Multiphonon inelastic scattering of helium atoms from crystal surfaces

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Energy-resolved measurements of diffuse multiphonon inelastic He scattering from the NaCl(001) surface are presented for a range of energies and temperatures which span the region from quantum-mechanical to semiclassical behavior. A theoretical model developed for explaining the scattering process gives good quantitative agreement with the data and shows that the strong dependence of the scattering distribution on the nature of the atom-surface interaction can be used to obtain important information on the He-surface potential.

Studies of single-phonon collisions of He atoms with crystal surfaces have proven to be an exceptionally effective way of obtaining information on surface dynamics.[1-4] However, the elementary processes involved in the interaction, even in the case of a simple noble-gas-atom projectile, are still not well understood. These fundamental processes are important to a range of surface problems in addition to scattering, including sticking, adsorption, desorption, and accommodation. Although the conditions for dominant single-phonon scattering are well known, the experimental measurements nearly always have an important inelastic background which is usually ascribed to coherent multiphonon exchange or incoherent scattering by impurities. Most previous experimental studies of the multiphonon regime have been classical limit experiments using heavy projectile atoms and high energies,[5] although recently it has been recognized that multiphonon processes can be responsible for certain peaks observed in the inelastic spectrum of He surface scattering.[6] There has been extensive previous theoretical work in inelastic atom-surface scattering in the multiphonon limit,[7-17] some of which has been heavily oriented towards numerical calculations.[18,19] In this paper we address the problem of neutral monoenergetic beams of He atoms colliding with alkali-halide crystal surfaces over a range of conditions which bridges the gap from purely quantum-mechanical to semiclassical measurements. This combined experimental and theoretical approach demonstrates not only that the multiphonon component can be well explained, but more importantly that it leads to valuable new information on the dynamics of the interaction process, information which cannot readily be obtained from the single-phonon intensities.

The experimental work on the alkali halides was carried out on a helium-atom scattering apparatus located at Florida State University which has been described previously.[20] Briefly, a high intensity, nearly monoenergetic ($\Delta v/v \approx 1\%$) He beam is directed onto a crystal surface and a mass-sensitive detector, with a fixed angle of 90° with respect to the incident beam, detects both the elastically and inelastically scattered intensity using the time-of-flight method. In this work all measurements were taken with the incident angle equal to 45°, which places the detector at the specular angle.

This work grew out of observations made on the elastic-scattering behavior of He atoms from alkali-halide surfaces in the specular direction, measured as a function of the beam energy and temperature of the crystal. It was noted that the specular elastic signal decreased exponentially with target temperature as expected for a Debye-Waller effect. The loss from the diffraction intensities appeared in an inelastic foot around the elastic peak which grew in size as the elastic signal decreased with increasing temperature.[21,22]

The NaCl crystal ($7 \times 10 \times 2$ mm^3) was cleaved in air and then inserted into the sample chamber which was baked to about 473 K for a day, after which the pressure dropped to the mid 10^{-10} torr range. Then the crystal was flashed to about 500–600 °C for 10–20 min. After this, the crystal surface was clean: it produced good angular distributions (with sharp diffraction peaks agreeing with bulk lattice spacings) and the time-of-flight spectra produced good phonon peaks (the dispersion curve agreed with previous studies).[21,23,24]

The crystal temperature was varied over the range of about 120–700 K. Computer control with a thermocouple was used to stabilize and measure the crystal temperature. However, the alkali-halide temperature was measured on the stage holding the crystal and some temperature gradient is believed to have been present across the crystal, especially during the highest and lowest temperature measurements. No corrections were attempted for this temperature gradient.

Figure 1 shows several time-of-flight spectra converted

to phonon-energy gain and/or loss taken over a range of crystal temperatures for NaCl(001) in the $\langle 100 \rangle$ direction with incident momentum $k_i \approx 9.25$ Å^{-1}. At low temperatures the specular scattering is almost completely elastic as shown by a sharp peak at the zero energy exchange [see Fig. 1(a)], and the evidence for inelastic scattering is hidden below this sharp peak. For spectra made at progressively increasing crystal temperatures, the elastic signal decreases and an inelastic "foot" grows around the base of the specular elastic peak. The elastic signal decreases nearly exponentially with temperature, while the multiphonon inelastic foot increases in intensity and broadens. With further increase in temperature, the elastic peak disappears and the inelastic peak both decreases in amplitude and broadens.

In order to explain these and other results, we have developed a pseudopotential approach to the scattering problem, in which the basic assumption is that the transition matrix T_{fi} for the scattering can be written as a pairwise summation

$$T_{fi} = \sum_l \tau_{fi}^l e^{-i\mathbf{k}\cdot[\mathbf{r}_l + \mathbf{u}_l(t)]}, \tag{1}$$

where the subscripts f and i indicate matrix elements

taken with respect to particle states of the incident and final scattered atom, and $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$ is the difference in final and initial scattered particle momentum. The scattering amplitude of the lth unit cell τ^l is taken to be independent of the vibrational displacement of the cell. This pseudopotential form allows for multiple scattering within each unit cell and with other unit cells, but assumes that each cell remains rigid under the influence of the surface vibrations. This should be a reasonable approximation for scattering by the large numbers of small energy, long wave-vector phonons expected to make up the multiphonon background.

The transition amplitude of Eq. (1) has been justified using the fundamental many-body scattering theory of Brako and Newns.[25,26] Using their formalism the unit-cell scattering amplitude τ^l is found, to lowest order, to be the scattering matrix (the S matrix evaluated at the energy shell) of the rigid or elastic interaction potential.

When the transition matrix of Eq. (1) is used with the generalized Fermi golden rule, after suitably averaging over the crystal modes,[27,28] the differential scattering intensity appears as the Fourier transform of the exponential of the time-dependent displacement correlation function,

$$\frac{dR}{d\Omega_f\, dE_f} = \frac{m^2 |\mathbf{k}_f|}{8\pi^3 \hbar^5 k_{iz}} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{l,l'} \tau_{fi}^{l\,*} \tau_{fi}^{l'} e^{-i\mathbf{k}\cdot(\mathbf{r}_l - \mathbf{r}_{l'})} e^{-W_l(\mathbf{k})} e^{W_{l'}(\mathbf{k})} \exp\langle\langle \mathbf{k}\cdot\mathbf{u}_{l'}^*(0) \mathbf{k}\cdot\mathbf{u}_l(t)\rangle\rangle, \tag{2}$$

where $e^{-2W_l(\mathbf{k})}$ is the classic expression for the Debye-Waller factor, and $\hbar\omega = E_f - E_i$ is the energy exchanged with the scattered particle.

The elastic and single-phonon contributions to the scattered intensity are obtained upon expanding the time-dependent exponential of the correlation function to zero or first order, respectively. The multiple-phonon part consists of the remaining terms of the expansion. The elastic and single-phonon terms have exactly the same form as the usual Born approximation or distorted-wave Born-approximation treatments using pairwise potentials, except that for the distorted-wave Born approximation the Debye-Waller factor must be inserted by supplementary means.[1,29] The sum over lattice sites in Eq. (2) converges rapidly, so we expand the displacement in normal modes of the crystal labeled by parallel momentum $\mathbf{Q}$ and develop the correlation in a series based on expansion in $\mathbf{Q}\cdot\mathbf{R}_l$, where $\mathbf{R}_l$ is the parallel component of $\mathbf{r}_l$. The resulting expressions can be evaluated explicitly for simple phonon models, and a dispersionless phonon model, equivalent to a Debye distribution for the energy exchange, and a two-dimensional Debye model for parallel momentum exchange has been shown to be adequate.[25] For He-atom projectiles, only the outermost layer of surface atoms participates actively in the scattering, and the final expression for the differential reflection coefficient is

$$\frac{dR}{d\Omega_f\, dE_f} = \frac{m^2 |\mathbf{k}_f|}{8\pi^3 \hbar^5 k_{iz}} |\tau_{fi}|^2\, e^{-2W(\mathbf{k})} S(\mathbf{K},\omega) I(\mathbf{K},\omega)\,. \tag{3}$$

This is the product of a form factor $|\tau_{fi}|^2$, a Debye-Waller factor, a structure factor $S(\mathbf{K},\omega)$, and an energy exchange factor $I(\mathbf{K},\omega)$. The latter two factors are given by

$$S(\mathbf{K},\omega) = \sum_l e^{-i\mathbf{K}\cdot\mathbf{R}_l} \exp\left[\frac{-\omega_0 k_B T \mathbf{R}_l^2}{2\hbar v_R^2}\right] \tag{4}$$

and

$$I(\mathbf{K},\omega) = \int_{-\infty}^{\infty} dt\, e^{(\omega+\omega_0)t} \exp\left[\frac{2W(\mathbf{k})\sin(\omega_D t)}{\omega_D t}\right], \tag{5}$$

where $\mathbf{K}$ is the parallel momentum transfer, v_R is approximately the Raleigh velocity of the surface modes, ω_D is the Debye frequency, and T is the surface temperature. The evaluation is made in the high-temperature limit. The energy shift $\hbar\omega_0$ has the value $\hbar^2 k^2/2M$ with M the mass of the surface atom, and arises naturally from the zero-point motion of the crystal. In the case of a semiclassical collision with a high-energy incident projectile, $\hbar\omega_0$ is approximately $4E_i m/M$. However, in general $\hbar\omega_0$ depends on the energy exchange $\hbar\omega$. The energy dependence of $\hbar\omega_0$ ensures that the beam of incident projectiles can on average either lose or gain energy upon collision with the surface, depending on the relative value of the incident energy E_i compared to the surface energy $k_B T$. The Debye-Waller exponent $2W(\mathbf{k})$ is equal to the expected value $3\mathbf{k}^2 k_B T/M\omega_D^2$.

Equation (3), with the elastic and single-phonon terms

subtracted off, has been used for all calculations and comparisons with data presented here. The remaining quantity to be specified is the form factor $|\tau_{fi}|^2$. For this we have adopted the transition amplitude obtained from the distorted-wave Born approximation, a Mott-Jackson matrix element for perpendicular motion, and a cutoff factor for parallel motion.[30] The Mott-Jackson factor is the matrix element of the repulsive exponential potential $V = \exp(-\beta z)$ with β the stiffness or range parameter, and it has an approximate exponentially decreasing behavior as a function of the difference in per-

pendicular momentum, $|\hbar k_{fz} - \hbar k_{iz}|$. For metals β is typically somewhat larger than 2 Å^{-1}. The cutoff factor is approximately $\exp(-2K^2/Q_c^2)$, where for metals Q_c is about 1 Å^{-1} as determined through measurements of the intensities of single-phonon peaks.[30]

A number of semiclassical theories have been presented for inelastic atom-surface scattering, and these generally find that the structure factor is a Gaussian in K and the energy exchange factor is a Gaussian in $\omega - \omega_0$, so that the scattered intensity is approximated by[6,12,13,15,25]

$$\frac{dR}{d\Omega_f\, dE_f} \propto \frac{1}{(\omega_0 T)^{3/2}} \exp\left[-\frac{\hbar(\omega - \omega_0)^2 + 2\hbar v_R^2 K^2}{4k_B T\omega_0}\right].$$

$$(6)$$

For the energy exchange factor [Eq. (5)] the classical limit is obtained upon carrying out the time integral by the method of steepest descents. However, this provides a condition of validity for this approximation which is $2W(k) > 6$, a condition which is rarely valid for He scattering and certainly not satisfied in the experiments reported here. The number $2W(k)$, incidentally, is roughly equal to the average number of phonons (virtual or real) exchanged in a scattering event. The semiclassical approximation to $I(K, \omega)$ gives a peak dependence which decreases as $T^{-1/2}$, while both the measurements and Eq. (3) show an increase in multiphonon intensity with T at lower temperatures and decreasing behavior only at very high temperatures.

The semiclassical expression for parallel momentum exchange is obtained from Eq. (4) in the limit of an isotropic continuum, but this approximation is also not satisfied for He scattering. The discrete nature of the crystal lattice, and the concomitant minimum wave vector for phonons, makes $S(K, \omega)$ go to unity in the semiclassical limit. In the quantum regime $S(K, \omega)$ has peaks when K equals a surface reciprocal-lattice vector, and for nonsimple unit cells it can have additional structure between the reciprocal-lattice vector positions. As ω_0 and T become larger, the summation in Eq. (4) becomes more rapidly convergent, and in the semiclassical limit only the term $l = 0$ is important, implying scattering from a single surface atom. This means that in the semiclassical limit the only difference between coherent multiphonon scattering from a perfectly ordered surface, and incoherent inelastic scattering from a defect or disorder is in the respective form factors.

The heavy lines shown in Fig. 1 are a best-fit calculation of the multiphonon contribution from Eq. (3) with $\beta = 5.6$ Å^{-1}, $Q_c = 200$ Å^{-1}, and an effective Debye temperature of 270 K. Both β and Q_c are large compared to the values cited above for metals, and with such a large value of Q_c there is effectively no cutoff correction in parallel momentum. These large values imply a correspondingly weak cutoff behavior in both parallel and perpendicular momentum exchange and are to be expected for the highly corrugated alkali-halide surfaces; such surfaces are not only strong elastic scatterers with many important diffraction peaks, but they are also strong inelastic scatterers. The effective surface Debye temperature is expected to be smaller than the bulk
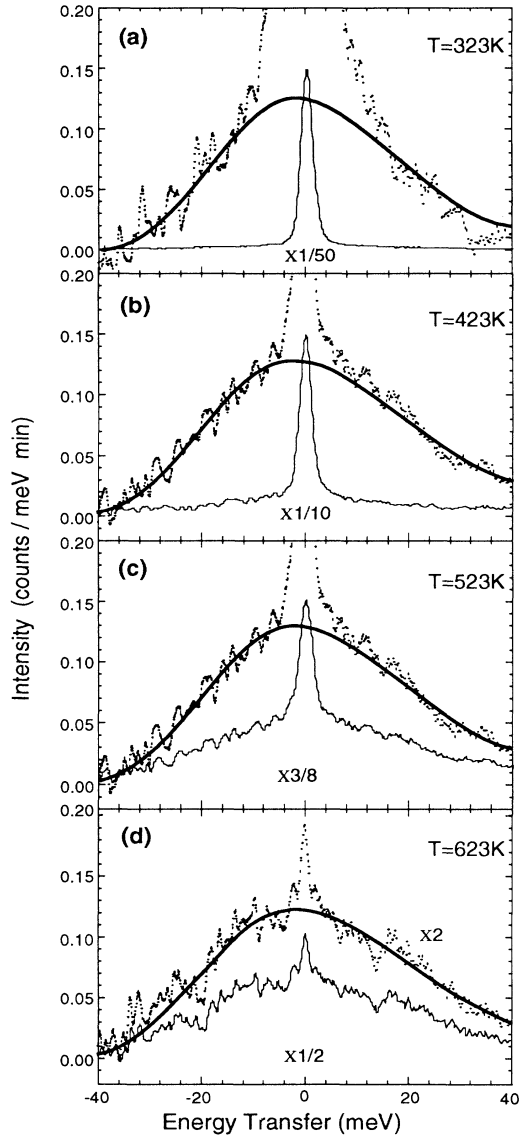
FIG. 1. Scattered intensity vs energy exchange for an incident beam of 44-meV He atoms incident on a clean NaCl(001) surface in the ⟨100⟩ direction for several surface temperatures. The vertical scales are for the dotted curves, which are the data expanded to show the inelastic foot. The light solid line is the data reduced to show the relative size of the elastic peak to the inelastic foot. The heavy solid lines are the theoretical calculations from Eq. (3).

value of 321 K because of the larger mean-square amplitude of the surface atomic cores as compared to the bulk. However, the Debye temperature is not expected to be as small as the value that might be measured, for example by an electron-scattering experiment, because of the insensitivity of the He projectile to high-frequency vibrations.[31] In the present instance we regard the effective Debye temperature as an experimental parameter whose value is well defined by comparison of theory to the experiment. The incident energy is 44 meV and the inelastic foot is roughly centered about the elastic peak, implying very small average energy gain or loss. When a lower-energy beam is used, the multiphonon peak shifts to the energy gain side (not shown), indicating that the reflected He, on the average, has gained energy from the surface. This shift is predicted by the theory.

Additional measurements have been carried out for He scattering from metal surfaces, in particular Al(111) and Cu(100). The appearance of the multiphonon background for metals is quite different; in the case of the alkali halides, the background forms a distinct and broad foot under the elastic peak, while for the metals the inelastic background is considerably less intense and simply tapers away from the elastic peak. This behavior is explained well by the theory of Eq. (3), the smaller values of β and Q_c for metals cause the form factor τ_{fi} to decrease more rapidly with energy exchange.[28] The very large value for Q_c with this crystal implies that the momentum cutoff portion of the matrix element is not very important for He scattering off of NaCl. Preliminary work on KBr and CsF also shows this behavior. This is a very interesting result as it shows that not only is the diffuse multiphonon intensity very strongly modulated by the interaction potential through the form factor, but also differences in the nature of the interaction for different types of surfaces readily can be observed. Clearly, it is the difference in interaction matrix elements, and not anything relative to the phonon distribution, which explains the net difference in the appearance of the multiphonon foot for the alkali-halide and the metal surfaces. This may well be the most important contribution of this work, because here we can extract physical information not obtainable by other methods. Since the multiquantum background is a collective average of the effects of exchanging several phonons, it is not strongly dependent on the details of the phonon spectral density, and simple phonon models suffice for the calculations. Consequently, measurements of the diffuse multiphonon backgrounds give directly the form factor (or transition-matrix modulus) of the potential. It can be argued that the single-phonon intensities also give this information, but there are two major differences: (i) the single-phonon peaks depend very strongly on the phonon spectral density and it is not simple to separate this from the effects of the potential, and (ii) the diffuse multiphonon intensity gives the form factor at all energies and momenta, and not just at those values where there happens to be a convenient single-phonon peak.

Figure 2 compares the measured and calculated temperature dependences of the intensity and width of the multiphonon foot for the NaCl (001) ⟨100⟩ experiment.
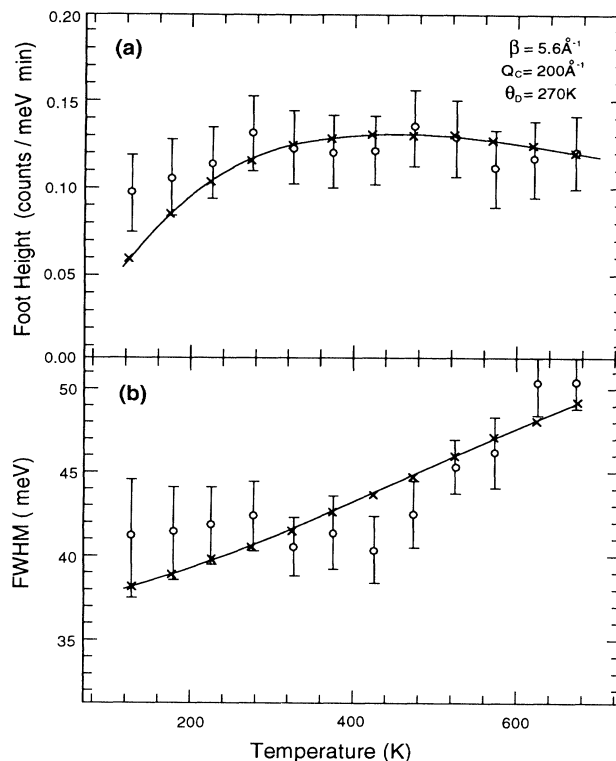

FIG. 2. Foot height and full width at half maximum (FWHM) vs temperature for the data in Fig. 1. The solid lines are fits to the theory to guide the eye. The ×'s are the calculated values from the theory, and the circles are the experimentally determined widths.

The error bars in this figure were estimated from the data before the theoretical fits were attempted, and are a conservative estimate of the experimental resolution for the inelastic data. We believe that the relative minimum in the data around 400 K is experimental noise. The multiphonon peak intensity increases slowly with T at lower temperatures, and then ultimately decreases as the semiclassical regime at very large T is approached. The full width at half maximum increases rather slowly and nearly linearly over the range of temperatures observed, and this is supported by the calculations shown by the solid line. The theory is in good agreement, and this behavior clearly shows the transition from the quantum-mechanical regime to the large quantum number, semiclassical regime. For $T=600$ K, the value of $2W$ is between 4 and 5 (and hence the most probable number of phonons exchanged in a collision is 4 or 5). Thus the true classical regime for this value of the He incident energy lies at surface temperatures greater than 800 K.

We have demonstrated here that the diffuse multiphonon intensity of He scattering from surfaces can be precisely measured and we have developed a theoretical model which is in excellent agreement with the data. Precise knowledge of the coherent multiphonon background is important in correctly extracting the intensities of diffraction or single-phonon peaks from the data, and also for separating out the incoherent inelastic contri-

bution due to defects on the surface. Observation of the multiphonon contribution provides an interesting picture of the transition from the quantum-mechanical regime to the semiclassical regime of large numbers of exchanged quanta. The somewhat surprising result of this work is that the shape of the multiphonon background as a function of energy exchange and momentum transfer is strongly dependent on the interaction potential. This fact, coupled with the knowledge that the multiphonon intensity is not strongly dependent on the details of the phonon spectrum, implies that such measurements may be used to obtain directly experimental values of the scattering form factor. The interpretation of single-phonon peak intensities provides a good example of the importance of an independent measurement of the form factor. The single-phonon intensity, even in the simplest theoretical models,[30,32] is a product of the form factor and the spectral density of the crystal. Such an expression is given by the single-phonon term of Eq. (2) and it is noted

that, within the approximation of Eq. (1), the form factor is the same for both single and multiple quantum contributions. The above remarks show that measurements of the diffuse multiphonon intensity can be used to independently determine the form factor, thus providing the information necessary to unambiguously extract the phonon spectral density.

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