Argon scattering from Ru(0001): Calculations and comparison with experiment

W. W. Hayes and J. R. Manson
Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634, USA
(Received 27 October 2006; revised manuscript received 15 January 2007; published 28 March 2007)

Recently reported measurements of Ar atom scattering from Ru(0001) at thermal and hyperthermal energies exhibited a number of characteristics that are unusual in comparison with other systems for which molecular beam experiments have been carried out under similar conditions: the measured energy losses are unusually small, some of the angular distributions exhibited an anomalous shoulder feature in addition to a broad peak near specular, and quantum mechanical diffraction was observed under conditions for which it was not expected. The data are analyzed and compared to calculations with classical scattering theory. Many of the unusual features observed in the measurements are explained but only upon using an effective surface mass of 2.3 Ru atomic masses, which implies collective effects in the Ru crystal. The bigger effective mass leads to substantially larger Debye-Waller factors and explains and confirms the observations of diffraction features. It also leads to the interesting conclusion that Ru is a metal for which molecular beam scattering measurements in the purely quantum mechanical regime can be performed with a range of atomic and molecular projectiles with masses substantially heavier than He.

DOI: 10.1103/PhysRevB.75.113408 PACS number(s): 68.49.Bc, 34.50.Dy, 34.50.Pi, 82.20.Rp

An extensive experimental investigation of the Ru(0001) surface using scattering of beams of Ar atoms at thermal and hyperthermal energies has recently been reported by Berenbak *et al.*[1,2] Several unusual features were noted in the scattered intensities, including elastic diffraction peaks in the energy-resolved spectra. Although diffraction peaks have been observed with Ar scattering on other surfaces,[3–5] and in fact the Debye-Waller behavior of such peaks is well explained,[6] diffraction is not normally expected on Ru with such large incident energies.

The purpose of this paper is to analyze these Ar/Ru(0001) scattering data in terms of a theory that has successfully described argon as well as other rare gas scattering from insulator and metal surfaces.[7–10] In these previous studies of rare gas scattering under classical conditions of high incident energy, large temperatures, and large projectile masses, classical scattering theory provided a quite reasonable description of the energy, angular, and temperature dependence of the scattered distributions.

A potentially important finding to come out of the comparisons is that in order to obtain agreement between theory and experiment it was necessary to choose an effective mass for the surface that was larger than that of a single Ru atom by a factor of 2.3, whereas for most rare gas–metal systems previously investigated a larger effective mass was not necessary. A larger effective mass can be interpreted as being due to collective phenomena in the metal in which the projectile scatters off of an effective target of more than one substrate atom. The effective mass is not a unique feature of Ar scattering because the analysis of a recent study of N_2 molecular scattering from the Ru(0001) surface[11] found it necessary to choose the surface mass to be the same 2.3 Ru atoms.[12] Additional support for the idea of larger collective masses for Ru comes from the analysis of atomic and molecular scattering[1,11] using the washboard model[13] and classical trajectory molecular dynamics simulations.[14]

The theory used here has been described elsewhere[15–17] and the interaction potential is chosen to be a strongly repulsive barrier whose corrugation vibrates under the influence of the underlying surface substrate atoms. The theory depends on a single parameter, arising from the fundamental condition of conservation of momentum parallel to the surface, and this is usually presented as a velocity v_R.[15] The parameter v_R is completely determined by the phonon spectral density at the classical turning point, thus its determination by comparison with experiment may provide useful information about the surface dynamics. However, it is usually treated as a parameter,[15,16] and crude estimates of its value give results of the order of the Rayleigh phonon velocity. For the work presented here, the value of v_R is chosen to be 3200 m/s which can be compared with measured values for the Rayleigh velocity of 3608 m/s for the Ru(0001) $\langle 11\bar{2}0\rangle$ direction and 3494 m/s for the $\langle 1\bar{1}00\rangle$ azimuth.[18] The experimental incident beam had a rather large energy spread.[1] This energy width has little effect on calculated angular distributions, since they are integrated over all final energies. However, a large energy width of the incident beam can have noticeable effects on the energy resolved spectra. For the calculated results presented here, the differential reflection coefficient was convoluted with the experimentally measured energy distribution function.[1]

A series of five measured energy-resolved intensity spectra as functions of final energy are shown in Fig. 1 for an incident energy $E_i=0.08$ eV, incident polar angle $\theta_i=40°$, and with the detector positioned at the final angle $\theta_f=20°$. The surface temperatures range from $T_S=140$ to 850 K as marked. These spectra are characterized as smooth, broad, single-peaked structures which get broader with a longer high-energy tail at increasing temperature. The position of the peak, or most probable energy, remains essentially the same for all temperatures.

These energy-resolved spectra exhibit no evidence of quantum mechanical features such as sharp diffuse elastic or single surface phonon peaks. The expected classical nature under these conditions can be verified by evaluating the Debye-Waller factor $\exp(-2W)$ where the simplest approximation gives

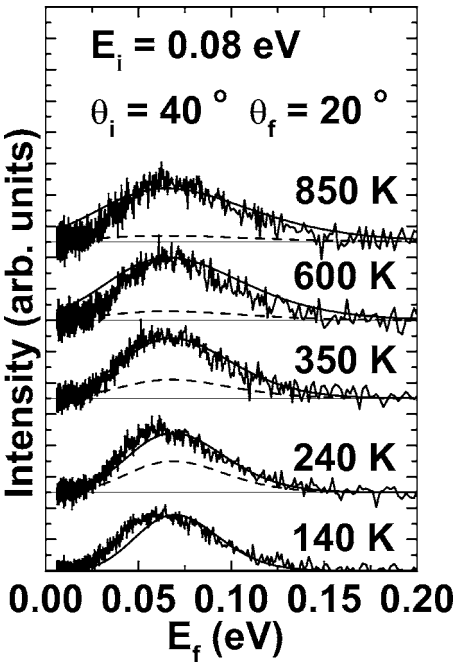

FIG. 1. Energy-resolved spectra of Ar scattered from Ru(0001) at temperatures ranging from 140 to 850 K as marked. The incident energy is E_i=0.08 eV, the incident angle is θ_i=40°, and the final angle is θ_f=20°. The theoretical calculations, normalized to the data at each temperature, are shown as smooth solid curves, and the calculated intensities relative to that at T_S=140 K are shown as dashed curves.

$$2W = \frac{3(\mathbf{p}_f - \mathbf{p}_i)^2 T_S}{M_C k_B \Theta_D^2} = \frac{6\Delta E_0 T_S}{k_B \Theta_D^2}, \tag{1}$$

where T_S is the surface temperature, M_C is the surface mass, and ΔE_0 is the recoil energy which is directly determined through comparison of these classical calculations with measurements. The exponent $2W$ is a measure of the approximate number of phonons created or destroyed in a collision and when it is large the scattering is purely classical. Using for the surface mass M_C the mass of a single Ru atom and a value of 216 K for the Debye temperature[1] Θ_D, the value of $2W$ in the region of the most probable final energy is about 16 even at the lowest temperature. Such a large value would reduce all quantum features to negligible intensity, and indicate clear classical conditions.

Calculations are shown as solid lines and for each temperature the calculations were normalized to the data at one point near the most probable intensity. The experimental data were reported in arbitrary units, and information about relative intensities at different temperatures was not determined. The theory predicts a decrease in the most probable intensity with T_S, and these relative theoretical calculations are shown as the dashed lines, normalized to the data at the lowest temperature of 140 K. The calculations match the general features of the data reasonably well, the increase in the high-energy tail is well predicted, but the calculations predict a slightly larger increase of broadening with temperature than that observed.

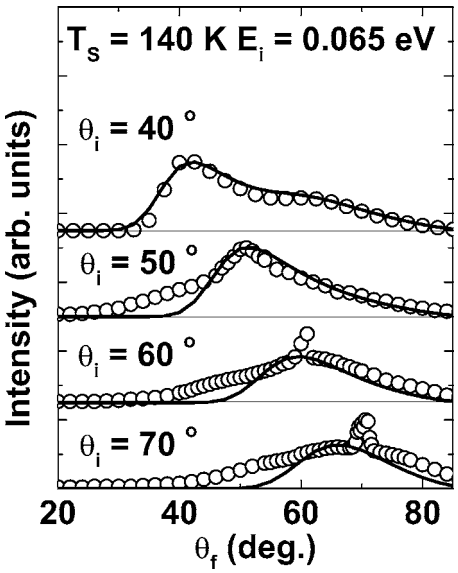

FIG. 2. Angular distributions for Ar/Ru(0001)-(1×1)H in the $\langle 11\bar{2}0\rangle$ direction with E_i=0.065 eV, T_S=140 K, and four different incident angles ranging from 40° to 70° as marked. The symbols are experimental data and the dashed curves are calculations normalized to match the experimental data in the vicinity of the maximum in the background.

However, as mentioned above, all calculations presented in this paper were carried out with an effective surface mass of 2.3 Ru atomic masses. The reason for this is that a smaller effective mass produces too much energy loss to the surface and gives curves that are too broad and do not match the most probable final energies observed in the data of Fig. 1. Without this larger effective mass, the calculated most probable final energy is less than half that observed. The value of the effective mass will also affect the Debye-Waller factor, implying that the value of $2W$ should be divided by 2.3. This would change the typical value calculated above to $2W \approx 7$ at the lower temperature and ranging up to over 30 at the higher temperatures, but these values are still large and within the range indicating classical scattering conditions.

Figure 2 shows angular distributions taken with a low incident energy of 0.065 eV, a surface temperature of 140 K, and four incident angles from 40° to 70° separated by 10° intervals. These data were taken on Ru(0001) with an ordered (1×1) hydrogen monolayer and a low-energy electron diffraction analysis enabled the surface azimuthal orientation to be determined as the $\langle 11\bar{2}0\rangle$ direction. At the incident angle closest to normal θ_i=40° the experimental points consist of a broad peak with a rather pronounced shoulder at about θ_f=60° and for the more grazing incident angles a diffraction feature gradually appears at the specular position. For θ_i=40° the value of $2W \approx 12$ at the specular position would seem to preclude the possibility of seeing a quantum peak, because even taking into account the effective mass would reduce this to about 5 which is still a rather large value for observing quantum effects. However, at the larger, more grazing angles the $2W$ value becomes smaller and for θ_i=70° where $2W \approx 3$ (evaluated with the effective mass of a single Ru atom) a distinct specular diffraction peak is observed.

The calculations shown as solid curves in Fig. 2 were carried out assuming the same effective mass M_C as for a clean Ru(0001) surface. There is little reason to suspect that the tightly bound hydrogen overlayer would have a noticeable effect on the scattering of a heavy projectile such as Ar. However, this question was directly addressed by some of the authors of Ref. 1 in a series of experiments in which Ar scattering measurements from clean and (1×1) hydrogen-covered Ru(0001) were compared directly under otherwise identical conditions. Negligible differences in the scattered spectra were observed as a result of the adsorbed hydrogen layer.[19]

At the incident angle of 40°, where the Debye-Waller evaluation clearly indicates classical scattering conditions, the calculations agree very well with the data, and this agreement includes the interesting shoulder feature. At the more grazing angles, since the exponent $2W$ near the specular position varies approximately as $\cos^2\theta_i$, the Debye-Waller factor quickly increases allowing the specular quantum diffraction peak to appear. In fact, if the effective mass is used $2W$ becomes approximately 1 at the largest angle of 70°, making this case clearly in the quantum regime. For these larger angles where quantum effects are important, the present classical mechanical calculations are not expected to be valid, and they explain only qualitatively the broad background under the specular peak.

The good agreement for the clearly classical scattering conditions for $\theta_i=40°$ is quite interesting. In the calculations, the reason for the shoulder appearing in the neighborhood of $\theta_f=60°$ is due to the nature of the differential reflection coefficient. Its most important feature is the product of two Gaussian-like functions, one in the energy transfer $E_f-E_i-\Delta E_0$ and the other in the parallel momentum transfer $\mathbf{P}$. Although the angular distribution consists of an integral over all final energies, the dominant contribution to this integral comes from the region of final energies in the neighborhood of the minima of the argument of the Gaussian-like functions in the differential reflection coefficient. Typically, this results in a scattered angular distribution that has a single broad peak in the general neighborhood of the specular position. For given incident and final angles, the argument of the exponential of the differential reflection coefficient does not necessarily vanish, because this would require the simultaneous conditions $E_f-E_i-\Delta E_0=0$ and $\mathbf{P}=0$. However, the shoulder at $\theta_f\approx60°$ appearing in Fig. 2 can be associated with conditions in which these simultaneous requirements are satisfied, i.e., conditions in which the minimum of the argument of the Gaussian-like function in the differential reflection coefficient actually is zero.

In order to understand this better, it is of interest to consider each of the two Gaussian-like functions separately. In the range of final energies $0<E_f<\infty$ the condition $E_f-E_i-\Delta E_0=0$ is always satisfied if the mass ratio $m/M_C<1$ for any combination of incident and final angles. The condition $\mathbf{P}=0$ is usually not simultaneously satisfied. However, under certain special circumstances both may be simultaneously satisfied. One of these circumstances is when θ_i is near normal and θ_f is larger and there is net energy loss to the surface, precisely the conditions of Fig. 2. The condition $E_f-E_i-\Delta E_0=0$ requires $E_f<E_i$, and the in-plane parallel momentum transfer which is proportional to $\sqrt{E_i}\sin\theta_i-\sqrt{E_f}\sin\theta_f$ can also simultaneously vanish because $\sin\theta_f>\sin\theta_i$, and in fact this may occur at more than one angle. It is of interest to note that classical stochastic trajectory calculations with model potentials for the scattering of Ar from metal surfaces have also exhibited shoulderlike features in scattered angular distributions.[20]

This explanation of the shoulder appearing in Fig. 2 leads immediately to suggestions for further interesting experiments. In particular, energy-resolved measurements for final angles near specular and near the position of the shoulder should be able to separate out the effects of the two Gaussian-like terms in the differential reflection coefficient. This should provide a more precise value of the parameter v_R which, in turn, will provide physical information on the correlations of the surface electron density at nearby separations.[21]

The reasoning behind the preceding statement is as follows. The quantity v_R is actually a well-defined weighted average of all phonon velocities parallel to the surface.[15] It arises because of the fundamental condition of conservation of momentum parallel to the surface for each of the many phonons transferred. Because in a classical scattering event, many phonons are generated, this translates into the Gaussian-like function in parallel momentum transfer $\mathbf{P}$ appearing in the differential reflection coefficient. This Gaussian-like function is a correlation function, and its Fourier transform, which is a Gaussian-like correlation function in positions parallel to the surface, provides an effective length R_C over which the collision samples the correlations of the surface. If the Gaussian like function in the differential reflection coefficient is expressed in terms of this correlation length according to

$$\exp\left(-\frac{2v_R^2\mathbf{P}^2}{4k_BT_S\Delta E_0}\right)=\exp\left(-\frac{\mathbf{P}^2R_C^2}{\hbar^2}\right), \tag{2}$$

the temperature and energy dependence of R_C can be evaluated in terms of the Debye-Waller exponent of Eq. (1) and for the present Ar/Ru system the result is $R_C=1.9/\sqrt{2W}$ Å.

The present theoretical analysis appears to resolve the question of why diffraction peaks are so readily visible in the Ar/Ru(0001) system. The observed energy resolved spectra and angular distributions can be explained only if the Ar beam is assumed to be scattering from a collection of more than one surface atom with an effective mass of approximately 2.3 Ru atomic masses. The same effective mass is what appears in the denominator of the Debye-Waller exponent $2W$ of Eq. (1), which implies that $2W$ is actually 1/2.3 times smaller, and consequently the Debye-Waller factor much larger, allowing quantum effects to be readily seen at small incident energies and low surface temperatures.

This observation of collective effects leads to an interesting prediction. The unusual nature of the Ru surface, with its large effective mass for both atomic Ar and molecular N_2 scattering, means that ruthenium presents a unique system in which surface structure and dynamics could be studied by quantum mechanical scattering of a range of atomic and molecular projectiles with relatively large masses, but at inci-

dent energies that are readily achievable in, for example, typical He scattering experiments.[22] Using projectiles with widely differing masses and electronic distributions, quantum diffraction and single phonon measurements can provide interesting comparative structural and dynamical information on the surface electron density at different classical turning point distances from the outermost surface layer. For example, a comparative examination of both He and Ne atom diffraction from hydrogen-covered nickel and rhodium surfaces was able to demonstrate clear anticorrugating effects due to the hybridization of the orbitals of the incoming atoms with the unoccupied metal states.[23] The availability of quantum mechanical projectiles with widely different masses and electronic properties for probing Ru surfaces could lead to similar important comparative studies on this system.

We would like to thank B. Berenbak and A. W. Kleyn for helpful discussions and for making their data available to us. This work was supported by the U.S. Department of Energy under Grant No. DE-FG02-98ER45704.

[1] B. Berenbak, S. Zboray, B. Riedmuller, D. C. Papageorgopoulos, S. Stolte, and A. W. Kleyn, Phys. Chem. Chem. Phys. **4**, 68 (2002).
[2] B. Berenbak, Ph.D. thesis, Vrije Universiteit Amsterdam, The Netherlands, 2000.
[3] E. K. Schweizer and C. T. Rettner, Phys. Rev. Lett. **62**, 3085 (1989).
[4] E. K. Schweizer, C. T. Rettner, and S. Holloway, Surf. Sci. **249**, 335 (1991).
[5] F. Althoff, T. Andersson, and S. Andersson, Phys. Rev. Lett. **79**, 4429 (1997).
[6] A. Šiber and B. Gumhalter, Phys. Rev. Lett. **81**, 1742 (1998).
[7] A. Muis and J. R. Manson, J. Chem. Phys. **107**, 1655 (1997).
[8] A. Muis and J. R. Manson, J. Chem. Phys. **111**, 730 (1999).
[9] Jinze Dai and J. R. Manson, J. Chem. Phys. **119**, 9842 (2003).
[10] Massimo F. Bertino, J. R. Manson, and W. Silvestri, J. Chem. Phys. **108**, 10239 (1998).
[11] H. Mortensen, E. Jensen, L. Diekhöner, A. Baurichter, A. C. Luntz, and V. V. Petrunin, J. Chem. Phys. **118**, 11200 (2003).
[12] Hailemariam Ambaye and J. R. Manson, J. Chem. Phys. **125**, 084717 (2006).
[13] J. C. Tully, J. Chem. Phys. **92**, 680 (1990).
[14] R. J. W. E. Lahaye, Ph.D. thesis, Vrije Universiteit Amsterdam, The Netherlands, 1995.
[15] R. Brako and D. M. Newns, Phys. Rev. Lett. **48**, 1859 (1982); R. Brako, Surf. Sci. **123**, 439 (1982).
[16] H.-D. Meyer and R. D. Levine, Chem. Phys. **85**, 189 (1984).
[17] J. R. Manson, Phys. Rev. B **43**, 6924 (1991).
[18] J. Braun, K. L. Kostov, G. Witte, L. Surnev, J. G. Skofronick, S. A. Safron, and Ch. Wöll, Surf. Sci. **372**, 132 (1997).
[19] B. Riedmüller, I. M. Ciobîcă, D. C. Papageorgopoulos, B. Berenbak, R. A. van Santen, and A. W. Kleyn, Surf. Sci. **465**, 347 (2000).
[20] Henry J. Castejón, Surf. Sci. **564**, 156 (2004).
[21] W. W. Hayes and J. R. Manson, Phys. Rev. B **74**, 073413 (2006).
[22] *Helium Atom Scattering*, edited by E. Hulpke, Springer Series in Surface Sciences Vol. 27 (Springer-Verlag, Heidelberg, 1992).
[23] K. H. Rieder, G. Parschau, and B. Burg, Phys. Rev. Lett. **71**, 1059 (1993).