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Potassium adsorption and an unoccupied surface state on Fe(001)

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Abstract. Spin-polarized photoemission studies of potassium adsorption on an Fe(001) surface provide evidence of a minority-spin surface state sitting immediately above the Fermi level on the clean surface. This state of d_{z^2} symmetry is associated with the surface state predicted in first-principles calculations and the state utilized in chemically selective scanning tunnelling microscopy studies of the Fe(001) surface.

1. Introduction

The magnetic properties of surfaces and thin films remain an area of great interest. Theoretical studies indicate that the low dimensionality and reduced coordination in the surface region can result in enhanced magnetic moments [1]. While these theoretical predictions have never been confirmed directly, it is possible to verify other aspects of the calculation. In particular the spin-polarized surface states that are responsible in part for the surface magnetic structure [2] have been identified and characterized. Tunnelling into such d-derived surface states [3] and into image or barrier-resonance states [4] has recently been used in the development of chemically selective imaging in scanning tunnelling microscopy (STM). Indeed in a recent STM study of chromium deposition on an Fe(001) surface [3], tunnelling into a surface state of d_{z^2} symmetry located immediately above the Fermi level was used to label the Fe atoms and tunnelling out of a state of the same symmetry immediately below the Fermi level was used to identify the chromium atoms. Aside from this STM study showing the existence of the Fe surface state there has been no study confirming its minority-spin polarization predicted by calculation. Earlier spin-polarized photoemission studies of the Fe(001) surface found evidence of a majority-spin surface state in the vicinity of the Fermi level but the incident light polarization was such that there would be no sensitivity to states of d_{z^2} symmetry [5]. A recent spin-polarized inverse photoemission study found no evidence of surface states in the vicinity of the Fermi level [6]. Indeed in the latter study the emission at the Fermi level was dominated by a majority-spin bulk feature.

In the present paper we report the results of a spin-polarized photoemission study of the Fe(001) surface using p-polarized incident light allowing a sensitivity to states of d_{z^2} symmetry. By using alkali atom adsorption we are able to provide evidence of a minority-spin surface state sitting immediately above the Fermi level at the centre of the zone on the clean surface. It has previously been shown in a number of studies of alkali atom

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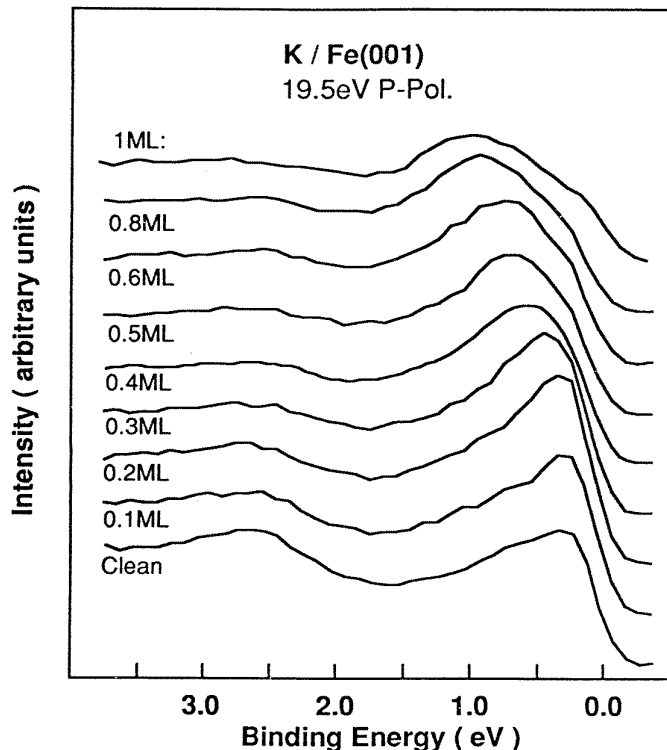


Figure 1. Spin-integrated photoemission spectra recorded along the surface normal from an Fe(001) crystal with varying coverages of potassium as indicated. The incident photon energy is 19.5 eV and the angle of incidence is 70° .

adsorption on transition metal surfaces that the presence of an alkali atom will cause a shift in the binding energy of the surface electronic structure associated with the clean surface [7, 8]. In particular, studies of Cs adsorption on W and Ta(001) [7] surfaces show that with increasing coverage the surface states may be shifted by up to 1.0 eV. The shift in energy was attributed to the formation of strong covalent bonds between the d-like surface states and the Cs 6s-derived valence states. Depositing potassium on the Fe(001) surface, we observe that with increasing coverage a minority-spin state moves below the Fermi level and becomes visible in the photoemission spectrum. We associate this state with the minority-spin surface state predicted in calculations of the electronic structure of the clean surface and the empty state observed in the STM study.

The experimental findings are compared with self-consistent electronic structure calculations for five-layer Fe(001) films with a $p(2 \times 2)$ potassium overlayer on either side. The all-electron full-potential linearized-augmented-plane-wave (FLAPW) method using the spin-polarized exchange–correlation potential of von Barth and Hedin has been employed [9].

2. Experimental details

The experimental studies reported in this paper were all carried out on the U5 spin-polarized photoemission facility at the NSLS [10]. Briefly, the photoelectrons are detected with a

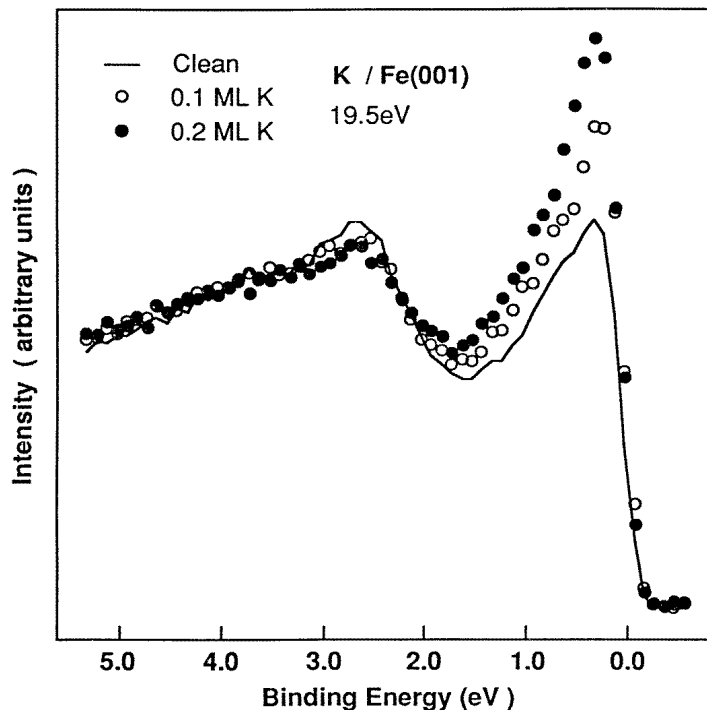


Figure 2. As figure 1, but restricted to the low-coverage regime. The spectra are normalized in the background region between the binding energies of 5.0 and 4.0 eV.

hemispherical analyser backed by a low-energy spin polarimeter of the type described by Unguris *et al* [11]. Electrons are collected in a solid angle of $\pm 1^\circ$ and the overall energy resolution is typically 0.3 eV. The Fe(001) crystal was manufactured in the form of a picture frame with each leg along a (001) direction and magnetized for spin-polarization studies using a coil wound around one leg. The crystal was initially cleaned by repeated argon-ion bombardment and annealing cycles. The surface contamination level was monitored initially using Auger electron spectroscopy and in the final stages using photoelectron spectroscopy. Potassium was evaporated from an SAES getter and the coverage was monitored using Auger electron spectroscopy. Work-function changes were determined by monitoring the change in the complete width of the photoemission spectrum with a small voltage applied to the sample. The maximum work-function change of 2.3 eV, corresponding to a work function of approximately 2.3 eV, was found at a coverage of 0.65 monolayers of potassium. Above this coverage the work function was again observed to show a slight increase with a value of approximately 2.6 eV at saturation coverage.

3. Results

Figure 1 shows the spin-integrated spectra recorded along the surface normal from the clean Fe(001) surface and the same surface following adsorption of potassium up to saturation coverage. The incident photons are p polarized with an energy of 19.5 eV. The coverages in the figure are given in terms of the overlayer rather than the substrate. From the figure we see that the intensity of the peak at the Fermi level increases up to a potassium coverage

of 0.2 ML and then slowly disperses to higher binding energy with increasing coverage.

Figure 2 highlights the low-coverage regime. It is clear that there is very little change in the binding energy of the peak even though the intensity increases substantially. This observation is consistent with a peak moving from immediately above the Fermi level to below as the potassium is initially adsorbed on the surface.

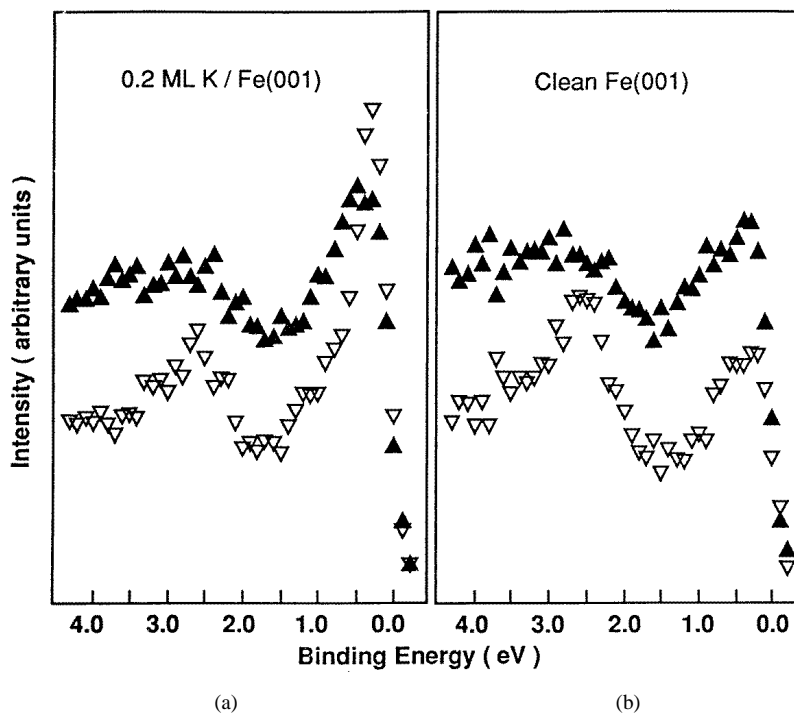


Figure 3. Spin-polarized spectra recorded from (a) the clean Fe(001) surface and (b) the same surface with 0.2 ML of adsorbed K. The incident photon energy is again 19.5 eV.

Figure 3 shows spin-resolved spectra recorded along the surface normal from the clean surface and the surface covered with 0.2 ML potassium. The incident photon energy is again 19.5 eV and any bulk k -conserving transitions will be close to the H point. With no minority-spin bands of the correct symmetry below the Fermi level at this point [12], the peaks in the minority-spin spectrum from the clean surface spectra, figure 3(a), both correspond therefore to transitions from surface states [1]. In particular the peak at a binding energy of 2.5 eV represents the surface resonance previously identified by Brookes *et al* [2]. In the majority-spin spectrum the peak immediately below the Fermi level corresponds to a direct transition from a bulk band close to the H point [12].

All of the features in the spectra from the potassium-covered surface, figure 3(b), are identical to those in the clean spectrum except the strong increase in the minority-spin peak immediately below the Fermi level and the reduction of intensity in the minority-spin resonance at a binding energy of 2.5 eV. The minority-spin peak at the Fermi level corresponds to the potassium-induced peak in the spin-integrated spectra of figures 1 and 2. We note that a spin-polarized photoemission spectrum recorded from the monolayer coverage of potassium also showed that the alkali-induced feature carried minority spin.

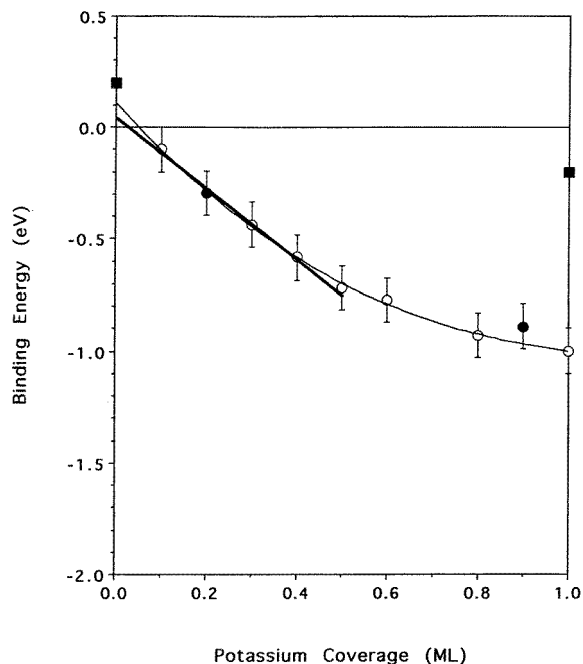


Figure 4. The binding energy of the K-induced feature in the photoemission spectra as a function of potassium coverage. The open circles indicate measurements taken from spin-integrated spectra and the filled circles measurements taken from spin-resolved spectra. The filled squares indicate the binding energies calculated for the clean and saturation covered surfaces. The bold solid line indicates the results of a linear fit to the experimental data in the low-coverage region. The thin line indicates the results of a polynomial fit to the experimental data.

4. Discussion

To obtain a better understanding of our data we plot in figure 4 the binding energy of the potassium-induced feature as a function of coverage. Using a linear fit in the low-coverage region, extrapolation to zero coverage leads to a predicted binding energy for this state of 0.04 ± 0.1 eV above the Fermi level. Using a polynomial fit over the entire coverage range leads to a predicted binding energy of 0.11 ± 0.1 eV above the Fermi level for zero coverage. These values may be compared with the binding energy of 0.17 eV above the Fermi level observed for the surface state in the STM study and the binding energy of about 0.2 eV above the Fermi level found for a minority-spin surface state in the FLAPW calculations; for the $p(2 \times 2)$ K overlayer, this state is calculated to be a few tenths of an eV below the Fermi level. We therefore associate the peak observed to move through the spectra in our photoemission studies with alkali-induced changes in the binding energy of the same minority-spin surface state.

Our FLAPW calculation of a $p(2 \times 2)$ potassium overlayer on Fe(001), corresponding approximately to the saturation coverage, finds a magnetic moment around the potassium site of $\sim 0.05\mu_B$ and $2.4\mu_B$ on the Fe surface atoms. The magnetic moments on the subsurface atoms change by only $0.01\mu_B$. The calculated change in surface Fe moments from $2.9\mu_B$ for the clean surface to $2.4\mu_B$ for the potassium-covered surface is consistent with the observation in the present study of the filling of the minority-spin surface state.

This will result in a reduction of the surface magnetic moment. One might anticipate that the reduction in the surface moment might result in a reduction in the background spin polarization. However, in the present study the spin polarization in the background showed little change as the potassium coverage increases from zero to one monolayer.

The calculated charge densities of the minority-spin surface resonance at higher binding energy and the surface state immediately above the Fermi level have both been published elsewhere [2, 4]. The surface resonance has considerable weight within the bulk whereas the surface state is highly localized within the surface region. This difference accounts for the different response of the two features to the presence of the alkali atom, a behaviour that has also been demonstrated in earlier studies of Cs adsorption on Mo(001) [7].

Although not reproduced here, studies of the potassium 3p core level show that as the coverage proceeds up to the monolayer level the binding energy decreases from 18.7 eV at the lowest coverage to 18.2 eV at the monolayer coverage. Spin-polarization studies reveal no detectable polarization consistent with the minimal moment found in our calculation for the K site.

In summary, our studies of potassium adsorption on the Fe(001) surface provide strong evidence for the presence of a minority-spin surface state sitting immediately above the Fermi level on the clean surface. In carrying out these studies we are able to demonstrate the spin character of the state employed in the earlier STM study [3]. Furthermore, the symmetry of this state is consistent with the d_{z^2} symmetry predicted in the first-principles calculation.

Acknowledgments

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