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Scattering of hyperthermal argon atoms from clean and D-covered Ru(0001) surfaces

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Hyperthermal Ar atoms were scattered from a Ru(0001) surface held at temperatures of 180, 400 and 600 K, and from a Ru(0001)-(1×1)D surface held at 114 and 180 K. The resultant angular intensity and energy distributions are complex. The in-plane angular distributions have narrow (FWHM ≤ 10°) near-specular peaks and additional off-specular features. The energy distributions show an oscillatory behavior as a function of outgoing angle. In comparison, scattered Ar atoms from a Ag(111) surface exhibit a broad angular intensity distribution and an energy distribution that qualitatively tracks the binary collision model. The features observed for Ru, which are most evident when scattering from the clean surface at 180 K and from the Ru(0001)-(1×1)D surface, are consistent with rainbow scattering. The measured TOF profiles cannot be adequately described with a single shifted Maxwell-Boltzmann distribution. They can be fitted by two components that exhibit complex variations as a function of outgoing angle. This suggests at least two significantly different site and/or trajectory dependent energy loss processes at the surface. The results are interpreted in terms of the stiffness of the surface and highlight the anomalous nature of the apparently simple hcp(0001) ruthenium surface. © 2011 American Institute of Physics. [doi:10.1063/1.3518042]

I. INTRODUCTION

Understanding the dynamics of atom and molecule scattering from surfaces provides knowledge useful in the development of applications involving processes such as sputtering, plasma etching, and heterogeneous catalysis. However, detailed understanding at the molecular level can be hard to obtain because a variety of phenomena may occur simultaneously under process conditions. Understanding of simple systems is a gateway to the understanding of more complex ones. Therefore, we study the interactions of inert gas atoms in this work as a prelude to studies with open shell atoms.1 A variety of model systems involving the interaction of noble gas atoms with well-characterized sample surfaces have been used to investigate the specifics of energy exchange at surfaces.2,3 It is well established that the interactions of noble gas atoms are physisorption mediated, involving a relatively shallow attractive well and a repulsive wall.

The scattering of atoms from surfaces can be divided into regimes on the basis of the energy of the incident particle (Ei). For the thermal energy regime (Ei < 1 eV), atoms generally see the surface as rather flat. In this situation scattering can be reasonably well described by the hard cube model, in which parallel momentum is conserved and only perpendicular momentum gets transferred to the cube.4 When the particle energy exceeds thermal energy (hyperthermal regime), structure scattering will occur. In this regime, the interactions typically involve individual surface atoms. When a surface appears like a rippled mirror,5 or exhibits the individual surface atom corrugation, surface rainbows may be observed.5 The simplest collision model to qualitatively describe atom scattering in this regime is the binary collision model between two hard spheres.3 Previous studies have shown the transition between thermal and hyperthermal energy regimes.7,8 At even higher particle energies of tens to a few hundred eV, a number of ion scattering studies involving alkali ion-metal surface systems have been carried out,5,9 showing even more complex scattering processes.

To date, extensive studies involving noble gas atoms with hyperthermal energies scattering from metal,1,7,8,10–15 semiconductor,11,16 and graphite17 surfaces have been performed. The Ar/Ru(0001) system has been investigated using supersonic molecular beam techniques for incident particle energies ranging from 0.08 to 2.32 eV.10 The results were interpreted with reference to the washboard model5 and trajectory calculations. At the high end of the energy range, the angle-resolved energy of scattered Ar could be qualitatively described by the washboard model. Classical trajectory calculations did not describe the experimental results very well, although the correspondence could be improved by modifying the Debye temperatures. Quantum mechanical diffraction features were identified in the angular intensity distributions from the bare and H-covered Ru(0001) for Ar incident at energies of 80 and 65 meV, respectively.10,18 Similar features were observed on the W(100)-2H surface.19 Subsequently, the Ru experimental results at 65 and 80 meV were compared with calculations involving a mixed quantum-classical scattering theory.20,21 The results were explained using an effective mass equivalent to 2.3 Ru atoms, implying collective effects of the target atoms in the Ru crystal.

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In this paper, the scattering of hyperthermal Ar atoms (average energy ~6.3 eV) from bare and D-covered Ru(0001) surfaces is presented. The current beam energy is significantly higher than in previously studies. By comparison, with measurements from Ag(111) we gain insight into the nature of the Ru surface. The results shown in the following sections indicate that the Ru(0001) behaves like a corrugated pseudostatic surface.

II. EXPERIMENTAL

The experiments were performed in an ultrahigh vacuum apparatus with a triply differentially pumped plasma source. The unique features of the apparatus have been described previously.\textsuperscript{1,2,23} Briefly, the system contains a cascaded arc source.\textsuperscript{24} Ar (purity 99.999\%) plasma is generated by discharge at three symmetrically-mounted cathode tips and is transported through a \( \phi = 2.5 \) mm channel in a stack of 5 floating, mutually-isolated copper plates before expanding into the first vacuum stage of the beamline. The second stage of the beamline, which particles enter via a skimmer, contains a double slit (0.5\% duty cycle) chopper in order to produce a pulsed beam, a beam flag to block the beam, and a pair of deflector plates in order to eliminate charged particles. The third stage functions as a buffer chamber.

The sample is mounted in the center of the scattering chamber on a three-axis goniometer.\textsuperscript{25} It can be moved aside, allowing measurement of the incident beam. The angular full width at half maximum (FWHM) of the direct beam is \( \sim 1.6^\circ \). This chamber contains an ion sputter gun, a residual gas analyzer to monitor the background gas, and a differentially-pumped rotatable quadrupole mass spectrometer (QMS).

The Ru crystal used was oriented to within 0.1\(^\circ\) of the (0001) face. The surface was cleaned by repeated cycles of Ar\(^+\) sputtering followed by annealing to 1500 K for several minutes and then annealing for several minutes at 1200 K in an O\(_2\) atmosphere (1 \( \times 10^{-8} \) mbar). The final cleaning step was Ar\(^+\) sputtering followed by annealing to 1500 K for several minutes and 1530 K flashing. The surface temperature \( T_S \) was monitored with a K-type thermocouple spot welded to the side of the crystal. The surface cleanliness was checked by reference to the temperature programed desorption (TPD) spectra of CO and H\(_2\)(D\(_2\)).\textsuperscript{26}

For the time-of-flight (TOF) experiments, the flight time of the Ar atoms was measured from the chopper to the rotatable QMS in the scattering chamber. The chopper-to-sample and sample-to-ionizer distances were 24 cm and 18 cm, respectively. Corrections for a trigger delay and for the flight time of ions through the QMS have been applied to the raw data.\textsuperscript{1} The incident particle energy, final energies as a function of scattering angle, and angular flux intensity distributions were all derived from individual TOF measurements after fitting with shifted Maxwell-Boltzmann distributions convoluted over the finite chopper opening time and over the spread of arrival times of particles at the surface.\textsuperscript{23,27}

In this study the incident Ar beams had an average energy \( \langle E_i \rangle \) of \( \sim 6.3 \) eV. Our beams had a broad energy distribution \( E_{FWHM}/(E_i) \sim 0.98 \). The TOF spectra of scattered Ar were fitted with a combination of two shifted Maxwell-Boltzmann distributions. The motivation for using two components is detailed in the following sections. Both components appear to be associated with scattering processes, since the slowest distribution is always much faster than a surface thermal energy distribution. The fits of the two components (each component having three fitting parameters) were unconstrained and independent of each other. After fitting and transformation from the time to energy domains employing the Jacobian and density to flux conversion (multiplication by \( \nu \)), a sum of scattered Ar energy distributions was derived. The average energies presented in this paper are the mean values obtained from integration of these energy distributions (not the peak energy values).

In order to minimize the influence of adsorption from the residual gas (primarily H\(_2\) and CO) during scattering from the bare Ru(0001) surface at \( T_S \) of 180 K and 400 K, the sample was flashed to 1530 K before each individual TOF measurement. The post-TOF coverage of these adsorbates was quantified by TPD. The coverages of CO were negligible and the final H coverage was \( < 0.1 \) ML in all cases. For the experiments on the Ru(0001)-(1×1)D surface, the deuterium overlayer was prepared by background dosing at a partial pressure of \( 2 \times 10^{-7} \) mbar D\(_2\) (purity 99.8\%) for 14 min. H(D) atoms preferentially bind in the fcc threefold-hollow sites.\textsuperscript{28} The saturation coverage is unity relative to Ru surface atoms.\textsuperscript{29} The resulting surface is quite inert to background contamination,\textsuperscript{30} such that several TOF spectra could be collected without requiring renewal of the surface.

III. RESULTS

A. Angularly resolved intensity distributions

The in-plane intensity distributions arising from scattering of Ar incident at 40\(^\circ\) (\( \theta_i \)) with respect to the surface normal are shown in Fig. 1. Figure 1(a) shows the results for Ar scattering from the bare surface at the three different surface temperatures. Results from the D-covered surface are shown in Fig. 1(b). For comparison purposes, the angular distribution from the bare surface at \( T_S = 180 \) K is reproduced in this panel as a dashed line. All intensities shown are represented as a fraction of the corresponding direct beam intensity.

It can be seen in Fig. 1(a) that decreasing the surface temperature results in an increase in the peak intensity and a corresponding decrease in the FWHM of the angular distribution. The effect is relatively minor when the temperature is decreased from 600 to 400 K, but is more pronounced when the temperature is further reduced to 180 K. In addition to the main peak, which has a temperature-independent maximum at a super-specular angle (\( \theta_i \sim 46^\circ \)), the angular distribution at \( T_S = 180 \) K has a shoulder at \( \theta_i \sim 6^\circ \). There is also an indication of a second shoulder at \( \theta_i \sim 35^\circ \).

The addition of D to the surface at \( T_S = 180 \) K has no significant effect on the maximum intensity of the angular distribution. Further reducing the temperature of the D-covered surface to 114 K results in a small increase in the maximum intensity. The effect is on the same order of magnitude as was
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FIG. 1. Angle-resolved flux distributions of Ar atoms ($\langle E_i \rangle \sim 6.2$ eV; $\theta_i = 40^\circ$) scattered from (a) Ru(0001) and (b) Ru(0001)-(1x1)D. The angular distribution from the bare surface at $T_S = 180$ K is replotted in the panel (b) as a dashed line. The scattered intensities are normalized to the intensity of the corresponding direct beam. The lines connecting the data points are intended to guide the eye.

observed when $T_S$ was reduced from 600 to 400 K. The angular distributions at $T_S = 180$ and 114 K have almost identical features. The shoulder that is evident in the scattering from the bare surface at 180 K has resolved into a clear peak at $\theta_f \sim 60^\circ$ for both measurements from the D-covered surface. This peak is slightly more intense at $T_S = 114$ K. There is also a significant increase in the intensity of the sub-specular wing of the angular distribution ($\theta_f = 30^\circ$–$40^\circ$) as compared with the bare surface, but this feature does not resolve into a distinct peak. The central peak has an asymmetry which becomes more pronounced with decreasing temperature and with the addition of D.

Figures 2(a) and 2(b) show the corresponding results for Ar scattering at $\theta_i = 60^\circ$. Again the maximum intensity occurs at a super-specular angle ($\theta_f \sim 65^\circ$). For the bare surface, the peak intensity of the angular distribution again increases with decreasing surface temperature. In this case, a substantial change is already observed upon decreasing from 600 to 400 K. Unlike the results obtained at $\theta_i = 40^\circ$, adding D to the surface at 180 K results in a significant reduction in the peak intensity. This intensity increases again when the sample temperature is reduced to 114 K, but it remains lower than that measured from the bare surface at 180 K. As was the case for $\theta_i = 40^\circ$, an additional shoulder/peak is evident at lower $T_S$ along a super-specular scattering angle ($\theta_f \sim 72^\circ$), and there is a wing on the sub-specular side of the main peak ($\theta_f = 50^\circ$–$55^\circ$). The asymmetry of the central peak is more obvious at this incidence angle.

B. Angularly resolved energy distributions

Figure 3 shows the results of our determination of the average energy of the scattered Ar on the basis of TOF measurements. Figures 3(a) and 3(b) show the angle-resolved ratios of the average final particle energy $\langle E_f \rangle$ over the average incident particle energy $\langle E_i \rangle$ for $\theta_i = 40^\circ$ as a function of $\theta_f$. Figure 3(a) shows the results for the bare surface and Fig. 3(b) shows those for the D-covered surfaces, with the 180 K clean surface data reproduced for comparison purposes. The lines through the data points are intended to guide the eye. Two simple models are also included on the panels. The solid line that decreases as the outgoing angle increases represents parallel momentum conservation, while the dashed-dotted line that increases with outgoing angle represents the binary collision model for a single hard-sphere scattering of the incident Ar from an isolated ruthenium atom (mass ratio $m_{Ar}/M_{Ru} = 40/101$).

The energy ratios determined for the bare surface [Fig. 3(a)] show complex behaviour. $\langle E_f \rangle/\langle E_i \rangle$ at a given $\theta_f$ is generally larger at higher $T_S$, but the overall shape of the distribution is temperature independent. If one were to apply a simple linear fit to the energy ratio curves in this panel, then the overarching trend would be of a gradual decrease as $\theta_f$ is increased. This is suggestive of a non-negligible contribution from parallel momentum conserving scattering events. However, this trend is disrupted by a clear region of increased $\langle E_f \rangle/\langle E_i \rangle$ for $\theta_f$ between $40^\circ$ and $60^\circ$. Adding D to the
surface [Fig. 3(b)] results in two significant changes: the increase in the average energy now occurs over a narrower range of outgoing angles ($\theta_f = 40^\circ$–$50^\circ$) and there is a substantial decrease in the average energy of the particles scattered to small outgoing angle (which alters the overarching trend to one of increasing $\langle E_f \rangle / \langle E_i \rangle$ as $\theta_f$ increases). The latter behavior was previously observed in the molecular beam study of Ar scattering from Ru(0001) and the effect was tentatively assigned to the influence of hydrogen (which was seeded in that beam) adsorption on the surface.\textsuperscript{10} The current measurements confirm that this conjecture is correct.

Figures 3(c) and 3(d) show the corresponding datasets for $\theta_i = 60^\circ$. At this incidence angle the energy distributions are even more complex. For the bare surface [Fig. 3(c)] the overall trend is one of increasing $\langle E_f \rangle / \langle E_i \rangle$ with increasing outgoing angle. This behavior is qualitatively indicative of the binary collision model and suggests that any contribution from parallel momentum conserving scattering events is reduced at this incidence angle. However, two peaks (located at $\theta_f \sim 50^\circ$ and $\sim 65^\circ$) are clearly evident in the energy distribution.

Adding D to the surface [Fig. 3(d)] again results in a decrease in $\langle E_f \rangle / \langle E_i \rangle$ at small outgoing angles, which is qualitatively similar to the behavior observed at $\theta_i = 40^\circ$. In addition, the peak structure is altered. While the peak at $\theta_f \sim 65^\circ$ is largely unchanged, the other peak has become less prominent and its maximum $\langle E_f \rangle / \langle E_i \rangle$ has shifted to $\theta_f \sim 60^\circ$.

C. Comparison with results from Ag(111)

To highlight the unusual nature of the intensity and energy distributions measured from the Ru(0001) surface, it is instructive to compare the results with comparable measurements from the Ag(111) surface. This is done in Fig. 4, where the results of scattering from the two surfaces at $T_s = 600$ K are presented. The results from the Ag(111) surface shown in Fig. 4 have been reported previously.\textsuperscript{1} Although they have a different bulk structure, Ru (hcp) and Ag (fcc), have similar standard atomic weights ($M_{\text{Ru}} = 101$ and $M_{\text{Ag}} = 108$), and their respective (0001) and (111) faces have an equivalent top-layer atomic arrangement. The surface Debye temperatures have been reported as 216 K (Ref. 31) for Ru(0001), and 155 K (Ref. 32) and 165 K (Ref. 33) for Ag(111).

Figures 4(a) and 4(b) show a comparison of the in-plane angular intensity distribution of Ar scattered from Ru(0001) and Ag(111) for $\theta_i$ of 40$^\circ$ and 60$^\circ$, respectively. The contrast is particularly dramatic at $\theta_i = 40^\circ$, where there is a factor of 4.6 difference in the maximum peak intensity. The angular distribution from Ru(0001) is much sharper than that from Ag(111) at both incident angles. At $\theta_i = 40^\circ$ the FWHM are $\sim 10^\circ$ and $\sim 25^\circ$ for Ru(0001) and Ag(111), respectively; at $\theta_i = 60^\circ$ the corresponding values are $\sim 8.8^\circ$ and $\sim 13.3^\circ$. (The QMS angular acceptance is $\sim 1.6^\circ$ assuming a point source at the sample position). For this beam energy the Ag(111) FWHM value at $\theta_i = 40^\circ$ is broader than results reported for $E_i$ in the range 0.5–2.6 eV,\textsuperscript{7,14} while the Ru(0001)
FIG. 3. Angle-resolved final-to-initial energy ratios ($\langle E_f \rangle / \langle E_i \rangle$) of Ar scattered from (a) Ru(0001) and (b) Ru(0001)-(1×1)D for $\theta_i = 40^\circ$, and from (c) Ru(0001) and (d) Ru(0001)-(1×1)D for $\theta_i = 60^\circ$. In (b) and (d) the results from the bare surface at $T_S = 180$ K are replotted as a dashed line. The lines connecting the data points are intended to guide the eye. Two simple models are illustrated on the panels. Solid lines correspond to parallel momentum conservation and dashed-dotted lines represent the model of single-collision hard sphere scattering of Ar from an isolated ruthenium atom (mass ratio of 40/101).

FWHM is comparable to a previous result ($\sim 11^\circ$) for $E_i = 2.09$ eV under a similar experimental condition ($T_S = 550$ K).34

Figures 4(c) and 4(d) show the corresponding comparison of $\langle E_f \rangle / \langle E_i \rangle$ as a function of outgoing angle. The $\langle E_i \rangle / \langle E_i \rangle$ ratios of Ag were previously determined on the basis of fitting a single shifted Maxwell-Boltzmann distribution to the scattered TOF spectra.1 In Figs. 4(c) and 4(d) these ratios have been recalculated on the basis of the two-component fitting outlined in the experimental section. This was done to
FIG. 4. Angle-resolved flux distributions of Ar ($\langle E_i \rangle \sim 6.5$ eV) scattered from Ru(0001) and Ag(111) at (a) $\theta_i = 40^\circ$ and (b) $\theta_i = 60^\circ$, and the corresponding angle-resolved $\langle E_f \rangle/\langle E_i \rangle$ ratios from those surfaces at (c) $\theta_i = 40^\circ$ and (d) $\theta_i = 60^\circ$. In panels (c) and (d), the dashed-dotted lines represent the models of single-collision hard sphere scattering of Ar from an isolated Ag atom (mass ratio of 40/108). $T_S$ was 600 K in all cases.

ensure equivalent treatment of all datasets. In the case of Ag(111), the extra component results in a small improvement in the quality of the overall fit to the slow tail of the TOF spectra. As a consequence, the $\langle E_f \rangle/\langle E_i \rangle$ derived are slightly lower than those determined using a single component fitting.

The simplicity of the Ag(111) energy distributions is in stark contrast to the complexity of the correspond-
ing Ru(0001) distributions. For both incidence angles, the \((E_f)/\langle E_i \rangle\) of Ar scattered from Ag(111) increases with increasing \(\theta_i\). The trend is qualitatively very similar to the simple binary collision model, although at both incident angles the average energy ratio is higher than would be expected from that simple model. The deviation from the \(m_A/M_{Ag} = 40/108\) model is largest for \(\theta_i = 60^\circ\). The results can be interpreted either in terms of the effective mass of the surface being larger than the atomic mass of a single Ag atom (scattering from a collective mass) or by the scattering being dominated by multiple forward collisions.\(^3\)\(^5\) The \((E_f)/\langle E_i \rangle\) determined for Ar scattering from Ru(0001) at \(T_S = 600\) K are far more complex than those of Ag(111) and show no correspondence with any simple collision model.

D. Two-component TOF fitting

In the previous study of Ar and N scattering from Ag(111), the measured TOF spectra were analyzed by fitting a single shifted Maxwell-Boltzmann distribution.\(^1\) The resultant fits were sufficient to accurately represent the data. The main discrepancy was in the correspondence of the fit to the tail (slow component) of the TOF spectra. There was no significant variation in the quality of the single component fit as a function of \(\theta_i\). In contrast, in the case of the Ru TOF measurements, and in particular for certain outgoing angles, a single component fit was insufficient to accurately represent the spectra. The shape of the TOF distributions measured from Ru changed as a function of the outgoing angle such that the requirement for at least a two-component fitting was unavoidable. This is illustrated by Fig. 5, which compares three contour plots, each constructed from sets of individually measured TOF spectra. In all cases, the raw spectra at the individual outgoing angles have been normalized to a peak intensity of one. The normalization is done in order to allow the changes in the time distribution of the scattered particles to be observed independent of the absolute scattered intensity.

Figure 5(a) shows the contour plot for scattering of Ar from Ag(111) at \(\theta_i = 40^\circ\) and \(T_S = 600\) K. This shows an essentially constant time profile as a function of \(\theta_f\). The peak of the distribution shifts to shorter time as \(\theta_i\) increases, which reflects the smoothly increasing \((E_f)/\langle E_i \rangle\) shown in Fig. 4(c). In other respects the distributions do not vary dramatically. The shape and width of the distribution and the relative contribution from any slow component are independent of the outgoing angle.

Figure 5(b) shows the contour plot for scattering of Ar from Ru(0001) at \(\theta_i = 40^\circ\) and \(T_S = 600\) K. It is immediately clear that the time profile of the TOF distributions no longer has a simple correspondence with \(\theta_i\). Figure 5(c) shows the corresponding contour plot for scattering of Ar from Ru(0001)-(1×1)\(D\) at \(\theta_i = 40^\circ\) and \(T_S = 114\) K. Under these conditions the variations in the time profile of the TOF spectra as a function of \(\theta_i\) are even more extreme. The shapes of the associated Ru \((E_f)/\langle E_i \rangle\) traces [see Figs. 3(a) and 3(b)] are clearly discernible in the angular variation of the contour maxima shown in Figs. 5(b) and 5(c).

Several raw TOF spectra are reproduced alongside their associated contour plot in Fig. 5. The individual two-component fits and the overall fitting curve used describe the measured distributions also shown. Note that the fitting was unconstrained and that there was no physical interpretation behind the fitting procedure. Hence, we do not make any claims regarding the accuracy or uniqueness of the allocation of intensity between the two components shown in Fig. 5. It is for this reason that we present overall average energies (which are dependent only on the quality of the overall fits) in Figs. 3 and 4, rather than the average energies of the two individual components.

IV. DISCUSSION

The physisorption potential well (\(<\ 70\) meV)\(^3\)\(^6\) will have a negligible effect on our incident hyperthermal (\(\sim\ 6.3\) eV) atoms. The scattering behavior of such atoms will be determined by the shape of the surface potential, the effective surface mass and by the thermal motion of individual surface atoms. The addition of D to the surface should not have a large effect on the surface potential. However, the effective surface mass and the motion of the surface atoms may be altered by D-induced changes to the lattice interactions.

A. Ar scattering from Ru(0001): Angular distributions

For the angular intensity distributions, the surface temperature dependence observed from Ru(0001) is qualitatively understandable in terms of the influence of temperature on surface atom motion. Raising the temperature increases the vibrational amplitude and displacement of the surface atoms, which will reduce the intensity of the near-specular peak and broaden the distribution. Nonetheless, the angular distributions remain surprisingly narrow as compared with those measured from Ag(111). The additional peaks/shoulders at super- and sub-specular angles are enhanced when the surface temperature is reduced, and in particular when D is added to the surface. Since reducing the temperature results in dampening of atomic motion, this suggests that D adsorption also acts to suppress the motion of individual surface atoms.

The features observed in the Ru angular distributions can be attributed to surface rainbows. It is possible to observe surface rainbows when scattering hyperthermal particles.\(^6\) However, vibrations and thermal displacement of surface atoms typically act to wash out rainbow features in most scattering systems. This effect was simulated by Lahaye et al. for Ar scattering from static \((T_S = 0\) K) and \(T_S = 600\) K Ag(111) surfaces with an incidence angle of \(40^\circ\).\(^1\)\(^4\) Rainbow features at different outgoing angles were readily evident from the static surface for incident atoms with energies ranging from 0.1 to 100 eV. In contrast, for the simulations done at \(T_S = 600\) K, all surface rainbow features disappeared due to thermal effects. Ar with \(E_i = 1\) eV scattered from the static surface exhibited surface rainbow features at \(\theta_f \sim 35^\circ\) and \(\sim 55^\circ\) with a sharp main (split-)peak centered at \(\sim 45^\circ\). For \(E_i = 10\) eV, the rainbow scattering features remained visible and the splitting of the central peak was clearly resolved. The positions of the two left-hand-side (small \(\theta_i\)) peaks shifted to smaller \(\theta_i\) with increased \(E_i\). In contrast, the two rainbow peaks at larger \(\theta_i\) did...
FIG. 5. Contour plots produced from Ar TOF spectra after normalization to a peak intensity of one: Ar scattered from (a) Ag(111) at $\theta_i = 40^\circ$ and $T_S = 600$ K; (b) Ru(0001) at $\theta_i = 40^\circ$ and $T_S = 600$ K; (c) from Ru(0001)-(1 $\times$ 1)D at $\theta_i = 40^\circ$ and $T_S = 114$ K. The right-hand-side panels show some representative raw TOF spectra for the three surfaces and the associated two-component fits. The measurement for (a) and (b) were done at 400 Hz chopper frequency, and for (c) at 200 Hz chopper frequency. The times shown represent the flight time from the chopper to the ionizer (i.e., the trigger delay and QMS flight-time corrections have been applied).
not shift. See Lahaye et al. for a detailed explanation of this behavior. Note that given our broad energy distribution, the 1 eV and 10 eV simulations represent reasonable lower and upper limits of the spread of particle energies present in our beam. Ar atoms with energies between these values account for ~90% of the total beam.

A broad range of incident $E_i$ should result in the rainbow peaks at small $\theta_i$ (which have an energy dependence) being smeared over a range of $\theta_f$, while those at larger $\theta_i$ (which are energy-independent) should remain relatively sharp and well-defined. The angular distributions from D-covered Ru(0001) are compatible with this expectation. The asymmetric central peak is sharp on the high $\theta_f$ side but broadened on the low $\theta_f$ side. This is consistent with it being an amalgamation of two rainbow peaks: one (right-hand side/larger $\theta_f$) being energy independent and the other (left-hand side/smaller $\theta_f$) shifting as a function of the incident particle energy. Considering the two outer rainbow features in the data from Ru(0001), there is a reasonably well-defined peak at $\theta_f \sim 60^\circ$ in contrast to a broad shoulder at $\theta_f = 30^\circ$–$40^\circ$. The fact that the peak at $\theta_f = 60^\circ$ is visible despite the broad energy distribution of the incident beam indicates that it is an energy-independent feature. The shoulder at small $\theta_f$ may be the net result of the smearing of an energy-dependent left-most rainbow peak. Based on the correspondence between the simulated Ar/Ag(111) and our measured angular distributions from Ru(0001), the low $T_S$ and D-covered Ru appear to behave like pseudostatic surfaces, with the consequence that associated rainbow features remain discernible under experimental conditions.

As mentioned above, the simulation results for Ar scattering from Ag(111) at $T_S = 600$ K suggest that surface rainbow effects get washed out due to displacement of atoms from their equilibrium positions and the actual vibration of surface atoms. Thermal displacement of Ru atoms and the associated kinetic energy of vibration would be expected to attenuate rainbow scattering features in a similar manner. However, the angular intensity distributions from Ru(0001) at $T_S = 600$ K remain much sharper than those from Ag(111) and remnants of the rainbow features, though less obvious at this temperature, persist in the angular distribution. This implies that the Ru surface has a much lower atomic displacement and is markedly stiffer (smaller vibrational amplitude) than the Ag surface.

Based on the reported surface Debye temperatures, the estimated root mean square (rms) displacements at $T_S = 600$ K of Ag(111) and Ru(0001) in the harmonic approximation are 0.17–0.18 Å and 0.14 Å, respectively. These values do indeed indicate smaller thermal displacement of Ru atoms, although the absolute difference between Ag and Ru does not seem to be dramatic. Ru displacement will be reduced both by lowering the temperature and by adding hydrogen to the surface. The rms Ru atomic displacement at a surface temperature of 180 K is estimated to be $\sim 0.075$ Å, based on a surface Debye temperature of 216 K in the harmonic approximation. With a 10% increase in the surface Debye temperature upon hydrogen adsorption, the rms displacement becomes even less, and surface atoms will be located even closer to their equilibrium positions.

It should be noted that there is a large disparity in the values of the Ru bulk Debye temperature that have been reported (415–600 K). These values are generally higher than those of the other transition and of the noble metals. Based on the bulk values reported and associating the single reported value for the Ru surface Debye temperature (216 K) with the lower limit, the corresponding range of Ru surface Debye temperatures would approximate to 216–312 K. Any increase in the surface Debye temperature translates into a reduced rms displacement at a given temperature.

Tentative support for a higher-than-reported Ru surface Debye temperature is provided by the efforts of Berenbak et al. to simulate the results of their molecular beam measurements on the Ar/Ru(0001) system. Calculations done on the basis of bulk, and surface Debye temperatures of 415 and 216 K, respectively were not satisfactory in reproducing the experimental results. However, the level of agreement was improved by increasing the Debye temperatures in their trajectory calculations. An increase of a factor of 1.5–2.0 resulted in the calculations exhibiting energy distribution trends that were qualitatively similar to the experimental results and to the washboard model.

The features observed for Ar scattered from Ru at $\theta_f = 60^\circ$ at low $T_S$ and with D added to the surface are reminiscent of those at $\theta_f = 40^\circ$. The asymmetric central peak is again broader on the small $\theta_f$ side than on the large $\theta_f$ side. There is also evidence of additional features at both smaller and larger $\theta_f$. Although the feature on the large $\theta_f$ side of the main peak does not fully resolve into a distinct peak, it is more evident than the wing on the small $\theta_f$ side. This is again indicative of the large $\theta_f$ features being more independent of the incident particle energy than the small $\theta_f$ features.

B. Ar scattering from Ru(0001): Energy distributions

The shapes of the energy ratio curves in the current study also have similarities to the results of Lahaye et al. from static Ag(111) surface for $E_i = 1$ and 10 eV, although the measured values of $\langle E_i \rangle / \langle E_f \rangle$ for Ru(0001) are consistently lower than the simulation. The simulations show an increase in relative energy between the outgoing angles of 40° and 50° (described as a “kink”). A similar kink is evident in the average energy distributions shown in Figs. 3(a) and 3(b). Note that the width and position of the energy kink measured for the D-covered Ru surface is in very good agreement with that reported by Lahaye et al. for the static Ag(111) surface. In contrast to the rainbow features observed in the measured angular distributions, which get more washed out at elevated $T_S$, the energy kink remains clearly evident even at $T_S = 600$ K.

Lahaye et al. identified this feature as arising from trajectories with reduced energy loss resulting from zig-zag collisions through the center site. The presence of D in the threefold-hollow sites can be expected to modify features associated with trajectories through such sites. This is indeed what is evident in Fig. 3(b), where the presence of D modifies (decreases) the width of the measured energy kink. The other major change that is induced by the addition of D is a
drop in $\langle E_i \rangle/\langle E_i \rangle$ at small $\theta_i$. This suggests that the small number of Ar atoms that are scattered in this direction arise primarily from trajectories associated with the threefold-hollow sites.

The preceding discussion, which relates to the energy distributions measured at $\theta_i = 40^\circ$ should also be applicable to the corresponding measurements for $\theta_i = 60^\circ$. Unfortunately, comparable static surface trajectory calculations for this angle of incidence are not currently available, so no judgment can be made regarding the level of agreement. Assuming the associations made on the basis of comparison with the $\theta_i = 40^\circ$ simulations also hold at $\theta_i = 60^\circ$, then features that change upon adsorption of D (more energy loss at small $\theta_i$ and modification of the peaks) should also be assigned to center site scattering trajectories. More detailed discussion of the oscillations seen for $\theta_i = 60^\circ$ is unwarranted in the absence of supporting trajectory calculations.

Rainbow features in energy-resolved scattering of atoms with hyperthermal energies have previously been reported experimentally and theoretically. As illustrated by Fig. 5, the variations in $E_f$ as a function of $\theta_i$ arise from changes in the relative contribution of distinct components in the TOF profiles, rather than from an angle-dependent variation in the energy of a single component. The TOF distributions appear to contain significant contributions from independent sets of trajectories. The fact that these sets remain identifiable, rather than being washed out by thermal effects, is again indicative of scattering from a relatively static surface.

In order to exhibit distinct components, different sites on the Ru surface must generate in-plane scattering trajectories that have very different energy losses. This points to impact-site-dependent energy loss, such as was reported for the Ar/Pt(111) system with hyperthermal incident energies. Note that the slower scattered atoms appear to be most prominent at the outgoing angles associated with the outermost features evident in the angular distributions. Based on Lahaye et al., these features are due to scattering from the surroundings of the atop site (up- and down-hill potential). These trajectories are dominated by interactions between individual atomic cores and are thus more likely to experience a lower effective surface mass (higher energy loss). The zero temperature calculations of Kulginov et al. illustrate that scattering from a static surface can indeed lead to multiple values of $\langle E_i \rangle/\langle E_i \rangle$ along a single $\theta_i$. They identified the lower branches of their $\langle E_i \rangle/\langle E_i \rangle$ curves as being associated with scattering from a single surface atom, while the upper branch was due to simultaneous interaction with multiple atoms near the hollow sites. Alternatively, it is conceivable that the components observed in the scattering from Ru could arise from differences in the scattering of low and high energy incident particles. In effect the Ru surface may be acting like a crude energy filter.

As can be seen in Figs. 4(c) and 4(d), the values of $\langle E_i \rangle/\langle E_i \rangle$ as a function of $\theta_i$ for scattering from Ru are often much lower than the comparable values from Ag, in particular for $\theta_i = 60^\circ$. In some cases the final energy of the Ar/Ru data is even lower than the binary collision model, especially at large $\theta_i$. This may be the result of out-of-plane scattering. Lahaye et al. reported on the out-of-plane results of Ar scattering from Ag(111) (static and $T_S = 600$ K). Since there is a good correspondence between our measured in-plane distributions from Ru and the in-plane simulations for the static Ag surface, a similar correspondence in the out-of-plane scattering should be anticipated. The general trend observed by Lahaye et al. was that out-of-plane scattering increased with $E_i$. For a broad energy incident beam, this implies that the in-plane scattered distribution will be preferentially weighted toward the lower energy incident particles. Hence, the energy distribution of the particles scattered in-plane will not retain a simple direct correspondence with the energy distribution of the incident beam. The effect would be to reduce $\langle E_i \rangle/\langle E_i \rangle$. Hence, the absolute values of $\langle E_i \rangle/\langle E_i \rangle$ determined for a broad energy beam should be treated with caution. However, conclusions can still be drawn on the basis of relative comparisons.

The unique features in the angular intensity and energy distributions measured, and their apparent similarity with static surface simulations point to a remarkable stiffness of the Ru surface. This is consistent with previous reports on the nature of the Ru(0001) surface. The surface lattice dynamics of Ru(0001) were studied by Heid et al. They found evidence of a strong softening of longitudinally-polarized vibrations, which was attributed to a very large softening of the intralayer coupling in the outermost atomic layer. This softening is in contrast to a substantial strengthening of the first-to-second inter-layer coupling. These are quite anomalous features as compared with other metals surfaces. A strong inter-layer coupling and a weak intra-layer coupling supports the suggestion by Hayes et al. that the effective mass of the Ru surface is dominated by the interaction of first layer atoms with the second layer. Such a substantial difference between inter- and intra-layer coupling strength, giving rise to large site and trajectory dependent variations in the net energy loss, could result in the complex TOF distributions that we measured. The energy loss may vary depending on whether the induced displacement of the surface atoms is primarily lateral with or perpendicular to the surface atomic plane. Perpendicular displacement can be anticipated to represent the maximum distortion of the strong inter-layer coupling, leading to the highest effective mass and the lowest energy loss. However, since all atomic displacement will involve some perturbation of all atomic couplings, the energy loss associated with any given displacement is not inherently obvious. Trajectory calculations using an appropriately modelled surface are necessary in order to elucidate the link between specific Ru atom displacements and the associated energy loss by incident Ar.

V. CONCLUSIONS

Results for both the angular flux and energy distributions of Ar scattering from Ru(0001) are qualitatively reminiscent of simulation results for scattering from a static Ag(111) surface. Rainbow features are visible in both the angular flux and energy distributions measured from Ru. Reducing the surface temperature and adding D to the surface, both of which reduce surface atomic motion, enhance the rainbow features. The results point to a remarkable stiffness of the Ru surface.
That Ru can be expected to be “stiffer” than other metal surfaces is indicated by its relatively large Debye temperatures. However, the effect appears to be much more pronounced than might be anticipated on the basis of reported Debye temperatures. The uniqueness of the Ru(0001) surface could prove immensely valuable in refining modelling of atomic scattering and in improving the correspondence between simulation and experiment.

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