Surface phonons on Al(111) surface covered by alkali metals

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We investigated the vibrational and structural properties of the Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-AM (AM = Na, K, Li) adsorbed systems using interaction potentials from the embedded-atom method. The surface relaxation, surface phonon dispersion, and polarization of vibrational modes for the alkali adatoms and the substrate atoms as well as the local density of states are discussed. Our calculated structural parameters are in close agreement with experimental and *ab initio* results. The obtained vibrational frequencies compare fairly well with the available experimental data.

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I. INTRODUCTION

Studies of alkali-metal (AM) adsorption on metal surfaces have been of considerable interest for several decades. This is partly related to the important technological applications of these systems due to the promoter effects of alkali adsorbates in heterogeneous catalysis and the adsorption-induced change of the work function. On the other hand, these investigations have played an important role in understanding of the nature of the adsorption mechanism.¹⁻³ For the most part, there have been experimental and theoretical studies devoted to the alkali-metal adsorption on aluminium rather than on any other substrate.⁴⁻¹⁵ The main common feature of these adsorption systems is that they have different structures at low temperatures and at room temperature. This is due to the fact that at room temperature the adsorption process involves a temperature-activated vacancy formation on the surface, and the adsorbate atoms occupy these vacancies to form ordered substitutional structures. The same structures also occur if the adatoms are adsorbed at low temperature and the substrate subsequently is heated to room temperature.² This transition is irreversible, indicating that the low-temperature structures are metastable.

A large amount of work has been devoted to the adsorption of 1/3 ML of AM on the Al(111) surface. In addition to the experiments and theoretical calculations that focused on the electronic properties of the adsorbate-induced ordered phases such as surface band structure and surface density of states over a wide range of coverage,^{6,16} their structural characteristics such as adsorbate-induced surface relaxation and adsorbate-substrate bond length were intensively investigated by different experimental techniques.^{4,9-13} It was shown by using surface extended x-ray-absorption fine structure (SEXAFS) measurements,⁴ that at room temperature Na atoms occupy sixfold-coordinated sites substituting the surface Al atoms. However, due to the mismatch of the atomic radii the substitution is not perfect and the Na adlayer lies above the substrate. This conclusion has been confirmed by a detailed low-energy electron-diffraction (LEED) analysis of the system⁹ as well as by the normal-incidence standing x-ray wavefield adsorption (NISXW) study^{10,11} and

is also supported by the high-resolution soft x-ray photoelectron (core-level) spectroscopy (SXPS).¹² The direct evidence that at room temperature the ordered Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Na phase is realized has been obtained by a scanning-tunneling microscopy (STM) of the Na adsorption behavior.¹³ The substitutional adsorption for 1/3 ML of lithium on the Al(111) surface was first suggested by Nagao *et al.*¹⁷ from measurements of the vibrational spectrum of this system. Then, using low-energy electron-diffraction measurements¹⁸ it was shown that Li adsorption leads to the formation of a binary surface alloy Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Li which structure was found to be qualitatively the same as the corresponding Na phase. The similar results have also been obtained for 1/3 ML of potassium on the Al(111) surface.^{5,7,14,15,19} The only difference is that for Li the structure is more substitutional than for the larger alkali metals because of the smaller radius. The experimental results have been supported by *ab initio* total energy calculations based on the density-functional theory.^{4,6,7,14} For Na, the calculations showed that the substitutional adsorption with ($\sqrt{3} \times \sqrt{3}$)R30° periodicity is energetically favorable due to the low vacancy formation energy. The reason has been attributed to the substrate effect: the formation of an in-plane covalent bonding between the top-layer Al atoms. An analysis of the electronic structure of the reconstructed surface^{6,16} showed that in the case of the ordered Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Na phase the Al-Na interaction dominates and the adsorbates are more ionic due to the enhanced screening by the substrate electron density. Unlike the Na results, the calculated adsorption energies for K were found to be equal within the accuracy ± 0.03 eV for all the geometries considered. Therefore, the preference of the substitutional sites is less pronounced in this case and is explained as a consequence of the ionic nature of the Al-K bonding.

On the other hand, to understand the bonding in the adsorbate-induced superstructures and to study the influence of adsorbate-adsorbate interactions on the vibrational properties of the alkali-adsorbed systems Nagao *et al.*¹⁷ have investigated the coverage dependence of atomic

vibrations using high-resolution electron energy loss spectroscopy (HREELS). The observed vibrational frequencies at the $\bar{\Gamma}$ point for both Na and Li adsorbates on the Al(111) surface remained almost constant over the coverage range considered within the precision of 0.3 meV. This was explained in terms of the screening of adsorbate-adsorbate interactions by the substrate Al electron density that suggests the substitutional character of adsorption for these system.^{6,16} Nagao *et al.*²¹ have also carried out a detailed experimental investigation of the surface phonon dispersion for Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Na along the $\bar{\Gamma}K'$ symmetry direction. They have obtained two acoustic modes: *R1*, with a frequency of 12.5 ± 0.2 meV at the $\bar{\Gamma}$ point and a strongly dispersing mode *R2* above the bulk phonon edge. Another surface localized mode has been observed at the BZ boundary below the bulk continuum. The obtained results were interpreted in terms of semiempirical lattice dynamical model based on the first-neighbor force constant fitted to the bulk empirical data. The phonon mode at the $\bar{\Gamma}$ point was assigned to a resonance characterized by motion of adatoms (Na, Li) along the normal (*Z*-polarized) to the surface. The vibrational modes of alkalis on Al(111) have also been studied by inelastic He-atom scattering (HAS) technique.²² The measurements were performed for various Na and K adsorption structures including $(\sqrt{3} \times \sqrt{3})R30^\circ$. As a common feature, almost constant energy vibrational modes were observed for all the geometries considered. This implies weak lateral adatom interaction and agrees well with the previous works.^{6,16,17} There are two theoretical calculations for Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Na.^{6,20} Ishida and Morikawa²⁰ considered the Na adsorption on a jellium with the electron density of Al to study the structural and vibrational properties over a wide coverage range. The stretching frequency of the Na-jellium bond which corresponds to the vibration of all the adatoms in phase relative to the substrate has been obtained from the curvature of the total energy as a bond length function at the equilibrium. In contrast to the experimental results this frequency was found to decrease monotonously with increasing coverage. This discrepancy can arise from the simplified structure of the surface. Another theoretical study, the *ab initio* pseudopotential calculation, was performed by Neugebauer and Scheffler,⁶ who considered the vibration of adatoms against a rigid substrate. They have evaluated the adsorption energy as a function of adsorbate height above the unrelaxed Al(111) surface and then estimated the stretching frequency of the adatom vibration normal to the surface.

Thus, in spite of the fact, that the structure of the Al(111) surface with 1/3 ML coverage of alkali metals has been investigated in detail, there is no comprehensive understanding of their vibrational properties. In this paper we study the phonon dispersion, polarization of vibrational modes for the adsorbate and substrate atoms, and the local density of phonon states of the ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase formed by the alkali-metal atoms (Na, K, and Li) on the Al (111) surface. We also evaluate equilibrium crystal structure for these systems.

II. COMPUTATIONAL METHOD

The calculations are performed using the embedded atom method (EAM).²³ The parameters of the method are deter-

FIG. 1. The atomic structure of the Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -alkali metal (Na, Li, and K) substitutional adsorbed systems (side view as a central projection on the $[11\bar{2}]$ plane). The larger and darker circles represent alkali metal atoms and light circles indicate Al atoms.

mined by fitting to experimental data such as sublimation energy, equilibrium lattice constant, elastic constants, and vacancy formation energy of the pure metals. Our EAM interatomic potentials were applied before to the calculation of phonons on the clean low-index surfaces of Al, Na, and Li.^{24–26} The pair potential component for the different alloying elements is constructed in the form proposed in Ref. 27. Using molecular-dynamics technique based on the EAM interaction potentials we first relax the adsorbed systems to the equilibrium configuration at zero temperature. The atomic structure of the Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -AM systems is shown in Fig. 1.

The calculations of vibrational characteristics are carried out in the thin film model. We used two-dimensional periodic slabs consisting of 31 layers of Al (it is sufficient to avoid interference effects) with 1/3 ML coverage of alkali metal adsorbates.

III. RESULTS AND DISCUSSION

A. Clean surface

First, we calculated the phonon spectrum of the clean Al(111) surface with $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell. The two-dimensional (2D) Brillouin zone (BZ) is shown in Fig. 2 in comparison to that of the conventional (1×1) unit cell. In this case the BZ of the clean surface and the surface with adsorbates is the same and one can directly compare the phonon band structure of the clean and adsorbate-covered surfaces.

The calculated phonon dispersion curves along the high symmetry directions of the irreducible part of BZ are shown in Fig. 3 (the surface modes are denoted by filled circles). The surface mode frequencies at high symmetry points are summarized in Table I together with the experimental Rayleigh wave (RW) frequencies. As one can see, at the $\bar{\Gamma}$ point four surface modes exist. The lower of them is a vertically (*Z*) polarized mode, the others are mainly associated with in-plane vibrations of surface atoms. The BZ, corresponding to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell (Fig. 2), is three times less than that of the conventional (1×1) unit cell. As a result of the folding, the $\bar{K}$ point of the initial BZ is reflected to the $\bar{\Gamma}$ point of the reduced BZ. So, the surface modes obtained at the $\bar{\Gamma}$ and $\bar{M}'$ points correspond to those at the $\bar{K}$ and $\bar{M}$

FIG. 2. Surface Brillouin zone for the (1×1) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface structures. The irreducible part of the BZ for $(\sqrt{3} \times \sqrt{3})R30^\circ$ is hatched.

points for the Al(111) surface with the conventional (1×1) unit cell.²⁴ As one can see the calculated RW frequency compares well with the HREELS measurements²¹ at the $\bar{M}'$ ($\bar{M}$) symmetry point and is slightly smaller than the experimental value obtained with helium-atom inelastic scattering (HAS).^{28,29} The discrepancy is larger at the $\bar{M}'$ ($\bar{M}$) than at the $\bar{\Gamma}$ ($\bar{K}$) point but does not exceed 6%. In Fig. 4 we plot the local density of states (LDOS) for the first three layers of the surface. The calculated LDOS's show features quite typical for the (111) fcc surface. In the first layer (S) there are prominent peaks around 14–18 meV for Z polarization and at 30 meV for in-plane polarization. Both peaks diminish in the second layer (S-1) and disappear in the third one (S-2). As one can see the effect of the surface is confined to the first two layers. Further we will discuss the alterations of the surface modes that are inherent to the clean Al(111) surface and appearance of new surface states due to the AM adsorption.

FIG. 3. Calculated phonon dispersion curves for Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$. The surface states are denoted by filled circles.

B. Na on Al(111)

To obtain the equilibrium structure we relaxed the surface using a molecular-dynamics method. The Na atoms were initially arranged above the sixfold sites of the relaxed Al(111) substrate in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Then the atoms were allowed to move according to the calculated forces until the equilibrium positions were achieved. The calculated bond length between the Na adatom and its nearest-neighbor Al atom, $d_{\text{Na-Al}}$, is 3.22 Å. This value compares well with the LEED result, $d_{\text{Na-Al}} = 3.21 \pm 0.01$ Å,⁹ and lies between the value of $d_{\text{Na-Al}} = 3.31 \pm 0.03$ Å found in the SEXAFS study⁴ and the values of $d_{\text{Na-Al}} = 3.10 \pm 0.06$ Å and $d_{\text{Na-Al}} = 3.21$ Å obtained by NISXW measurements^{10,11} and in the *ab initio* total energy DFT calculation,⁶ respectively. The present results also show that the effect of the Na adsorption on the outermost interlayer spacing of the substrate consists of decreasing of its magnitude in comparison with the equilibrium clean Al(111) surface. It is known that clean fcc metal (111) surfaces show very small (a few percent) changes in the outermost layer spacing.^{24,30,31} An analysis of interatomic interactions in the adsorbate induced superstructure shows that the force constants between the nearest-neighbor Al atoms from the top and the second (subsurface) atomic layers are increased by 16%–19% in comparison to the clean surface. The relative contractions of the first and second interlayer distances of the Al substrate are found to be $\Delta_{12} = -5.14\%$ and $\Delta_{23} = -0.15\%$ with respect to the bulk spacings. The values for Δ_{12} obtained in the LEED study⁹ and in the *ab initio* pseudopotential calculations⁶ are slightly smaller: -3% and -2.5% , respectively. Another structural effect induced by the Na adsorption is appearance of a small rippling $\delta_4 = 0.0017$ Å in the fourth substrate layer, where atoms located directly beneath the Na adatoms move slightly outward, while those located under the surface Al atoms have a small inward displacements. The deeper interlayer spacings remain unperturbed from the bulk value.

The calculated surface phonons for the Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Na are shown by filled circles in Fig. 5, the experimental data from Ref. 21 are depicted by open circles. The surface mode frequencies at high symmetry points are summarized in Table I. Unlike the case of the clean Al(111) surface with $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell, a few modes appear below the bottom of the bulk spectrum along the entire BZ edge. One of them is mainly connected with displacements of adsorbates along the normal to the surface and near the $\bar{M}'$ point and on moving to the zone center it couples with the in-plane motion of the top-layer Al atoms. The other is a mixed transverse mode associated with vibrations of the top-substrate and adlayer atoms in the sagittal plane like RW. Both modes are strictly localized at the surface only in the limit of the short wavelengths where they split off the bulk band and are almost dispersionless. At small wave vectors they enter the bulk phonon region and assume a resonant character. At the $\bar{K}'$ point the frequencies of these modes are 10.6 meV and 11.2 meV, respectively. As one can see from Fig. 5 they are very close to each other in energy and on moving to the $\bar{M}'$ point become almost degenerate. Experimentally, Nagao *et al.*²¹ have observed a strongly surface localized mode (S1) within the

TABLE I. Surface phonon frequencies (meV) and polarizations at the symmetry points. X, Y, Z displacements coincide with $[1\bar{1}0]$, $[11\bar{2}]$, and $[111]$ directions, respectively.

	$\bar{\Gamma}$		$\bar{K}'$		$\bar{M}'$
Clean Al(111)- $(\sqrt{3} \times \sqrt{3})$					
18.2 ^a	$(Z)_s$	13.15	$(Z)_{s,s-1}$	10.75	$(Z)_s$
18.03	$(Z)_s$	13.36	$(Z)_{s,s-1}$	16.5 ^a , 15.5 ^b	$(Z)_s$
19.73	$(XY)_s + (Z)_{s-1}$			15.50	$(Z)_s$
25.35	$(XY)_s$			15.50	$(XY)_{s,s-1}$
27.05	$(XY)_s$			24.71	$(XY)_{s,s-1}$
				30.52	$(XY)_s$
Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Na					
12.5 $\pm$ 0.2 ^b	$(Z)R1$	11.25 ^b	$(Z)S1$	9.64	$(ZY)Al_{s,s-1}$
12.4 ^c	$(Z)Na$	10.59	$(Z)Na$	9.68	$(Z)Na + (XY)Al_s$
14.5 ^d	$(Z)Na$	11.17	$(ZY)Na, Al_{s,s-1}$	11.29	$(YZ)Na, Al_{s-1,s-2}$
12.80	$(Z)Na$	12.53	$(XY)Al_{s,s-1}$	12.99	$(XY)Na, Al_s$
19.52	$(XY)Na, Al_s + (Z)Al_{s-1}$	13.23	$(XY)Na, Al_s + (Z)Al_{s-1}$	13.75	$(XY)Na, Al_s$
20.64	$(Z)Al_s$			14.64	$(XY)Al_s + (Z)Al_{s-1}$
23.74	$(XY)Na, Al_s$			24.61	$(XY)Al_{s,s-1}$
26.35	$(XY)Al_{s,s-1}$			30.03	$(XY)Al_{s,s-1}$
Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Li					
17.6–18.1 ^e	$(Z)Li$	10.63	$(XY)Al_s$	9.14	$(YZ)Al_{s,s-1}$
19.36	$(Z)Al_s + (XZ)Al_{s-1}$	11.62	$(YZ)Al_{s,s-1}$	11.17	$(Z)Al_{s,s-1}$
19.94	$(XY)Al_s + (Z)Al_{s-2}$	13.36	$(XY)Al_{s,s-1}$	12.98	$(YZ)Al_{s,s-1}$
21.30	$(Z)Li$	13.98	$(Z)Al_{s-1}$	14.06	$(Z)Li + (XY)Al_s$
25.39	$(XY)Al_s + (YZ)Al_{s-1}$	26.18	$(Z)Li + (XY)Al_s$	15.05	$(XY)Al_s + (Z)Al_{s-1}$
26.67	$(XZ)Al_{s,s-1}$			19.15	$(Z)Li, Al_s + (YZ)Al_{s-1}$
29.53	$(XY)Li, Al_s$			27.87	$(XY)Li, Al_{s,s-1}$
				31.40	$(XY)Li, Al_{s,s-1}$
Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -K					
1.78	$(XY)K$	4.34	$(Z)K$	4.43	$(Z)K$
4.22	$(Z)K$	9.31	$(X)K$	8.19	$(X)K$
18.90	$(XY)Al_s + (Z)Al_{s-1}$	9.76	$(XY)K, Al_s$	8.81	$(XY)K, Al_s + (YZ)Al_{s-1}$
20.47	$(Z)Al_s$	10.05	$(Y)K + (XY)Al_s$	10.05	$(Y)K$
24.77	$(XY)Al_{s,s-1}$	11.79	$(Z)Al_{s,s-1}$	10.38	$(Z)Al_{s-1}$
25.60	$(XY)Al_{s,s-1}$			12.61	$(YZ)Al_{s,s-1}$
				14.84	$(XY)Al_s + (YZ)Al_{s-1}$
				24.03	$(XY)Al_{s,s-1}$
				28.21	$(XY)Al_{s,s-1}$

^aReferences 28 and 29, HAS experiment.

^bReference 21, HREELS experiment.

^cReference 6, *ab initio* calculation.

^dReference 20, jellium calculation.

^eReference 17, HREELS experiment.

bulk band gap near the $\bar{K}'$ point. This mode with a frequency of about 10.8–11.5 meV near the BZ boundary³² was assigned to atomic displacements similar to the RW of the clean surface. In the HAS measurements²² along the $\bar{\Gamma K}$ direction a similar nearly constant-energy surface mode was observed away from the bulk phonon bands at energies of about 9.2 meV. The frequency obtained in the present

calculation for this mode at the $\bar{M}'$ point ($\bar{\Gamma K}$ direction) is of 9.6–9.7 meV. Thus, we have obtained two modes strongly localized at the surface region (adlayer and the top substrate layer) with energies close to the experimental values and can suppose that the obtained experimentally surface mode S1 (open circles in the figure) probably has a mixed Al-Na character.

FIG. 4. Local densities of states for Al(111)-($\sqrt{3} \times \sqrt{3}$).

Another surface mode found in the experiment²¹ and also obtained in the present calculation is a resonance *R2* extending along the $\bar{\Gamma}K'$ direction. This transverse acoustic branch is similar to the Rayleigh mode as well as *S1* but is observed above the bulk phonon edge. A similar phonon mode is obtained in our calculation along the $\bar{\Gamma}M'$ direction. It is also observed in the HAS measurements²² at approximately 1–2 meV higher than the Rayleigh curve of the clean Al(111) surface.^{28,29} Such behavior is connected with the normal (*Z*) component of the force constant between the nearest-neighbor Al and Na atoms. As follows from the analysis of the force constants this component is nonzero in the case of the adsorbate-induced superstructure unlike the clean surface since the Na adlayer is not completely embedded and lies above the top substrate atoms. This makes the *R2* mode move up into the bulk bands.

FIG. 5. Calculated phonon dispersion curves for Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Na. The surface states are indicated by filled circles. The experimental data from Ref. 21 are shown by open circles.

As in the case of the clean surface, we have obtained four surface modes at the $\bar{\Gamma}$ point. The lower one is a new adsorbate-induced acoustic mode (*R1*) which can be regarded as the backfold of the *R2* mode due to the new ($\sqrt{3} \times \sqrt{3}$)R30° periodicity. It appears only for wave vectors close to the BZ center as well as it was found in the experiment.^{17,21} This mode (*R1*) is a surface resonance which is mainly characterized by the vertical motion of adatoms. But it also involves displacements of the substrate atoms and couples with the neighboring bulk phonon modes. Its vibrational amplitude decreases slowly on moving inside the substrate. The frequency of this mode at the $\bar{\Gamma}$ point is 12.8 meV. In the experiment, Refs. 17 and 21, the surface resonant mode *R1* was observed at 12.5 ± 0.2 meV. As for the theoretical values, one of them was obtained from the jellium-model calculation²⁰ of the total energy as a function of bond length and was found to be around 14.5 meV. Another value of the stretching frequency obtained from the *ab initio* pseudopotential total energy calculation of the adsorption energy as a function of adsorbate height above the unrelaxed Al(111) surface⁶ is 12.4 meV. As one can see our result agrees well with the measured and calculated values of the frequency except for that reported for the rather simplified jellium surface structure.

The upper three modes at the $\bar{\Gamma}$ point are typical for Al(111) but unlike the clean surface, two of them have a mixed character with displacements of both Na and substrate atoms. It should be noted that almost all the surface modes found on the clean Al(111) surface remain. They only degenerate with the adsorbate phonons and assume a mixed character except for a few ones. The presence of the adsorbates also leads to a small alteration of their frequencies while their polarizations remain the same as for the clean surface. Of considerable interest is the degree to which the force constants at the clean Al(111) surface change upon the Na adsorption. The analysis of the interatomic interactions shows that the in-plane force constants between the nearest-neighbor Al atoms do not practically change whereas the interlayer force constants are increased by 16%–19% in comparison to the clean surface. The interaction between the ad-

sorbates and the nearest-neighbor substrate Al atoms is rather strong and comparable to the in-plane bonding. But the normal (Z) component of the force constant is not negligible in this case since the adsorbates lie above the top substrate atoms and the substitutional geometry is not perfect. As for the Na—Na interaction, it is very weak. The similar conclusion was derived from the electron band energy calculations of the reconstructed surface^{6,16} which showed that in the case of the ordered $\text{Al}(111)-(\sqrt{3}\times\sqrt{3})R30^\circ\text{-Na}$ phase the Al—Na interaction dominates since the Na—Na interaction is well screened by the substrate electron density.

In Fig. 6 we present the calculated local density of states for the first three layers of the $\text{Al}(111)-(\sqrt{3}\times\sqrt{3})R30^\circ\text{-Na}$ structure. For the top layer Na and Al atoms the results are shown separately. As one can see, the first and second layer Al atoms have significantly different local densities as compared to those of the clean $\text{Al}(111)$ surface. Their LDOS's without any sharp peaks are very similar to each other and show bulklike features. In addition, there is an enhancement of modes in the lower frequency range up to 8 meV compared to the clean surface. For Na, a prominent low-frequency peak with maximum displacements along the surface normal is observed. As for the in-plane vibrations of adatoms their LDOS is distributed over a large frequency range with a small peak at 23–24 meV.

C. Li on $\text{Al}(111)$

Like in the previous case, we first relaxed the $\text{Al}(111)-(\sqrt{3}\times\sqrt{3})R30^\circ\text{-Li}$ structure to obtain the equilibrium geometry. After relaxation, Li atoms and nearest-neighbor substrate atoms have a distance of $d_{\text{Li-Al}}=3.10$ Å. This result is in reasonable agreement with the value of $d_{\text{Li-Al}}=2.88$ Å obtained in the LEED study.¹⁸ The adsorption of Li also leads to decreasing in the first interlayer spacing of the substrate compared to the clean $\text{Al}(111)$ surface in agreement with the experimental data.¹⁸ The calculated relative contractions of the first and second interlayer spacings of the substrate are the follows: $\Delta_{12}=-5.10\%$ and $\Delta_{23}=-0.18\%$ with respect to the bulk value. They are close to those obtained in the case of Na adsorption. The experimental value of $\Delta_{12}=-2\pm 1\%$.¹⁸ Like in the previous case a small rippling $\delta_4=0.0016$ Å in the fourth layer of the substrate is observed. The deeper interlayer spacings are the same as in the bulk.

The calculated phonon dispersion curves for the $\text{Al}(111)-(\sqrt{3}\times\sqrt{3})R30^\circ\text{-Li}$ are shown in Fig. 7. As one can see from Table I, at the $\bar{\Gamma}$ point we have obtained an adlayer localized resonance with vertical polarization at a frequency of 21.3 meV. A similar mode at the $\bar{\Gamma}$ point was observed by Nagao *et al.*¹⁷ in the HREELS measurements at about 18 meV. Like the case of sodium, new surface modes appear beneath the bulk phonons but they are localized on the substrate. The modes associated with vibrations of Li adatoms shift towards the higher energies due to the reduced mass of the Li atoms and most of them couple with the motion of substrate atoms. In Fig. 8 one can see the local density of states. While the LDOS's for the subsurface (S-1) and the next Al layers are very similar to those obtained in the case of Na adsorption the densities of states for the top layer Li

FIG. 6. Local densities of states for $\text{Al}(111)-(\sqrt{3}\times\sqrt{3})R30^\circ\text{-Na}$.

and Al atoms differ substantially. In this case we have a pronounced peak at 16–20 meV for vertically polarized Al(S) modes which is similar in shape to the corresponding peak for the clean $\text{Al}(111)$ surface (Fig. 4) but is shifted to higher frequencies. An enhancement of lower frequency modes is also observed as in the case of Na. It is a common

FIG. 7. Calculated phonon dispersion curves for Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Li. The filled circles show the surface states.

feature for all the adsorbed structures considered. For the local density at the adlayer, now one can see two prominent peaks. One of them corresponds to the normal vibrations of adatoms and the other is connected with Li displacements within the surface plane. Both peaks are shifted to higher frequencies pointing a stiffening of the corresponding force constants compared to the case of Na.

D. K on Al(111)

The calculation of the equilibrium position showed that the nearest-neighbor Al-K distance amounts to 3.67 Å. This result is in good agreement with $d_{K-Al}=3.58$ Å obtained by LEED measurements⁵ and the DFT calculation values of 3.70 Å (Ref. 6) and 3.48 Å.³³ The main difference with the previous cases is a larger distance of K adatoms above the surface. As a consequence the adsorbate-substrate interactions become weaker. On the other hand we obtain the stronger interaction between adsorbates (K-K). From the force constant analysis it follows that the Al-K interaction is 4.5 times less than the Al-Al one. This agrees well with the data from the electronic structure calculations^{6,16} which indicate a less efficient substrate-mediated screening in the case of K. The relative contractions of the first and the second interlayer Al spacings are $\Delta_{12}=-4.15\%$ and $\Delta_{23}=-0.13\%$ with respect to the bulk distance. In contrast to the adsorbed Na and Li we did not obtain the fourth layer rippling due to the higher adsorbate position and as a consequence the weaker adsorbate-substrate interaction.

The calculated phonon dispersion curves are shown in Fig. 9. Like in the previous cases, there is a surface mode in the $\Gamma K'$ and $\Gamma M'$ directions which follows the clear substrate RW but is located above the bulk phonon edge. A similar mode was observed in the HAS measurements.²² The vertically polarized adlayer mode at the Γ point was obtained at a frequency of 4.22 meV. We also estimated its frequency from the analysis of the force constants and atomic masses. A similar mode for Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Na was obtained at a frequency of 12.80 meV. The normal component of the force constant between K and the nearest-neighbor substrate atom is approximately 5.3 times less than in the case of Na.

FIG. 8. Local densities of states for Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Li.

The K atomic mass is 1.7 times as large than the mass of Na. Hence, the vertical frequency of K adatoms on the Al(111) substrate must be approximately 3 times softer than that for Na atoms as we indeed obtain in the present phonon calculation. As a common feature, the K adsorption results in arising new surface modes beneath the bottom of bulk

FIG. 9. Calculated phonon dispersion curves for Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -K. The filled circles show the surface states.

phonons. Thus, over the entire BZ, except the area of small momenta, an almost dispersionless low-frequency mode is observed. It is strongly localized in the adlayer and is caused by vertical vibrations of the adsorbates. The next group of three modes with close frequencies is associated with in-plane vibrations of potassium and top-layer Al atoms. The lowering of the in-plane polarized modes localized on the substrate atoms (compared to the Na or Li adsorption) is connected with the softening (12%) of the force constants responsible for the Al-Al in-plane interaction for Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -K while in the cases of Na and Li adsorption they do not practically change compared to the clean surface. The observed “splitting” of the X- and Y-polarized adlayer modes is connected with different atomic surrounding in $[1\bar{1}0]$ and $[11\bar{2}]$ directions. It should be noted that the main difference of the Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -K spectrum from those obtained for Na and Li adsorption is that the K-localized modes lie (except for the $\bar{\Gamma}$ point) only beneath the bulk phonon modes. In Fig. 10 we present the calculated LDOS's for the first three layers. They have similar features as those obtained in the case of Li. The only difference is that the peaks in the local density at the adlayer reveal a shift to lower frequencies.

IV. CONCLUSION

We have presented the results of a comparative study of the vibrational and structural properties of the Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -AM superstructures. Upon analysis of the structural characteristics one can see that the effect of the AM adsorption on the substrate consists of decreasing in the outermost interlayer spacing compared to the clean Al(111) surface. For Li and Na adsorbates these changes are very close in magnitude while for K adatoms the contraction is somewhat smaller. Such behavior is related to the changes in force constants between the substrate atoms from the top and sub-surface layers. They are increased by 16%–19% in comparison to the clean surface. Another structural effect induced by the AM adsorption is a small rippling in the fourth substrate layer, where atoms located directly beneath the Li(Na) ada-

FIG. 10. Local densities of states for Al(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ -K.

toms move slightly outward, while those located under the surface Al atoms have a small inward displacements. This effect is not observed for K due to the weaker adsorbate-substrate interaction. The calculated lengths of the Al-AM bonding are in agreement with both experimental and *ab initio* results. They are arranged in order of magnitude according to the adsorbate masses.

It should be noted that almost all the surface modes obtained for the clean Al(111) surface remain. They only assume a mixed character coupling with the adsorbate phonons except for a few ones. The presence of the adsorbates also leads to a small alteration of their frequencies. Unlike the case of the clean surface, for the Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-AM superstructures a few modes appear below the bulk spectrum. As a rule, they correspond to vibrations of the top-substrate and adlayer atoms except for the case of Li where they are localized on the substrate. Comparing our results with those measured along the $\bar{\Gamma}K'$ symmetry direction for the Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Na structure²¹ one can suppose that the obtained experimentally surface state S1 has a mixed Al-Na character. The adlayer localized modes, most of them are accompanied by the motion of substrate atoms, are located in the bulk continuum for Li adsorption and lie only beneath the bulk phonon spectrum (except for the $\bar{\Gamma}$ point) in the case of K. The calculated frequencies of the adsorbate localized modes at the $\bar{\Gamma}$ point are in agreement with the experimental data obtained for the Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Na and Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-Li

superstructures.^{17,21} We have also found a similar mode for the Al(111)-($\sqrt{3} \times \sqrt{3}$)R30°-K structure. The analysis of these frequencies shows that they depend not only on atomic masses but on the adsorbate-substrate interactions, too. This interaction between the adatoms and the nearest-neighbor substrate Al atoms is rather strong for Li and Na. For K, the large distance of adatoms from the substrate results in the much weaker adsorbate-substrate interaction and the stronger interaction between the adatoms than in the previous cases. This agrees well with the electronic structure calculations^{6,16} which indicate a less efficient substrate-mediated screening in the case of K.

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