Multiphonon excitation and quantum decoherence in neon scattering from solid surfaces

Amjad Al Taleb,^{1,*} Gloria Anemone,¹ W. W. Hayes,² J. R. Manson,^{3,4} and Daniel Farías^{1,5,6}

¹Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain

²Physical Sciences Department, Greenville Technical College, Greenville, South Carolina 29606, USA

³Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634, USA

⁴Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 Donostia, San Sebastian, Spain

⁵Instituto "Nicolás Cabrera", Universidad Autónoma de Madrid, 28049 Madrid, Spain

⁶Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain

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We present angle- and energy-resolved analysis of Ne scattering from a Ni(111) surface at moderate beam energy and surface temperature. Variation of the surface temperature allows the transition from a pure quantum regime, where single-phonon events are observed, to the classical regime, where multiphonon excitations are observed. The latter can be reproduced by classical calculations. Therefore, our data lie on the border between the coherent quantum regime and the incoherent classical regime.

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I. INTRODUCTION

The scattering of noble-gas atoms from surfaces has been a method of choice for studying the structure and vibrational properties of surfaces due to the inertness, low-energy, and presumed simplicity of the gas-surface interaction [1,2]. Helium is the preferred projectile in this type of surface analysis due to its low mass and thus relatively large wavelength; on the other hand, neon has been shown in many cases to give richer information about the surface [3,4]. The use of heavy-noble-gas atoms is, however, disfavored, especially on hot surfaces, due to increasing thermal attenuation of the scattered beam, known as the Debye-Waller effect [5], where incoherent dynamics play an increasing role in the scattering process compared with the quantum part [6].

Quantum effects can persist in atom-surface scattering even at high translational energies in spite of an expected transition from the quantum to the classical regime due to a small de Broglie wavelength, where energy-loss processes through purely mechanical exchange have been predicted to have an important effect on the distribution of the scattered lobe of projectiles [7]. For example, grazing-angle atom scattering with keV energies has produced quantum diffraction patterns because only a small amount projectile energy is dissipated to the crystal lattice under channeling conditions even for elevated surface temperatures [8–10].

An even more intriguing result is the restoration of quantum coherence in Ne scattering from $c(2\times 2)$ Li/Cu(100), where the low-energy out-of-plane phonons are suppressed, and since high-frequency phonons are not easily excited in a low-energy collision, which is the case for Ne scattering, phonon exchange is rendered ineffective. This results in the quenching of the Debye-Waller factor, which has been shown to be related to the phonon density of states (spectral density) [11–13].

It is becoming clearer that the quantum-to-classical transition is not simply a matter of "size": for instance, while clusters of very few metallic atoms exhibit classical behavior [14], cold diluted gases containing tens of thousands of atoms can still show entanglement [15,16]. The coupling of a coherent system with its environment leaks quantum information to the surroundings and results in the decoherence of the observed system, as has been shown for 1000–3000 K C_{70} [17].

While grazing-angle scattering measurements are an interesting example of the persistence of quantum coherence despite the high projectile energies, we show here how the coherence can be almost completely lost for low beam energies due to a small increase in the surface temperature as we compare our data to the earlier Ne scattering work of Feuerbacher and Willis [18] from this same surface. We show angle-resolved and energy-resolved scattering measurements of Ne atoms with translational energy of 66 meV from a Ni(111) surface at temperatures up to 420 K. Although the Debye-Waller factor can be relatively large for this system, as evidenced by the appearance of a well-defined quantum specular diffraction peak at lower temperatures, increasing the temperature from 300 to 420 K results in losing all single-phonon features in the time-of-flight (TOF) data. We also show that a classical model gives very good agreement with the measured data at these slightly higher temperatures despite the presence of a small quantum specular reflection from the surface.

The investigation of the quantum-to-classical boundary is certainly an important issue, and here we discuss the possibility of using atom-surface scattering experiments to explore this subject. A second motivation for understanding inelastic losses in atom-surface scattering is the need to improve the reflectivity of mirrors for potential use in scanning matter-wave microscopy [19–22]. Yet another need for understanding the nature of classical features is that in some circumstances they can appear as peaks in the energy-resolved spectra that mimic the appearances of single-phonon quantum excitations; for example, a classical feature can be mistaken for an anomalous phonon dispersion when its energy is mistakenly plotted as a function of parallel momentum transfer [23]. In this paper we identify a single-peak feature that is clearly classical in origin and due to multiple phonon transfers, but as the system upon lowering the surface temperature is made to enter the quantum regime in which true single-surface-phonon peaks

^{*}Corresponding author: amjad.altaleb@uam.es

appear, this classical peak persists. If the position of this classical peak is blindly and erroneously plotted on the surface phonon dispersion curve for Ni(111) it exhibits the appearance of an anomalous mode.

II. EXPERIMENT

All the data shown in this work, except for those in Fig. 2, were measured from a Ni(111) surface using a high-resolution He-atom-scattering (HAS) time-of-flight spectrometer. Essentially, the He-atom beam, produced in a high-pressure free jet expansion of the gas, is modulated by a rotating disk chopper for TOF measurements. The helium atoms scattered from the sample, after traveling through three differentially pumped stages along the 1.7-m-long drift tube, are detected by means of a mass-sensitive detector. The angle between the incident and scattered beams, the source-to-detector angle in planar geometry, is fixed at a total angle $\theta_{SD} = \theta_i + \theta_f = 105.4^\circ$.

The angular distributions are measured by rotating the crystal in angular steps of $\Delta \theta_i = 0.04^\circ$ around a normal to the scattering plane, defined by the incident and outgoing beams and the normal to the surface. More details on this spectrometer are found elsewhere [24,25].

The Ni(111) single crystal used in the study is a disk with a diameter of 8 mm and a thickness of 2 mm. The crystal was mounted on the sample holder, which can be heated by electronic bombardment or cooled to 100 K using liquid nitrogen. Sample temperature was measured with a C-type thermocouple spot-welded to the sample edge. Clean Ni(111) surfaces were prepared in UHV by repeated cycles of ion sputtering (1.5 KeV, $P_{Ar} \simeq 1 \times 10^{-5}$ mbar) and flash annealing at ~1400 K. The base operating pressure in the sample chamber is 5×10^{-10} mbar. The cleanliness and azimuthal alignment of the sample was monitored by means of the analysis of HAS angular distributions, as well as by low-electron energy diffraction (LEED).

The data shown in Fig. 2 are a set of diffraction measurements conducted in a different HAS apparatus [26] by scattering of Ne with a fixed angle of incidence θ_i on a Ru(0001) surface and moving the detector inside the scattering chamber to obtain in-plane as well as out-of-plane diffraction intensities as a function of the final scattering angle θ_f .

The detector correction factor

Due to the low probability of ionizing noble gases, the detector design requires a long ionization region where the probability of ionizing a gas atom increases with the time the projectile spends in passing through the detector, and this time is inversely proportional to the speed or momentum of the projectile. The importance of this effect increases for lower projectile speeds and for increasing energy exchange when scattering from the surface because the detector correction changes the shape of the peak which can result in a shift in the peak position as well as its intensity. Therefore, the conversion of the measured TOF spectra intensities, denoted by $I_t(t_{SD})$, to the intensities in the energy domain, denoted by the differential reflection coefficient $I_{\Delta E}(\Delta E)$, are

given by [27]

$$I_{\Delta E}(\Delta E) = \frac{t_{el}}{t_{SD}} I_t(t_{SD}) \left| \frac{dt}{dE} \right|_{t_{SD}}$$
$$= \frac{t_{el}}{t_{SD}} I_t(t_{SD}) \frac{(t_{SD}^i)^3}{m(S_{SD})^2}$$
$$= I_t(t_{SD}) \frac{t_{el}}{mv_e^2}, \qquad (1)$$

where |dt/dE| is the Jacobian relating the time and energy domains. Other terms in Eq. (1) are the time of flight between the surface and the detector t_{SD} , t_{el} is the time of flight for an elastically scattered projectile, S_{SD} is the distance between the surface and the detector, v_f is the final speed, and *m* is the projectile atom mass. The factor t_{el}/t_{SD} is the detector correction. The detector correction does not have an appreciable effect on the widths of the peaks but rather affects their intensities and maximum positions. In this work we have applied the detector correction to the theoretical calculations rather than the experimental data.

III. THEORETICAL MODEL

In the classical smooth-surface model (SSM) the transition rate $w(\mathbf{p}_f, \mathbf{p}_i)$ for scattering of a projectile atom with incident momentum \mathbf{p}_i into a state of final momentum \mathbf{p}_f is given by [28–30]

$$\omega(\mathbf{p}_f, \mathbf{p}_i) \propto \frac{1}{(4\pi k_B T \Delta E_0)^{3/2}} |\tau_{fi}|^2 \times \exp\left\{-\frac{(E_f - E_i + \Delta E_0)^2 + 2v_R^2 \mathbf{P}^2}{4\pi k_B T \Delta E_0}\right\}, \quad (2)$$

where E_i and E_f are the initial and final energies of the projectile, **P** is the component of the momentum transfer parallel to the surface, $\Delta E_0 = (\mathbf{p}_f - \mathbf{p}_i)^2/2M$, with *M* being the effective mass of the surface, is the classical recoil energy, *T* is the surface temperature, the Boltzmann constant is denoted by k_B , and v_R is a weighted average of phonon speeds parallel to the surface [28,29]. The matrix element τ_{fi} is the transition matrix of the interaction potential taken with respect to the initial and final states of the projectile atom. As in previous studies, it is approximated by the value obtained for a rigid repulsive hard-wall potential where it is proportional to the surface, $\tau_{fi} \propto p_{fz}p_{iz}$.

The parameters of the calculation using the SSM model were fitted by weighted least squares, giving lower weight to data points close to $\Delta E = 0$ since they show a substantial quantum component. The surface effective mass was M = 164.1 amu, equivalent to the mass of 2.8 Ni atoms. The phonon average velocity was $v_R = 2606.5$ m s⁻¹. These values are consistent with those used previously for heavy-rare-gas scattering from clean metal surfaces [31,32].

Equation (2) has successfully described scattering spectra for several systems such as heavy-rare-gas scattering from molten metals [33] or other clean-metal-substrate targets [32,34]. In order to compare the transition rate of Eq. (2) with experiment it must be converted into a differential reflection coefficient. The differential reflection coefficient



FIG. 1. Angular distributions, taken with fixed $\theta_{SD} = \theta_i + \theta_f = 105.4^\circ$, of He and Ne scattered from Ni(111) at different surface temperatures and plotted on a logarithmic scale. The incident energy is 66 meV. The vertical line at 0° is for visual guidance. The inset is a close-up of the vicinity of the specular peak where the intensity is plotted in a linear scale.

is obtained by multiplying $w(\mathbf{p}_f, \mathbf{p}_i)$ by a Jacobian which is proportional to the magnitude of the final momentum p_f and dividing by the incident atomic flux, which is proportional to p_{iz} .

IV. RESULTS

A. Angular diffraction

Figure 1 shows angular distributions, taken with fixed θ_{SD} and plotted as a function of $\Delta \theta_i$ relative to the specular position, of He and Ne atoms scattered from a clean Ni(111) surface. The beam energy in all these spectra is 66 meV, and the incident direction is along the high-symmetry direction $\overline{\Gamma M}$. The black spectrum exhibits He-diffraction peaks from a cold Ni(111) surface (100 K); the position of the peaks corresponds to a periodicity of (2.48 ± 0.02) Å, in agreement with the nearest-neighbor distance on the Ni(111) surface. Increasing the surface temperature to 300 K (red spectrum) lowers the intensities of the diffraction and specular peaks and gives rise to a broad background peak resulting from inelastic scattering. This background is slightly shifted to the left (subspecular) in comparison with the spectrum measured at 100 K.

The inelastic background is more prominent in the angular distribution spectra recorded for Ne scattering. Diffraction peaks are visible in the spectrum measured from a cold surface (green spectrum) at $\Delta \theta_i = \pm (5.9 \pm 0.6)^\circ$ from the specular position. When the surface temperature is increased, the intensity of both the specular and diffraction peaks is strongly reduced (blue spectrum). This behavior is similar to the one observed for He scattering; however, there is a noticeable difference. In comparison with the case of He scattering the asymmetry in the inelastic background is observed even for the cold surface in the case of Ne, and it is shifted to the right (supraspecular). We have chosen the temperature 420 K for our measurements because the Ni(111) surface quickly



FIG. 2. In-plane angular distributions of Ne scattered from Ru(0001) at different surface temperatures with a fixed beam energy of 151 meV (blue to red) or different beam energies with a fixed surface temperature 330 K (shades of green). The two sets of measurements were carried out at two different fixed angles of incidence as indicated in the legend. The spectra indicated with arrows of the same color in the different panels share the same $T \approx 300$ K and $E_i = 151$ meV and differ in the angle of incidence.

gets contaminated with adsorbates from the residual gases in the scattering chamber (mainly H_2) below this value. This contamination is very easily detected by HAS due to the large cross section of He scattering from single defects on the surface [1].

The effect of increasing surface temperature on the Ne specular peak is not limited to Ni(111), as it was also measured on a different surface with the same qualitative result. Figure 2 shows Ne angular distribution spectra on Ru(0001) taken on a different machine with fixed incident angle θ_i and variable final angle θ_f . Two separate sets of data were taken; the main panel is for $\theta_i = 60^\circ$ (curves colored blue to red) with a single incident energy of 151 meV and several different surface temperatures, and the inset shows $\theta_i = 45^\circ$ (shades of green) at a fixed temperature of 330 K and several incident energies as marked. Increasing the surface temperature gradually reduces the intensity of the specular peak, which remains visible up to 300 K, whereas the inelastic background intensity increases to completely dominate the spectra above 600 K. The transition from quantum scattering into the classical regime can also be observed by varying the incident energy while keeping the surface temperature fixed. This is illustrated by the series of spectra in the inset in Fig. 2, where the data were collected at the single surface temperature of 330 K. We see that the Ne specular peak is still visible, albeit with very low intensity, for $E_i = 108$ meV but disappears at $E_i = 151 \text{ meV}$. A comparison of the two spectra taken at nearly the same temperature of \approx 300 K, indicated with arrows of their respective colors, illustrates the effect of changing the

TABLE I. Parameters used in fitting the angular distribution spectra in Fig. 1 by two Gaussian peaks. A is the area under the inelastic peak normalized to the elastic peak for each spectrum. C is the shift (in degrees) of the center of the inelastic peak relative to the elastic peak. FWHM and FWHM_e are the widths (in degrees) of the inelastic and elastic peaks, respectively. Beam energy is 66 meV, and T is the surface temperature.

Gas	<i>T</i> (K)	Α	С	FWHM	FWHM _e
He	100 300	0.4 0.9	$0.04 \\ -0.10$	0.76 0.53	0.13 0.14
Ne	150 420	5.3 61.4	0.23 0.00	4.38 7.80	0.21 0.21

angle of incidence from $\theta_i = 60^\circ$ to $\theta_i = 45^\circ$ while keeping the other parameters fixed. Here the loss of a specular peak is a result of increasing the component of the projectile momentum perpendicular to the surface.

It is interesting to start with a simple case to see if we are able to understand Ne scattering from a surface near the quantum-classical transition region. In this work, we present a systematic study performed at fixed incident energy (66 meV) and surface temperature (420 K) for Ne scattering from Ni(111). These conditions correspond to the blue spectrum shown in Fig. 1.

Table I summarizes the results of performing a two Gaussian peak fit to all the spectra shown in Fig. 1. The intensity (area under the peak) of the inelastic peak relative to that of the elastic peak is shown by A. While this value is smaller than 1 in the case of He scattering, it increases up to 61 for Ne scattering, indicating that inelastic scattering becomes the most important feature for this system. Actually, the background in the He spectra follows mostly a $1/\Delta K^2$ form, where ΔK is the momentum exchange parallel to the surface, rather than a Gaussian distribution. This is an effect of surface defects, which also appears in the Ne angular distributions as a fit residual but with less significance. Therefore, the intensities for He peaks in Table I serve only for a qualitative comparison.

C in Table I gives the angular shift (in degrees) of the center of the inelastic peak relative to the elastic one. We have shown a similar comparison in an earlier work where the inelastic peak shifts by changing the surface temperature or the beam energy for He scattering from graphene (Gr) passivated Ni(111) [35]. This explains why the angular distributions of the scattering of heavy Ne from a hot surface and of light He from a cold surface are symmetric, while the inelastic peak in the case of Ne scattering from a cold surface is supraspecular and that of He scattering from a hot surface is subspecular.

The widths of the inelastic peak (FWHM) and the elastic peak (FWHM_e) are shown in the last two columns in Table I. While the elastic peak maintains its width for different surface temperatures, as expected from the Debye-Waller model [1], the width of the inelastic peak increases significantly. The broadening of the inelastic peak with increasing temperatures agrees with the predictions of the SSM model of Eq. (2) and with the calculations done with a classical theory in Pollak and Miret-Artés [36] for the scattering of Ar from the Ag(111) surface.

B. Debye-Waller factor

The thermal attenuation of all quantum peaks is often described in terms of a Debye-Waller (DW) factor $\exp\{-2W(T)\}$, and specifically for the specular diffraction beam, the intensity appears in the form

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

The validity of the SSM theoretical model for classical scattering used in this paper [5], discussed in Sec. III, requires that the DW exponent 2W(T) is much larger than 1 [1]. However, we could not obtain the value of 2W(T) directly by measuring the thermal attenuation behavior of Ne scattering from Ni(111) mainly due to two factors: (1) the surface gets contaminated quickly at low temperatures, affecting the specular peak intensity, and (2) the inelastic background overcomes the specular peak quickly with increasing surface temperatures. Therefore, we have performed a comparative extrapolation by comparing the values of the mass-normalized factor for He and Ne scattering from Gr/Ni(111). Since this is an inert surface, it remains clean at low temperatures. In addition, the effective surface mass M in Gr/Ni(111) is sufficiently high and expected to be similar to that of clean Ni(111) due to the strong Gr-Ni bond [35,37]. These properties allow measurement of the Debye-Waller factor for Ne scattering from Gr/Ni(111), and the resulting values of 2W(T) are expected to be similar for Ne scattering from clean Ni(111), as discussed further below, since these surfaces show similar low-energy phonon dispersions which are largely responsible for the inelastic scattering [13,35].

Figure 3 shows the thermal attenuation behavior of the specular intensity for the scattering of Ne and He from Gr/Ni(111) (black and red curves, respectively) and for He scattering from bare Ni(111) (green). In this plot, the intensity *I* indicates the area under the deconvoluted elastic peak, which



FIG. 3. Thermal attenuation of the intensity of specularly scattered He from Ni(111) (green pentagons) compared to He (black squares) and Ne (red circles) from Gr/Ni(111). The values of the Debye-Waller exponent 2W(T) have been normalized by dividing by the projectile mass *m*, measured in amu. The values of I_0 are chosen such that for all three systems the measured intensities are the same at the lowest temperatures measured. Lines are exponential fits. The incident beam energy is 66 meV.

TABLE II. Temperature gradient of the Debye-Waller exponent normalized to the mass (in amu) of the projectile atom for bare and Gr-covered Ni(111) surfaces. The normalized DW argument 2W/mT is in K⁻¹ amu⁻¹.

	Gr/N	i(111)	Ni(111)
	Не	Ne	He
2W(T)/mT	1.24×10^{-3}	1.18×10^{-3}	7.96×10 ⁻²

has been normalized with respect to the intensity of the elastic peak measured at the lowest surface temperature, denoted by I_0 . This value was then normalized to the atomic mass of the projectile, resulting in the standard equation for the specular peak intensity [38]:

$$\frac{\ln[I(T)/I_0]}{m} = \frac{-2W(T)}{m} = -\frac{24(E_i \cos^2 \theta_i + D)T}{Mk_B \Theta_D^2}, \quad (4)$$

where E_i is the incident energy of the beam, D is the well depth of the projectile-surface potential, and Θ_D is the surface Debye temperature.

The results of fitting the data in Fig. 3 to Eq. (4) are summarized in Table II. Within the experimental error, essentially the same mass-normalized DW factor is obtained for both He and Ne atoms scattered from Gr/Ni(111). Furthermore, Table II shows that the normalized Debye-Waller exponent for He scattering from clean Ni(111) is only about 20% smaller than that for scattering from Gr/Ni(111) at any given temperature. As stated above, this similarity in the Debye-Waller behavior of the clean and Gr-covered surfaces is expected because graphene binds tightly to Ni(111), and this tight binding is evidenced by the fact that the dispersion curves of the lowenergy phonons from the two surfaces are quite similar [13,35].

One of the main underlying reasons for the analysis of the Debye-Waller factors in this work is to show that 2W(T) for Ne scattering from clean Ni(111) in the temperature range of our experiments is large enough for the classical SSM of Eq. (2) to be valid. However, as mentioned above, it was not possible to measure directly the Debye-Waller factor for Ne and clean Ni(111) because of problems of surface contamination at temperatures smaller than 420 K. From the data shown in Fig. 3 and Table II the value of 2W(T) for Ne scattering from the Gr/Ni(111) surface can be extrapolated to give $2W(420) \approx 10$, implying that the classical theory is valid for that system. If we make the reasonable assumption, as was directly measured for He scattering, that also for Ne and clean Ni(111) the 2W(420)is only slightly smaller than for the Gr-covered surface, using Eq. (4), we get $2W(420) \approx 7$, a value significantly larger than unity, and thus, the classical theory can be applied.

It should also be mentioned that for very heavy atomic projectiles at low energies there is evidence that, due to longer collision times, the mass dependence of 2W becomes proportional to $m^{1/2}$ instead of m [39–43]. Although the normalized 2W data shown in Fig. 3 and Table II imply that such behavior does not apply to the lighter-mass Ne at the relatively large energy of 66 meV, it is of interest to note that even if $m^{1/2}$ scaling were to be assumed, the value of 2W(420)



FIG. 4. Time-of-flight spectra of Ne scattered from Ni(111) (left) and their conversion to energy-exchange domain (right). The incident energy is $E_i = 66$ meV, and the surface temperature T = 420 K. Blue spectra correspond to specular condition $\theta_i = \theta_f$. The vertical lines indicate the center of the elastically scattered peak at t = 2.9 ms and $\Delta E = 0$ meV. Red dashed lines are visual guides following the maxima of the spectra. Angles of incidence relative to the specular position $\Delta \theta_i$ (degrees) and the components of k_i (Å⁻¹) parallel to the surface are indicated next to each spectrum.



FIG. 5. Energy-resolved spectra taken at $\Delta \theta_i = \pm 4^\circ$ and $\pm 8^\circ$ from Fig. 4 compared with scaled-to-maximum theoretical calculations. The experimental data are shown as black points, and the calculations from the theory of Eq. (2) are the red solid curves.

would be about 3 or larger. A value in this range is still large enough for the classical SSM theory to be valid.

C. Time-of-flight measurements

TOF spectra measured by scattering of a 66 meV Ne beam from a Ni(111) surface at 420 K for different incident angles are presented in Fig. 4. The data are shown in both flighttime and energy-exchange domains after normalizing their intensities by dividing by the maximum for each spectrum. The value (in degrees) of the incident angle $\Delta \theta_i$ relative to the specular position is shown next to each spectrum in the left panel. In the right panel, the component of the beam wave vector parallel to the surface is indicated for each spectrum (in Å⁻¹). The blue spectrum corresponds to the specular condition (i.e., $\theta_i = \theta_f = 52.7^\circ$).

The absence of single-phonon features is noted, in contrast to the data reported by Feuerbacher and Willis [18]. It is worth mentioning that the data presented in Ref. [18] were recorded with the Ni(111) surface at 300 K, whereas in the current study the TOF data have been measured with the Ni(111) surface at 420 K. Another important difference with respect to the work in Ref. [18] is the novel observation here of multiphonon dispersion features, as discussed in more detail below.

The energy-resolved spectra of Fig. 4 are explained rather well by the SSM theory of Eq. (2) as discussed above in Sec. III. Shown in Fig. 5 are individual spectra taken at incident angles of $\Delta \theta_i = \pm 4^\circ$ and $\pm 8^\circ$ relative to the specular position, with the data plotted as points and the calculations as solid curves. The positions and shape of the calculated peaks match those of the measurements over a large range of the most probable energy transfer from $\Delta E < -20$ meV to greater than +40 meV.

Figure 6 shows a comparison of widths (FWHM) and relative intensities between the experimentally measured (black) and theoretically calculated (red) TOF spectra using the smooth-surface model. The widths (top panel) and intensities (bottom panel) are presented as a function of the angle of incidence $\Delta \theta_i$ measured relative to specular position, and the





FIG. 6. Comparison of the width (top panel) and intensity (bottom panel) of the time-of-flight spectra between experiment (black circles with dashed lines) and theory (red circles with solid lines). Experimental data were taken from spectra in the energy-exchange domain (right panel in Fig. 4). Indicated values on the horizontal axes are $\Delta \theta_i$ relative to the specular position (bottom axis) and the corresponding value of the component of k_i parallel to the surface (top axis).

corresponding values of the component of k_i parallel to the surface are indicated on the top axis.

The calculated FWHM values increase monotonically with increasing values of $k_{i||}$. In the experimental points, the only outlier is the peak width at the specular condition, but this is because the intensity at this point is dominated by the elastic specular diffraction peak and its broadness due to the angular spread of the incident beam. As can be seen from the angular distributions presented in Fig. 1, an important component of the intensity of scattered Ne atoms at this angle is due to coherent elastic scattering, which explains the presence of a sharper TOF peak. Excluding the TOF spectrum taken at the specular condition, the theoretical model qualitatively reproduces the experimental data to a reasonable degree.

The bottom panel of Fig. 6 shows the intensities of the TOF spectra as a function of incident angle $\Delta \theta_i$, measured relative to the specular position. The data points for θ_i near the specular position appear artificially large, again because of the dominance of the elastic intensity in the region near the specular position. The data point at $\Delta \theta_i = -1^\circ$ is apparently spurious. The calculations of the classical smooth-surface model predict the same general trends as observed in the



FIG. 7. Blue circles are measured phonon dispersion curves using He scattering from a Ni(111) surface. Dashed gray lines are calculations of the Rayleigh wave (RW) and longitudinal resonance (LR) modes [44]. Red circles are the measured anomalous dispersion curve (actually a multiple phonon feature) by Ne scattering obtained from Fig. 4. Green circles are calculations performed with the SSM model (discussion and parameters in Sec. III). Red dotted lines are example scan curves for selected $\Delta \theta_i$ as indicated on each curve.

experiment; that is, the intensities are largest at incident angles near the specular position, and these intensities diminish as the incident angle deviates from the specular region.

Figure 7 shows the dispersions of the surface phonon modes of Ni(111), namely, the Rayleigh wave (RW) and the longitudinal resonances (LR) measured by helium scattering (blue dots). The two modes are well resolved and match the calculated surface phonon modes of Ni(111) shown by dashed gray lines [44] (an example of the TOF spectra measured by HAS can be found in Ref. [35]). The He TOF measurements were conducted over a range of different surface temperatures from 100 to 460 K.

Shown as red dotted curves in Fig. 7 are several representative scan curves for Ne, labeled by their corresponding incident angles $\Delta \theta_i$. The scan curve is obtained from combined conservation of energy and parallel momentum for a single phonon transfer and, for given experimental conditions of incident angle and energy, gives ΔE as a quadratic function of ΔK . Only those phonon modes that intersect or touch the scan curve can be observed under the given experimental conditions.

The peak positions of the energy-resolved inelastic spectra of Fig. 4 are shown in Fig. 7 as red dots, where they give the appearance of a dispersive phonon mode of large energy as a function of ΔK . However, this is clearly a false, or anomalous, mode because it is a multiphonon feature and cannot be assigned a specific value of ΔK according to the single-phonon scan curve. The way these points were assigned was that for each inelastic spectrum of Fig. 4 its most probable energy (the peak position energy) was assigned a value of ΔK according to where that peak energy fell on the scan curve for the corresponding incident angle $\Delta \theta_i$, i.e., essentially the same way such a ΔK assignment is made for a peak due to a true single-phonon excitation. However, since the inelastic features of Fig. 4 are classical and multiphonon in nature, the application of the single-phonon scan curve is inappropriate.

In addition to the fact that this anomalous mode persists at a temperature and incident energy sufficiently large that no other single-phonon peaks appear, there are additional indications that it is not a single-phonon excitation. For example, its "apparent" phonon dispersion lies at energies much larger than any surface mode expected for the Ni(111) crystal face. Another indication is that the anomalous mode appears for positive ΔE only in the fourth quadrant of Fig. 7 and for negative ΔE only in the second quadrant, whereas data points for the known RW and LR phonon modes appear in all quadrants of Fig. 7. The appearance of the anomalous mode only in the fourth and second quadrants of Fig. 7 is predicted by the classical calculations of the SSM theory.

V. DISCUSSION AND CONCLUSIONS

In this paper we have made a comparative analysis of He and Ne scattering from a clean Ni(111) surface. Using the heavierrare-gas projectile Ne provides an interesting system with which to examine the decoherence transition from quantummechanical coherence to classical incoherent scattering, and this is studied mainly as a function of increasing surface temperature and also by increasing the incident translational energy. The mechanism causing the quantum decoherence is the excitation of multiple quanta of vibrational modes. At lower temperatures and smaller incident energies, where the Debye-Waller factor is not significantly smaller than unity, the Ne scattering spectrum exhibits clear quantum-mechanical features, e.g., specular and other nonzero reciprocal lattice vector diffraction peaks as well as single-quantum phonon excitation peaks for the known surface-localized RW and LR modes of the Ni(111) face. As either the temperature or incident energy is increased, the Debye-Waller factor becomes smaller, to the point where all sharp quantum excitation features are suppressed, and only a classical, multiphonon peak feature survives. Remnants of this classical, multiphonon feature persist even at the lower temperatures and energies where clear quantum features are observed, and we showed that if this classical feature is misinterpreted as a single-phonon peak, it can appear as an anomalous dispersive mode in a graph of surface phonon dispersion curves.

This anomalous dispersion mode is of interest in part because there is a long history of classical multiphonon features being potentially misinterpreted as single-phonon excitation in atom-surface energy-resolved spectra [23]. This anomalous feature in the energy-resolved spectra appears as a broad peak in the intensity but not broader than is routinely observed for some known single-phonon peaks, such as those due to the LR mode on close-packed metal surfaces. Thus, we performed a careful analysis of this feature in order to exclude its identification as a single-phonon peak. Although the anomalous peak persists and is apparent in the Ne/Ni(111) energy-resolved scattering spectra at lower temperatures and energies where true quantum peaks appear, as shown in Fig. 4, it is the sole peak that remains at T = 420 K and $E_i = 66$ meV because the Debye-Waller factor is so small that all quantum features are suppressed. Additionally, the anomalous dispersion mode appears at energy and parallel momentum combinations for which no surface-localized phonon modes are expected to appear on Ni(111); that is, for a given parallel momentum (falsely) obtained by assigning its energy a position on the single-phonon scan curve, its apparent energy is much too large to be a believable mode of Ni(111). Further evidence of the multiphonon nature of the anomalous mode comes from comparison with the classical SSM theory in Sec. III. The behavior of the intensities and FWHMs of the anomalous mode as a function of incident angle θ_i are qualitatively explained. The SSM calculations explain quantitatively the shape of the false anomalous dispersion curve when plotted in a phonon energy vs parallel wave vector graph. In particular, the SSM calculations explain why the anomalous mode appears only in the second and fourth quadrants of the graph in Fig. 7; that is, the multiphonon feature appears to have positive parallel momentum when Ne loses energy (net phonon creation) and negative parallel momentum when Ne gains energy (net phonon annihilation). Thus, this anomalous inelastic feature can be clearly identified as multiphonon and hence classical and incoherent in nature.

There are other reasons why Ne can be a particularly interesting probe for surface scattering experiments. Because the outer electrons of Ne are less tightly bound than those of He, despite being in a closed-shell configuration, they can make virtual exchange excursions into the empty *D*shell states of transition metals such as Ni as the Ne atom approaches close to the surface. This mechanism of interaction, which is much less active for He projectiles, gives rise to anticorrugation effects; that is, the Ne interaction potential can have significantly different corrugation than that encountered by He.

The Ne/Ni(111) system has been investigated previously by Feuerbacher and Willis [18] using similar incident Ne energies and an ambient (300 K) temperature Ni(111) target, and they observed what appeared to be single quantum excitation of phonon modes. Our investigation indicates that at temperatures lower than about 420 K the Ni(111) surface rapidly becomes contaminated, most likely due to a small partial pressure of hydrogen in the vacuum chamber. This contamination is indicated not only by the character of the Ne scattering spectra but also through observations of elastic scattering of He atoms at temperatures below 420 K, which showed clear features indicating scattering from surface defects. Consequently, we conclude that the earlier work of Feuerbacher and Willis did not exhibit Ne scattering from clean Ni(111), but rather, the surface was hydrogen covered. Consequently, the apparent coherence in their work was more likely a result of limiting Ne access to in-plane phonons by partial coverage of the surface with hydrogen.

In conclusion, we have demonstrated, for the system of Ne atoms scattering from Ni(111), the transition from the regime of quantum mechanics, distinguished by sharp diffraction and single-phonon peaks in the scattering spectra, to the classical regime which exhibits only a single peak feature in both the angular-resolved and energy-resolved spectra. This transition is exhibited by varying either the surface temperature or the incident translational energy over relatively small and easily accessible ranges. Thus, the Ne/Ni(111) system presents an interesting example of the transition from a quantum coherent state, through decoherence, and onward to the classical incoherent state, and the mechanism of the observed decoherence is the excitation of multiple quanta of phonon modes.

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