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Multiphonon background in atom–surface scattering

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A quantum mechanical theory for the multiphonon inelastic background appearing in the energy resolved measurements of low energy atom–surface scattering is presented. Simple expressions for the differential reflection coefficient are given for the semiclassical and extreme semiclassical limits of high surface temperatures and large atomic translational energies. Measurements of the inelastic background give directly the form factor of the interaction potential for inelastic scattering. It is shown that there can be either net gain or loss of energy by the scattered particles, depending on the relative incident particle energy to the surface temperature. The relation to previous semiclassical theories is discussed.

1. Introduction

Atom–surface scattering, and particularly He–surface scattering at thermal energies, has proven to be an extremely sensitive and useful method of surface analysis [1]. When a nearly mono-energetic and well collimated beam of atoms is directed towards a surface, the intensity backscattered towards the detector consists of four major components which can be divided roughly into the following categories: elastic diffraction peaks, single surface phonon inelastic peaks, the diffuse elastic, and the diffuse inelastic contributions. The latter two categories may be further divided into coherent and incoherent contributions, with the incoherent part coming from defects and imperfections on the surface.

Elastic diffraction peaks have been, and continue to be extensively studied; their positions in momentum space provide immediate information on surface structure, and through comparison with dynamical calculations, also provide a way of determining the atom–surface interaction potential [2]. The other elastic contribution, the diffuse elastic background which appears in the energy resolved intensity as a sharp elastic peak at all angles and parallel momentum exchange, is due to scattering from imperfections (defects, adsorbates, steps, vacancies, etc.) in the otherwise regularly ordered surface. Precise measurements of the diffuse elastic intensity have provided details of the differential cross section of adsorbates on the surface [3] and of surface steps [4], and fine structure in the diffuse intensity has been used to obtain information on the ordering of steps at lattice row positions on the surface [5].

The inelastic peaks due to exchange of single surface phonons give immediately the surface phonon dispersion relations, again simply from the positions of these peaks in the space of energy and momentum exchange. In principle the single phonon peaks, through dynamic calculations, can be related to the phonon spectral density, and can be used to extract the available information about surface dynamics. However, in practice this has proved difficult to accomplish because the total intensity of an inelastic peak also depends strongly on the atom–surface interaction potential, and both the potential and the spectral density are strongly varying functions of energy and momentum, thus it is difficult to separate the contributions of each of these two unknown quantities.

In addition to the inelastic peaks, there is always an inelastic background which arises from multiphonon transitions with the coherent surface [6], or from incoherent inelastic scattering with defects [7]. This multiphonon intensity has been very little exploited for obtaining detailed surface sensitive information, and is the subject of this paper. For a perfectly ordered surface, the inelastic background arises from multiphonon in-

elastic transfers between the particle and surface, and is totally coherent. We show here that the multiphonon background is not only readily observable under semiclassical conditions of large projectile energy and high surface temperatures, but it also should be non-negligible and observable under conditions in which elastic and single phonon exchange are the dominant scattering channels. At low surface temperatures the diffuse inelastic background will exhibit a characteristic structure dependent on the form of the crystal lattice. Perhaps most importantly, the coherent multiphonon background depends on the atom–surface interaction potential in very much the same way as does the single phonon intensity. However, the single phonon intensity depends very strongly on the details of the phonon spectral density, whereas the multiphonon contribution does not since exchange of several quanta of energy tends to average over details of the phonon spectral density. This insensitivity to details in the phonon dynamics means that, through the use of simple phonon models, the information on the atom–surface interaction potential (i.e., the form factor for inelastic scattering), can be extracted. This inelastic form factor is too a good approximation, identical with that for the single phonon intensity. Thus from the multiphonon intensity one can extract the necessary information on the interaction potential to allow the unambiguous determination of the spectral density from the single phonon peak intensities.

The theoretical approach taken here is fully quantum mechanical in nature, but allows an immediate limit to the semiclassical and classical scattering regimes. We discuss briefly how the semiclassical result evolves into an equilibrium distribution for the scattered particles in the limit of high surface temperature and low incident energies, and relate this theory to other semiclassical theories of multiphonon scattering.

2. Theory

A suitable point for starting a calculation of multiphonon scattering from the initial atomic projectile state of momentum $\hbar \boldsymbol{k}_i$ to the final state of momentum $\hbar \boldsymbol{k}_f$ is the transition rate of the generalized golden rule

$$w(\boldsymbol{k}_f, \boldsymbol{k}_i) = \frac{2\pi}{\hbar} \left\langle \sum_{\{n_f\}} |T_{fi}|^2 \delta(E_f - E_i) \right\rangle . \tag{1}$$

The particle state transition rate of eq. (1) has been summed over all final many-body quantum states $\{n_f\}$ of the crystal, and the brackets $\langle\ \rangle$ signify an average over initial crystal states.

The transition matrix T_{fi} requires a calculation of the full many body problem, a practical impossibility, so a reasonable approximation must be made. A form which is satisfactory for the small frequency and long wavelength phonons which are expected to dominate in multiphonon exchange is a pairwise summation of contributions from all surface unit cells located at the positions $\boldsymbol{r}_j$.

$$T_{fi} = \sum_j \tau_{fi}^j \, e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_j + \boldsymbol{u}_j)}, \tag{2}$$

where $\boldsymbol{k} = \boldsymbol{k}_f - \boldsymbol{k}_i$ is the wavevector exchange, $\boldsymbol{u}_j$ is the displacement from equilibrium of the jth unit cell and τ_{fi} is the scattering amplitude from the jth unit cell. In the following we will assume that τ_{fi} is independent of phonon displacement, and depends only on $\boldsymbol{k}_f$ and $\boldsymbol{k}_i$. The approximations embodied in eq. (2) are that the collision is rapid compared to the relevant phonon periods, and that the environment of each unit cell is similar (i.e., small frequencies and long wavelengths) but it does include multiple scattering with adjacent unit cells. Eq. (2) is central to the results which follow. The condition of small frequencies and large wavelengths implies that multiphonon scattering should be dominated by frequencies much smaller than the Debye frequency and wavelengths much larger than the lattice spacing. The results of the calculations discussed in section IV below indicate that in practice eq. (2) is a reasonable approximation. Its relation to more general treatments of inelastic scattering, and particularly to inelastic scattering in the presence of bound state resonances, is taken up again at the end of section 3.

With the approximate form of eq. (2) for the transition rate, all many-body sums can be carried

out in the harmonic crystal approximation and upon multiplying by the appropriate densities of states for scattering of a particle into the final state, the differential reflection coefficient becomes

$$\frac{\mathrm{d}R}{\mathrm{d}\Omega_\mathrm{f}\,\mathrm{d}E_\mathrm{f}} = \frac{m^2|\boldsymbol{k}_\mathrm{f}|}{8\pi^3\hbar^5 k_{\mathrm{i}z}}\int_{-\infty}^{+\infty}\mathrm{d}t\;\mathrm{e}^{-\mathrm{i}\omega t} \times\sum_{j,j'}\tau_{\mathrm{fi}}^{j}\tau_{\mathrm{fi}}^{*j'}\;\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_j-\boldsymbol{r}_{j'})} \times\mathrm{e}^{-W_j(\boldsymbol{k})}\;\mathrm{e}^{-W_{j'}(\boldsymbol{k})}\;\mathrm{e}^{\langle\boldsymbol{k}\cdot\boldsymbol{u}_j^*(0)\boldsymbol{k}\cdot\boldsymbol{u}_{j'}(t)\rangle}, \tag{3}$$

where m is the mass of the projectile atom, $\exp(-W_j(\boldsymbol{k}))$ is the classic expression for the Debye–Waller factor, and $\hbar\omega = E_\mathrm{f} - E_\mathrm{i} = \hbar^2(k_\mathrm{f}^2 - k_\mathrm{i}^2)/2m$ is the projectile energy exchange. Eq. (3) represents the fraction of particles scattered from an incident plane wave of momentum $\hbar\boldsymbol{k}_\mathrm{i}$ into final energy range $\mathrm{d}E_\mathrm{f}$ and final solid angle $\mathrm{d}\Omega_\mathrm{f}$, and is in the form of the time Fourier transform of the exponentiated displacement correlation function. In the harmonic approximation, the displacement correlation function can be decomposed in harmonic modes of the crystal substrate

$$\begin{aligned}\langle\boldsymbol{k}\cdot\boldsymbol{u}_{j'}^*(0)\boldsymbol{k}\cdot\boldsymbol{u}_j(t)\rangle &= \sum_{\alpha,\alpha'=1}^{3}k_\alpha k_{\alpha'}\sum_{\boldsymbol{Q},\nu}\frac{\hbar}{2NM\omega_\nu(\boldsymbol{Q})}e_\alpha(\boldsymbol{Q},\nu) \times e_{\alpha'}^*(\boldsymbol{Q},\nu) \times\mathrm{e}^{\mathrm{i}\boldsymbol{Q}\cdot(\boldsymbol{R}_j-\boldsymbol{R}_{j'})}\{[2n_\nu(\boldsymbol{Q})+1]\cos(\omega_\nu(\boldsymbol{Q})t) \\ &\quad -\mathrm{i}\sin(\omega_\nu(\boldsymbol{Q})t)\},\end{aligned} \tag{4}$$

where M is the crystal atom mass, $e_\alpha(\boldsymbol{Q},\nu)$ is the αth component of the polarization vector for the $(\boldsymbol{Q},\nu)$ vibrational mode of frequency $\omega_\nu(\boldsymbol{Q})$, and $n_\nu(\boldsymbol{Q})$ is the Bose–Einstein statistical factor. Eq. (4) has been written in the form for a Bravais lattice, but the extension to systems with several atoms in the unit cell basis is straightforward. The displacement correlation function is readily evaluated by any of a number of standard methods, such as the slab method [8] or by Greens function methods [9], and the Fourier transform and sum over lattice sites of eq. (3) are rapidly convergent under numerical calculation provided the 0- and 1-phonon terms are first subtracted out. The 0- and 1-quantum terms are the 0th- and first-order expansion of the exponential of the displacement correlation function in eq. (3), and these contributions can be evaluated separately and the results correspond to the essential features of many theoretical treatments of the elastic [10] and single phonon scattering [11].

Instead of carrying out detailed numerical calculations with exactly calculated phonon spectral densities, we will use simpler models in keeping with the philosophy of this approach, which is that the multiphonon background should be relatively independent of details of the particular phonon distribution. Also, in keeping with this spirit, a great simplification can be achieved by making an expansion of the displacement correlation function in small $\boldsymbol{Q}$. Then, through terms of order $(\boldsymbol{Q}\cdot\boldsymbol{R}_j)^3$ the differential reflection coefficient (3) takes the form

$$\frac{\mathrm{d}R}{\mathrm{d}\Omega_\mathrm{f}\,\mathrm{d}E_\mathrm{f}} = \frac{m^2|\boldsymbol{k}_\mathrm{f}|}{8\pi^3\hbar^5 k_{\mathrm{i}z}}|\tau_{\mathrm{fi}}|^2\,\mathrm{e}^{-2W(\boldsymbol{k})}S(\boldsymbol{K},\omega) \times I(\boldsymbol{K},\omega). \tag{5}$$

This is the product of a form factor $|\tau_{\mathrm{fi}}|^2$, the Debye–Waller factor, a structure factor $S(\boldsymbol{K},\omega)$, and an energy exchange factor $I(\boldsymbol{K},\omega)$, given by

$$S(\boldsymbol{K},\omega) = \sum_j \mathrm{e}^{-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}_j}\,\mathrm{e}^{-F_j(T)} \tag{6}$$

and

$$I(\boldsymbol{K},\omega)\int_{-\infty}^{+\infty}\mathrm{d}t\;\mathrm{e}^{-\mathrm{i}(\omega+\omega_0)t}\;\mathrm{e}^{Q(t)} \tag{7}$$

with

$$F_j(T) = \sum_{\alpha,\alpha'=1}^{3}k_\alpha k_{\alpha'}\sum_{\boldsymbol{Q},\nu}\frac{\hbar(\boldsymbol{Q}\cdot\boldsymbol{R}_j)^2}{2NM\omega_\nu(\boldsymbol{Q})}e_\alpha(\boldsymbol{Q},\nu) \times e_{\alpha'}^*(\boldsymbol{Q},\nu)[2n_\nu(\boldsymbol{Q})+1] \tag{8}$$

and

$$Q(t) = \sum_{\alpha,\alpha'=1}^{3}k_\alpha k_{\alpha'}\sum_{\boldsymbol{Q},\nu}\frac{\hbar}{2NM\omega_\nu(\boldsymbol{Q})}e_\alpha(\boldsymbol{Q},\nu) \times e_{\alpha'}^*(\boldsymbol{Q},\nu)[2n_\nu(\boldsymbol{Q})+1]\cos(\omega_\nu(\boldsymbol{Q})t) \tag{9}$$

and $\omega_0 = \hbar k^2/2M$. The energy $\hbar\omega_0$ arises from zero point motion of the lattice and is the result of a further approximation of replacing the $\sin(\omega_\nu(Q)t)$ function in eq. (4) by its argument. This approximation is not necessary, but it is quite accurate in the semiclassical region where $\hbar\omega_0$ is interpreted as the energy loss to the surface of an energetic incident particle. However, $\hbar\omega_0$ is not a constant and in general depends on energy and momentum exchange; it is perhaps better to interpret it as being the result of recoil motion of the crystal, and the consequences of its energy dependence are important in discussing the total energy transfer from particle to crystal (which can be either positive or negative depending on the relative incident energy and crystal temperature), and in discussing the approach to equilibrium of the scattered gas in the limit of a hot surface and a cold incident beam.

3. The semiclassical limit

The semiclassical limit is the regime of high crystal temperatures and large projectile energies. When the substrate temperature measured in units of $k_B T$ is higher than any of the phonon energies, the Bose–Einstein factor $n_\nu(Q)$ can be replaced by $k_B T/\hbar\omega_\nu(Q)$ and the functions $F_j(T)$ and $Q(t)$ in eqs. (6) and (7), which are essentially proportional to the mean square vibrational displacement of a surface atom, increase linearly with T. In addition, both these functions increase with k^2. Considering first the structure factor of eq. (6), in the limit of large T and large k only the one term with $j = 0$ in the sum over lattice cells will survive and $S(K, \omega)$ approaches unity. Physically, the structure factor can be interpreted as the function describing the coherent contributions to the multiphonon intensity coming from all the surface unit cells. The presence of the damping factor $\exp(-F_j(T))$ in the summand indicates that the coherence region for multiphonon scattering is limited. As T and k increase, this coherence region becomes smaller, and in the extreme semiclassical limit all coherence between different surface atoms is lost and each scatters independently. Thus, in the extreme semiclassical limit the only difference between the multiphonon contribution from the ordered surface or the multiphonon contribution from isolated point defects on the surface is the respective form factors and vibrational frequency spectrum, as both scatter as incoherent sources.

The energy exchange factor $I(K, \omega)$ of eq. (7) is evaluated in the semiclassical limit by carrying out the Fourier transformation by the method of steepest descents after expanding $Q(t)$ as a power series in t. The result is that the differential reflection coefficient becomes proportional to a Gaussian function in energy exchange $\hbar\omega$ with an energy shift $\hbar\omega_0$.

$$\frac{dR}{d\Omega_f\, dE_f} = \frac{m^2 |k_f|}{8\pi^3\hbar^5 k_{iz}} |\tau_{fi}|^2 \sqrt{\frac{\hbar\pi}{\omega_0 k_B T}} \times \exp\left[-\frac{\hbar(\omega+\omega_0)^2}{4k_B T\omega_0}\right]. \tag{10}$$

Implicit in the steepest descent approximation is the validity criterion which can be expressed in terms of the Debye–Waller exponent as $2W(k)/6 \gg 1$. The Debye–Waller exponent is the most useful parameter for judging the importance of the multiphonon component in atom-surface scattering [12], since its value can be interpreted as the average number of real or virtual phonons transferred in a scattering event. It is important to note that the condition $2W(k) > 6$ is rarely met in thermal energy He scattering, and in fact is often not satisfied even for surface scattering of higher mass noble gas atoms.

The extreme semiclassical result of eq. (10) shows that, apart from the density of the final states factor of $|k_f|$ and the form factor $|\tau_{fi}|^2$, the differential reflection coefficient is a Gaussian in energy exchange with a width which increases as $[\omega_0 T]^{1/2}$ and a maximum amplitude which decreases with $T^{-1/2}$. The compensating effects of increasing width and decreasing amplitude insure that the integral of the differential reflection coefficient over all angles and energies is constant as a function of temperature, as required by the condition of unitarity. The elastic and single phonon contributions have become so small as to contribute negligibly to the scattering

intensity; all the backscattered particles are in the inelastic background.

Eq. (10) is the extreme semiclassical result for a point particle interacting with the lattice. There is still another limit for a large, massive particle colliding with the substrate, where the surface lattice can be regarded as a continuum. In this case the summation over lattice cells in the structure factor of eq. (6) can be approximated by an integral, with the result that $S(\boldsymbol{K}, \omega)$ becomes a Gaussian in parallel momentum exchange and the differential coefficient is

$$\frac{\mathrm{d}R}{\mathrm{d}\Omega_\mathrm{f}\,\mathrm{d}E_\mathrm{f}} = \frac{m^2|\boldsymbol{k}_\mathrm{f}|}{4\pi^3\hbar^5 k_{\mathrm{i}z}}|\tau_\mathrm{fi}|^2 v_\mathrm{R}^2\left(\frac{\hbar\pi}{\omega_0 k_\mathrm{B}T}\right)^{3/2} \times \exp\left[-\frac{\hbar(\omega+\omega_0)^2 + 2\hbar v_\mathrm{R}^2 K^2}{4k_\mathrm{B}T\omega_0}\right]. \tag{11}$$

In eq. (11) v_R is approximately the Rayleigh phonon velocity, and we have made the assumption in evaluating the structure factor that for parallel momentum exchange, the phonon spectral density is dominated by the Rayleigh phonon modes [13,14].

A question of interest is the average energy gained or lost by a monoenergetic beam of particles scattering from a surface. This can be obtained by weighting the differential reflection coefficient by the energy exchange $\hbar\omega$ and then summing over all final energies and angles

$$\overline{\Delta E} = \int \mathrm{d}\Omega_\mathrm{f}\int \mathrm{d}E_\mathrm{f}\hbar\omega\frac{\mathrm{d}R}{\mathrm{d}\Omega_\mathrm{f}\,\mathrm{d}E_\mathrm{f}}\Big/\int \mathrm{d}\Omega_\mathrm{f}\int \mathrm{d}E_\mathrm{f} \times \frac{\mathrm{d}R}{\mathrm{d}\Omega_\mathrm{f}\,\mathrm{d}E_\mathrm{f}}. \tag{12}$$

The average energy exchange can be evaluated exactly in the extreme semiclassical limit in which the energy and angular dependence of $|\boldsymbol{k}_\mathrm{f}|$, $|\tau_\mathrm{fi}|^2$ and ω_0 are neglected. In this limit, using the differential reflection coefficient of either eq. (10) or (11) it is readily shown that the incident projectile always looses to the surface an average amount of energy equal to $\hbar\omega_0$. However, even in the semiclassical limit the energy dependence of $|\boldsymbol{k}_\mathrm{f}|$, $|\tau_\mathrm{fi}|^2$ and particularly ω_0 cannot always be neglected, and it is easy to show that in general an incident particle can either loose or gain energy upon collision. Because of the energy and angular dependence of the form factor $|\tau_\mathrm{fi}|^2$ it is not a simple question to predict the conditions for energy gain or loss, but the key parameter is the ratio of $k_\mathrm{B}T$ to that part of the incident energy due to motion normal to the surface. When the temperature is small compared to the incident energy the projectile will loose energy, but when the incident energy is small compared to $k_\mathrm{B}T$ the projectile can gain energy.

As an example of a case where the particle can gain energy upon collision with the surface it is of interest to discuss the approach to an equilibrium distribution of a scattered gas arising from a very low energy beam of atoms incident on a very hot surface [15]. In the limit $E_\mathrm{i} \to 0$ we have for the energy exchange and energy shift

$$\hbar\omega = E_\mathrm{f} - E_\mathrm{i} \to E_\mathrm{f},$$

$$\hbar\omega_0 = \frac{\hbar^2}{2m}(\boldsymbol{k}_\mathrm{f} - \boldsymbol{k}_\mathrm{i})^2 \to \frac{m}{M}E_\mathrm{f}. \tag{13}$$

Then the differential reflection coefficient of eq. (11) takes the form

$$\frac{\mathrm{d}R}{\mathrm{d}\Omega_\mathrm{f}\,\mathrm{d}E_\mathrm{f}} \propto T^{-3/2}\exp\left(\frac{-E_\mathrm{f}[1+m/M]^2}{4k_\mathrm{B}Tm/M}\right). \tag{14}$$

The Gaussian in energy exchange has gone over to an exponential in the final energy of the scattered particle. This can be related to the energy E of a crystal atom through the well known expression for the energy exchanged in a two particle collision [16]

$$E_\mathrm{f} = 4E\frac{m/M}{(1+m/M)^2}, \tag{15}$$

leaving the differential reflection coefficient in the form

$$\frac{\mathrm{d}R}{\mathrm{d}\Omega_\mathrm{f}\,\mathrm{d}E_\mathrm{f}} \propto T^{-3/2}\exp(-E/k_\mathrm{B}T). \tag{16}$$

The differential reflection coefficients of (14) or (16) clearly show not only that the incident low-

energy beam of particles has gained energy in the surface collision, but in addition show that the particles leave the surface with an energy distribution obeying the exponential law of the Maxwell–Boltzmann distribution function [17].

At this point it is of interest to relate the present results, which were derived from a transition matrix formalism, to other treatments of multiphonon scattering. The closest work to this is the semiclassical approximation of Brako and Newns based on the many-body evolution operator [18]. The semiclassical limits of eqs. (10) and (11) are completely equivalent to the results of Brako and Newns in the limit of a rapid collision, except for the fact that the Brako–Newns results do not contain the form factor $|\tau_{fi}|^2$. This shows that a major approximation embodied in the assumption of eq. (2) is a rapid collision scattering process; in semiclassical terms the scattering event is one in which the total impulse over the time of the collision can be approximated by $\hbar\boldsymbol{k} = \hbar(\boldsymbol{k}_f - \boldsymbol{k}_i)$. The Brako–Newns approach can be readily carried out in a completely quantum mechanical form, and a reexamination of the problem from the standpoint of quantum mechanical S-matrix or evolution operator theory shows that the Brako–Newns results should, in general, be multiplied by a form factor. This form factor, which plays the same role as τ_{fi} in the above results, is to a first approximation given by the off-energy-shell scattering matrix for transitions of the incident atomic projectile from state $\boldsymbol{k}_i$ to state $\boldsymbol{k}_f$ under the influence of the elastic part of the atom–surface interaction potential [15]. This justification of the reduced scattering amplitude τ_{fi} now allows us to make some statements about scattering under conditions of resonance with the bound states in the adsorption well of the potential. The most important of these resonances, sometimes referred to as selective adsorption resonances, are caused either by purely elastic diffraction or are assisted by single phonon exchange [1]. Contrary to what might be expected, it has been demonstrated that there is not an unusually large increase in multiphonon interactions under conditions of resonance; if an experiment is carried out near conditions of resonance and under conditions where the scattering is dominated by single phonon processes, it continues to be dominated by single phonon processes when the initial conditions are slightly changed to induce a resonance [18]. However, in spite of the fact that the scattering may be dominated by single phonon events, the same calculation shows that the full width at half maximum (FWHM) of the resonance feature increases with temperature, and this conclusion is in agreement with experimental measurements. This observation clearly shows that the scattering amplitude τ_{fi}, under conditions of resonance, cannot be considered to be independent of the vibrational displacement of the unit cell. The displacement dependence of τ_{fi} leads to a temperature dependent form factor near conditions of resonance, but this is not a difficult problem to surmount as ref. [18] gives the prescription for calculating this temperature dependent form factor. We should also note in connection with this discussion of resonant processes that under semiclassical conditions, such as when eqs. (10) or (11) are valid, resonances are no longer observed because the diffraction and single phonon contributions are negligibly small compared to the total multiphonon contribution.

4. Calculations

A comparison of the theory with recent experimental results of Bishop et al. [19] for the scattering of He by the (001) surface of NaCl is shown in fig. 1. The incident He energy is 28 meV, the surface temperature is 773 K, and the experimental configuration is that of a specular scan in which both the incident and detector directions make an angle of 45° with respect to the surface normal. The scattering plane is aligned with the ⟨110⟩ direction of the crystal face. The multiphonon background as measured by a time-of-flight analysis, here converted to energy exchange, shows the multiphonon background as a distinct and broad foot upon which stands the sharp elastic specular peak. This inelastic foot is well explained by the calculation shown as a solid line. The calculation is the differential reflection coefficient of eq. (5) carried out for a simple

Debye model of the phonon frequency distribution, and the Debye temperature is 330 K. The form factor is taken to be a constant, indicative of the strong scattering nature of the strongly repulsive and highly corrugated alkali halide surface.

This is a case which is in the intermediate region between the purely quantum mechanical regime and the extreme semiclassical regime as $2W(k)$ is approximately equal to 3 near the elastic peak, and it is an interesting case because it shows clearly a situation in which the scattered particles have, on average, gained energy from the surface. The maximum in the inelastic foot is about 10 meV on the energy gain side of the elastic peak. The position of this maximum is well matched by the theory in spite of the fact that the energy shift $\hbar\omega_0$ in the neighborhood of the elastic peak is about 6 meV, and this demonstrates the importance of the energy dependence of the energy shift and the density in phase space of final particle states in determining net energy gain or loss.

Fig. 2 shows further calculations of the total inelastic background for the same system as in fig. 1 at both higher and lower temperatures. The high temperature calculation is for $T = 1000$ K

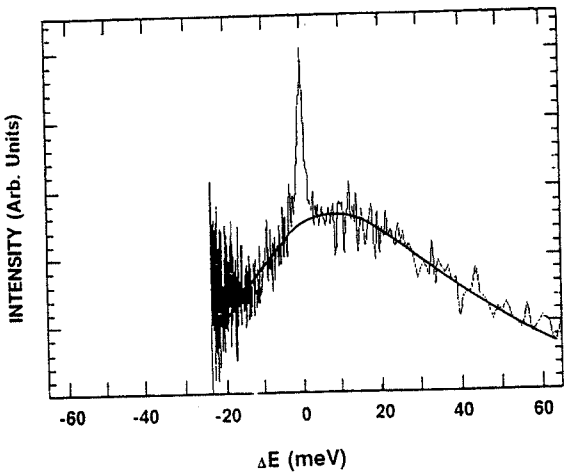

Fig. 1. The differential reflection coefficient as a function of energy exchange for a beam of He incident of a NaCl(001) surface in the ⟨110⟩ direction. The incident He energy is 28 meV, the surface temperature is 773 K, and the incident and detector angles are both 45°. The solid curve is the present calculation.

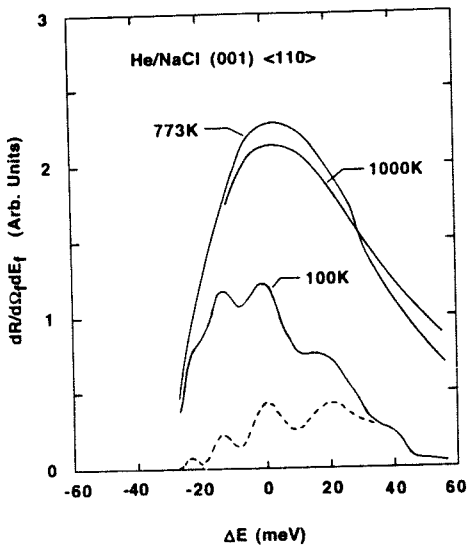

Fig. 2. Calculated differential reflection coefficients for the system of fig. 1 for three different surface temperatures: 773, 1000 and 100 K. For the 100 K calculation the solid line is the total inelastic contribution and the dashed curve is the multiphonon contribution.

and, compared to the curve for $T = 773$ K, shows a broader width in the energy exchange and a decreased maximum amplitude. This behavior is characteristic of the semiclassical result of eq (10), and at this temperature the system is just entering the extreme semiclassical regime. The low temperature calculations in fig. 2 are for $T = 100$ K and show the characteristic oscillations that arise in the multiphonon background from the structure factor in eq. (5). The structure factor for this calculation is shown separately in fig 3. For the $T = 100$ K curve the multiple phonon contribution has been drawn in as a dashed line in addition to the total inelastic background which includes the single quantum part. The single phonon part is the largest contributor at this low temperature, but in the Debye approximation it is a relatively smoothly varying contribution, the structure appears entirely in the exchange of larger numbers of phonons. It is clear that the majority of the energy exchanged by the particle is through the single phonon term, and that near energy will be lost to the surface by the particles contrary to the situation at the higher temperatures.

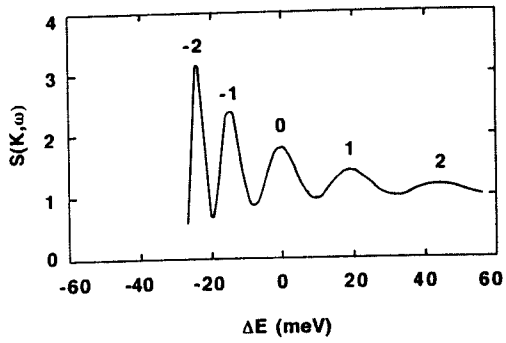

Fig. 3. The structure factor for the $T = 100$ K calculation of fig. 2 plotted as a function of energy exchange. The numbers above the peaks give the order of the corresponding diffraction reciprocal lattice vector in the ⟨110⟩ direction.

The structure factor shown in fig. 3 is calculated from eq. (8) using a two-dimensional Debye model with a Rayleigh phonon velocity $v_R = 2540$ m/s as determined by Bishop et al. [19]. It is not periodic in reciprocal space because of the energy dependence of the exponential damping factor $\exp(-F_j(T))$, although it does show distinct peaks at all reciprocal lattice vector positions. Because the damping factor causes incomplete destructive interference, there can under some circumstances be small additional structure peaks between the diffraction peak positions. Such additional peaks appear, for example, in the ⟨110⟩ direction of the close packed hexagonal (111) surface of an fcc crystal. The structure factor has been plotted as a function of energy exchange rather than as a function of K in order to show the relation to fig. 2, and the reciprocal lattice vector positions in the ⟨110⟩ direction are noted above each peak.

5. Conclusions

We have developed a theory which can be used as a framework for explaining and drawing useful physical information from the inelastic background appearing in time-of-flight energy resolved measurements of low energy atom–surface scattering. The theory is quantum mechanical but is extended into the semiclassical regime of large energies and high surface temperatures, where simple and useful expression for the multiphonon inelastic background are presented. We have shown that in the quantum mechanical regime, the inelastic background will show marked structure due to the coherent nature of the scattering process. Questions of average energy gain or loss by an incident atomic beam are discussed within the context of the theory. It is shown that even in the semiclassical limit an atom can, on average, either gain or lose energy to the surface depending on whether the incident energy is smaller or greater than $k_B T$. The approach to an equilibrium distribution for the gas scattered by the surface from a very low energy monoenergetic beam is briefly discussed as well as the relation to earlier semiclassical theories. The results are illustrated by calculations and comparisons with experiment for the case of He scattering by a NaCl(001) surface.

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