Anticorrugation in Inelastic He-Atom Scattering from Rh(111) Surfaces

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Recent measurements supported by *ab initio* calculations have shown that the interaction of He atoms with transition metal surfaces is anticorrugating, i.e., the electron density seen by He is higher in the bridge positions than in the on-top positions. By shifting the electron charge density away from the atomic positions and using the Esbjerg-Norskov approach to determine the interaction potential, we evaluate the inelastic reflection coefficients of He with Rh(111). The structure factor introduced by the anticorrugation explains, in a simple way, the high intensity observed for the resonant mode. [S0031-9007(98)05499-4]

In the last fifteen years, the spectroscopy of vibrational motion of atoms in or on crystal surfaces has developed in an impressive manner. Two powerful experimental techniques are now available: inelastic scattering of He atoms (HAS) [1,2] and off-specular inelastic electron scattering (EELS) [3,4]. These techniques allow one to measure, with the same accuracy, the dispersion relation of surface phonons on clean crystals through the surface Brillouin zone.

For the noble and transition metals [5,6], the HAS provides information on the dispersion curve of the Rayleigh surface phonon (RW). In addition, a striking resonance within the bulk band was observed. This mode, corresponding mainly to a longitudinal vibration, was called longitudinal resonance (LR). In the time-of-flight experiments, the intensity of this resonance is sometimes higher than the intensity of the Rayleigh mode; whereas, in the EELS spectra, its intensity is much smaller than the RW intensity. This discrepancy between the two results has been the object of controversial discussions for a long time.

A test case, to investigate this puzzle, was the (111) surface of copper. The phonon frequencies obtained with the two techniques overlap to within the experimental errors and uncertainty; they are in very good agreement. However, at the same time, two different pictures of the surface lattice dynamics of Cu(111) have emerged from an independent analysis of the EELS [7] and HAS data [8].

The longitudinal mode, quite localized at the surface, has a polarization sensitive to the leading force constant between atoms in the surface layer. The authors of Ref. [7] suggested that there is a rather slight softening (15%) of this force constant which explains the intensity of LR peaks. With such a model, an excellent quantitative account of the energy variation of the excitation cross section was found, from the application of multiple scattering theory to a description of the loss processes. The above picture fails to account for the intensity variation found in the HAS experiments. The theoretical helium loss spectrum gives a resonance weaker than the one observed. Our unpublished calculations [8] showed that the simultaneous fit of surface phonon frequencies and HAS intensities requires a very large unphysical softening (70%) of the surface force constant, and a large stiffening of the force constant (70%) between first and second layer atoms to enhance the intensity of the LR, and at the same time fit the RW dispersion curve. Calculations performed with this phonon model for the off-specular excitation cross section generate spectra in disagreement with the EELS spectra [9].

Subsequent theoretical calculations based on the local density approximation for Ag, Cu [10], Al [11], and Na [12] showed that the softening of the intralayer and interlayer surface force constants are ≲20%. These calculations reproduce the observed frequencies quite well, but, with these modest modifications of the force constants, it is not possible to explain the enhanced HAS intensity of the LR observed in the noble and transition metals. The first attempt to solve this paradox was given by Kaden *et al.* [13]. They evaluate the HAS spectra of copper by using a semiempirical lattice dynamical model similar to the bond charge model of semiconductors. In this approach, the lattice vibrations couple to those of the fictitious bonding charges. Another attempt to explain the spectra was the use of an oblate potential [14] which is reducing the corrugation as does the bonding charge model. Apparently the problem was solved. However, recent measurements of Rieder and collaborators [15] have thrown new light on the interpretation of the elastic HAS spectra and on the role of the atom-surface interaction, reopening the problem.

In the past, the interaction potential was derived by Esbjerg and Norskov [16], who argued that the interaction energy of the He atom with the surface is simply proportional to the unperturbed electron density of the substrate at the position of the He atom. Doubts on the validity of this approach were put forward by Rieder and Garcia [17]. To improve the description of the interaction potential, several attempts have been made [18–20].

To interpret the elastic He-atom scattering measurements performed on Rh(110) and on Ni(110) using the Esbjerg and Norskov procedure, Rieder *et al.* [15] conclude that the corrugation of the unperturbed charge

density is shifted away from the atomic positions. The electron density at the short bridge position appeared in the HAS to be higher than the one on the top positions. On the contrary, the scattering of Ne atoms reflects the corrugation of the surface unperturbed electron density. A physical explanation has been given by Petersen *et al.* [21]. Their calculations, based on density functional theory, show that, for He, there is evidence of anticorrugation in the He-Rh surface potential. Their interpretation differs from the Rieder arguments. The nature of the interaction is determined by electron polarizations and hybridizations with only the *d* electrons close to Fermi level. The interaction potential energy evaluated for He is anticorrugated with respect to the unperturbed density of electrons of Rh surface layer. For He-atom fixed energy, the He-atom turning point is higher on the short bridge configuration than in the on-top position, and the He atom sees the maximum of the electron charge profile of the Rh substrate on the bridge position. The Ne $2p$ states interact with the substrate in different manners, and the result is that the Ne atom sees the corrugation of the ideal surface. This is also in agreement with Rieder's interpretation of the elastic scattering data. We will show that the anticorrugation is the key point in order to reconcile HAS and EELS experiments.

This paper addresses the analysis and application of the He-Rh(111) surface anticorrugating potential to the interpretation of the inelastic time-of-flight spectra. Very accurate measurements of the phonon frequencies for the (111) surface are available for Rh [22] as well as recent measurements of the bulk phonon frequencies [23].

We will consider the total potential $V(r)$, composed of a repulsive part V_R of the Esbjerg-Norskov form plus an attractive V_A van der Waals interaction, with the inclusion of the Tang-Toennies [24] correction to reduce the attraction at close range from the surface atoms. To include mathematically, in this He atom-surface interaction, the effect of the anticorrugation discussed previously, we write the total He-(111) surface potential as a sum of pairwise potentials of the type

$$V(\mathbf{r}) = \sum_{\mathbf{R}_l, \mathbf{b}_l \neq 0} v(\mathbf{r} - \mathbf{R}_l - \mathbf{b}_l), \qquad (1)$$

where the $\mathbf{b}_l$ are the midpositions of the neighboring atoms, i.e., the center of the bridge positions. The $\mathbf{b}_l$ are introducing a basis in the surface Bravais hexagonal cell shifting the charge profile with respect to the underlying atoms.

The repulsive part of the potential for Rh is obtained with a superposition of atomic charges in the self-interaction corrected local density approximation of the type $A \exp(-\beta r)$ with $\beta = 2.57$ Å [25]. With the total potential, we evaluate, at the particle energy (20–30 meV), the turning point of He for the top and for the bridge position on the Rh(111). The corrugation defined as the difference between these two turning points is

$\xi = -0.07$ Å. This value is close to the value found by Petersen [21] in the short bridge direction for the Rh(110), and to the value derived by Rieder [15] from experiments.

In order to study the experimental time-of-flight spectra, we evaluate the reflection coefficient in the distorted wave Born approximation. The matrix elements of the gradient of the total potential given in Ref. [26], using the potential of Eq. (1), are multiplied by the structure factor of the basis, that, for the (111) surface, is given by

$$S(\mathbf{Q}) = \frac{1 + 2\cos(\pi Q/2Q_M)}{3}, \qquad (2)$$

where $\mathbf{Q}_M$ is the momentum at the $\bar{M}$ point of the two-dimensional Brillouin zone (2DBZ). We note that in the case of corrugated surfaces $S(\mathbf{Q}) = 1$.

To evaluate the reflection coefficient, one should know the surface phonon frequencies and polarization vectors in the whole 2DBZ. At present, *ab initio* local density approximation calculations are available for the bulk Rh along high symmetry directions [23] and surface calculations for some selected points of the 2DBZ for the (110) and (100) surfaces [27]. These calculations indicate that (i) the bulk interactions are long ranged and noncentral, and (ii) the effect of the surface is to slightly modify the surface force constants by about 20%, with respect to their bulk value. To evaluate the surface phonons on the whole 2DBZ, we have chosen a semiempirical potential that fulfills requirements (i) and (ii). We have used a central potential with long range interactions up to 10 n.n. (nearest neighbors) and noncentral interactions up to 2 n.n. [28]. With long interactions, we can reproduce with great accuracy the edges of the bulk projected bands on the surface. In the surface region, we have modified (by less than 20%)
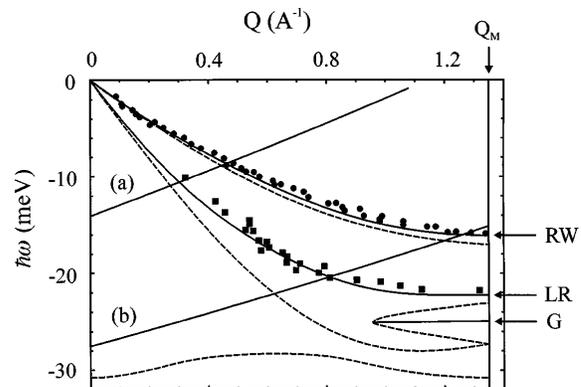

FIG. 1. Surface phonon frequencies of Rh(111) with Q along the [11$\bar{2}$] direction. Solid lines represent the surface modes. RW: Rayleigh wave; LR: resonance mainly of longitudinal character; G: gap mode not measured in the experiments of Ref. [22]. The dashed curves refer to the edges of the projected bulk bands. The curve close to the RW is the transverse edge and the one below LR is the longitudinal edge of the projected bulk phonons. The curves *a* and *b* are the scan curves representing the conservation of energy $\hbar\omega$ and lateral momentum $\mathbf{Q}$ for $\theta_i = 40.50°$ and $\theta_i = 34.00°$, respectively.
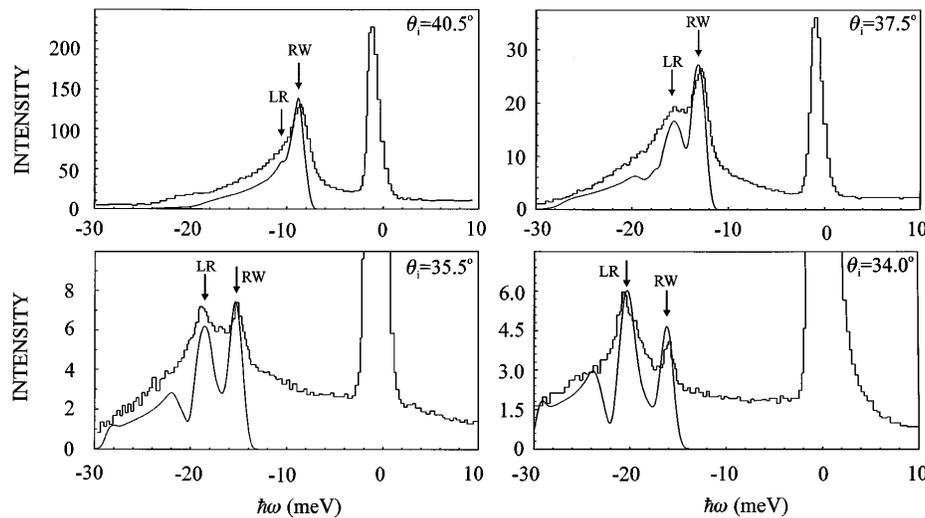
FIG. 2.   Comparison between the measured time-of-flight spectra of Ref. [22] (histograms) and the evaluated reflection coefficients (full lines). The arbitrary constant existing between the evaluated reflection coefficient and the measured spectra has been taken to fit the maximum of the Rayleigh peak for $\theta_i = 40.50°$.

the intraplanar and interplanar (surface-first interior plane) force constants to fit the Rayleigh mode at the $\bar{M}$ point.

The calculated surface phonon frequencies are depicted in Fig. 1 together with the measured phonon frequencies [22]. The dashed lines represent the edges of the bulk phonons projected on the (111) surface, and the full lines represent the surface localized modes. The quality of the fit to surface measurements is very good. With the eigenvalues and eigenvectors relative to the surface layer, we evaluate the reflection coefficient [26].

In Fig. 2, we compare some evaluated reflection coefficients with the He-Rh(111) scattering spectra of Witte *et al.* [22] for the symmetry direction $\bar{\Gamma}\bar{M}$. Close to the specular ($\theta_i = 45.25°$) for the $\theta_i = 40.50°$ geometry (see the scan curve *a* of Fig. 1), the lateral momentum of the Rayleigh wave is $Q_{RW} \simeq 0.47$ Å^{-1} and that of the LR is $Q_{LR} \simeq 0.3$ Å^{-1}. In this range of small Q, the structure factor is slowly varying, so that only the Rayleigh peak is dominating the cross section (see Fig. 2). By increasing the momentum transfer, i.e., by decreasing θ_i, the
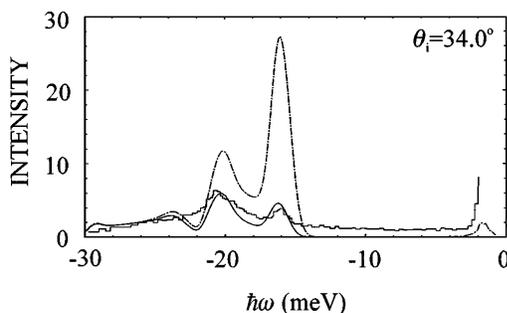
structure factor is rapidly decaying on the Rayleigh mode. For the extreme subspecular angle $\theta_i = 34.00°$ (see the scan curve *b* in Fig. 1), we have $Q_{RW} \simeq 1.3$ Å^{-1} and $Q_{LR} \simeq 0.8$ Å^{-1}. For this value of Q, the structure factor strongly reduces the intensity of the Rayleigh peak, with respect to the LR peak, as shown in Fig. 2. The $S(\mathbf{Q})$ is responsible for the large intensity at the LR, particularly at large momentum. The reflection coefficients with $S(\mathbf{Q}) = 1$ for all the subspecular angles do not show this effect, and only the Rayleigh structure is very intense as it occurs with the EELS scattering, where there is no anticorrugation. In Fig. 3, where, for comparison, the reflection coefficient with and without the structure factor for the extreme subspecular geometry are presented, one sees immediately the anticorrugation effect of the structure factor.

In conclusion, the anticorrugating effect is fully explaining the anomalous height of the LR observed by He scattering. As $\mathbf{Q}$ increases, the structure factor decreases the height of the RW peak and, at large momentum, the LR intensity takes over the RW intensity, making clearly visible the little structure observed by EELS. Therefore, the anticorrugation reconciles the EELS and HAS experiments for what concern the intensities of the observed spectra.

FIG. 3.   The evaluated reflection coefficient for $\theta_i = 34.00°$. Full curve with $S(\mathbf{Q})$ given by Eq. (2). Dotted curve with $S(\mathbf{Q}) = 1$. Note the dramatic enhancement of the ratio of LR to RW intensity.

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