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Coverage-dependent frequency for Li-atom vibrations on Cu(111)

S.-Å. Lindgren, C. Svensson, L. Walldén, A. Carlsson, and E. Wahlström
Physics Department, Chalmers University of Technology, Göteborg, Sweden

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Electron-energy-loss spectra recorded for monolayer amounts of Li adsorbed on Cu(111) show a loss peak associated with Li vibrations perpendicular to the substrate. The loss energy shifts from 38 meV at low coverage to 43 meV at 0.3 ML and remains constant for coverages between 0.3 and 0.5 ML. The loss intensity passes a maximum at a Li coverage of 0.15 ML and gradually decreases such that it is difficult to resolve a loss peak at coverages above 0.5 ML. The high loss energy indicates that the adatom resides on the surfaces rather than in substitutional sites. The frequency shift is much too large to be explained by dipole-dipole interactions. The above results are obtained with the evaporation source loaded with the natural Li isotope mixture (92.6% ^{7}Li, 7.4% ^{6}Li). Measurements with ^{6}Li show that the increase of the vibration frequency with increasing coverage is not an isotope effect. [S0163-1829(96)09439-8]

I. INTRODUCTION

Alkali metals adsorbed on metal substrates attract interest as prototype examples of simple chemisorption systems and as examples of simple metal quantum-well systems.[1–3] Of practical interest is the low work-function values obtained and the strong modification of adsorptive properties often found when metal surfaces are covered with submonolayers of alkali metal.[1] Present interest is furthermore stimulated by the observation of unexpected sites, on top or substitutional, for alkali-metal atoms adsorbed on low index surfaces of noble and transition metals as well as on Al.[4–8] Recently, also some vibrational properties of alkali-metal overlayers have been studied. With electron-energy-loss spectroscopy (EELS) the frequency and loss intensity for adatom-substrate stretch vibrations have been measured at different monolayer coverages for a few systems.[9–14] Using He-scattering the frequency of lateral oscillations has been determined as well as the frequencies of the organ-pipe-like modes of a-few-atomic-layers-thick alkali-metal films on a metal substrate.[15,16]

Two characteristic features of the previous EELS data for Na and K on Cu(111) are a nearly coverage-independent vibration frequency and a strongly coverage-dependent loss intensity. The latter passes a maximum at a low coverage of around 0.15 ML, and decreases to a low level for coverages above half of a full monolayer of alkali metal. This intensity variation reflects the changing character of the electronic structure of the adlayer as the coverage changes and is of interest for the current discussion regarding how the adatom-substrate bond is best described at different coverages,[17] for example, whether at low coverage the adatom is to be regarded as partly ionic or as neutral but strongly polarized.

Given the strong coverage dependence for properties such as the desorption energy, which decreases considerably with increasing coverage,[18] it is surprising that the vibration frequency remains nearly constant when the adsorbed amount is changed. The main motivation for the present EELS study of Li on Cu(111) is to find out whether a constant stretch frequency is a common feature of alkali metals adsorbed on a close-packed surface. Previous results for Li on Cu(110) revealed a sizeable upwards shift of the frequency, from 33 to 35 meV, upon changing the coverage between zero coverage and 0.3 ML while no shift was noted when Na was adsorbed on the same surface.[10] A complication with the Cu(110)/Li system is that the surface reconstructs. Another reason for our interest in Li as adsorbate is that the size of the atom ought to make it more likely than for Na and K that the atom assumes a similar substitutional site as found for the lighter alkali metals on Al(111).

II. EXPERIMENT

The electron-energy-loss spectra are recorded with a Leybold ELS 22 spectrometer using samples prepared by Li evaporation at a slow rate (200 sec/ML) onto a Cu(111) crystal cleaned by Ar-ion bombardment and heating. The spectra are obtained in the specular direction at an incidence angle of 60°, a primary energy of 5 eV and with the sample usually held at room temperature (RT). Spectra obtained with the sample cooled to 160 K gave loss energies and loss intensities similar to those recorded at RT and shown below. Li is evaporated from a Mo crucible which fits into an aluminium oxide oven tube wrapped with Ta foil to reduce heat losses and placed inside a water-cooled stainless steel tube. After outgassing of the source in a separate vacuum chamber at temperatures somewhat higher than used for the evaporation, the Li could be evaporated at a pressure of around 2×10^{-10} mbar in the measuring chamber, which has a base pressure of 5×10^{-11} mbar. After each deposition the source is isolated from the main chamber by a straight-through valve. For samples prepared in this manner there is little evidence of contamination during the first two hours. This gives time to measure loss spectra for one or two different coverages in one experimental run. As discussed previously for Na and K, residual water vapour is a main source of contamination and strongly affects the loss spectrum.[19] Most of the measurements were made with the evaporation source filled with natural Li, which contains 7.4% ^{6}Li. To check for possible isotope effects loss spectra were also recorded for the lighter isotope.

The work function changes upon Li deposition at RT is

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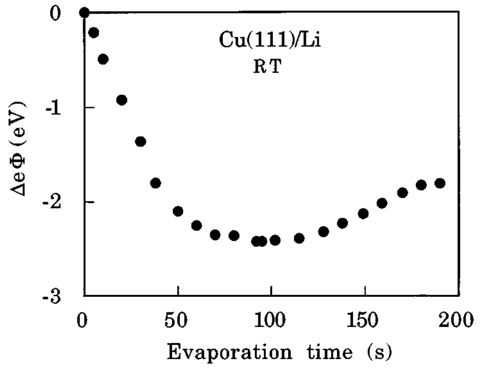

FIG. 1. Work-function change upon deposition of Li on Cu(111) plotted against Li evaporation time.

measured by the diode method using the monochromator of the spectrometer to produce the incident electron beam.

III. RESULTS

Upon deposition of Li atoms on Cu(111), the work function shows the coverage dependence typical for alkali-metal adsorption on metals. There is first a rapid, then slower decrease to a minimum, which occurs at around half of full monolayer coverage (Fig. 1). This is followed by an increase by around 0.6 eV to a value which remains nearly constant upon continued deposition. The coverage values given below are based on the assumption that saturation of the work-function change occurs at full monolayer coverage. The maximum reduction of the work function is 2.4 eV and at saturation it is 1.85 eV. Since the work function of Cu(111) is 4.95 eV the full monolayer value corresponds to a work function of 3.1 eV, slightly higher than the value reported for Li (2.9 eV).[20]

In Fig. 2 are shown energy-loss spectra for different Li coverages on Cu(111). The numbers by the curves give the Li coverages in monolayers. As the Li coverage is increased a Li-adsorption-induced loss peak shifts from a loss energy of 38 meV at low coverage to around 43 meV for coverages above 0.3 ML (Fig. 3, filled circles). These are the loss energies measured for natural Li, which contains 92.6% ^{7}Li and 7.4% ^{6}Li. With 95% ^{6}Li in the evaporation source a similar shift in loss energy is observed as the coverage is increased (Fig. 3, open circles).

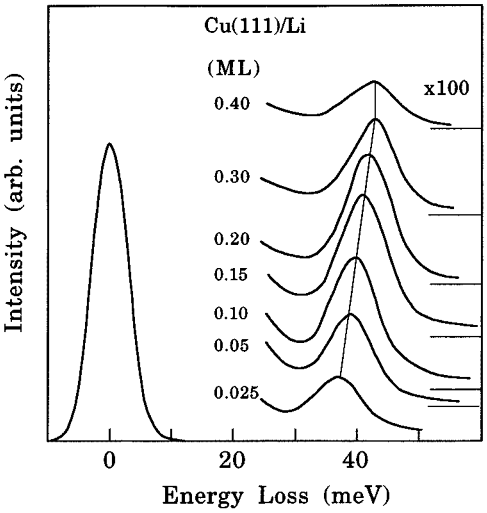

FIG. 2. Electron-energy-loss spectra for Cu(111) covered by different amounts of Li indicated in the diagram. The numbers by the curves give the Li coverage in monolayers.

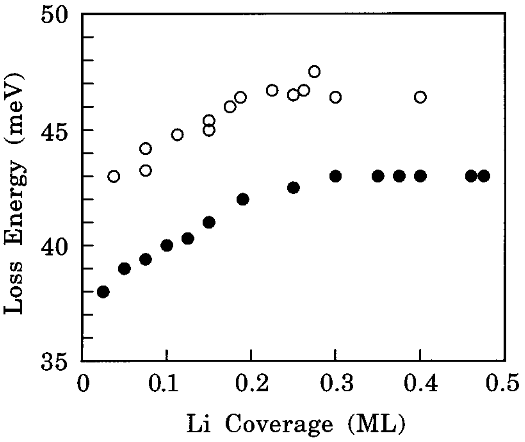

FIG. 3. Loss energy vs Li coverage for Cu(111)/Li for the natural Li isotope mixture (filled circles) and for ^{6}Li (open circles).

The coverage dependence for the relative loss intensity of the Li-Cu stretch vibration is shown in Fig. 4. For low Li coverages the loss intensity increases rapidly and passes a maximum at around 0.15 ML. If the deposition is continued the loss intensity decreases almost linearly with Li coverage and for coverages above half of a full atomic layer it is difficult to resolve a loss peak.

If the sample is left in the experimental chamber for several hours contamination by residual gases produces a strong change of the loss spectrum (Fig. 5) with an intense loss peak appearing at 64 meV and a shift of the Li induced loss peak from 40 to 36 meV. For Na on Cu(111) it was shown that a corresponding loss peak observed in that case is due to adsorption of water vapor.[19] For Cu(100)/Li exposed to residual water vapor a strong loss peak at 74 meV loss energy was assigned to LiOH standing upright on the surface with the Li end down.[12]

IV. DISCUSSION

The similarity of the work-function change induced by Li adsorption to that observed for Na, K, and Cs indicates that

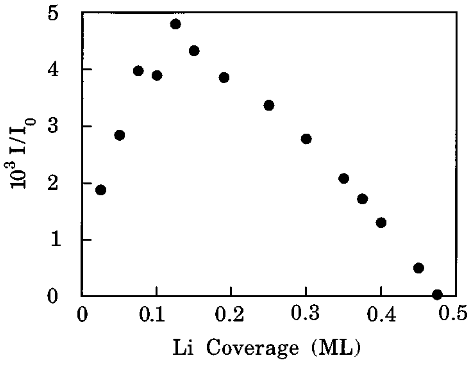

FIG. 4. Relative loss intensity vs Li (natural isotope mixture) coverage for Cu(111)/Li.

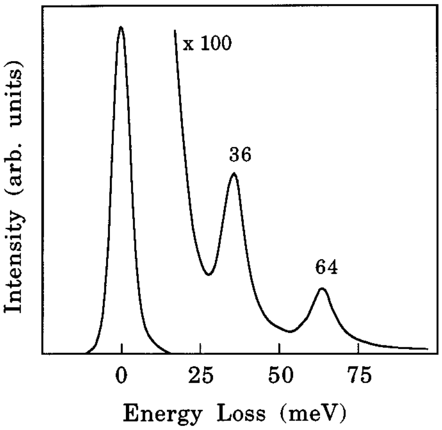

FIG. 5. Electron-energy-loss spectrum for Cu(111) covered by 0.13 ML of Li recorded 28 h after the evaporation. A peak due to contamination appears at 64-meV loss energy and the Li-adsorption-induced loss peak has shifted to a loss energy of 36 meV from a value of 40 meV immediately after Li deposition.

also Li resides on top of the substrate rather than in substitutional sites. This view is supported also by the high loss energy. For Li on Al(111) the alkali atom is adsorbed in substitutional sites and then a much lower loss energy (18 meV) is observed.[13] The fact that the coverage dependence of the work function is similar to that observed for the heavier alkali metals furthermore indicates that Li atoms are also uniformly distributed on the substrate surface at low and intermediate monolayer coverages. From the slope at low coverage of the coverage dependence of the work function one obtains a value for the Li dipole moment of 0.9 eÅ. Recently, by low-energy electron diffraction Li has been found in substitutional sites for Cu(111)/Li.[21] The disruption of the substrate surface, however, occurs at higher coverages than those probed here. At RT substitution is observed only if full monolayer coverage is exceeded.

The loss energy and the intensity of the Li-adsorption-induced loss peak suggests that it is due to the excitation of adatom vibrations perpendicular to the surface. An extrapolation to zero coverage of the loss energies measured with different amounts of Li on the surface gives a loss energy of 38 meV. The loss energies measured for Li (38 meV), Na (21 meV) and K (13 meV) means that for $\omega^2 M$, where M is the mass of the alkali-metal atom, nearly equal values are obtained for Li and Na while the value is 30% lower for K. The different value of $\omega^2 M$ for K may be due to a different adsorption site for K. We note that for the heavy alkali-metal atoms the preferred site at high monolayer coverage is on top of the substrate atoms rather than above hollows. This is observed for Cu(111) as well as for Ni(111).[4,22–25]

In qualitative terms the vibration frequency and the intensity depends on the coverage as expected when dipole-dipole interactions are important. According to theory[26] the frequency is given by the expression

$$\omega^2=\omega_0^2+\frac{Q^2\Sigma}{M_r(1+\alpha_e\Sigma)}, \tag{1}$$

where Q is the dynamic charge, α_e is the electronic polarizability, and M_r is the reduced mass. Σ is a lattice sum $\Sigma_{ij}(1/r)_{ij}^3$, which for a hexagonal lattice is equal to $8.9n^{3/2}$ where n is the surface density of atoms. For the loss peak intensity one obtains[26]

$$\frac{I_{\text{loss}}}{I_{\text{el}}}=\frac{\pi\hbar}{2a_0E\cos\theta_1}(1-2\vartheta_E)^{1/2}F(\vartheta_C)\frac{Q^2}{M_r\omega}\frac{n}{(1+\alpha_e\Sigma)^2}, \tag{2}$$

where $\vartheta_E=\hbar\omega/2E$, E is the primary energy, and θ_1 is the incidence angle. a_0 is the Bohr radius and $F(\vartheta_c)$ depends of the incidence angle, the primary energy, and the loss energy. By measurement of both the loss energy and the intensity one should then be able to determine the dynamic charge and the polarizability at different Li coverages. However, the agreement between theory and experiment is only apparent since unreasonable values are obtained for the dynamic charge and the polarizability if the above expressions are used. The reason for this is that the measured frequency shift is far too large to be explained by the dipole-dipole interaction for values of the dynamic charge of the order of unity. Some other mechanism must therefore be responsible for the frequency shift. In the low coverage limit the dynamic charge can instead be determined from the loss intensity since the dynamic screening factor, $1+\alpha_e\Sigma$, is then close to unity. The value obtained in this way, $0.4e$, is of the same order as the values determined for Na $(0.5e)$ and for K $(0.6e)$. These values agree well with theoretical estimates obtained from the derivative $d\mu/dz$ of the induced dipole moment μ with respect to the distance, z of the alkali atom above the surface of an $r_s=2$ jellium[27,28] or of Al(111).[17]

The most interesting observation in the present work is thus the large frequency increase with increasing coverage. Total-energy calculations for alkali-metal atoms on a jellium substrate indicate a shift in the direction opposite to the observed.[29] The fact that the present frequency shift is too large to be ascribed to dipole-dipole interactions and that no similar shifts are observed for Na and K suggests that the mechanism behind the shift is particular for Li. One difference with Li is that the adatom vibrates with a frequency above the upper limit of the substrate phonon spectrum. The more decoupled motion for Li ought to mean that the thus-far-presented theoretical estimates should be more relevant for Li than for the heavier alkalis. However, this is obviously not the case.

The observed frequency shift for Li could possibly be an isotope effect. As this was not anticipated, most of the measurements were made with the evaporation source loaded with natural Li. For the lighter isotope one expects a frequency approximately 3 meV higher than that for ^{7}Li. The low content of ^{6}Li (7.4%) should make the corresponding loss peak intensity small at low Li coverage. At high coverage the situation may be different. Infrared absorption measurements of CO stretch frequencies for isotope mixtures show that the excitation probability is far from proportional to the content at coverages high enough for the excitation to jump from one molecule to another.[30,31] One observes a transfer of absorption intensity such that already at a content of 4% of ^{12}C^{16}O and 96% ^{12}C^{18}O the absorption intensity is approximately the same for the two modes at full monolayer coverage. The degree of intensity transfer depends on the dynamic charge, the frequency difference and the width of the absorption lines. In the present case the observation of similar shifts for natural Li and ^{6}Li (Fig. 3) demonstrates that the frequencies are well enough separated that the intensity transfer is unimportant, at least for coverages below 0.5 ML.

Regarding frequencies, we finally note that the observation of an upward shift with increasing alkali-metal coverage is not unique for Li. Recently such a shift was reported for Cs adsorbed on Ru(0001),[14] a case where the isotope effect discussed above is not important. The relative increase for Ru(0001)/Cs is even larger (30%) than for Cu(111)/Li (13%) and also for Cs very large values for the dynamic charge are required in order to account for the shift using the expression given above. With reasonable values chosen for dynamic charge and polarizability the authors estimate that dipole coupling explains approximately 25% of the observed shift. He and Jacobi[14] suggest that an important contribution to the shift comes from a delocalization of the mode with substrate atoms becoming increasingly involved as the coverage increases. Since the Li frequency is appreciably higher than the substrate frequencies this mechanism should be more important for heavier alkali metals, which disagrees with the observation of nearly coverage-independent frequencies for Na and K on Cu(111). The experiments made so far thus give examples of either a quite strong or a very weak coverage dependence for the characteristic loss energy. In either case the behavior is not easily explained.

The gradual decrease of loss intensity as the Li coverage exceeds 0.2 ML is ascribed to the transformation from a partly ionic adsorbate at low coverage to a metal overlayer with an electron density at full monolayer coverage nearly equal to that of bulk Li. For the metal monolayer the field from the incident electron will be screened, and this explains the low loss intensity at high monolayer coverage. For the screening to be efficient it is sufficient that frequencies in the range of the loss frequency are screened. The screening will therefore be important already at quite low valence electron densities outside of the alkali-metal ion cores. This may explain in qualitative terms why the vibrational loss is suppressed already at half of full monolayer coverage.

Our final comment concerns the spectral change due to contamination, which as in previous experiments is likely due to residual water vapor. When Na- and K-covered Cu(111) is exposed to water vapor the loss spectrum shows two loss peaks at low loss energy (18 and 36 meV for Na, and 13 and 26 meV for K).[19] For water-vapor exposed Na this means that the low-energy component is at 3 meV lower loss energy than the mode observed when there is only Na on the surface while for K the energy of the low-energy loss is practically unaffected by the exposure. As discussed previously the doublets observed upon water-vapor exposure can be explained in terms of NaOH and KOH molecules standing upright on the surface with the alkali end down. For the present system the two loss peaks observed, at 36 and 64 meV, for the presumably water-vapor-exposed surface are too close in energy to be characteristic of LiOH molecules with this orientation. In a recent Cu_4-LiOH cluster calculation simulating adsorption on Cu(100) loss energies of 10 and 100 meV are estimated for the Cu-Li and Li-OH stretches, respectively, for LiOH standing upright on the surface.[32]

V. CONCLUSIONS

The electron-energy-loss spectrum for Li on Cu(111) shows a loss peak ascribed to Li vibrations perpendicular to the substrate. The loss energy surprisingly increases and by a large amount, from 38 meV at low Li coverage to 43 meV at 0.3 ML. The observation of similar shifts for natural Li and ^{6}Li shows that the shift is not an isotope effect characteristic of isotope mixtures with a small separation between isotope shifted frequencies. The loss intensity shows the coverage dependence characteristic of alkali-metal adsorbates with a strong intensity for the loss peak only when the Li coverage is below half of a full atomic layer. The dynamic charge obtained from the loss intensity recorded at low coverage $(0.4e)$ and the static charge obtained from the work-function change are sizeable and similar in magnitude, indicating that the adsorbed Li atom can be described as partly ionic at low coverage. The loss energy, the loss intensity, and the Li-induced work-function change show that the Li atoms reside on the substrate surface and not in substitutional sites when the Li coverage is in the monolayer range.

ACKNOWLEDGMENT

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