

Ionicity of Alkali-Metal Adsorbates

Riffe, Wertheim, and Citrin [1] reported the core level binding energies (BE's) of surface layer W atoms when alkali metals are adsorbed on W(110). For low coverage and for first-layer saturation coverage, they find only very small shifts from the BE values for a clean surface. They conclude that there is little, if any, charge transfer from the adsorbed alkali to W, even in the limit of low coverage. At low coverages, adsorbed alkali atoms have long been believed to be fully ionic [2]. In this Comment, we show that these small BE shifts are fully consistent with large ionic character of an adsorbate.

We used idealized point charge (PC) models of ionic adsorbates. A $PC=+1$ represents a cationic adsorbate, the character [3] that we have found for K/Cu(100). A $PC=-1$ represents an anionic adsorbate, the character that has been found [4] for F/Ag(111). We examine the BE shifts for a Cu surface using the same cluster model for Cu(100) as in our previous study [3] of K/Cu(100); the effects shown for Cu should hold for other metal surfaces. The PC is in a fourfold site above a Cu_{25} cluster [3]; it is placed near the equilibrium adsorbate distance, z , found for $Cu_{25}K$, $z(PC=+1)=3.0$ Å, and $Cu_{25}F$, $z(PC=-1)=1.8$ Å. Self-consistent-field (SCF) wave functions were obtained for $Cu_{25}PC^+$, where $PC^+=+1$, and $Cu_{25}PC^-$; the charge on Cu_{25} maintains the proper neutrality for substrate (Cu_{25}) plus adsorbate (PC).

We use initial state BE's given by Koopmans' theorem [5] (KT). Final state relaxation, which screens the core hole, is neglected because there is a large body of evidence [5] which suggests that this neglect may not be serious. In Table I, the shifts of the KT BE's, $\Delta E_B(nl)$, for the $3s$ and $3p$ core levels of the four Cu atoms nearest the adsorbate are given under the heading SCF. The $\Delta E_B(nl)$ are the difference of the BE's for $Cu_{25}PC^-$ or $Cu_{25}PC^+$ from neutral Cu_{25} ,

$$\Delta E_B(nl) = E_B(nl; Cu_{25}PC) - E_B(nl; Cu_{25}). \quad (1)$$

For both $Cu_{25}PC^+$ and $Cu_{25}PC^-$, the ΔE_B are small; for $Cu_{25}PC^+$, the values are somewhat larger than the extremely small shifts reported by Riffe, Wertheim, and Citrin [1]. It is important to stress that the key feature of our result is that the ΔE_B are small; the absolute value or even the sign is less important. This is because there are other effects [5] which could lead to changes of ~ 0.1 eV in the ΔE_B . One of these is a differential final state relaxation energy between $Cu_{25}PC$ and Cu_{25} . Another is limitations in the representation of the Cu surface conduction band given by the Cu_{25} cluster. The main point is that this calculated $\Delta E_B \lesssim 0.1$ eV is much smaller than expected from the large electrostatic potential due to ionic adsorbates.

We estimate this electrostatic effect by fixing the substrate density as that for the isolated charged Cu_{25} cluster and adding the point charge to this frozen orbital

TABLE I. SCF and FO BE shifts for core levels of the adsorption site Cu atoms; see Eq. (1).

	$Cu_{25}PC^+$		$Cu_{25}PC^-$	
	SCF	FO	SCF	FO
$\Delta E_B(3s)$ (eV)	-0.13	+1.56	+0.02	-2.99
$\Delta E_B(3p)$ (eV)	-0.12	+1.56	+0.02	-3.00

(FO) cluster. The ΔE_B for the FO $Cu_{25}PC$ clusters represent only the effect of the electrostatic potential arising from the PC; they do not include polarization of the substrate charge to screen the potential of the PC. These FO ΔE_B , given in Table I, are quite large. The electrostatic potential due to a cation, $PC=+1$, increases the Cu core level BE's by ~ 1.5 eV, while that due to an anion [6], $PC=-1$, lowers the Cu BE's by ~ 3.0 eV. The larger magnitude of the FO ΔE_B for $PC=-1$ occurs because the $PC=-1$, which models F/Cu, is closer to the Cu(100) surface, by 1.2 Å, than is $PC=+1$, which models K/Cu. The contribution of the response of the highly polarizable metal surface to the presence of the PC is given by the difference between the FO and SCF ΔE_B . This polarization contribution is almost equal in magnitude and opposite in sign to the electrostatic contribution. Effectively, the polarization screens the point charge and this explains why the ΔE_B due to an ionic adsorbate will be very small.

In conclusion, the small surface W(4f) BE shifts found [1] for low coverage of alkali metals on W(110) are quite consistent with the strong evidence [2,3] for the ionicity of adsorbed alkali atoms.

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