atoms is derived from maxima in ion scattering spectra and geometries from angular dependencies. Figure 3 shows the energy spectrum of 1-keV $^4He^+$ scattered "up the staircase" from Pd(331) covered with D, at α = 77.5°, θ = 25°, -185°C and $P(D_2)$ = 2.7 x 10^-5 Pa. Only D and Pd are present in significant amounts. Two peaks attributable to $^4He^+/D$ are clearly present at relative energies, E/E_0, for the upper maximum of 0.65 and of 0.18

for the lower maximum. The identity of those two peaks as being $^4He^+/D$ was firmly established in Ref. 1 and substantiated here by varying θ. The locations are close to those calculated by Eq (1): E/E_0 = 0.61 (upper), and 0.18 (lower). The lower peak did not exhibit consistently reliable experimental variation, e.g., its intensity in Fig. 3 is anomalously high, and so we concentrate on the upper peak. The upper peak energy, however, is higher than the calculated value by 7%. No sufficiently large systematic error in energy calibration or measured angles could be located to explain the discrepancy, which led us to question the single-event, binary collision scenario of Eq. (1). The true scattering angle of Fig. 3 appeared to be 2°-3° less than the presumed 25°. Adding support to this possibility are the α-scan data.

Figure 4 is a representative α scan of $^4He^+/D$(ads) scattering intensity versus angle, α, taken at the preferred θ = 25° angle. From several sets of data, the upper maximum occurs at 76.5° ± 2°; the lower maximum was consistently about 3° higher for reasons we have not as yet explored. Two questions arose: 1) Why should the α plot be peaked in a well defined maximum at α = 76.5° ±2°? 2) Why is the upper energy in Fig. 3 higher than expected? Shadow cones provide a single unified answer to both questions and, further, give atomic locations.

Figure 5 is a shadow-cone plot of 1-keV $^4He^+$ scattered by ^{106}Pd by a ZBL potential and ZBL screening.[8] The plot is superimposed on the Pd(331) "up the staircase" geometry in the experimental {110} plane of incidence at 8° below the (111) terrace, that is, α = 76° from the surface normal corresponding approximately to Fig. 4. At this α angle, the cone edge intersects surface Site 2 of Fig. 2, and passes 1°-2° below position 3 with greatly enhanced $^4He^+$ flux at an energy within 1 eV of E_0. By this simple construct, the observed α = 76.5° ±2° peak position of Fig. 4 is explained quantitatively by D occupancy at Sites 2 or 3. The shadow cone also has a strong implication for the upward shift of E/E_0 of the upper peak in Fig. 3.

A close examination of the shadow cone of Fig. 5 reveals that the cone boundary as it crosses Site 2 is almost, but not quite, parallel to the incident beam direction; the cone diameter is still expanding and the edge is at a small angle of ~1° to the incident ions. The $^4He^+/D$ scattering angle is lowered from 25° by that amount which in turn raises the calculated energy ratio to ~0.67 which agrees with the observed value.

The shadow cone edge passes over Site 1 at α ≈ 70° which is below the range of observed values. The major reason the $^4He^+/D$ (Site 1) scattering event is not observed is that the scattered trajectory directly intersects Pd atoms in the next row up. Consequently, Site 1 even if occupied would not be detected in the present set of experiments. To complete the full examination of all such possible sites, azimuthal scattering data, e.g., parallel to the <110> ledges, would be needed. Studies of other vicinal surfaces would be invaluable.

Sites 2 and 3 both satisfy the geometrical constraints imposed by Figs. 3, 4 and 5. It is interesting to consider an argument based upon covalent radii which favors Site 2. Covalent radii are Pd - 1.28Å; H - 0.32Å; the sum is 1.60Å. D may differ slightly from H due to different zero-point energies but not enough to alter our conclusions. The metallic Pd-Pd distance along the <110> chains in Fig. 2 is 2.743Å which does not leave enough space for a co-linear, covalent D configuration. For quasi-threefold Site 2, the unrelaxed crystallographic Pd-D separation is 1.58Å, which is close to the sum of 1.60. From our data we do not, of course, claim to locate D precisely within the (111) terrace plane or above it closer than a few tenths of an Å.

In conclusion, $^4He^+$/D(ads) forward scattering data have located D adsorption symmetry sites on the Pd(331) stepped surface. The results favor surface positions directly above the bulk octahedral void sites.

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Figure Captions

1. "Up-the-staircase" scattering geometry for 1 keV $^4He^+$ in the {110} plane of incidence on stepped Pd(331). The angle of incidence, α, is measured relative to the (331) surface normal; θ is the laboratory scattering angle. $^4He^+$ beam comes in 8° below the (111) terrace plane.

2. Hard sphere model of Pd(331). The incident beam is perpendicular to the <110> ledge. Possible adsorption Sites 1, 2 and 3 are marked.

3. Energy distribution of 1 keV $^4He^+$ scattered from Pd(331)/D(ads). α = 77.5°, θ = 25°, sample T. -185°C, P(D_2): 2.7 x 10^{-4} Pa, 325 nA incident beam current. Vertical scale is log_{10} of signal counts normalized by incident beam ion dose (0.5 μC/channel). Dashed curve: cleaned Pd(331) without D.

4. Alpha scan of $^4He^+$/D(ads) scattering intensity versus angle of incidence, α, for scattering angle θ = 25°.

5. ZBL shadow-cone plot for 1 keV $^4He^+$/^{106}Pd superposed on the Pd(331) "up the staircase" direction. The cone edge shown here intersects adsorption Site 2 at α = 76°.

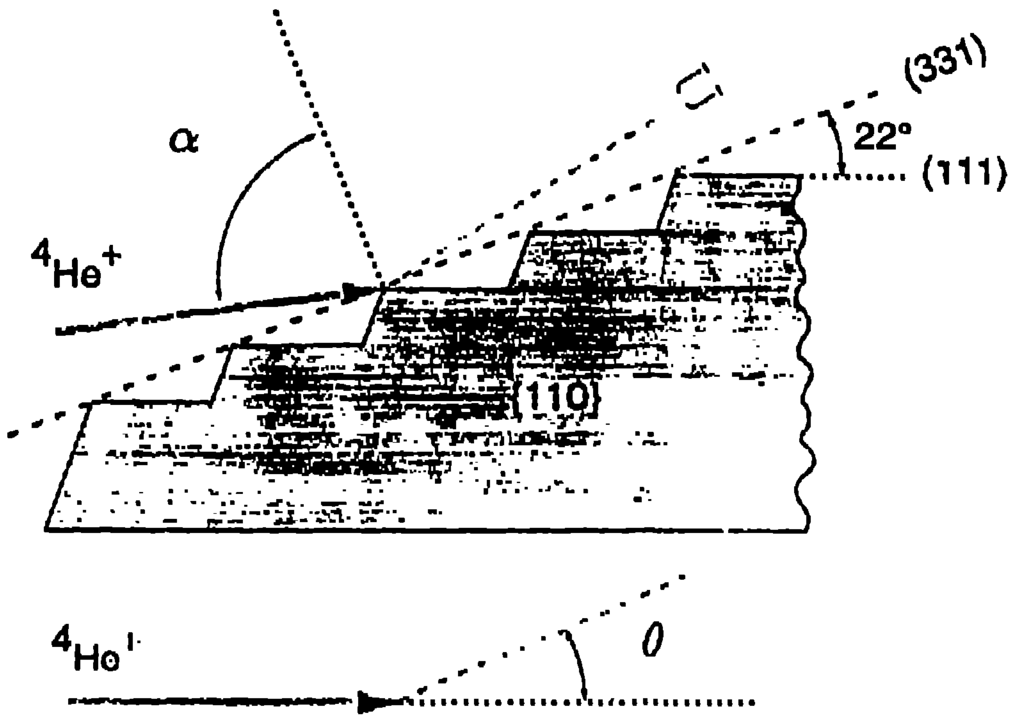

Figure 1

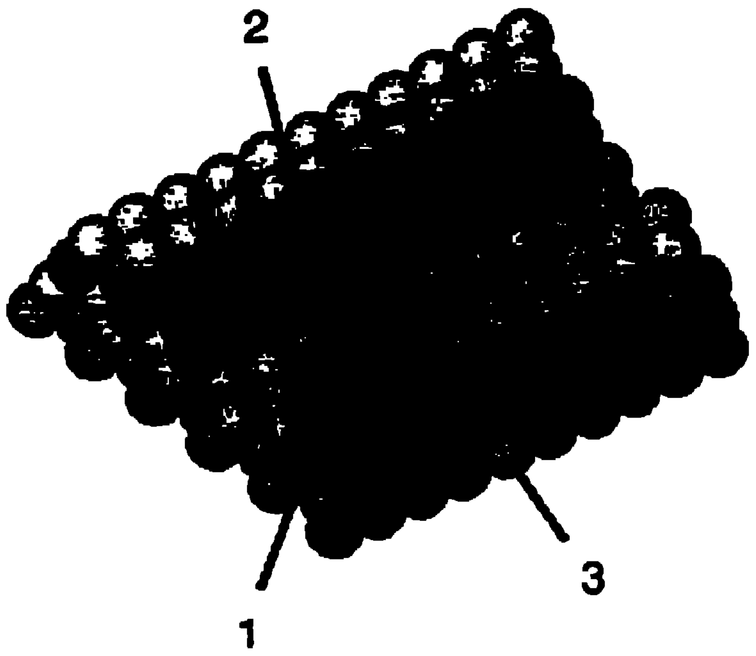

Figure 2

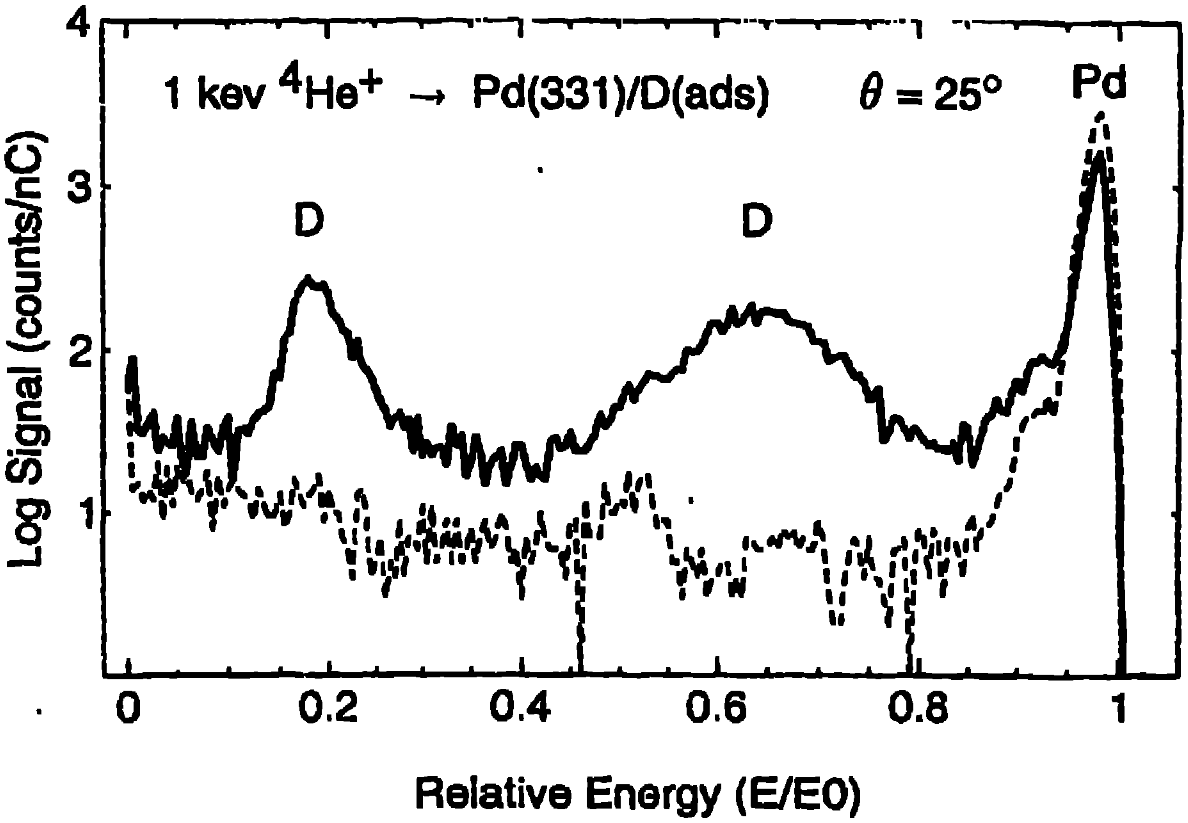
1 kev $^4He^+$ → Pd(331)/D(ads)
$\theta = 25°$
Pd
D
D
Log Signal (counts/nC)
Relative Energy (E/E0)
0
0.2
0.4
0.6
0.8
1
1
2
3
4

Figure 3

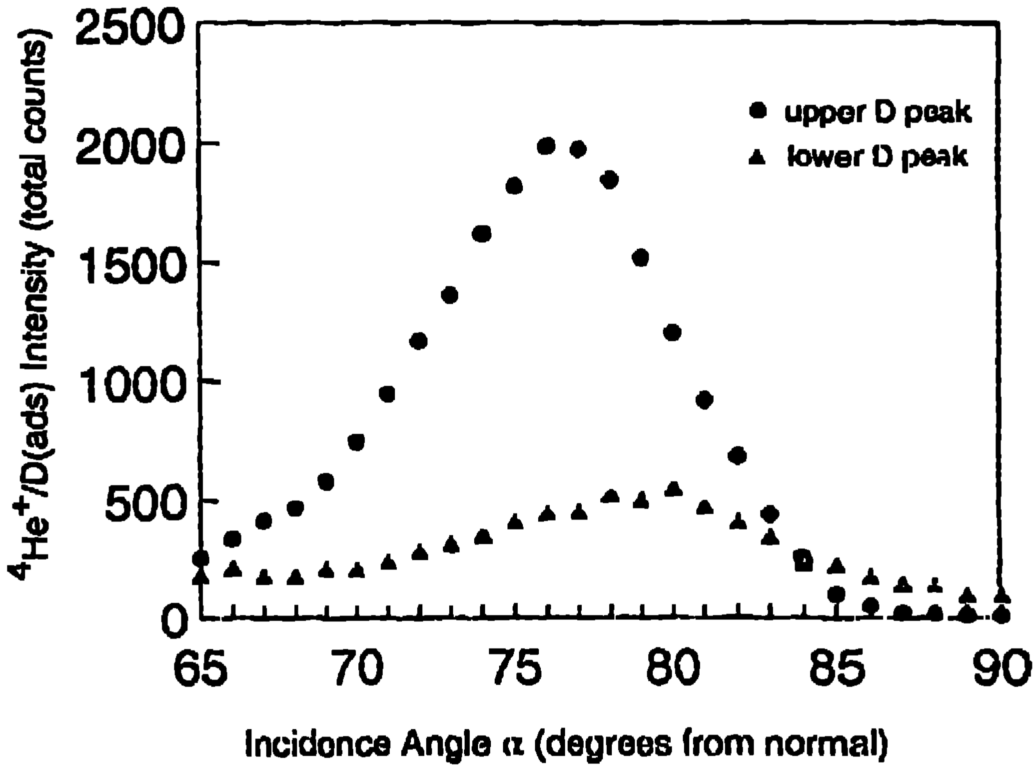
2500
2000
1500
1000
500
0
65
70
75
80
85
90
upper D peak
lower D peak
4He+/D(ads) Intensity (total counts)
Incidence Angle α (degrees from normal)

Figure 4

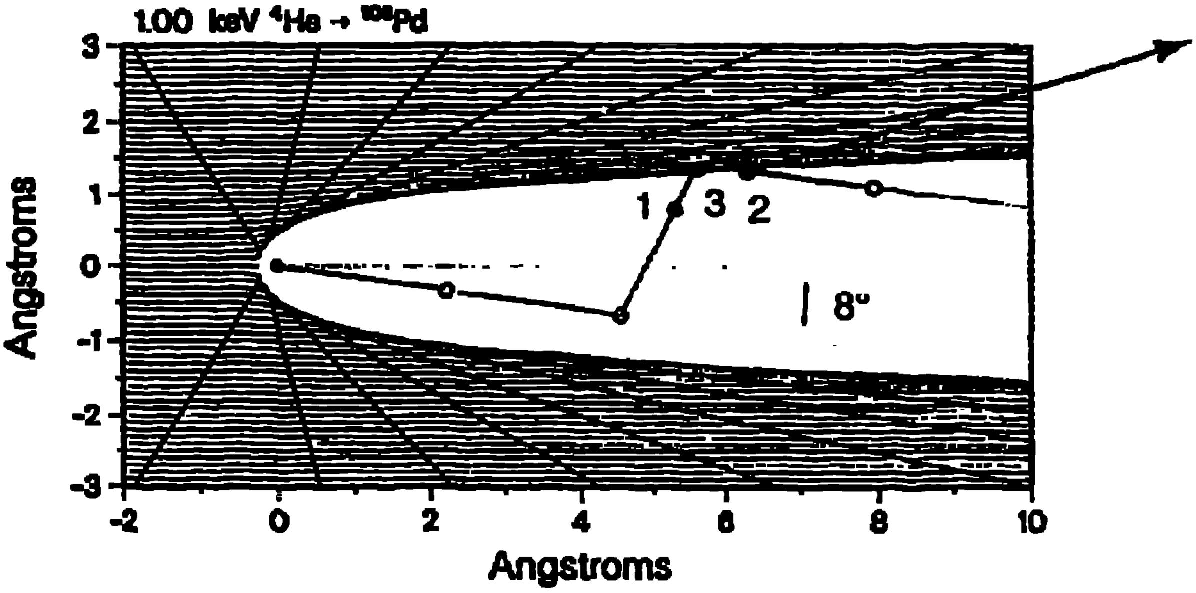
1.00 keV ⁴He → ¹⁰⁶Pd
Angstroms
Angstroms
1
3
2
8°
3
2
1
0
-1
-2
-3
-2
0
2
4
6
8
10

Figure 5