

UNOCCUPIED ELECTRONIC STATES OF POTASSIUM AND SODIUM ON Ag(110)*

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Abstract

Unoccupied electronic states induced by alkali adsorption on a Ag(110) surface were investigated by inverse photoemission. In addition to electrostatically induced level shifts the formation of energy bands in periodic overlayers was monitored. Despite their chemical similarity considerable differences exist between potassium and sodium induced empty electronic states. The relation of the observed unoccupied bands to the two-dimensional bandstructure of an unsupported alkali metal layer is discussed.

Introduction

The adsorption of alkali atoms on metal surfaces has been studied extensively in the past 60 years because there is a lot of interest in these systems from the applied as well as the fundamental point of view. Alkali covered metal substrates are used as low work function cathodes, promoters in heterogeneous catalysis, but also as simple model systems for chemisorption studies.

The first qualitative quantummechanical description of alkali adsorption was given by Gurney already in 1935. Refined quantitative models were developed more than 30 years later by Lang, Muscat and Newns and others (Lang, 1971; Lang and Williams, 1978; Muscat and Newns, 1974, 1984). In the Gurney model the discrete *s*-electron valence level of the isolated alkali atom broadens into a resonance upon adsorption on the metal due to the interaction with the metal substrate. At low coverages this so called *s*-resonance is centered above the Fermi energy E_F . Only the tail of the resonance extends below E_F . Therefore the *s*-resonance is mostly unoccupied and as a consequence the bonding to the metal is strongly ionic. The partly ionic alkali atoms and their image charges in the metal form dipoles at the surface leading to a lowering of the work function. At sufficiently high coverage interactions

* Dedicated to Prof J. Giber on the occasion of his 60th birthday.

between the alkali atoms reduce the dipole moment per adatom thereby slowing down the work function decrease. At a certain coverage the depolarization just offsets the increasing number of dipoles and thus the characteristic minimum in the work function versus coverage curve is produced as shown for example in the inset of Fig. 3 for adsorption of sodium and potassium on a Ag(110) surface. The depolarization mechanism may be envisioned as follows: With increasing coverage the s -resonance is pushed down towards the Fermi level. In the Gurney model this is due mainly to an electrostatic effect. As a consequence the s -resonance becomes occupied to a larger extent and the dipole moment per adatom is reduced. The bonding changes from strongly ionic to predominantly metallic character.

This simple model nicely explains the qualitative work function change $\Delta\Phi$ reported in a wealth of alkali/metal adsorption studies (see Bonzel, 1987, and references therein). On the other hand these $\Delta\Phi$ measurements support the model only indirectly making a direct observation of the alkali valence levels highly desirable. Most photoemission (PES) investigation up to now have failed to detect any occupied alkali induced state near E_F . Only measurements by Lindgren and Walldén, 1978 and 1980, using low photon energies for studying the adsorption of Cs and Na on Cu(111) and a recent PES investigation of K/A1(111) (Horn *et al.*, 1988) showed an alkali induced feature just below E_F appearing at coverages of approximately one half of a monolayer, which could be explained in terms of a partially refilled alkali s -resonance. Using electron spectroscopy by deexcitation of metastable noble gas atoms (MDS) for the study of K/Cu(110) Woratschek *et al.*, 1985, were able to detect K-induced features just below the Fermi energy already at very low coverages indicating that even a single adsorbed alkali atom is not completely ionized. In this paper we will show complementary data on the unoccupied alkali induced states obtained by inverse photoemission (IPE) for the adsorption of Na and K on a Ag(110) surface.

Experimental

Experiments were carried out in an UHV system with a base pressure below 10^{-8} Pa. The Ag(110) surface was cleaned by Argon ion sputtering and subsequent annealing up to approximately 1000 K. The IPE facility consists of an electrostatically focussed electron gun with BaO cathode and a Geiger Müller counter with Iodine filling and a CaF_2 window (Dose, 1977) yielding an overall resolution of 0.8 eV FWHM. The counter was mounted in the plane of incidence at an angle of 51° relativ to the electron gun. The angle θ of the incident electron beam could be varied by rotating the sample around an axis perpendicular to the plane of incidence. All measurements were done

along the line $\bar{\Gamma}\bar{Y}$ of the surface Brillouin zone (SBZ). Work function changes were measured via the diode method using the IPE electron gun. Alkali overlayers were prepared in the case of K by dosing the sample at room temperature with the proper amount of alkali from an SAES getter source or in the case of Na by adsorbing multilayers of alkalis at 100 K and subsequent partial thermal desorption in order to reach the desired coverage. Both methods yield essentially identical overlayers (Behm et al., 1987). Throughout this article the coverage Θ is defined as the ratio of the number of adsorbed alkali atoms to the number of Ag-atoms in the topmost layer ($8.45 \cdot 10^{14} \text{ cm}^{-2}$). Relative coverages were obtained by thermal desorption spectroscopy

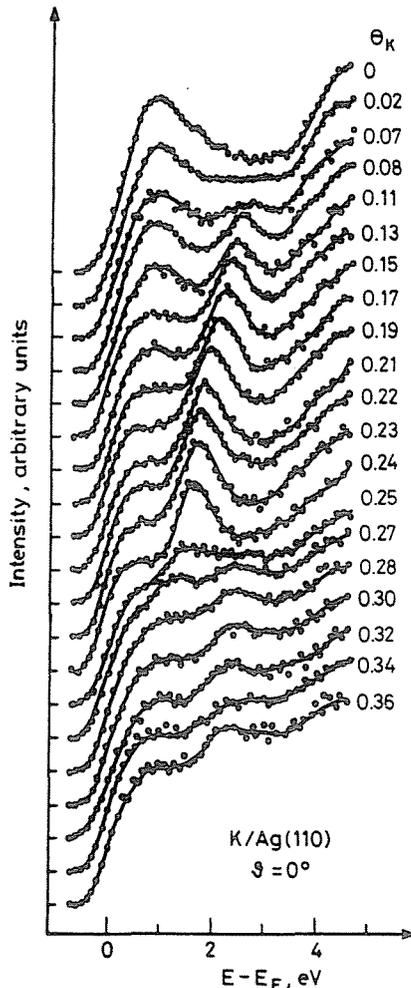


Fig. 1. IPE spectra of K/Ag(110) as a function of potassium coverage Θ_K . The spectra were taken at normal electron incidence

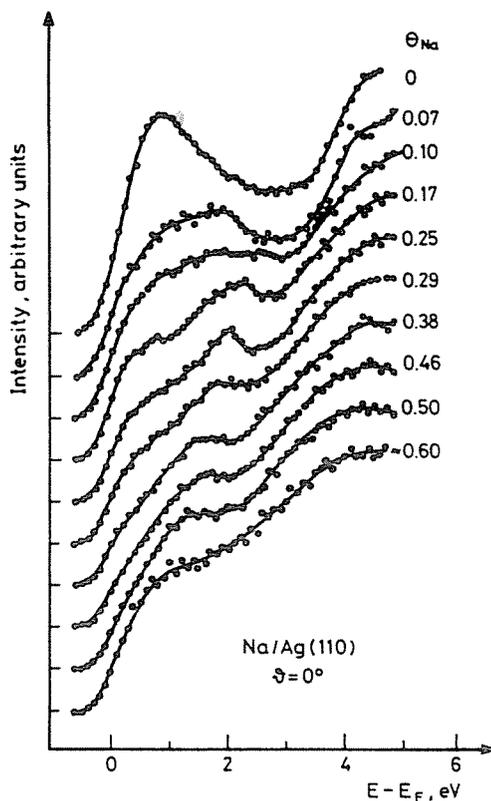


Fig. 2. IPE spectra of Na/Ag(110) as a function of sodium coverage Θ_{Na} . The spectra were taken at normal electron incidence

and converted to absolute values by assuming the minimum of the work function to occur at a coverage of one half of a close packed layer of metallic K or Na, i.e. the work function minimum was associated with a value of $\Theta_{\text{K}} = 0.32$ and $\Theta_{\text{Na}} = 0.5$, respectively. Although a long-range periodic ordering of the adsorbate layer was indicated by the observation of LEED patterns, a coverage determination by LEED was not possible due to an alkali induced reconstruction occurring already at low coverages (Hayden *et al.*, 1983).

Results and discussion

Figures 1 and 2 show a series of IPE spectra taken at normal incidence for various potassium and sodium coverages. A spectrum of the clean Ag(110) surface is also shown for comparison. IPE spectra of Ag(110) are discussed in detail by Altmann *et al.*, 1986. Upon adsorption of potassium a new structure

appears already at coverages below $\Theta_K = 0.1$ at energies around 2.5 eV above the Fermi level. With increasing coverage this K induced feature shifts towards the Fermi energy. Up to a coverage of $\Theta_K \approx 0.24$ the peak increases in intensity while at higher coverages a rapid intensity decrease is observed accompanied by the appearance of an additional feature near 2.5 eV above E_F . Upon adsorption of sodium an analogous alkali induced peak is observed showing a similar behaviour with regard to the coverage dependence of peak energy and peak intensity although the Na induced features are much less pronounced. In the case of Na the emergence of a second peak at higher coverage cannot clearly be discerned. The energy positions of the alkali induced structures as a function of coverage is plotted in Fig. 3. We assign this strongly shifting peak to an alkali p_z derived level for the following reasons:

As predicted by theory and observed by MDS the s -resonance should be partly occupied even at low coverage. Therefore the s -resonance is expected to be located near the Fermi energy. In contrast extrapolation of our data to zero coverage yields peak energies of 3.1 and 2.6 eV above E_F for K and Na respectively. Furthermore theoretical and experimental evidence indicates that near half monolayer coverage (\approx work function minimum) the bonding becomes essentially metallic and therefore the s -resonance should be half filled and centered at the Fermi level. For periodic adsorbate structures as they are observed in most cases for alkalis — also in the present experiment — the wave vector $k_{||}$ is a good quantum number. Accordingly, rather than considering just the density of states one should take into account band

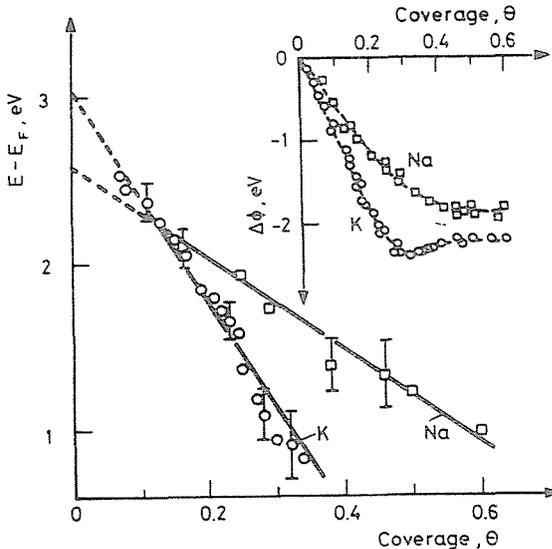


Fig. 3. Energy position of the p_z derived unoccupied level for K/Ag(110) and Na/Ag(110) as a function of coverage Θ . The inset shows the accompanying work function change

formation. Instead of a half filled s -resonance one should then consider a half filled s -band. This means that the bottom of the s -band at $\bar{\Gamma}$, corresponding to $\mathbf{k}_{\parallel}=0$, has to be located considerably below E_F . In contrast our measurements indicate a peak position approximately 1 eV above E_F . Therefore the observed feature cannot be due to the s -resonance or s -band and we assign it to a level derived mainly from p -states of the isolated alkali atom. In the adsorbed state, however, the local symmetry is rather low allowing s , p_z and d_{z^2} derived levels to mix. An analysis by Lang, 1989, shows that the unoccupied level considered here has nearly pure p_z character for Na but contains non-negligible d -admixture in the case of K. For simplicity we henceforth call it p_z -resonance in both cases. The shift observed parallels the one expected for the s -resonance. The latter however cannot be observed because of interference with the Ag induced peak right at E_F .

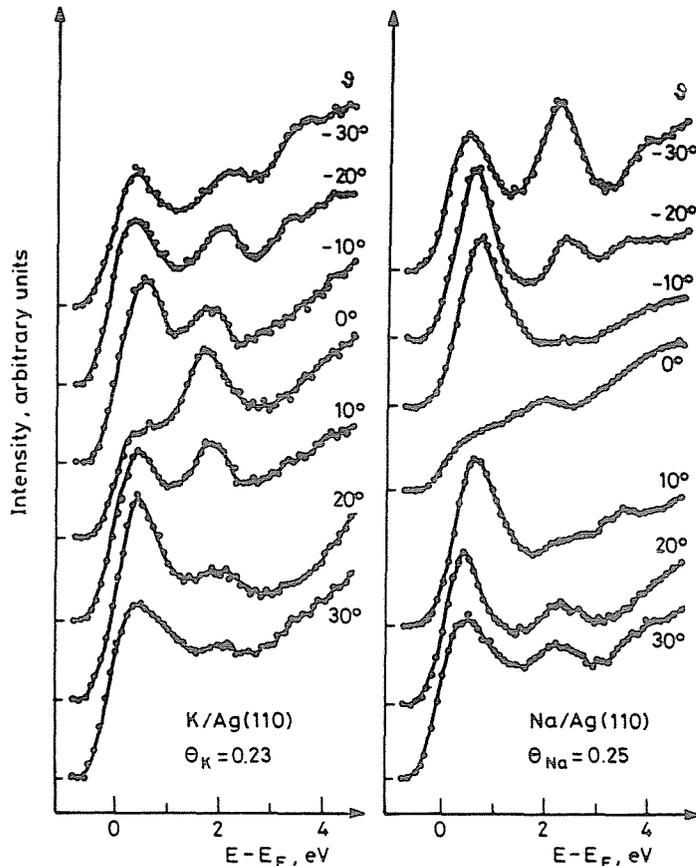


Fig. 4. IPE spectra for K/Ag(110) and Na/Ag(110) at various angles of incidence for coverages of $\Theta_K=0.23$ and $\Theta_{Na}=0.25$ respectively. Spectra were taken along the line $\bar{\Gamma}\bar{Y}$ of the SBZ

Electron energy loss spectroscopy (EELS) measurements of various alkali/metal systems (e.g. Andersson and Jostell, 1975; Soukiassian et al., 1982 and 1985; Rangelov and Sumev, 1987) show a strongly coverage dependent loss which changes from 3–4 eV at low alkali coverages to approximately 1–3 eV at half monolayer coverage. The existence of an alkali induced state of p character which shifts from 2–3 eV above E_F at low coverages to roughly 1 eV above E_F near half monolayer coverage (as is observed here) can explain these EELS data as a transition from an occupied level with partial s character to an alkali p derived empty state. From a combination of PES and EELS in the study of Cs/W(100) Soukiassian et al., 1985 derived a shift of the unoccupied level which varied linearly with coverage up to about half a monolayer. The data in Fig. 3 exhibit just such a behaviour, this time however verified by a direct measurements.

Further support for the p_z assignment is given by the observed dispersion behaviour. Fig. 4 shows IPE spectra taken at various angles of incidence for coverages $\Theta_K=0.23$ and $\Theta_{Na}=0.25$. The corresponding E versus $k_{||}$ diagrams are displayed in Figs 5 and 6. The dispersion of the K induced structure can be followed nicely and ranges from ≈ 1.7 eV at $\vartheta=0^\circ$ to ≈ 2 eV at $\vartheta=\pm 30^\circ$. Such an upward dispersion is expected for a band of either s or p_z character. Bandstructure calculations for unsupported hexagonal monolayers of alkali metals (Wimmer, 1983) show a parabolic upward dispersion of the p_z band at $\bar{\Gamma}$ with an effective mass $m^*/m \approx 1.2$ for potassium. From our data an effective mass $m^*/m \approx 3.3$ can be derived (A slightly lower reduced mass $m^*/m \approx 2.5$ was erroneously given in the original paper by Jacob et al., 1987)

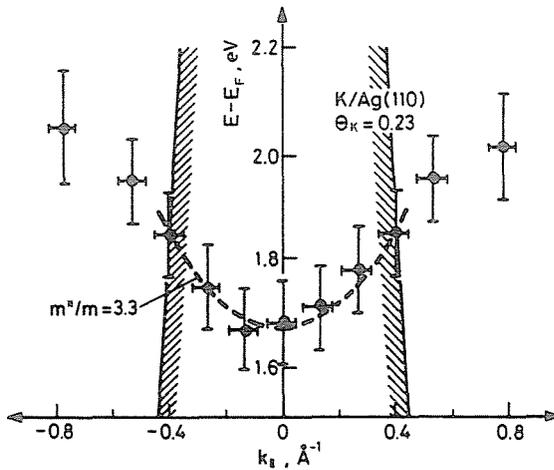


Fig. 5. Energy versus $k_{||}$ plot of the K p_z derived unoccupied state for a coverage of $\Theta_K=0.23$. The interpolating parabola corresponds to an effective mass of $m^*/m \approx 3.3$. Unshaded areas indicate gaps of the projected bulk bandstructure (Eckhardt et al., 1984)

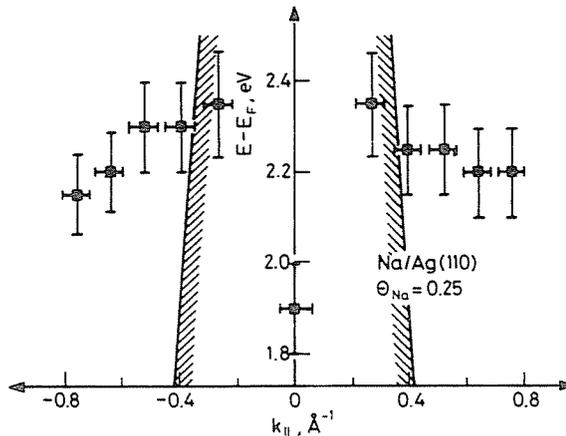


Fig. 6. Energy versus $k_{||}$ plot for Na/Ag(110), $\Theta_{\text{Na}} = 0.25$. Unshaded areas indicate gaps of the projected bulk bandstructure (Eckhardt *et al.*, 1984)

which is consistent with the coverage in the experiment being only $\approx 1/3$ of the coverage for which the calculations were done. It is surprising, though, that the calculations for an unsupported layer reproduce the electronic structure of an adsorbed layer qualitative quite well.

The observation of band formation already at such low coverages has another consequence: When talking about energetic positions of the alkali induced resonances in the Gurney or other theoretical models we always talk about the maxima in the density of states distribution. However what is measured in k -resolved IPE spectroscopy is the energy position of a band at a well defined point of the Brillouin zone. The regions of the Brillouin zone which contribute most to the density of states are those close to the zone boundary. Consequently the maximum of the density of states in dispersing bands is always associated with the band energy close to the zone boundary rather than the energy of the band at $\bar{\Gamma}$. However the strong downward shift with increasing coverage of the p_z level — ≈ 2.1 eV for K and ≈ 1.6 eV for Na — has been measured at $\bar{\Gamma}$ and therefore has to be attributed at least partially to the increasing bandwidth. This is also consistent with the observed larger shift in the case of potassium as compared to the case of sodium. The K $4p$ wavefunction is spatially more extended than the Na $3p$ wavefunction. Thus at equal coverages the overlap will be larger for potassium leading to a broader band and a larger shift to lower energies of the p_z level at the $\bar{\Gamma}$ point.

Heskett *et al.*, 1987 and 1988, observed a similar downward shift of the p_z derived level at $\bar{\Gamma}$ for low coverages of sodium on Al(111). A measurable dispersion was observed at $\Theta_{\text{Na}} = 0.33$ and found to be even more pronounced at $\Theta_{\text{Na}} = 0.5$ (this coverage was assigned by the authors to the completion of

the first monolayer). Again this shows that the dispersion has to be considered when measured peak shifts are interpreted.

Instead of choosing this more chemically oriented interpretation of the observed levels in terms of bands derived from atomic orbitals, Lindgren and Walldén, 1988, used an alternative, more formal approach. They explained the observed unoccupied levels for a monolayer of Na on Al(111) (Heskett et al., 1987) as resonances in the alkali overlayer using a simple phase accumulation model (Echenique and Pendry, 1978) based on a phenomenological one-electron potential. Salmi and Persson, 1989, refined this approach using a self consistent potential derived from a jellium description of the Al substrate and the alkali overlayer. Although this approach seems to be remarkably successful if applied to complete monolayers it can hardly be used to describe the electronic energy bands at submonolayer coverages where high coverage dependent effective masses are observed.

In the following we consider the system Na/Ag(110) in more detail. In this case the dispersion cannot be followed throughout the Brillouin zone since the weak Na induced structure at normal incidence vanishes when increasing the angle of incidence to about $\pm 10^\circ$. At $\pm 20^\circ$ a peak appears at approximately 0.4 eV higher energy which shows a small downward dispersion with increasing k_{\parallel} . At $\vartheta = -30^\circ$ this peak dominates the IPE spectrum in marked contrast to the relatively weak structure observed for potassium at this angle. In order to clarify the nature of this peak IPE spectra were taken at $\vartheta = -30^\circ$ (this approximately corresponds to the \bar{Y} point of the clean SBZ) for various coverages of sodium (see Fig. 7). On clean Ag(110) a strong IPE transition is observed with a final state energy of 1.8 eV. Altmann et al., 1986, identified this peak as a crystal induced surface state located in the gap of the projected bulk bandstructure near \bar{Y} . With increasing Na coverage initially this peak shows little change in intensity but a pronounced shift to higher energy. At $\Theta_{\text{Na}} \approx 0.15$, however, this trend is suddenly reversed and for $\Theta_{\text{Na}} > 0.15$ the IPE peak shows the familiar behaviour of dropping down in energy towards E_F as more Na is added onto the surface. We would like to point out that the dispersion is rather dramatically affected by sodium adsorption. Around \bar{Y} strong dispersion is observed for the clean surface ($m^*/m \approx 0.9$, Altmann et al., 1986), whereas for the Na covered surface the dispersion is much smaller (Fig. 6). In the case of potassium adsorption this state is quenched already at low coverages.

Finally we return to Fig. 1 in order to discuss the origin of the second alkali induced structure in the normal incidence spectra of K/Ag(110) for coverages $\Theta_K \geq 0.25$, which corresponds to roughly 1/3 of a closed packed metallic monolayer of potassium. This feature is tentatively assigned to the K 3d derived level as suggested by the calculations of Wimmer, 1983, for free monolayers of alkali metals. They show that the second unoccupied band at

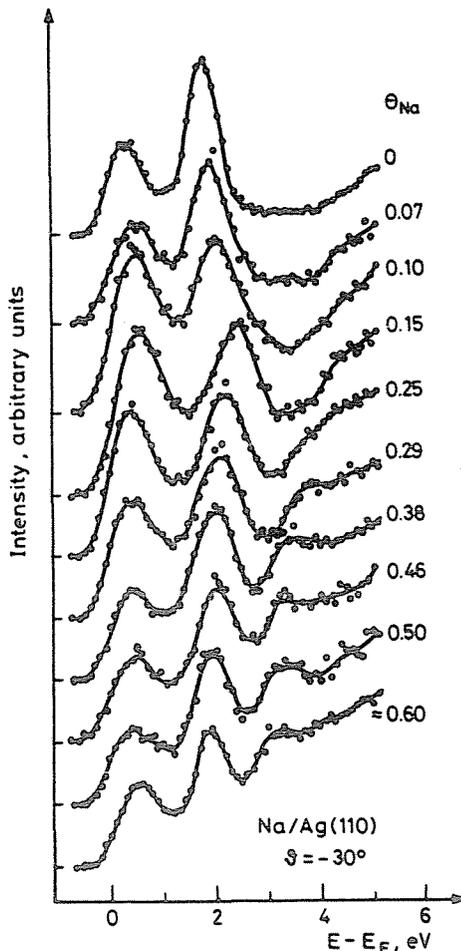


Fig. 7. IPE spectra of Na/Ag(110) as a function of sodium coverage Θ_{Na} . The angle of incidence is -30°

$\bar{\Gamma}$ is located approximately 1.5 eV above the p_z derived band and has mainly d character. Heskett et al., 1988, also observed a second alkali induced unoccupied state for Na/Al(111) at roughly the same fraction of the monolayer coverage and likewise assigned it to a Na d derived band. As mentioned above such a state could not be clearly identified for Na/Ag(110).

Summary

We observed unoccupied p_z and d derived levels for potassium and sodium adsorbed on a Ag(110) surface. With increasing coverage the p_z derived level shows a strong shift at $\bar{\Gamma}$ towards the Fermi level in agreement with previous EELS results. Even for submonolayer coverages the observed shift is partly due to bandformation and not only due to electrostatic effects. The measured dispersion is qualitatively similar to calculated bandstructures for free monolayers of alkali metals. Adsorption of sodium leads to a modification of a crystal induced surface state located in the gap of the projected bulk bandstructure near \bar{Y} .

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