THEORY OF SURFACE SCATTERING AND DETECTION OF SURFACE PHONONS*

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A formal theory for the investigation of crystal surfaces by the scattering of particles is developed. Expressions satisfying the condition of unitarity are presented for diffraction as well as one-phonon inelastic scattering, including the effects of surface bound states. The possibility of detection of surface phonons by scattering of low-energy He atoms from a cleaved surface is investigated.

The scattering of penetrating particles (neutrons, photons, electrons) has proved most useful to investigate the structure and the elementary excitations of solids in the bulk, partly because it is amenable to a detailed theoretical analysis in the Born approximation. We propose to show in this Letter that the methods of quantum scattering theory can provide a framework for analyzing the scattering of nonpenetrating particles and deducing information on the surface properties of solids. We shall discuss specifically the scattering of light rare-gas atoms, such as He, from perfect cleaved surfaces of simple solids, such as LiF or Si, with the aim of studying the surface-phonon spectrum. However, the method applies as well to other particles, such as low-energy electrons, and their interactions with any kind of elementary excitation near the surface (e.g., plasmons).

We describe first the kinematics of the scattering process. A particle with wave vector $\vec{p}_i$, having components $\vec{P}_i$ parallel to the surface and p_{zi} perpendicular to it, is reflected into the state of momentum $\vec{p}_f$, with components $\vec{P}_f$ and p_{zf}. In elastic scattering $\vec{P}_f=\vec{P}_i+\vec{G}$, where $\vec{G}$ is a reciprocal lattice vector of the surface, and $\vec{p}_i^{\,2}=\vec{p}_f^{\,2}$. Here, and in the following, the convention is that p_{zi} must be negative and p_{zf} positive for an actual process. In one-phonon–exchange processes (absorption or emission) $\vec{P}_f-\vec{P}_i=\vec{G}\pm\vec{Q}$ and $(\hbar^2/2m)\times(\vec{p}_f^{\,2}-\vec{p}_i^{\,2})=\pm\hbar\omega(\vec{Q},\nu)$, where $\omega(\vec{Q},\nu)$ is the frequency of a phonon of momentum $\vec{Q}$ parallel to the surface and label ν. For surface (Rayleigh) phonons[1] ν is a discrete label, and knowledge of ω and $\vec{Q}$ completely defines the scattering angles; hence the measurement of energy and momentum transfer for a given order of diffraction (i.e., for a given $\vec{G}$) is sufficient to give the dispersion relation $\omega(\vec{Q},\nu)$ vs $\vec{Q}$. For bulk or mixed[2] phonons ν is a quasicontinuum label involving the momentum perpendicular to the surface, and for a given energy the scattered beam exhibits a spread in angles. If for the moment we assume that there is only an acoustic branch, it is rather easy to show[3] that for a given energy transfer there is no overlap in scattering angles for the three types of phonons, and the well defined beam due to the surface phonons is the most widely separated from the elastically scattered part.

A formal theory of surface scattering can be developed starting from the two-potential formalism of Gell-Mann and Goldberger.[4] The total potential V due to the scattering surface is divided into a "large" part U of a simple form, and a remainder $V-U$ to be treated approximately. In our case it is natural to relate U to $\langle V\rangle$, the thermal average of V over the vibrations of the solid. Usually V is taken as a sum of atomic potentials V_a, each having Fourier transform $V_a(\vec{Q},q_z)$. We define

$$U_{\vec{K}}(z)=\sum_l\int(dq_z/2\pi)\exp[iq_z(z-z_l)]\times V_a(\vec{K},q_z)\exp[-W_l(\vec{K})-W_l(q_z)], \quad (1)$$

where the sum runs over atomic planes parallel to the surface and W_l is the Debye-Waller exponent[5] for atoms in the lth plane.[6] Then $\langle V\rangle=\sum_{\vec{G}}U_{\vec{G}}(z)e^{i\vec{G}\cdot\vec{R}}$ and we choose $U=U_{\vec{0}}(z)$. The eigenfunctions of U for outgoing wave (+) and incoming (−) boundary conditions will be denoted by $\chi^{(\pm)}$; 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 $\chi^{(\pm)}(p_z;z)$. When U gives rise to total reflection of the incident particles, $\chi^{(+)}(-p_z;z)=e^{i\delta}\times\chi^{(-)}(p_z;z)$, where $e^{i\delta}$ is in fact the S matrix for U scattering. In the following we drop the label (±) with the understanding that (−) and (+) are always associated with positive and negative p_z, respectively. There may also be bound states, $\chi_b(z)$.

The T matrix for V scattering can then be written

$$T_{fi}=\exp(i\delta_i)[\tfrac{1}{2}iN_i^{-1}\delta_{fs}+t_{fi}], \quad (2)$$

where $N=mL/2\hbar^2|p_z|$ is π times the density of states for perpendicular motion (L is the size of the quantization box), δ_{fs} indicates that the first

term in (2) is present only for the specularly reflected beam, and t_{fi} obeys the equation

$$t_{fi} = v_{fi} + \sum_c v_{fc}(E - E_c + i\epsilon)^{-1} t_{ci} \tag{3}$$

with $v_{fi} = \exp(-i\delta_i)[\chi_f^{(-)}, (V-U)\chi_i^{(+)}]$. The reflection coefficient R is computed by averaging $4\pi N_i \times |T_{fi}|^2 \delta(E_f - E_i)$ over initial phonon states and summing over final phonon states. Unitarity requires that the sum of R over all emerging beams be equal to 1.

For very low incoming energies there is no diffraction and only inelastic scattering about the specular beam is allowed. To lowest order $t_{fi} = v_{fi}$ ("distorted-wave Born approximation") and the reflection coefficient, upon keeping only the one-phonon absorption terms, is found to be

$$R(\vec{p}_z, \vec{p}_i) = (\pi m/\hbar^2 \rho |p_i|) \sum_\nu [n(\vec{Q}, \nu)/\omega(\vec{Q}, \nu)] |\vec{e}(\vec{Q}, \nu) \cdot (\nabla U_{\vec{Q}})_{fi}|^2 \delta(\hbar(\vec{p}_i^{\,2} - \vec{p}_f^{\,2})/2m + \omega(\vec{Q}, \nu)). \tag{4}$$

Here $\vec{Q} = \vec{P}_f - \vec{P}_i$, ρ is the mass density of the scattering material, $n(\vec{Q}, \nu)$ and $\vec{e}(\vec{Q}, \nu)$ are, respectively, the occupation number and the polarization vector for the $(\vec{Q}, \nu)$ phonon mode, and $(\nabla U_{\vec{Q}})_{fi}$ is the matrix element between $\chi(p_{zf}; z)$ and $\chi(p_{zi}; z)$ of the vector $(i\vec{Q}U_{\vec{Q}}, dU_{\vec{Q}}/dz)$. A similar formula holds for phonon emission. For the actual calculations reported below we chose a simplified potential of the form $V(z-u_z)$ and computed the surface displacement u_z in the continuum isotropic elastic theory with a Debye cutoff. Then instead of (1) we have simply $U(z) = \langle V \rangle = \int (dq/2\pi) \exp[iqz - W(q)] V(q)$ and in (4) we have only the z component of ∇U, namely dU/dz. The physical meaning of (4) is then transparent. The effective scattering potential is the expansion of $U(z-u_z) - U(z)$ to first order in u_z, since $\hbar n |e_z|^2/2\rho\omega$ is, in the classical limit, nothing but the square of the amplitude of perpendicular displacement of the surface due to the $(\vec{Q}, \nu)$ mode of oscillation at thermal equilibrium. A plot of the differential scattered intensity versus scattering angle for helium on silicon is given in Fig. 1 for a perpendicularly incident beam, when $V(z)$ is approximated by a step function.

To show the approximations to be made in a more general treatment, we consider the case when the only emerging elastic beams are the specular beam s, and one diffracted beam g. From (3) the approximate soluble equations are

$$\begin{aligned} t_{si} &= -iN_g v_{sg} t_{gi} + \sum_f v_{sf}(E_i - E_f + i\epsilon)^{-1} t_{fi}, \\ t_{gi} &= v_{gi} - iN_s v_{gs} t_{si} + \sum_f v_{gf}(E_i - E_f + i\epsilon)^{-1} t_{fi}, \\ t_{fi} &= v_{fi} - iN_g v_{fg} t_{gi} - iN_s v_{fs} t_{si}, \end{aligned} \tag{5}$$

where f denotes a continuum or bound state that can be reached from i by the absorption or emission of a single phonon. After squaring and averaging, v_{gi} is effectively replaced by $\exp(i\delta_i) \times (U_{\vec{G}})_{gi}$, and similarly for v_{fg}; while v_{fi} will involve $(\nabla U_{\vec{Q}})_{fi}$ or $(\nabla U_{\vec{G}+\vec{Q}})_{fi}$ and similarly for v_{fg} and v_{sf}. Equations of the type (5) lead to a completely unitary treatment of diffraction and one-phonon processes.[7] For example, a reflection coefficient corresponding to Eq. (4) but satisfying the unitarity condition is obtained by using

$$t_{fi} = v_{fi}\{1 + N_s[\sum_p N_p |v_{sp}|^2 + \sum_b |v_{sb}|^2 (E_i - E_b + i\epsilon)^{-1}]\}^{-1}, \tag{6}$$

which is the solution of (5) when diffraction is neglected. The sum over p in (6) represents a sum over the phonon quantum numbers $\vec{Q}$, ν of the continuum states, while the sum over b is the contribution from the bound states and can be greatly simplified by noting that the dominant terms are those with $E_b \simeq E_i$.

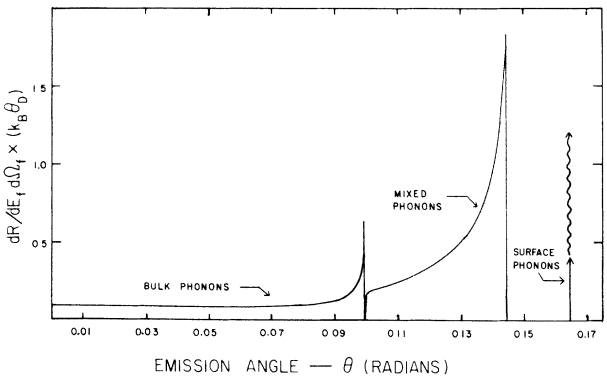

FIG. 1. The inelastic scattering of a low-energy (4°K) beam of helium which is incident perpendicularly on a silicon surface at room temperature (300°K). The differential scattered intensity $dR(\vec{p}_f, \vec{p}_i)/dE_f d\Omega_f$ is plotted against scattering angle θ for the absorption of phonons of the Debye energy ($\Theta_D = 658$°K). The surface phonon contribution is a δ function of strength shown by the straight line. There is no possibility of phonon emission at this energy.

Another important case is the possibility of diffraction occurring resonantly in and out of an intermediate bound state b, of energy $E_b \simeq E_i$ and parallel momentum $\vec{P}_i + \vec{G}$. Through solving another set of equations similar to (5) we find that the essential features of the specular elastic beam are well described by

$$R(\vec{p}_s, \vec{p}_i) = |1 - 2i\Gamma_{el}/(E_i - E_b + i\Gamma_{tot})|^2, \qquad (7)$$

where $\Gamma_{el} = N_i |(U_{\vec{G}})_{sb}|^2$ and Γ_{tot} is Γ_{el} plus the contribution of phonon scattering. The inelastic one-phonon absorption coefficient is similar to (4) except that $(\nabla U_{\vec{Q}})_{fi}$ is replaced by $(\nabla U_{\vec{Q}})_{fi} + (\nabla U_{\vec{G}+\vec{Q}})_{fb}(U_{\vec{G}})_{bi}/(E_i - E_b + i\Gamma_{tot})$. The general case of several diffracted and several bound states can be treated in a manner similar to the simpler cases outlined above.

In conclusion, we have shown that surface scattering can be treated by taking matrix elements of the effective potential (1) between wave functions of the smoothed average potential U. The essential point is the introduction of the reduced matrix t. These results generalize previous treatments of surface scattering.[8] The angular distribution and intensity of the one-phonon scattering have been computed as an example in the simplest possible case. For actual experiments it is better to use nonnormal incidence so as to increase the angular separation between elastic and one-phonon beams, and there is really no need to use an incoming beam of very low energy.

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EXCITON-ENHANCED RAMAN SCATTERING BY OPTICAL PHONONS

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The theory of exciton-enhanced Raman scattering is formulated in terms of the scattering of polaritons by optical phonons via the exciton part of the coupled modes. The expression for the exciton contribution to the scattering tensor is given, within a constant factor, in terms of the same parameters that determine the exciton contribution to the frequency-dependent dielectric constant. The theory also provides a new mechanism for the exciton contribution to the electro-optic effect.

Leite and Porto[1] have reported a marked enhancement of Raman scattering by LO phonons in CdS at low temperatures (77°K) at frequencies near the absorption edge, and have explained their results in terms of Loudon's theory[2] of resonant Raman scattering via electron-hole-pair intermediate states. Birman and Ganguly[3] have, however, pointed out that the creation of virtual excitons dominates the resonance Raman scattering by LO to TO phonons and have interpreted Leite and Porto's data on this basis. More recent data[4] for CdS indicate that the ratio of the