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Formation of free-electron-like resonant bands for alkali-metal overlayers on simple metals

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The electronic structure of hexagonal close-packed alkali-metal monolayers on the semi-infinite jellium is studied to simulate the ordered $(\sqrt{3}\times\sqrt{3})R30°$ monolayers on Al(111). The calculated electron band structure is in good agreement with recent photoemission and inverse photoemission experiments, yet it is different from the band structure of isolated monolayers in some important aspects.

Since the pioneering work of MacRae *et al.*,[1] alkali-metal adsorption on metal substrates has attracted much attention in connection with the realization of two-dimensional metals. The appearance of overlayer plasmons in electron energy-loss-spectroscopy experiments above some critical coverage (Θ) suggests that the nature of the overlayers changes rather crucially depending on the ratio of the adatom-adatom interaction to adatom-substrate interaction.[2-4] One crucial aspect of the overlayer metallization is its electron band structure, i.e., energies of adatom resonant (or true surface) states as a function of the wave vector parallel to the surface $\mathbf{k}_{\parallel}$. Heskett *et al.*[5] studied unoccupied bands of the Na monolayer on Al(111) by inverse photoemission spectroscopy (IPES), whereas very recently Horn *et al.*[6] succeeded for the first time in observing a partially occupied free-electron-like band for K/Al(111) by photoemission spectroscopy (PES). On the theoretical side, some of the previous electronic structure calculations which adopted conventional slab methods predicted the existence of free-electron-like bands derived from adatom valence states.[7,8] However, it is not clear whether discrete bands of a thin slab correspond to peak energies of adatom resonances on the semi-infinite substrates, and moreover, slab calculations give no information on the width or shape of resonances which is indispensable for comparison with experiments. Actually, as will be shown later, in contrast to such slab calculations, the alkali valence p_z state does not form a sharp resonant band on simple metal substrates. In the present paper we report, for the first time, calculated band structures of alkali-metal overlayers on a semi-infinite substrate, employing "jellium" as a substrate. The model corresponds to an extension of the well-known work of Lang and Williams[9] on the single atom adsorption on jellium to the finite Θ regime. The results obtained reveal the existence of rather sharp free-electron-like overlayer resonances over a wide energy range. They are in good agreement with the recent experiments, but different from the band structure of isolated monolayers on some important points. We use the atomic units where the units of length and energy are equal to 0.529 Å and 27.2 eV, respectively.

The left-hand side of Fig. 1 shows the calculational geometry. Details of the calculational method are described in Ref. 10. The method is a fully three-dimensional one which introduces no approximation such as taking the average of the potential energy in the planar direction,[11] and the semi-infinite calculation is performed by use of the embedding method of Inglesfield.[12] In the present work, we simulate the ordered alkali-metal monolayers on Al(111) with the $(\sqrt{3}\times\sqrt{3})R30°$ structure ($\Theta=\frac{1}{3}$ in units of Al monolayers) for which recent IPES and PES experiments[5,6] were performed. The Al(111) substrate is represented by a jellium with $r_s=2.1$ a.u. The alkali-metal ion cores are expressed by the norm-conserving pseudopotential,[13] and adatoms form a hexagonal lattice with the nearest-neighbor lattice constant $a_{\parallel}=9.35$ a.u. The distances between the adatom and jellium edge are chosen as 3.0 and 4.0 a.u., for the Na and K layers, respectively, which correspond approximately to the total-energy minimum.[14]

The right-hand side of Fig. 1 shows a contour map of the difference charge $\delta\rho(\mathbf{r})$ for the Na overlayer on a vertically cut plane which contains adatoms at an interval of $a_{\parallel}$. Here $\delta\rho(\mathbf{r})$ is defined as the charge density of the

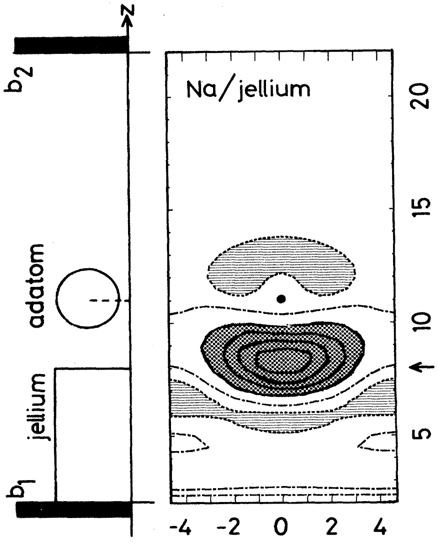

FIG. 1. Left-hand side: calculational geometry for alkali-metal overlayers on the semi-infinite jellium. Right-hand side: contour map of the difference charge $\delta\rho(\mathbf{r})$ for the Na adlayer. The shaded and hatched areas indicate the regions where $\delta\rho(\mathbf{r})\geqq 0.001$ a.u. and $\delta\rho(r)\leqq -0.0005$ a.u., respectively.

alkali-metal–covered jellium surface minus the superposed density of the isolated Na layer and bare jellium. The electron density accumulates in the Na-jellium interface as a result of the formation of a metallic adatom-substrate bond. The bond charge contour as well as the main charge-depletion region in the vacuum side of a Na atom is very similar to those calculated previously with a slab method for a Na square lattice on the jellium with a similar atomic density.[15,16] The charge redistribution shown in Fig. 1 results in an electric dipole layer to lower the work function; the work function of the jellium substrate, 3.8 eV, is reduced to 2.6 and 2.3 eV for the Na and K overlayers, respectively.

The solid lines in Fig. 2 show the adatom-*induced* density of states (DOS) defined by

$$\rho_a(\varepsilon,\Theta)=\int_{\mathrm{SBZ}}\frac{d\mathbf{k}_{\parallel}}{(2\pi)^2}[\rho_a(\mathbf{k}_{\parallel},\varepsilon,\Theta)-\rho_a(\mathbf{k}_{\parallel},\varepsilon,\Theta=0)]\,, \tag{1}$$

where

$$\rho_a(\mathbf{k}_{\parallel},\varepsilon,\Theta)=-\frac{2}{\pi}\int_R d\mathbf{r}\,\mathrm{Im}G(\mathbf{r},\mathbf{r},\mathbf{k}_{\parallel},\varepsilon,\Theta)\,. \tag{2}$$

In Eq. (2), $G(\mathbf{r},\mathbf{r}',\mathbf{k}_{\parallel},\varepsilon,\Theta)$ denotes the Green's function with the one electron-energy ε and wave vector $\mathbf{k}_{\parallel}$, and the integration in Eq. (2) is done in a sphere around an adatom. Its radius R is chosen as 4.5 a.u. for both Na and K atoms. The dashed, dot-dashed, and dotted lines show the decomposition of $\rho_a(\varepsilon,\Theta)$ into the s, $p_{\parallel}$ (p_x+p_y), and p_z components, respectively. Although qualitative features of $\rho_a(\varepsilon,\Theta)$ for the Na and K overlayers are quite similar to each other in the occupied part below the Fermi level E_F, there is considerable difference in the unoccupied part; $\rho_a(\varepsilon,\Theta)$ for the K overlayer has spiky peaks above E_F which are absent in $\rho_a(\varepsilon,\Theta)$ for Na. The difference comes from the d bands of the K overlayer which are located in a considerably lower-energy range as compared with those of Na. By comparing $\rho_a(\varepsilon,\Theta)$ in Fig. 2 with that given by Lang and Williams[9] in the limit of $\Theta\rightarrow 0$ for Na, it is seen that the sharp resonant peak located about 1 eV above E_F in the limit of $\Theta\rightarrow 0$ is completely lost at the present Θ. This indicates a formation of wide overlayer bands due to the large overlap of neighboring orbitals, which is discussed in detail in the following.

To examine the energy dispersion of adatom resonant bands, we show in Fig. 3 $\rho_a(\mathbf{k}_{\parallel},\varepsilon,\Theta)$ for the Na overlayer along the $\bar{\Gamma}$-$\bar{M}$ line in the surface Brillouin zone (SBZ), which corresponds to angle-resolved spectra in PES and IPES experiments. The dashed, dot-dashed, and dotted lines show decomposition of $\rho_a(\mathbf{k}_{\parallel},\varepsilon,\Theta)$ into s, $p_{\parallel}$, and p_z partial DOS, respectively. $\rho_a(\mathbf{k}_{\parallel},\varepsilon,\Theta)$ has much richer structures than $\rho_a(\varepsilon,\Theta)$ in Fig. 2. The lowest peak, contributed strongly by s and also by the p_z state in its upper half, disperses upward with increasing $\mathbf{k}_{\parallel}$, and crosses E_F in the middle of the $\bar{\Gamma}$-$\bar{M}$ line. In contrast to the case of isolated monolayers,[17] the p_z resonance is greatly broadened, and does not form a separated peak in $\rho_a(\mathbf{k}_{\parallel},\varepsilon,\Theta)$ due to the adatom-substrate interaction. The wave function corresponding to the energy region of the p_z resonance has an antibonding character with respect to

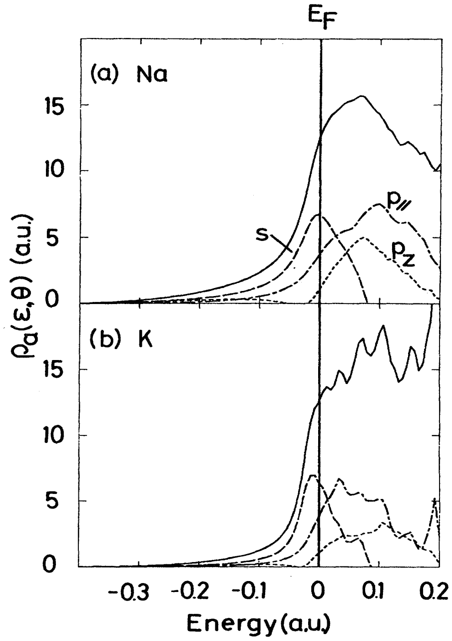

FIG. 2. The calculated adatom-induced DOS, $\rho_a(\varepsilon,\Theta)$ and its decomposition into s, $p_{\parallel}$, and p_z components for the Na and K overlayers. The total, s, $p_{\parallel}$, and p_z DOS are shown by solid, dashed, dot-dashed, and dotted curves, respectively. E_F denotes the Fermi level.

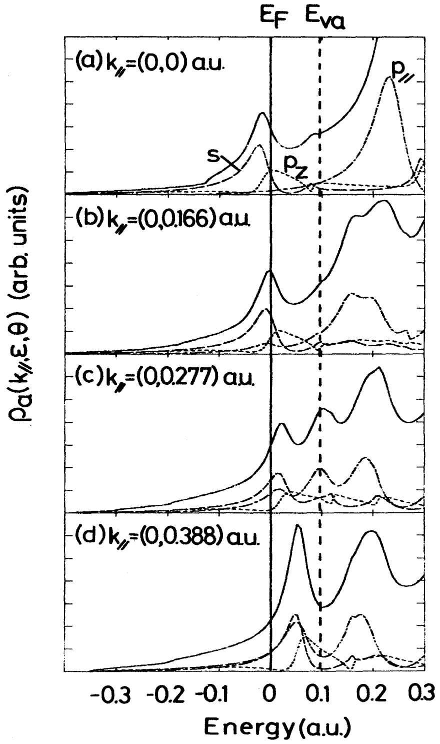

FIG. 3. The calculated $\rho_a(\varepsilon,\mathbf{k}_{\parallel},\Theta)$ for the Na overlayer along $\bar{\Gamma}$-$\bar{M}$ line. (a) and (d) correspond to $\bar{\Gamma}$ and $\bar{M}$, respectively. E_{va} denotes the vacuum level.

the adatom-substrate bonding, and polarizes toward the vacuum side of the overlayer. On the other hand, the $p_{\parallel}$-like peak located about 6.5 eV above E_F at $\bar{\Gamma}$ splits into two bands which disperse downward with increasing $\mathbf{k}_{\parallel}$. The lower one with a larger energy dispersion almost degenerates with the s-like band at $\bar{M}$ [Fig. 3(d)].

The solid lines in Fig. 4 show the band structure of the Na overlayer on the jellium along high-symmetry lines in SBZ, which is obtained from the peak energies of $\rho_a(\mathbf{k}_{\parallel},\varepsilon,\Theta)$. These bands have finite widths as shown in Fig. 3 and are not discrete states. Along $\bar{\Gamma}$-$\bar{M}$, we also showed the center of gravity of the broad p_z resonance by dot-dashed lines. The energy difference between the s and p_z resonances is ~ 1 eV, which is less than half of the corresponding value for the isolated monolayer. In the case of the K overlayer, the band structure above E_F is more complicated due to the existence of d bands, and we show only the dispersion of the lowest s-like band by dashed lines. Its bandwidth is a little larger than that for Na because of the larger orbital overlapping among adatoms. The free-electron-like band structure in Fig. 4 indicates the weak adatom-substrate bonding at higher Θ as well as formation of metallic overlayers. Moreover, the effective mass of the lowest s-like band for Na estimated from the dispersions along $\bar{\Gamma}$-$\bar{M}$ and $\bar{\Gamma}$-$\bar{K}$ is $1.0-1.1 m_e$ (electron mass). The formation of free-electron-like bands for overlayers at higher Θ is not a very obvious fact because they originate from rather weak ion core potentials and are easily modified by stronger substrate potentials.[18] One important point is that the calculated Na band structure in Fig. 4 has quite small energy splittings at zone boundaries. For example, the s and $p_{\parallel}$ resonances are almost degenerate at $\bar{M}$, whereas the corresponding energy splitting in the band structure of the isolated monolayer amounts to ~ 0.5 eV.[17] This may be explained by the following two reasons: (1) The high-density metal substrate can screen the periodic alkali-metal ion core potentials more effectively than the isolated layer; (2) since the wave functions of the alkali-metal valence states are delocalized into the substrate, they are less affected by the periodicity of the ion core potentials than those in the isolated monolayer.

The filled circles in Fig. 4 show the K 4s-like band on Al(111) along $\bar{\Gamma}$-$\bar{M}$ recently measured by Horn *et al.*[6] by PES. The experimental band is in good agreement with the calculated one, except one $\mathbf{k}_{\parallel}$ point near $\bar{M}$, where it may become difficult experimentally to identify the resonant peak because it completely overlaps with the structure at the Fermi edge. The open circles in Fig. 4 show the results of an IPES experiment by Heskett *et al.*[5] for the Na overlayer of Al(111). They observed two broad structures which disperse upward along the $\bar{\Gamma}$-$\bar{M}$ and $\bar{\Gamma}$-$\bar{K}$ lines. By comparing them with the band structure of an isolated Rb monolayer,[17] they attributed the higher and lower ones to the Na d and p_z states, respectively. As for the observed higher structure, there seems to be no corresponding state in the present calculation; Na d states are located in much higher energies. The observed structure might be related with the change in the electronic structure of Al(111) or might be an image-potential state as suggested by Heskett *et al.* themselves. Regarding the observed lower band, its energy location is in fair agreement with the center of gravity of the p_z resonance shown by dot-dashed lines. Although Na 3p_z does not form a sharp resonance, its broad structure might really be observed because of its larger cross section as compared with Na 3s in IPES. In the same way, the reason why the unoccupied part of the lowest s-like band was not observed might be related with its smaller cross section in IPES.

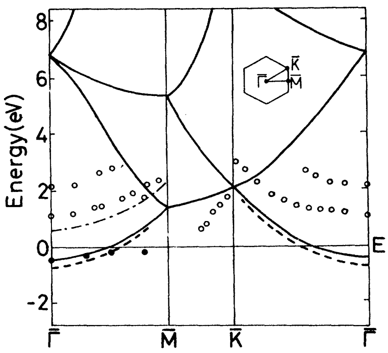

FIG. 4. Electron band structures of the Na and K overlayers on the jellium. The open and filled circles indicate experimental data taken from Refs. 5 and 6, respectively.

In conclusion, the electronic structure of alkali-metal monolayers on the semi-infinite jellium is studied to simulate the ordered monolayers on Al(111). Rather sharp free-electron-like bands are formed in a wide energy range, indicating formation of metallic overlayers. The calculated band structure is in agreement with recent experiments, yet it is modified from that of isolated monolayers in some important points.

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[1] A. U. MacRae, K. Muller, J. J. Lander, J. Morrison, and J. C. Phillips, Phys. Rev. Lett. **22**, 1048 (1969).

[2] J. Cousty, R. Riwan, and P. Soukiassian, J. Phys. (Paris) **46**, 1693 (1985).

[3] U. Jostell, Surf. Sci. **82**, 333 (1979).

[4] H. Ishida and M. Tsukada, Surf. Sci. **169**, 225 (1986).

[5] D. Heskett, K.-H. Frank, E. E. Koch, and H.-J. Freund, Phys. Rev. B **36**, 1276 (1987).

[6] K. Horn, A. Hohlfeld, J. Somers, Th. Lindner, P. Hollins, and A. M. Bradshaw, Phys. Rev. Lett. **61**, 2488 (1988).

[7] E. Wimmer, A. J. Freeman, J. R. Hiskes, and A. M. Karo, Phys. Rev. B **28**, 3074 (1983).

[8] G. A. Benesh and J. R. Hester, Surf. Sci. **194**, 567 (1988).

[9] N. D. Lang and A. R. Williams, Phys. Rev. B **18**, 616 (1978); **16**, 2408 (1977).

[10] H. Ishida, Phys. Rev. B **39**, 5492 (1989).

[11] P. A. Serena and N. Garcia, Surf. Sci. **189/190**, 232 (1987); W. Ning, C. Kailai, and W. Dingsheng, Phys. Rev. Lett. **56**, 2759 (1986).

[12] J. E. Inglesfield, J. Phys. C **14**, 3795 (1981).

[13] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[14] The value for Na is determined from the total-energy minimization. Since pseudopotential calculations for heavier alkali-metal atoms underestimate the interatomic distance, we used the value determined by N. D. Lang, S. Holloway, and J. K. Norskov, Surf. Sci. **150**, 24 (1985) in the limit of $\Theta \rightarrow 0$ for K.

[15] H. Ishida, Phys. Rev. B **38**, 8006 (1988).

[16] H. Ishida and K. Terakura, Phys. Rev. B **36**, 4510 (1987).

[17] E. Wimmer, J. Phys. F **13**, 2313 (1983).

[18] S. Ciraci and I. P. Batra, Phys. Rev. B **37**, 2955 (1988).