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Vibrations of adsorbed alkali-metal atoms: Na on Cu(111)

S.-Å. Lindgren, C. Svensson, and Lars Walldén
Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

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Vibrations of alkali-metal atoms adsorbed on a metal surface are observed by electron-energy-loss spectroscopy. From the loss intensity recorded for Na on Cu(111) a dynamic dipole charge of 0.5*e* is obtained at low alkali-metal coverage. The dynamic dipole charge is found to decrease gradually with increasing coverage making the loss peak due to Na vibrations difficult to observe for coverages above approximately half of a full monolayer.

As prototype examples of simple chemisorption systems, alkali-metal atoms adsorbed on metals have been studied extensively.[1] According to the standard picture, which has emerged from the previous work, the alkali-metal valence level becomes broadened and largely emptied as the atom is adsorbed. Evidence for the charge transfer comes mainly from the strong work-function reduction observed at low coverage implying a large induced dipole moment. In a couple of cases substrate derived states, which accommodate transferred electrons, have been identified.[2]

In previous work it has often been assumed that due to the rather empty *ns* level the adsorbate has a considerable net positive charge. However, in a series of recent articles[3-5] it has been concluded that the adsorbate is strongly polarized but essentially neutral at all coverges. This conclusion is based on self-consistent electronic-structure calculations that reproduce the work-function change typical of alkali-metal-atom adsorption: a rapid decrease to a minimum and then, on continued deposition, some increase which saturates at around full monolayer coverage. One concern in a discussion of the bond is that it is not always clear how to distinguish, based on a calculated charge distribution, between a strongly polarized adatom and one from which charge has been transferred but only a short distance. Experimentally, core-level binding energies are often measured to get information on charge transfer. For adsorbed alkali-metal atoms there are cases where core-level binding energies or excitation thresholds are higher at low than at high coverage indicating a more ionic adsorbate at low coverage.[6-10] There are, however, also systems for which no binding-energy shifts are recorded when the coverage is changed.[11,12] For a W(110) substrate the recent observation of a surface core-level shift, which remains constant when alkali-metal atoms are adsorbed, was interpreted in terms of neutral adatoms.[13] Yet another way to probe the character of the bond is to put the adatom in motion and find out to what extent the screening charge moves together with the core. For an adsorbate with an ionic character one expects that the charge producing the dynamic dipole at vibration frequencies is of the same order as the charge producing the static dipole, while for a nearly netural adsorbate the dynamic charge is expected to be small compared with that of the ionic case.

Here we use electron-energy-loss spectroscopy to obtain information on the vibrations of the Cu(111)/Na adsorption system. Samples are prepared by evaporation of the alkali metal from a heated breakseal ampoule onto a Cu(111) substrate which is cleaned by argon-ion bombardment (500 eV) followed by heating (625 K). After Na has been deposited the spectra recorded with a Leybold ELS23 spectrometer show a peak at 21-meV loss energy (Fig. 1). The angle of incidence is 60° and the primary energy 5 eV. The loss intensity measured in the specular direction passes a maximum at around 20% of full monolayer coverage [Fig. 2(a)]. Coverages are obtained from the evaporation times using as a reference the time needed to make the work-function change saturate, which is assumed to occur at around full monolayer coverage. If, as in Fig. 1, the coverage Θ is given as the ratio between the number of adsorbed atoms and the number of atoms in the outermost substrate layer, then Θ is close to 0.5 at full monolayer coverage. The work-function change is measured by the diode method. During deposition the pressure is around 6×10^{-11} mbar and during measurement around 3×10^{-11} mbar. Under these conditions approximately 1 h of measuring time is available be-

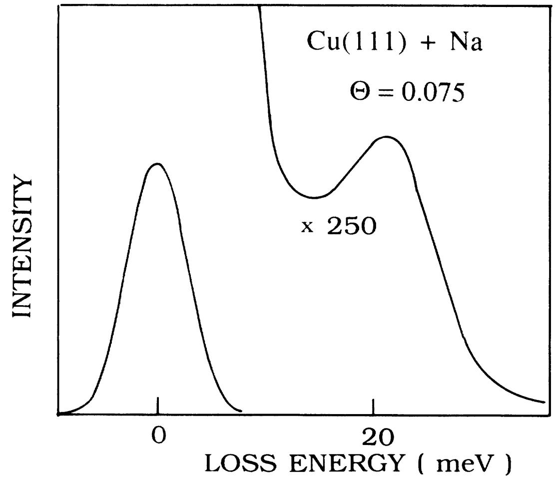

FIG. 1. Electron energy-loss spectrum recorded in the specular direction with 5-eV primary electron energy and 60° incidence angle from Cu(111) covered by 20% of a full monolayer of Na. The peak at 21-meV loss energy is associated with Na vibrating normally to the substrate.

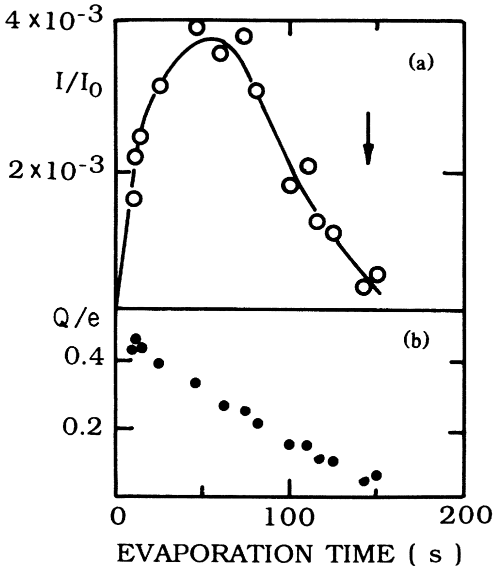

FIG. 2. (a) The intensity of the loss peak I relative to the intensity of the elastic peak I_0 for Na covered Cu(111) plotted against the Na coverage given as the evaporation time. The vertical arrow indicates the evaporation time necessary to produce the work-function minimum. A saturated monolayer is obtained after approximately 350s evaporation time. (b) The dynamic dipole charge derived via dipole scattering theory from the intensities shown in the upper panel.

fore a peak due to contamination appears at ~37 meV loss energy.

We associate the 21-meV loss energy with Na atoms vibrating in the direction perpendicular to the substrate. From the measured loss intensity combined with dipole scattering theory one may determine a dynamic dipole moment μ and an effective dynamic charge Q related via $\mu = Q(h/2M_r\omega)^{1/2}$, where M_r is the reduced mass. Using an approximate expression for the intensity[14-16] and assuming that the reduced mass can be approximated by the mass of the Na atom we obtain $Q = 0.5e$ at low Na coverage. The experimental parameters necessary for this determination are the incidence angle (60°), the acceptance angle (1.5°), and the primary energy (5 eV). When the same expression is used at higher coverage one obtains a dynamic dipole moment which drops almost linearly with increasing coverage [Fig. 2(b)]. An extrapolation to zero dynamic dipole moment of a line drawn through the points in the diagram gives a coverage somewhat higher than needed to produce the work-function minimum.

It is interesting to compare the experimentally obtained Q value with calculations of how the induced static dipole moment varies with the distance between substrate and adsorbate. Results of such calculations are available for Na adsorbed on $r_s = 2$ jellium[17] and for Li on jellium with $r_s = 2.0$, 2.65, or 3.28.[18] A characteristic feature for the alkali-metal adsorbates is the linear dependence of the induced dipole moment on the adatom-substrate distance z over a wide distance range. The Li results indicate that the slope $d\mu/dz$ is not very sensitive to the jellium density. For Na on $r_s = 2$ jellium, Lang and Williams[17] obtain a value for the slope which corresponds to an effective charge of around 0.4e.

From the work-function change $e\Delta\Phi$ measured at low coverage, a static dipole moment μ_s of around 0.9 e Å is obtained from $\Delta\Phi = n\mu_s\epsilon_0^{-1}$ if n is the surface density for the adsorbate. The calculated equilibrium distance for Na adsorbed on $r_s = 2$ jellium is 1.6 Å outside the jellium edge.[3,17] For a real substrate one should compare this distance with the distance between the adatom and a plane drawn half an interlayer separation outside a plane through the outermost substrate atoms. From low-energy electron diffraction (LEED) data for $c(2\times2)$Na on Ni(100) (Refs. 19 and 20) a value of ~1.4 Å is obtained. With distances in this range one thus obtains a static dipole charge of roughly 0.6e. The static and dynamic charges are thus not very different. The low energy-loss intensity at high monolayer coverage suggests that the dynamic charge of the dipole is small at high coverage. For high coverages the adsorbate thus behaves as expected for an essentially neutral particle.

Although the present description of the adsorbate is different from that given by Ishida[4] the values calculated by him are of considerable interest as far as more well-defined quantities are concerned than the net charge of the adsorbate which depends on the atomic volume considered. Of particular interest is the estimate made for the vibration frequency of Na adsorbed on a slab of jellium with the density of Al. According to the present measurement the frequency remains constant as the coverge is changed to within an experimental uncertainty of around 1 meV. The adsorption energy of alkali-metal adsorbates typically decreases by around a factor of 2 as the coverage is increased[21,22] and one would expect the vibration frequency to reflect this change of adsorption energy. However, according to Ishida's calculations, the coverage dependence of the adsorption energy is as strong as that observed and yet the vibration frequency, which is estimated to be ~17 meV, is found to decrease only slightly with increasing coverage.[3]

In conclusion, Na adsorption on Cu(111) produces a characteristic loss of 21 meV for backscattered low-energy electrons with a maximum loss intensity at around 20% of full monolayer coverage. From dipole scattering theory a dynamic charge of around 0.5e is obtained at low coverage if it is assumed that the loss is due to excitation of Na vibrations perpendicularly to the surface and that the reduced mass of the oscillator is the mass of Na. The dynamic charge decreases almost linearly with increasing coverage reaching to an extrapolated zero charge at around 60% of full monolayer coverage. The ionic character of the adsorbate at low coverage is indicated by the facts that the charges producing the static and dynamic dipoles are of similar size and that each charge is a considerable fraction of an elementary charge.

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