# Resonance-Enhanced Atom Scattering from Surface Phonons

D. Evans, V. Celli, and G. Benedek[a]
*Department of Physics, University of Virginia, Charlottesville, Virginia 22901*
and
J. P. Toennies
*Max-Planck-Institut für Stromungsforschung, D-3400 Göttingen, Federal Republic of Germany*
and
R. B. Doak
*Bell Laboratories, Murray Hill, New Jersey 07974*

(Received 23 December 1982)

Phonon-assisted resonances with surface bound states are shown to give important effects in time-of-flight spectra of He scattered from a LiF (100) surface. The comparison with theory indicates that inelastic resonances produce sharp distortions in the response of the surface phonon spectrum. At low temperature, theory predicts that resonances can locally amplify the phonon response by an order of magnitude.

PACS numbers: 63.20.Dj, 68.30.+z

Time-of-flight (TOF) spectroscopy of atom scattering from crystal surfaces has been successfully used to obtain detailed information on the dispersion of surface vibrations.[1,2] High-resolution TOF spectra show, besides the sharp peaks corresponding to Rayleigh waves (RW), a complex structure which reflects the bulk phonon density projected onto the surface. From a theoretical point of view, the TOF spectra are related to the phonon densities through the coupling coefficients, the Bose factor, and the Debye-Waller factor. These quantities are fairly well known in the framework of the distorted-wave Born approximation,[3,4] the eikonal approximation,[5] or the hard corrugated surface model.[6] Thus, one could in principle derive the surface phonon densities from the inelastic scattering intensities and gain a full knowledge of the dynamical behavior of clean surfaces and adsorbate layers. In practice, it is highly desirable to base the data analysis mostly on model-independent kinematic considerations; the full theory is then used to assign with confidence the observed structure to particular physical processes.

A discussion of the effects of bound-state resonances on the angular distributions of scattered intensity has already been presented.[7] In this Letter we show that phonon-assisted resonances with surface bound states have dramatic effects on the atomic TOF spectra. The interference between the directly scattered beam and the beam passing through a bound state can give a sharp maximum (or minimum) corresponding to the particular phonon momentum and energy required to accomodate the incident atom in the bound state. As long as such resonant features cannot be distinguished from the singularities of the phonon density, the atom scattering spectroscopy of surface phonons suffers from a serious limitation. The kinematics of phonon-assisted resonance was first considered by Cantini, Felcher, and Tatarek in connection with angular distributions.[8] Here we have calculated separately the nonresonant and resonant contributions to the inelastic scattering intensities and compared them to the experimental results for some situations where kinematics indicates that resonances should be seen.

Time-of-flight spectra of $^4$He scattered from a LiF (001) surface along the $\langle 100 \rangle$ direction were recorded with the apparatus and procedure of Ref. 1. The experiments measured the in-plane intensity at a final angle complementary to the incident angle $\theta_i$. Figure 1 shows the inelastic intensity plotted as a function of the parallel momentum transfer $K$, for two slightly different values of the incident momentum ($k_i = 6.06$ and $6.14$ Å$^{-1}$), at the same incident angle ($\theta_i = 64.2°$). The two experimental spectra show remarkable differences, especially in the intensity of the Rayleigh wave near $-3.45$ Å$^{-1}$. The calculation based on the breathing shell model for surface lattice dynamics and nonresonant scattering theory for a hard corrugated surface[6] (Fig. 1) is unable to reproduce the details of either spectrum, nor can it account for the differences between the two spectra.

Kinematics indicates that the discrepancies arise from inelastic resonances. The condition for a resonance assisted by a phonon of frequency

 

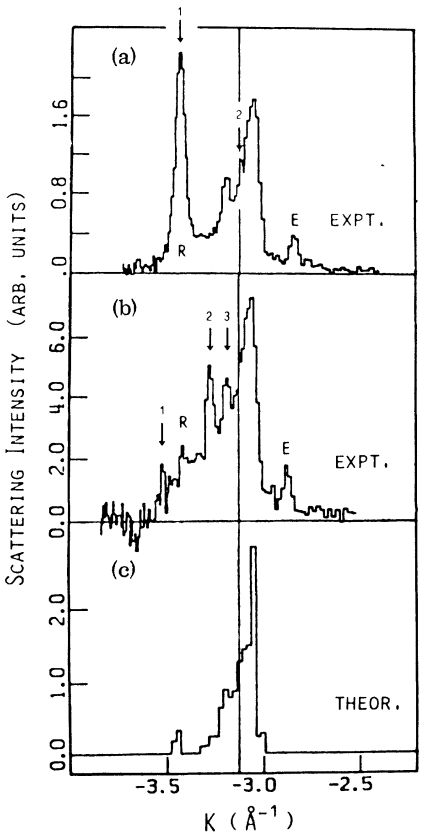


FIG. 1. TOF spectra of He scattering from LiF(001) along ⟨100⟩ for $\theta_i = 64.2°$ and slightly different values of the incident momentum [(a) $k_i = 6.06$ and (b) 6.14 Å$^{-1}$]. Arrows mark inelastic resonances for $\vec{N} = (1,1)$ and $n = 1,2,3$. Rayleigh wave peaks ($R$) are shown together with the incoherent elastic peaks ($E$). (c) The calculated nonresonant reflection coefficient has practically the same shape for both sets of experimental parameters.

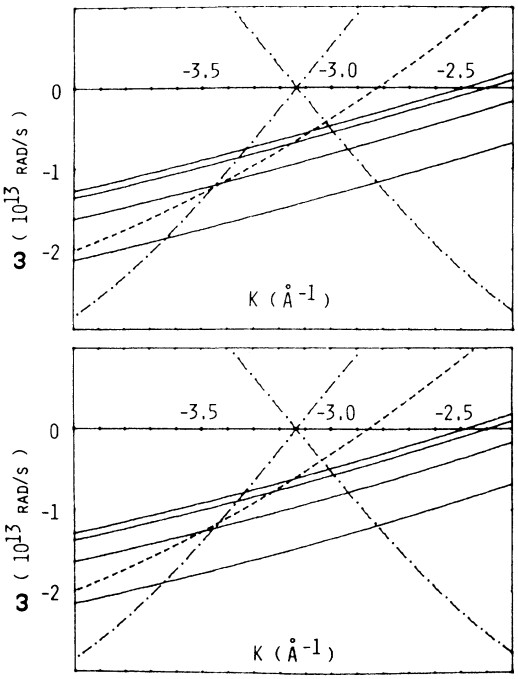


FIG. 2. Parabolas representing the inelastic-resonance condition for $\theta_i = 64.2°$, $k_i = 6.06$ (above) and 6.14 Å$^{-1}$ (below), $\vec{N} = (1,1)$ and $n = 0,1,2,3$ (full lines), with the corresponding scan curve (dashed line) and the RW dispersion curves (dot-dashed lines).

$\omega$ and parallel wave vector $\vec{Q} = \vec{K} - \vec{G}$ (where $\vec{G}$ is a surface reciprocal-lattice vector) is

$$\hbar\omega = (\hbar^2/2m)(\vec{K}_i + \vec{K} + \vec{N})^2 - E_i - |\epsilon_n|, \qquad (1)$$

where $m$ is the atomic mass, $K_i = k_i \sin\theta_i$ and $E_i$ are the incident parallel wave vector and energy, $\vec{N}$ is the surface reciprocal-lattice vector coupling the final state to the bound state, $-|\epsilon_n|$ ($n = 0, 1, 2, 3$) are the bound-state energies,[9] and $\omega$ and $K$ are related through the energy-conservation law

$$\hbar\omega = E_i[-1 + (1 + K/K_i)^2 \tan^2\theta_i]. \qquad (2)$$

The functions defined by Eqs. (1) and (2) are plotted in Fig. 2, together with the RW dispersion curves. The resonances occur wherever these two functions intersect; experimentally visible resonances are indicated by arrows in Fig. 1. Figure 2 explains the spectacular enhancement of the RW scattering observed for $k_i = 6.06$ Å$^{-1}$ by showing that the resonance with $\vec{N} = (1,1)$, $n = 1$ occurs exactly on top of the RW. For $k_i = 6.14$ Å$^{-1}$ this resonance is shifted outside the region of allowed one-phonon processes and the RW peak becomes small, in agreement with theory. Also, the resonant intensity becomes weak, but is not vanishing, indicating that *many-phonon processes are present in the background.* Another resonance [$\vec{N} = (1,1)$, $n = 2$] appears at about $-3.22$ Å$^{-1}$, enhancing the scattering due to *bulk acoustic phonons.*

We have shown that sharp enhancement is found where resonances are predicted, but can any resonant mechanism provide an explanation for the observed amplitudes? We calculated the resonant intensities by generalizing the Celli, Garcia, and Hutchison formalism[10] to include inelastic processes.[11] The atom-surface potential is divided into a laterally smooth attractive part, $V_a$, and a short-range repulsive part, $V_r$, which contains the static and dynamic surface corrugations. The elastic and inelastic scattering matrices for $V_r$ are assumed to be known, and are denoted respectively by $S(\vec{G}', \vec{G})$ and $S(\vec{G}+\vec{Q}, \vec{G})$. Here $\vec{G}$ stands for parallel momentum $\vec{K}_i + \vec{G}$ and energy

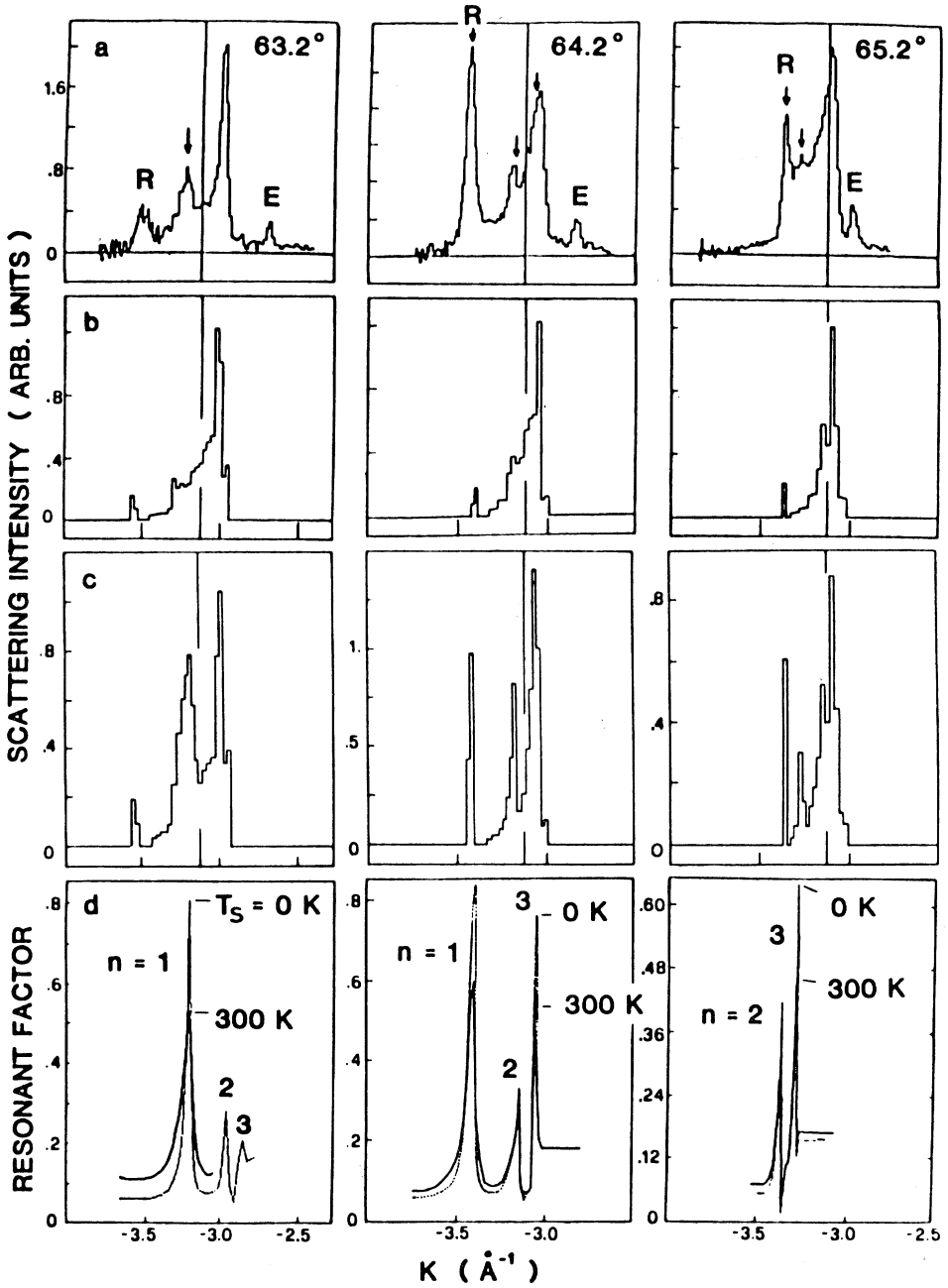


FIG. 3. TOF spectra for He scattering from LiF(001) along ⟨100⟩ for $k_i = 6.06$ Å$^{-1}$ and $\theta_i = 63.2°$, 64.2°, and 65.2°. The experimental data (a) are compared to the calculated nonresonant spectra (b) and to the results of the full calculation (c). The resonant factor alone is shown in (d) for two values of the surface temperature $T_s$. The plot for $T_s = 300$ K (full line) is multiplied by 3. The effect of $T_s$ is included in the manner of Hutchison (Refs. 11 and 13), with the assumption of a root-mean-square surface displacement $0.090T_s$ Å. The maxima [marked by arrows in (a)] correspond to the inelastic resonances for $\vec{N} = (1,1)$ and $n = 1,2,3$ [as shown in (d)]. Almost degenerate with the $n = 2$ peak, and affecting its shape, is an out-of-plane inelastic resonance for $\vec{N} = (2,0)$ and $n = 0$, which by itself gives a minimum.

$E_i + D$, where $D$ is the well depth; $\vec{G}+\vec{Q}$ stands for parallel momentum $\vec{K}_i+\vec{G}+\vec{Q}$ and energy $E_i+\hbar\omega+D$. The effect of adding $D$ to the energy is to change the perpendicular momentum from $k_z$ to $p = (k_z^2 + 2mD/\hbar^2)^{1/2}$. The calculation of the $S$-matrix elements for a hard corrugated wall is described below.

The elastic and inelastic amplitudes $B(\vec{G})$ and $B(\vec{G}+\vec{Q})$ for scattering from $V_a+V_r$ are obtained by

solving the equations

$$B(\vec{G}) = S(\vec{G}, 0)(k_{iz}/p_i)^{1/2} + \sum_{\vec{N}} S(\vec{G}, \vec{N}) R(\vec{N}) B(\vec{N}), \quad (3)$$

$$B(\vec{G}+\vec{Q}) = S(\vec{G}+\vec{Q}, 0)(k_{iz}/p_i)^{1/2} + \sum_{\vec{N}} S(\vec{G}+\vec{Q}, \vec{N}) R(\vec{N}) B(\vec{N}) + \sum_{\vec{N}} S(\vec{G}+\vec{Q}, \vec{N}+\vec{Q}) R(\vec{N}+\vec{Q}) B(\vec{N}+\vec{Q}). \quad (4)$$

Here $R(\vec{N})$ and $R(\vec{N}+\vec{Q})$ are reflection amplitudes from $V_a$, which have modulus one for beams in the well and are negligible otherwise. Thus the sums over $\vec{N}$ are in fact restricted to states in the well, and we can first solve for the elastic and inelastic amplitudes in the well, $B(\vec{N})$ and $B(\vec{N}+\vec{Q})$, and then compute $B(\vec{G})$ and $B(\vec{G}+\vec{Q})$ for the outgoing beams.

The first term in Eq. (4) is just the scattering amplitude for $V_r$ alone. One can divide this out to obtain the factor containing the resonances. The second term describes the inelastic scattering out of the elastic beams in the well, and is important when the incoming beam is at resonance [i.e., some $B(\vec{N})$ is large]. Under such a condition the entire inelastic spectrum is affected. The third term describes elastic transitions out of the inelastic beams in the well, and is important when the outgoing beam is at resonance; it produces sharp structures in the TOF spectra at well defined phonon momenta.[8,11]

The elastic hard-wall matrix elements have been obtained by solving the Rayleigh equation with the iterative method of Lapez, Yndurain, and Garcia.[12] The inelastic matrix elements are obtained by a simple generalization of this procedure. To first order, each phonon mode can be treated separately; further, a classical treatment of the phonon field gives the correct answer, provided that the Bose-Einstein factor is introduced. We are then left to solve the static problem with a corrugation $\zeta(\vec{R}) + 2D_{\vec{Q}} \cos(\vec{Q}\cdot\vec{R})$, where $\zeta(\vec{R})$ is the static corrugation and $D_{\vec{Q}}$ is phonon induced. The Rayleigh equations are then solved to first order in $D_{\vec{Q}}$. The resulting inelastic amplitudes are approximately

$$S(\vec{G}+\vec{Q}, 0) = 2ik_{iz} D_{\vec{Q}} A(\vec{G}+\vec{Q}), \quad (5)$$

where $A(\vec{G}+\vec{Q})$ is computed in the same way as for the elastic amplitudes, but for final energy $E_i + \omega$. The important point is that all the inelastic amplitudes $S(\vec{G}+\vec{Q})$ are proportional to $D_{\vec{Q}}$. Finally, then, $|B(\vec{G}+\vec{Q})|^2$ is given by the product of the surface-projected phonon density times a resonant factor that does not depend on the phonon displacements.

A comparison of theory and experiment is shown in Fig. 3 for $k_i = 6.06$ Å$^{-1}$ and for three closely spaced incident angles. In order to display the effect of resonances, we have also plotted, in Fig. 3(d), the resonant factor $(k_{fz}/k_{iz})|B(\vec{G}+\vec{Q})|^2/|D_{\vec{Q}}|^2$. The complete theory [Fig. 3(c)] is obtained by including temperature effects through a Debye-Waller factor[11,13] corresponding to $T_s = 300$ K. The bound-state energies and the surface corrugation amplitude are taken from Hoinkes's review article.[9] One can see that both the location and the calculated strength of the resonances are needed for a qualitative agreement with the experimental spectra. In particular the resonant factor for $\theta_i = 63.2°$ shows the broadening effect of the Debye-Waller factor at $T_s = 295$ K, which reproduces fairly well the observed resonance widths. For $\theta_i = 64.2°$ the intense resonance $n = 1$ accounts for the observed enhancement of the RW peak. On the other hand, the resonance $n = 3$ is slightly apart from the sharp peak in the phonon density, yielding only a broadening of the experimental peak.

It is interesting to note that at low temperature theory predicts extremely sharp and intense resonances which can locally amplify the scattering intensity by an order of magnitude. This effect could be exploited to tune certain particular phonons, e.g., optical surface phonons, which are weakly involved in atom scattering, and thus make their response observable through resonance-induced amplification.

[a]Permanent address: Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Istituto di Fisica dell'Università, Milano, Italy.

[1]G. Brusdeylins, R. B. Doak, and J. P. Toennies, Phys. Rev. Lett. 44, 1417 (1980), and 46, 437 (1981).

[2]B. Feuerbacher and R. F. Willis, Phys. Rev. Lett. 47, 526 (1981).

[3]R. Manson and V. Celli, Surf. Sci. 24, 495 (1971).

[4]V. Bortolani, A. Franchini, F. Nizzoli, G. Santoro, G. Benedek, and V. Celli, Surf. Sci. 128, 286 (1983).

[5]A. C. Levi, Nuovo Cimento B 54, 357 (1979).

[6]G. Benedek and N. Garcia, Surf. Sci. 80, 563 (1978), and 103, L143 (1979).

[7]G. Brusdeylins, R. B. Doak and J. P. Toennies, J. Chem. Phys. 75, 1784 (1981).

[8]P. Cantini, G. P. Felcher, and R. Tatarek, Phys. Rev. Lett. 37, 606 (1976).

[9]H. Hoinkes, Rev. Mod. Phys. 52, 933 (1980).

[10]V. Celli, N. Garcia, and J. Hutchison, Surf. Sci. 87, 112 (1979).

[11]P. Cantini and R. Tatarek, Phys. Rev. B 23, 3030 (1981).

[12]C. Lopez, F. J. Yndurain, and N. Garcia, Phys. Rev. B 18, 970 (1978).

[13]J. S. Hutchison, Phys. Rev. B 22, 5671 (1980).