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High-Resolution Electron Energy Loss Spectroscopy of Cs Vibration on the Ru (0001) Surface *

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By using a newly implemented high-resolution electron energy loss spectrometer with better resolution, a new loss at a energy near to double energy of the Cs-Ru stretching vibration, and its dependence on Cs coverage for Cs overlayer on Ru (0001) were observed. Since the energy is slightly smaller than the double energy of the Cs-Ru vibration (intrinsic loss), overtone excitation must be responsible for this new loss observed, but two-phonon process is not excluded.

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Alkali metal (AM) adsorption on transition metal surfaces is considered as a simple model system which attracted much interest in surface physics.[1,2] An AM atom is very electropositive, and forms an ns-derived resonance upon approaching the metal surface. It has the tendency to transfer its valence electron to the metal surface during adsorption. With the increasing AM coverage, the ns-derived resonance shifts downward and becomes increasingly filled because of the lateral interaction introduced by the surrounding adatoms, and finally a full metallic overlayer is formed.

While the electronic and structural properties of these systems have been extensively studied, only little is known about the vibrational properties of these systems.[3-9] Recently, we reported a very large upward shift in energy of Cs-Ru vibration with Cs coverage.[9] Size and direction of this shift are not understood yet. From the known decrease of the Cs-Ru bond strength with coverage[10-12] one would expect a decrease of the Cs-Ru stretching frequency opposite to what is observed.[9]

In this contribution we report on high-resolution electron energy loss spectroscopy (HREELS) measurements for Cs overlayers on Ru (0001) with a newly implemented HREEL spectrometer. A new loss at an energy near to double energy of the Cs-Ru stretch vibration (intrinsic loss) was observed, for the first time, for this kind of AM on metal system. Compared with the intrinsic loss, this new loss has different coverage dependence in intensity. Based on the energy difference from the double energy of the Cs-Ru stretch vibration, we attributed this new loss to overtone excitation. However, since the energy difference is samll, two-phonon process is not excluded, yet.

The experiments were carried out in an ultrahigh-vacuum apparatus (in Fritz-Haber-Institut der MPG, Berlin, Germany) with a base pressure of 1×10^{-11} mbar. The apparatus is described elsewhere.[13] In brief, it consisted of two chambers. The upper one contained an argon-ion gun, a quadrupole mass spectrometer, a low-energy electron diffraction (LEED) optics, and a Cs effusion cell for sample preparation; the lower one housed a recently implemented HREEL spectrometer (DELTA 0.5, Vacuum Science Instruments, Germany). HREEL spectra were taken at a 60° angle of incidence with respect to the surface normal and in specular geometry. The primary energy was 4.0 eV, and the energy resolution 1.9 meV. Typically, count rates in the elastic peak of about 3×10^5 counts per second were achieved. Submonolayer Cs coverages were achieved by an appropriate choice of the annealing temperature of the substrate covered by a full monolayer of Cs at room temperature.[10] These values were cross-cheched with the loss energy as a function of coverage from Ref. 9.

The Cs overlayer on Ru (0001) is characterized by lateral repulsive interaction giving rise to a liquid-like behavior and ring-like diffraction patterns in LEED for submonolayer coverages, and locking into commensurate adsorption sites at appropriate coverages, e.g., for $\theta_{Cs} = 0.25$, a (2×2) LEED pattern is formed.[10] Figure 1 exhibits HREEL spectra for submonolayer coverages of Cs adsorbed on Ru(0001) at 300 K. The most prominent loss features around 8 meV are due to the Cs-Ru stretching vibration perpendicular to the surface.[9] The loss energy shifts upwards and reaches a maximum at $\theta_{Cs} = 0.19$. The loss intensity increases with coverage, and decreases again at larger coverages. The decrease in intensity is due to a nearly linear decrease of the dynamic charge involved in the vibration.[9] At $\theta_{Cs} = 0.25$ the Cs-Ru mode is not observable any longer, since the Cs overlayer achieves metallic conductivity in lateral direction which screens any dipole fluctuation. The energy-gain peaks of the Cs-Ru mode can also recognized at negative loss energies. Their intensity is a measure of the occupation of the first excited state at given sample temperature of 300 K.

The new and most remarkable result of Fig. 1 is the observation of the new losses of the Cs-Ru stretch mode at about 17 meV, indicative for an excitation from the ground state ($n = 0$) to the second excited

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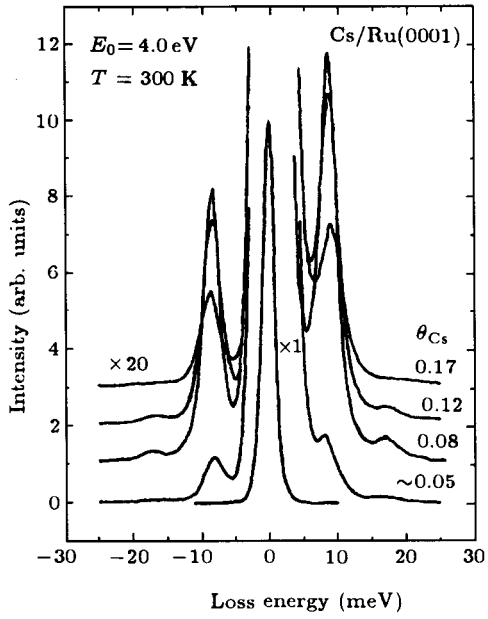

Fig. 1. HREEL spectra for a Ru(0001) surface covered by different amounts of Cs. The parameter is the Cs coverage θ_{Cs}. The first curve from the bottom is measured at a Cs coverage $\theta_{Cs} = 0$, which shows the peak of the elasitically scattered electrons with a sensitivity factor of ×1. Primary energy of the electrons and surface temperature T are indicated.

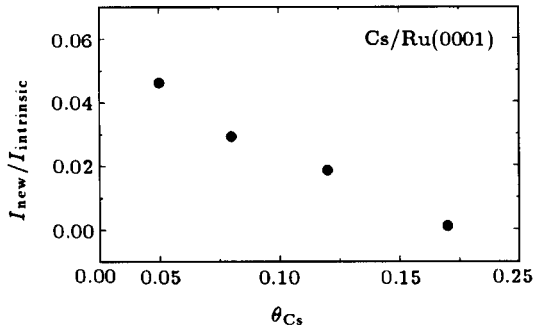

Fig. 2. Intensity ratio of the new loss to intrinsic loss as a function of Cs coverage θ_{Cs} for submonolayer amounts of Cs on a Ru(0001) surface.

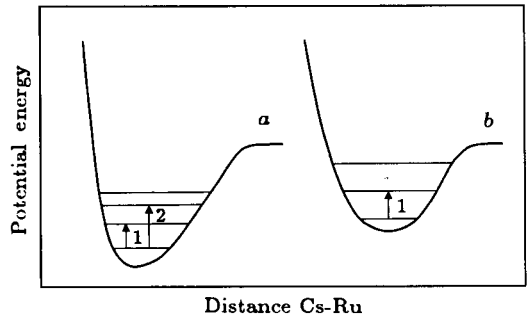

Fig. 3. Schematic potential energy curves perpendicular to the Ru surface for low (curve *a*) and high (curve *b*) Cs coverage, where 1: intrinsic, and 2: overtone excitation are also indicated.

state ($n = 2$). The three spectra for $\theta_{Cs} = 0.05$, 0.08, and 0.12 show clearly this kind of excitation. Even at the energy-gain side, the peaks associated with the new losses can be clearly seen. Since the HREEL spectra were taken in specular geometry, only dipole active mode is allowed. For a harmonic oscillator, the direct excitation from the ground state to the second excited state ($n = 2$), i.e., the two-quantum transition is dipole forbidden, since the matrix element of the normal coordinate between $n = 0$ and $n = 2$ levels vanishes. Therefore, these new losses must be overtone excitation, or excitation via two phonon process. For an anharmonic oscillator, the anharmonic term gives rise to non-vanishing matrix element between $n = 0$ and $n = 2$ states (overtone excitation), while excitation via two phonon process is also through multiple scattering even for harmonic potential. By applying some curve fitting and background subtraction, the energy of this new loss, e.g., at 17.0 meV for $\theta_{Cs} = 0.08$, is slightly smaller than double energy of intrinsic loss $2 \times 8.6\,\text{meV} = 17.2\,\text{meV}$. Thus the overtone excitation must be responsible for those new losses observed. But the two-process cannot be excluded, because the energy difference is small.

Another interesting point in Fig. 1 is the change in intensity with Cs coverage for this new loss. The new loss peak cannot be observed any longer in the HREEL spectrum for $\theta_{Cs} = 0.17$. By subtracting background, and integrating the peak area, the intensity ratio of the new loss to the intrinsic loss is calculated, and the change of this ratio with Cs coverage is shown in Fig. 2, apparently, the changes in intensity for the new and the intrinsic loss have different coverage dependence. The ratio decreases with increasing Cs coverage and approaches zero at $\theta_{Cs} = 0.17$.

Considering this new loss as related to overtone excitation, one can immediately recognize that such a change in intensity implies coverage dependent change of potential energy. The potential energy changes from anharmonic to harmonic with coverage, e.g., at $\theta_{Cs} = 0.17$, the Cs oscillator becomes nearly harmonic where no overtone excitation appears. From thermal desorption spectroscopy[10–12] it is known that the bond energy decreases with coverage. Assuming simple first-order kinetics it changes from 2.2 eV at $\theta_{Cs} \approx 0$ to 1.7 eV at $\theta_{Cs} = 0.17$. Based on above discussion, the potential energy curve has been sketched in Fig. 3, where intrinsic excitation and overtone excitation are also indicated. At lower Cs coverage, the potential is anharmonic (curve *a* in Fig. 3), while at higher coverage, it becomes harmonic (curve *b* in Fig. 3).

The change of potential energy curve may also explain the large (30%) upward shift of the loss energy with θ_{Cs} which we observed recently.[9] The lateral dipole coupling effect[14,15] leads to a shift into the same direction, but the size of this effect is expected to be only in the percent region. Therefore, dipole coupling alone cannot account for the observed size of the shift. Even the change of the reduced mass with Cs coverage, which is the response of the substrate to the

vibration of the adatoms, is not enough to explain the total upward shift.[9] Only when the potential energy curve changes strongly as sketched in Fig. 3 the additional upward shift in the intrinsic loss energy with coverage can be explained.

Now the question arises of why the character of the Cs-Ru bond changes so strongly with coverage. The lateral interaction between Cs adatoms in repulsive which results in a decrease of adsorption energy with Cs coverage.[10–12] The origin for the shape change of potential energy curve with Cs coverage may be related to the change of the local structure in which both AM adatom and the substrate surface are involved.

In the following, we discuss briefly on the evidences relevant to the structure change of AM-metal adsorption. Up to now, very little is known about the change of the AM-metal bond length with AM coverage, since most of the structural investigations were carried out only for one or two coverages of the corresponding long-range-order phases. Only a few studies have focused on the change in bond length with AM coverage, e.g., for the systems K/Ni(111),[16] K/Ni(100),[17] Rb/Al(111),[18] and Cs/Ag(111).[19] While for the first three systems no coverage dependence were detected within the limit of error,[17] the Cs-Ag bond length was reported to increase by 0.3 Å when the AM-coverage increased from 0.15 to 0.30.[19] For Cs/Ru two structures have been determined: for $\theta_{Cs} = 0.25$, the LEED pattern is of (2×2) symmetry, and the Cs atoms occupy top-sites, while for $\theta_{Cs} = 0.33$, the LEED pattern is $\sqrt{3}$ symmetry, and the Cs atoms are shifted to threefold hollow sites.[10] The Cs-Ru layer distance does not change within the limit of error. For small Cs coverages where the bond changes as we reported above, nothing is known about the structure. The Cs overlayer in this coverage region has 2D liquid-like behavior, and LEED study can not be used to determine the structure.

In the case of Li adsorption on Cu(110),[7,8] the total upward shift with Li covergage is about 10%. In order to explain this total shift, also here the change of the Li-Cu bond must be taken into consideration. To our opinion this system is similar to the Cs/Ru(0001) system and the same mechanism, i.e., change of the potential energy curve, is involved for the following reason. The energy of the Li-Cu mode lies above the Cu phonon bands whereas for Cs/Ru it lies in the lower part of the phonon spectrum. In both cases the interaction with the substrate phonon bands is weak and the supposedly undistorted AM-metal vibration is observed.

In conclusion, we carried out HREELS measurements for the system of Cs/Ru(0001), observed a new loss, and the change in intensity for this new loss for an AM on metal systems for the first time. Since the energy of this new loss is slightly smaller than the double energy of the Cs-Ru stretch vibration (intrinsic loss), it must be associated with overtone excitation due to anharmonicity. But the two-phonon process is not excluded, because the energy difference is small. Meanwhile, the results showed strong coverage dependence of the Cs-Ru bond, i.e., change of the potential energy curve with Cs coverage, which accounts for the large upward shift in vibrational energy measured for some AM oscillators on metal surfaces reported previously.[7,9] Due to low Cs-Ru stretch frequency and the resulting weak coupling to the Ru phonon bands, we consider this system as a prototype for AMs on transition metal surfaces. It would be worth starting an *ab-initio* calculation for this system which is vibrationally characterized by this work.

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