PHYSICAL REVIEW B VOLUME 24, NUMBER 6 15 SEPTEMBER 1981

Inelastic electron scattering from surface vibrational modes of adsorbate-covered Cu(100)

S. Andersson and M. Persson
Department of Physics and Institute of Theoretical Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

(Received 6 July 1981)

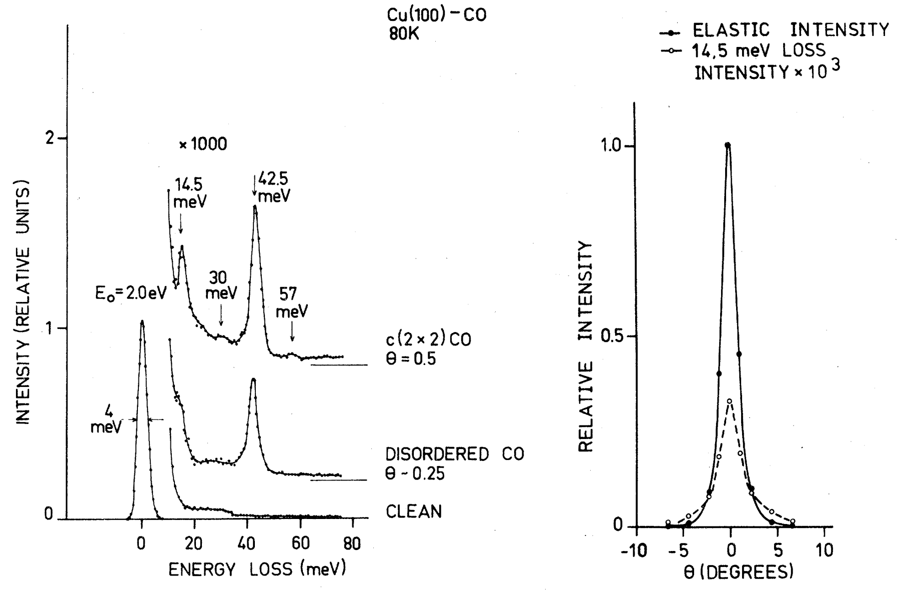
The excitation of surface vibrational modes of Cu(100) covered with ordered adsorbate lattices of CO, CH_3O, and S has been investigated by electron-energy-loss spectroscopy. The influence of the adsorption site symmetry on the surface-mode-excitation cross section is analyzed and shown to provide important information about the adsorption site.

Recently it has been reported in a few instances[1–3] that vibrational modes in the energy range of the metal substrate phonon band can be observed by high-resolution electron-energy-loss spectroscopy (EELS) from single-crystal metal surfaces covered with ordered adsorbate lattices. It was shown by Ibach and Bruchmann[3] that these modes may be associated with metal surface phonons at certain points of the surface Brillouin zone determined by the dimension of the adsorbate structure unit mesh. The purpose of this work is to demonstrate how knowledge about adsorption sites can be obtained from EELS investigations of such surface vibrational modes. Our discussion concerns particularly some ordered adsorbate lattices on Cu(100) and is based on simple arguments concerning the symmetry properties of the surface phonons and the symmetry of the adsorption site. We will adopt the surface vibrational mode notation given by Allen, Alldredge, and de Wette[4] in their theoretical study of fcc crystal slabs and also make a direct comparison with the surface phonon energies for a Cu(100) crystal slab calculated by Castiel, Dobrzynski, and Spanjaard.[5]

The EELS measurements reported in this work were obtained using a new high-resolution electron spectrometer which has been briefly described elsewhere.[6] The specimen and the analyzer can be rotated such that the polar angles of incidence and analysis can be varied independently. The scattering plane containing the incident and the analyzed electron beams is defined by the Cu(100) specimen surface normal and the [100] direction in the surface plane. The energy of the incident electron beam quoted in the spectra refers to the specimen vacuum level. Vibrational loss spectra have been recorded for the following simple ordered adsorbate structures: Cu(100)-$c(2\times2)$CO, -$c(2\times2)CH_3O$, and -$p(2\times2)$S. The Cu(100) crystal was cleaned routinely by argon ion bombardment—annealing and a final brief heating to 950 K prior to adsorption. The formation of the ordered surface structure was monitored by low-energy electron diffraction (LEED). The CO adsorption was performed at 80-K substrate temperature. The Cu(100)-$c(2\times2)CH_3O$ structure was formed by reacting methanol with preadsorbed oxygen on the Cu(100) surface at the reaction conditions for which Sexton[7] found the most intense CH_3O vibrational loss spectrum. This turns out to correspond to the condition for establishing an ordered $c(2\times2)CH_3O$ structure. The $p(2\times2)$S structure was formed by adsorbing 3×10^{-5} torr sec H_2S at 300-K substrate temperature.[8]

Figure 1(a) shows the low-energy region of the EELS spectra for CO adsorbed on Cu(100). The 42.5-meV peak is associated with the CuC stretching vibration and its intensity is approximately proportional to the CO coverage. The peak at 14.5-meV behaves differently, its intensity increases abruptly when the $c(2\times2)$CO structure develops. The corresponding vibrational mode is evidently related to the existence of the $c(2\times2)$ structure. A direct consequence of forming the $c(2\times2)$ structure is that the M point of the substrate surface Brillouin zone (SBZ) becomes equivalent to the $\bar{\Gamma}$ point of the $c(2\times2)$ SBZ [see Fig. 2(a)]. This means that surface vibrational modes at $\bar{M}$ may be excited at $\bar{\Gamma}$, i.e., close to the specular direction in the EELS experiment. This will correspond to a situation where the adsorbed species in the $c(2\times2)$ lattice move in phase. Angular measurements of the 14.5-meV [see Fig. 1(b)] and 42.5-meV loss peaks reveal that these modes are excited by dipole scattering; i.e., the loss intensity peaks sharply around the specular direction.

If we equate the maximum phonon energy $\hbar\omega_{\max}$ of the Cu(100) slab calculation to the maximum phonon energy of bulk copper,[9] which is 30 meV, we get an energy of 14 meV for the surface phonon S_1 at $\bar{M}$.[4] This observation strongly supports the interpretation of the 14.5-meV peak in terms of the excitation of a surface mode originating from $S_1(\bar{M})$ and has implications for the structure of the Cu(100)-$c(2\times2)$CO system. The symmetry properties of the phonon mode, which differ with respect to the adsorption site, is exhibited in the cross section for exciting the mode. We will illustrate this by analyzing three different adsorption sites: (i) on top position; (ii) hol-



(a) (b)

FIG. 1. (a) Electron-energy-loss spectra from the Cu(100)-CO system measured in the specular direction, $\theta = 0°$, for an energy 2 eV and angle 50° of the incident electron beam. (b) Experimental elastic peak intensity (solid circles) and 14.5-meV loss peak intensity (open circles) for Cu(100)-$c(2\times2)$CO vs collection angle θ (positive towards the surface normal).

low position; and (iii) bridge position. When deriving the symmetry labels of a phonon mode at $\bar{\Gamma}$, it is sufficient to examine the corresponding displacement field in an extended basis of surface atoms which has the full point-group symmetry. This is shown schematically in Fig. 2(b) for the three adsorption sites and $S_1(\bar{M})$. As discussed by Allen *et al.*,[4] along $\bar{\Gamma}$-$\bar{M}$ the bare surface phonon mode S_1 is polarized strictly within the sagittal plane predominantly normal to the surface. At $\bar{M}$ it is, due to symmetry, strictly normal to the surface and strictly localized in the first layer since the dynamical matrix decouples[10] the parallel and normal components of the phonon displacement field which belong to different irreducible representations E and A_1 for odd layers, E and B_1 for even layers with respect to the C_{4v} group of the wave vector.

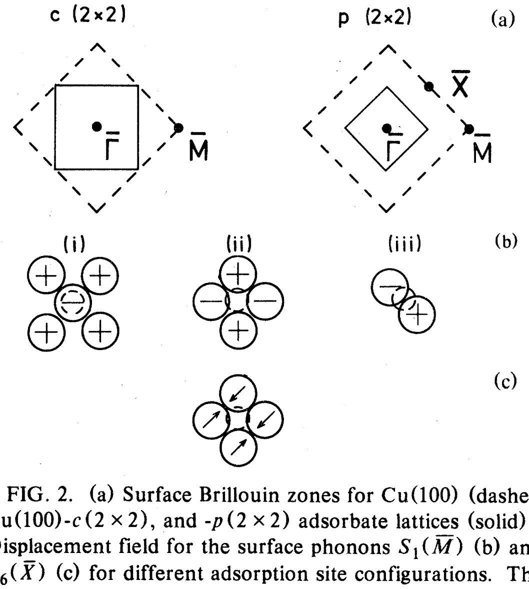


FIG. 2. (a) Surface Brillouin zones for Cu(100) (dashed), Cu(100)-$c(2\times2)$, and -$p(2\times2)$ adsorbate lattices (solid). Displacement field for the surface phonons $S_1(\bar{M})$ (b) and $S_6(\bar{X})$ (c) for different adsorption site configurations. The solid and dashed circles indicate the substrate surface and the adsorbate ion cores, respectively.

For cases (i) and (ii) above the symmetry group is a symmorphic space group with C_{4v} as the point group. The dipole active displacement field for the fundamental CuC and CO stretching vibrations are both totally symmetric (belong to symmetry class A_1) with respect to the point group. Dipole activity will then be symmetry allowed for the dressed surface phonon mode[11] $S_1(\bar{M})$ for the on top configuration (i) since the bare mode $S_1(\bar{M})$ is totally symmetric in that case. In the hollow site configuration, (ii), $S_1(\bar{M})$ belong to symmetry class B_1 and will then be symmetry forbidden to be dipole active since the dipole moment normal to the surface is totally symmetric.

For dipole scattering from an ordered surface structure consisting of N primitive cells of area n^{-1}, the differential cross section at small scattering angles is given by[12]

$$\frac{d\sigma}{d\Omega}=nN\left(\frac{me}{\pi\epsilon_0\hbar}\right)^2|\mu_\nu(\vec{k}_1^{\parallel}-\vec{k}_0^{\parallel})|^2\left|\frac{\vec{k}_1}{\vec{k}_0}\right|\frac{1}{\cos\alpha}\frac{|\vec{k}_1^{\parallel}-\vec{k}_0^{\parallel}|^2}{|\vec{k}_1-\vec{k}_0|^4}\ , \tag{1}$$

where $\vec{k}_0$, $\vec{k}_1$ and $\vec{k}_0^{\parallel}$, $\vec{k}_1^{\parallel}$ are the wave vectors and their surface components of the incident and scattered electrons, respectively, α is the angle of incidence, and $\mu_\nu(\vec{q}_\parallel)$ is the normal component of the dipole matrix element in a primitive cell for a one-phonon excitation ν with wave vector $\vec{q}_\parallel=\vec{k}_1^{\parallel}-\vec{k}_0^{\parallel}$. For the bare mode $S_1(\overline{M})$ we may write[12]

$$\mu_\nu(\vec{q}_\parallel)=\sum_i e_i\xi(\vec{x}_i),\quad i=1,2\ , \tag{2}$$

where $\vec{x}_i$ is the position vector, e_i is the effective charge, $\xi(\vec{x}_i)=\xi_0\exp(i\vec{q}\,'_\parallel\cdot\vec{x}_i)$ is the displacement field of the surface ion core i in the basis, and $\vec{q}\,'_\parallel$ is the wave vector in the substrate SBZ. Close to $\overline{\Gamma}$ for (i) and (ii) above we get

$$\begin{aligned}&\text{(i)}\quad |\mu_\nu(\vec{q}_\parallel)|\approx|(e_1+e_2)\xi_0|\ ,\\&\text{(ii)}\quad |\mu_\nu(\vec{q}_\parallel)|\approx|e'\xi_0\vec{q}_\parallel\cdot(\vec{x}_1-\vec{x}_2)|,\\&\qquad\qquad e'=e_1'=-e_2'\ .\end{aligned} \tag{3}$$

Hence for small $\vec{q}_\parallel$, $d\sigma/d\Omega$ will be strongly suppressed in the symmetry-forbidden case (ii); $|\vec{q}_\parallel\cdot(\vec{x}_1-\vec{x}_2)|^2<0.01$ for the experimental conditions in this work.

The symmetry group of the bridge site configuration (iii) is a symmorphic space group with C_{2v} as the point group. Figure 2(b) shows the extended basis for one of the two possible orientations. The bare mode $S_1(\overline{M})$ belongs to symmetry class B_1 with respect to C_{2v} and by the same arguments as in the previous case the dressed mode is symmetry forbidden to be dipole active.

Hence it is only the on top configuration that is compatible with the assignment of the dipole active low-energy loss as the dressed mode $S_1(\overline{M})$. This conclusion is consistent with the LEED analysis of the Cu(100)-$c(2\times2)$CO system.[13]

We now turn to another example of a $c(2\times2)$ adsorbate structure, that of CH_3O on Cu(100). From his EELS measurements Sexton[7] concluded that the CH_3O species formed on Cu(100) were adsorbed with the oxygen end towards the metal substrate. Figure 3 shows the lower-energy range of the EELS spectrum for the Cu(100)-$c(2\times2)CH_3O$ system recorded at 80-K substrate temperature. The 38- and 125.5-meV loss peaks correspond to the CuO and the CO stretching vibrations, respectively, of the adsorbed CH_3O species. Angular measurements reveal that both these modes are dipole excited. We would then expect the dressed mode $S_1(M)$ to be dipole active for adsorption in the on top configuration. There is, however, no corresponding low-energy-loss peak discernible in the EELS spectrum and the symmetry argument thus strongly suggests that the CH_3O species adsorb in a more open substrate site than CO does. The low CuO stretching frequency observed supports this picture. The EELS spectrum for the Ni(100)-$c(2\times2)$O system[14] shows a similar appearance as that for Cu(100)-$c(2\times2)CH_3O$, i.e., no low-energy loss corresponding to $S_1(\overline{M})$ is observed. This is in accordance with our symmetry argument since oxygen is known to adsorb in the fourfold hollow site (see references in Ref. 1).

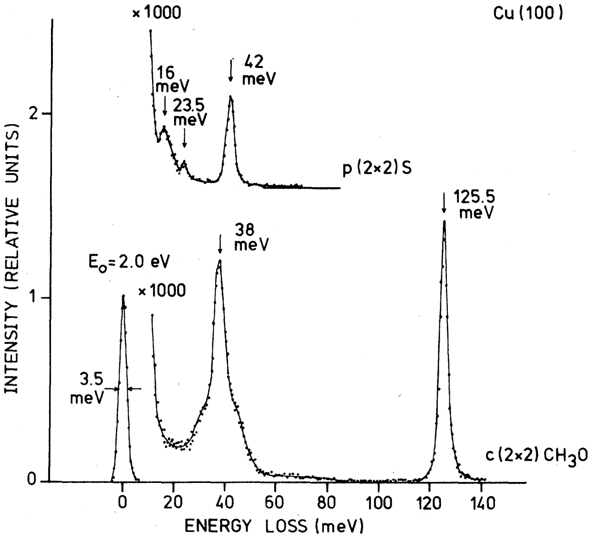


FIG. 3. Electron-energy-loss spectra from the $c(2\times2)CH_3O$ and $p(2\times2)$S structures on Cu(100). Conditions as in Fig. 1.

We will finally consider the Cu(100)-$p(2\times2)$S system. The corresponding EELS spectrum recorded at 300-K substrate temperature is shown in Fig. 3. In analogy with the Ni(100)-$p(2\times2)$S system[1] we interpret the 42-meV loss peak as the CuS stretching vibration for S adsorbed in the hollow site configuration. For the $p(2\times2)$ adsorbate lattice both the $\overline{X}$ and $\overline{M}$ points of the substrate SBZ are equivalent to the $\overline{\Gamma}$ point of the $p(2\times2)$ system SBZ [see Fig. 2(a)]. Applying the same arguments as given above for the bare surface phonon modes in the *first* Cu layer, one predicts, for the hollow site configuration, one loss originating from $S_6(\overline{X})$ [see Fig. 2(c)].[4] At the $\overline{X}$ point in the substrate SBZ there are no symmetry restrictions for the mode $S_5(\overline{X})$ to be strictly localized in the *second* layer[4] and the $p(2\times2)$S layer can then couple to $S_5(\overline{X})$ via the first copper layer. This is symmetry allowed for the hollow site configuration. $S_6(\overline{X})$ is found at 24.5 meV in the Cu(100) slab calculation[5] and $S_5(\overline{X})$ is presumably located near the bottom of the bulk band which is at 14 meV. These phonon energies agree reasonably well with the experimental loss energies 23.5 and 16 meV, respectively.

We conclude by noticing that important knowledge about adsorption sites can be obtained from simple arguments concerning the symmetry properties of the surface phonons and the symmetry of the adsorption sites. In more complex structural situations lattice dynamical calculations will be required to resolve ambiguities concerning mode frequencies.

We want to thank N. V. Richardsson and R. Ryberg for valuable suggestions during the course of this work, which was supported by the Swedish Natural Science Research Council.

---

[1] S. Andersson, Surf. Sci. 79, 385 (1979).

[2] W. Erley, H. Wagner, and H. Ibach, Surf. Sci. 80, 612 (1979).

[3] H. Ibach and D. Bruchmann, Phys. Rev. Lett. 44, 36 (1980).

[4] R. E. Allen, G. P. Alldredge, and F. W. de Wette, Phys. Rev. B 4, 1661 (1971).

[5] D. Castiel, L. Dobrzynski, and D. Spanjaard, Surf. Sci. 59, 252 (1976).

[6] S. Andersson, *Vibrations at Surfaces* (Namur, Belgium, 1980) (in press).

[7] B. A. Sexton, Surf. Sci. 88, 299 (1979).

[8] J. L. Domange and J. Oudar, Surf. Sci. 11, 124 (1968).

[9] E. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Phys. Rev. 155, 619 (1971).

[10] E. Wigner, in *Symmetry in the Solid State,* edited by R. S. Knox and A. Gold (Benjamin, New York, 1964), p. 173.

[11] We assume that the overlayer causes a weak perturbation of the bare mode so the dressed mode is well defined.

[12] E. Evans and D. L. Mills, Phys. Rev. B 5, 4126 (1972).

[13] S. Andersson and J. B. Pendry, Phys. Rev. Lett. 43, 363 (1979).

[14] S. Lehwald and H. Ibach, in *Proceedings of the International Conference on Vibrations at Surfaces, Namur, Belgium, 1980* (in press).