

# Friction Anisotropy at Pd(100)/Pd(100) Interfaces

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Friction anisotropy was studied between two Pd(100) single-crystal surfaces sliding in an ultrahigh vacuum environment. Friction measurements were made using Pd(100)/Pd(100) interfaces modified by adsorption of octane at coverages ranging from 4 to 40 molecular monolayers (ML). The relative crystallographic orientation of the two Pd(100) surfaces was systematically varied and friction measurements were made at each orientation as a function of octane coverage. These measurements have revealed that friction is anisotropic with respect to Pd(100) lattice orientation. When the surfaces were aligned, forming a commensurate interface, and sheared along the  $\langle 110 \rangle$  direction with 4 ML of octane at the interface, the static friction coefficient was  $\mu_s > 8.0 \pm 2.0$ . A minimum in the static friction coefficient was obtained when the two Pd(100) surfaces with 4 ML of octane at the interface were misoriented by  $\theta = 45^\circ$ . Under these conditions, the static friction coefficient for sliding along the  $\langle 110 \rangle$  direction of the stationary surface was  $\mu_s = 4.0 \pm 2.0$ . Higher coverages of octane decreased the friction, but friction anisotropy persisted for coverages of octane up to 20 ML at the interface. Wear scars were observed on both surfaces indicating that plastic deformation occurred during sliding. The observation of friction anisotropy in the presence of disordered overlayers of octane and during shearing of surfaces that deform plastically suggests that friction anisotropy originates with the properties of the bulk crystal lattices rather than surface lattice commensurability. These results corroborate the findings of a previous study of friction anisotropy between Ni(100) surfaces (*Langmuir* 2000, 16(22), 8343).

## 1. Introduction

Friction anisotropy is defined as the dependence of friction on the relative orientation of two crystalline surfaces forming a solid–solid interface. It is not easily observable in most engineering applications but is a fundamental tribological phenomenon. New and emerging technologies such as microelectromechanical systems require precise control of friction at the atomic or molecular level because lubricating films and coatings used in these applications are typically only a few molecular layers in thickness.<sup>1,2</sup> Friction between surfaces in sliding contact is dependent on the structure of the surfaces and their orientation with respect to one another and with respect to the sliding direction. Friction anisotropy can be studied either by varying the shearing direction of two surfaces at a fixed relative orientation or by fixing the shearing direction and varying the relative crystallographic orientation of the two surfaces. Both have been used extensively to explore the origins of friction anisotropy.<sup>3–12</sup>

The work described in this paper investigates the effect on friction of the relative lattice orientation of two identical single crystalline surfaces in sliding contact.

Two surfaces brought into contact with one another undergo either elastic or plastic deformation. The origins of friction anisotropy under these two conditions are likely to be quite different. Under conditions of elastic deformation, there is no permanent change of the contacting surfaces as a result of bringing them in and out of contact. In this case, it has been suggested that surface lattice commensurability, or alignment of the surface atomic lattices with respect to one another, is the primary cause of friction anisotropy.<sup>6–9,13,14</sup> Plastic deformation occurs when there is a permanent, irreversible change of one or both of the surfaces during sliding contact. Metal surfaces typically undergo plastic deformation under all conditions of contact. Studies of friction anisotropy between plastically deforming surfaces of single crystalline metals have suggested that surface lattice commensurability effects are not the primary cause of friction anisotropy. Instead, it is the bulk properties of the crystal lattices such as the orientation of slip planes or anisotropy of the bulk mechanical properties that leads to friction anisotropy.<sup>3–5,15</sup> Much work has been done to identify and differentiate the possible origins of friction anisotropy; however, no one theory yet explains or predicts all observations.

A recent study by Ko and Gellman delved into the issue of friction anisotropy by measuring friction between two Ni(100) single-crystal surfaces prepared to be truly clean in an ultrahigh vacuum (UHV) environment.<sup>3</sup> The relative misorientation angle between the Ni(100) surface lattices was varied while measuring the friction forces during sliding along a fixed direction. A marked decrease in friction occurred when the crystals were misoriented by  $45^\circ$ . That study examined friction at several misorientation

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angles and used surfaces modified by adsorbed sulfur and ethanol. At a misorientation angle of  $45^\circ$ , the static coefficient of friction was approximately 50% lower than at all other misorientation angles. This friction anisotropy was unchanged by the presence of thin films of adsorbed ethanol. The presence of wear scars on the Ni(100) surfaces indicated that the conditions of sliding contact led to plastic deformation of the near-surface region during sliding. This led to the suggestion that friction anisotropy was predominantly caused by the movement of atomic slip planes in the bulk of the crystal and was not due to surface lattice commensurability. That study was the first to examine friction anisotropy between single-crystal metal surfaces sliding under conditions of plastic deformation in the controlled environment of a UHV apparatus.

Several research groups have studied friction anisotropy between surfaces sliding under conditions in which plastic deformation of one or both of the surfaces occurred. In one such study, Enomoto and Tabor used a diamond stylus sliding across the surface of a diamond(100) single crystal.<sup>4</sup> Sliding occurred more easily along the  $\langle 100 \rangle$  direction than along the  $\langle 110 \rangle$  direction. The wear tracks formed during sliding exhibited different characteristics after sliding in the different directions in the sense that more surface cracking and pit formation was observed when sliding along some directions than others. At very small loads when plastic deformation was not observed, the friction anisotropy disappeared. Enomoto and Tabor claimed that the friction anisotropy observed when the contact pressure exceeded some critical value was due to surface and subsurface damage produced in preferred crystallographic directions by the sliding process. In another tribological study under conditions of plastic deformation, Martin and co-workers investigated the superlubricity of molybdenum disulfide ( $\text{MoS}_2$ ) coatings.<sup>5</sup> Using a UHV reciprocating pin-on-flat tribometer, they found that friction decreased by an order of magnitude and was reduced to the noise level of their measurement after seven cycles of sliding. This apparent vanishing of the friction force was attributed to friction anisotropy of the low-energy basal planes of the  $\text{MoS}_2$  grains which were oriented by intercrystallite slip. In other words, sliding induced misoriented  $\text{MoS}_2$  grains to reorient and align along the sliding direction. These studies illustrate that friction anisotropy can be observed between surfaces that undergo plastic deformation during sliding contact.

In addition to studies of friction anisotropy under conditions of plastic deformation, there are many studies that have explored the origins of friction anisotropy between elastically interacting surfaces. Perhaps one of the most well studied systems is that of two mica surfaces interacting elastically in a crossed-cylinder configuration in a surface forces apparatus.<sup>6,13,14</sup> Israelachvili and McGuiggan measured adhesion and friction forces between mica surfaces with water present at the interface.<sup>6</sup> They found that both friction and adhesion forces were dependent on the orientation of the two surfaces, with the highest forces occurring when the surface lattices were aligned. Misorientation of the surface lattices by just  $\pm 1^\circ$  resulted in a 50% decrease in the adhesion force. These effects extended through four molecular layers of liquid at the interface. Hirano and co-workers studied the static and dynamic friction forces between mica single crystals as a function of the lattice misfit angle.<sup>7</sup> They found friction to be anisotropic with respect to the lattice misfit, or misorientation angle, with a minimum occurring at  $30^\circ$  and an increase when rotating toward  $0^\circ$  or  $60^\circ$ . The friction versus misorientation angle had sixfold symmetry which reflected the pseudo-hexagonal symmetry of the mica

cleavage surfaces. Hirano and co-workers attributed this friction anisotropy to the commensurability between contacting lattices. In another study with surfaces under elastic contact, Sheehan and Lieber used an atomic force microscope to characterize the sliding of molybdenum oxide ( $\text{MoO}_3$ ) nanocrystals on single-crystal  $\text{MoS}_2$  surfaces.<sup>8</sup> They observed lattice-directed sliding in which the  $\text{MoO}_3$  nanocrystals moved only along specific directions of the  $\text{MoS}_2$  surface lattice indicating that friction was highly anisotropic. The friction anisotropy observed in those studies suggests that the orientation or commensurability of surface lattices plays an important role in friction under conditions of elastic contact.

In addition to experimental investigations, friction anisotropy has been studied through the use of simulations and modeling. He, Muser, and Robbins used molecular dynamics simulations to investigate the origins of static friction between surfaces modified by adsorbed layers of Lennard-Jones atoms.<sup>9</sup> Their investigation found that friction is similar at incommensurate interfaces between the surface lattices but higher for the special case of a commensurate interface. Depondt, Ghazali, and Lévy also used molecular dynamics simulations to study friction.<sup>10</sup> Their simulation system was composed of a single layer of adsorbate deposited on the (001) surface of an fcc substrate. The friction force was strongly anisotropic. Rajasekaran, Zeng, and Diestler performed a study of friction anisotropy using a statistical thermodynamic description of the atomic force microscope experiment, with a single-atom tip sliding over a hexagonal close-packed substrate under constant load.<sup>11</sup> They found that static friction forces are highly anisotropic, and furthermore they found that there is a particular sliding direction in which friction is extremely low. Finally, in a report by Sokoloff, molecular dynamics simulations were used to calculate the friction force generated at an incommensurate interface between two crystalline surfaces.<sup>12</sup> The friction force at an incommensurate interface was 13 orders of magnitude lower than that at the commensurate interface. These simulation and modeling studies have provided further insight into the anisotropic nature of sliding surfaces.

We have studied friction anisotropy between Pd(100) surfaces under the highly controlled conditions of a UHV chamber in an effort to corroborate findings of our previous study using Ni(100) surfaces.<sup>3</sup> The dependence of friction on the relative misorientation of crystalline surface lattices was systematically studied between Pd(100) single crystals in the presence of thin layers of octane and under conditions of plastic contact. Friction was anisotropic with respect to the relative misorientation angle between the crystals and exhibited the same anisotropy as was observed between the Ni(100) surfaces. In essence, we have matched the conditions of the previous study by Ko and Gellman and have corroborated their observations of friction anisotropy between face-centered cubic (100) surfaces under conditions of plastic deformation.

## 2. Experimental Section

**2.1. Ultrahigh Vacuum Chamber and Tribometer.** All experiments were conducted in a stainless steel UHV chamber with a base pressure below  $10^{-10}$  Torr achieved through the use of a Varian StarCell 400 ion pump and supplemented by a water-cooled titanium sublimation pump. The UHV chamber is equipped with a variety of instruments for in situ surface preparation and analysis. These include a quadrupole mass spectrometer, low-energy electron diffraction (LEED) optics, an  $\text{Ar}^+$  ion sputter gun for surface cleaning, and leak valves for introduction of gases or vapors into the chamber. In addition to

these instruments, the chamber is equipped with a unique UHV tribometer for the measurement of friction between pairs of highly characterized surfaces, both of which have been subjected to the same preparation and analysis procedures.

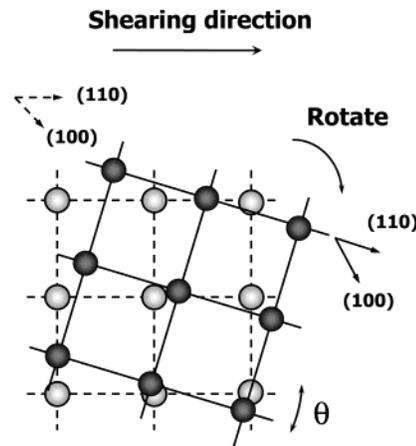
Two Pd(100) single crystals, purchased from Monocrystals Inc. with 1-cm nominal diameter, were mechanically polished to a mirror finish using diamond and alumina pastes. One sample was polished to have a radius of curvature of  $\sim 4$  cm while the other was polished to be flat. This ensures that there are no edge contacts during a friction measurement and that the surfaces interact in a pin-on-flat configuration. Topography measurements using an atomic force microscope revealed an rms roughness value of approximately 8 nm, with a maximum  $\Delta z$  (peak-to-valley) value of 80 nm. The curved sample was spot-welded between two tantalum wires at the end of a UHV manipulator. The manipulator allows motion in the  $x$ ,  $y$ , and  $z$  (vertical) directions as well as rotation about the vertical axis of the chamber. Motion in the  $x$  and  $y$  directions was controlled using motorized micrometers capable of speeds from 0.5 to 200  $\mu\text{m}/\text{sec}$ . The sample could be heated resistively to  $T > 1000$  K and cooled to  $T < 100$  K through mechanical contact with a liquid nitrogen reservoir. Temperatures were measured using a chromel–alumel thermocouple junction spot-welded to the back of the curved Pd(100) sample.

The second, flat Pd(100) crystal used in the friction measurements was spot-welded between two tantalum wires and mounted in a copper frame which was clamped onto the UHV tribometer. This tribometer allows the simultaneous, real-time measurement of both normal and shear forces at the interface formed when the manipulator crystal is brought into contact with and sheared relative to the stationary tribometer crystal. A brief description of the UHV tribometer will be given here as a more detailed description has been published previously.<sup>16</sup> The tribometer crystal can be heated to  $T > 900$  K by electron bombardment from a thoriated tungsten filament located behind the crystal and can be cooled to  $T \sim 120$  K by mechanical contact with a liquid nitrogen reservoir. The temperature was measured with a chromel–alumel thermocouple spot-welded to the edge of the crystal.

The response of the tribometer to an applied force was calibrated outside the UHV chamber over a force range of 5–250 mN using weights of known mass. Both normal and shear forces were individually calibrated and the responses were linear over the calibration range. After installing the tribometer into the UHV chamber, the samples were aligned optically to ensure that their surface normals were parallel. They were also positioned such that the sliding motion of the manipulator sample was parallel to the surface of the tribometer sample. Friction measurements were made by first bringing the curved, manipulator sample into contact with the flat and fixed tribometer sample under a load of  $F_N \approx 25$  mN. The samples were held in contact for a few seconds before the manipulator sample was sheared against the tribometer sample at a constant speed of  $v_s = 20$   $\mu\text{m}/\text{sec}$ . Normal and shear forces ( $F_N$  and  $F_S$ ) were measured simultaneously over a sliding distance of 600–800  $\mu\text{m}$ . The samples were then separated and the manipulator sample moved slightly by a rotation of  $\pm 1.5^\circ$  from the normal and by raising or lowering  $\pm 2$  mm before making another contact. This ensured that each single-pass friction measurement occurred with contact at different points on the sample surfaces. At least 12 single-pass friction measurements were performed at any given set of experimental conditions to obtain a statistically meaningful measure of the friction coefficient,  $\mu = F_S/F_N$ .

## 2.2. Pd(100) Surface Preparation and Characterization.

Prior to any friction measurements, both Pd(100) samples were cleaned in vacuo under identical conditions. Multiple cycles of annealing and Ar<sup>+</sup> ion sputtering were employed to remove surface atmospheric contaminants and surface oxidation. The surfaces were then annealed to  $T = 1000$  K in  $5 \times 10^{-6}$  Torr of oxygen exposed to the surface through a doser. This oxygen treatment was used to remove carbon which reacts with the oxygen and desorbs as CO or CO<sub>2</sub>.<sup>17–20</sup> The surfaces were finally



**Figure 1.** Schematic illustration of the contact geometry between the Pd(100) surfaces on the manipulator and on the tribometer. The manipulator sample (filled circles) is rotated by misorientation angle ( $\theta$ ) with respect to the fixed tribometer sample (open circles). The shearing direction is always along the  $\langle 110 \rangle$  direction of the fixed tribometer sample.

annealed to  $T = 1000$  K for 15 min to generate ordered crystalline surfaces. Surface cleanliness was verified using several methods. First, molecular oxygen was adsorbed onto the clean surface at various temperatures and temperature-programmed desorption (TPD) experiments were performed. On the clean Pd(100) surface, oxygen ( $m/q = 32$ ) desorbed at  $\sim 800$  K while no significant CO or CO<sub>2</sub> formation was observed. Next, sharp LEED patterns were obtained indicating that the surface was well ordered. Finally, the surfaces were exposed to molecular oxygen which has been shown to form an ordered  $c(2 \times 2)$  overlayer on the clean Pd(100) surface.<sup>21</sup> The  $c(2 \times 2)$  overlayer was observed using LEED following exposure at room temperature to 10 L ( $1 \text{ L} = 1 \times 10^{-6}$  Torr·sec) of oxygen from a doser. This overlayer was then desorbed by heating to 1000 K to leave a clean, ordered Pd(100) surface.

Octane was used as a thin-film lubricant. The octane was purified by several freeze–pump–thaw cycles to remove condensed gases until no contaminants were detected using mass spectrometry. Octane was then adsorbed onto the clean Pd(100) surfaces by filling the chamber with octane vapor introduced to the system through a leak valve. The two samples were positioned in the chamber such that they received equal exposures to octane. Exposures were measured in Langmuirs with pressures uncorrected for ion gauge sensitivity, and coverages were calibrated using TPD.

## 2.3. Determination of Surface Lattice Misorientation.

The relative misorientation angle of the Pd(100) samples was varied to study friction anisotropy. A schematic illustration of the contact geometry is shown in Figure 1. Laue diffraction was used to determine the surface lattice orientation of the flat Pd(100) sample and, once mounted on the tribometer, it was fixed in position and remained so for the duration of this study. The orientation of the tribometer sample was fixed with its  $\langle 110 \rangle$  direction along the sliding direction. Laue diffraction was also used to determine the orientation of the curved Pd(100) sample mounted on the manipulator. The lattice misorientation angle between the two samples was varied by removing the curved sample mounted on the manipulator, physically rotating and then remounting it. Within the UHV chamber, LEED was used to verify the initial orientation and the orientation after removal and remounting. The relative misorientation was defined as  $\theta = 0^\circ$  when the manipulator sample had its  $\langle 110 \rangle$  direction along the sliding direction and parallel to the  $\langle 110 \rangle$  direction of the sample on the tribometer. The relative misorientation angles chosen for this study were  $\theta = 0^\circ, 30^\circ, 45^\circ, 55^\circ, 75^\circ, 90^\circ$ , and  $135^\circ$ . Since palladium has a face-centered cubic bulk structure, the  $\langle 100 \rangle$  surface is a fourfold symmetric surface and, therefore, the

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0°/90° misorientation angles are degenerate, as are the 45°/135° misorientation angles.

### 3. Results

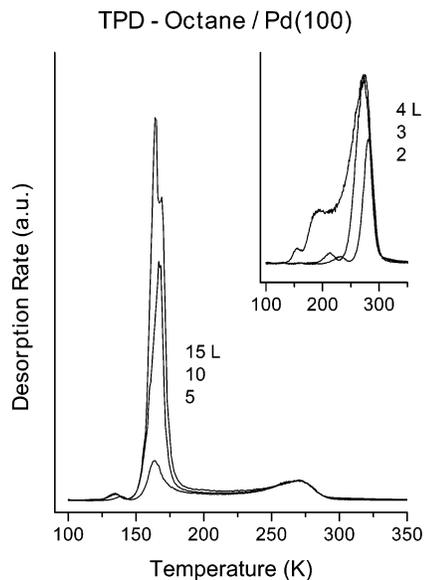
#### 3.1. Friction between Clean Pd(100) Surfaces.

Friction measurements were made first between the clean Pd(100) surfaces. In general, the measurement of friction between perfectly clean metal surfaces in UHV is difficult because the atoms of the metals interact with one another directly to form strong metallic bonds between the two surfaces. This phenomenon is known as cold-welding and can cause the two surfaces to stick together irreversibly. Even when cold-welding does not occur, friction is high, and adhesion is strong. Friction between the clean Pd(100) surfaces was immeasurably high at all misorientation angles. The surfaces stuck to one another during shearing until the shear forces reached the maximum value for which the tribometer had been calibrated. Sliding never occurred during shearing of the clean surfaces held at a misorientation angle of 45°. As a result, the maximum shear force,  $F_s$ , reached during shearing could only be used to estimate a lower limit on the static friction coefficient,  $\mu_s$ . When sliding at a misorientation angle of  $\theta = 0^\circ$  (lattices aligned), cold-welding occurred leaving the two Pd(100) crystals stuck together. At that point, the apparatus had to be disassembled and the samples had to be physically separated from one another and manually repolished. Following this incident, no further measurements of friction between clean Pd(100) surfaces were attempted.

**3.2. Octane Adsorption on Pd(100).** In this study of friction between Pd(100) surfaces and in the previous study using Ni(100) single crystals, friction has been measured with clean surfaces and with the surfaces modified by the presence of an adsorbate or lubricant. Octane was chosen for use as the lubricant in this study for several reasons. First, it is a small chain hydrocarbon which can adsorb and desorb reversibly from the Pd(100) surfaces without decomposing. Adsorption on a Pd(100) surface would cause the decomposition of an alcohol such as ethanol.<sup>22</sup> The second reason for choosing octane is that it is the smallest alkane which can adsorb to form multilayers on the Pd(100) surfaces within the achievable temperature range.

The coverage of octane on the Pd(100) surfaces was calibrated using TPD. The clean Pd(100) surfaces were exposed to octane vapor while being held in the same positions as would be used in exposures performed prior to friction measurements. The sample was then positioned in front of the mass spectrometer and heated at a constant rate (2 K/s) while monitoring the signal of the primary ionization fragment of octane ( $m/q = 43$ ). Desorption spectra of octane from the Pd(100) surfaces are shown for different exposures to octane in Figure 2. Following low exposures, the TPD spectra exhibit a single desorption peak at 273 K which saturates in intensity at an exposure of 3.25 L. This peak is associated with those octane molecules that are adsorbed directly onto the Pd(100) surfaces and form the first monolayer (ML). The area under the saturated high-temperature desorption peak was defined as that of the monolayer and was used to determine octane coverages above 1 ML. At high exposures, a second desorption peak appeared at 170 K arising from desorption of molecules forming the multilayer.

**3.3. Friction between Lubricated Pd(100) Surfaces.** Following the preliminary friction studies using clean Pd(100) surfaces, all experiments were conducted

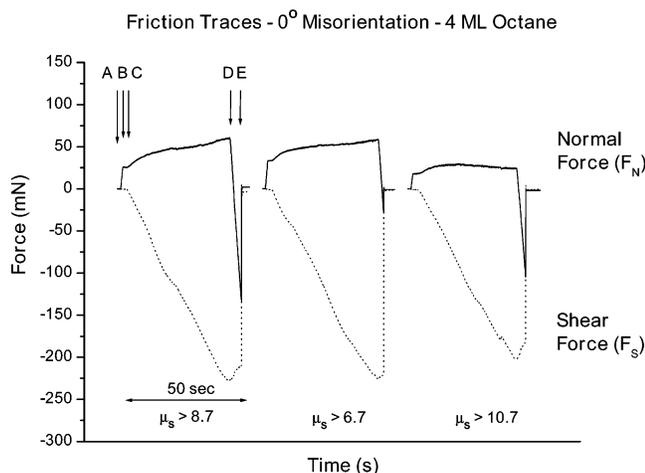


**Figure 2.** Temperature-programmed desorption spectra of octane on the Pd(100) surface. The inset shows the desorption spectra for low coverages on the surface. The exposure required to obtain one monolayer of adsorbed octane was 3.25 L (1 L =  $10^{-6}$  Torr·sec). Desorption of the monolayer occurs at  $T = 273$  K (inset) and desorption of the multilayer occurs at  $T = 165$  K. All octane coverages were determined relative to the area under the monolayer TPD spectrum. Heating rate = 2 K/s. Mass/charge = 43 ( $C_3H_7^+$ ).

with surfaces modified by the presence of adsorbed octane. Friction measurements were made with surfaces modified by five different coverages of octane ranging from 4 to 40 ML at the interface and at seven misorientation angles. Two sets of friction measurements will be described in detail, those made at lattice misorientation angles of 0° and 45°. The first set of measurements was made between samples which were aligned such that their surface lattices were commensurate and the lattice misorientation angle was 0°. The surfaces were first exposed to octane to give coverages of 2 ML on each surface and thus 4 ML at the interface formed when the surfaces were brought into contact. A total of 12 friction measurements were made between the samples under this set of conditions. Three typical single-pass friction versus time traces are shown in Figure 3. Referring to the first trace shown in Figure 3, friction measurements were obtained using the following sequence of steps. At point A, the surfaces were out of contact. The manipulator sample was brought into contact with the tribometer sample at point B, resulting in an increase in the normal force,  $F_N$ . Between points B and C, the surfaces were held in contact for a short period of time. At point C, the manipulator sample was sheared at a constant velocity relative to the stationary tribometer sample. This resulted in an increase of the shear force,  $F_s$ . The shear force continued to increase until movement of the manipulator sample was stopped at point D. At point E, the manipulator sample was separated from the tribometer sample and the shear and normal forces returned to zero. During separation of the two samples, a large, negative normal force was generated indicating a tensile stress at the interface. This negative pull-off force indicates intermetallic adhesion between the two samples. Adhesive forces were commonly observed when shearing with thin lubricant layers at the Pd(100)/Pd(100) interface.

With the two Pd(100) surfaces aligned at 0° misorientation and separated by only 4 ML of adsorbed octane, no sliding was observed during shearing. Instead, the shear force increased monotonically until it reached the limit to

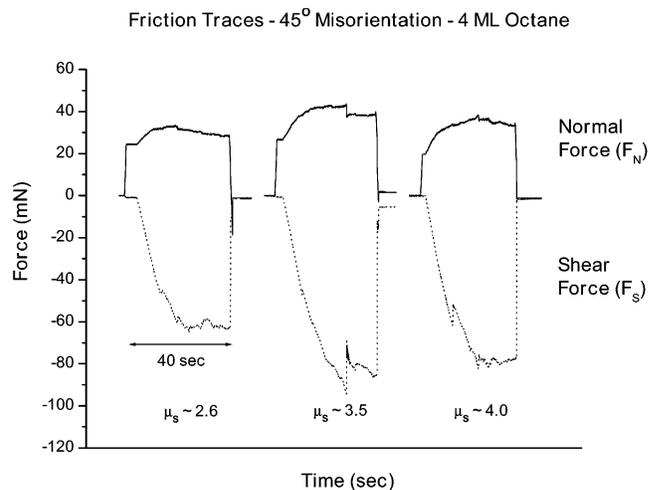
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**Figure 3.** Three randomly selected single-pass friction traces for measurements made between two Pd(100) surfaces lubricated by 4 ML of octane and aligned at  $0^\circ$ . The upper trace (solid line) is the applied normal force and the lower trace (dashed line) is the shear force during sliding. Friction for this set of conditions can be characterized as “stick”. No sliding occurred as can be seen by the steady increase of the shear force until shearing was terminated. High adhesion is also observed as indicated by the negative normal force as the surfaces were separated. Sliding conditions were  $F_N \approx 25$  mN,  $v_s = 20$   $\mu\text{m}/\text{sec}$ , and  $T \approx 120$  K.

which the tribometer had been calibrated. At that point, the force measurement was stopped and the surfaces were separated. Shearing was terminated at this point to prevent permanent damage to the tribometer. These measurements, therefore, yield only a lower limit for the static friction coefficient. Under these conditions of high friction and adhesion, friction coefficients were calculated by dividing the shear force at the point at which shearing was stopped by the applied load. The results of 12 such measurements yield a lower limit on the static friction coefficient of  $\mu_s < 8.0 \pm 2.0$ . The friction traces of Figure 3 are representative of all friction measurements made between Pd(100) surfaces lubricated with 4 ML of octane and at all misorientation angles other than  $45^\circ$  (and  $135^\circ$ ).

A set of friction measurements was made between the Pd(100) samples with the manipulator sample rotated by  $45^\circ$  with respect to the sample on the tribometer. As in the set of measurements made at a misorientation angle of  $0^\circ$ , both surfaces were modified by adsorption of 2 ML of octane. Figure 4 shows three typical single-pass friction traces measured during sliding under these conditions. There is an obvious difference between the traces obtained at  $45^\circ$  misorientation (Figure 4) and those obtained at  $0^\circ$  misorientation (Figure 3). The most notable difference is that sliding was achieved during shearing of the samples misoriented by  $45^\circ$  and the interaction between the surfaces can be characterized as “slip”. In other words, instead of increasing monotonically during shearing the friction force reached a maximum or steady state during shearing indicating slip at the interface. There were, however, a few instances of shearing at the  $45^\circ$  misorientation during which “stick” and “stick-slip” dominated the interaction between the surfaces. Stick-slip sliding is characterized by large fluctuations of the shear force during shearing. The behavior at  $45^\circ$  misorientation is in contrast to the behavior of the surfaces misoriented by  $0^\circ$  which can always be characterized as “stick”. For the samples misoriented by  $45^\circ$ , the friction coefficient was calculated by dividing the shear force at the onset of sliding by the applied load. This yielded an average static friction coefficient of  $\mu_s = 4.0 \pm 2.0$ . This average friction coefficient

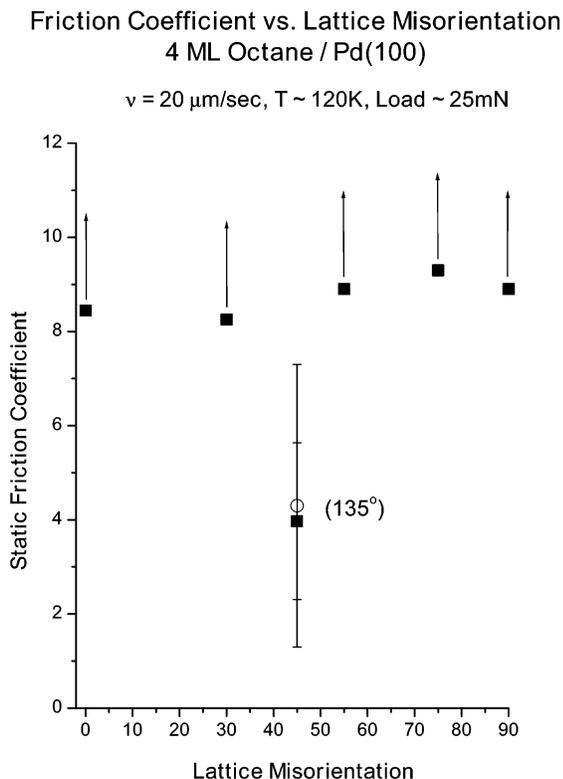


**Figure 4.** Three randomly selected single-pass friction traces for measurements made between two Pd(100) surfaces lubricated by 4 ML of octane and rotated to a misorientation angle of  $45^\circ$ . The upper trace (solid line) is the applied normal force and the lower trace (dashed line) is the shear force during sliding. Friction for this set of conditions can be characterized as “slip” or “stick-slip”. Sliding was initiated upon shearing and negligible adhesion occurred as the surfaces were separated. Sliding conditions were  $F_N \approx 25$  mN,  $v_s = 20$   $\mu\text{m}/\text{sec}$ , and  $T \approx 120$  K.

is half the value of the lower limit on the friction coefficient found for the commensurate samples misoriented by  $0^\circ$ . This is the first indication of friction anisotropy at the interface.

Friction measurements were also made between Pd(100) surfaces each modified by the adsorption of 2 ML of octane and then brought into contact at misorientation angles of  $30^\circ$ ,  $55^\circ$ ,  $75^\circ$ ,  $90^\circ$ , and  $135^\circ$ . Figure 5 shows the average static friction coefficient measured between Pd(100) surfaces modified by 2 ML of adsorbed octane at all seven misorientation angles. Each data point represents the average of at least 12 single-pass friction measurements, and the error bars indicate one standard deviation from the mean. For those misorientation angles at which sliding was never initiated during shearing, the data point indicates the average of the lower limits on the static friction coefficient obtained from each of the 12 measurements. The only misorientation angles at which sliding occurred during shearing and at which the static friction coefficient could be measured were  $45^\circ$  and  $135^\circ$ . The fourfold rotational symmetry of the Pd(100) surfaces renders these two misorientation angles equivalent. The apparent minimum in the static friction coefficient at these angles is a clear indication of friction anisotropy at the Pd(100)/Pd(100) interface.

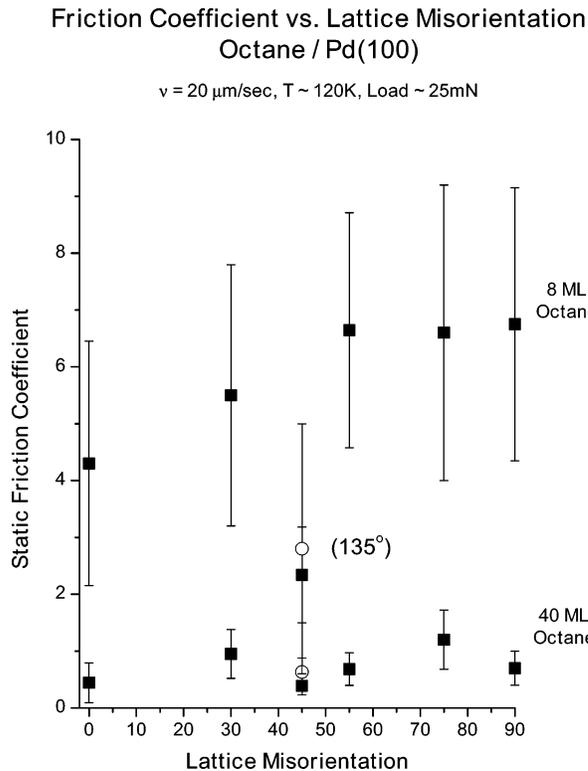
Additional friction measurements were made at all seven misorientation angles using surfaces that had been modified by adsorption of octane at coverages up to 40 ML. This was done to assess the effect of thicker adsorbed layers on friction anisotropy. As for the measurements made using 4 ML of octane at the interface, the clean Pd(100) surfaces were prepared by cooling to below 120 K followed by exposure to octane vapor. Figure 6 shows the static friction coefficient as a function of misorientation angle for 8 and 40 ML of octane at the sliding interface. With 8 ML of octane at the interface, sliding was observed during shearing, and thus the friction coefficient was measurable at each misorientation angle. In contrast, shearing of the interface with 4 ML of octane did not result in sliding (at most misorientation angles). With 8 ML of octane present, sliding was highly irregular, however, and



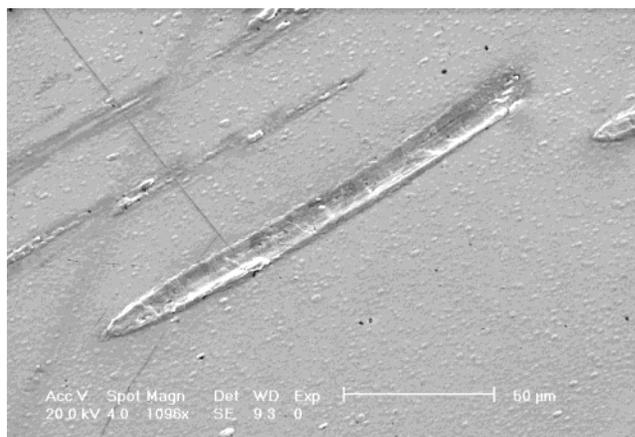
**Figure 5.** Static friction coefficient as a function of lattice misorientation angle between two Pd(100) surfaces with 4 ML of octane at the sliding interface. Each data point represents the average of at least 12 single-pass friction measurements. A minimum in the static friction coefficient occurred at a misorientation angle of  $45^\circ$  (and  $135^\circ$ ). At all other misorientation angles, friction was not measurable and the data points put a lower limit on the static friction coefficient ( $\mu_s > 8.3$ ). Sliding conditions were  $F_N \approx 25\text{mN}$ ,  $v_s = 20 \mu\text{m/sec}$ , and  $T \approx 120\text{K}$ .

can be characterized as stick-slip at most misorientation angles with adhesion still playing an important role in the interaction between the surfaces. This caused a wide variance in the measured friction coefficient as indicated by the large error bars in Figure 6 for the friction coefficients measured with 8 ML of octane at the interface. Despite the high variance in the friction coefficients, friction anisotropy can be observed even in the presence of 8 ML of octane. Friction coefficients are high and similar in magnitude for all misorientation angles other than  $45^\circ$  and  $135^\circ$ .

While misorientation angles other than  $0^\circ$  and  $90^\circ$  produce incommensurate interfaces between the Pd(100) surfaces, the friction between the two only decreased at  $45^\circ$  (and  $135^\circ$ ). This is in contrast to some previous studies which have shown that friction can decrease with relatively minor misorientation of surface lattices.<sup>8,9</sup> Those previous studies, however, examined friction anisotropy between surfaces interacting elastically, while in the present study of friction between Pd(100) surfaces plastic deformation of the surfaces occurs during sliding. Plastic deformation is observed in the form of wear scars which can be seen in scanning electron micrographs of the surface of the tribometer crystal obtained after making several hundred friction measurements (Figure 7). These wear scars have widths of  $\sim 5 \mu\text{m}$ . This suggests that plastic deformation is occurring on a scale that is likely to dwarf any effects of surface roughness or asperities. Friction anisotropy between the Pd(100) surfaces does not show the characteristics expected for friction anisotropy due to surface lattice commensurability and is observed with octane at



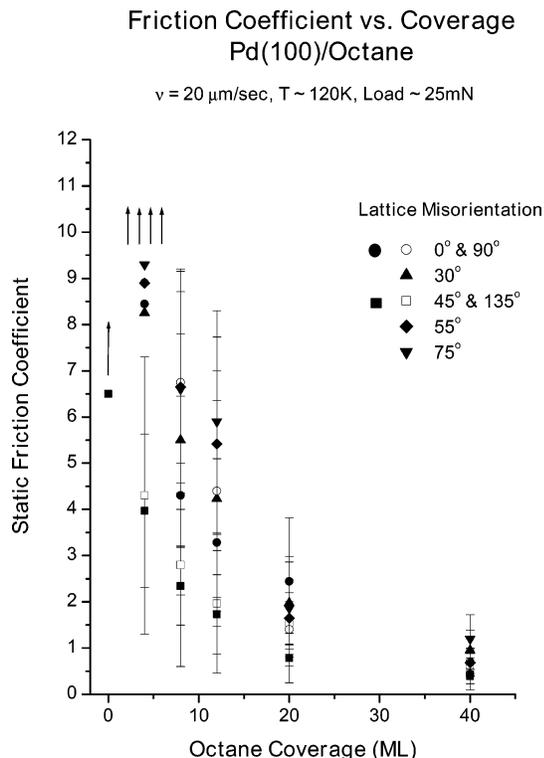
**Figure 6.** Static friction coefficient as a function of lattice misorientation angle between two Pd(100) surfaces with 8 and 40 ML of octane at the sliding interface. Each data point represents the average of at least 12 single-pass friction measurements with error bars of one standard deviation. With 8 ML of octane at the interface, a minimum in the friction coefficient occurred at a misorientation angle of  $45^\circ$  (and  $135^\circ$ ). With 40 ML of octane at the sliding interface, no friction anisotropy was observed and all friction coefficients were in the range  $\mu_s \sim 0.5-1.0$ . Sliding conditions were  $F_N \approx 25\text{mN}$ ,  $v_s = 20 \mu\text{m/sec}$ , and  $T \approx 120\text{K}$ .



**Figure 7.** Scanning electron micrograph of the flat Pd(100) surface show wear tracks made from a single-pass friction measurement. The width of the tracks is approximately  $10 \mu\text{m}$  and the length is about  $150 \mu\text{m}$ .

the interface and under conditions of plastic deformation. These facts suggest that friction anisotropy originates from the bulk properties of the crystal lattices rather than the properties of the surface lattices.

At sufficiently high coverages of adsorbed species between the Pd(100) surfaces, the effects of the substrate on friction should be damped to the point that friction anisotropy is no longer observable. Friction measurements were made with 20 and 40 ML of octane present at the



**Figure 8.** Static friction coefficient as a function of octane coverage between two Pd(100) surfaces for all misorientation angles studied. The minimum friction coefficient occurred consistently for a misorientation angle of 45° (and 135°) at all coverages. Friction anisotropy is observed for octane coverages of  $\leq 12$  ML at the interface. At an octane coverage of 20 ML friction anisotropy is not observable, and at a coverage of 40 ML friction has been reduced to that of bulk lubrication by octane. Sliding conditions were  $F_N \approx 25$  mN,  $v_s = 20$   $\mu$ m/sec, and  $T \approx 120$  K.

interface. Sliding occurred during shearing of the surfaces and the friction coefficient was measurable at both coverages. Figure 6 shows the friction coefficients as a function of misorientation angle with 40 ML of octane at the interface. No friction anisotropy is observed and the friction coefficient has been reduced to that of bulk lubrication by octane.

Figure 8 shows the static friction coefficient as a function of octane coverage for all misorientation angles. At zero coverage, there is a data point for the clean surfaces obtained at a misorientation angle of 45° for which the error bar points upward indicating the data point represents a lower limit on the friction coefficient. Additional attempts at shearing clean Pd(100) surfaces at different misorientation angles resulted only in stick of the samples, and in one instance, cold-welding of the surfaces. At higher octane coverages, the static friction coefficient decreases and is measurable for all misorientation angles. The friction coefficient at 45° (and 135°), however, is approximately half that at other misorientation angles. This is easily seen for octane coverages of 4, 8, and 12 ML. With an octane coverage of 20 ML at the interface, friction at 45° and 135° is lower than for the other misorientations; however, all values are approaching that of bulk lubrication. Finally, with 40 ML of octane at the interface, the friction coefficients at all misorientation angles are approximately equal.

#### 4. Discussion

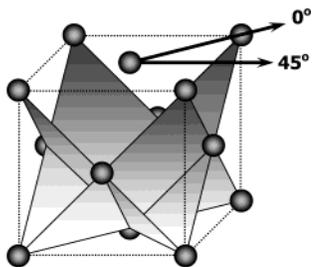
##### 4.1. Friction Anisotropy at Pd(100)/Pd(100) Interfaces.

Friction anisotropy is a fundamental phenom-

enon but is not readily observable under conditions of engineering applications. This is due simply to the fact that most engineering metals are polycrystalline. Polycrystalline metals may be desirable for practical reasons, but it would be impossible to begin a study of friction anisotropy with such materials as they are comprised of many crystallites of varying size and random orientation. Thus, they are isotropic in the average orientation of their surface lattices and friction measurements made between surfaces of most engineering metals average over all possible relative orientations of the single crystalline grains that come into contact. In this study, single crystalline metal samples have been used to produce interfaces between two surfaces such that the relative orientation of their lattices can be controlled and friction anisotropy can be studied systematically.

Two single crystalline metals oriented to expose the same crystallographic face can be brought into contact to form an interface which can be characterized as commensurate or incommensurate. The commensurate case uniquely occurs when the surface lattices of the two crystals are in exact registry or alignment with one another and have periodicities that are integer multiples of one another. When the surface lattices are rotated away from the commensurate orientation, they form an incommensurate interface. This concept is important when thinking about friction in that it defines two conditions for the interaction of individual atoms across the interface. For commensurate contact, sliding of one surface over the other requires all the atoms of one surface to move in phase past those of the other surface. For the incommensurate case, the atoms of one surface adopt all possible relative positions with respect to the atoms in the other surface. Under these conditions, the friction force between the two surfaces will be zero if the atoms are rigidly fixed into position. If friction were due only to atomic interactions at the surface, that is, atoms interacting elastically via their atomic potentials, then perhaps commensurability would be the primary factor determining friction anisotropy. Friction would be high for orientation angles at which the lattices are in commensurate contact and zero for angles at which the surfaces were in incommensurate contact. The results of this study, however, indicate that something other than elastic interactions between rigid surfaces is contributing to friction anisotropy between crystalline metal surfaces. As seen in Figure 7, wear tracks were made on the surfaces of the crystals during each single-pass friction measurement. This indicates that plastic deformation occurred in the near-surface region. This is in contrast to most previous studies of friction anisotropy that have been performed using surfaces in elastic contact.<sup>6-8</sup> The electron micrograph of Figure 7 shows that during shearing the samples are irreversibly damaged at the surface and in the near-surface region of the bulk. The bulk properties of the crystals must, therefore, play a role in determining the manner in which they interact and the origin of friction anisotropy.

The friction between two Pd(100) single crystals was anisotropic with respect to the relative misorientation of their surface lattices. While it was impossible to investigate the effects of friction anisotropy between truly clean surfaces, the results presented here clearly indicate that sliding occurred along preferred crystallographic directions even in the presence of a lubricant. Friction anisotropy was observable with as much as 20 ML of octane at the sliding interface. Octane forms an amorphous layer on the Pd samples and thus ought to mask effects of substrate lattice periodicity. Friction was the same, however, for all misorientation angles other than 45° at



**Figure 9.** The fcc lattice unit cell with the (100) surface exposed at the top. The four (111) slip planes are shown in the bulk of the unit cell and project out to the (100) surface. The  $\langle 110 \rangle$  shearing direction is marked as  $0^\circ$ . When the two surfaces were aligned, shearing occurred along the  $0^\circ$  direction for both and friction was high. When the two surfaces were misaligned by  $45^\circ$ , the friction was lowest. Under these conditions, the shearing occurs along the  $0^\circ$  direction for one crystal and along the  $45^\circ$  direction for the other.

which the friction was reduced by approximately 50%. This is consistent with the friction anisotropy previously observed using Ni(100)/Ni(100) interfaces.<sup>3</sup>

**4.2. Origins of Friction Anisotropy.** All periodic crystal lattices contain slip planes along which atoms are most densely packed.<sup>23,24</sup> These slip planes are also those in the structure that are most widely separated from one another. When sufficient stress is applied to a crystal lattice to cause deformation, the easiest way for the lattice to release this stress is by allowing the movement of atoms along slip planes in the bulk of the lattice. Palladium has a bulk face-centered cubic (fcc) structure. In an fcc crystal, the (111) planes are the slip planes, and the preferred slip directions along these planes are the  $\langle 110 \rangle$  directions. For the crystal surface configuration used in this study, sliding was always along the  $\langle 110 \rangle$  direction in the (100) plane of the surface of the fixed, stationary tribometer crystal (Figure 9). When the manipulator crystal was oriented such that the  $\langle 110 \rangle$  directions of the two (100) surfaces were aligned, the surface lattices were commensurate and shearing occurred along  $\langle 110 \rangle$  directions of both samples. After the manipulator crystal was rotated to  $45^\circ$  misorientation, the shearing direction for the tribometer crystal remained along its  $\langle 110 \rangle$  direction, but shearing for the manipulator crystal was along its  $\langle 100 \rangle$  direction. Friction was lower under these conditions than at any other misorientation angle.

It has been proposed that the cause of friction anisotropy in nickel, another fcc metal, is due to subsurface deformation along slip planes in the bulk of the crystal.<sup>3</sup> The results of this study corroborate that previous claim. Two independent studies have now been conducted using fcc single crystals oriented to expose the (100) face and both studies have revealed friction anisotropy in which friction is reduced at a lattice misorientation angle of  $45^\circ$  while shearing along the  $\langle 110 \rangle$  direction. This reduction in friction has been by approximately 50% in both studies.

(23) VanVlack, L. H. *Elements of Materials Science and Engineering*, 6th ed.; Addison-Wesley Publishing Company, Inc., 1990.

(24) Shackelford, J. F. *Introduction to Materials Science for Engineers*, 4th ed.; Prentice-Hall: New Jersey, 1996.

Friction anisotropy of a different type has been previously studied by Buckley and Johnson who made friction measurements between single-crystal copper samples that expose surfaces of different structure (100 and 111) both in air and in a vacuum.<sup>15</sup> It was shown that friction anisotropy was related to the preferred slip systems of the bulk crystal. Friction was lower when the interface between sliding surfaces had the (111) structure of the preferred slip planes for fcc metals.

Since plastic deformation occurs at interfaces between metal surfaces, it is likely that the surface lattice commensurability is a negligible contributor to the observed friction anisotropy at Pd(100)/Pd(100) interfaces. If surface lattice commensurability effects were dominant, a reduction in friction should occur with any rotation away from the commensurate interface,  $\theta = 0^\circ$ . Instead, friction was reduced only for the  $45^\circ$  misorientation angle. This is also interesting from another standpoint. If the movement of slip planes in the bulk of the crystal because of plastic deformation is the only cause for friction anisotropy in this system, then reduction of friction should be a smooth function of the misorientation angle. In the commensurate case, the shearing direction is directly opposing two of the four slip planes as shown in Figure 9. As the samples are rotated away from the alignment, the shearing direction is rotated until at  $45^\circ$  it lies midway between all four of the slip planes of the fcc crystal as they project into the surface. This is the point of minimum friction in our experiments, yet there is no reduction of friction for any other misorientation angles. At this point in time, there is no quantitative theory that appears to predict this behavior.

## 5. Conclusions

The friction anisotropy between Pd(100) surfaces was studied in the highly controlled and reproducible environment of a UHV chamber. Friction measurements made between a pair of clean single-crystal Pd(100) surfaces modified by adsorption of octane have revealed that friction is anisotropic with respect to the relative orientation of crystalline lattices. A minimum in the friction occurred when the surfaces were rotated by  $45^\circ$  with respect to each other. This friction anisotropy was observed with octane films up to 12 ML in thickness at the interface between the sliding surfaces. With 20 or 40 ML of octane at the interface, the effect of friction anisotropy was no longer evident. Plastic deformation of both samples was confirmed by SEM. This study corroborates the findings of a previous study of friction anisotropy between Ni(100) surfaces and suggests that for sliding systems where plastic deformation is occurring, friction anisotropy originates from deformation of the bulk lattice along slip planes in the crystal and not from surface lattice commensurability.

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