IL NUOVO CIMENTO VOL. 20 D, N. 7-8 Luglio-Agosto 1998

Dynamical properties of Rh(111):H(1×1) surface$(^*)$

G. SANTORO, A. FRANCHINI and V. BORTOLANI

INFM e Dipartimento di Fisica, Università di Modena
Via Campi 213/A, 41100 Modena, Italy

(ricevuto il 23 Gennaio 1998; approvato il 19 Febbraio 1998)

Summary. — In the experimental He atom scattering time-of-flight spectra of rhodium covered with hydrogen there is no evidence of the anomalous high intensity of the resonant mode present in the clean surface. In this paper we explain the different behaviour of clean and covered rhodium (111) surface in terms of the "corrugating" effect of the electron density of hydrogen atoms. For clean surface the surface electronic density is shifted with respect to the lattice atomic positions, *i.e.* there is an "anticorrugating" effect that enhances the intensity of the longitudinal resonant mode which becomes dominant for some scattering geometries. For the covered surface the hydrogen atoms remove the anticorrugation, the charge profile becomes corrugated and the intensity of the longitudinal resonant vibrational mode remains very weak with respect to the Rayleigh wave intensity.

PACS 63.20.Dj – Phonon states and bands, normal modes, and phonon dispersion.
PACS 63.20.Pw – Localized modes.
PACS 01.30.Ee – Monographs and collections.

Rhodium is known to be an active heterogeneous catalyst for several chemical reactions. The adsorption of hydrogen on metal surfaces is of great interest since the chemisorbed H is an intermediate in many catalytic reactions. In this paper we investigate the surface dynamical properties of the hydrogen-covered Rh(111) surface. The surface phonon dispersion branches for rhodium have been measured with inelastic He-atom scattering (HAS) for the clean and hydrogen-covered (111) surface [1]. Significant changes of the dynamical properties of the surface after the hydrogen adsorption have been found. In particular the disappearance of the very intense resonance observed for a number of metals [2, 3]. In addition to the Rayleigh mode (RW) several features at high energy appear in the He time-of-flight spectra. The He beam diffraction has the specific property of being sensitive to the outermost layer of atoms and is especially valuable

$(^*)$ In honour of Prof. Gianfranco Chiarotti on the occasion of his 70th birthday.

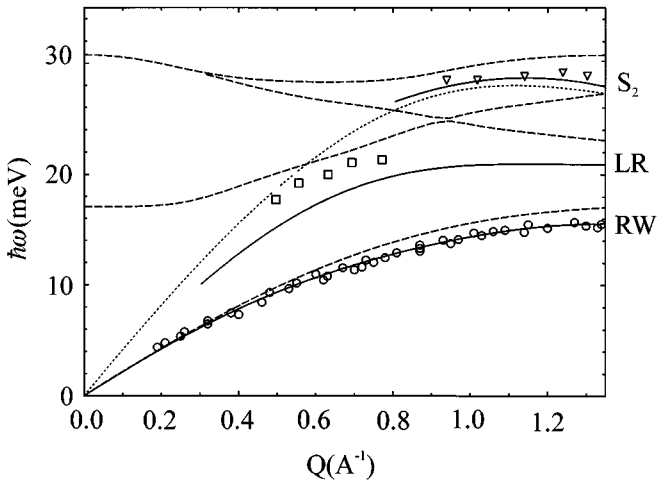

Fig. 1. – Surface phonons along the $\bar{\Gamma}\bar{M}$ direction. Dashed lines: bulk phonons edges. Continuous lines: our results. Open symbols: He scattering data [1].

in deducing adatom configurations of the light adsorbate as hydrogen on metallic surfaces. Elastic He beam diffraction gives detailed information on the surface structure [4]. Rieder and coworkers have shown that the interaction of the He atoms with the rhodium surface is anticorrugating, *i.e.* the electron density seen by the He atom is higher in the bridge position than in the on-top position [5]. The interaction is shifting the charge profile with respect to the underlying atoms. In a previous paper [6] we have shown that this anticorrugation is introducing a structure factor in the matrix elements of the He surface potential. This structure factor allows us to explain in a simple way the very high intensity observed experimentally for the resonant mode (LR) in the clean Rh(111) surface. Here we want to show that the presence of the hydrogen adsorbed on the surface is altering in a significant manner the He surface interaction in such a way that the He atom "sees" the charge profile of the surface atoms, without any shifting effect.

To this purpose we evaluate the reflection coefficients and we compare these with the hydrogen-covered Rh(111) surface time-of-flight spectra. The evaluation of the surface phonon dispersion relation based upon model calculations using bulk force constants is now possible because very recently the bulk phonons of Rh have been measured [7]. Also *ab initio* calculations which fit very well the experiments have been recently performed [8]. However, to perform the lengthy calculation of the reflection coefficients it is convenient to use a simplified force constants model. The model contains long-range interactions up to 10th n.n. and non-central forces up to 2nd n.n. in agreement with *ab initio* calculations. The surface force constants in the first and second layer have been obtained from a fit of surface phonons at the zone boundary. We found variation of about 20% of the surface constants with respect to the bulk ones. The He-surface interaction is obtained as the sum of a repulsive Born-Mayer and an attractive Van der Waals term. The reflection coefficients have been evaluated in the distorted Born approximation [9].

The evaluated surface phonons branches along the $\bar{\Gamma}\bar{M}$ direction are shown in fig. 1 together with the experimental data. The agreement in quite remarkable. The Rayleigh branch is well reproduced on the entire direction. Also the presence of the longitudinal resonance LR is well reproduced. The peak at high energy can be explained by the high

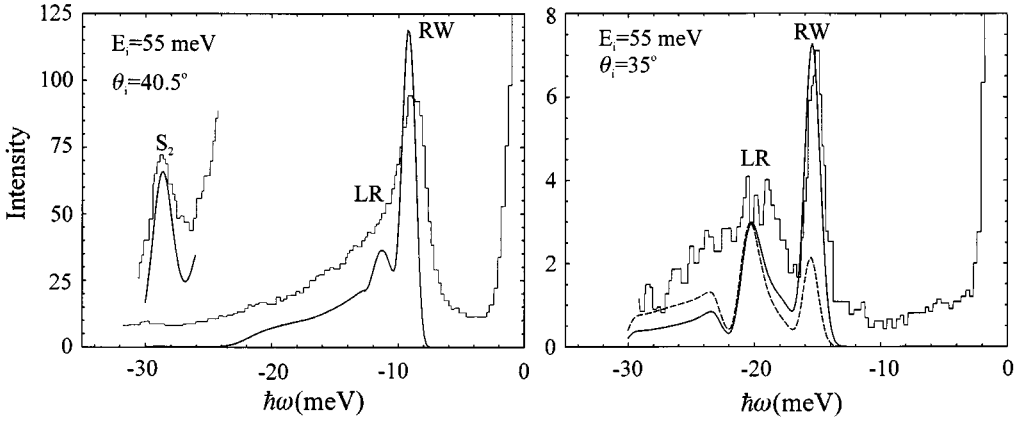

Fig. 2. – Comparison between the measured time-of-flight spectra of ref. [1] (histograms) and the evaluated reflection coefficients without structure factor (full lines) and with structure factor (dashed lines). The arbitrary constant existing between the evaluated reflection coefficient and the measured spectra has been taken to fit the maximum of the Rayleigh peak for $\theta_i = 36.50°$.

density of states in the bottle-neck around $\bar{M}$.

A better understanding of the high-frequency modes comes from the evaluation of the reflection coefficients presented in fig. 2. In these calculations we have assumed that the He-surface interaction is proportional to the charge of the surface atoms, in other words we assume that the charge profile of the surface is not modified by the interaction with the He atom. We note that the intensity of the Rayleigh peak dominates that of the LR peak in the whole direction. This can be understood by remembering that the structure factor used for the clean surface is a rapidly decaying function of the momentum transfer. In the measurements the momentum of the RW mode is always much larger than the

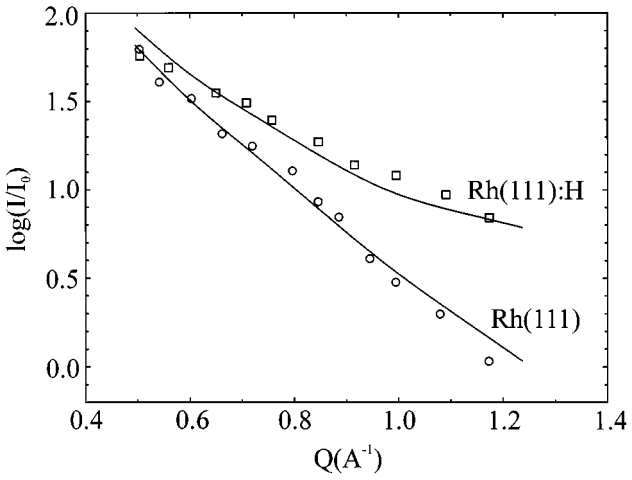

Fig. 3. – Comparison of the calculated absolute intensity of RW for hydrogen-covered surface and clean surface (continuous line) with measured [1] intensities (open symbols).

momentum of the LR mode, so that in the spectra of the clean surface the intensity of the RW mode is strongly reduced with respect to the LR, as shown by the dashed lines in fig. 2 for the scattering geometry $\theta_i = 35°$. In the calculations for the hydrogenated surface we assume that the structure factor is unity, so that there is not a strong reduction of the intensity in the spectra at large momentum transfer and it is also possible to obtain the peak of the S_2 mode, as shown for the $\theta_i = 40.50°$ geometry in fig. 2.

The effect of the corrugation is also evident in fig. 3, where we have drawn the intensity of the RW mode as a function of momentum. One sees that for the anticorrugated clean surface the decaying of the RW mode is much faster than the decay of the RW mode for the H-covered surface, as found in the experiments.

In conclusion our model, based on the corrugating effect of hydrogen adsorbed onto the Rh(111) surface, is able to explain the experimental data of the lattice dynamics of the H-covered surface and the differences in the time-of-flight spectra with respect to the clean surface.

* * *

Partial financial support of Grant NATO CRG971622 is acknowledged.

REFERENCES

[1] WITTE G., TOENNIES J. P. and WÖLL CH., *Surf. Sci.*, **323** (1995) 228.
[2] HARTEN U., WÖLL CH. and TOENNIES J. P., *Phys. Rev. Lett.*, **55** (1985) 2308.
[3] HARTEN U., TOENNIES J. P. and WÖLL CH., *Faraday Disc. Chem. Soc.*, **80** (1985) 137.
[4] RIEDER K. H., *Phys. Rev. B.*, **27** (1983) (RC)7799.
[5] RIEDER K. H., PARSCHAU G. and BURG B., *Phys. Rev. Lett.*, **71** (1993) 1059.
[6] SANTORO G., FRANCHINI A. and BORTOLANI V., *Phys. Rev. Lett.*, **80** (1998) 2378.
[7] EICHLER A., BOHNEN K. P., REICHARDT W. and HAFNER J., *Phys. Rev. B*, **57** (1998) 324.
[8] XIE J. and SCHEFFLER M., *Phys. Rev. B*, **57** (1998) 4768.
[9] BORTOLANI V., FRANCHINI A. and SANTORO G., in *Electronic Structure, Dynamics and Quantum Structural Properties of Condensed Matter*, edited by J. T. DEVREESE and P. VAN CAMP (Plenum Press) 1985, p. 401.