

## INELASTIC SURFACE SCATTERING OF NON-PENETRATING PARTICLES\*

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This paper is an extension of the authors' earlier work to include a treatment of one-phonon inelastic scattering of particles which do not penetrate appreciably into the crystal. A full quantum-mechanical treatment of the lattice vibrations is used throughout, and the results are not restricted to small scattered intensities. Calculations are presented for the scattering of helium atoms by a simplified model of the crystal surface.

### 1. Introduction

The scattering of non-penetrating particles has proven to be a very useful technique for determining the surface properties of a crystal. However, there is presently a large amount of unexplained experimental data available<sup>1-4</sup>) which, if properly analyzed, would surely lead to a much better understanding of the crystal surface. The theoretical description of surface scattering has been developing for many years, the fundamental work being contained in the series of papers by Lennard-Jones, Devonshire, and co-workers<sup>5-8</sup>). Recently there has been a great deal of renewed interest in the area mainly in connection with the interpretation of low energy electron diffraction data<sup>9-13</sup>). However, existing theories of the scattering of non-penetrating particles have been developed either from a classical standpoint<sup>14-16</sup>), or within the framework of the Born approximation<sup>5-8, 17-19</sup>), and none of these treat the many body features of the scattering process in a systematic manner.

This paper is an extension of the authors' earlier work<sup>20, 21</sup>) to include scattering processes in which energy may be exchanged at the surface. The

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complete quantum mechanical description of the lattice vibrations is used throughout and the theory meets the requirement of unitarity; i.e. the total number of scattered particles always equals the number of incoming particles.

The kinematics of the scattering process is quite simple. An incoming particle with wave vector  $p_i$ , having components  $P_i$  parallel to the surface and  $p_{zi}$  perpendicular to it, is reflected into the final state of wave vector  $p_f$ , with components  $P_f$  and  $p_{zf}$ . If no energy is exchanged between the particle and the surface then

$$P_f - P_i = G, \quad (1.1)$$

where  $G$  is a reciprocal lattice vector of the surface, and energy conservation implies

$$p_f^2 - p_i^2 = 0. \quad (1.2)$$

In the case of inelastic processes the right-hand side of (1.1) contains the parallel wave vector of all exchanged phonons, and (1.2) is replaced by the corresponding equation containing the phonon frequencies. The convention is that the crystal lies in the region  $z < 0$ , hence the perpendicular wave vector  $p_{zi}$  of an incoming particle is negative, while the perpendicular component  $p_{zf}$  for a final scattered particle is positive.

The next three sections of this paper are concerned with developing the theory of inelastic surface scattering with particular applications to the "distorted wave Born approximation" and the unitary treatment of one-phonon exchange. In section 5 these results are used to calculate the spectrum of particles scattered from a simple crystal model.

## 2. Development of the theory

The theory of inelastic surface scattering can be developed along several equivalent lines but perhaps the most convenient for our purposes is the two-potential formalism of Gell-Mann and Goldberger<sup>22</sup>). Since we are interested in the energy region in which none of the incoming particles penetrates appreciably into the surface, the total interaction potential  $V_i$  is divided into a "large" part  $U$  exhibiting total reflection and a remainder  $v = V_i - U$  which must be treated approximately.

As discussed in I<sup>21</sup>) we can relate the potential  $U$  to the thermal average of the total interaction potential. If  $V_i$  is chosen to be a sum over all lattice sites of two-body atomic potentials, i.e.

$$V_i = \sum_l v^a(r - r_l - u_l), \quad (2.1)$$

where  $u_l$  is the small displacement from equilibrium of the crystal ion at

position  $r_i$ , then it is shown in I that the thermal average can be written as

$$\langle V_i \rangle = N \sum_G \sum_m \sum_q \exp [iG \cdot R + iq(z - z_m)] \exp [-W_m(G, q)] v_{G,q}^2, \quad (2.2)$$

where  $N$  is the number of lattice sites on the surface,  $W_m(G, q)$  is the Debye-Waller factor for ions in the  $m$ th plane parallel to the surface,  $v_{G,q}^2$  is the Fourier inverse of the atomic two-body potential, and  $R$  is the projection of the position vector on the surface. By making the definition

$$U_G(z) = N \sum_m \sum_q \exp [iq(z - z_m)] \exp [-W_m(G, q)] v_{G,q}^2, \quad (2.3)$$

the thermal average takes the simple form

$$\langle V_i \rangle = \sum_G e^{iG \cdot R} U_G(z). \quad (2.4)$$

It has proven to be most convenient to take the potential  $U$  such that it gives rise to total specular reflection only. The obvious choice is

$$U = U_{G=0}(z). \quad (2.5)$$

The eigenfunctions of  $U$  for outgoing wave (+) and incoming wave (-) boundary conditions will be denoted by  $\chi_r^{(\pm)}$ ; they are products of a vibrational wave function for the solid, a plane wave for particle motion parallel to the surface, and a normal wave function  $\chi^{(\pm)}(p_{zr}; z)$  which obeys the equation

$$\left( \frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + \frac{\hbar^2 p_{zr}^2}{2m} - U \right) \chi^{(\pm)}(p_{zr}; z) = 0. \quad (2.6)$$

Eq. (2.6) can have solutions for  $p_{zr}^2 < 0$  corresponding to surface bound states.

The transition rate  $w_{fi}$  from some initial state  $i$  to some final state  $f$  is given in terms of the transition matrix  $T_{fi}$  by

$$w_{fi} = \frac{2\pi}{\hbar} |T_{fi}|^2 \delta(E_f - E_i), \quad (2.7)$$

where  $E_f$  and  $E_i$  are the final and initial energies of the entire system. The subscript  $f$  or  $i$  is a collective label for the wave vector ( $\mathbf{P}, p_z$ ) of the scattered particle and the number of phonons  $\{n\}$  in each vibrational mode of the crystal. The reflection coefficient  $R(p_f, p_i)$  discussed in I is found by dividing the transition rate by the incident particle flux  $j_i = \hbar p_{zi}/mL$  (where  $L$  is the quantization length), and then summing over all final phonon states and averaging over all initial phonon states

$$R(p_f, p_i) = \frac{2\pi}{\hbar j_i} \sum_{(n_f)} \sum_{(n_i)} \rho(\{n_i\}) |T_{fi}|^2 \delta(E_f - E_i), \quad (2.8)$$

where  $\rho(\{n_i\})$  is the distribution of initial phonon states. For inelastic scattering the experimentally measurable quantity is the differential scattered intensity or differential reflection coefficient  $dR/dE_f d\Omega_f$ . This is obtained upon multiplying the reflection coefficient by the available volume in phase space for a final scattered particle

$$\frac{dR(p_f, p_i)}{dE_f d\Omega_f} = \left(\frac{L}{2\pi}\right)^3 \frac{2\pi m |p_f|}{\hbar^3 j_i} \sum_{\{n_f\}} \sum_{\{n_i\}} \rho(\{n_i\}) |T_{fi}|^2 \delta(E_f - E_i). \quad (2.9)$$

Thus all information on the scattering process depends upon knowledge of the matrix element of the transition operator taken between initial and final states,  $\phi_i$  and  $\phi_f$ , of the unperturbed system. Gell-Mann and Goldberger<sup>22</sup> have shown that this matrix element is equivalent to

$$T_{fi} = (\phi_f, U\chi_i^{(\pm)}) + t'_{fi}, \quad (2.10)$$

where the reduced transition matrix  $t'_{fi}$  obeys an integral equation involving only  $v$ ,

$$t'_{fi} = (\chi_f^{(-)}, v\chi_i^{(+)}) + \sum_c (\chi_f^{(-)}, v\chi_c^{(-)}) \frac{1}{E_i - E_c + i\epsilon} t'_{ci}. \quad (2.11)$$

At this point we note that since  $U$  is chosen to give rise only to specular reflection of low energy incoming particles, the outgoing wave eigenfunction  $\chi_i^{(+)}$  (where  $i$  denotes the set of quantum numbers describing the incident beam) can differ from the incoming wave eigenfunction  $\chi_s^{(-)}$  (where  $s$  denotes the quantum numbers of the specular beam) only by a phase factor depending on the absolute value of the perpendicular momentum, i.e.

$$\chi_i^{(+)} = e^{i\delta_i} \chi_s^{(-)}, \quad (2.12)$$

where

$$\delta_i = \delta_i(|p_{zi}|) = \delta_i(p_{zs}). \quad (2.13)$$

In fact,  $e^{i\delta_i}$  is the scattering matrix ( $S$ -matrix) for the potential  $U$ .

The first term on the right-hand side of (2.10) is simply the transition matrix for  $U$ -scattering and is shown in I to be given by

$$(\phi_f, U\chi_i^{(+)}) = \frac{i\hbar^2 |p_{zi}|}{mL} e^{i\delta_i} \delta_{fs}, \quad (2.14)$$

where the Kronecker  $\delta$ -function implies that it contributes only to specular scattering.

It is convenient to define a new reduced  $t$ -matrix  $t_{fs}$  according to

$$t_{fi} = t'_{fi} e^{-i\delta_i}, \quad (2.15)$$

so that eq. (2.10) becomes

$$T_{fi} = e^{i\delta_i} \left\{ \frac{i\hbar^2 |p_{zi}|}{mL} \delta_{fs} + t_{fs} \right\}, \quad (2.16)$$

and (2.11) is cast into the form

$$t_{fs} = v_{fs} + \sum_g v_{fg} \frac{1}{E_i - E_g + i\varepsilon} t_{gs}, \quad (2.17)$$

where

$$v_{fg} = (\chi_f^{(-)}, v\chi_g^{(-)}). \quad (2.18)$$

The problem now reduces to one of finding solutions for the  $t$ -matrix of (2.17). In general this is impossible to do exactly; however, if we neglect the principal part contribution to the sum over intermediate continuum states in (2.17) we are left with an approximate integral equation which can be solved, i.e.

$$t_{fs} = v_{fs} - i\pi \sum_c v_{fc} \delta(E_i - E_c) t_{cs} + \sum_b v_{fb} \frac{1}{E_i - E_b} t_{bs}. \quad (2.19)$$

The sum over  $c$  in (2.19) runs over all continuum states while the sum over  $b$  runs over all discrete states of the potential  $U$ . It is obvious that this approximation neglects the intermediate interactions with energy non-conserving continuum states, but the contributions from all bound states are kept regardless of energy conservation. The  $\delta$ -function in (2.19) can be used to carry out the sum over perpendicular momentum leaving

$$t_{fs} = v_{fs} - i \sum_{K_c} \sum_{\{n_c\}} v_{fc} N_c t_{cs} + \sum_{K_b} \sum_{\kappa_b} \sum_{\{n_b\}} v_{fb} \frac{1}{E_i - E_b} t_{bs}, \quad (2.20)$$

where  $N_c = mL/2\hbar^2 p_{zc}$  is  $\pi$  times the density of states for perpendicular motion, and the total energy of a particle in a bound state  $b$  is given by  $\hbar^2 (K_b^2 - \kappa_b^2)/2m$ .

It is shown in the Appendix that eq. (2.20) leads to results which obey the quantum mechanical condition of unitarity for both elastic and inelastic scattering. The case of elastic surface scattering has been discussed in I, and we wish to consider here the extension of those results to the case of one-phonon inelastic scattering.

### 3. Distorted wave Born approximation

The simplest approximation to the  $T$ -matrix is the "distorted wave Born approximation" and is obtained upon replacing  $t_{fs}$  by  $v_{fs}$  in (2.16). Since the specular scattering is of no interest in the Born approximation, the first term

on the right of (2.16) will never enter and we can replace  $v_{fs}$  by matrix elements of the true interaction potential  $V_i$ . The reflection coefficient for particles scattered from the initial state  $k_i$  to the final state  $k_f$  is then

$$R(k_f, k_i) = \frac{2\pi}{\hbar j_i} \sum_{(n_f)} \sum_{(n_i)} \rho(\{n_i\}) |(\chi_f^{(-)}, V_i \chi_i^{(-)})|^2 \delta(E_f - E_i). \quad (3.1)$$

The sums over phonon states can be carried out using the methods of solid state field theory as developed by Van Hove<sup>23</sup>) and the results are

$$\begin{aligned} R(k_f, k_i) &= \frac{1}{\hbar^2 j_i} \int_{-\infty}^{\infty} dt \exp[i\hbar(k_f^2 - k_i^2)t/2m] \int dr \int dr' \chi_s^{(-)*}(r) \\ &\times \chi_f^{(-)}(r) \chi_f^{(-)*}(r') \chi_s^{(-)}(r') \sum_l \sum_{l'} \sum_k \exp[ik' \cdot (r' - r_l) - ik \cdot (r - r_l)] \\ &\times v_k^{a*} v_k^a \exp[-W_l(k) - W_{l'}(k') + Q_{ll'}(k, k'; t)]. \end{aligned} \quad (3.2)$$

The term  $W_l(k)$  is the Debye-Waller exponent and depends only on that component of  $l$  which counts crystal planes parallel to the surface. The exponent  $Q_{ll'}(k, k'; t)$  is essentially the two-particle correlation function discussed in detail by Glauber<sup>24</sup>). For a monatomic lattice it has the explicit form

$$\begin{aligned} Q_{ll'}(k, k'; t) &= \frac{\hbar}{2NM} \sum_{Q, \nu} \frac{\left[ k \cdot e^* \left( l \left| \frac{Q}{\nu} \right. \right) \right] \left[ k' \cdot e \left( l' \left| \frac{Q}{\nu} \right. \right) \right]}{\omega_\nu(Q)} \\ &\times \{ (n_\nu(Q) + 1) \exp[iQ \cdot (R_l - R_{l'}) + i\omega_\nu(Q)t] \\ &+ n_\nu(Q) \exp[-iQ \cdot (R_l - R_{l'}) - i\omega_\nu(Q)t] \}, \end{aligned} \quad (3.3)$$

where  $M$  is the mass of a lattice ion,  $n_\nu(Q)$  is the Bose-Einstein occupation number and  $e \left( l \left| \frac{Q}{\nu} \right. \right)$  is the unit polarization vector for a phonon of parallel wave vector  $Q$  and other labels  $\nu$  (perpendicular wave vector, polarization, etc.). The polarization vector also depends only on the component of  $l$  which counts planes parallel to the surface.

It is apparent from (3.3) that the factor  $\exp[Q_{ll'}(k, k'; t)]$ , through its dependence on  $t$ , contains all the possibilities for energy transfer. The elastic (zero-phonon) and inelastic (one-phonon, two-phonon, etc.) reflection coefficients are obtained by expanding  $\exp[Q_{ll'}(k, k'; t)]$  in powers of  $Q_{ll'}(k, k'; t)$ . From the zeroth order term, upon carrying out the trivial sums and integrations and recalling the definition (2.3), we obtain the elastic reflection coefficient

cient in the form

$$R^{(0)}(k_f, k_i) = \frac{2\pi m}{\hbar^2 k_{zi}} \sum_{G \neq 0} |(\chi^{(-)}(k_{zf}; z), U_G(z) \chi^{(-)}(k_{zs}; z))|^2 \times \delta(K_f - K_i - G) \delta\left(\frac{\hbar^2}{2m} [k_f^2 - k_i^2]\right) \quad (3.4)$$

It is seen that  $R^{(0)}$  is non-vanishing only for wave vectors  $K_f$  that satisfy the condition of Bragg diffraction.

The inelastic scattering in which a single phonon is exchanged is obtained from the first order expansion of  $\exp[Q_{II'}(k, k'; t)]$ . Again many of the sums are trivial and the differential reflection coefficient for one-phonon inelastic scattering can be written

$$\begin{aligned} \frac{dR(k_f, k_i)}{dE_f d\Omega_f} &= \frac{m^2}{2\hbar^4 N M k_{zi}} \sum_G \sum_{Q, \nu} \frac{|k_f|}{\omega_\nu(Q)} \\ &\times \left\{ |(\chi^{(-)}(k_{zf}; z), \nabla \cdot U_{-Q-G, \nu}(z) \chi^{(-)}(k_{zs}; z))|^2 (n_\nu(Q) + 1) \right. \\ &\times \delta(K_f - K_i + Q + G) \delta\left(\frac{\hbar}{2m} [k_f^2 - k_i^2] + \omega_\nu(Q)\right) \\ &+ |(\chi^{(-)}(k_{zf}; z), \nabla \cdot U_{Q-G, \nu}(z) \chi^{(-)}(k_{zs}; z))|^2 n_\nu(Q) \\ &\times \delta(K_f - K_i - Q + G) \delta\left(\frac{\hbar}{2m} [k_f^2 - k_i^2] - \omega_\nu(Q)\right) \Big\}, \quad (3.5) \end{aligned}$$

where the reduced vector potential  $U_{Q+P, \nu}(z)$ , and the divergence operator  $\nabla$  are defined by

$$U_{Q+P, \nu}(z) = N \sum_i \sum_q \exp[iq(z - z_i)] v_{Q+P, q}^2 \exp[-W_i(Q + P, q)] e\left(l \left| \frac{Q}{\nu} \right.\right), \quad (3.6)$$

and

$$-i\nabla \cdot U_{Q+P, \nu}(z) = \left(Q + P, -i \frac{\partial}{\partial z}\right) \cdot U_{Q+P, \nu}(z). \quad (3.7)$$

The physical meaning of (3.5) is as follows. The term proportional to  $n_\nu(Q) + 1$  describes processes in which a single phonon is emitted into the surface, while the term proportional to  $n_\nu(Q)$  describes single phonon absorption. The conservation of energy and parallel momentum is given by the  $\delta$ -functions. The appearance of the divergence operator  $\nabla$  suggests, as expected, that the effective potential for one-phonon scattering is just the first order term in a Taylor expansion of the complete thermally averaged interaction potential,  $U$ .

The extension of this procedure to include scattering by any number of phonons is straightforward. For instance the two phonon differential scattered intensity is obtained from (3.3) by replacing  $\exp[Q_{II'}(k, k'; t)]$  by  $\frac{1}{2}[Q_{II'}(k, k'; t)]^2$ .

One would expect the Born approximation to be good for scattering of low energy particles by a low temperature surface with a shallow potential well. However, at present no experiments have been carried out in this region. In order to explain existing data, such as those of Fisher et al.<sup>1)</sup>, we must have a more exact theory. As mentioned in section 2, a more satisfactory result is obtained by solving (2.20) exactly for the reduced  $t$ -matrix and this is done in the next section.

#### 4. Unitary treatment of one-phonon inelastic scattering

We first consider the solution of eq. (2.20) for a situation in which there is only one-phonon inelastic scattering about the specular beam. The reduced  $t$ -matrix for the specular beam is given by

$$t_{ss} = -i \sum_{K_p} \sum_{\{n_p\}} v_{sp} N_p t_{ps}, \quad (4.1)$$

where  $\{n_p\}$  differs from  $\{n_i\}$  by the absorption or emission of a single phonon. The matrix element  $v_{ss}$  has been omitted since it never contributes to the elastic or one-phonon scattering. Eq. (4.1) represents a virtual phonon process in which the same phonon is absorbed and then re-emitted (or vice versa). The inelastic part of the scattering is given by

$$t_{ps} = v_{ps} - i v_{ps} N_s t_{ss}. \quad (4.2)$$

Eqs. (4.1) and (4.2) completely define the  $t$ -matrix for this simple case since any other processes which might be included will necessarily involve two or more phonons.

Solving for the full  $t$ -matrix of eq. (2.16) gives

$$T_{ss} = \frac{i \exp[i\delta_i]}{2N_i} \left\{ \frac{1 - N_s \sum_{p'} |v_{sp'}|^2 N_{p'}}{1 + N_s \sum_{p'} |v_{sp'}|^2 N_{p'}} \right\}, \quad (4.3)$$

and

$$T_{ps} = \exp[i\delta_i] \frac{v_{ps}}{1 + N_s \sum_{p'} |v_{sp'}|^2 N_{p'}}, \quad (4.4)$$

where  $\sum_p$  now implies  $\sum_{K_p} \sum_{\{n_p\}}$  as in eq. (4.1). As one can check, the inherent unitarity of eq. (2.16) insures that

$$N_s |T_{ss}|^2 + \sum_p N_p |T_{ps}|^2 = 1.$$



The  $T$ -matrix for nonspecular scattering differs from the Born approximation of the previous section by the factor

$$1/(1 + N_s \sum_p |v_{sp}|^2 N_p)$$

appearing in the denominator.

In order to find the experimentally measurable quantities it is necessary to insert (4.3) and (4.4) into (2.8) or (2.9). However, the process of carrying out the sums and averages over phonon states is far more difficult than in the case of Born scattering. This difficulty can be circumvented without destroying the unitarity by averaging the term

$$N_s \sum_p |v_{sp}|^2 N_p$$

before the  $T$ -matrix is inserted into the transition rate of (2.7). The desired expression can be obtained by the methods of Glauber<sup>24</sup>), or by computing first

$$N_s \langle \sum_p |v_{sp}|^2 N_p \rangle = N_s \sum_{\{n_s\}} \rho(\{n_s\}) \sum_{K_p} \sum_{\{n_p\}} |v_{sp}|^2 N_p, \quad (4.5)$$

without any restriction on  $\{n_p\}$  as in the derivation of (3.2) in the previous section, and keeping only the first order term in the expansion of

$$\exp [Q_{II'}(k, k'; t)].$$

The result is seen to be the integral of the one phonon reflection coefficient (3.5), divided by 4. Explicitly:

$$\begin{aligned} N_s \left\langle \sum_p |v_{sp}|^2 N_p \right\rangle^{(1)} &= \frac{2\pi^2 \hbar N_s}{NM} \sum_{K_p} \sum_{Q, \nu} \frac{N_p}{\omega_\nu(Q)} \\ &\times \{ |\chi^{(-)}(k_{zs}; z), \nabla \cdot U_{-Q, \nu}(z) \chi^{(-)}(k_{zp}; z)|^2 (n_\nu(Q) + 1) \delta(K_p - K_s + Q) \\ &+ |\chi^{(-)}(k_{zs}; z), \nabla \cdot U_{Q, \nu}(z) \chi^{(-)}(k_{zp}; z)|^2 n_\nu(Q) \delta(K_p - K_s - Q) \}, \quad (4.6) \end{aligned}$$

where  $U_{Q, \nu}(z)$  and the divergence operator  $\nabla$  are defined as in (3.6) and (3.7) respectively.

When (4.6) is substituted for  $N_s \sum_p |v_{sp}|^2 N_p$  the  $T$ -matrix for specular scattering (4.3) becomes independent of phonon variables and the phonon sums in the reflection coefficient of (2.8) give unity. The result is given below in (5.21). In the case of inelastic scattering the substitution of (4.6) into the denominator of (4.4) effectively decouples the numerator from the denominator and removes all phonon dependence from the denominator. Consequently, when this expression for the inelastic  $T$ -matrix is inserted into the differential scattered intensity (2.9) the result differs from the results of (3.5) with

$G=0$  only by the multiplicative factor

$$\frac{1}{|1 + N_s \langle \sum_p |v_{sp}|^2 N_p \rangle^{(1)}|^2}. \quad (4.7)$$

The determination of the scattering matrix for more complicated systems is a straightforward matter. For instance, if we add to the example of eq. (4.1) and (4.2) the possibility that the particle can undergo a diffraction into the intermediate bound state  $b$ , the  $t$ -matrix is defined by the following set of three linear equations

$$t_{ss} = -i \sum_p v_{sp} N_p t_{ps} + v_{sb} \frac{1}{E_i - E_b} t_{bs}, \quad (4.8a)$$

$$t_{bs} = v_{bs} - i v_{bs} N_s t_{ss} - i \sum_p v_{bp} N_p t_{ps}, \quad (4.8b)$$

$$t_{ps} = v_{ps} - i v_{ps} N_s t_{ss} + v_{pb} \frac{1}{E_i - E_b} t_{bs}. \quad (4.8c)$$

If instead of the bound state, the diffraction process carries the particle into a continuum state  $g$  the above equations become

$$t_{ss} = -i \sum_p v_{sp} N_p t_{ps} - i v_{sg} N_g t_{gs}, \quad (4.9a)$$

$$t_{gs} = v_{gs} - i v_{gs} N_s t_{ss} - i \sum_p v_{gp} N_p t_{ps}, \quad (4.9b)$$

$$t_{ps} = v_{ps} - i v_{ps} N_s t_{ss} - i v_{pg} N_g t_{gs}. \quad (4.9c)$$

Discussions of these two examples with particular emphasis on the possibility of the incoming particle undergoing a resonant scattering with the bound state have appeared in previous papers<sup>20, 21</sup>).

As a final illustration of the one-phonon approximation we consider the case in which the incoming particle can be resonantly scattered into a bound state by an inelastic process. If we introduce into the example of eqs. (4.8) the set of bound states  $d$ , which can be obtained from the initial state by a one-phonon process, then the  $t$ -matrix is defined by the set:

$$t_{ss} = v_{sb} \frac{1}{E_i - E_b} t_{bs} - i \sum_p v_{sp} N_p t_{ps} + \sum_d v_{sd} \frac{1}{E_i - E_d} t_{ds}, \quad (4.10a)$$

$$t_{bs} = v_{bs} - i v_{bs} N_s t_{ss} - i \sum_p v_{bp} N_p t_{ps} + \sum_d v_{bd} \frac{1}{E_i - E_d} t_{ds}, \quad (4.10b)$$

$$t_{ps} = v_{ps} - i v_{ps} N_s t_{ss} + v_{pb} \frac{1}{E_i - E_b} t_{bs} - i \sum_{p'} v_{pp'} N_{p'} t_{p's} + \sum_d v_{pd} \frac{1}{E_i - E_d} t_{ds}, \quad (4.10c)$$

$$t_{ds} = v_{ds} - i v_{ds} N_s t_{ss} + v_{db} \frac{1}{E_i - E_b} t_{bs} - i \sum_p v_{dp} N_p t_{ps} + \sum_{d'} v_{dd'} \frac{1}{E_i - E_{d'}} t_{d'i}. \quad (4.10d)$$

Eqs. (4.10a) and (4.10b) describe processes in which the energy of the scattered particle does not change, while eqs. (4.10c) and (4.10d) describe processes in which the particle absorbs or emits a phonon during the scattering process.

At first glance it would appear that eqs. (4.10) are a set of coupled integral equations for which it would be impossible to find exact solutions. However the one-phonon approximation affords a great simplification. The  $t$ -matrix elements  $t_{ps}$  and  $t_{ds}$  must have an overall exchange of exactly one phonon, and this implies that the matrix elements in the last two terms of eqs. (4.10c) and (4.10d) can describe diffraction only. Because we allow only a single diffraction process connecting a bound state to the continuum these two equations become

$$t_{ps} = v_{ps} - i v_{ps} N_s t_{ss} + v_{pb} \frac{1}{E_i - E_b} t_{bs} + v_{pd} \frac{1}{E_i - E_d} t_{ds}, \quad (4.11a)$$

and

$$t_{ds} = v_{ds} - i v_{ds} N_s t_{ss} + v_{db} \frac{1}{E_i - E_b} t_{bs} - i v_{dp} N_p t_{ps}. \quad (4.11b)$$

The  $t$ -matrix for this system is now given by (4.10a), (4.10b), and (4.11). Again this is a set of linear equations which can be solved by the standard techniques of matrix algebra.

It is now apparent that the extension of this procedure to systems containing any number of diffraction states and any number of continuum states is straightforward<sup>25</sup>), and we need not write it out in detail here. The advantage of the one-phonon approximation is that in every case the set of integral equations (2.20) is reduced to a set of linear equations which can be solved by standard matrix algebra.

There remains but one matter to be discussed and that is how to actually carry out the phonon summations in (2.8) and (2.9) once the  $t$ -matrix (and thence the  $T$ -matrix) has been determined. This was a rather straightforward process in the Born approximation of section 3, but for the more complicated  $t$ -matrices of this section there are as yet no simple methods for carrying out the averaging process. Thus it has been necessary to develop an approximate averaging procedure as indicated by the treatment of the first example in this section. First we assume that all diffraction matrix elements are to be taken using the thermally averaged potential defined by (2.4). Secondly we must average separately such terms as

$$N_s \sum_p |v_{sp}|^2 N_p$$

which appears in eqs. (4.3) and (4.4) for example. These two steps will produce suitable averaged expressions for all  $t$ -matrix elements describing elastic processes. For the one-phonon  $t$ -matrix elements these two steps produce expressions which are the sums of several terms, and in each term there will remain a single un-averaged one-phonon matrix element. The inelastic  $t$ -matrix in this form can be substituted into the formal expression for the differential scattered intensity and the desired thermally averaged results will be obtained by carrying out the phonon sums as in section 3 and keeping only the contributions due to single phonon exchange. This procedure consists simply of averaging individually many of the various terms in each  $T$ -matrix element before insertion into the reflection coefficient. It can readily be shown that under this approximation the contribution of the diagonal matrix element  $v_{rr}$  is non-vanishing only for exchange of two or more phonons and hence will never enter in the one-phonon approximation<sup>25</sup>). However, the results still obey the very important property of unitarity.

### 5. Numerical calculations and discussion

A great variety of physical effects (elastic and inelastic scattering, diffraction, adsorption) is described by the general formulae of the previous section. In the discussion of real systems, it is most desirable to introduce further simplifications based on the relative importance of the various processes. In some cases order of magnitude arguments can easily be made, while for other effects detailed model calculations are necessary.

We illustrate here the case of scattering of a very cold beam by absorption of phonons from a warm surface. The incoming beam energy is assumed to be so low that diffraction cannot take place, i.e. eqs. (1.1) and (1.2) have no solution for  $G \neq 0$  and  $p_{zf}^2 > 0$ . In practice this can be realized by using a He beam at liquid He temperatures. The scattering surface is assumed to be at temperatures comparable to its Debye temperature. Under these conditions phonon absorption is dominant, since most emission processes are forbidden by energy conservation. We want to estimate the intensity of the inelastically scattered beams and determine whether surface phonons give rise to a distinct peak that can be used to study their dispersion relation. A crude description of the surface phonons will be sufficient and we can neglect all effects of the discrete nature of the crystal, except for the introduction of a Debye cutoff in the phonon spectrum. The crystal can then be replaced by a semi-infinite isotropic continuum whose surface can undergo perpendicular vibrations. The model scattering potential we use is

$$V_i = V_0 S(-z + u_z), \quad (5.1)$$

where  $V_0$  is the strength of the interaction,  $u_z$  is the small displacement from equilibrium in the perpendicular direction, and the step function is defined by

$$S(z) = \begin{cases} 1, & z > 0, \\ 0, & z < 0. \end{cases} \quad (5.2)$$

This potential is not entirely realistic, especially in view of the fact that it does not include the possibility of a bound or adsorption state near the crystal surface. Nevertheless, it should give reasonable qualitative results, especially for particles which absorb a phonon upon collision with the surface, and in any case it indicates the range of validity of the Born approximation when adsorption is not important.

Considering first the case of Born scattering discussed in section 3, we proceed to evaluate the averaged potential (2.3) and the vector potential for inelastic scattering (3.6). Since the crystal model does not exhibit any periodic structure there can be no diffraction and the thermally averaged potential will contain only the single term  $U_G(z) = U_0(z)$ . The process for evaluating the sums in (2.3) is outlined in I and gives

$$U_0(z) = U = - \frac{V_0}{(2\pi \langle u_z^2 \rangle)^{1/2}} \int_{-\infty}^{\infty} \exp(-\frac{1}{2}x^2 \langle u_z^2 \rangle) dx, \quad (5.3)$$

assuming that the surface Debye-Waller factor is of the usual form

$$W(q) = \frac{1}{2}q^2 \langle u_z^2(z=0) \rangle. \quad (5.4)$$

The vector potential of (3.6) can be readily determined since there is no sum over lattice sites. It has only the  $z$ -component given by

$$[U_{Q\nu}(z)]_z = e_z \left( \frac{Q}{\nu} \right) U, \quad (5.5)$$

where  $e_z \left( \frac{Q}{\nu} \right)$  is the perpendicular component of the phonon polarization vector at the surface. It is seen from (5.3) that the sharp step-function is "smeared" by the thermal vibrations. However, for any reasonable  $V_0$  the effect of the smearing turns out to be small. Hence at first we simply neglect the difference between  $U$  and  $V$ ; the matrix elements of  $dU/dz$  [see (5.8) below] become then independent of  $V_0$ , for incident energy  $\hbar^2 k_{zi}^2/2m$  less than  $V_0$ . We shall comment later about deviations from this limit.

There are three distinctly different types of phonons that can exist near the surface of an isotropic continuum and these are surface (Rayleigh) waves<sup>26</sup>, mixed waves<sup>27, 28</sup>, and bulk waves<sup>29</sup>. For the case of Rayleigh phonons the

frequency is completely defined by the parallel momentum, i.e.

$$\omega_v(Q) = \omega(Q) = c_t \xi |Q|, \quad (5.6)$$

where  $c_t$  is the velocity of transverse waves and  $\xi$  satisfies the well known Rayleigh condition

$$\xi^6 - 8\xi^4 + 8\xi^2(3 - 2c_t^2/c_l^2) - 16(1 - c_t^2/c_l^2) = 0 \quad (5.7)$$

( $c_l$  is the velocity of longitudinal waves). Thus after inserting (5.5) into (3.5) we need only to carry out the sum over parallel phonon wave vector  $Q$ . For phonon absorption the differential scattered intensity is

$$\begin{aligned} \frac{dR(k_f, k_i)}{dE_f d\Omega_f} &= \frac{m^2}{8\pi^2 \hbar^4 \rho k_{zi}} \frac{|k_f|}{\omega(Q)} \left| \left( \chi^{(-)}(k_{zf}; z), \frac{dU}{dz} \chi^{(-)}(k_{zs}; z) \right) \right|^2 \\ &\times |e_z(Q)|^2 n(Q) \delta \left( \frac{\hbar}{2m} [k_f^2 - k_i^2] - \omega(Q) \right), \end{aligned} \quad (5.8)$$

where  $Q = K_f - K_i$  and  $NM/L^2$  has been replaced by  $\rho$ , the mass density of the solid. A similar expression with  $n(Q)$  replaced by  $n(Q) + 1$  describes phonon emission. The square of the perpendicular component of the phonon polarization vector is<sup>29</sup>)

$$|e_z(Q)|^2 = \frac{\{|Q| + \kappa_t b\}^2}{\left\{ \frac{\kappa_t^2 + Q^2}{2\kappa_t} + b^2 \frac{\kappa_t^2 + Q^2}{2\kappa_t} + 2b|Q| \right\}}, \quad (5.9)$$

with

$$\kappa_{t,i} = (Q^2 - \omega^2/c_{t,i}^2)^{\frac{1}{2}}, \quad (5.10)$$

and

$$b = 2(1 - \xi^2)^{\frac{1}{2}} / (2 - \xi^2). \quad (5.11)$$

For bulk and mixed phonons the index  $v$  labels both the perpendicular phonon momentum and the polarization. However, there is only a single polarization for mixed modes, and only one polarization of the bulk modes has a non-vanishing perpendicular component. Hence the sum over  $v$  in (3.5) can be converted to an integral over the perpendicular component of momentum,  $q$ , and the differential scattered intensity for phonon absorption becomes

$$\frac{dR}{dE_f d\Omega_f} = \frac{m^2 |k_f|}{8\pi^3 \hbar^4 k_{zi} \rho \omega} \left| \left( \chi^{(-)}(k_{zf}; z), \frac{dU}{dz} \chi^{(-)}(k_{zs}; z) \right) \right|^2 \left( \frac{dq}{d\omega} \right) |e_z|^2 n(\omega), \quad (5.12)$$

where

$$\omega = \frac{\hbar}{2m} [k_f^2 - k_i^2].$$

For bulk phonons the density of modes for perpendicular motion, or  $dq/d\omega$ , can be obtained simply by remarking that the total energy of transverse and longitudinal motion must be the same as in the bulk, up to terms of order  $1/L$ . Let  $\theta_l$  and  $\theta_t$  be the angles at which the longitudinal and transverse part of the wave are incident on the surface<sup>25</sup>). For the bulk modes with a non-vanishing perpendicular displacement at the surface we obtain<sup>28, 29</sup>):

$$\frac{dq}{d\omega} \frac{4a_l^2 a_t}{(1 - a_l)^2 + a_t^2} = \frac{(1 + a_l)^2}{c_l \cos \theta_l} - \frac{a_t^2}{c_t \cos \theta_t}, \quad (5.13)$$

$$|e_z|^2 = \frac{[(a_l - 1) \cos \theta_l - a_t \sin \theta_t]^2}{(1 - a_l)^2 + a_t^2}, \quad (5.14)$$

where  $a_l$  and  $a_t$  are the amplitudes of the longitudinal and transverse waves arising from a unit longitudinal wave impinging on the surface. Explicitly:

$$a_l = \frac{c_t^2 \sin 2\theta_t \sin 2\theta_l - c_l^2 \cos^2 2\theta_l}{c_t^2 \sin 2\theta_t \sin 2\theta_l + c_l^2 \cos^2 2\theta_l}, \quad (5.15)$$

$$a_t = \frac{2c_l c_t \sin 2\theta_l \cos 2\theta_t}{c_t^2 \sin 2\theta_t \sin 2\theta_l + c_l^2 \cos^2 2\theta_l}. \quad (5.16)$$

For mixed phonons the longitudinal part does not propagate in the medium and  $q$  labels the perpendicular wave number of the transverse part. Then

$$dq/d\omega = 1/c_t \cos \theta_t, \quad (5.17)$$

$$|e_z|^2 = \frac{2\alpha^2 \sin^2 2\theta_t}{\cos^4 2\theta_t + 4\alpha^2 \sin^2 \theta_t \sin^2 2\theta_t}, \quad (5.18)$$

where

$$\alpha = (\sin^2 \theta_t - c_t^2/c_l^2)^{\frac{1}{2}} \quad (5.19)$$

and  $\alpha\omega/c_l$  is the attenuation constant of the longitudinal part of the wave.

The differential scattered intensity for one-phonon absorption computed from eqs. (5.8) and (5.12) is shown in fig. 1. This is a plot of the scattering of a low energy  $\text{He}^4$  beam  $[(\hbar^2/2m) k_i^2 = (4^\circ\text{K})k_B]$  perpendicularly incident on an isotropic crystal at room temperature ( $300^\circ\text{K}$ ). The longitudinal and transverse sound velocities were evaluated from the values of the elastic constants for silicon tabulated in the American Institute of Physics Handbook<sup>30</sup>). The differential scattered intensity is plotted against scattering angle for the absorption of phonons of the Debye energy ( $\theta_D = 658^\circ\text{K}$ ). The surface phonon contribution is a  $\delta$ -function of strength shown by the straight line, while the bulk and mixed phonons exhibit a spread in angles. Note that each of the three types of phonons scatters particles over a separate range of angles, with the well defined beam due to the surface phonons

most widely separated from the specular beam. For absorption of lower energy phonons the picture is quite similar to fig. 1 except that the various beams are scattered closer to the normal.

It should be pointed out here that there is a discrepancy between the results shown in fig. 1 and the previously reported results of the same calculation<sup>20</sup>). In the earlier paper the mixed and bulk phonon part was in error and the surface phonon contribution was inadvertently multiplied by a factor of two.

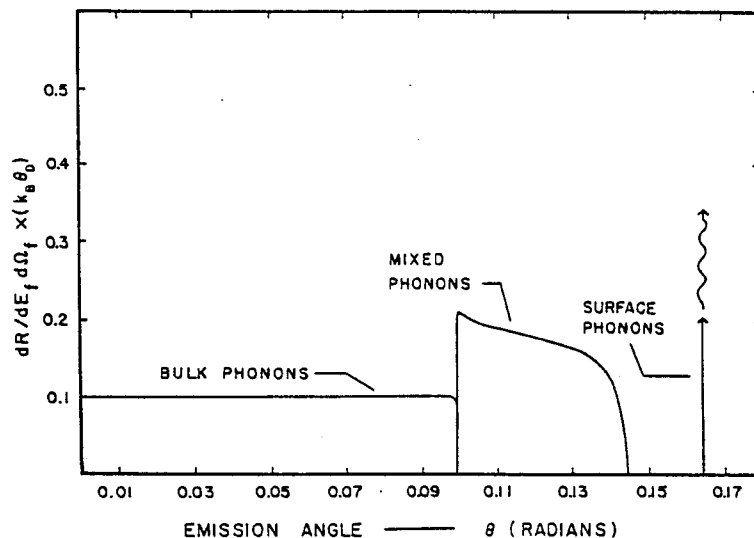


Fig. 1. The differential scattered intensity versus scattering angle  $\theta$  for absorption of Debye energy phonons by  $\text{He}^+$  atoms at a silicon surface. The helium beam is perpendicularly incident with an energy  $(\hbar^2/2m) k_i^2 = (4^\circ \text{K}) k_B$ .

The phonon emission calculation has also been performed for this case and the features of the differential scattered intensity are similar to fig. 1. However, because the scattering potential (5.1) does not contain a well near the surface, the magnitude of the phonon emission intensity is smaller than that for absorption by a factor of  $10^{-3}$  and is completely negligible.

It has been shown in section 4 that to make the above calculation into one which obeys the condition of unitarity we need only multiply all the scattered intensities by (4.7). The quantity

$$N_s \langle \sum_p |v_{sp}|^2 N_p \rangle^{(1)} \quad (5.20)$$

of eq. (4.6) has been evaluated for the same system and initial conditions as described above and its value is 0.0084. Thus the unitary differential scattered



intensities differ from that of fig. 1 by the factor 0.984. We recall that (4.6) gives the total inelastic reflection coefficient in the Born approximation, divided by 4. Then the total inelastic reflection coefficient in the unitary theory is  $R_{in} = 4 \times 0.984 \times 0.0084 = 0.033$ . Of this number 0.004 is due to bulk phonons, 0.007 is due to the mixed phonons, and 0.022 is due to the Rayleigh phonons.

The specular reflection coefficient from (4.3) and (2.8) together with the averaging approximation of section 3 is

$$R_{el} = \frac{\left| 1 - N_s \left\langle \sum_p |v_{sp}|^2 N_p \right\rangle^{(1)} \right|^2}{\left| 1 + N_s \left\langle \sum_p |v_{sp}|^2 N_p \right\rangle^{(1)} \right|^2}, \quad (5.21)$$

and for the system at hand has the value 0.967.

It is interesting that the surface and mixed phonon contributions to the total inelastic scattering are considerably larger than the bulk contribution. For a surface wave this can be explained qualitatively by noting that its energy lies in a small region near the surface, while the energy in a bulk wave is spread throughout the volume. Classically speaking the  $N$  atoms at the surface contribute  $3Nk_B T$  to the total energy of the crystal, of which  $Nk_B T$  is associated with the motion perpendicular to the surface. There are  $N$  surface phonons, each carrying energy  $k_B T$ , and it can be shown that these oscillate almost entirely in the direction perpendicular to the surface. The mean penetration depth  $\lambda$  of a surface phonon is determined by some average over the damping constants given in (5.10). If  $a$  is the interatomic spacing, we can reason that a portion  $a/\lambda$  of the perpendicular energy of each surface atom is due to the surface phonons. Rough estimates lead to a value of  $a/\lambda$  of about 0.5. The mixed phonons are combinations of transverse bulk waves and longitudinal surface waves, both of which exhibit perpendicular displacement. Since the transverse waves involved travel relatively close to the surface and hence give a large perpendicular displacement we would expect the mixed mode scattering to be much larger than that of bulk modes.

This calculation is only meant to suggest the order of magnitude of the inelastic surface scattering and not to give the precise location of the cutoffs and peaks in the differential reflection coefficient, such as are seen in fig. 1, except for long-wavelength phonons. This is because the Debye approximation is certainly inadequate for short wavelength phonons. On the other hand, it is just for these phonons that surface scattering may provide new information, not obtainable by the ultrasonic methods. It is easy to see from simple kinematics, as reflected by the  $\delta$ -functions in (3.5), that the angular separation between the surface phonon peak and the other scattered beams, at fixed energy loss, will be greater when the various branches of the phonon spectrum bend over instead of being linear.

Within the framework of the above model, the surface is described by the following parameters: the crystal potential  $V_0$ , the Debye temperature  $\theta_D$ , the longitudinal and transverse sound velocities and the temperature  $T$ . We have not undertaken to vary systematically all these parameters, in addition to the incident beam parameters. However, we have run a number of tests. We have checked that the results are not sensitive to the magnitude of  $V_0$ , within reasonable limits, even if the thermally smeared potential  $U$  is used. A calculation for  $V_0 = 1$  eV, the other parameters being the same as in fig. 1, shows that the net effect of replacing  $V$  by  $U$  is a reduction of the inelastically scattered intensities by about 2%. In fact, the Debye-Waller factor (5.4) turns out to be unimportant for all realistic temperatures (up to 10000°K for the case of Si, but it should be remembered that  $\theta_D = 638^\circ\text{K}$  is higher than in most materials). The temperature dependence of one-phonon scattering is then governed by the phonon occupation numbers  $n_\nu(Q)$  in (3.5), that is, the scattering is proportional to the mean square displacement of the surface. At 500°K the total number of inelastically scattered particles in Born approximation is about 10% of the incident beam, all other parameters being the same as in fig. 1. Thereafter the increase with temperature is approximately linear. The unitary correction is trivial to apply, but in practice it amounts only to a few percent, for such a low-energy incoming beam.

For higher incoming energies the inelastic scattering becomes larger, being approximately proportional to the incoming particle momentum. Thus a calculation for the same surface as in fig. 1 shows that 10% of a He beam with incident energy  $20 k_B$  will be inelastically scattered. Computations at higher incoming energies must include diffraction and an extrapolation of the present calculations is not meaningful.

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#### Appendix I. Proof of unitarity

For a potential which exhibits no forward scattering the unitary condition<sup>31)</sup>

$$\sum_c S_{fc} S_{ci}^\dagger = \delta_{fi} \quad (\text{A.1})$$

becomes

$$-(2\pi i)^2 \sum_c \delta(E_f - E_c) T_{fc} \delta(E_i - E_c) T_{ci}^\dagger = \delta_{fi}. \quad (\text{A.2})$$

[For  $i=f$ , replacing  $\delta(E_f - E_c)$  by the density of states  $N_f/\pi = mL/2\pi\hbar^2 p_{zf}$ , the equation can be written  $\sum_c w_{ci} = j_i$ , where  $w_{ci}$  is the transition rate (2.7) and  $j_i = \hbar p_{zi}/mL$  is the incident current. We also have  $\sum_{pf} R(p_f, p_i) = 1$  from (2.8), or  $\int dR = 1$ , from (2.9).] Inserting (2.10) for the  $T$ -matrix gives

$$\begin{aligned} & - (2\pi i)^2 \sum_c \delta(E_f - E_c) (\phi_f, U \chi_c^{(+)} ) \delta(E_i - E_c) (\phi_c, U \chi_i^{(+)} ) - \delta_{fi} \\ & - (2\pi i)^2 \sum_c \delta(E_f - E_c) (\phi_f, U \chi_c^{(+)} ) \delta(E_i - E_c) t_{ci}^\dagger \\ & - (2\pi i)^2 \sum_c \delta(E_f - E_c) t_{fc}' \delta(E_i - E_c) (\phi_c, U \chi_i^{(+)} )^\dagger \\ & - (2\pi i)^2 \sum_c \delta(E_f - E_c) t_{fc}' \delta(E_i - E_c) t_{ci}^\dagger = 0. \end{aligned} \quad (A.3)$$

The first two terms of (A.3) cancel since they are equivalent to eq. (A. 2) for scattering by the potential  $U$ . Using (2.14) and (2.15) the condition of unitarity becomes

$$t_{fs} - t_{fs}^\dagger + 2\pi i \sum_c t_{fc} \delta(E_i - E_c) t_{cs}^\dagger = 0. \quad (A.4)$$

However, starting from the defining equation for the  $t$ -matrix

$$t_{fs} = v_{fs} + \sum_c v_{fc} G_c t_{cs}, \quad (A.5)$$

it can be readily shown that

$$t_{fs} - t_{fs}^\dagger - \sum_c t_{fc} (G_c - G_c^\dagger) t_{cs}^\dagger = 0. \quad (A.6)$$

A comparison of (A. 6) with (A. 4) shows that the condition of unitarity will be satisfied if the imaginary part of the Green's function is  $-i\pi$  times a  $\delta$ -function in energy. Since the approximate Green's function which we have used is

$$G_c = -i\pi\delta(E - E_c) \quad (A.7)$$

for continuum states and is the exact Green's function for bound states it follows directly that the  $t$ -matrix of eq. (2.20) is unitary.

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