Radiation Effects and Defects in Solids, 1991, Vol. 117, pp. 221–226
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ENERGY EXCHANGE IN ATOM-SURFACE COLLISIONS

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A theoretical treatment of inelastic scattering of low energy particles from surfaces is developed which treats the regime of multiple quantum phonon exchange. Good agreement is obtained with recently measured multiphonon backgrounds in the scattering of He by alkali halide and metal surfaces over a large range of surface temperatures and incident conditions. The results show that the multiphonon scattered intensity can give important information on the particle-surface interaction potential.

1 INTRODUCTION

Measurements of energy exchange in the collision of a particle with a surface can give important information of the interaction potential and on the vibrational dynamics of the surface, information which ultimately depends on the surface bonding forces.[1] The advent of precise time-of-flight experiments in the collisions of atomic beams with surfaces has lead to a great deal of interest in explaining the observed elastic diffraction peaks and the inelastic intensity peaks due to exchange of single surface phonons.[2] In this paper we wish to address the question of multiple quantum energy exchange processes that occur in the collision of a particle with a surface.

The multiphonon contribution to the scattering process is observed as a diffuse inelastic background upon which the elastic and single phonon peaks appear. Although it appears as a diffuse background intensity it is nonetheless still coherent, and under many circumstances can exhibit features such as broad peaks or valleys.[3] Thus one important reason for studying the multiphonon contribution is to better understand how to subtract the diffuse inelastic background in order to obtain accurate elastic and single phonon intensities. However, we find that the shape of the multiphonon background is not only dependent on the phonon spectral density of the surface, but is even more strongly dependent on the nature of the particle-surface interaction. This strong dependence is shown to be able to provide a great deal of information on the nature of the particle-surface interaction.

The theory developed here is quantum mechanical, and thus is capable of treating the case of scattering of small mass particles such as He. We also take the semiclassical limit which is valid for higher surface temperatures, higher energy particles, and larger mass particles. We made comparisons with recent data for the scattering of He by NaCl (100) and metal surfaces. In both cases the theory explains the diffuse inelastic background. Furthermore, the comparison of the shape of the calculated inelastic background shows that the He-surface interaction is markedly different for an alkali halide than for a metal. Data taken at low surface temperatures and low energies, well within the quantum mechanical regime, show that the shape of the

inelastic background is strongly dependent on the periodic structure of the surface substrate.

2 THEORY

It is most convenient to develop the theory starting from 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[4]

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

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 particle momentum. The scattering amplitude of the unit cell τ_{fi}^{l} is taken to be independent of the vibrational displacement of the l^{th} atom. This pseudopotential form allows for multiple scattering within the unit cell and with other unit cells, but assumes that the cell remains rigid under the influence of the surface vibrations. It should be a reasonable approximation for scattering by the large numbers of small energy, long wavevector phonons expected to make up the multiphonon background.

When the transition matrix of Eq. (1) is combined with the generalized Fermi golden rule, after suitably averaging over the crystal modes[5] the differential scattered intensity appears as the Fourier transform of the exponential of the time dependent displacement correlation function:

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

where $\exp(-W_l(\mathbf{k}))$ is the classic expression for the Debye-Waller factor, and $\hbar\omega = E_f - E_i$ is the particle energy exchange. The exponent $\langle\langle \mathbf{k}\cdot\bar{\mathbf{u}}_{l'}(0)\mathbf{k}\cdot\mathbf{u}_l(t)\rangle\rangle$ is the time dependent displacement correlation function of the particles at positions l and l', and can be developed in terms of the normal modes of the crystal and expressed as

$$\begin{aligned}\langle\langle n_i | \mathbf{k}\cdot\bar{\mathbf{u}}_{l'}(0)\mathbf{k}\cdot\mathbf{u}_l(t) | n_i \rangle\rangle = & \sum_{\alpha,\alpha'=1}^{3} k_\alpha k_{\alpha'} \sum_{\mathbf{Q},\nu} \frac{\hbar}{2NM\omega_\nu(\mathbf{Q})} \\ & \times e_\alpha(\mathbf{Q}, \nu) \, \bar{e}_{\alpha'}(\mathbf{Q}, \nu) \, e^{i\mathbf{Q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})} \\ & \times \{[2n(\omega_\nu(\mathbf{Q})) + 1] \cos(\omega_\nu(\mathbf{Q})t) - i \sin(\omega_\nu(\mathbf{Q})t)\},\end{aligned} \tag{3}$$

where k_α is the alpha cartesian component of $\mathbf{k}$, M is the mass of a surface particle, $\omega_\nu(\mathbf{Q})$ is the normal mode frequency, and $e_\alpha(\mathbf{Q}, \nu)$ is the normal mode polarization vector.

The elastic and single phonon contributions to the scattered intensity are obtained upon expanding the time dependent exponential to zero or first order, respectively,

and the multiphonon part is 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.[6]

In practice Eqs. (2) and (3) can be used as the starting point for a completely numerical calculation of the multiphonon scattering. The time dependent displacement correlation function (3) can be evaluated using any standard calculational method for surface vibrations such as the slab calculation or Green function methods. Then the Fourier transform over time in (2) is well behaved (after subtracting off the zero and single phonon parts) and can be carried out. More importantly the sum over lattice positions in (2) converges rapidly and usually only a few terms are needed.

3 MODEL CALCULATIONS AND SEMICLASSICAL LIMIT

Making use of the rapid convergence of the lattice sum, we can expand the crystal displacement in a series in $\mathbf{Q} \cdot \mathbf{R}_l$, where $\mathbf{R}_l$ is the parallel component of $\mathbf{r}_l$. We also make use of the fact that for He scattering only the outermost layer of surface atoms participates actively in the inelastic scattering. Then the differential reflection coefficient can be cast into the following form:

$$\frac{dR}{d\Omega_f dE_f} = \frac{m^2 |\mathbf{k}_f|}{8\pi^3 \hbar^5 k_{iz}} |\tau_{fi}|^2 e^{-2W(\mathbf{k})} S(\mathbf{K}, \omega) I(\mathbf{K}, \omega). \tag{4}$$

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 $I(\mathbf{K}, \omega)$.

If we further simplify the model by choosing a Debye model for the phonon frequency distribution function, the structure factor and energy exchange factor are given by the explicit functions

$$S(\mathbf{K}, \omega) = \sum_l e^{-i\mathbf{K} \cdot \mathbf{R}_l} \exp\left[\frac{-\omega_0 k_B T \mathbf{R}_l^2}{2\hbar v_R^2}\right], \tag{5}$$

and

$$I(\mathbf{K}, \omega) = \int_{-\infty}^{\infty} dt\, e^{-i(\omega+\omega_0)t} \exp\left[\frac{2W(\mathbf{k}) \sin(\omega_D t)}{\omega_D t}\right], \tag{6}$$

where $\hbar\mathbf{K}$ is the parallel momentum transfer, v_R is approximately the Rayleigh velocity for 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 $\hbar^2 k^2/2M$ and arises naturally from the zero point motion of the crystal. $\hbar\omega_0$ is recognized as being the energy given up to the surface by a semiclassical particle. The Debye-Waller exponent $W(\mathbf{k})$ is equal to the expected value.

Equation (4) with the Debye model of (5) and (6) has been used for all calculations and comparisons with data presented below. The remaining quantity to be specified is the form factor $|\tau_{fi}|^2$. For this we have adopted expressions obtained from the distorted wave Born approximation, a Mott-Jackson matrix element for perpendicular motion and a cutoff factor for parallel motion.[7,8] 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 decays roughly exponentially with the difference in perpendicular momentum, $|\hbar k_{fz} - \hbar k_{iz}|$. For metals, β is typically somewhat larger than $2\,\text{Å}^{-1}$. The cutoff factor has the form $\exp(-\mathbf{K}^2/Q_c^2)$ where for metals Q_c is about $1\,\text{Å}^{-1}$ as determined through measurements of the intensities of single phonon peaks.[8]

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 $\mathbf{K}$ and the energy exchange factor is a Gaussian in $\omega - \omega_0$, so that the scattered intensity is approximated by[9,10]

$$\frac{dR}{d\Omega_f dE_f} \propto \frac{1}{(\omega_0 T)^{3/2}} \exp\left[-\frac{\hbar(\omega - \omega_0)^2 + 2\hbar v_R^2 \mathbf{K}^2}{4k_B T\omega_0}\right]. \tag{7}$$

This expression is obtained by approximating both the structure factor (5) and the energy exchange factor (6). For the energy exchange factor the semiclassical 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 $2W(\mathbf{k}) > 6$, a condition which is rarely valid for He scattering and often not valid for many experiments involving the scattering of heavier particles. The number $2W$, incidentally, is roughly equal to the average number of virtual or real phonons exchanged in a scattering event. The semiclassical approximation to $I(\mathbf{K}, \omega)$ gives a peak dependence which decreases as $1/\sqrt{T}$, while both Eq. (3) and many measurements show an increase in multiphonon intensity with T at lower temperatures and decreasing behavior only at very high temperatures.

The part of the semiclassical expression (7) depending on parallel momentum exchange is obtained from (6) in the limit of an isotropic continuum, but this approximation is also not satisfied for the scattering of most small mass particles. The discrete nature of the crystal lattice, and the concomitant minimum wave vector for phonons, makes $S(\mathbf{K}, \omega)$ go to unity in the semiclassical limit. In the quantum regime $S(\mathbf{K}, \omega)$ has peaks when $\mathbf{K}$ equals a surface reciprocal lattice vector, and for non-simple unit cells it can have additional structure between the reciprocal lattice vector positions. As ω_0 and T become larger, the summation in Eq. (7) 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 scattering from a defect or disorder is in the respective form factors.

4 COMPARISON WITH EXPERIMENT

Recently, Skofronick *et al.*[11,12] have carried out extensive investigations of both single phonon and multiphonon scattering of He by alkali halides. Figure (1) shows an energy resolved scan of the scattering of a 44 meV He beam from a NaCl (001) surface in the ⟨100⟩ azimuthal direction at a temperature of 523 K. The experiment is a so-called "specular" scan configuration, in which $\theta_i = \theta_f$, and in this case θ_i is 45°. The increasing amount of background noise on the energy loss side is simply an artifact of the conversion from the experimentally measured time-of-flight intensities to the energy exchange scale. The solid curve is the present calculation. The effective Debye temperature is determined by comparison of measurements of the specular intensity with the Debye-Waller factor. The cutoff parameter Q_c is $5\,\text{Å}^{-1}$ and the range parameter is $\beta = 6\,\text{Å}^{-1}$, which is a very weak dependence of the form factor on the

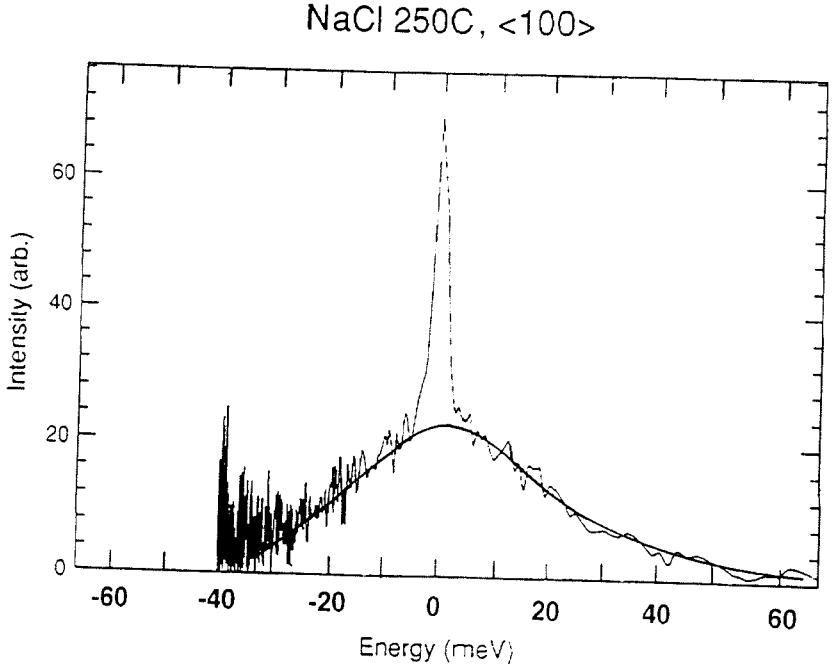

FIGURE 1 The scattered intensity as a function of energy exchange for He scattering on a NaCl (001) surface in the ⟨100⟩ direction. The incident beam wavevector is 9.2 Å^{-1}, and the angle of incidence and the detector angle are both 45°, measured from the surface normal. The solid curve is the present calculation and the surface temperature is 523 K.

energy and momentum exchange. The value of v_R is unimportant, as the structure factor $S(\mathbf{K}, \omega)$ is essentially unity for this system even for temperatures of order of the Debye temperature.

The agreement between theory and experiment is excellent, and this agreement extends to all temperatures measured, from $T = 200$ K to 800 K. There is a small increase in the multiphonon background with T, and a small nearly linear increase with T in the full width at half maximum of the multiphonon intensity; both of these behaviors agree well with calculations. Note that the extreme semiclassical approximation of (7) would predict a decrease in elastic intensity at $T^{-3/2}$ and a $T^{1/2}$ dependence for the width, clearly in disagreement with experiment. The value of $2W$ is about 4 (implying that 4 real phonons exchanged per collision), and the energy shift $\hbar\omega_0$ is about 10 meV. This energy shift, although arising from zero point motion, is clearly non-negligible; without it the experimental and calculated curves cannot be made to agree regardless of how the parameters are varied.

Excellent agreement with experiment has also been obtained for the multiphonon inelastic intensity of He scattered by the close packed surfaces of metals. In particular the (111) surfaces of the fcc metals Al, Cu and Pt have been examined.[4] For these metal surfaces we find that Q_c is about 1 Å^{-1} and β is somewhat larger than 2 Å^{-1}, which compare very favorably with values obtained from elastic and single phonon scattering. However, these values of Q_c and β are much smaller than those found for the alkali halides, and the resulting large differences in the shape of the inelastic background underscores the importance of the interaction potential in multiphonon exchange.

5 CONCLUSIONS

We have presented here a treatment of inelastic surface scattering which is capable of providing straightforward ways of calculating multiquantum components of the

scattered intensity in particle-surface collisions. The motion of the particle and the surface are treated quantum mechanically, and the transition to the correspondence limit of large numbers of quanta, and to the semiclassical limit for particle motion are straightforward. The treatment is based on a pseudopotential approximation for the scattering amplitude from each unit cell, which is a good approximation for multi-quantum processes involving the exchange of low energy, long wavelength phonons. A number of calculations show excellent agreement with the multiphonon inelastic background observed in He scattering experiments. This approach shows the limits to which information on surface vibrational properties can be obtained from analysis of an experiment, without extensive knowledge of the specific and detailed nature of the He-surface interaction potential. We have found that the multiphonon inelastic background in a surface scattering experiment is strongly dependent on the nature of the interaction potential, but rather weakly dependent on the details of the phonon spectrum and hence can be calculated using simple models for the surface vibrations. In addition to its usefulness in subtracting off background, the comparison with experiment of calculated multiphonon intensities determines the form factor, and thus provides useful information on the interaction potential.

ACKNOWLEDGEMENTS

We would like to thank the SURA/ORAU/ORNL Summer Cooperative Program for support during the course of this work. One of us (J. R. M.) would like to thank the Alexander von Humboldt Foundation for support.

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