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MOLECULAR BEAM STUDY OF HYDROGEN-DEUTERIUM EXCHANGE ON LOW AND HIGH MILLER INDEX PLATINUM SINGLE CRYSTAL SURFACES

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MOLECULAR BEAM STUDY OF HYDROGEN-DEUTERIUM EXCHANGE ON LOW AND HIGH MILLER INDEX PLATINUM SINGLE CRYSTAL SURFACES*

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ABSTRACT

The hydrogen-deuterium exchange reaction takes place readily on a platinum single crystal with high Miller index (997), but not detectably on a platinum single crystal of low Miller index (111). The difference in reactivity is ascribed to the large density of atomic steps present on the high index surface that are responsible for the dissociation of the diatomic molecules.

The dissociation of hydrogen on solid surfaces is an initial step in many important surface reactions.[1] Hydrogen dissociation can be conveniently studied by monitoring the hydrogen-deuterium exchange reaction

$$H_2 + D_2 \xrightarrow{\text{surface}} 2HD$$

taking place in the presence of the surface. The scattering of a mixed hydrogen-deuterium molecular beam from the solid surface can be a particularly useful technique to investigate the surface

dissociation mechanism of hydrogen.

Molecular beam scattering studies have shown that this exchange reaction takes place readily on Ni(111) and Pt(111) oriented thin films.[2,3] Classical studies have shown that the reaction takes place readily on a variety of polycrystalline solid surfaces.[4] On the other hand, the formation of HD, indicating hydrogen dissociation, was not readily detected during molecular beam scattering studies from the (100) single crystal face of platinum.[5] It is apparent from these contradictory results that the polycrystalline and thin film surfaces contain surface sites that are responsible for dissociation, while the single crystal surface does not. In order to verify the nature of surface sites where dissociation of the hydrogen molecules occurs we have studied the hydrogen-deuterium exchange on the (111) face of platinum and on the (997) high Miller index face of platinum. This high Miller index face is characterized by an ordered arrangement of atomic steps (of one atom height) separated by atomic terraces of (111) orientation and nine atoms wide.[6] The two crystal faces differ only in the density of atomic steps.

A schematic diagram of the experimental apparatus[7] is shown in Fig. 1. The incident molecular beam is modulated by a variable frequency chopper and then scattered from the crystal surface, whose surface geometry and chemical composition are monitored by low energy electron diffraction and auger electron spectroscopy. The crystal surface is cleaned by heating in an ambient of 10^{-5} Torr O_2 and is kept clean by operating the scattering chamber at contaminating gas pressures below

10^{-9} Torr. The species scattered or desorbed from the surface are detected by a quadrupole mass spectrometer as a function of angle from the surface normal. The exchange reaction is followed by measuring the modulated HD signal as a function of scattering angle and surface temperature by lock-in detection. The experiments were performed both with a mixture of hydrogen and deuterium in the incident beam, and also with a pure deuterium beam scattered from the crystal in a hydrogen ambient ($\sim 10^{-8}$ Torr). All of the experiments reported here were from surfaces free of contamination as indicated by the auger spectra.

The scattering distributions of the reactants (H_2 and D_2) and the product (HD) are shown for the two crystal faces in Fig. 2. The distribution is broadened and has its maximum at the specular angle for hydrogen and deuterium from both crystal surfaces. The scattering distribution is much broader for the stepped surface than for the (111) surface, however, and the maximum intensity at the specular angle is lower. No hydrogen deuteride signal was detected from the (111) surface for any surface temperature between 300°K and 1000°K or for any angle from the surface normal. Hydrogen deuteride is readily detected, however, from the stepped surface over this temperature range. The angular distribution of the hydrogen deuteride leaving the stepped surface is shown in Fig. 3 with the scale expanded. The distribution is seen to be cosine-like. Integration of the deuterium and hydrogen deuteride angular distributions indicates that between 5% and 10% of the incident deuterium beam is converted to hydrogen deuteride at a surface temperature of 1000°K.

In conclusion, we have detected the formation of hydrogen deuteride on scattering mixed hydrogen-deuterium beams from the stepped surface and on scattering deuterium from the stepped surface in a hydrogen ambient. Under identical experimental conditions, no hydrogen deuteride was seen to form at the (111) single crystal surface. The angular distribution of the hydrogen deuteride desorbed from the stepped surface is cosine-like, indicating that the hydrogen deuteride has come to thermal equilibrium with the surface prior to desorption.

Studies of the exchange at modulation frequencies as low as 40 Hz have shown large hydrogen deuteride phase lags. These studies, which are still in progress, indicate that the hydrogen deuteride molecule must have a surface lifetime of the order of milliseconds.

The observation that hydrogen deuteride is readily formed on the stepped surface and is not detectable on the (111) surface indicates that the dissociation of hydrogen takes place at the atomic steps on the surface. These results also explain why hydrogen deuteride is formed readily on polycrystalline and thin film metal surfaces while the exchange could not be readily detected on low Miller index (low step density) single crystal surfaces. More experiments are underway to explore the detailed mechanism of the surface exchange reaction.

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*This work supported by United States Atomic Energy Commission.

†N.S.F. Predoctoral Fellow

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4. J. C. Bond, Catalysis by Metals, (Academic Press, New York, 1962).
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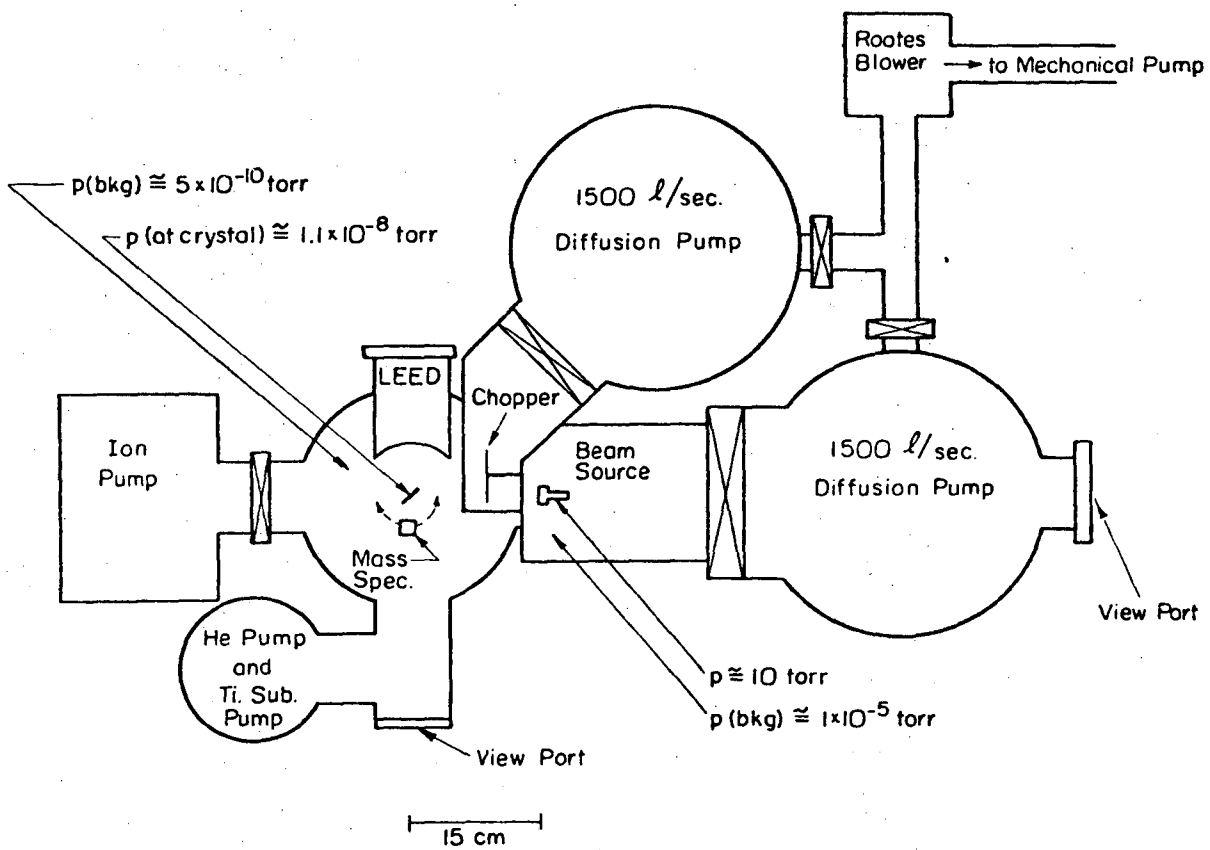
FIGURE CAPTIONS

Fig. 1. Molecular Beam Surface Scattering Apparatus

Fig. 2(a). Angular distribution of H_2 and D_2 scattered from D + (111). Heavy arrow indicates angle of incidence. Schematic of surface shown above.

Fig. 2(b). Angular distribution of H_2, D_2 and HD scattered from the stepped platinum crystal surface. Schematic of surface shown above.

Fig. 3. Angular distribution of HD scattered from the stepped surface as in Fig. 2(b) with scale expanded. Heavy arrow indicates angle of incidence.



MOLECULAR BEAM SURFACE SCATTERING APPARATUS

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Fig. 1.

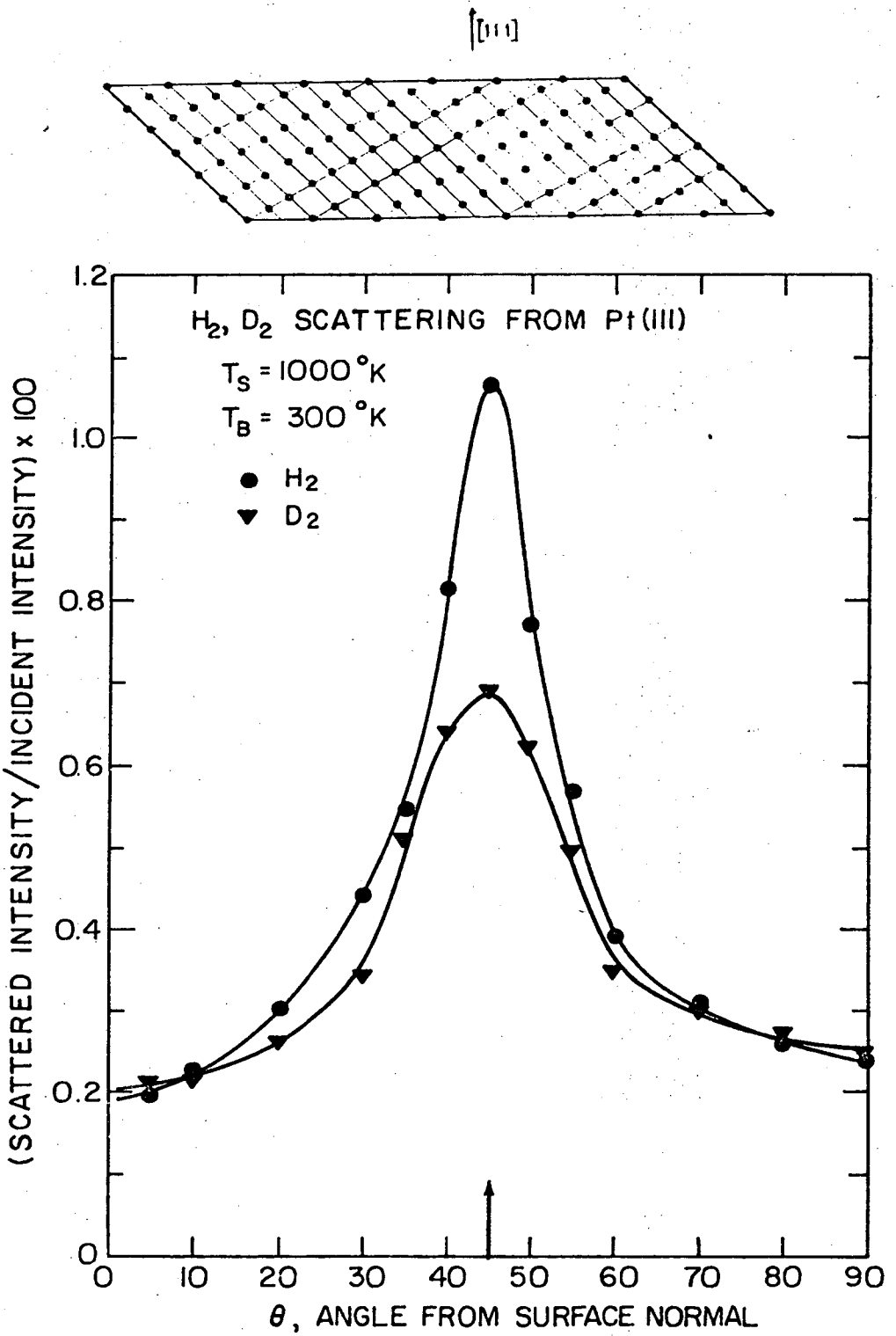

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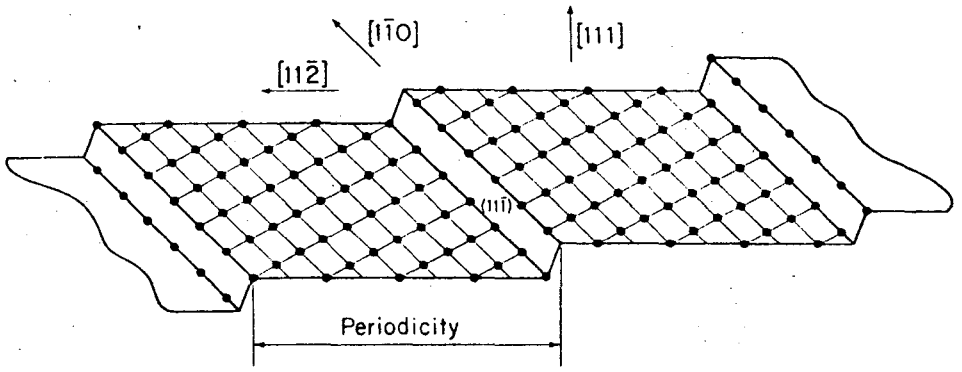
Fig. 2.



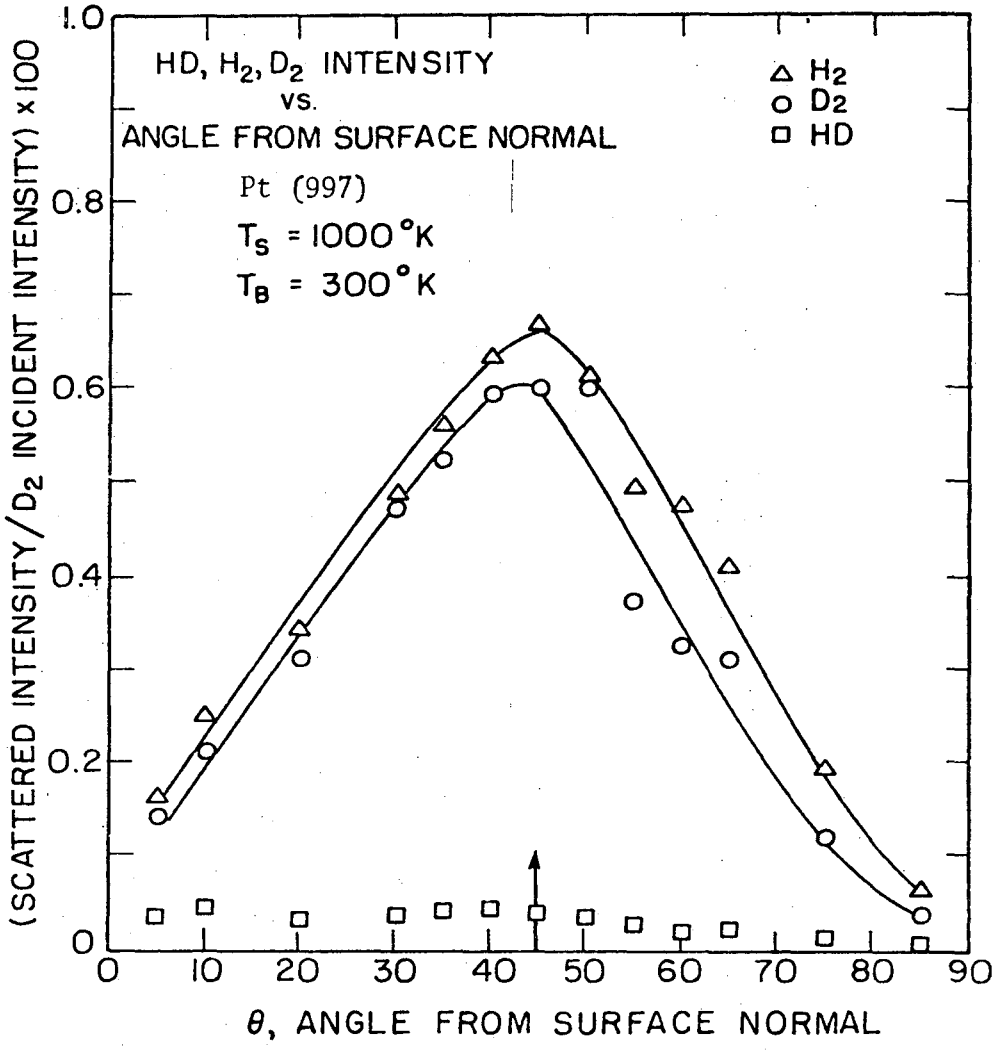


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Fig. 3.

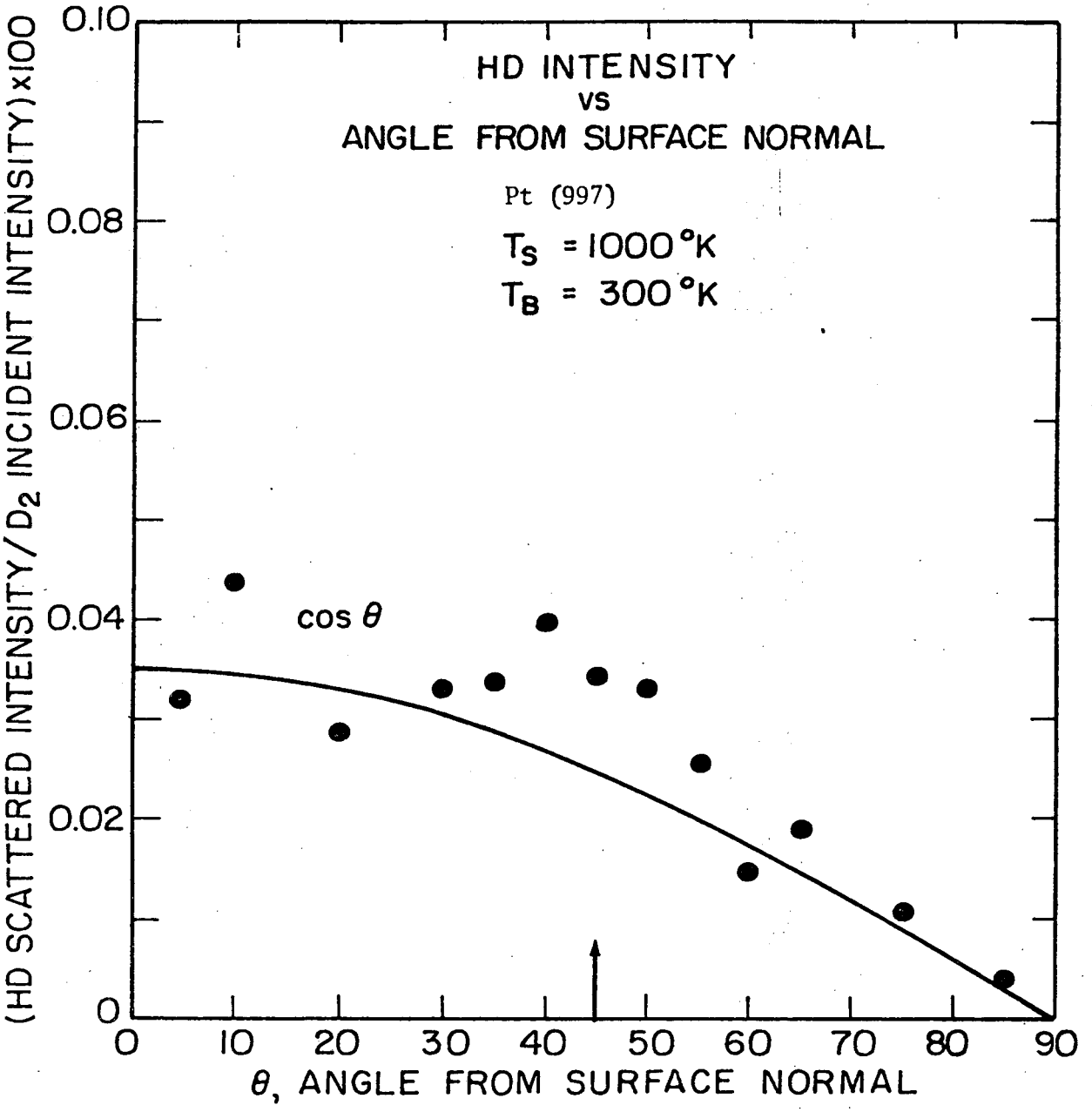

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Fig. 4.

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