PHYSICAL REVIEW B VOLUME 53, NUMBER 7 15 FEBRUARY 1996-I

Vibrational analysis of cesium on Ru(0001)

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(Received 11 July 1995)

We report a high-resolution electron-energy-loss spectroscopy study of the coverage dependence of the Cs-Ru stretch vibration at 300 K. Surprisingly, the frequency of Cs-Ru stretch vibration shifts upward by about 30% with Cs coverage for $0 \leqslant \theta_{Cs} \leqslant 0.19$. Only a quarter of this shift can be explained through lateral dipole-dipole interaction. We discuss two further mechanisms that may cause the other part of the shift. A slight decrease of the stretch frequency for $\theta_{Cs} > 0.19$ is associated with the metallization of the alkali-metal layer including a structural change.

Alkali-metal (AM) overlayers on transition metal (M) surfaces attracted much interest in surface physics since they have been considered as simple examples of adsorption on surfaces.[1–5] An AM atom is very electropositive, forms an ns-derived valence resonance upon approaching the metal surface, and has the tendency to transfer its valence electron to the metal surface during adsorption. With increasing AM coverage, the ns-derived resonance shifts downward and becomes increasingly filled because of the depolarization introduced by the surrounding adatoms, and finally, a full metallic overlayer is formed. Recently, it was shown in a calculation for AM adsorption on Al(111) (Refs. 6 and 7) that there is an induced charge at the interface between the AM and the metal substrate as a response of the metallic substrate which screens the partially ionized AM atom. The latter calculations are in full agreement with the pioneering work of Lang and Williams,[4] and support the Langmuir-Gurney model of ionic bonding[1,2] at least for the zero-coverage limit.

Whereas electronic properties of the AM on metal systems have been extensively studied,[8] knowledge about the vibrational properties of these systems is very scarce.[9–15] Here we report results of a high-resolution electron-energy-loss (HREELS) investigation on the Cs stretch vibration of the system Cs/Ru(0001). The frequency of the Cs-Ru stretch shifts upward with Cs coverage below $\theta_{Cs}=0.19$, and then shifts downward. The upward shift of the Cs-Ru stretch mode is very surprising since, from the strong decrease of the binding energy, one would expect an opposite shift. In the following we discuss possible explanations for this unexpected result.

The experiments were carried out in an ultrahigh-vacuum apparatus with a base pressure of 1×10^{-11} mbar. The apparatus consisted of two chambers. The upper chamber 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 chamber housed a high-resolution electron-energy-loss spectrometer (HREELS) for recording vibrational spectra, which was developed and mounted at the laboratory of Ibach.[16] HREEL spectra were taken at a 60° angle of incidence with respect to the surface normal and in specular geometry if not mentioned otherwise. The primary energy was 1.5 eV, and the energy resolution was 3.8 meV. Typically, count rates in the elastic peak of about 3×10^5 counts per second were achieved. Sample mounting and preparation has already been described elsewhere.[17]

The Cs overlayer on Ru(0001) is characterized by lateral repulsive interaction giving rise to a liquidlike behavior and ringlike diffraction patterns in LEED, and locking into commensurate adsorption sites at appropriate coverages, e.g., for $\theta_{Cs}=0.25$, a (2×2) LEED pattern, and for $\theta_{Cs}=0.33$ a $\sqrt{3}$ LEED pattern (monolayer) is formed.[18,19] Figure 1 shows some typical HREEL spectra for Cs adsorbed on Ru(0001) at 300 K. The loss peaks associated with the Cs-Ru stretch mode, located between 6.6 and 8.9 meV, increase in intensity with coverage for smaller coverages, and decrease again for larger coverages. As can be seen from Fig. 1, the energy-gain

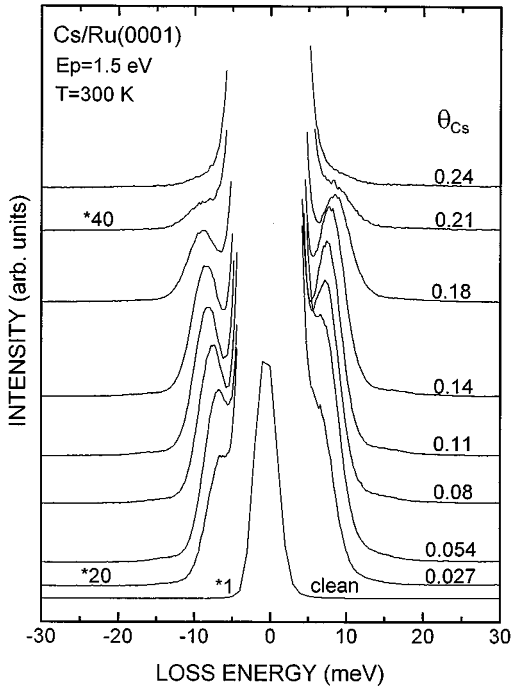

FIG. 1. HREEL spectra for a Ru(0001) surface. The parameter is the Cs coverage θ_{Cs}, which is the number of Cs atoms relative to the number of surface atoms. Primary energy E_P and sample temperature T are indicated. The incidence angle of the electron beam is 60° with respect to the surface normal, and the reflected beam is analyzed.

0163-1829/96/53(7)/3658(4)/$06.00

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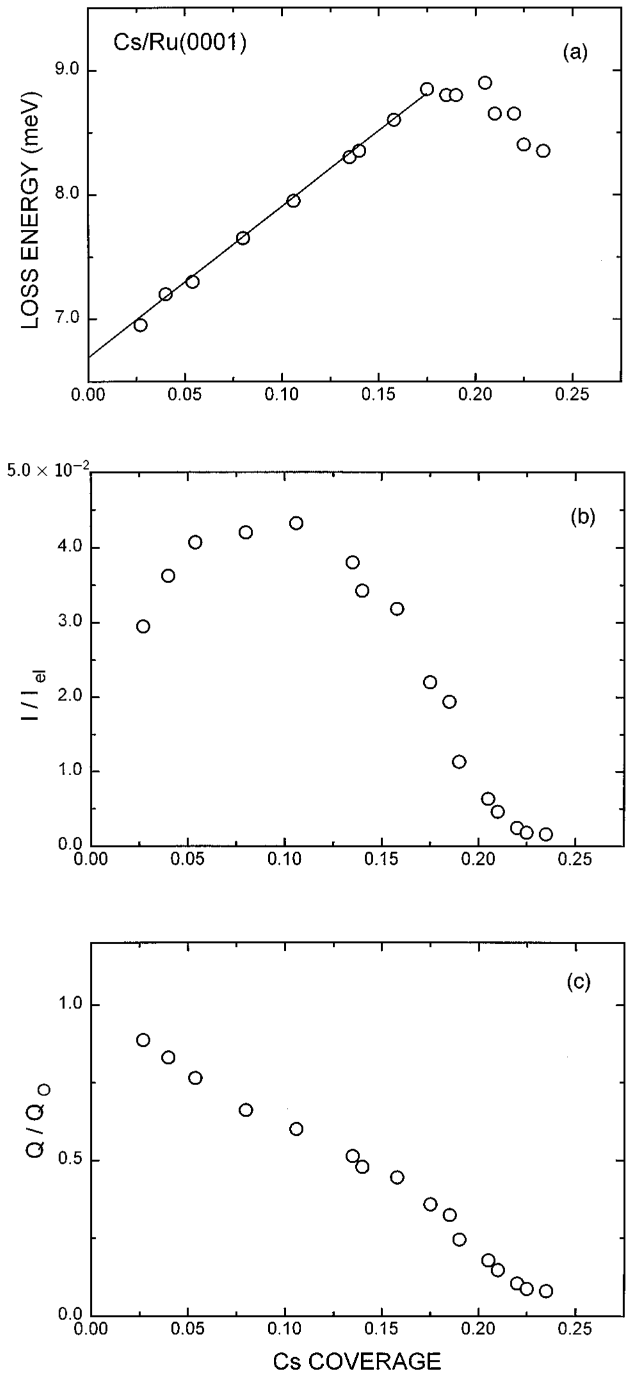

FIG. 2. (a) Loss energy of the Cs-Ru vibrational mode vs Cs coverage for Cs/Ru(0001). (b) Intensity of the Cs-Ru stretch vibration relative to the intensity of the elastic peak for the same surface. (c) Relative dynamic charge Q/Q_0 (see text).

peak of the Cs-Ru stretch mode (at negative loss energy) is also observed at 300 K. The relative intensities of energy-loss and -gain peaks are in good agreement with the value calculated from the vibrational energy and sample temperature.

Figures 2(a) and 2(b) show the vibrational energy and intensity of the Cs-Ru stretch mode as a function of Cs coverage. These data are obtained by fitting the HREEL spectra using a standard deconvolution technique and Gaussian line shapes. The vibrational energy $\hbar\omega$ is taken as the average of loss and gain peak positions. Using the measured loss intensity, one can determine a dynamical dipole moment μ from dipole-scattering theory.[20–23] An effective charge Q can then be calculated from $\mu = Q(\hbar/2M_r\omega)^{1/2}$, with M_r being the reduced mass.[22] Figure 2(c) shows the calculated effective charge as a function of coverage. Here a rigid Ru substrate is assumed, i.e., $M_r = M_{\mathrm{Cs}}$, and the following experimental parameters are used: the incidence angle (60°), the half-angle of acceptance (1.5°), and the primary energy of 1.5 eV. The effective charge $Q_0 = 1.1e^-$ is determined from extrapolation with $\theta_{\mathrm{Cs}} \to 0$.

It is interesting to compare the dynamic charge Q_0 with the charge of the static dipole, since the same order of those charges indicates the ionic bonding characteristics of the AM-*M* bond.[11] The static dipole of 11 D (for $\theta_{\mathrm{Cs}} \to 0$) was reported based on work-function measurements.[18,24] If the image plane is set at half an interlayer separation [2.1 Å for Ru(0001)] outside the topmost substrate plane, and a Cs height of 3.15 Å, obtained from LEED data for (2×2)-Cs on Ru(0001),[19] is taken, a static charge of about $1.15e^-$ can be deduced, which is equal to the dynamic charge within the limits of error.

In Fig. 2(a), the total upward shift in frequency of Cs-Ru stretch with coverage is about 2.3 meV, i.e., the relative shift amounts to about 30%. This value is large compared to the results for the lighter alkali metals.[9–14] Based on the dipole-coupling theory,[23,25] using the parameters of electronic polarizability $a_e = 43.6$ Å^3,[24] and vibrational polarizability $a_v = Q^2/M_r\omega^2$ (Ref. 23) (for the effective charge we take Q_0) the calculated upward shift amounts to 7.5%. This leaves about 23% of upward shift to be explained.

Another effect, which can be responsible for the increase of ω_0, is the response of the substrate to the vibration of the adatoms. With coverage the stretch mode changes from a localized or resonant vibrational excitation in the zero-coverage limit to a delocalized surface mode at the full monolayer. In order to estimate the size of this effect we assume that this transition may be described as a change in the reduced mass of the adsorbate-substrate system. A maximum shift is calculated, if at the zero-coverage limit the substrate lattice is considered as rigid.[26] When a full monolayer is formed, the substrate atoms in the surface region can respond to the move of adatoms, and the adatoms, together with the substrate atoms, vibrate and form a surface dipole-active mode. If this surface mode is confined to the outermost layer of the substrate, and the same force constant is taken as for the localized mode, one can derive the following relation:

$$\omega^2/\omega_0^2 = 1 + (M_{\mathrm{ad}}/M_{\mathrm{sub}})\,\theta_{\mathrm{ad}}, \tag{1}$$

where ω_0 is the frequency at the zero-coverage limit. Substituting the masses of Cs and Ru, and the coverage of 0.19 into this formula, an upward shift of about 12% can be calculated. This indicates that about half of the total upward shift can be explained by a change in a response of the substrate atoms. One recognizes that this effect is smaller than the total shift.

There is still about one-third of the total upward shift to be explained. We believe that a change of the force constant of the AM-*M* bond is responsible for the remaining part. In general, an increase of the force constant implies a strengthening of the bond between the adsorbate and substrate. But the alkali-metal adsorption energy decreases largely with coverage,[18,19,24] which implies a bond weakening with coverage. It is apparent that the force constant, i.e., the curvature of the potential energy well and the adsorption energy, have different coverage dependencies, which is confirmed by HREELS measurements for Li, Na, and K on copper surfaces for which no downward shifts were observed.[10–13] It seems that any missing decrease in stretching frequency, despite a strong decrease of the binding energy, is a general phenomenon of the AM-M bond. Qualitatively this may be explained by a change of the curvature of the AM-M potential-energy surface near to its minimum. At small coverages the screening charge may be laterally more extended than at higher coverages, giving rise to a rather flat potential and a low stretch frequency.

The change in vibrational energy at $\theta_{\rm Cs}=0.19$ [Fig. 2(a)] is associated with the onset of the overlayer metallization, since a decrease in ω is expected for a lateral interaction of the Cs atoms. At $\theta_{\rm Cs}=0.25$ the Cs layer is ordered within a 2×2 structure[18,19] and is metallic, as can be recognized from the fact that the Cs-Ru stretch mode intensity approaches zero at this coverage. Any dipole fluctuation becomes screened out at this point, and electronic excitations become observable.[27] Interestingly, at $\theta_{\rm Cs}=0.19$ the 2×2 LEED pattern begins to be seen.[18,19] Therefore, we believe that within some small patches a 2×2 structure is formed in which the Cs atoms are close enough to overlap laterally with their wave functions and develop a metallic state. These patches grow until, at $\theta_{\rm Cs}=0.25$, the adlayer is completely metallic. The patches below $\theta_{\rm Cs}=0.25$ need not be static, but may fluctuate in time and location. It is known from LEED intensity analysis that Cs sits in on-top positions at this coverage, i.e., the change in slope at $\theta_{\rm Cs}=0.19$ seems to be connected with the moving of the Cs atom to the on-top position.

In the case of Li adsorbed on Cu(110),[13] the total upward shift is about 10%, to which the lateral dipole-dipole interaction contributes about 3%. Therefore, a shift of about 7% was left to be explained. If the coverage is set to 1, the calculated upward shift arising by the response of the substrate layer to the Li-overlayer is about 5%. This implies that, in order to explain the total shift, the change of force constant should also be taken into consideration. Surprisingly, no upward shift with coverage was found for Na and K on Cu(110).[10,13] The reason for this may be the strong interaction between the AM-M mode and the surface resonance on Cu(110).[13] The adsorbate-induced reconstruction also makes those systems more complicated.

In this paper we have studied some most important aspects of the vibrational behavior of the Cs/Ru(0001) surface. The upward shift of the Cs-Ru stretch frequency by 30% for $0\leqslant\theta_{\rm Cs}\leqslant0.19$ is discussed in terms of three different effects. The dipole-dipole interaction contributes by 7.5%, and the response of the substrate surface layer by 12%. The remaining 10% may be due to an increase of the curvature of the potential-energy surface near to the equilibrium position. We argue that this may be due to a lateral squeezing of the screening charge with increasing coverage. For these reasons, in general, a constant or even increasing AM-M stretch frequency is observed, although the AM is thermally strongly destabilized at higher coverages. Generally one expects that the AM-M stretch mode becomes softer when the AM atoms interact laterally. Such a decrease in frequency is observed for $\theta_{\rm Cs}>0.19$. We believe that the metallization starts locally at $\theta_{\rm Cs}=0.19$. Interestingly, at this coverage a first indication of the 2×2 structure appears, so that the change in shift at $\theta_{\rm Cs}=0.19$ may also be connected with the move of the Cs atoms to the on-top position, which is found in the 2×2 structure at $\theta_{\rm Cs}=0.25$.

We believe that the Cs/Ru(0001) system is a very important prototypical alkali-metal-on-transition-metal adsorption system which we have now characterized vibrationally, and which awaits a theoretical modeling in the near future.

We are grateful to P. Geng and H. Dietrich for technical assistance, and to Dr. Hongyue Shi who contributed to early measurements on this system.

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