Observation of valence-band structure in the LVV Auger spectra of thin epitaxial sodium layers

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Electron-impact-induced Auger spectra at energies below 30 eV were measured from epitaxial sodium films on Cu(001) from a submonolayer up to several layers and assigned to sodium LVV transitions. According to well established deconvolution and background-correction techniques, the line shape of the Na $L_{2/3}VV$ transition could be used to determine the sodium valence-band density of states. In agreement with photoemission investigations of the Na density of states, our results also suggest a strong narrowing of the valence band with respect to the calculated density of states for a nearly-free-electron metal. Since CVV Auger transitions cannot occur in isolated alkali-metal atoms due to the lack of a second valence s-shell electron, the onset of the Na LVV signal during the growth of the first monolayer unambiguously marks the first stage of an alkali s-level-derived valence-band-like state. Thus, the present model study of Na/Cu(001) demonstrates that CVV Auger spectroscopy can be used as a powerful method to investigate the intriguing electronic behavior during alkali-metal adsorption.

I. INTRODUCTION

Alkali metals (AM's) are considered to be the simplest metals from a theoretical point of view, and therefore many of their properties such as crystal structure, lattice vibrations, and electronic structure can be calculated by means of first-principle methods. In the latter case, however, sophisticated valence-band calculations involving self-energy corrections[1] reveal only small deviations from the results obtained from local-density-approximation (LDA) calculations,[2] or from the fundamental Sommerfeld theory of a free-electron gas.[3] In the case of sodium, one of these deviations is a narrowing of the valence-band width by about 10% due to many-body effects.[1] This is at variance with angle-resolved photoemission results by Jensen and Plummer,[4] which show that the sodium valence band is narrowed by an amount of about 20%. The experiments of Jensen and Plummer stimulated theoretical work to explain this discrepancy by considering more carefully the self-energy corrections in a modeling of the energy spectra of the final (excited) state of a photoemission process.[5]

Here we present a detailed investigation of the density of states (DOS) of sodium by line-shape analysis of the Na $L_{2/3}VV$ Auger transition. Our results also demonstrate a strong narrowing of the sodium valence band with respect to the free-electron value, and with respect to theoretical line-shape calculations.[6,7] We suggest that, as in the case of photoemission, the sodium CVV Auger energy spectra can only be described exactly by going beyond the basic models in order to correctly describe the many-body interactions during the Auger process.

The investigation of the alkali-metal valence-band density of states is of great interest in another context. The alkali-metal-induced occupied electronic states near the Fermi level during adsorption on clean metal surfaces are generally interpreted as s-valence resonance[8–10] or discrete valence electronic states.[11] They are populated as a function of coverage leading to a varying net charge transfer from the AM adatoms to the metal substrate.

This interpretation, however, is still controversial,[12] and any additional method, which also probes valence-band-like states, is of interest in order to provide additional information about the electronic structure of adsorbed alkali-metal atoms. Since Auger electron spectroscopy (AES) is a well established valence-band probing method, it is indeed surprising that, to our knowledge, AES so far has been neither used nor proposed for a dedicated monitoring of the development of alkali-metal valence bands during adsorption. In particular, the very first stage of the alkali-metal s-level-derived valence band can be unambiguously identified by the onset of the CVV transitions, which cannot occur in isolated alkali-metal atoms due to the lack of a second electron in the outer s shell. Conversely, if the outer s shell of alkali atoms becomes delocalized due to an increasing atomic density, i.e., the formation of a bandlike state, Auger transitions involving one core electron and two valence electrons become possible.

The present coverage-dependent alkali-metal Auger measurements were carried out within the framework of a multitechnique study involving low-energy electron diffraction (LEED), work-function change measurements, electron-energy-loss spectroscopy (EELS), and thermal helium-atom scattering (HAS) of the Na/Cu(001) epitaxial system at 80-K substrate temperature.[13] The Na $L_{2/3}VV$ transitions studied here were so far only considered to be obstacles in photoemission,[4] in the investigation of sodium segregation on a lithium surface[14] and in a study of sodium oxidation.[15] Our experiments show a distinct onset of the Na $L_{2/3}VV$ transition just prior to the formation of a half monolayer, indicating the beginning metallization of the sodium overlayer. These results will mainly be compared with photoelectron spectroscopy data reported in the literature.[16] Alkali-metal CVV Auger spectroscopy turns out to be a powerful complementary method by not only indicating the existence of alkali-metal-induced occupied s states (as in the case of photoemission), but also by revealing simultaneously the existence of an intrinsic bandlike behavior of these states

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even in the coverage regime between 0.5 and 1 mono-layer. In addition, line-shape changes of the Na $L_{2/3}VV$ transition during the growth of the first three monolayers provide information about the evolution of the electronic band structure during epitaxial alkali-metal film growth.

The paper is organized as follows: After presenting the experimental details in Sec. II, the results will be dis-cussed in Sec. III beginning with an introductory survey about sodium film growth on CU(001). In Sec. III A the Na LVV nature of the observed Auger transition will be demonstrated. In Sec. III B results from direct electron-energy-loss spectroscopy (EELS) and AES loss-satellite observations will be compared in order to discuss the ori-gin of electronic excitations in ultrathin AM films. Sec-tion III C deals with the intensity and line-shape behavior of the Na $L_{2/3}VV$ Auger transition during the formation of the first three monolayers. A detailed DOS investiga-tion by AES from a six-monolayer-thick sodium film will be presented in the last part of Sec. III, before concluding with a discussion in Sec. IV.

II. EXPERIMENT

All measurements presented in this paper, except the helium atom scattering measurements,[17] were performed in an ultrahigh-vacuum (UHV) chamber equipped with a cylindrical mirror analyzer (CMA) — Auger spectrometer (Perkin-Elmer, model 10-155), a LEED system, and an electron gun for the investigation of work function changes by the diode method. Electron-energy-loss spec-troscopy was performed in normal incidence using both the CMA and the four-grid LEED screen as a retarding field analyzer in order to avoid artifacts within the CMA measurements due to the limited angle acceptance of a CMA. Data acquisition during AES and EELS measure-ments was done with a analog/digital converter linked to a standard lock-in electronics and a personal computer. Commercial SAES-Getters were used as sodium sources.[18] The copper (001) surface was prepared by re-peated cycles of 800-eV argon-ion bombardment and an-nealing at 800 K.

Since AES is a surface-sensitive technique, clean sodi-um surfaces from well-ordered crystals are required for the DOS investigation. Unfortunately, however, due to their softness, their reactivity, and their low melting tem-peratures, the preparation of alkali-metal surfaces under UHV conditions is possible only via in situ epitaxial growth. In a recent study[19] of the layer-by-layer growth of sodium on Cu(001), we investigated the exact growth mode of thick alkali-metal films by combining AES, LEED, and helium-atom scattering. These well-defined sodium films with thicknesses ranging from a fraction of a monolayer up to tens of monolayers were characterized by phonon spectroscopy (inelastic HAS),[20] and in the present study by AES valence-band spectroscopy.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the results from several different tech-niques for the behavior during sodium thin-film growth on Cu(001) at 80 K substrate temperature.[13] The AES in-

vestigation of the electronic properties was done simul-taneously with EELS, work-function change, and LEED investigations. They were complemented by HAS experi-ments in another apparatus in order to study not only the electronic but also the related structural aspects.[19,21]

The growth of sodium on Cu(001) occurring in a layer-by-layer way is indicated by the distinct oscillations of the specular scattered helium-atom intensity.[22] For coverages less than one half monolayer the sodium ada-toms form a lattice gas (LG), as revealed by the appear-ance of sharp He-diffraction peaks with the periodicity of the substrate, which cannot be observed from the pure Cu(001) surface.[21] The first ordered superstructure is a $c(2\times3)$ structure at $\Theta = \frac{2}{3}$ ML (monolayer), and was ob-served by LEED and HAS. The first full monolayer ($\Theta = 1$ ML) consists of a $c(2\times2)$ structure, followed by hexagonal bilayers and trilayers, as indicated by sharp LEED diffraction patterns and by helium-atom diffraction. Work-function change measurements reveal the typical work-function minimum upon alkali-metal ad-sorption on metal surfaces. Finally, no evidence for sodi-um copper intermixing could be observed.
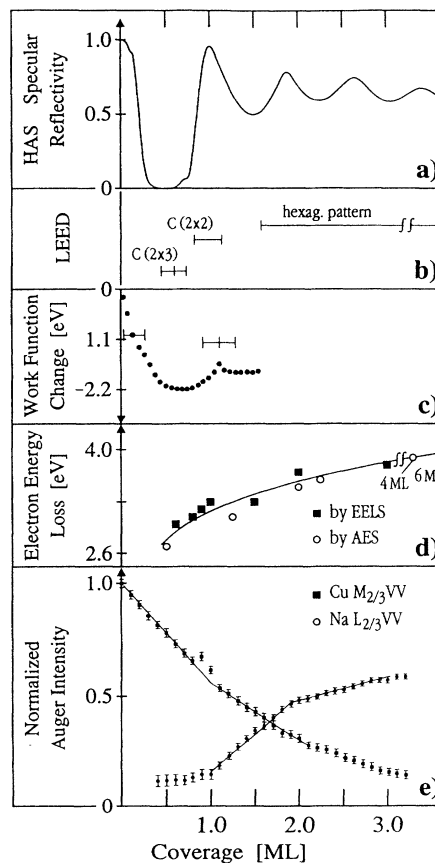

FIG. 1. Overview showing the evolution of signals from five different experimental techniques during the growth of sodium on Cu(001) at $T = 80$ K. While the LEED, AES (primary ener-gy: 2000 eV), EELS, and work-function measurements have been done simultaneously, the HAS data were obtained in a separate apparatus.

A. Principal features of the Na $L_{2/3}VV$ Auger peak

Auger spectra obtained as a function of the sodium coverage are shown in Fig. 2 for various coverages of $\Theta=0.5$, 1.25, 2.25, 4.0, and 6.0 ML. Apart from the expected Cu $M_{2/3}VV$ Auger transitions at around 60 eV,

TABLE I. Electron binding energies in an isolated sodium atom (Ref. 45).

Shell	Electron binding energy
$1s(K)$	1072 eV
$2s(L_1)$	63 eV
$2p(L_{2/3})$	31 eV
$3s(M_1)$	1 eV

five distinct features labeled by peaks $A-E$ are observed in the low-energy side of the spectra. All spectra plotted in Fig. 2. are normalized with respect to the peak-to-peak height of peak C, which is the most important feature observed.

Following Ref. 14, peaks D (at 31.5 eV) and E (at 40.0 eV) can be easily identified as the $L_{2/3}L_{2/3}V$ and $L_{2/3}V$ Auger transitions, respectively, by a simple calculation involving the electronic binding energies in sodium atoms or ions. Table I lists the electronic binding energies in free sodium atoms, and from these energies it is obvious that Auger transitions are not possible below 30 eV in isolated sodium atoms. Applying the same energy considerations to peaks A, B, and C (29.2 eV), only peak C can also be attributed to an Auger transition. It is assigned to the sodium $L_{2/3}VV$ transition, which can only occur in condensed sodium because of the lack of a second valence electron in isolated alkali-metal atoms. Thus it is obvious, from the results of Fig. 2(a), that an electronic valence s-band-like state has already developed at coverages of about half a monolayer. We will come back to this important point in Sec. III C, where the oneset of the Na $L_{2/3}VV$ transition is monitored.

Since the observed Na $L_{2/3}VV$ transition lies in the energy range of the strongly varying secondary electron background, misleading assignments to distinct features in the true secondary electron background have to be ex-
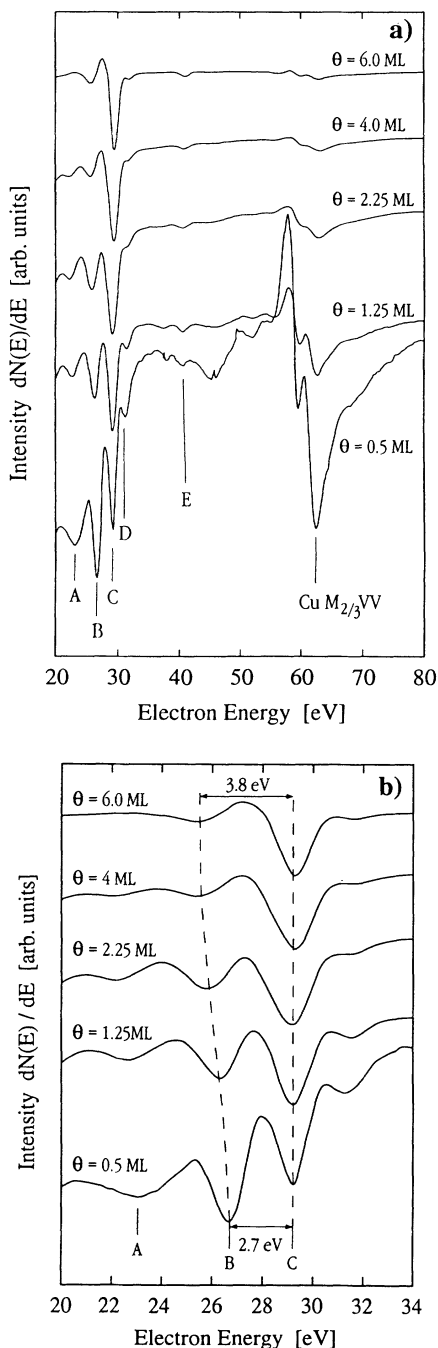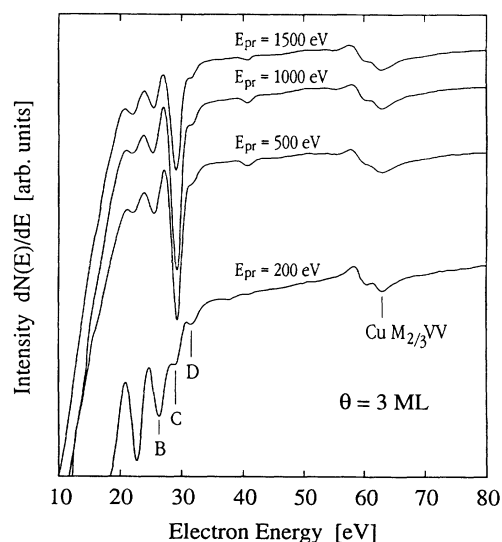
FIG. 2. (a) Overview of the differentiated measured energy distribution of electron impact (primary energy: 1500 eV) induced Auger electrons from Na/Cu(001) as a function of the sodium coverage. E and D denote the Na $L_{2/3}L_{2/3}V$ and Na $L_1L_{2/3}V$ Auger transitions. Peaks C, B, and A denote the Na $L_{2/3}VV$ transition and two corresponding loss features. (b) Close-up of the spectra of (a) showing the energy shifts of peaks A and B.

FIG. 3. Na LVV Auger spectra from three sodium monolayers as a function of the primary energy.

cluded. This was done by measuring the LVV transitions with different primary electron-beam energies. While the true secondary electron background is expected to vary significantly when changing primary beam energies, Auger transition line shapes should remain unaffected to a certain extent. By means of this assumption, the Auger nature of peak C was demonstrated. This is shown in Fig. 3 for the case of three monolayers. The energy positions of all five peaks remain constant when the primary beam energy is increased from 200 to 1500 eV. Thus peaks A and B are also related to an Auger process and, due to the impossibility of further Auger transitions in this energy range, have to be attributed to loss structures with respect to the main $L_{2/3}VV$ peak. The energy difference between the $L_{2/3}VV$ peak and the first and second loss structures (peaks B and A) is 3.8 and 7.8 eV, respectively. Since this is nearly equal to or twice the sodium surface plasmon energy reported by several authors,[23] they are thus assigned to single and multiple plasmon losses.

B. A comparison of electronic excitation spectroscopy by EELS and AES

In order to identify peaks A and peak B as loss structures conclusively, electron-energy-loss distributions were measured as a function of the sodium coverage and are presented in Fig. 4. Two intense losses at 3.8 and 7.8 eV are seen in the spectrum obtained from three monolayers of sodium. The loss spectrum of the clean Cu surface re-
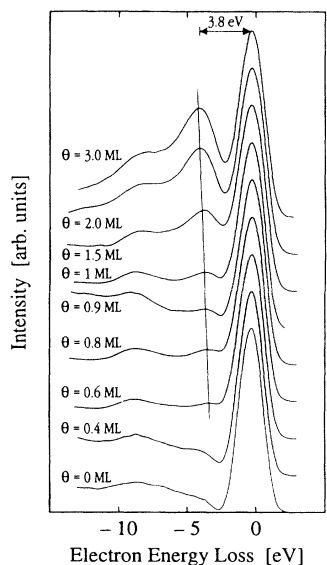

FIG. 4. Electron-energy-loss spectra from Na/Cu(001) recorded with the four grid LEED screen and a primary energy of 60 eV at different Na coverages. Whereas for coverages beyond 1.5 monolayers no differences between the spectra recorded with the CMA and the LEED screen could be observed, the loss features in the CMA measurements have been slightly less pronounced in the low coverage regime, due to the limited angle acceptance of the CMA.

veals a typical broad loss structure due to intraband transitions. Sodium adsorption weakens this feature and induces an inelastic feature beginning at $\Theta = 0.6$ ML with an energy loss of 3.0 eV. Further adsorption causes a strong increase of this inelastic intensity. In addition a small increase of the energy change from 3.0 to 3.8 eV for three monolayers can be observed [see also Fig. 1(d)]. This agrees with high-resolution electron-energy-loss spectroscopy (HREELS) measurements,[24] which also show such a thickness dependence of the surface plasmon frequencies of thin alkali-metal films. As a verification of our EELS data, this increase of the surface plasmon energy is also evident in the close-up of the Na $L_{2/3}VV$ Auger spectra of Fig. 2(a), shown in Fig. 2(b), by the increase of the energy difference between the loss structures and the main Auger $L_{2/3}VV$ peak [see also Fig. 1(d)]. In contrast to the EELS spectra of Fig. 4, there can be no doubt about this energy shift, because the loss intensity is decreasing with respect to the main $L_{2/3}VV$ signal.

Although the determination of electronic excitation energies by studying loss satellites in CVV AES is not a straightforward method, it may contribute to the discussion about the nature of electronic excitations within adsorbed alkali metals. While EELS loss peaks from the monolayer region and above are commonly interpreted as collective (plasmon) excitations, loss features in the low-coverage region between 0.5 and 1 ML have been explained either as single-particle s-p excitation of the (more or less ioniclike) AM adatom,[25–27] or as collective excitations of the adlayer electron system with a decreased electronic density with respect to the bulk value.[28,24] Since the latter only applies if a valence-band-like state already exists, the existence of this state should be demonstrated in a pure EELS work by an adequate additional method, such as angle-resolved photoemission. In contrast to this, our Auger method is based on the very existence of a valence-band-like state, and therefore the energy losses suffered by the Na $L_{2/3}VV$ Auger electrons can be attributed to plasmon excitations even in the coverage regime of 0.5 to 1 ML. A recent theoretical study by Ishida and Liebsch[29] provided a novel explanation for the observation of distinct electron-energy-loss features from alkali-metal submonolayer films, attributing them to a threshold enhancement in the EELS loss function. This is not inconsistent with our observations, and we are thus not able to make a clear distinction between the excitation mechanisms mentioned above. In addition, the reversal of the intensity ratio between the loss signal and the $L_{2/3}VV$ signal at about one monolayer [see Fig. 2(a)] also suggests a drastic change in the loss mechanism and therefore in the electronic system with the onset of the growth of the second monolayer. A similar behavior has been observed for Na/Al(111) by Heskett et al.[27] in the case of EELS. Since the intensity of the loss peaks in the low-coverage regime always exceeds the $L_{2/3}VV$ signal, the excitation mechanism in these cases cannot be explained by a simple model of Auger electrons which are exciting plasmons on their way to the surface. Rather an intrinsic plasmon excitation during the Auger transition has to be assumed.

C. Sodium valence-band spectroscopy during the initial film growth

A promising feature of CVV AES in alkali-metal adsorption experiments is the possibility of studying the earliest stages of alkali s-level-derived-bandlike states by the development of the CVV signal during the adsorption of the first monolayers. This was done by comparing the copper $M_{2/3}VV$ and sodium $L_{2/3}VV$ Auger intensities shown in Fig. 1(e) with the EELS, work-function change, LEED, and HAS measurements.

The Cu $M_{2/3}VV$ Auger signal decreases linearly during the formation of each monolayer, as expected for the sodium layer-by-layer growth. An onset on the Na $L_{2/3}VV$ signal appears at approximately half the time needed to evaporate the first monolayer. This is in good agreement with results obtained from photoemission and metastable deexcitation spectroscopy (MDS) investigations on Na/Cu(001) (Ref. 16) or other alkali-metal–metal systems,[8–11] which also show occupied alkali-induced electronic states for coverages much lower than one full monolayer. In the case of Na/Ca(001), photoemission results by Walldén[16] reveal no significant change of the intensity close to the Fermi level during the formation of the first half monolayer. Therefore no occupied Na $3s$-derived states have been observed in the low-coverage limit, confirming the model of an almost total charge transfer from the alkali s resonance into the substrate in the low-coverage limit. Further sodium evaporation, however, reveals a strong photoemission intensity increase close to the Fermi level after the work-function minimum has been reached. Walldén attributes this to the appearance of Na $3s$-derived valence states.

It is important to note that the existence of an occupied Na $3s$ level at half a monolayer as found by Walldén is only one requirement for our Na CVV Auger transitions to become possible. In addition, this resonance has to be a bandlike state. By detecting the Na $L_{2/3}VV$ transitions, we therefore demonstrate directly that even in the low-coverage regime, where the $c(2\times3)$ superstructure begins to form, the $3s$ resonance in Na/Cu(001) belongs to an energy band containing delocalized electrons. It should be mentioned here that angle-resolved UPS measurements or other band-state-sensitive measurements, which would provide direct information about the bandlike character of the alkali s-level-derived states, have so far been restricted to a single monolayer. Thus our AES results reported here demonstrate directly the bandlike (delocalized) character of occupied alkali s-level-derived states even in the case of low coverages between 0.5 and 1 ML, where the interatomic distance between the alkali-metal atoms exceeds the value of the bulk material by a factor up to 1.3. This result can, however, be compared with inverse photoemission data[30] obtained from the $(\sqrt{3}\times\sqrt{3})R\,30°$ Na overlayer on Al(111), where the Na-Na distance exceeds the Na bulk value by a similar factor of 1.36. These experiments show a distinct dispersion of an unoccupied AM-induced electronic state. There is therefore no reason why occupied states in the case of enlarged AM-AM distances within the AM adlayers should not show dispersion, which supports our

above interpretation.

Further evidence can be drawn by comparing the Na $L_{2/3}VV$ intensities with the appearance of the work-function minimum upon sodium deposition. According to Gurney's picture,[31] it is commonly assumed that the formation of such a work-function minimum is due to the downward shift, respectively, refilling of alkali s resonances[12] with increasing alkali-metal coverage. Since the onset of the Na $L_{2/3}VV$ signal lies close to the work-function minimum, this refilling is already accompanied by a lateral two-dimensional (2D) bandlike smearing of the s-state resonance. Thus not only the adsorbate substrate interaction[32] but also the adsorbate-adsorbate interaction significantly changes at the work-function minimum, leading to the formation of a metallic bond within the sodium monolayer. This strongly supports Rhead's suggestion[33] that the work-function minimum generally indicates a two-dimensional condensation of the adsorbed atoms. In addition, Argile and Rhead, in a recent paper,[34] were able to link the well-known change in the work-function minimum of the uptake mode of coadsorbed oxygen on AM-precovered metal surfaces [O/K/Cu(001)] to two-dimensional condensation. We have also observed such a change in the oxygen uptake mode of O/Na/Cu(001) (Ref. 13) around the work-function minimum. In addition, He-atom diffraction clearly demonstrates lattice-gas formation instead of the formation of ordered islands for coverages below the work-function minimum.[21] We thus have several consistent experimental data which together give strong evidence for the onset of condensation within the sodium adlayer in a narrow coverage interval around the work-function minimum.

For coverages beyond one full monolayer, a strong increase of the Na $L_{2/3}VV$ intensity is observed (Fig. 1). Its development now suggests a behavior usually expected for the adsorbate signal during the growth of the first monolayer.[35] In addition, as already mentioned, the line shape tends to become normal in the sense of the associated loss structure during the growth of the second and third layers (Fig. 2). Further deposition reveals no significant change in the line shape, while the intensity slowly approaches a saturation value. From this it can be concluded that the three-dimensional arrangement of sodium atoms during the growth of the second and third monolayers still affects the evolution of the sodium valence band, as indicated by large differences between the AES spectra obtained from 1.25, 2.25, and 4 monolayers (Fig. 2).

Further detailed AES experiments on different AM-adsorption systems are of great interest in order to understand our preliminary results. They should be performed with an improved energy resolution and with different substrate materials in order to exclude interatomic transitions. Since the sodium $L_{2/3}VV$ process occurs in the low-energy range, UV-excited AES would also be helpful in order to avoid disturbances by true secondary electrons. As a first step toward a detailed study of the alkali-metal-induced bandlike states, we made a DOS investigation of thick sodium films, where the Na $L_{2/3}VV$ spectra only show one distinct loss feature. Thus intrin-

sic excitations during the Auger event can be excluded, and a well-established deconvolution technique can be applied for data analysis in order to obtain the true Auger signal, as described in Sec. III D.

D. Bulk sodium valence-band spectroscopy and quantitative line-shape analysis

The use of AES as a DOS probing method was first recognized by Lander in 1953,[36] and has been widely used until the advent of more sophisticated methods, such as photoemission with synchrotron radiation. Nevertheless many interesting results about the DOS of various metals could be and are still obtained by CVV Auger line-shape analysis.[37] For detailed information, we refer to the review article by Madden.[38]

The two most difficult problems in obtaining true Auger line shapes arise from the subtraction of the secondary electron background and the removal of distortions of the Auger signal resulting from extrinsic losses suffered by some of the Auger electrons when leaving the solid. In order to overcome these problems, several approaches have been proposed and applied in the literature. In our case following the data analysis method used

by Madden and Houston[39] for the Li KVV transition, the secondary electron background was subtracted by a scheme proposed by Sickafuss[40] and successfully applied by several authors.[38] The background-corrected signal was then corrected for loss features related to the Na $L_{2/3}VV$ Auger process by applying ten iterations of the Van Cittert deconvolution technique.[41] The system response function needed for this loss deconvolution was modeled using an inelastic backscattered electron spectrum obtained with the CMA Auger spectrometer with a primary electron energy comparable to the Auger electron energy.[42] The simulation study by Madden and Houston[43] in which the validity and limits of this approach are discussed indicates that it is entirely appropriate for our purpose.

Figure 5(a) shows the initial derivative Auger spectrum obtained from six monolayers and its fitted background. Clearly the fit describes only the part of the secondary electron background which has a positive second derivative. The background-corrected and -integrated Auger spectrum is shown in Fig. 5(b) together with the relevant energy-loss spectrum, which was used as the response function in the following iterative deconvolution. Figure 5(c) shows the results obtained after each step of the
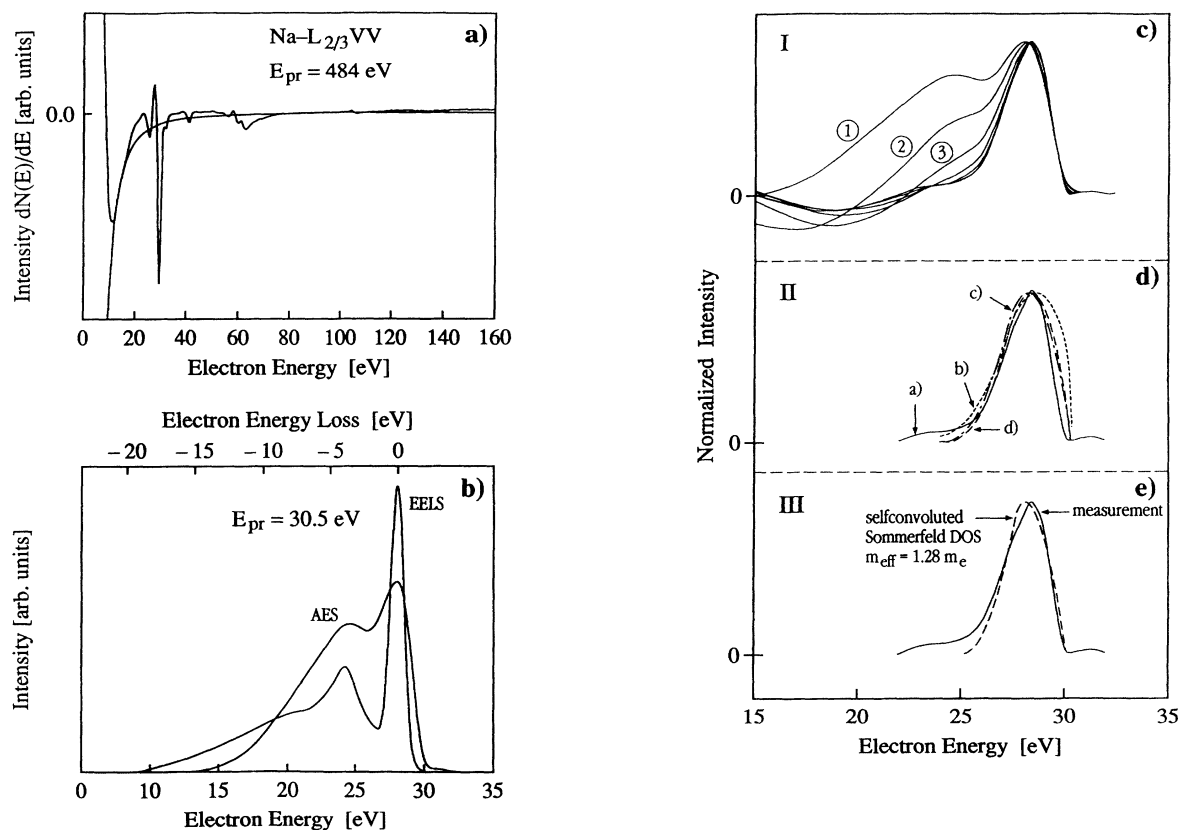

FIG 5. Results of the deconvolution procedure for the sodium valence-band spectroscopy by AES. (a) Na $L_{2/3}VV$ Auger initial derivative spectrum from six monolayers together with the fitted background. (b) Background-corrected and -integrated Na $L_{2/3}VV$ Auger spectrum and the EELS spectrum, which has been used for the modeling of the system response function. (c) Consecutive steps of the Van-Cittert deconvolution. (d) Final result of the Van-Cittert deconvolution (curve a) compared to theoretical line-shape calculations by Almbladh, Morales, and Grossman (Ref. 7) (curves b,c, and d). (e) Final result of the Van-Cittert deconvolution compared to the convoluted sodium DOS as obtained by the basic Sommerfeld theory with $m_{\text{eff}} = 1.28 m_e$.

iteration, indicating a fast convergence after six steps. Undesirable wings at the ends of the spectrum appear as a consequence of the Van Cittert deconvolution technique.[43] The final result after ten steps (curve a) is now compared in Fig. 5(d) with recent theoretical calculations by Almbladh, Morales, and Grossman (curves b, c, and d).[7] In all three models the electronic states are calculated within the framework of the LDA. Whereas for the calculation of curve b only the influence of the core hole and its screening has been considered, curve c has been calculated by additionally taking surface effects into account. Model (d), however, totally ignores the core hole screening and the existence of the surface and therefore its result (curve d) differs only very slightly from the convoluted DOS of bulk sodium as obtained from the Sommerfeld theory of a free-electron gas. While, to a first approximation, the differences between these models are rather small, our experimental curve is significantly narrower, indicating a narrowed Na valence band with respect to the free-electron model. This is in agreement with the photoemission measurements by Jensen and Plummer.[4] They found a free-electron-like parabolic valence band, which is strongly narrowed with respect to the Sommerfield theory, leading to an effective electron mass of $1.28m_e$. Theoretical work has been undertaken to explain this discrepancy by considering more sophisticatedly the self-energy corrections in a modeling of the energy spectra of the final (excited) state of the photoemission process.[5]

In the calculated line shapes of Fig. 5(d), the interaction between the Auger electron and the correlated valence-band hole state left behind is only considered within the LDA and the well established approximation of the Hohenberg-Kohn-Sham ground-state potential for the calculation of exchange and correlation effects.[7] In view of the small differences of curves b, c, and d of Fig. 5(d), we therefore believe that the Na $L_{2/3}VV$ linewidth is more affected by quasiparticle self-energy corrections than by core-hole screening or surface effects. In order to obtain an idea of the amount of this self-energy correction we compare in Fig. 5(e) our result with a convoluted DOS based on the Sommerfeld theory but with an effective mass of $1.28m_e$, as proposed by Jensen and Plummer.[4] The agreement between these two curves is surprisingly good as far as the linewidths are concerned.

We therefore hope that our experimental results will lead to further theoretical work to explain the reported narrowing of the sodium DOS observed by AES.

IV. DISCUSSION AND SUMMARY

In the present investigation alkali-metal CVV Auger spectroscopy was applied to the study of the electronic energy levels during alkali-metal adsorption. As expected, an intense CVV Auger line around 29 eV was observed for coverages higher than 0.4 monolayers during epitaxial growth of sodium on Cu(001). In the case of thick sodium films the observed lines could be assigned to the pure sodium $L_{2/3}VV$ transition due to the limited electron mean free paths, whereas for low coverages the possibility of interatomic transitions involving a sodium

2p core electron and two copper valence-band electrons has to be considered. The corresponding line shape of such a transition would to a first approximation reflect the convolution of the apparatus response function with the self-convolution of the copper DOS. As in the case of a pure copper surface, however, this would lead only to a single-peak structure regardless of the peaked 3d-electron contribution of the Cu DOS.[44] Therefore the multipeak structure of peaks $A-C$ (Fig. 1) cannot be the result of interatomic transitions even in the case of low coverages. In addition, the peak maximum of an interatomic transition should lie about 5 eV below a CVV transition involving free-electron-like states, where the DOS maximum would be at the Fermi level. However, we did not see any significant energy shift of peak C, which during adsorption develops into the $L_{2/3}VV$ Auger peak of (bulk) sodium. Only peaks A and B undergo a slight energy shift, which is much smaller than 5 eV and—more importantly—is in the opposite direction. Moreover, this shift has been linked successfully to increasing electronic excitation energies within the sodium adlayer, when interpreteting peaks A and B as loss peaks with respect to the main sodium $L_{2/3}VV$ peak. There are other experimental findings which rule out the possibility of an interatomic transition even if varying matrix elements which strongly favor interatomic transitions involving only s-like copper states are considered. First of all, the overall line shape of the observed transition remains constant during the entire coverage regime. Second, if in the low-coverage regime at about one-half monolayer interatomic transitions are observed, they already should appear with beginning adsorption showing a linear intensity increase instead of an onset. Since the origin of Auger electrons of interatomic transitions would be confined to the Na/Cu interface, we should also observe a decreasing absolute intensity rather than an increasing intensity of interatomic events in view of the layer-by-layer sodium growth. We thus conclude that the reported structure over the whole coverage interval consists of a main $L_{2/3}VV$ signal and corresponding loss satellites. The fact that they already appear during the formation of the first monolayer then leads to the conclusion that AM-induced or AM s-level-derived occupied states represent an energy band even at coverages between one-half and one full monolayer. Finally, the observation of an onset instead of a monotonic increase of the Na $L_{2/3}VV$ signal might well be linked to a sudden change in the adatom-adatom interaction, and two-dimensional condensation within the adlayer.

The line shape of the Na $L_{2/3}VV$ transition undergoes a significant change between one-half and three monolayers, indicating both increasing electron excitation energies and a strongly varying DOS in the sodium film. Unfortunately we were not able to carry out a quantitative line shape analysis in this range of coverage, because of the lack of deconvolution techniques, when intrinsic excitations during the Auger event have to be accounted for. In the case of thick sodium films, however, we could perform a detailed Na $L_{2/3}VV$ line-shape analysis in order to investigate the sodium transition DOS. By comparing our results with theoretical calculations, strong

evidence for a remarkably narrowed sodium valence band with respect to the results of basic many-body calculations has been found.

In conclusion, we have shown that CVV Auger electron spectroscopy can be used as a powerful tool in order to investigate the electronic behavior during the entire range of alkali-metal thin-film growth.

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