Calculation of potential cutoff for one-phonon atom-surface scattering

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A cluster calculation for Cu(111), Ag(111), and Au(111) shows that the lateral Fourier transform of the charge deformation due to a displacement of a single surface atom is a Gaussian $\exp(-Q^2/2Q_c^2)$. This is proportional to the scattering amplitude for one-phonon exchange atom-surface scattering and produces a cutoff in the cross section. The values of Q_c are evaluated for the above-mentioned surfaces, explaining very well the experimental observations. We also find a simple formula that should be useful to experimentalists in calculating the cutoff.

Inelastic atom-surface scattering has been proved to be a very efficient tool for the study of surface phonon dispersion relations.[1-5] However, the knowledge of the projected phonon density of states $\langle u^2(\vec{Q},\omega)\rangle$ is not sufficient to determine the one-phonon cross section. Here $\vec{Q}$ and ω are the lateral momentum and the phonon frequency, respectively, and $\langle\ \rangle$ indicates the ensemble average. In addition, the coupling matrix elements between the incident particle and the atom displacement $\vec{u}_1$ at the surface play an important role. Considerable work has been done on the atom-surface inelastic coupling potential. For metals, the experiments have shown a rapid decay of the cross section near the Brillouin-zone (BZ) edge.[2,3] In addition, no phonons have been observed beyond the first BZ.[4,5] However, for alkali-halides Brusdeylins, Doak, and Toennies[1] have observed phonons up to the second BZ. Several mechanisms have been proposed for explaining the above experiments: (i) the size effect of the incident particle and the correlation of the atom displacements in the surface unit cell;[6] (ii) reduction of the Debye-Waller exponent due to coupling between the atom wave vector and the cross-correlated surface atom displacements;[7] (iii) the softness of the atom-surface interaction potential;[8] and (iv) the charge deformation due to atomic motion, which is also related to the softness.[3,9]

In this paper we calculate for the first time the cutoff parameters due to charge deformation, by using a cluster of atoms. We also present simple analytical formulas for the determination of the softness parameter and of the cutoff parameter Q_c, which reproduce with good accuracy the values obtained with the full calculation.

In order to proceed, we take the Esbjerg-Norskov[10] He-surface interaction potential

$$V(\vec{r}) = \alpha\rho(\vec{r})\ ,\tag{1}$$

where $\alpha = 375$ eV/a.u. $\rho(\vec{r})$ is the surface charge density averaged with the atom electrostatic potential and $\vec{r} = (\vec{R}, z)$ is the position vector. In the case of elastic-scattering experiments on Cu(110), Ag(110), and Au(110) (1×2) it has been shown that formula (1) works well[11] when the charge density is calculated with Clementi and Roetti atomic wave functions.[12] The reason why a superposition of atomic charges can be used in formula (1) is that the impinging He atom experiences the charge density at large distance from

the surface atoms, where the surface states and the bonding effects are negligible. In fact, for the typical thermal energies E_i of the incident atoms ($\lesssim 30$ meV) the turning point is in the range 7–8 a.u. We notice that the averaging effect of the He atom on the surface charge density at the experimental incident energies E_i is a minor correction.[10,11]

The one-phonon exchange interaction potential is

$$V_{ph}(\vec{r}) = \sum_l \vec{u}_1 \cdot \vec{\nabla}_1 V(\vec{r})\ ,\tag{2}$$

where l labels the atoms and $\vec{u}_l$ the relative displacements. By using a superposition of atomic charge density $\rho_a(\vec{r})$ in formula (1), we have

$$V(\vec{r}) = \alpha\sum_l \rho_a(|\vec{r}-\vec{r}_l|)\ ,\tag{3}$$

where $\vec{r}_l$ is the position vector of the lth atom. We believe that the use of atomic wave functions in the evaluation of Eq. (3) is also reasonable for inelastic scattering: For small atomic displacements, the modification in the charge profile should be dominated by the wave functions of the displaced atom. Equation (2) is evaluated at the turning point z_t of the He atom for a fixed E_i. It can be shown[11,13] that for large values of z the repulsive part of the potential[14] can be written as

$$V(\vec{r}) = E_i \exp\{-\beta[z-z_0-D(\vec{R})]\}\ ,\tag{4}$$

where β is the softness parameter[15] and $D(\vec{R})$ is the corrugation function. The turning point $z_t(\vec{R})$ is the value of z for which Eq. (3) becomes equal to E_i (in our case 17.5 meV) for a fixed $\vec{R}$. The corrugation is measured with respect to z_t evaluated at $\vec{R}=0$, i.e., $D(0)=0$. With this choice z_0 is equal to $z_t(0)$. We remark that $D(\vec{R})$ depends also on the atomic positions $\vec{r}_1$.

We have evaluated $\rho(\vec{r})$ with a 30-atom cluster. With this charge we have obtained the values of the turning point and of the corrugation $D_0(\vec{R})$ for the atoms in the ideal lattice positions. In addition, we have evaluated the new turning point and the new corrugation $D_{\vec{s}}(\vec{R})$ for a given dis-
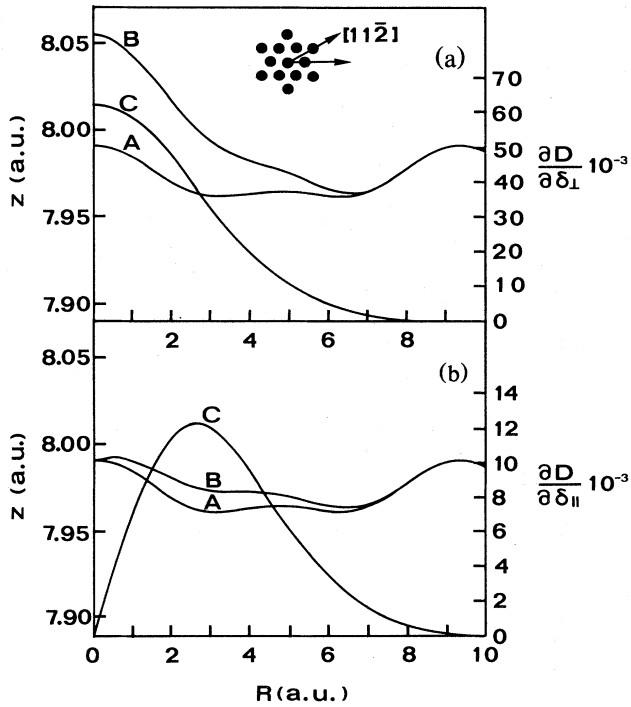
FIG. 1. Corrugation profiles and their derivatives $\partial D(\vec{R})/\partial \vec{\delta}$ for Ag(111) and $\vec{R}$ along $[11\bar{2}]$. Curve A: $D_0(\vec{R}) + z_0$. Curve B: $D_{\vec{\delta}}(\vec{R}) + z_0$. Curve C: $\partial D(\vec{R})/\partial \vec{\delta}$. In (a) $\vec{\delta}$ is along the z direction, in (b) $\vec{\delta}$ is along $\vec{R}$. In both cases, $\delta = 0.1$ a.u. The inset shows the surface geometry.
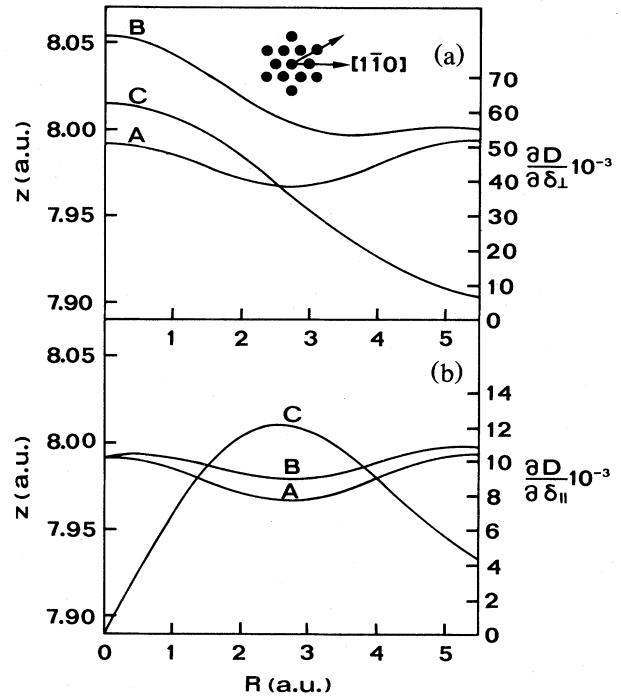
FIG. 2. As in Fig. 1 for $\vec{R}$ along $[1\bar{1}0]$.

placement $\vec{\delta}$ of the atom in $\vec{r}_1 = 0$. The calculation has been carried out for the (111) surfaces of Ag, Au, and Cu using the s atomic wave functions[12] for $[11\bar{2}]$ and $[1\bar{1}0]$ directions of symmetry and $E_i = 17.5$ meV. Typical examples are presented in Figs. 1 and 2 for Ag. As can be seen in Figs. 1 and 2 the amplitude of the corrugations is much smaller than the value of the turning point z_t. In the same figures are presented the calculated derivatives $\partial D(\vec{R})/\partial \vec{\delta}$ for $\vec{\delta}$ along z and $\vec{R}$. In the former case the derivative is a Gaussian of the type $\exp(-\frac{1}{2}Q_c^2 R^2)$ and in the latter case $\partial D(\vec{R})/\partial \vec{\delta}$ is the derivative of the same Gaussian divided

by β.

We can now write the gradient of the potential with respect to the atomic displacement $\vec{\delta}$ as

$$\vec{F}(\vec{R},z) = \beta E_i e^{-\beta(z-z_0)} \frac{\partial D(\vec{R})}{\partial \vec{\delta}} . \qquad (5)$$

The softness parameter β can be determined by matching the logarithmic derivatives of formulas (1) and (4) at the turning point z_t. The values of β and of the turning point z_t for $\vec{R} = 0$ are summarized in Table I, together with the values of Q_c. We found that β varies in the unit cell less than one over a thousand, indicating the validity of the factorization of the potential in Eq. (4). We also notice that our results remain unchanged to within 1% by varying α in the range 300–750 eV/a.u.

For the evaluation of the inelastic scattering amplitudes

TABLE I. Values of $z_t(0)$, β, and Q_c obtained from the cluster calculation. $\bar{z}_t$, $\bar{\beta}$, and $\bar{Q}_c$ are the approximated values of Eqs. (7) and (11).

	z_t (a.u.)	$\bar{z}_t$ (a.u.)	β (a.u.$^{-1}$)	$\bar{\beta}$ (a.u.$^{-1}$)	Q_c (a.u.$^{-1}$)	$\bar{Q}_c$ (a.u.$^{-1}$)
Cu	8.04	7.26	1.06	1.10	0.38	0.39
Ag	8.00	7.54	1.15	1.17	0.39	0.40
Au	8.09	7.59	1.11	1.12	0.39	0.39

we need the R Fourier transform of the gradient,[8,9,16,17] that is,

$$F_\perp(\vec{Q},z) = \beta B \exp(-\beta z) \exp(-Q^2/2Q_c^2) \quad (\vec{\delta} \text{ along } z) \ , \tag{6}$$

$$F_\parallel(\vec{Q},z) = iQB \exp(-\beta z) \exp(-Q^2/2Q_c^2) \quad (\vec{\delta} \text{ along } \vec{R}) \ ,$$

where $B = 2\pi E_i \exp(\beta z_0)/AQ_c^2$ and A is the area of the surface unit cell. These equations represent the most important result of this paper. They state that the cross section is proportional to a Gaussian in Q for shear-vertical vibrations, while it is proportional to the same Gaussian times Q for longitudinal vibrations. We have previously shown[9] that these factors determine the fast decreasing of the cross section at large Q because the projected density of states and the matrix elements, connected with the softness of the potential, decrease less rapidly.

The evaluation of $D(\vec{R})$ over the entire unit cell requires a cluster calculation. However, approximated values $\bar{z}_t$, $\bar{\beta}$, and $\bar{Q}_c$ can be obtained by considering the charge density of a single atom. In fact, z_t is so large for the energy E_i under consideration, and the wave functions are so rapidly decaying in this region, that $z_t(0)$, β, and Q_c are mainly determined by the properties of a single atom. The formula that is a very practical one is as follows:

(1) Take only the two outermost components of the s wave functions, i.e., for Ag those with the two smaller exponents among the $5s$ electrons.

(2) Calculate the approximated turning point $\bar{z}_t$ created by this charge.

(3) Calculate the logarithmic derivative along z of the potential defined by Eq. (1) with the approximated charge and match to the logarithmic derivative of a potential of the type $\exp(-\bar{\beta}r)$ evaluated along the z direction. By using atomic wave functions in the form of Clementi and Roetti[12] we obtain

$$\bar{\beta} = [2\xi - 2(n-1)/\bar{z}_t] \ , \tag{7}$$

with

$$\xi = \frac{\xi_0 + (\xi_0 + \xi_1) \exp[-(\xi_1 - \xi_0)\bar{z}_t](\xi_1/\xi_0)^{n+1/2}c_1c_0}{1 + 2\exp[-(\xi_1 - \xi_0)\bar{z}_t](\xi_1/\xi_0)^{n+1/2}c_1/c_0} \ , \tag{8}$$

where c_1, c_0 and ξ_1, ξ_0 are the coefficients and the exponents of the outer ns electron wave function. As an example, for Ag in the $5s^2$ state (Clementi and Roetti,[12] p. 233) $\xi_0 = 1.041\,86$ a.u.$^{-1}$, $\xi_1 = 1.650\,08$ a.u.$^{-1}$, $c_0 = 0.510\,23$, $c_1 = 0.394\,85$).

(4) Our potential at the turning points reads

$$V(\vec{r}) \propto \exp[-\bar{\beta}(R^2 + z^2)^{1/2}] \ , \tag{9}$$

where $\bar{\beta}$ and $\bar{z}_t$ have been determined before. Since $R \ll \bar{z}_t$ for all the values of interest of R, Eq. (9) can be expanded as

$$V(\vec{r}) \propto \exp(-\bar{\beta}z) \exp(-\bar{\beta}R^2/2\bar{z}_t) \ . \tag{10}$$

This potential has the same factorized form of the potential

in Eq. (4). Similarly it can be easily verified that the gradient of Eq. (10), with respect to the motion of the atom, is formally similar to the gradient given by Eq. (5), after the identification

$$\bar{Q}_c = (\bar{\beta}/\bar{z}_t)^{1/2} \ . \tag{11}$$

All the approximated values are given in Table I and the comparison with the full cluster calculation is good for $\bar{\beta}$ and $\bar{Q}_c$, which are the physical parameters that define the interaction.

The same analysis can be carried out for the alkali halides. For example, in He/LiF(001) a good estimate of the turning point is obtained by summing the ionic radius of F$^-$ (2.3 a.u. according to Tosi and Fumi[18]) to the atomic radius of He (2.02 a.u.), that is, $\bar{z}_t = 4.32$ a.u. Consequently $\bar{\beta} \simeq 1.7$ a.u.$^{-1}$ and $\bar{Q}_c \simeq 0.66$ a.u.$^{-1}$. We observe that the value of Q_c for LiF is much larger than the values of Table I relative to metals. Therefore, in LiF the phonon exchange can be detected over several Brillouin zones.[1]

In conclusion, we have proved that the Esbjerg-Norskov potential, which works well[11] for the interpretation of the diffraction data of Cu, Ag, and Au, presents a cutoff that reduces the cross section of the one-phonon exchange interaction. This cutoff factor has a Gaussian form $\exp(-Q^2/2Q_c^2)$. This Gaussian arises from the two-dimensional Fourier transform of the gradient of the charge associated with the motion of a single surface atom. We notice that this cutoff is not due to the correlate motion of the atoms in the surface unit cell.[6] The cutoff is just associated with the deformation of charge produced by a single moving atom and exists because of the softness of the potential; in other words, the He atoms are sampling the weak tail of the exponentially decaying wave functions.

Another interesting point concerns the size of the incident particles which modifies the values of α in the potential. By using Ne atoms instead of He, the value of α becomes larger.[19] Consequently, z_t increases and Q_c decreases. This explains why in Ne/Ni(111) the surface phonons are observed only up to $\frac{2}{3}$ of the BZ (Ref. 3) while in He/Ni(111) surface phonons are detected over the entire BZ,[3,20] but not beyond.[20]

We finally remark that the cutoff factor could also explain the asymmetry of the measured spectra in metals, with respect to phonon gain or loss in energy and momentum. In fact, in the one-phonon cross section[9] the kinematic condition selects surface phonons with different values of Q, so that processes with large Q are strongly damped by the cutoff.

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