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Diffuse inelastic scattering of atoms from surfaces

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We consider the large-angle diffuse scattering of thermal-energy atoms by defects or adsorbates on a surface. We obtain the Debye-Waller factor for the thermal attenuation of the incoherent elastic peak. When the Debye exponent is small, the diffuse inelastic contribution is dominated by the single-phonon exchange, and is proportional to the frequency distribution function of the defect or adsorbate. We discuss its magnitude compared to the multiphonon background.

I. INTRODUCTION

Elastic and inelastic scattering of neutral atoms at low energies has provided a large quantity of detailed information about the structure and vibrational properties of surfaces.[1] Defects and adsorbates have been intensively investigated by observing the decrease in coherent diffraction intensities as a function of surface coverage.[2,3] Recently a new class of experiments has demonstrated that the diffuse elastic intensity scattered at large angles away from the specular can provide detailed information on the differential cross sections of defects and adsorbates.[4,5] In this paper we wish to examine the nature of this large-angle diffuse scattering, with particular attention paid to the inelastic part due to exchanges of phonons with the surface.

In a typical experiment on an ordered surface with a highly monoenergetic incident beam, one observes diffraction peaks at angles defined by energy and parallel-momentum conservation. The intensity of these peaks can be large or small compared to the specular beam, depending on the smoothness of the surface corrugation. A time-of-flight analysis of the intensity scattered between the diffraction peak positions virtually always reveals combinations of an elastic peak and of inelastic peaks, due to features in the phonon spectral density such as Rayleigh modes. Measurements of the inelastic peak positions have been used to determine dispersion relations for the surface modes of a large number of materials. The elastic peak is due to scattering from defects or disorder on the surface and usually appears with the same linewidth as the incident or specular beam. It serves as a very useful reference point for determining the inelastic peak positions, and in addition, measurements of its intensity as a function of parallel-momentum transfer have revealed structures which can be related to the size and shape of defects[4] or adsorbates[5] on the surface. These elastic and inelastic structures rise out of a diffuse inelastic background that appears at all angles and energies, is dependent on incident energy and crystal temperature, and is usually considered to be due to multiphonon exchanges with the surface.

We examine here the details of this diffuse inelastic background by considering the large-angle scattering from a smooth substrate surface with a dilute concentration of defects or adsorbates. We find that the large-angle inelastic scattering must, in general, be diffuse, and that at any given angle it has a broad frequency spectrum, an exception being the case of adsorbates with dispersionless Einstein-like modes.[6] An interesting point, however, is that under the conditions of most experimental observations the diffuse inelastic contribution is predominantly due to single-phonon exchanges, with the multiphonon contribution being substantially smaller. In addition we derive the Debye-Waller thermal attenuation factor for the diffuse elastic peak.

In the next section we develop the theory for large-angle scattering from surface defects, and in Sec. III we consider the inelastic part using simple Debye and Einstein models for the phonon spectral densities. In Sec. IV we give an explicit calculation of the scattering amplitude of an isolated defect on a smooth surface, and in Sec. V we conclude with a summary of the results.

II. SCATTERING FROM DEFECTS

We develop the theory for scattering by a small coverage of defects, here considered to be adsorbates or other point-scattering centers. We consider the coverage to be sufficiently dilute that multiple scattering between defects can be ignored; then the principal result looks very similar to that commonly used for neutron or x-ray scattering from the bulk. We begin with the transition rate between the initial state i and final state f of the entire system,

$$w_{fi}=\frac{2\pi}{\hbar}|T_{fi}|^2\,\delta(E_i-E_f)\,, \tag{1}$$

where the unperturbed Hamiltonian is

$$H_0=-\frac{\hbar^2}{2m}\nabla^2+U+H^c\,, \tag{2}$$

where H^c is the crystal Hamiltonian and the remaining two terms in (2) comprise the unperturbed particle Hamiltonian which includes a static distorting potential U. Thus, for a typical unperturbed state of the system, i stands for the momentum of the scattering particle $\mathbf{k}_i$ and the quantum numbers of the unperturbed crystal $\{n_i\}$. Since only initial and final particle states can be measured in the experiment, we must sum the transition rate over all possible final crystal states and average over all initial crystal states. This produces a particle transition rate $w(\mathbf{k}_f,\mathbf{k}_i)$ given by

$$w(\mathbf{k}_f,\mathbf{k}_i)=\left\langle \sum_{\{n_f\}} w_{fi} \right\rangle , \tag{3}$$

where the angular brackets $\langle \cdots \rangle$ represent the average over initial-crystal states. We make the van Hove transformation[7] which consists of representing the energy δ function as an integral and defining time-dependent operators in the interaction picture as

$$T(t)=e^{iH^c t/\hbar}\,T\,e^{-iH^c t/\hbar} . \tag{4}$$

The sum over final crystal states can be carried out using closure and we have

$$w(\mathbf{k}_f,\mathbf{k}_i)=\frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt\, e^{-i(\varepsilon_i-\varepsilon_f)t/\hbar}\langle T_{if}(0)T_{fi}(t)\rangle , \tag{5}$$

where ε_i and ε_f are particle energies. We assume that multiple scattering between different defects is negligible, and also assume that we are interested in the intensity sufficiently far from specular that we can ignore the scattering from the flat substrate surface between centers. Then the transition matrix can be written as a sum of atomiclike scattering amplitudes, each multiplied by a phase factor

$$T_{fi}=\sum_l \tau_{fi}^{(l)} e^{-i\mathbf{k}\cdot(\mathbf{R}_l+\mathbf{u}_l)} , \tag{6}$$

where $\mathbf{k}=\mathbf{k}_f-\mathbf{k}_i$ is the total momentum exchanged by the scattering particle, the sum extends over all surface defect positions $\mathbf{R}_l$, and $\mathbf{u}_l$ is the displacement from the equilibrium position due to vibrational motion. If, in addition, all scattering centers are assumed to be identical, Eq. (6) takes the form

$$T_{fi}=\tau_{fi}\sum_l e^{-i\mathbf{k}\cdot(\mathbf{R}_l+\mathbf{u}_l)} . \tag{7}$$

This form is further justified and the approximations leading to it are clarified in Sec. IV below, where we exhibit an explicit calculation for a hard surface in the eikonal approximation. We note here that τ_{fi} is not simply an atomic scattering amplitude for the defect; it must also include multiple scattering with the surrounding substrate surface. The transition rate of Eq. (5) now becomes

$$\begin{aligned}w(\mathbf{k}_f,\mathbf{k}_i)=\frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt\, e^{-i(\varepsilon_i-\varepsilon_f)t/\hbar}&|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2\\ &\times\sum_{l,j}\langle e^{i\mathbf{k}\cdot[\mathbf{R}_l(0)+\mathbf{u}_l(0)]}\\ &\qquad\times e^{-i\mathbf{k}\cdot[\mathbf{R}_j(t)+\mathbf{u}_j(t)]}\rangle ,\end{aligned} \tag{8}$$

where we have made the further assumption that τ_{fi} does not depend on the crystal operators (see Sec. IV below). Equation (8) has the general form of the fundamental equation for a large class of scattering treatments involving a many-body target:[8]

$$w(\mathbf{k}_f,\mathbf{k}_i)=\frac{2\pi}{\hbar}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 S(\mathbf{k},\omega) , \tag{9}$$

where $\omega=(\varepsilon_f-\varepsilon_i)/\hbar$. It is the product of a form factor $|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2$ for the scattering centers, and a dynamical structure factor $S(\mathbf{k},\omega)$ which depends on the average over positions of the scattering centers.

We examine the Fourier transform of the structure factor as it appears in Eq. (8):

$$S(\mathbf{k},t)=\sum_{l,j} e^{i\mathbf{k}\cdot\mathbf{R}_l(0)}e^{-i\mathbf{k}\cdot\mathbf{R}_j(0)}\langle e^{i\mathbf{k}\cdot\mathbf{u}_l(0)}e^{-i\mathbf{k}\cdot\mathbf{u}_j(t)}\rangle . \tag{10}$$

If all vibrational modes of the crystal and defects satisfy the harmonic approximation, the vibrational average can be carried out by standard methods:[9,10]

$$\begin{aligned}\langle e^{i\mathbf{k}\cdot\mathbf{u}_l(0)}e^{-i\mathbf{k}\cdot\mathbf{u}_j(t)}\rangle&=e^{-\langle[\mathbf{k}\cdot\mathbf{u}_l(0)]^2\rangle/2}\\ &\quad\times e^{-\langle[\mathbf{k}\cdot\mathbf{u}_j(t)]^2\rangle/2}\\ &\quad\times e^{\langle\mathbf{k}\cdot\mathbf{u}_l(0)\mathbf{k}\cdot\mathbf{u}_j(t)\rangle}\\ &=e^{-2W(\mathbf{k})}e^{Q_{lj}(\mathbf{k},t)} ,\end{aligned} \tag{11}$$

in which $\exp(-2W)$ is the Debye-Waller factor, where $W=\langle(\mathbf{k}\cdot\mathbf{u}_l)^2\rangle/2$ is independent of the position l parallel to the surface. Real-energy transfers between the surface and scattered particle are governed by the correlation function

$$Q_{lj}(\mathbf{k},t)=\langle\mathbf{k}\cdot\mathbf{u}_l(0)\mathbf{k}\cdot\mathbf{u}_j(t)\rangle . \tag{12}$$

We consider briefly the case of elastic scattering which corresponds to the zeroth-order term in the expansion of $\exp[Q_{lj}(\mathbf{k},t)]$. The structure factor (10) is then independent of t:

$$S(\mathbf{k})=\sum_{l,j}\langle e^{i\mathbf{k}\cdot\mathbf{R}_l(0)}e^{-i\mathbf{k}\cdot\mathbf{R}_j(0)}\rangle . \tag{13}$$

For randomly distributed scattering centers, the sum over positions can be replaced by its average value over an ensemble of distributions and we find, as usual,

$$S(\mathbf{k})=\eta , \tag{14}$$

where η is the total number of scattering centers. (This same result holds for the diffuse part of the scattering from a random lattice gas.[11]) If, instead, the defects were arranged in an ordered array on the surface we would have

$$S(\mathbf{k},t)=\eta^2\sum_{\mathbf{G}}\delta_{\mathbf{k},\mathbf{G}} , \tag{15}$$

where $\mathbf{G}$ is the set of surface reciprocal-lattice vectors. (This is also the result for the coherent part of the scattering by a random lattice gas.[11]) Using (14) for a random distribution of scattering centers on the surface, we obtain for the transition rate

$$w(\mathbf{k}_f,\mathbf{k}_i)=\eta\frac{2\pi}{\hbar}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 e^{-2W(\mathbf{k})}\delta(\varepsilon_f-\varepsilon_i)\ . \tag{16}$$

The quantity which is usually measured is the differential reflection coefficient $dR/d\varepsilon_f d\Omega_f$, which is obtained from (16) by dividing by the incident flux normal to the surface $j_i=|\hbar k_{iz}|/m$, and multiplying by the density of states for a final scattered particle:

$$\frac{dR^{(0)}}{d\varepsilon_f d\Omega_f}=\eta\frac{m^2|\mathbf{k}_f|}{\hbar^4|k_{iz}|(2\pi)^2}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 e^{-2W(\mathbf{k})}\delta(\varepsilon_f-\varepsilon_i)\ . \tag{17}$$

This is essentially the result which has been used to explain the experimental observations of structure in the diffuse scattering of He by steps[4] or by adsorbed CO (Ref. 5) on a smooth Pt(111) surface. We note that our consideration of the vibrational motion of the crystal shows that the diffuse elastic peak is multiplied by a Debye-Waller factor similar to that which is associated with diffraction peaks.

We now move to the problem of inelastic scattering, where we must evaluate the displacement correlation function of Eq. (12). We assume at first that the impurities just "ride along" with the phonons of the unperturbed surface. With this approximation we can write the vibrational amplitude of the jth scattering center in terms of normal modes as

$$\mathbf{u}_j(t)=\sum_{\mathbf{Q},\nu}\left[\frac{\hbar}{2NM\omega_\nu(Q)}\right]^{1/2}\mathbf{e}(\mathbf{Q},\nu)\times\left(a^\dagger_{-\mathbf{Q},\nu}e^{i\mathbf{Q}\cdot\mathbf{R}_j+i\omega_\nu(\mathbf{Q})t}+a_{\mathbf{Q},\nu}e^{-i\mathbf{Q}\cdot\mathbf{R}_j-i\omega_\nu(\mathbf{Q})t}\right)\ , \tag{18}$$

where $\mathbf{Q}$ is the parallel-phonon momentum, ν represents additional phonon quantum numbers such as Rayleigh-mode branch or normal momentum of bulk modes, $\mathbf{e}(\mathbf{Q},\nu)$ is the polarization vector, and $a^\dagger_{\mathbf{Q},\nu}$ is the phonon-creation operator. The polarization vector is related to the frequency distribution function $\rho_{\alpha\beta}$ in the usual way:

$$\sum_{\mathbf{Q},\nu}\mathbf{e}_\alpha(\mathbf{Q},\nu)e_\beta(\mathbf{Q},\nu)\delta(\omega-\omega(\mathbf{Q},\nu))=\rho_{\alpha\beta}(\omega)\ . \tag{19}$$

The displacement correlation function can then be straightforwardly evaluated as

$$\langle\mathbf{k}\cdot\mathbf{u}_l(0)\mathbf{k}\cdot\mathbf{u}_j(t)\rangle=\sum_{\mathbf{Q},\nu}\frac{\hbar|\mathbf{k}\cdot\mathbf{e}(\mathbf{Q},\nu)|^2}{2NM\omega_\nu(\mathbf{Q})}\{n_\nu(\mathbf{Q})e^{i\mathbf{Q}\cdot(\mathbf{R}_j-\mathbf{R}_l)-i\omega_\nu(\mathbf{Q})t}+[n_\nu(\mathbf{Q})+1]e^{-i\mathbf{Q}\cdot(\mathbf{R}_j-\mathbf{R}_l)+i\omega_\nu(\mathbf{Q})t}\}\ , \tag{20}$$

where $n_\nu(\mathbf{Q})$ is the Bose-Einstein factor,

$$n_\nu(\mathbf{Q})=[\exp(\hbar\omega_\nu(\mathbf{Q})/k_BT)-1]^{-1}\ ,$$

with k_B Boltzmann's constant. To obtain the single-phonon contribution to the transition rate of Eq. (8), we expand $\exp[Q_{lj}(\mathbf{k},t)]$ in Eq. (11) and keep the linear term. This leads to

$$w^{(1)}(\mathbf{k}_f,\mathbf{k}_i)=\frac{1}{\hbar}\int_{-\infty}^{\infty}dt\ e^{-i(\varepsilon_i-\varepsilon_f)t/\hbar}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2e^{-2W(k)}\times\sum_{\mathbf{Q},\nu}\frac{|\mathbf{k}\cdot\mathbf{e}(\mathbf{Q}\nu)|^2}{2NM\omega_\nu(\mathbf{Q})}\sum\{e^{i(\mathbf{K}+\mathbf{Q})\cdot(\mathbf{R}_j-\mathbf{R}_l)}e^{-i\omega_\nu(\mathbf{Q})t}n_\nu(\mathbf{Q})+e^{i(\mathbf{K}-\mathbf{Q})\cdot(\mathbf{R}_j-\mathbf{R}_l)}e^{i\omega_\nu(\mathbf{Q})t}[n_\nu(\mathbf{Q})+1]\}\ . \tag{21}$$

The sum over particle positions, just as in the elastic case of Eq. (14), gives a factor of η for a random distribution, or for the diffuse scattering by a lattice gas. Thus the final expression for the differential cross section becomes

$$\frac{dR^{(1)}}{d\varepsilon_f d\Omega_f}=\eta\frac{m^2|\mathbf{k}_f|}{\hbar^3|k_{iz}|(2\pi)^2}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2e^{-2W(\mathbf{k})}\times\sum_{\mathbf{Q},\nu}\frac{|\mathbf{k}\cdot\mathbf{e}(\mathbf{Q},\nu)|^2}{2NM\omega_\nu(\mathbf{Q})}\{\delta(\varepsilon_i-\varepsilon_f+\hbar\omega_\nu(\mathbf{Q}))n_\nu(\mathbf{Q})+\delta(\varepsilon_i-\varepsilon_f-\hbar\omega_\nu(\mathbf{Q}))[n_\nu(\mathbf{Q})+1]\}\ . \tag{22}$$

Considering now the general case when the impurities affect the phonon spectrum, we see that in Eq. (18) we must replace $\mathbf{e}(\mathbf{Q},\nu)\exp(i\mathbf{Q}\cdot\mathbf{R}_j)$ by a general polarization vector $\mathbf{e}_j(\mathbf{Q},\nu)$ that depends on $\mathbf{R}_j$ in an unknown way and is characterized by three quantum numbers that we still write as $(\mathbf{Q},\nu)$, even though $\mathbf{Q}$ is no longer a wave vector. The only property of $\mathbf{e}_j(\mathbf{Q},\nu)$ that we need is that its phase varies randomly with $\mathbf{R}_j$, so that, in the analog of Eq. (21), we can still discard all terms with $l\neq j$. Equation (22) is then the general result for the single-phonon contribution to the diffuse scattering from a dilute collection of scattering centers. It consists of the phonon-creation part proportional to $n_\nu(\mathbf{Q})+1$ and the destruction part proportional to $n_\nu(\mathbf{Q})$ and both are multiplied by a Debye-Waller factor. We note that one of the sums over $\mathbf{Q},\nu$ can be trivially carried out using the energy δ function, and consequently the differential reflection coefficient is usually diffuse, and the only structure is that appearing in the phonon spectral density. This structure, of course, is very sharp for a dispersionless mode in which ω is independent of $\mathbf{Q}$, i.e., an Einstein mode.[12] These points are illustrated by the model calculations in the next section.

III. DEBYE AND EINSTEIN MODELS

We now take the results of the preceding section and illustrate them by considering some simple forms for the spectral density for vibrations of the scattering centers. The single-phonon contribution to the scattering is obtained from Eq. (8) with Eq. (11) expanded to first order in $Q_{lj}(\mathbf{k},t)$:

$$w^{(1)}(\mathbf{k}_f,\mathbf{k}_i)=\frac{1}{\hbar^2}\int_{-\infty}^{\infty}dt\, e^{-i(\varepsilon_i-\varepsilon_f)t/\hbar}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 e^{-2W(\mathbf{k})}\sum_{l,j}e^{i\mathbf{K}\cdot(\mathbf{R}_l-\mathbf{R}_j)}\langle \mathbf{k}\cdot\mathbf{u}_l(0)\mathbf{k}\cdot\mathbf{u}_j(t)\rangle \ . \tag{23}$$

From the arguments after Eq. (21) it is clear that the diffuse contribution comes only from those terms with $l=j$, i.e., it is the incoherent contribution. Then we have

$$w^{(1)}(\mathbf{k}_f,\mathbf{k}_i)=\frac{\eta}{\hbar^2}\int_{-\infty}^{\infty}dt\, e^{-i(\varepsilon_i-\varepsilon_f)t/\hbar}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 e^{-2W(\mathbf{k})}\langle \mathbf{k}\cdot\mathbf{u}(0)\mathbf{k}\cdot\mathbf{u}(t)\rangle \ . \tag{24}$$

For simplicity we will assume that only vibrations in the direction perpendicular to the surface are important. This is usually the case because the normal momentum transfer $q=k_{iz}+k_{fz}$ is typically considerably larger than the parallel momentum. Thus we are making the replacement $\langle \mathbf{k}\cdot\mathbf{u}(0)\mathbf{k}\cdot\mathbf{u}(t)\rangle \approx q^2\langle u(0)u(t)\rangle$, where u is assumed to be the normal component of $\mathbf{u}$, although we note that it is a straightforward matter to keep all the components. Now, in terms of the frequency distribution function $\rho(\omega)$ we can write the correlation function as

$$\langle u(0)u(t)\rangle=\frac{\hbar}{2M}\int_{-\infty}^{\infty}\frac{d\omega}{\omega}\rho(\omega)e^{i\omega t}n(\omega)\ , \tag{25}$$

where M is the effective mass of the surface defect and $n(\omega)$ is again the Bose-Einstein factor. This correlation function substituted into Eq. (24) leads to a differential reflection coefficient of the form

$$\frac{dR^{(1)}}{d\varepsilon_f d\Omega_f}=\eta\frac{m^2|\mathbf{k}_f|q^2}{2\hbar^3|k_{iz}|(2_\pi)^2M}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 \times e^{-2W(\mathbf{k})}\frac{\rho(\Omega)n(\Omega)}{\Omega}\ , \tag{26}$$

where $\Omega=(\varepsilon_f-\varepsilon_i)/\hbar$. Note that since $n(-\omega)=-[n(\omega)+1]$ this expression contains both energy-loss (phonon creation) and energy-gain (phonon annihilation) events. Equation (26) describes totally diffuse scattering at all final angles with the only structure due to the phonon distribution coming from its linear dependence on $\rho(\omega)$. The temperature dependence is contained in the Debye-Waller factor and in the Bose-Einstein factor.

As a specific example we can look at the Debye model in which $\rho(\omega)=3\omega^2/\omega_D^3$, where ω_D is the Debye frequency. Then

$$\frac{dR^{(1)}}{d\varepsilon_f d\Omega_f}=\eta\frac{3m^2|\mathbf{k}_f|q^2}{2\hbar^3M|k_{iz}|(2\pi)^2\omega_D^3}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 \times e^{-2W(\mathbf{k})}|\Omega|n(\Omega) \tag{27}$$

and it is understood that $dR^{(1)}/d\varepsilon_f d\Omega_f=0$ if $|\Omega|>\omega_D$. A second example is the Einstein model, in which the spectral density consists of a single strong peak, $\rho(\omega)=\delta(\omega-\omega_E)$. In this case the differential reflection coefficient also shows the same sharply peaked structure,

$$\frac{dR^{(1)}}{d\varepsilon_f d\Omega_f}=\eta\frac{m^2|\mathbf{k}_f|q^2}{2\hbar^3k_{iz}M(2\pi)^2\omega_E}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 \times e^{-2W(\mathbf{k})}n(\omega_E)\delta(\omega-\omega_E)\ . \tag{28}$$

Diffuse scattering from several species of adsorbates on surfaces has been shown to exhibit such dispersionless Einstein vibrational modes.[6,13,14]

It is of interest to consider the multiple-phonon contribution to the diffuse elastic scattering and to compare its importance to the above single-phonon terms. The two-phonon contribution is obtained from Eq. (8) with Eq. (11) expanded to second order in $Q_{lj}(\mathbf{k},t)$. Using the simplified displacement correlation function of Eq. (25) leads to

$$\frac{dR^{(2)}}{d\varepsilon_f d\Omega_f}=\eta\frac{m^2|\mathbf{k}_f|}{8\hbar^2|k_{iz}|(2\pi)^2M^2}q^4|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2e^{-2W(\mathbf{k})} \times\int d\omega\frac{\rho(\omega)n(\omega)}{\omega}\frac{\rho(\Omega-\omega)n(\Omega-\omega)}{\Omega-\omega}\ . \tag{29}$$

This depends on the convolution of the phonon spectral density with itself. This simplifies in the high-temperature limit $k_BT>\hbar\omega_D$, where $n(\omega)\rightarrow k_BT/\hbar\omega$, and if we further consider a Debye model for $\rho(\omega)$, the integral over ω gives a factor of $2\omega_D-|\Omega|$ (and zero for $|\Omega|>2\omega_D$). Then

$$\frac{dR^{(2)}}{d\varepsilon_f d\Omega_f}=\frac{\eta 9m^2|\mathbf{k}_f|k_BT^2}{4\hbar^4k_{iz}(2\pi)^2M^2\omega_D^5}q^4|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 \times e^{-2W(\mathbf{k})}\left[\omega_D-\frac{|\Omega|}{2}\right]\ . \tag{30}$$

If we evaluate the single-phonon contribution of Eq. (27) in the same high-temperature limit, we obtain the ratio of the two-phonon contribution to that of single phonons to be the following for $|\Omega| < 2\omega_D$:

$$\frac{R^{(2)}}{R^{(1)}} = \frac{3q^2 k_B T}{2\omega_D^2 M} = 12\frac{m}{M}\frac{E_n}{\hbar\omega_D}\frac{k_B T}{\hbar\omega_D} , \tag{31}$$

where the effective normal energy of the scattered particle is defined by $E_n = \hbar^2 q^2/8m$. The result of Eq. (31) is sometimes referred to as the Weare parameter,[15] and we note that it is also of the same form as the Debye-Waller exponent W for the same one-dimensional Debye phonon distribution. Thus under circumstances in which Eq. (31) gives values $\ll 1$, and this corresponds to many experimental situations, the diffuse inelastic scattering is dominated by the single-phonon contribution.

IV. SCATTERING AMPLITUDE FOR ISOLATED DEFECTS

In this section we calculate explicitly the transition-matrix amplitude for a dilute coverage of adsorbates on a flat surface. We assume that the surface can be treated as a hard reflecting mirror and that the adsorbates are represented by hard hemispheres on that surface.[5] We will use the eikonal approximation, since it is sufficient to exhibit the features of more exact solutions and justifies readily the statements above Eqs. (6) and (7).

The usual starting point for developing the eikonal approximation for surface scattering is the Rayleigh ansatz, in which the wave function is represented as a plane wave incoming toward the surface and a distribution of outgoing scattered waves:

$$\psi(\mathbf{r}) = e^{-ik_{iz}z} e^{i\mathbf{K}_i\cdot\mathbf{R}} + \sum_{\mathbf{K}} C(\mathbf{K}) e^{i(\mathbf{K}_i+\mathbf{K})\cdot\mathbf{R}} e^{ik_{fz}z} \tag{32}$$

with $k_{fz} = [k_{iz}^2 + \mathbf{K}_i^2 - (\mathbf{K}_i+\mathbf{K})^2]^{1/2}$ for elastic scattering. The hard surface is defined by a corrugation function $\xi(\mathbf{R})$ such that the boundary condition on ψ at the hard surface is

$$\psi(\mathbf{R}, z = \xi(\mathbf{R})) = 0 . \tag{33}$$

The eikonal approximation consists of assuming that the dependence of k_{fz} on $\mathbf{K}$ is very weak, which leads directly to the evaluation of the amplitude $C(\mathbf{K})$:

$$C(\mathbf{K}) = -\frac{1}{L^2}\int d\mathbf{R}\, e^{-i\mathbf{K}\cdot\mathbf{R}} e^{-iq\xi(\mathbf{R})} , \tag{34}$$

where $q = k_{iz} + k_{fz}$, and the integral is over the entire surface.

For the inelastic case considered here, where there is energy loss or gain by the particle at the surface, the most straightforward extension of the above treatment is to replace k_{fz} by

$$k_{fz} = [k_{iz}^2 + k_i^2 - (\mathbf{K}_i + \mathbf{K})^2]^{1/2} \pm \hbar\omega/2m .$$

As in Sec. III above this ignores any parallel momentum exchanged by the phonon.

If we now assume that the scattering centers are hard bumps, well separated, and each occupying an area S_l, we can rewrite Eq. (34) in the form

$$C(\mathbf{K}) = -\frac{1}{L^2}\sum_l \int_{S_l} d\mathbf{R}\, e^{-i\mathbf{K}\cdot\mathbf{R}} e^{-iq\xi(\mathbf{R})} + \frac{1}{L^2}\sum_l \int_{S_l} d\mathbf{R}\, e^{-i\mathbf{K}\cdot R} - \frac{1}{L^2}\int d\mathbf{R}\, e^{-i,\mathbf{K}\cdot\mathbf{R}} . \tag{35}$$

The last term, in which the integral is over the entire surface, is a δ function describing specular scattering. This arises because we have subtracted and added the middle term, which is an integral, over the flat surface underneath each of the bumps. This middle term is the Fraunhofer contribution, while the first term is the illuminated-face contribution. Since we are interested in scattering at large values of parallel-momentum transfer $\mathbf{K}$, we can neglect the δ-function contribution at $\mathbf{K}=\mathbf{0}$. If we now assume that all of the bumps are identical, we have

$$\begin{aligned} C(\mathbf{K}) &= -\frac{1}{L^2}\int_S d\mathbf{R}\, e^{-i\mathbf{K}\cdot\mathbf{R}} (e^{-iq\xi(\mathbf{R})} - 1) \sum_l e^{-i\mathbf{K}\cdot\mathbf{R}_l} \\ &= \frac{1}{L^2} c(\mathbf{K}) \sum_l e^{-i\mathbf{K}\cdot\mathbf{R}_l} , \end{aligned} \tag{36}$$

with $\mathbf{R}_l$ is the equilibrium origin of the lth center and the integral is carried out over only one of them.

Under many circumstances there are multiple semiclassical hits which may contribute to scattering at a given final angle, but the eikonal approximation only accounts for single hits. An important example occurs when the second hit is a backreflection by the mirror surface. When such terms occur they can be accounted for by adding in an "image" contribution to the illuminated-face term corresponding to the transfer of perpendicular momentum $q' = k_{iz} - k_{fz}$. In this case $c(\mathbf{K})$ becomes

$$c(\mathbf{K}) = -\frac{1}{L^2}\int d\mathbf{R}\, e^{-i\mathbf{K}\cdot\mathbf{R}} (e^{-iq\xi(\mathbf{R})} - e^{-i\mathbf{q}'\xi(\mathbf{R})} - 1) . \tag{37}$$

The relationship between the transition matrix and $C(\mathbf{K})$ is obtained by comparing forms of the asymptotic wave function and is given by

$$C(\mathbf{K}) = \frac{m}{L^2\hbar^2|k_{fz}|}\tau(\mathbf{k}_f, \mathbf{k}_i) e^{i\delta} , \tag{38}$$

where δ is an unimportant phase. This together with Eq. (36) justifies the form chosen for the transition matrix in Eq. (7) above.

We illustrate the above results by making the explicit calculation for the case when the perturbing bump is a hemisphere. Then we have

$$\xi(\mathbf{R}) = \begin{cases} 0, & R \geq a \\ (a^2 - R^2)^{1/2}, & R < a . \end{cases} \tag{39}$$

The simplest term is the Fraunhofer part, which is just the integral over a flat circle of radius a,

$$\frac{1}{L^2}\int d\mathbf{R}\,e^{-i\mathbf{K}\cdot\mathbf{R}}=\frac{2\pi a}{L^2}\frac{J_1(Ka)}{K}\ , \tag{40}$$

where $J_1(Ka)$ is the Bessel function of order 1. For the illuminated-face contribution we can obtain a solution using stationary-phase methods.[16] This is sometimes referred to as the primitive semiclassical approximation:

$$-\frac{1}{L^2}\int d\mathbf{R}\,e^{-i\mathbf{K}\cdot\mathbf{R}}e^{-iq\xi(\mathbf{R})}=\frac{2\pi i}{L^2}\frac{e^{-ia\mathbf{k}\cdot\hat{\mathbf{n}}}}{\mathbf{k}\cdot\hat{\mathbf{n}}}\ , \tag{41}$$

where

$$\mathbf{k}\cdot\hat{\mathbf{n}}=k_f^2+k_i^2+2k_ik_f\cos(\theta_f+\theta_i)\ , \tag{42}$$

and in the expression where q is replaced by q' the result is of the same form as (41) except that $\mathbf{k}\cdot\hat{\mathbf{n}}$ is replaced by

$$\mathbf{k}'\cdot\hat{\mathbf{n}}'=k_f^2+k_i^2-2k_ik_f\cos(\theta_f-\theta_i)\ . \tag{43}$$

Thus for the case of a hemispherical bump we have

$$c(\mathbf{K})=\frac{2\pi a}{L^2}\left[\frac{ie^{-ia\mathbf{k}\cdot\hat{\mathbf{n}}}}{a(\mathbf{k}\cdot\hat{\mathbf{n}})}-\frac{ie^{-ia\mathbf{k}'\cdot\hat{\mathbf{n}}'}}{a(\mathbf{k}'\cdot\hat{\mathbf{n}}')}+\frac{J_1(Ka)}{K}\right]\ . \tag{44}$$

It is a straightforward matter to obtain a somewhat better solution for $c(\mathbf{K})$ by considering the atomic scattering cross section from a hard sphere, together with its image contribution accounting for a second reflection from the flat surface. One can again apply the stationary-phase approximation. For elastic scattering $|\mathbf{k}_f|=|\mathbf{k}_i|$, and for normal incidence the result is identical with Eq. (44).[5]

V. CONCLUSIONS

In this paper we have considered the diffuse scattering by a collection of defect centers on an otherwise flat surface substrate. Our treatment does not consider the large contribution to the total scattering cross section due to the long-range van der Waals part of the defect or adsorbate potential,[17] but this contribution appears only very near the specular direction. The results are then valid for large-angle scattering ($\gtrsim 10°$), or equivalent for large parallel-momentum transfer.

We show that the reflection intensities can be directly related to the structure factor for the distribution of defects. We are primarily interested in the nature of the incoherent diffuse inelastic contribution. We find that, for sufficiently low surface temperatures, the incoherent diffuse inelastic scattering is dominated by the single-phonon term $R^{(1)}$, according to Eq. (31). It is also interesting to compare $R^{(1)}$ to the total two-phonon scattering intensity $R^{(2)}_{\text{tot}}$.

The comparison is relevant because even for a perfect surface the two-phonon processes are "diffuse" in the sense that they give contributions in regions of the $\omega\mathbf{K}$ space where one-phonon (coherent) processes are kinematically forbidden. In the simple model where the defects "ride along" with the surface and have the same mass as surface atoms, we have, in analogy with Eq. (31),

$$\frac{R^{(2)}_{\text{tot}}}{R^{(1)}}=\frac{3q^2k_BT}{2\omega_D^2M\eta}\ . \tag{45}$$

As a by-product of our analysis, we also determine the Debye-Waller thermal attenuation factor which multiplies the incoherent elastic diffuse intensity: in the simplest approximation, it has the standard form $\exp[-\langle(\mathbf{k}\cdot\mathbf{u})^2\rangle]$, where $\mathbf{u}$ is the displacement of the defect. Although these results have been obtained for defects or adsorbates on a flat surface substrate, it is straightforward to make the extension to surfaces with periodic structure and exhibiting diffraction effects.

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