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SURFACE LATTICE DYNAMICS OF NICKEL

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Abstract.- In the framework of a central and angular force constants model, we have evaluated the phonon spectrum and the loss function of the Ni(111) surface covered with Oxygen. We explain quantitatively the main features of the observed electron energy loss spectra.

1. Introduction.- In this work we are interested in the surface optical phonons of the Ni(111) surface for which very accurate high resolution electron energy loss (EELS) experiments are available⁽¹⁾. The detection of these surface vibrations with EELS occurs through the dipole coupling. The dipole is provided by fraction of monolayers of Oxygen adsorbed on the metallic surface. As a consequence there are problems of interpretation of the experimental spectra because one has to discriminate between the modes of the substrate and the modes induced by the adsorbate. In order to solve this problem we show here that a realistic surface phonon calculation is needed. Our results indicate that the observed peaks relate to the phonons of the substrate for the Rayleigh wave, but otherwise are due to the adsorbed layer.

2. Calculation of the EELS spectrum.- In the dipole coupling approximation, the EELS scattering cross section has the form:

$$\frac{d\sigma}{d\Omega} \propto \frac{k_B T}{\omega^2} \left| \frac{w_z(\vec{Q}_\parallel, l_z=0, \omega)}{\sqrt{m_{l_z=0}}} - \frac{w_z(\vec{Q}_\parallel, l_z=1, \omega)}{\sqrt{m_{l_z=1}}} \right|^2$$

Here w_z is the normal component of the polarization vector of the excited phonon with parallel momentum $\vec{Q}_\parallel$ and frequency ω . l_z labels the atomic planes and m_{l_z} is the mass of the atoms in the l_z plane. It is clear from this equation that the modes which are detectable are those having a non zero normal component of the sum of the polarization vectors in the surface unit cell. In order to evaluate the surface phonon field of Ni we use the slab method, in the framework of a central and angular force constants parametrization⁽²⁾. We present here the calculations for the measured EELS spectra relative to the Ni(111):O p(2x2) and to the Ni(111):O ($\sqrt{3} \times \sqrt{3}$)R30° geometries, depicted in Fig.1. In both configurations the Oxygen is bound to three Ni in a C_{3v} position.

We firstly consider the p(2x2) geometry. In this case the M point of the 2-dimensional Brillouin zone of the ideal (111) surface is folded in Γ , so that EELS detects the M phonons. The experimental results⁽¹⁾ are reported in Fig.2a. Three peaks are

Fig. 1 : a) Ni(111):O $p(2 \times 2)$ geometry. ● Oxygen atoms, (A), (B), (C) Ni atoms in the first three layers. b) the same for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ geometry.

present. The one at 72 meV, which is far outside the phonon spectrum of Ni, is clearly due to the motion of the Oxygen relative to the three coordinate Ni atoms. It corresponds to the A_1 normal mode of a pyramidal x_3y molecule⁽³⁾. As it can be seen from Fig.3, this mode gives a dipole moment along the C_{3v} axis, i.e. the surface normal. The lowest peak can be interpreted in terms of the surface phonons of the clean Ni (111) surface⁽²⁾. In fact, near this frequency there is the Rayleigh wave of the M point which is mainly polarized normal to the surface. The other peak at 32.8 meV, inside the phonon spectrum of Ni, cannot be explained in terms of the phonons of the clean surface. The modes of the M point around this frequency are longitudinal and do not couple with the impinging electrons. To clarify the nature of this peak we have performed a full calculation of the phonons of the covered surface. We have considered the interaction of Oxygen with the three nearest neighbouring Ni atoms by introducing one central and one angular force constant. By any arbitrary choice of these force constants the calculated EELS cross section shows three structures. The one at lowest frequency remains related to the Rayleigh mode of the substrate. The other two peaks are connected with the A_1 (higher frequency peak) and A_2 (central peak) modes of the x_3y molecule. For this molecule, the frequency of the A_1 mode is mainly due to the value of the Ni-O central force constant, while the frequency of A_2 depends on the Ni-O-Ni angular force constant. To determine the force constants of the x_3y molecule we note that, even if the free Ni_3O molecule does not exist, the surface potential is able to stabilize such a molecule. By using the EELS data relative to a very low disordered coverage of Oxygen we fit the peak at 72 meV with the central force constant and the peak at 30 meV with the angular force constant. The results obtained with these parameters are reported in Fig.2b. The lowest peak is still related to the Rayleigh wave of the clean surface. The presence of the Oxygen atom does not modify the frequency and polarization of this mode. The highest peak remains at the energy position of the A_1 mode of the molecule. The other peak at 32.8 meV, in perfect agreement with the experiment, results slightly shifted with respect to the energy of the A_2 mode of the free molecule, while the polarization remains the same. The frequency shift can be understood in terms of the indirect O-O interaction caused by the sub-

Fig. 2 : a) and b) experimental and calculated EELS intensities for the $p(2 \times 2)$ geometry. c) and d) the same for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ geometry.

strate.

The same analysis has been carried out for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ geometry. The experimental and calculated intensities are compared in Fig.2c and Fig.2d respectively. The two observed modes are related to the A_1 and A_2 modes of the molecule. The 29.8 meV peak is slightly shifted with respect to the corresponding mode of the $p(2 \times 2)$ geometry because of the different O-O interaction.

In conclusion, we have shown that a detailed calculation allows to explain the loss spectra of coated systems and to identify the origin of the experimental structures in terms of the modes of the substrate and those of the adsorbate species.

Fig. 3 : Normal modes of the x_3y pyramidal molecule that contribute to the EELS cross section.

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