Theoretical analysis of the electronic structure of the stable and metastable \( c(2 \times 2) \) phases of \( \text{Na on Al}(001) \):

Comparison with angle-resolved ultra-violet photoemission spectra

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Using Kohn-Sham wave functions and their energy levels obtained by density-functional-theory total energy calculations, the electronic structure of the two \( c(2 \times 2) \) phases of \( \text{Na on Al}(001) \) are analyzed; namely, the metastable hollow-site structure formed when adsorption takes place at low temperature, and the stable substitutional structure appearing when the substrate is heated thereafter above ca. 180 K or when adsorption takes place at room temperature from the beginning. The experimentally obtained two-dimensional band structures of the surface states or resonances are well reproduced by the calculations. With the help of charge density maps it is found that in both phases, two pronounced bands appear as the result of a characteristic coupling between the valence-state band of a free c(2 \( \times 2) \)-\( \text{Na monolayer and the surface-state/resonance band of the Al surface} \) that is, the clean (001) surface for the metastable phase and the unstable, reconstructed \( \langle \text{vacancy}\rangle \) for the stable phase. The higher-lying band, being \( \text{Na-}\)derived, remains ionic metallic for the unstable phase, whereas it lies completely above the Fermi level for the stable phase, leading to the formation of a surface-state/resonance band-structure resembling the bulk band-structure of an ionic crystal.

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I. INTRODUCTION

The adsorption of an alkali metal atom on a metal surface has attracted much attention in recent years partly due to the discovery of a variety of new adsorbate phases, in particular, structures that involve a reconstruction of the metal surface induced by the alkali metal (see, for example, references and therein). A common feature of these systems is that often there is a metastable phase at low temperature involving no reconstruction of the metal surface while at higher temperatures, the stable reconstructed phase occurs.

In the present paper we present a combined theoretical and experimental investigation of one such system, namely that of the \( c(2 \times 2) \) phases of \( \text{Na on Al}(001) \). Early dynamical-theory analyses of low energy electron diffraction (LEED) intensities concluded that \( \text{Na occupied the four-fold hollow site} \). It was not demonstrated by high resolution core-level spectroscopy (ESCA) and surface extended x-ray absorption near structure (SEXAFS) studies that the hollow site is taken only for preparations at low temperature (LT), and when excited, stable structure is formed by adsorption at room temperature (RT) or by heating of the LT phase above ca. 160 K. It was shown later by a density functional theory (DFT) study and by a new LEED analysis that in the RT phase the Na atom occupies substitutional sites, where every second Al atom in the top layer is displaced and a Na atom adsorbed in its place. The result of an x-ray photoelectron diffraction (XPD) study of the RT phase concluding that the surface contains two domains, and could not be explained.

In what follows, we perform a theoretical analysis of the electronic structure of the two \( c(2 \times 2) \) structures and compare the results with those of these experiments. The measurements have been performed in what we call a polar scan, modes which deliver displays of photoemission intensities as a function of energy and wave vector component parallel to the surface, lying in selected symmetry directions (\( \langle T \rangle \) and \( \langle X \rangle \) in the two-dimensional \( (2D) \) Brillouin zone (see Fig. 1). The displays yield directly 2D band structures of surface states/resonances (i.e., surface states or resonances, depending on the position of the states in or out of the gap of the 2D projected bulk bands), which may be compared with calculated results.

The basis of our theoretical analysis are the Kohn-Sham wave functions and their energy levels obtained by DFT total energy calculations. 2D band structures are derived and compared with the experimental results. The obtained, satisfactory agreement between theory and experiment may be regarded as a confirmation of the proposed atomic structure models mentioned above, and a useful basis for further studies of the properties of these surfaces.

A two single-state charge density distributions of occupied and unoccupied states are derived from the DFT calculation, and used for analyzing the character of the bands. The adsorption leads, in both LT and RT cases, to two main bands of surface state/resonances as the result of a coupling between the valence-state band of a free c(2 \( \times 2) \)-\( \text{Na monolayer and the surface-state/resonance band of the Al surface} \). Across the Fermi level the Al-derived band is shifted down, and the Na-derived band is shifted up. As a consequence, a charge transfer is taking place from the adsorbate directly into the pre-existent surface state/resonance of the substrate.
For the LT (hol low) structure, it is found that the coupling is relatively weak and the Al-derived state almost retains the perfect (1 1) periodicity of the clean surface. For the RT (substitutional) structure, the Al-derived state exhibits a clear (2 2) periodicity of the reconstructed Al surface. The Na-derived band of the RT structure is completely empty and leads, except for the still existing background bulk-continuum, to a surface electronic structure having a character of an ionic monolayer lying on the surface. We discuss possible consequences of this finding.

The paper is organized as follows: In Section II the experimental method is outlined and is followed in Section III by a description of the calculation methods. Section IV contains the results for the surface state/resonance band structures and the analysis of the character of the bands in terms of single-state charge density distributions. Also the charge transfer processes are analysed by using density differences. Section V contains the discussion and Section VI, the conclusion.

II. EXPERIMENT

The photoemission experiments were performed in a VG ESCALAB Mark II spectrometer modified for automated sequential angle-scanning data acquisition, and with a working pressure in the lower 10⁻¹¹ mbar region. Ultraviolet photoelectron spectroscopy (UPS) measurements were done using a monochromatized He I (21.2 eV) radiation from a discharge lamp. The 150-mm radius cesium sphere analyser was run with an energy resolution of 50 m eV. Contaminant-free surfaces were prepared by a combination of Ar⁺ sputtering and annealing at 500 °C. Na was evaporated from a carefully outgassed SAES getter source. Particular care was taken to ensure ultraclean Na deposits. All parts of the evaporation source, except the tiny exit slit, were surrounded with liquid-nitrogen-cooled walls. In this way, the pressure during evaporation could be kept as low as 2.5 10⁻¹¹ mbar. Na coverages were determined accurately (0.03 ML) from core-level photoelectron intensities. The sample temperature was measured with a thermocouple spot welded onto a dummy sample. Sample temperatures given here are corrected for this temperature difference and are estimated to be correct within 10 K.

In order to obtain two-dimensional band structures of surface states/resonances, polar scans along the M-X directions of the Al(001) surface Brillouin zone were performed, recording at each angular setting ( = 2) the entire photoelectron spectrum between 0.4 and 4.3 eV binding energy. The experimental data sets E(k) acquired in this way were mapped onto a regular (E-k) grid and visualized as gray-scale plots with low intensities in white and high intensities in black.

III. CALCULATION METHOD

The ab initio DFT total energy calculations, and comparison with LEED results are described in Refs. 6-8. The calculations were performed using the local-density approximation (LDA) for the exchange-correlation functional. Further details about the method can be found in Refs. 9-10.

The following two kinds of diagram have been used in the present analysis:

1. 2D band structures

For deriving 2D band structures we use the following procedure:

The projected density of states (DOS) onto a chosen atomic orbital, AO(r), is defined as

$$N_{AO}(\mathbf{k}) = \sum_{\mathbf{k}} N_{AO}(\mathbf{k}, \mathbf{r})$$

where the \( \mathbf{k} \)-resolved projected DOS is given by

$$N_{AO}(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{r}} \sum_{\mathbf{k}} d^2 r \frac{1}{\sqrt{(\mathbf{k} - \mathbf{r})^2 + z^2}}$$

We have used for \( \mathbf{AO}(\mathbf{r}) \) the eigenfunctions of the isolated pseudo-atom from which the pseudopotentials were derived for the total energy calculation. The integral was truncated at a cut-off radius \( r_c \). (We used here \( r_c = 3.7 \AA \).) In the standard supercell method using a slab geometry, a Kohn-Sham state, \( k_j, \mathbf{r} \), can be specified except for the presence of degeneracy, by indices \( k_j \) and \( \mathbf{r} \) (both discrete), the parallel wave vector and the energy, respectively. The lifetime broadening parameter, \( \Gamma \), is introduced for convenience in numerical work and for improving visibility of peaks in the resulting plots. (We take here \( \Gamma = 0.5 \, \text{eV} \).)
A simple sum of \( N_{Na} (k_{p};^n) \)'s are formed over atomic orbitals of a specified atom. For example, for Na we have,

\[
N_{Na} (k_{p};^n) = N_{Na3p} (k_{p};^n) + N_{Na3p_{y}} (k_{p};^n)
\]

The corresponding quantities, \( N_{Al}(k_{p};^n) \), are evaluated for the Al atoms in the uppermost layer. The maximum peak of these quantities was always found at the bottom of a surface state/resonance band lying at \( k_{p} \). Those peaks having a fractional ratio to the maximum higher than a properly chosen "maximum" (in the "Fraction" in Tab. 1), are selected and their positions in \( k_{p} \) space displayed, using squares for Na and circles for Al (see Tab. 1). The plots along \( X- \) and \( Z- \) are combined, and are presented in Figs. 2 and 3. We see that they produce satisfactorily 2D band structures to be compared to the experimental ones obtained.

The bulk-band continuum is separated into discrete bands due to the use of nine (nine layer) Al slabs. They appear in Figs. 2 and 3 as weak features. The discreteness of bulk bands may have caused a small energy shift of the surface resonance bands lying inside the bulk continuum, because they are replaced by one of the discrete bulk bands lying nearest to them.

We note that in Figs. 2 and 3 the theoretical bands for the LT and RT structures repeat themselves inside the \((1 \ 1 \ 1)\) Br"l"l"u"n zone, exhibiting the \( c(2 \ 2) \) periodicity. That is, the range \( \frac{1}{M} \) being referred to \((1 \ 1 \ 1)\) is halved, and the bands in the second half become mirror image of the first half. We call this here "back-folding" (cf. Ref. 3). It is a consequence of our use of density of states projected to one specified atom in each \( c(2 \ 2) \) surface unit cell. We note that this is obviously a theoretical construct and not quite adequate for representing fully the character of the wave functions of the bands, particularly in the LT structure. In fact, there is no information included about the relation between the values of wave functions around the two Al atoms in a unit cell (see Fig. 4). Thus, in reality the wave functions may happen to have approximatively the \((1 \ 1 \ 1)\) Br"l"l"u"n periodicity (the back-folding still occurs). The same would also result even for the clean-surface band if the artificial \( c(2 \ 2) \) unit cell would be imposed. In our back-folded band structure, a vanishing deviation from the \((1 \ 1 \ 1)\) Br"l"l"u"n periodicity would become visible only in a vanishing band gap at a new Br"l"l"u"n zone boundary, that is, in our case on the line halving the range \( \frac{1}{M} \).

On the other hand, the photoemission intensity would be determined by a matrix element.
**A. Clean Al(001)**

Figure 2a shows the experimental (left panel) and theoretical (right panel) band structures for the clean Al(001) surface. It can be seen that both exhibit a surface-state band which has a free-electron-like form. The parameters obtained by fitting to parabolas, as indicated by broken lines in Figure 2a, are shown in Table II. The energy position of the band at $E_0$, agrees well between theory and experiment, with values of 2.68 and 2.76 eV below the Fermi level, respectively. The theoretical value lies in the range of the results of other calculations, $2.6 - 2.9$ eV. The experimental value is in very good agreement with earlier studies.\(^1\)\(^2\)\(^3\) and\(^4\).

In Figure 2 (left panel) it can be seen that the experimental results display a number of additional features. Those which are common to all structures studied on this surface are assigned to bulk bands, as indicated by arrows. These bulk features do not appear in the calculated band structures (right panel), reflecting the fact that the density of states projected onto the uppermost Al atom is dominated by the surface states.

In Fig. 6a we display the single-state charge density distributions at $E_0$ for the main band. The two cross-sections (100) and (110) are defined in Fig. 4a. An important characteristic of the surface state of the clean Al(001) surface is that the charge density shows a pronounced maximum just on top of the surface Al atom. This can also be seen in the cross-section parallel to the

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**Fig. 2.** Comparison of experimental (left panel) and calculated (right panel) 2D band structures. The symbols used for the calculated bands are specified in Table I. (a) Clean surface, (b) LT phase (hollow site), and (c) RT phase (substitutional site).
surface through the electron density maxima as shown in Fig. 7a. This particular feature of the surface state is apparently crucial in the formation of the electronic structure of the LT phase, as we see below.

**B. LT c(2 2) hollow structure**

1. Al-derived band

In Fig. 2b we show the experimental (left panel) and calculated (right panel) surface state/resonances for the LT c(2 2) hollow structure. The lower lying main band is Al derived as indicated by the circles in the theoretical plot (cf. Table I). The position of the calculated band at lies somewhat lower in energy than the experimental value; compare 3.61 to 3.12 eV (see Table II). Notably the calculated results of the earlier theoretical work of Chulkov and Sikil is also 3.6 eV, although their non-self-consistent value of vertical distance 2.05 Å, from Na to Al is different from ours 2.35 Å, which is nearer to the experimental value 2.57 Å.

Compared to the position of the surface-state band of the clean Al(001) surface, the Al derived band lies lower in energy, by 0.93 and 0.36 eV, as obtained by the calculations and as determined from experiment, respectively. The nature of this downward shift will be discussed below. The discrepancies between theory and experiment may have been caused by the approximations used in the total energy calculation (use of LDA, Rydberg cut, k-point sampling etc).

The experimental results show clearly that the Al derived state does not have the c(2 2) periodicity, but rather the (1 1) periodicity of the clean surface. In fact, we nd it a significant experimental result that the main band in the LT phase has, throughout the whole range of M, almost the same form as that of the clean surface, being only shifted down.

**FIG. 4. Geometries of the c(2 2)Na/Al(001) surface structures:** (a) clean surface (b) LT phase (hollow site), (c) vacancy structure and (d) RT phase (substitutional site). The positions of perpendicular cross-sections used for charge density distributions are indicated. The white circles represent Na atom s and the grey circles Al atom s.

In Fig. 5b we display the single-state charge density distribution for the Al-derived band of the LT phase. The two sets of cross-sections di erently chosen for Al and Na (cf. Fig. 6c) are dened in Fig. 4b. It can be noticed in Fig. 5b that the maxima of charge density remain on top of the surface Al atom s, almost unchanged.
from those of the clean surface shown in Fig. 6a. This has also been pointed out by Chulkov and Silkin. In the cross-section parallel to the surface shown in Fig. 7b only a small deviation from the (1 1 0) structure is seen, having a c(2 × 2) period, with some indication of a character of a bonding state between the Na and Al atoms. The smallness of the deviation explains the similarity of the experiential band structures between the clean surface and the LT phase. It is to be noted that in the photoemission processes from this band, not only the initial states, but also the final states have apparently maintained approximately the same periodicity of the clean surface. The theoretical curves in Fig. 2b appear different, but this is only caused by the back-folding as already mentioned.

2. Na-derived band

In Fig. 2b dark spots can be seen at $\Gamma$ and $\bar{M}$ near the Fermi energy, $E_F$, in the experimental results. Although from the figure presented here it is perhaps difficult to distinguish, we noted in the experimental data that the dark feature at $\bar{M}$ for the LT phase is markedly different in character from that of the clean surface, in that the intensity for the LT phase is stronger and some tailing with dispersion is exhibited, as is the case also for the feature at $\Gamma$. From the calculated bands of the LT phase (right panel of Fig. 2b), we can see that there is a surface state/resonance band with an energy of about 0.7 eV below the Fermi level at $\Gamma$. As indicated by the open squares, it is a Na-derived band. We assign this band as arising from the experimental measured intensities at $\Gamma$ and $\bar{M}$ at 0.4 eV below the Fermi level. The existence of this band was not theoretically predicted by Beneš et al. and was also reproduced by Chulkov and Silkin. In Fig. 3a we show the same calculated band structure as in Fig. 2b, but where the energy region extends higher into the positive range. Here we can see that the part of the Na-derived band above $E_F$ exhibits marked band structure effects in the middle of $\bar{M}$, due to the c(2 × 2) periodicity of the adsorbed Na layer.

In Fig. 5a we show the band structure of a free c(2 × 2)-Na monolayer for comparison. It can be observed that at $\Gamma$ the lowest band lies 0.8 eV lower in energy as compared to the Na-derived band of the LT phase. Correspondingly the occupied part of the band is notably larger for the free monolayer.

Figure 5c displays the distribution of the Na-derived surface state/resonance at $\Gamma$ which clearly shows an antibonding character, the nodal line (not shown) running between the Na- and Al-layers. A comparison with Fig. 5b shows that the strongly smeared out character of the density between the Na atom and Al maintained, appearing however only in the upper half of the Na layer. The lower half is apparently cancelled by the Al surface states due to the antibonding coupling. A cross-section parallel to the surface passing through the electron density maximum on top of the Na atoms is shown in Fig. 7c.

W e see here a smeared out, free-electron-like distribution.

3. Formation mechanism of the two surface state/resonance bands

Combining the results above, we can conclude that the two bands are resulting from a coupling between the lowest lying (3s-derived) band of a free c(2 × 2) monolayer of Na and the surface state band of the clean Al(001) surface. Applying a simple two-term perturbation theory, as commonly done in molecular-orbital theory, this may be understood as being due to the formation of bonding and antibonding states, leading to the downward shift of the Al-derived band by 0.9 eV (calc.) with an increase in population and the upward shift of the Na-derived band by 0.8 eV (calc.) with a decrease in population. Alternatively, it may be understood, as in the case of ionic crystals, that the shifts occur as the result of Coulomb fields between the two oppositely charged ionic layers. The ionization is to be expected due to the cationic nature of Na, which donates electronic charge to the aluminum.
Al atom s are kept at those of the adsorption system,:

\[ \text{di: } = \text{tot: } A/\text{tot: } Al \]

\[ \text{med: } = \text{tot: } Al <(c(2)2) Na+ \]

which subtracts out the charge density of the free Na monolayer (Fig. 5b), showing exactly where charge has been enhanced and depleted. It can clearly be seen from di: and med: that charge enhancement occurs primarily at the maxima of the surface states, and indeed almost proportionally. We can also note in med: some regions of depletion, showing that the electron charge has been transferred from the upper half of the region between the Na atoms, where the density for the free Na layer (see Fig. 5b) is much larger than that of the Al surface states (see Fig. 6a). We may thus conclude that the electron transfer is occurring from Na atoms directly into the pre-existing surface states of Al.

It is noted in passing that this character of the LT phase shows a close analogy to the case of c(2 2)-C\textsubscript{s/W (001)}, both having the c(2 2) four-fold hollow structure. Although the electronic structure is much more complicated for C\textsubscript{s/W }, the essential feature of the charge transfer is the same. Thus, the maxima of the charge density distribution of the main surface state/resonances in a plane parallel to the surface passing through the electron density maxima (not the atom centres): The clean surface (a), the Al-derivative (b) and Na-derivative (c) bands of the LT (hollow) structure, respectively, and vacancy structure (d), the Al-derivative (e) and Na-derivative (f) bands of the RT (substitutional) structure, respectively. The dots represent the positions of the Na atom s. The contours begin at 1.0 and the contour spacing is 1.0. The units are 10\textsuperscript{-3} e\text{bohr}\textsuperscript{3}.

4d-derivative surface states of the clean W (001) surface lie on top of the surface W atom s (see Fig. 7 of Ref. 3). The maxima maintain their form upon Cs adsorption. Charge transfer takes place from Cs to these surface states. Hence, this case and ours may be regarded as representatives of the alkali metal on a metal system s for which the surface states of the substrate play an essential role.

The upper Na-derivative band is crossing the Fermi level and partly occupied, remaining "metallic". In Figs. 6c and 7c its free-electron-like character can be seen. We see in Figs. 6b and 6c that the charge density of the Al-derivative band lies well below the smeared out density of the Na-derivative band, and also below the position of the Na atom s. Thus, the traditional picture of a thin metallic in covering an originally metallic substrate remains qualitatively valid. We see below that this is not the case for the RT phase.

It is to be noted that the apparently weak influence of the Na adsorption on the Al surface states is limited to the high coverage of = 0.5 for the c(2 2) structure, for which the density maxima for the Na valence electrons (Fig. 5b) lie between the Na atom s and situated just at the same site as the surface state maxima. In fact, it has been found experimentally that at low coverages = 0 to 0.15 the surface states are deteriorated by Na adsorption.

FIG. 6. Charge density distribution of the surface state/resonance of the main bands at...
tion. Also it has been shown by DFT calculations for a active ordered-structure model, p(2 2) with coverage \( = 1/4 \), that the surface-state maxima are moved from the on-top sites to the bonding-line positions between the Na and Al atoms.

\[ \text{FIG. 8. Same as Fig. 6 for the RT phase (substitutional site). The positions of cross-sections are specified in Figs. 4c and 4d.} \]

C. RT c(2 2) substitutional structure

1. Al-derived band

Figure 2c shows the experimental (left panel) and calculated (right panel) surface state/resonance bands for the RT c(2 2) substitutional structure. It can be seen that the experimental surface state/resonance band clearly exhibits a c(2 2) periodicity, in contrast to the LT (hollow) structure. As we will see below, this is due to the significantly reconstructed Al(001) surface. The calculations (right panel) show good agreement with the experiment and indicate that the band is mainly Al-derived (circles) but has a small participation of Na (squares). The energy position of the main theoretical and experimental bands at \( -M \) are 2.14 and 2.31 eV, respectively.

The experimental results display some asymmetry in the intensity near \( k_x = 0.5 \) in \( -M \), i.e. a weakening on the left side and a strengthening and upward shift on the right. A few alternative explanations may be possible for this anomaly. Among others, it may be related to the closing of the bulk band gap in this region, causing the state to go from being a pure surface state to a surface resonance (see Fig. 10c of Ref. 4). Also, additional coupling to bulk states may be possible by surface Umklapp processes. The peak may become broad and complicated, as indicated by the split structure of the band near \( k_x = 0.5 \) in \( -M \).

\[ \text{An important finding in the present analysis is that the main band in the RT structure can be regarded as being derived from the surface state/resonance band of an active, reconstructed clean Al surface, that is, the vacancy structure, see Fig. 4c. In this structure the Na atom's are replaced by "vacancies" of the Al atoms. The surface state/resonance band structure of the vacancy structure is displayed in Fig. 3c. By comparison with Fig. 3b it is clearly shown that the main Al-derived band of the RT phase originates from that of the vacancy structure and is only somewhat shifted down in energy (by 0.81 eV) due to Na adsorption.} \]

Figures 8a and 8b show the single-state charge distribution for the main bands of the vacancy structure and the RT phase, respectively. Figures 7d and 7e show their cross-sections parallel to the surface passing through the electron density maxima. Similarly to the clean Al(001) surface, the maxima of charge density for the vacancy structure lie on top of the uppermost surface Al atom, having this time the c(2 2) periodicity. For the Al-derived band of the RT phase, the maxima also lie approximately at the same position as that of the vacancy structure with relatively small changes in their form. It can be noted that these states are rather strongly localized. This explains the well-developed c(2 2) character of the band found in Fig. 2c, and its relatively small dispersion (larger value of \( m^* \), see Table II).

Similarly to the LT phase, we find in Fig. 2c a few additional theoretical bulk bands which are not present for the clean surface. These are apparently introduced by the c(2 2) periodicity as surface Uhklapp processes. There is also indication of a third, relatively weak band lying at \( E_F \) and around \( -M \) in both the experimental and calculated band structures. From our analysis (not shown), this band can be regarded as being derived from a second, relatively weak, surface state/resonance band of the vacancy structure.

2. Na-derived band

In Fig. 3b we see that the Na-derived band (filled squares) is found only in the calculation, lying completely in the positive energy range, about 2.7 eV higher in energy than for the free c(2 2)-Na layer. Notably, this
is much larger than the downward shift of the Al-derived band (0.8 eV). This will be discussed below.

The single-state charge distribution of the unoccupied Na-derived state at +1 eV is shown in Fig. 8a, indicating again an antibonding character. Figures 8c and 7f show its smearing out, free-electron-like structure with the maximum residing this time above the Na atoms.

\[ \rho_{\text{tot}}, \rho_{\text{diff}}, \rho_{\text{resid}} \]

Fig. 9. Total charge density distribution, \( \rho_{\text{tot}} \) (left panel), density difference, \( \rho_{\text{diff}} \) (middle panel), and density redistribution, \( \rho_{\text{resid}} \) (right panel), of the LT phase hollow site.

The cross-section is in the (001) Na plane (see Fig. 4b). The units are 10^-3 e bohr^-3. In the left panel the first contour begins at 4.5 with a spacing of 4.0, for the middle panel the first contour begins at 0.6 with a spacing of 0.6, and in the right panel the contours are the same as the middle panel with the addition of a negative contour line (unshaded) at 0.6.

3. Formation mechanism of the two bands

We conclude that the two main bands are resulting, just as in the case of the LT phase, from the coupling between the states of a free c(2x2)-Na monolayer and the surface state/resonance of the Al surface, i.e., the vacancy structure in this case.

The electron transfer can also be regarded as occurring from Na atoms into the surface state/resonance of the vacancy structure. This can be seen clearly in comparing Fig. 10 with Fig. 8a. In the charge redistribution \( \rho_{\text{resid}} \) in Fig. 10 we note some regions of depletion: the electron charge has been transferred in this case mainly from the region on top of the Na atoms, where the density of the free Na layer dominates the density of the surface state/resonance of the vacancy structure. The charge depletion found in Fig. 10 also near the centres of the Al atom may be interpreted as a result of an upward shift of the maximum of the surface states induced by Na adsorption.

\[ \rho_{\text{tot}}, \rho_{\text{diff}}, \rho_{\text{resid}} \]

Fig. 10. Same as Fig. 9 for the RT phase (substitutional site). For the middle panel there is one contour line at 1.2, and in the right panel there are three negative contour lines (unshaded) at 1.8, 1.2, and 0.6.

These findings, combined with the unbalanced large upward shift of the Na-derived band and the existence of the third peak at +1 eV, both mentioned above, indicate that the coupling between the free Na monolayer states and the Al surface states/resonances takes place in a little more complicated way than in the LT case. It can no longer be interpreted in a simple two-term-coupling perturbation scheme. Apparently the coupling is too strong, and involves other states, namely, the p states of Na lying originally at +1 eV (Fig. 5a) and the second surface states/resonances of Al lying originally at 0 eV (Fig. 3c).

We have seen above that for the LT phase the traditional picture of a thin metallic film covering a metallic substrate remains qualitatively valid. For the RT phase, however, we find in Fig. 8b that the completely filled A-derived band has the maximum at the same height as the Na atoms. The maxima of the Na-derived band lie indeed higher, but they are empty. Thus, as far as the electronic states in the energy range near E_F are concerned, the A-derived band constitutes practically the "surface" of this structure. The Na monolayer (or the Na/Al composite monolayer) cannot be regarded as a metallic film on a metallic substrate; rather, except for the still existing background bulk continuum, the electronic structure of the monolayer may be viewed as being analogous to that of an ionic crystal, like NaCl, where the completely filled A-derived band replaces the valence band of Cl, and forms with the empty Na-derived band a "band-gap" of about 3.5 eV across the Fermi energy.

We note in passing that we find a similarity of the surface electronic structure of the RT phase to that of the system (c(2x2)-Na/A1(111)) with a c(2x2) monolayer double layer surface alloy with a similar, but more complex intermixing of Na and Al in the surface layers. For this system, we also find a similar A-derived band originating from the corresponding Na vacancy structure, and an empty Na-derived band. (The latter may be assigned to that found by Heskett et al., using inverse photoemission spectroscopy. The similarity indicates that also this layer cannot be regarded simply as a thin metallic layer.

V. DISCUSSION

For all three systems studied (A1(001) and the two c(2x2)-Na/A1(001) phases), we find good overall agreement of the surface state/resonance band structure between experiment and theory. In each case there is a prominent A-derived surface-state/resonance band, showing similar free-electron-like parabolic dispersion at the band bottom near +1 eV, as indicated by broken lines in Fig. 2. We find that the observed and calculated val-
ues of the Fermi wave vector, $k_F$, and the effective mass, $m$, of the main band (Tab. II) agree only roughly, probably due to the approximations used in calculation, as already mentioned. In any case these quantities are to be regarded as global parameters specifying only the geometry of the bands, and are not intended to indicate that the bands are free-electron-like. In fact, the wave functions of the Al-derived bands are rather strongly localized, as we see from the charge density distributions. The dispersion of the bands may be regarded as the result of the overlap between the localized wave functions.

The picture of charge transfer taken place from Na to the surface state/resonance of Al is also supported by the almost equal values of the work function change (decrease) $-1.6$ eV, obtained both experimentally and theoretically in the present work for the LT and RT phases. Obviously the value of $\Delta\phi_{\text{Na}}$, shown in Figs. 9 and 10, as the z-component of the dipole moment, as already mentioned, is a minimum at $m$-maxima of $\Delta\phi_{\text{Na}}$ and Al-derived states, respectively. This can be seen by comparison of Figs. 9 and 10 with Figs. 6b, c and Figs. 8b, c. In these figures, the vertical distances between the maxima of the Na- and Al-derived states are found to have the ratio of 1.0 to 0.6 between the LT and RT phases. On the other hand, a comparison between Figs. 5a and 2b, c shows that the decrease of the occupancy of the Na-derived states is about 0.6 for the LT phase, in contrast to 1.0 for the RT phase (being empty). This leads to the same amount of overlap between the two phases, as a product of charge and distance. It is essential in this consideration to note the fact that, while the forms of the Al-derived states remain almost unchanged, the forms of the Na-derived states change drastically, from that of Figs. 5b to those of Figs. 6c and 8c.

Our results verify the formation of the two surface state/resonance bands. Various experimental methods of studying surface electronic properties other than ultraviolet photoelectron spectroscopy, as used here, may be useful for finding out characteristic features induced by these two bands. Particularly, EELS (electron energy loss spectroscopy) and IPS (inverse photoemission spectroscopy) may be useful for studying the effects of the bands lying in the energy range above the Fermi level.

For the RT phase, the fact that the surface band structure is constituted of a filled band and an empty band with a gap of approximately 3.6 eV, may play an important role in various properties of the surface. We may think of, in addition to EELS, an analogous feature in optical excitation spectra near 3.5 eV and a corresponding anomaly in the dispersion curve of surface plasmon.

A significant effect may be expected in various surface-sensitive methods such as ion neutralization, metastable deexcitation, etc., which would reveal the dominant character of the surface states/resonances in the outermost surface region, and hence expose the difference in the character of these states between the LT and RT phases. We may also think of the relevance of the occupancy of surface states/resonances on surface diffusion and catalytic activity.

VI. CONCLUSION

We have analyzed the electronic structure of the metastable hollow and stable substitutud structures of c(2 × 2)-Na on Al(001). The calculated surface state/resonance bands agree well with those measured by angle-resolved photoemission experiments. It is found that in both phases, two pronounced bands appear as the result of a characteristic coupling between the valence-state bands of a free c(2 × 2)-Na layer and the surface-state/resonance bands of the corresponding (i.e. clean and reconstructed) Al surfaces. While the experimental band structure of the substitutional structure shows a clear c(2 × 2) character due to the sign change of the surface Al layer, the hollow structure does not: the main band, in fact, exhibits a quasi-periodicity like that of the clean surface. For the stable substitutional structure, the unoccupied surface state/resonance band lies completely above the Fermi level, leading to the formation of a surface-state band structure that resembles that of an ionic crystal. We await experimental verification of the predicted unoccupied surface state/resonance band, and of the dihedral surfaces in the properties of the LT and RT phases in relation to the character of the surface states/resonances.
Details about the determination and calibration of Na coverages can be found in Ref. [10].

TABLE I. Legend of the symbols used in calculated 2D band structures in Figs. 2 and 3. The "minimum fraction" is defined in the text (see III Calculation method).

| Structure          | Symbol          | Projected Atom | M in. Fraction |
|--------------------|-----------------|----------------|----------------|
| clean              | big circles     | A1             | 0.8            |
|                    | sm all circles  | A1             | 0.4            |
| LT                 | em pty squares  | Na             | 0.5            |
|                    | big circles     | A1             | 0.7            |
|                    | sm all circles  | A1             | 0.35           |
| RT                 | big squares     | Na             | 0.4            |
|                    | sm all squares  | Na             | 0.2            |
|                    | sm all circles  | A1             | 0.5            |
|                    | sm all circles  | A1             | 0.3            |
| vacancy            | big circles     | A1             | 0.5            |
|                    | sm all circles  | A1             | 0.3            |

TABLE II. Parameters specifying the main surface state/resonance bands in Figs. 2 and 3. The experimental values [10] are shown in brackets.

| Structure | E₀ [eV] | k₀ [Å⁻¹] | m [Å⁻¹] |
|-----------|---------|----------|---------|
| clean     | 2.68 (2.76) | 0.55 (0.60) | 1.05 (1.18) |
| LT        | 3.61 (3.12) | 0.64 (0.66) | 1.03 (1.29) |
| RT        | 2.14 (2.31) | 0.51 (0.62) | 1.12 (1.55) |
| vacancy   | 1.33     | 0.41     | 1.15    |