Quantum Decoherence Behavior in Neon Scattering from Ru(0001) and Graphene/Ru(0001) Surfaces: Experiment and Comparison with Calculations

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ABSTRACT: We report Ne atom scattering from clean Ru(0001) and from Ru(0001) covered with a single layer of graphene. For both systems, the quantum and classical regimes are observed and analyzed. The quantum to classical boundary is explored by varying both the surface temperature and the incident Ne kinetic energy. The classical smooth surface model is used to perform theoretical simulations in order to reproduce the angular distributions in the classical regime and determine the effective surface mass and hence allow determination of the Debye temperature. The theoretical calculations, in agreement with experiments, predict angular distributions that are subspecular at low energies and shift to



supraspecular with increasing incident energy. The energy-resolved spectra in the classical regime exhibit only a single and somewhat broad multiphonon peak, but this peak persists into the regime where quantum features are also observed; thus care must be taken to avoid misinterpretation of the multiphonon background peak as a single phonon feature.

I. INTRODUCTION

The employment of rare gas scattering to investigate the structural and dynamical properties of surfaces is a wellestablished technique.^{1,2} The use of heavier projectiles is in many cases unfavorable in atom scattering experiments. However, Ne atoms have been shown to be very sensitive to the surface structure when the incident energy and the surface temperature are in the neighborhood of room temperature or smaller.^{3–5} In fact, Ne scattering presented larger corrugation amplitudes than those obtained with He atoms. $^{6-9}$ This higher sensitivity makes the Ne atom beam an interesting candidate to be used as a probe in neutral atom microscopy, $^{10-13}$ in addition to its usage in fundamental studies. Investigation of the Ru(0001) surface by means Ne and Ar scattering in the quantum domain has already been reported in the past.¹⁴ These early studies confirm how a normal corrugation effect is observed with Ne, whereas anticorrugating effects are present in the cases of He and Ar.

Furthermore, Ne being a heavier rare gas than He readily allows the study of the scattering in the classical regime by increasing the incident beam energy or the surface temperature,¹⁵ permitting exploration of the decoherence mechanism in atom diffraction from surfaces.^{16,17} A recent study by Shichibe et al.¹⁸ demonstrated that using quantum and classical rare gas (He, Ar, Xe) atom scattering from graphene on metal

substrates, it is possible to quantify the graphene-substrate interaction in terms of Debye temperature. However, the behavior of Ne scattering from metal and graphene-terminated metal has not yet been thoroughly investigated in both the quantum and classical domains in a systematic manner providing angular distributions and time-of-flight measurements.

In this work we use Ne scattering to explore the quantum boundary, i.e., the transition between the coherent quantum regime and the incoherent classical regime, on two different surfaces, Ru(0001) and graphene-covered Ru(0001). For the first time a systematic study of Ne atom scattering from solid surfaces has been performed in the classical regime, recording both angular distributions and time-of-flight spectra.

The Ne scattering measurements carried out in the classical regime are analyzed with a classical theory of heavier rare gas scattering, called the smooth surface model (SSM).¹⁹⁻²³ The comparison between the theoretical and experimental data enables an evaluation of the effective surface mass as seen by the Ne projectiles in the collision.

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This work also measures the surface Debye temperature of Ru(0001) using a combination of measurements in the quantum and classical regimes. Knowledge of the surface effective mass obtained in the classical regime, combined with quantum mechanical measurements of the Debye–Waller attenuation of the specular diffraction peak, allows for an unambiguous determination of the surface Debye temperature.

In addition, the behavior of the peak position and spectral shape of the angular distributions has been explored as a function of the incident beam energy by comparison of experiment with calculations. Finally, in the classical regime where no evidence of quantum features is detected, energy-resolved scattering spectra exhibit only a single broad multiphonon peak, similar to the situation reported previously for Ne scattering on Ni(111).²⁴

II. EXPERIMENTAL SECTION

Ne scattering measurements were carried out in two different ultrahigh vacuum (UHV) chambers designed for atom scattering located at LASUAM (Laboratorio de Superficies de la Universidad Autónoma de Madrid). The first chamber contains a Thermal Energy Atomic and Molecular Scattering (TEAMS) apparatus which enables determination of absolute diffraction reflectivities. The angular distribution of scattered atoms, taken for fixed incident angle θ_i and variable final angle θ_{ρ} is recorded with a detector that is a quadrupole mass spectrometer mounted on a two-axis goniometer which can be rotated 200° within the X–Y plane and 15° out-of-plane.²⁵ With the target crystal moved out of the incident beam, the detector can be moved to receive directly the incident beam, thus permitting measurements of absolute reflection intensities.

The second setup is a high-resolution helium atom scattering apparatus with a time-of-flight arm (HAS-TOF) and a fixed angle of 105.4° between incident and outgoing beams.^{26,27} The angular distributions of diffracted beams are measured by continuous rotation of the crystal with angular steps of $\Delta \theta_i = 0.04^\circ$ around a normal to the plane defined by the incident and the outgoing beams. After scattering, Ne particles travel through three differentially pumped stages along a 1.7 m long time-of-flight drift tube, where they are detected by means of a mass-sensitive detector. At fixed angles the time-of-flight capability allows measurements of energy-resolved spectra. The energy resolution is about 0.5 meV.

In both systems the Ne beam is generated by introducing the Ne gas from a 60 bar reservoir into a high vacuum chamber (10^{-6} mbar) via a 10 μ m platinum nozzle. The incident beam energy can be varied in the TEAMS apparatus between 18 and 151 meV by regulating the nozzle temperature, with the corresponding energy spread varying from 2 to 14%, respectively, and similarly in the TOF machine up to a maximum of 92 meV. The angular resolution of the TEAMS apparatus is 1°, whereas that of the HAS-TOF apparatus is 0.13°.

The sample employed in this study is a Ru(0001) single crystal disk 2 mm thick with a diameter of 10 mm. Clean Ru(0001) surfaces were prepared in UHV by cycles of ion sputtering (1 keV $P_{\rm Ar} \simeq 2 \times 10^{-5}$ mbar), followed by oxygen exposures at 1150 K plus final flashes up to 1500 K. In both chambers, surface cleanliness and order were ensured by frequent monitoring of the angular distribution in the neighborhood of a specularly reflected He beam as well as through low energy electron diffraction (LEED) measurements.

In order to obtain a graphene surface on the clean Ru(0001) substrate, the sample was heated to 1100 K and maintained there during exposure to ethylene at pressure $P_{C_2H_4} = 5 \times 10^{-6}$ mbar for 10 min with subsequent slow cooling in UHV.^{28–30} The target temperature was measured with a type-C thermocouple spot-welded to the sample. The angular distributions presented in this work were measured after aligning the sample along the $\overline{\Gamma M}$ direction of Ru(0001), both on clean Ru(0001) and for graphene (Gr) on Ru(0001).

III. THEORETICAL METHOD

In the classical regime and for a potential energy surface that is flat except for small thermal vibrations, the smooth surface model (SSM) holds.^{19–23} The transition rate $w(\mathbf{p}_{\theta}\mathbf{p}_{i})$ for an atom with incident momentum \mathbf{p}_{i} to be scattered into a final state with momentum \mathbf{p}_{f} is¹⁹

$$w(\mathbf{p}_{\rm f}, \, \mathbf{p}_{\rm i}) \propto \frac{1}{(4\pi k_{\rm B}T\Delta E_{\rm 0})^{3/2}} |\tau_{\rm fl}|^2 \\ \exp\left(-\frac{(E_{\rm f} - E_{\rm i} + \Delta E_{\rm 0})^2 + 2\nu_{\rm R}^2 \mathbf{P}^2}{4\pi k_{\rm B}T\Delta E_{\rm 0}}\right)$$
(1)

where $\Delta E_0 = (\mathbf{p}_f - \mathbf{p}_i)^2 / 2M$ is the recoil energy, *M* is the effective mass of the surface, *T* is the surface temperature, E_i and E_f are the initial and final energies of the atom, v_R is a weighted average of phonon velocities parallel to the surface,^{31,32} and **P** is the surface-parallel component of the scattering vector $\mathbf{p}_f - \mathbf{p}_i$. The scattering form factor $|\tau_{\rm fi}|^2$ is the mod-squared transition matrix of the interaction potential. As in other studies using the SSM, it is approximated by its value for the potential of a hard repulsive wall, $\tau_{\rm fi} \propto p_{\rm fz} p_{\rm iz}$.

The expression which, in principle, should be compared with the energy-resolved inelastic spectra measured here is the differential reflection coefficient or intensity as a function of the final solid angle and final kinetic energy $dR(\mathbf{p}_{f}\mathbf{p}_{f})/dE_{f} d\Omega_{f}$ which is obtained from the transition rate upon multiplying by a Jacobian which is proportional to $|\mathbf{p}_{f}|$ and dividing by the incident flux which is proportional to p_{iz} . However, there is a correction that must be applied due to the energy dependence of the detectors. The detector efficiency is proportional to the time that the final scattered particle takes to pass through the ionization chamber, which is inversely proportional to the final momentum. This means that, for comparisons with the present experiments, the theoretical differential coefficient should multiplied by the detector correction factor of $1/p_{fr}$

The quantity to be compared with the measured angular distribution intensities is

$$\frac{dR}{d\Omega_{\rm f}} = \int_0^\infty dE_{\rm f} \; \frac{dR(\mathbf{p}_{\rm f}, \, \mathbf{p}_{\rm i})}{dE_{\rm f} \; d\Omega_{\rm f}} \frac{p_0}{p_{\rm f}} \tag{2}$$

where the factor $1/p_f$ is the detector correction and p_0 is an arbitrary constant having dimensions of momentum.

IV. RESULTS AND DISCUSSION

A. Quantum Decoherence of Diffraction. Figure 1a shows angular distributions of Ne atoms scattered from a clean Ru(0001) surface for an incident beam energy $E_i = 64$ meV, measured with the TEAMS apparatus. The attenuation of the specular peak with increasing surface temperature is readily observed. Ne scattering allows a clear visualization of the transition from the quantum to classical regimes. The black



Figure 1. Attenuation of the specular peak with increasing surface temperature of the Ru(0001) sample measured at two different incident energies and angles: (a) incident beam energy $E_i = 64 \text{ meV}$ and $\theta_i = 60^\circ$; (b) incident beam energy $E_i = 151 \text{ meV}$ and $\theta_i = 30^\circ$. The vertical dashed line denotes the specular position.

spectrum, corresponding to a surface temperature of 90 K, exhibits an evident elastic peak, but no other diffraction features. With increasing surface temperature, the intensity of the specular peak decreases and the background, due to inelastic scattering, begins to dominate (green and cyan spectra). At the highest surface temperature, only a broad classical peak is observed (magenta spectrum), and it presents a most probable final angle (peak position) that is shifted subspecular with respect to the specular diffraction position.

A detailed study of the behavior of the scattering as independent functions of the incident angle and incident energy has not been carried out, but the transition from quantum mechanical to classical behavior occurs at lower temperatures as both the incident angle is increased toward normal and as the incident energy is increased. An example is exhibited in Figure 1b, where four spectra have been collected at different surface temperatures, for a fixed nozzle temperature of 700 K corresponding to an incident energy of the Ne beam of 151 meV, and for an incident angle of $\theta_i = 30^\circ$. The existence of low-intensity, but well-resolved $(\overline{1}, 0)$ and (1,0) diffraction peaks can be seen in the lowest temperature (black curve) spectrum. This is the fingerprint of the existence of wellordered Ru(0001) domains and of the quantum nature of scattering under these conditions. The angular position of these peaks allows us to derive the lattice constant, $a = 2.70 \pm 0.02$ Å, which agrees well with the value obtained by scanning tunneling microscopy (STM)³³ and density functional theory $(DFT)^{34}$ for clean Ru(0001). The absence of similar first order diffraction peaks in Figure 1a appears to be due to a smaller relative corrugation observed by the Ne under the conditions of smaller energy and larger incident angle. When the temperature is raised to 330 K, slightly above room temperature, the elastic peak decreases and almost disappears and the broader inelastic contribution begins to dominate (red spectrum). At this temperature the situation is in the transition region between quantum and classical behavior. Note that for $E_i = 64$ meV and $\hat{\theta}_i = 60^\circ$ this transition situation happens at a higher temperature (820 K, blue spectrum in Figure 1a). At temperatures of 1100 K and higher the system has fully transitioned into classical scattering and only a broad multiphonon foot is observed. Also in this case an asymmetry in this inelastic background is observed as well as a subspecular shift of the peak position. However, this shift of this classical peak to the left of the specular position is distinctly less than that observed at a similar temperature for the lower energy case of Figure 1a.

Similar results were also obtained for Ne scattering from the Gr/Ru(0001) surface. Figure 2 shows several angular distributions of Ne atoms scattered from Gr/Ru(0001) taken at different surface temperatures from 90 to 980 K. The data in Figure 2a were recorded for a fixed incident angle $\theta_i = 40^\circ$ and incident energy of 43.1 meV. The existence of well-ordered domains can be appreciated in the black spectrum, where diffraction peaks are clearly observed and their intensity has the same order of magnitude as the specular peak. These peaks are a convolution with the moiré superstructures resulting from the mismatch of the lattice constant of the two surfaces, Ru(0001)and Gr/Ru(0001). The positions of the diffraction peaks close to the specular peak correspond to the 11th order of the Gr moiré pattern and are labeled with m(-11,0) and m(11,0). They are ascribed to a periodicity of the moiré lattice of 30 Å.^{33,3}

The very large intensity of the m(11,0) and m(-11,0) peaks in Figure 2a at the temperature of 90 K is not surprising as this phenomenon has been observed previously for He atom scattering from Gr/Ru(0001)³⁶ and from Gr/Al₂O₃.³⁷ In the previous case for He atom scattering the very strong m(11,0) diffraction peak matches nearly exactly the positions of the (1,0) peak of the clean Ru(0001) or Al₂O₃, respectively. However, as shown in Figure 2b, when the incident angle is increased, the positions of the diffraction peaks match with the first order of the Gr pattern. By using the in-plane Bragg diffraction condition for a hexagonal two-dimensional structure, the derived value of the lattice constant of Gr on Ru(0001), is *a* = 2.46 ± 0.02 Å, identical to that reported for Gr/Ru(0001),³³ and agrees well with 2.4612 Å, the periodicity of a single carbon layer in graphite.³⁹

As opposed to the situation for clean Ru(0001) in Figure 1, the two incident angles shown for the Gr/Ru(0001) system in



Figure 2. Attenuation of the Ne specular peak with increasing surface temperature for Gr/Ru(0001), measured at two different incident energies and angles: (a) $E_i = 43.1$ meV and $\theta_i = 40^\circ$; (b) $E_i = 151$ meV and $\theta_i = 50.5^\circ$. Note that the quantum features are lost when the surface temperature is increased and the maximum of the classical peak is shifted toward subspecular positions. The specular position is marked by the vertical dashed line.

Figure 2 are similar: 40° for the incident energy of 43.1 meV and 50.5° for 151 meV. This allows for a much clearer comparison of the effect of increasing the incident energy on the transition from quantum to classical behavior. At the larger incident energy shown in Figure 2b, this system makes the transition from quantum to classical at lower surface temperature. The specular and the diffraction peaks of Gr were detected only up to 150 K (magenta spectrum), due to the strong attenuation caused by the Debye–Waller effect and the high corrugation of Gr on Ru(0001). Also for this system broad and asymmetric peaks centered at subspecular final angles were detected for temperatures above room temperature. The value of the peak shift in this range of temperatures is strongly dependent on the translational energy of the beam. Similarly to the case of clean Ru(0001), the shift of the spectra for Gr/ Ru(0001) is more pronounced for the lowest incident energy. If the incident energy is raised to 151 meV, the most probable angle is very near the specular angle (see Figure 2b).

B. Surface Debye Temperature. Measurements of the thermal attenuation of the reflected beam provide information on the nature of the scattering, for example, whether it is quantum mechanical or classical, and can give an estimate of the surface Debye temperature. The intensity I(T) of a diffraction peak for a surface at a given temperature T is related to its value I_0 that it would have for a frozen lattice completely at rest by the relation¹

$$I(T) = I_0 e^{-2W(T)}$$
(3)

where $\exp\{-2W(T)\}$ is the Debye–Waller factor. A standard procedure is to evaluate the Debye–Waller exponent using a Debye model for the phonons at the surface, and then for sufficiently large *T* and for the specular diffraction peak one obtains

$$2W(T) = \frac{24m(E_{\rm i}\cos^2\theta_i + D)T}{Mk_{\rm B}\Theta_{\rm D}^{\ 2}}$$
(4)

where *m* is the mass of the impinging atoms, *D* is the potential well depth, $k_{\rm B}$ is Boltzmann's constant, and $\Theta_{\rm D}$ is the surface Debye temperature. The appearance of the physisorption well depth *D* added to $E_i \cos^2 \theta_i$, the energy associated with motion normal to the surface, accounts for the larger energy of the atomic projectile as it moves in the well.³⁸

The typical way of evaluating the Debye temperature Θ_D is through evaluation of 2W(T) over a range of temperatures. However, this is impractical for the system of Ne scattering from Ru because, as is evident from Figure 1, at high temperatures the specular peak is completely attenuated and disappears while at lower temperatures the surface is rapidly contaminated, most likely with adsorption of residual hydrogen in the vacuum chamber. At the lower temperatures, during the time needed to achieve a stable temperature, the reflection will be affected by varying degrees of contamination. For this reason we choose to obtain similar information from the incident normal energy dependence of the specular beam at fixed temperature as shown in Figure 3, which exhibits logarithmic attenuation plots for both He and Ne scattering from



Figure 3. Comparison of the thermal attenuation of the specular peak between He (red diamonds) and Ne (blue circles) scattered from Ru(0001). The specular intensity is represented as a function of $E_i \cos^2 \theta_i$. The surface temperature of Ru(0001) is maintained at 200 K for the He measurement and at 90 K for Ne.



Figure 4. (left panels) Comparison of the angular distributions for Ne scattering from Ru(0001) (a and c) and Gr/Ru(0001) (e and g) between experimental data (shown as blue points) and calculations (solid curves). Vertical arrows denote the specular position. (right panels) Most probable final angle as a function of incident energy for Ne scattering from Ru(0001) (b and d) and from Gr/Ru(0001) (f and h). Calculations of the most probable final angle for the angular distributions, shown as solid curves, predict subspecular scattering at low energies, shifting to supraspecular scattering at higher energies.

Ru(0001). The Ru(0001) surface temperature was fixed at 90 K in the measurement of Ne scattering and at 200 K in the measurement of He scattering. The values used for D are 13 meV for He and 22 meV for Ne.²⁸ By taking angular distributions as functions of the incident angle, once the incident energy has been set, more accurate and controlled measurements are possible. Before recording each angular distribution, a flash-annealing was made in order to ensure the cleanliness of the surface, and when the thermocouple marked a fixed temperature value, the measurements were started. In this way, the same experimental conditions for each spectra were assured. The logarithmic Debye–Waller attenuation of the specular peak for scattering of He atoms at a temperature of

200 K (red curve) and for Ne at 90 K (blue curve) from Ru(0001) is shown in Figure 3 as a function of $E_i \cos^2 \theta_i$. The experimental points are the intensity of the quantum mechanical specular diffraction peak only. The intensity *I* is the area of a Gaussian fit to the specular peak after subtracting off the background, in a manner similar to that applied previously to the scattering of He atoms from graphite.⁴¹ This was then normalized to the intensity of the direct incident beam, denoted by I_0 . According to eqs 3 and 4, the logarithmic plot of the normalized intensity versus $E_i \cos^2 \theta_i$ gives rise to a linear decrease in the logarithmic plot, and from the slope one obtains the product $M\Theta_D^2$. Thus, if the effective mass is known an evaluation of the Debye temperature can be made. Previous

work on heavier rare gas scattering from Ru(0001) suggests that a large effective mass needs to be considered, approximately 2.5 times the mass of a single Ru atom (M = 253 amu).⁴⁰ If such a mass is assumed, the surface Debye temperature is 288 ± 20 K for He/Ru(0001) in close agreement with the value of $\Theta_D = 295 \pm 10$ K for the first layer of Ru(0001) measured by Ferrari et al. using core-level photoelectron spectroscopy.⁴² These values are to be compared with the accepted bulk room temperature value of 415 K.⁴³ For Ne using this same effective mass the surface Debye temperature would be 505 ± 20 K. This value for Ne is clearly too large, implying that the effective surface mass should be larger for Ne. To have the same Θ_D as found for He, an effective mass of approximately 8 Ru atoms (809 amu) would need to be assumed.

However, the problem of independently measuring the effective mass can be resolved by making measurements in the classical regime of high incident energies and large surface temperatures. As shown in eq 1, in the classical regime all quantum diffraction is completely attenuated, and what remains is a broader inelastic distribution which is the consequence of large numbers of phonon excitations. This classical intensity of eq 1 depends on the effective mass M through the recoil energy ΔE_{0} , but does not depend on the Debye temperature. The physical reason why the Debye temperature does not appear is because in the classical regime so many phonons are transferred that the nature of the phonon distribution becomes unimportant; i.e., basically any reasonable distribution of phonons at the surface will lead to a result similar to eq 1.

The value of the effective mass M for Ne atoms scattering from clean Ru(0001) was chosen as the mass of 8 Ru atoms as mentioned above. This choice was based on fits of the SSM theory to the full widths at half-maximum (fwhm's) of the most basic measurements, i.e., the energy-resolved spectra such as shown in Figure 5. Although the choice of 8 Ru masses for the effective surface mass can be considered as only approximate, it gives reasonable predictions for the fwhm's of the energyresolved spectra as discussed below in connection with Figure 6. This choice also gives quite reasonable fits to the less basic energy-integrated angular distributions such as shown in Figure 4. However, it must be verified that use of the classical SSM model of eq 1 is valid. As stated above, the nature of the thermal attenuation can be used to indicate when a particular scattering system is in the classical regime. If the exponent 2W(T) is sufficiently large, then the Debye–Waller factor becomes so small that all quantum effects such as diffraction are suppressed and what remains is a classical scattered spectrum. Thus, in order to evaluate the effective mass M in the classical regime, what is necessary is to be assured that 2W(T) is significantly larger than unity. As an example, for Ne impinging with an incident energy $E_i = 64$ meV, on a clean Ru(0001) surface, the value of 2W(T) calculated using eq 4 at the specular position and at a surface temperature of 1100 K ranges from 4 (corresponding to $\theta_i = 60^\circ$) to 6 (corresponding to $\theta_i =$ 30°). Thus, even for the rather large effective mass equal to that of 8 Ru atoms, all of the measurements taken at temperatures as large as 1000 K have values of 2W that are greater than 1, although not necessarily much greater than 1. Nevertheless, even though the value of 2W in these experiments is not always much greater than unity, it is sufficiently large that the SSM of eq 1 can be expected to supply at least a reasonable qualitative prediction of the scattering behavior.

The physical meaning of an effective mass is that it indicates the approximate number of atoms that the incoming Ne interacts with in the collision. The value of approximately 8 Ru atoms found here is somewhat larger than the value previously found for Ar scattering from Ru(0001) which was, as indicated above, approximately 2.5 Ru atoms.⁴⁰

With the independent evaluation of the effective mass M, the Debye temperature measured through Ne scattering is determined to be about 282 K. This is a bit smaller, but still in reasonable agreement with the value of 295 K for the outermost layer of Ru(0001) as measured by core-level photoelectron spectroscopy.⁴²

C. Scattering Behavior in the Classical Regime. The left-hand column of Figure 4 shows a series of angular distributions measured on the TEAMS machine with fixed incident angle as marked, and plotted as a function of total scattering angle $\theta_i + \theta_f$ between the incident beam and detector position. Figure 4a shows an angular distribution taken with an incident energy of 151 meV, an incident angle of 60°, and a surface temperature of 1100 K. All spectra were recorded along the Γ M direction of the Ru(0001) substrate. Ne scattering from Ru(0001) exhibits a broad and symmetric peak centered at the total final scattering angle of approximately 119°. The calculation is shown as a solid line, and it was carried out assuming, as stated above, an effective mass of 8 Ru atoms. The value of $v_{\rm R}$ used in the simulation is 2500 m/s. Under these conditions, the experimental spectrum is well reproduced by the SSM. Figure 4b shows the most probable final angle $\theta_{\rm fMP}$ as a function of incident energy for Ne scattering from Ru(0001) for the same fixed conditions of $\theta_i = 60^\circ$ and $T_s = 1100$ K. The experimental points fall close to the calculated curve with the exception of the single outlying point at $E_i = 100$ meV. Figure 4b shows that for incident energy less than approximately 450 meV the most probable final angle is predicted to be subspecular. However, if the incident energy is raised to about 450 meV, the most probable angle is very near the specular angle, and for larger energies it is predicted to become supraspecular. Whether the angular distribution peaks are predicted to be subspecular or supraspecular depends primarily on the incident energy and angle. Calculations indicate it is not strongly dependent on other parameters such as the effective surface mass. For this reason, it is quite interesting to investigate this behavior for different angles of incidence θ_{i} . Figure 4c presents data recorded at a smaller incident angle, θ_i = 45°, but otherwise with similar experimental conditions, E_i = 151 meV and $T_{\rm S}$ = 1200 K. The experimental spectrum consists of a somewhat sharper peak than the one measured for $\theta_i = 60^\circ$, at a final total angle of approximately 90°. Furthermore, the experimental points present a visible asymmetry with respect to the peak maximum. This shoulder is well reproduced by the SSM, as shown in the solid curve. As shown in Figure 4d, the tendency of the most probable final angle as a function of the incident energy is also predicted. The behavior is similar to the one previously observed for $\theta_i = 60^\circ$, but the predicted recovery energy, i.e., the incident energy at which the most probable final angle is at the specular position, decreases to about 400 meV.

Similar results were also obtained for Ne scattering on the Gr/Ru(0001) surface, as shown in Figure 4e–h. Figure 4e shows angular distribution data for Ne scattering from graphene covered Ru(0001) at an incident energy of 151 meV, at a surface temperature of $T_{\rm S}$ = 1000 K, and for an incident angle of $\theta_{\rm i}$ = 50.5°. The calculation using an effective mass M = 8 Ru atoms and the same value of $v_{\rm R}$ = 2500 m/s

-10

a)

ntensity (a.u.)

-30

-20



E_i = 70 meV

-10

0

 Δ E (meV)

10

-20

Figure 5. Time-of-flight spectra, converted to an energy-transfer scale, for Ne scattered from Ru(0001) at incident energies ranging from 70 to 96 meV and temperature T = 1000 K. The values of the incident angle $\Delta \theta_i$ relative to the specular position are -2 and 2° as noted. The theoretical calculations, normalized to the data at each energy, are presented as black dashed curves, using an effective mass M = 8 Ru and a value of 2500 m/s for $v_{\rm p}$.

-30

40

E_. = 70 meV

30

10

0 ΔE (meV) 20

taken for the clean Ru(0001) surface is shown as a solid curve. The most probable final angle is well reproduced by the calculation, but the spectral shape of Ne scattering from Gr/ Ru(0001) is not as well reproduced by the SSM. The tail of the experimental data appears with a noticeable asymmetry with respect to the peak maximum, even to the point of suggesting the presence of two peaks. The same effect has been observed for Ar scattering on Gr/Ru(0001) by Shichibe et al., where it was explained with a stronger bond in the valley of the Gr moiré corrugation with respect to that in the region of the hill. This effect could be reproduced with two different effective masses, one corresponding to the tightly bound regions of graphene and a smaller effective mass associated with the more loosely bound moiré "hill".¹⁸ Figure 4f presents how the most probable final angle changes as a function of the incident energy in the same experimental conditions for the angular distribution in Figure 4e. From the comparison of the experimental points with the calculations, it is evident that the dependence of the most probable final angle is well reproduced by the theory. As pointed out in a previous section, Ne scattering from Gr/Ru(0001) presents a shift to the subspecular angle more pronounced than the one presented in Ne scattering on Ru(0001). This behavior can also be seen from the spectrum in Figure 4g, taken at a lower incident energy, $E_i = 43.1$ meV. Also in this case a clear asymmetry in the shape of the peak at supraspecular angles is evident. The SSM calculations shown as a solid curve qualitatively explain

the subspecular position, as shown in Figure 4h, where the theoretical calculations predict subspecular scattering at low energies, that shift from subspecular to supraspecular with increasing incident energy.

As mentioned above, both the parameter $v_{\rm R}$ and the effective mass are the same for clean Ru(0001) and graphene covered Ru(0001). This implies that the changes in the phonon spectrum introduced by the graphene monolayer do not appreciably change the multiphonon energy transfers in the classical collisions with Ne projectiles.

This subspecular to supraspecular shift as a function of energy in the angular distributions is apparently caused by a subtle shift in the fractional momentum transfers parallel and perpendicular to the surface. For collisions at low incident energies the fractional momentum transfer is larger in the perpendicular direction. At the recovery point, when the most probable final angle is at the specular position, the fractional momentum transfers in the parallel and perpendicular directions are equal. At larger incident energies the fractional momentum transfer in the parallel direction becomes dominant and the most probable final angle shifts to become supraspecular.

As stated above, the calculations of the peak shift in the righthand panels of Figure 4 are only weakly dependent on the choice of effective mass. For example, if in Figure 4b,d the effective mass is increased to 12 Ru masses the calculated curve comes slightly closer to the experimental data, while if M is

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taken to be 4 Ru masses the agreement is significantly worse. In both cases the recovery temperature is almost unchanged. However, with either the smaller or larger value of M the calculated energy-resolved spectra such as in Figure 5 become significantly worse. As stated above, our choice of approximately 8 Ru masses for the effective mass was based mainly on the widths of the energy-resolved spectra such as shown in Figure 5. This is because the energy-resolved spectra are the measurements that provide the most detailed information on the collision.

D. Time-of-Flight Measurements. Energy-resolved spectra were taken on the HAS-TOF apparatus with a fixed source-to-detector angle of 105.4°, and a series of representative results, converted from time-of-flight to energy transfer ΔE is presented in Figure 5. This series of TOF spectra was recorded by scattering Ne atoms on the clean Ru(0001) surface for three incident angles, $\Delta \theta_i = -2$, 0, and $+2^\circ$, relative to the specular position. For each incident angle, three different high surface temperatures were used at 750, 800, and 1000 K. The incident energies range from $E_i = 70$ to 91 meV, as marked in Figure 5. These spectra are characterized by the absence of quantum coherence features such as single-phonon or diffuse elastic peaks, as also observed for Ne scattering from the Ni(111) surface at 420 K.²⁴

Theoretical calculations using the smooth-surface model are represented in Figure 5 as black dashed lines, using the same effective mass M = 8 Ru atoms and $v_{\rm R} = 2500$ m/s as for the angular distributions. For each energy, the calculations were normalized to the data at the maximum of the corresponding experimental spectrum. The calculations show qualitatively the same general shape and width as exhibited by the data, although the calculations show consistently a shift of about 5 meV toward smaller final energies. The widths of the calculated peaks are quite sensitive to the chosen value of the effective mass, and this was the principal basis for the choice of taking Mto be approximately 8 Ru atomic masses. The peak position of the calculations is rather insensitive to the effective mass and is essentially unchanged if M is either increased or decreased by the mass of 4 Ru atoms. For example, for $E_i = 80$ meV and $\Delta \theta_i$ = 2° the peak position decreases by only 0.08 meV if the effective mass is taken to be 4 Ru atoms and increases by 0.07 meV if the mass is increased to that of 12 Ru atoms. On the other hand, the respective changes to the widths are significant. The smaller mass of 4 Ru atoms increases the 15 meV fwhm shown in Figure 6 by 4 meV, and the larger mass of 12 Ru atoms causes it to decrease by 3.5 meV. The insensitivity of the peak position to the effective mass is contrary to what would be predicted by a hard sphere collision model, where if the mass M were assigned to the target sphere the Ne projectile would lose less energy as M increased. This behavior appears to be due to the fact of the large angle of 105.4° between the incident beam and the detector direction. The discrepancy of roughly 5 meV in peak position between calculations and measurements may be a consequence of the experimental conditions not being fully into the classical regime. As discussed above, for these conditions the Debye-Waller exponent 2W is larger than unity, but not necessarily always much larger; thus the classical theory is not clearly applicable and may give only qualitative behavior.

Although the measured peak positions cannot be made to match the SSM theory, the shapes and widths of the broad peaks are similar. The widths increase with both temperature and incident energy, and this is exhibited in Figure 6, in which



Figure 6. Comparison between experimental and theoretical fwhm's of time-of-flight spectra converted to the energy-exchange domain as a function of the incident energy. Two different incident angles $\Delta \theta_i = 2$ and -2° relative to the specular position are shown. The surface temperature is 1000 K.

the fwhm's are shown as a function of energy for the two incident angles of $\Delta \theta_i = 2^\circ$ and $\Delta \theta_i = -2^\circ$ measured relative to the specular position. The theory predicts the fwhm's reasonably well, particularly for $\Delta \theta_i = 2^\circ$.

The classical multiphonon peaks such as exhibited in the inelastic spectra of Figure 5 can persist even at low temperatures and incident energies where quantum features such as diffuse elastic peaks or single surface phonon peaks can be observed. It has recently been shown, if care is not taken, that it is possible to misinterpret multiphonon features as being single-phonon peaks.²⁴ Figure 7 shows how the classical multiphonon peaks in Figure 5 can appear as an anomalous single-phonon dispersion curve. Plotted in Figure 7 is the energy transfer ΔE as a function of the parallel momentum transfer ΔK . In an atom-surface scattering event involving excitation of a single surface phonon of frequency $\omega(\Delta K)$, the conservation law for energy is $E_{\rm f} - E_{\rm i} = \hbar\omega(\Delta K)$ and conservation of parallel momentum demands that $K_f - K_i =$ ΔK , where $\hbar K_{\rm f}$ and $\hbar K_{\rm i}$ are the final and initial parallel momenta of the atom, respectively. Combining the two conservation laws results in a quadratic equation for ΔE = $\hbar\omega(\Delta \mathbf{K})$ as a function of $\Delta \mathbf{K}$ which is called the scan curve. For a given set of initial conditions, meaning incident energy and angle, only surface phonons with both $\Delta E = \hbar \omega (\Delta K)$ and ΔK lying on the scan curve can be observed. By systematically varying either the incident energy or angle, complete dispersion curves for all surface phonons can be mapped onto a graph such as in Figure 7. In Figure 7, for the fixed incident angles of $\Delta \theta_i = -2, 0, \text{ and } +2^\circ$, the solid curves with colors corresponding to different incident energies as indicated are the respective scan curves. The experimental data points, shown as blue diamonds, are positioned on each scan curve at the energy equal to the most probable final energy (peak position) of the corresponding energy-resolved spectrum such as in



Figure 7. Anomalous dispersion curve plot for Ne scattering from clean Ru(0001) showing the energy transfer value of the most probable final energy as a function of parallel momentum transfer of an assumed single surface phonon transfer of the same energy. The blue diamond data points were collected for T = 1000 K; they are the experimental anomalous dispersion points obtained from Figure 5. Black circles are theoretical calculations predicted by the SSM model. Single phonon scan curves for incident beam energies used in the experiment are calculated for $\Delta \theta_i = -2$, $\Delta \theta_i = 0$, and $\Delta \theta_i = 2$ for each incident energy as marked.

Figure 5. The predictions of the SSM classical theory are also shown as black filled circles. Although only three different incident angles $\Delta \theta$ are shown in Figure 7, it is clear that if a large enough range of $\Delta \theta$ values were plotted the most probable final energies would form a curve that resembles a single-phonon dispersion. A more extensive example for the case of Ne scattering from Ni(111) is discussed in ref 24. However, such a curve is a false, or anomalous dispersion because the energy transfers ΔE extracted from the most probable final energies such as exhibited in Figure 5 are due to multiphonon transfers and are not at all due to single-phonon features. Such multiphonon features are less expected for the case of He atom scattering, although they have been discussed.⁴⁴ On the other hand, for Ne scattering, and by extension for scattering of heavier rare gas projectiles, we have demonstrated here that many experimental measurements may be carried out at or near the decoherence boundary between quantum and classical physics. Thus, care must be taken to avoid misinterpretation of such anomalous dispersion features which are really due to multiphonon transfers.

V. CONCLUSIONS

The scattering of atoms from surfaces presents an interesting system for examining the decoherence transition from coherent quantum mechanical behavior at low temperatures and energies to the fully classical regime of high temperatures and energies, with the driving mechanism being excitation of increasingly larger numbers of phonons. In this work we consider the scattering of Ne atoms from clean Ru(0001) and from single layer graphene covered Ru(0001). Ne is an especially useful projectile for this study because its mass is sufficiently small so that, for both translational energies and target temperatures in the neighborhood of room temperature or smaller, its scattering spectra exhibit quantum features such as diffraction, single phonon excitation peaks, or diffuse elastic reflection due to defects and disorder. However, by increasing the target temperatures or incident beam energies to higher values readily obtainable in most experimental configurations, all quantum features are attenuated and what remains are scattering spectra that are explained by classical physics.

In this paper angular distributions of Ne scattered from both clean Ru(0001) and Gr/Ru(0001) taken at temperatures below ambient and energies below 100 meV showed clear specular diffraction as well as off-specular diffraction peaks. As either the temperature or incident Ne translational energy was increased, the quantum diffraction was suppressed by the Debye–Waller attenuation. At higher temperatures and larger energies only broad features were observed, and these were reasonably well described by the classical theory of the smooth surface model.

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Interestingly, the Ne atom scattering characteristics were rather similar for both the clean Ru(0001) and Gr/Ru(0001) targets. In the quantum regime both surfaces exhibited clear specular diffraction peaks as well as nonspecular diffraction. The nonspecular diffraction from Gr/Ru(0001) was strongly enhanced when the diffraction peak positions of the moiré overlayer pattern coincided with the diffraction peaks of the clean Ru(0001), and they became nearly as large as the specular peak. In the classical regime Ru(0001) exhibited broad peaks both in the angular distributions and in the energy-resolved spectra. The classical behavior of both Ru(0001) and Gr/Ru(0001) is reasonably well described by the smooth surface theoretical model using the same set of parameters for the effective mass *M* and $\nu_{\rm R}$.

The combination of successive measurements in either the quantum or classical domain allowed an evaluation of the surface Debye temperature as measured by Ne atom scattering. Measurements of the Debye–Waller attenuation factor in the quantum regime allow for evaluation of the product of the Debye temperature Θ_D and the effective surface mass M in the form $M\Theta_D^2$. Measurements in the classical regime depend on the same effective mass, but do not depend on the Debye temperature or on any other specifics of the phonon distribution. Thus, with an independent measure of M evaluated from fits to the classical scattering features, it is possible to make an evaluation of Θ_D for Ru(0001). This value is in agreement with a previous independent measurement using core level photoelectron spectroscopy.

An interesting observation is that for small incident Ne energies the broad classical angular distribution peaks, observed in the classical regime induced by high surface temperatures, were not centered about the specular angles, but were shifted distinctly in the subspecular direction. This behavior occurred for all measured incident angles, and as the incident energy increased, the most probable final angle of the broad classical peak shifted toward the specular position. Calculations with the smooth surface model agree well with this shift, and even predict that at a distinct energy called the "recovery energy" the most probable final angle would appear precisely at specular. For energies larger than the recovery energy, the classical peak would become supraspecular.

It is also noted that at or near the decoherence boundary investigated here, both quantum features and residual classical peaks in the background can appear simultaneously. Because the quasi-classical multiphonon feature appears in the energyresolved spectra as a peak, albeit somewhat broad, it is possible to mistake it as a putative single phonon quantum feature. Complicating this issue is the fact that the classical peak often shifts position as a function of controllable experimental parameters, notably changes of the incident angle, in a way that mimics a single phonon dispersion curve. Thus, care must be taken not to mistake multiphonon peak features as anomalous single phonon dispersion behavior.

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The authors declare no competing financial interest.

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REFERENCES

(1) Farías, D.; Rieder, K.-H. Atomic beam diffraction from solid surfaces. *Rep. Prog. Phys.* **1998**, *61*, 1575–1664.

(2) Rieder, K. H. Surface structural research with atom beam diffraction: helium versus neon. *Surf. Rev. Lett.* **1994**, *01*, 51–65.

(3) Rieder, K. H.; Stocker, W. Observation of Pronounced Neon Diffraction from Low-Index Metal Surfaces. *Phys. Rev. Lett.* **1984**, *52*, 352–355.

(4) Salanon, B. Ne diffraction from Cu (110). J. Phys. (Paris) 1984, 45, 1373-1379.

(5) Farías, D.; Patting, M.; Rieder, K. H. A helium atom scattering study of the H/NiAl(110) adsorption system. *J. Chem. Phys.* 2002, *117*, 1797–1803.

(6) Parschau, G.; Kirsten, E.; Bischof, A.; Rieder, K. H. Diffraction of He and Ne and selective adsorption of He on Rh (110). *Phys. Rev. B: Condens. Matter Mater. Phys.* **1989**, 40, 6012–6017.

(7) Apel, R.; Farías, D.; Tröger, H.; Kirsten, E.; Rieder, K. H. Atomic beam diffraction and resonant scattering studies of clean Rh (311) and the c (1×1) H phase. *Surf. Sci.* **1996**, *364*, 303–311.

(8) Rieder, K. H.; Parschau, G.; Burg, B. Experimental evidence for anticorrugating effects in He-metal interactions at surfaces. *Phys. Rev. Lett.* **1993**, *71*, 1059–1062.

(9) Annett, J. F.; Haydock, R. Anticorrugating effect of hybridization on the helium diffraction potential for metal surfaces. *Phys. Rev. Lett.* **1984**, 53, 838–841.

(10) Holst, B.; Allison, W. An atom-focusing mirror. Nature 1997, 390, 244.

(11) Fladischer, K.; Reingruber, H.; Reisinger, T.; Mayrhofer, V.; Ernst, W. E.; Ross, A.; MacLaren, D.; Allison, W.; Litwin, D.; Galas, J.; et al. An ellipsoidal mirror for focusing neutral atomic and molecular beams. *New J. Phys.* **2010**, *12*, 033018.

(12) Barredo, D.; Calleja, F.; Nieto, P.; Hinarejos, J.; Laurent, G.; Vázquez de Parga, A. L.; Farías, D.; Miranda, R. A Quantum-stabilized mirror for atoms. *Adv. Mater.* **2008**, *20*, 3492–3497.

(13) Anemone, G.; Al Taleb, A.; Eder, S. D.; Holst, B.; Farías, D. Flexible thin metal crystals as focusing mirrors for neutral atomic beams. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *95*, 205428.

(14) Minniti, M.; Diaz, C.; Cuñado, J. L. F.; Politano, A.; Maccariello, D.; Martin, F.; Farías, D.; Miranda, R. Helium, neon and argon diffraction from Ru (0001). *J. Phys.: Condens. Matter* 2012, 24, 354002.
(15) Kondo, T.; Mori, D.; Okada, R.; Sasaki, M.; Yamamoto, S. A molecular-beam study of the collision dynamics of methane and dynamics of methane and dynamics of methane and dynamics. *Phys. Rev. Phys. Rev. Cond.* 2012, 24, 35402.

ethane upon a graphitic monolayer on Pt (111). J. Chem. Phys. 2005, 123, 114712. (16) Bundaleski, N.; Soulisse, P.; Momeni, A.; Khemliche, H.;

Roncin, P. Decoherence in fast atom diffraction from surfaces. Nuclear. Nucl. Instrum. Methods Phys. Res., Sect. B 2011, 269, 1216– 1220.

(17) Roncin, P.; Debiossac, M. Elastic and inelastic diffraction of fast atoms, Debye-Waller factor, and Mössbauer-Lamb-Dicke regime. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *96*, 035415.

(18) Shichibe, H.; Satake, Y.; Watanabe, K.; Kinjyo, A.; Kunihara, A.; Yamada, Y.; Manson, J. R.; Sasaki, M.; Hayes, W. W. Probing interlayer interactions between graphene and metal substrates by supersonic rare-gas atom scattering. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *91*, 155403.

(19) Manson, J. R. Inelastic scattering from surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1991**, 43, 6924–6937.

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(20) Manson, J. R. Multiphonon atom-surface scattering. *Comput. Phys. Commun.* **1994**, *80*, 145–167.

(21) Hayes, W. W.; Manson, J. R. Rare gas collisions with molten metal surfaces. J. Chem. Phys. 2007, 127, 164714.

(22) Hayes, W. W.; Manson, J. R. Determination of the surface corrugation amplitude from classical atom scattering. *Phys. Rev. Lett.* **2012**, *109*, 063203.

(23) Hayes, W. W.; Manson, J. R. Classical and semiclassical theories of atom scattering from corrugated surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89*, 045406.

(24) Al Taleb, A.; Anemone, G.; Hayes, W. W.; Manson, J. R.; Farías, D. Multiphonon excitation and quantum decoherence in neon scattering from solid surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *95*, 075414.

(25) Nieto, P.; Barredo, D.; Farías, D.; Miranda, R. In-plane and outof-plane diffraction of H_2 from Ru(001). *J. Phys. Chem. A* **2011**, *115*, 7283–7290.

(26) Ernst, H. J.; Hulpke, E.; Toennies, J. P. Helium-atom-scattering study of the structure and phonon dynamics of the w(001) surface between 200 and 1900 K. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, 46, 16081–16105.

(27) Barredo, D.; Laurent, G.; Nieto, P.; Farías, D.; Miranda, R. High-resolution elastic and rotationally inelastic diffraction of D_2 from NiAl(110). *J. Chem. Phys.* **2010**, 133, 124702.

(28) Politano, A.; Borca, B.; Minniti, M.; Hinarejos, J. J.; Vázquez de Parga, A. L.; Farías, D.; Miranda, R. Helium reflectivity and Debye temperature of graphene grown epitaxially on Ru(0001). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *84*, 035450.

(29) Sutter, P.; Minniti, M.; Albrecht, P.; Farías, D.; Miranda, R.; Sutter, E. A high-reflectivity, ambient-stable graphene mirror for neutral atomic and molecular beams. *Appl. Phys. Lett.* **2011**, *99*, 211907.

(30) Vázquez de Parga, A. L.; Calleja, F.; Borca, B.; Passeggi, M. C. G.; Hinarejos, J. J.; Guinea, F.; Miranda, R. Periodically rippled graphene: growth and spatially resolved electronic structure. *Phys. Rev. Lett.* **2008**, *100*, 056807.

(31) Brako, R.; Newns, D. M. Differential cross section for atoms inelastically scattered from surfaces. *Phys. Rev. Lett.* **1982**, *48*, 1859–1862.

(32) Brako, R.; Newns, D. M. Energy and angular distribution of atoms scattered from surfaces. *Surf. Sci.* **1982**, *117*, 42–52.

(33) Marchini, S.; Günther, S.; Wintterlin, J. Scanning tunneling microscopy of graphene on Ru (0001). *Phys. Rev. B: Condens. Matter Mater. Phys.* 2007, 76, 075429.

(34) Wang, B.; Bocquet, M.-L.; Marchini, S.; Günther, S.; Wintterlin, J. Chemical origin of a graphene moiré overlayer on Ru (0001). *Phys. Chem. Chem. Phys.* **2008**, *10*, 3530–3534.

(35) Borca, B.; Barja, S.; Garnica, M.; Minniti, M.; Politano, A.; Rodriguez-García, J. M.; Hinarejos, J. J.; Farías, D.; Vázquez de Parga, A. L.; Miranda, R. Electronic and geometric corrugation of periodically rippled, self-nanostructured graphene epitaxially grown on Ru (0001). *New J. Phys.* **2010**, *12*, 093018.

(36) Maccariello, D.; Campi, D.; Al Taleb, A.; Benedek, G.; Farías, D.; Bernasconi, M.; Miranda, R. Low-energy excitations of graphene on Ru (0001). *Carbon* **2015**, *93*, 1–10.

(37) Anemone, G.; Climent-Pascual, E.; Yu, H. K.; Al Taleb, A.; Jiménez-Villacorta, F.; Prieto, C.; Wodtke, A. M.; De Andrés, A.; Farías, D. Quality of graphene on sapphire: long-range order from helium diffraction versus lattice defects from Raman spectroscopy. *RSC Adv.* **2016**, *6*, 21235–21245.

(38) Beeby, J. L. Scattering of Helium Atoms from Surfaces. J. Phys. C: Solid State Phys. 1971, 4, L359.

(39) Nelson, J. B.; Riley, D. P. The thermal expansion of graphite from 15 c. to 800 c.: Part I. Experimental. *Proc. Phys. Soc.* **1945**, *57*, 477–486.

(40) Hayes, W. W.; Manson, J. R. Argon scattering from Ru(0001): calculations and comparison with experiment. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, 75, 113408.

(41) Oh, J. P.; Kondo, T.; Hatake, D.; Nakamura, J. Elastic and inelastic scattering components in the angular intensity distribution of He scattered from graphite. *Surf. Sci.* **2009**, *603*, 895.

(42) Ferrari, E.; Galli, L.; Miniussi, E.; Morri, M.; Panighel, M.; Ricci, M.; Lacovig, P.; Lizzit, S.; Baraldi, A. Layer-dependent Debye temperature and thermal expansion of Ru(0001) by means of highenergy resolution core-level photoelectron spectroscopy. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *82*, 195420.

(43) Ho, C. Y.; Powell, R. W.; Liley, P. E. Thermal conductivity of the elements: a comprehensive review. *J. Phys. Chem. Ref. Data* **1974**, 3 (Suppl. 1), I-10.

(44) Celli, V.; Himes, D.; Tran, P.; Toennies, J. P.; Wöll, C.; Zhang, G. Multiphonon processes in atom-surface scattering. *Phys. Rev. Lett.* **1991**, *66*, 3160–3163.