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Inverse photoemission study of the Cu(100)c(2 × 2)–Mn phase

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Abstract. Momentum- (k -) resolved inverse photoemission spectroscopy (KRIPES) has been used to investigate the electronic structure of Mn deposited on Cu(100), including the substitutional surface alloy phase Cu(100)c(2 × 2)–Mn. A well-resolved unoccupied state 2.0 eV above the Fermi level is found to be associated with the Mn adsorbate; this state shows no evidence of dispersion in either perpendicular or parallel electron momentum and is associated with a localized Mn 3d state. This result is consistent with previous evidence that the Mn remains in an atomic-like high-spin ground state in this surface, and contrasts with its behaviour in thicker Mn films. Measurements following exposure of the surface to oxygen show a greatly enhanced oxidation rate, with evidence of bulk oxide formation not possible on the clean Cu(100) surface at room temperature under high-vacuum conditions.

1. Introduction

There has been increasing interest in the last few years in novel magnetic phases of alloys [1], ultra-thin films [2] and surfaces [3]. In dilute bulk alloys, one type of system of especial interest is the existence of local magnetism of high-spin states of solutes such as Mn in non-magnetic metal matrices, such as Ag or Cu, to form a spin glass. In the case of the Cu–Mn system, a rather different aspect of the implications of the magnetic properties has recently attracted some interest. In particular, structural studies of the deposition of Mn on a Cu(100) surface have identified a stable substitutional surface alloy phase, Cu(100)c(2 × 2)–Mn, in which the rather large degree of local corrugation (with the Mn atoms some 0.3 Å further out from the surface than the surrounding outer-layer Cu atoms); it has been suggested, on the basis of theoretical total energy calculations, that this phase is stabilized by the magnetic interactions of the locally exchange-split virtual bound state associated with the Mn atoms which exist in this surface [4, 5]. The existence of such local (quasi-atomic) high-spin states on the Mn atoms in this phase has been confirmed by x-ray absorption spectroscopy and core-level photoemission measurements [6]; parallel x-ray dichroism measurements, on the other hand, indicated that no long-range ferromagnetic phase is present at room temperature, although antiferromagnetic order could not be excluded.

As yet there appear to have been no measurements of the valence electronic structure of the Cu–Mn surface alloy, although some data on both the occupied and unoccupied valence states of polycrystalline samples of the Cu–Mn spin glass have been reported using ultraviolet photoemission and x-ray bremsstrahlung isochromat spectroscopy [7]. One complication of studying the occupied states in both Cu–Mn and the related Ag–Mn bulk alloy is that the majority-state occupied Mn 3d states appear to occur at a similar energy to the matrix (Cu or Ag) valence d band, leading to rather unsatisfactory Mn-state

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contribution measurements. Here we present the results of a momentum- (k -) resolved inverse photoemission (KRIPES) [8] study of Mn on Cu(100), including the $c(2 \times 2)$ alloy phase, which provides clear identification of a localized Mn 3d-related unoccupied state some 2 eV above the Fermi level, well-separated from the occupied part of the 3d state as may be expected for the high-spin state. We also present some results of measurements of the influence of oxygen exposure on this surface which show that the surface alloy has very greatly enhanced reactivity relative to that of the clean Cu surface, and indeed that the surface Mn not only appears to be capable of enhancing the rate of oxygen dissociation but also allows the production of true three-dimensional copper oxide.

2. Experimental details

The experiments were conducted in a purpose-built UHV spectrometer system equipped with low-energy electron diffraction (LEED) optics for characterization of the surface order, and a VSW HA50 hemispherical electron energy analyser for Auger electron spectroscopy to check the cleanness and surface composition. KRIPES measurements in the form of isochromats were conducted simultaneously at two photon energies, 11.5 eV and 10.0 eV, using a novel instrument [9] which exploits the chromatic aberration of a LiF lens in the spectral range close to its absorption edge at 11.7 eV. The basic principle of this type of instrument has been described by Childs *et al* [10], and our instrument uses two detectors set at different distances from the lens on the optical axis which collect different photon energies [8].

The Cu(100) sample was prepared by the usual combination of x-ray Laue alignment, spark-machining, mechanical polishing, and *in situ* argon-ion bombardment and annealing cycles until a clean well-ordered surface was obtained as indicated by Auger electron spectroscopy and LEED. Mn deposition was effected with the sample at a temperature of 100 °C from a commercial (WA Technology) Knudsen cell. The surface composition was monitored by Auger electron spectroscopy, with an approximate coverage calibration point being provided by the 0.5 ML ordered $c(2 \times 2)$ phase [4, 11]. Although the use of a temperature slightly above nominal room temperature was used for deposition as this seemed to lead to facile formation of the $c(2 \times 2)$ phase, we should note that higher temperatures could lead to significant diffusion of Mn into the underlying substrate. In particular, if a multilayer Mn film was grown (e.g. 2–4 ML) and annealed at 300 °C for 10–15 minutes, both the Auger electron spectroscopy and KRIPES spectra indicated that the resulting surface comprised only about 1 ML of Mn. This result is qualitatively consistent with reported observations based on STM studies [12], although we did not see the regeneration of a clean Cu(100) surface which the authors of [12] report. For the experiments on oxygen adsorption, exposures were achieved by introduction of dioxygen gas into the chamber, with pumping maintained to stream the gas flow and ensure purity.

3. Results and discussion

3.1. Electronic structure

Figure 1 summarizes the normal-incidence KRIPES data taken from the Cu(100) surface at different Mn overlayer coverages and at the two different isochromat energies. In the case of the clean Cu(100) surface spectra, the principal peak seen just above the Fermi level is due to an s–p-band direct transition [13, 14]. Notice that as the photon energy is increased, the final-state energy moves closer to the Fermi level as the direct transition shifts towards

the $\bar{\Gamma}$ point and away from the band gap at \bar{X} . One characteristic feature of the LiF lens dispersion system is that the higher-energy 11.5 eV isochromat shows better resolution (approximately 0.4 eV) than that recorded at 10.0 eV photon energy (approximately 0.7 eV) [9, 10], which improves the resolution of the image potential state seen some 4.5 eV above the Fermi level. Conspicuously, however, the high-energy side of the s-p band transition in the 11.5 eV isochromat appears broader. This is due to the presence of an intrinsic surface resonance some 1.2 eV above the Fermi level [15]; its presence is more clearly seen in the higher-energy isochromat because the dispersing s-p bulk transition overlaps less and suffers less instrumental broadening. All of these aspects of the $\text{Cu}(100)$ clean surface spectra are extremely well documented.

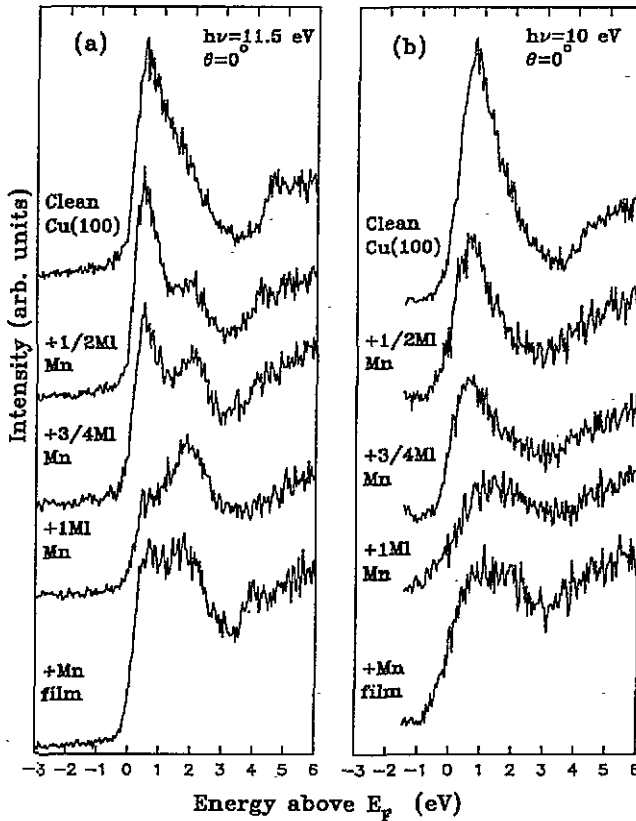


Figure 1. Normal-incidence KRIPES spectra recorded from clean $\text{Cu}(100)$ and after various coverages of Mn recorded in the form of 11.5 eV and 10.0 eV isochromats (a) and (b).

The effect of the addition of the Mn overlayer is seen very clearly in the 11.5 eV isochromats as a distinct peak which develops with increasing coverage. Notice that at the half-monolayer $c(2 \times 2)$ phase, the substrate s-p transition peak appears significantly sharper, presumably due to quenching of the intrinsic surface resonance by the Mn. The Mn-induced peak appears to lie 2.0 eV above the Fermi level, independently of coverage up to 1 ML. In the 10.0 eV isochromat spectra the existence of the Mn-induced peak is far less clear, due in part to the higher energy of the substrate s-p band transition and to the lower spectral resolution, although it also appears that the inverse photoemission cross-section

for transitions to the Mn peak may also be relatively somewhat lower. Difference spectra indicate, however, that the energetic position of the Mn feature is probably unchanged with photon energy, indicating no dispersion in perpendicular momentum. Such an absence of dispersion is to be expected, of course, for a surface-localized feature. Notice that in the 0.5 ML Mn spectra of figure 1 the image potential state has shifted down towards the Fermi level by several tenths of an eV, and indeed appears at an even lower energy on the relatively thick Mn film spectra; this can be attributed to a steady decrease of the work function as the Mn coverage is increased as reported previously [11]. A limiting decrease of 0.6 eV has been reported [11], and to a good approximation the image potential states track the vacuum level [8]; clearly the shift in the image potential state seen in figure 1 is consistent with this view.

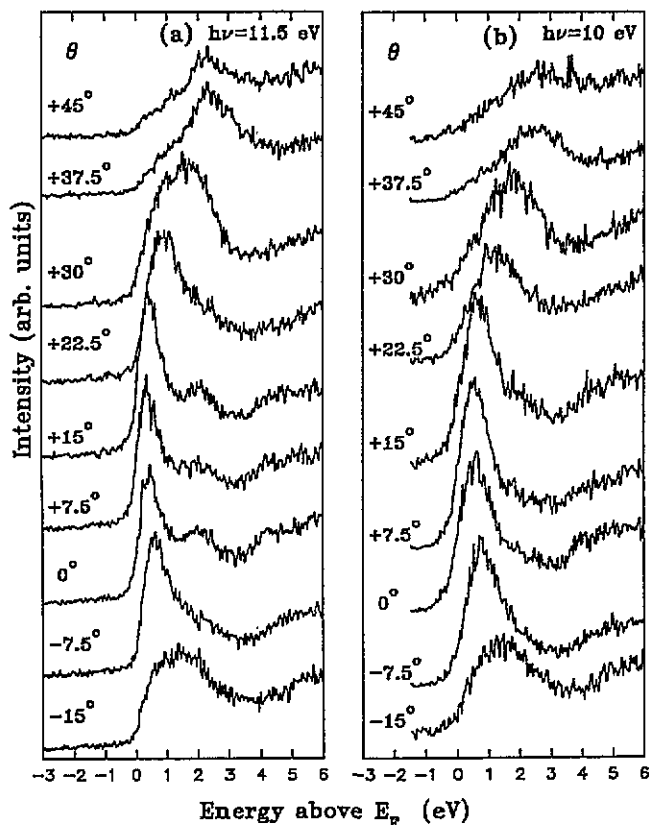


Figure 2. Incidence-angle dependence of KRIPES isochromats from the Cu(100)c(2 × 2)-Mn phase at (a) 11.5 eV and (b) 10.0 eV photon energies.

The effect of varying the parallel momentum transfer in KRIPES from the Cu(100)c(2 × 2)-Mn phase can be seen in the spectra of figure 2 recorded at a range of angles of incidence. In order to distinguish the contribution of the substrate s-p band transition, a similar set of spectra from the clean Cu(100) surface are shown in figure 3. This bulk transition disperses up in final-state energy as the parallel momentum increases, but the Mn state is clearly seen to remain at essentially the same energy to within about 0.2 eV. Notice that the existence of this Mn state in the 10.0 eV isochromats is somewhat clearer in this set than in those of

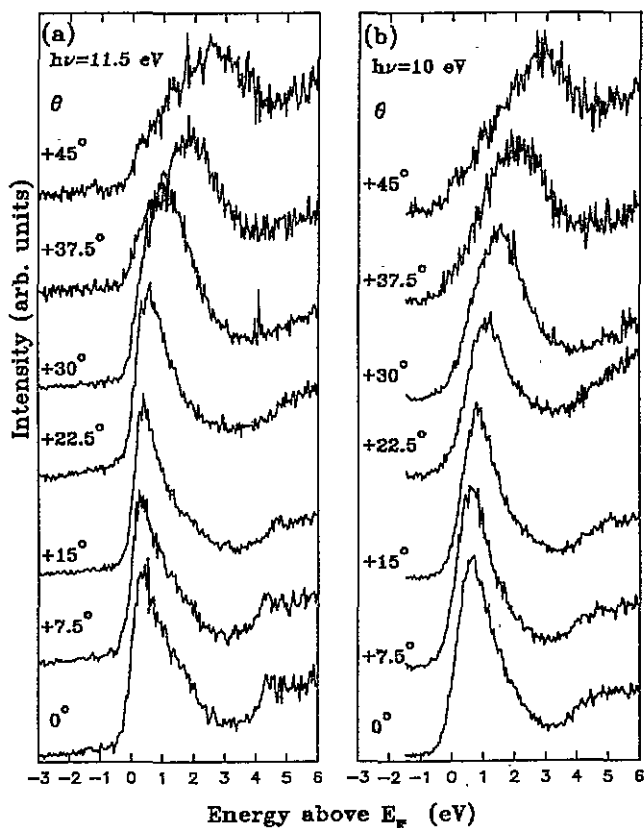


Figure 3. Incidence-angle dependence of KRIPES isochromats from clean $\text{Cu}(100)$ phase at (a) 11.5 eV and (b) 10.0 eV photon energies, recorded under the same conditions as for the $c(2 \times 2)\text{Mn}$ phase data of figure 2.

figure 1 because of its lack of dispersion relative to that of the substrate s - p band transition. These further data thus demonstrate significant localization parallel as well as perpendicular to the surface. We cannot, of course, totally exclude the possibility that the feature does form a very flat band via interactions parallel to the surface (even bulk d bands rarely show a large degree of dispersion), but the results favour the 2.0 eV feature being attributed to an essentially totally localized Mn 3d state. The fact that this state clearly lies well above the Fermi level is consistent with it being a totally unfilled minority-state band expected for the high-spin state.

In this context we note that the KRIPES recorded from a multilayer Mn film (figure 1) differ very substantially from those associated with coverages up to 1 ML. A rather broad flat-topped feature is now seen, the highest-energy component of which is a few tenths of an eV below the centre of the submonolayer feature, while the lower-energy component is cut off sharply at the Fermi level. The flat top suggests at least two components, consistent with a strong mixing of the Mn d states due to Mn-Mn neighbour interactions to form broader bands which straggle the Fermi level and lead to a substantial reduction in the magnetic moments on the Mn atoms.

Although there appear to be no previous KRIPES studies of the Cu-Mn surface phases, some comparable investigations have been made of the Ag-Mn system, both in the form

of a dilute bulk alloy [16] and of a 1 ML Mn film on Ag(111) [17], as well as an x-ray BIS study of both Ag-Mn and Cu-Mn dilute alloys [7]. The x-ray BIS spectra of the two alloys indicate unoccupied Mn 3d states in both systems at about 2.0 eV above the Fermi level. These data actually indicate the Mn-induced feature to be about 0.2 eV lower in the Cu matrix than in the Ag, although the resolution and signal-to-noise conditions of these data are probably not sufficient to render this difference significant. The normal-emission KRIPES spectra from the both the Ag-Mn alloy and the Mn monolayer on Ag(111), on the other hand, show an Mn-induced peak centred only slightly lower in energy (1.8 eV above the Fermi level) than that seen in figure 1; the authors of this work also report an asymmetry in the Mn-induced feature, visible after subtracting the clean surface spectrum, which they attribute to a crystal-field splitting of some 1.4 eV. Certainly our raw data give no hint of any such effect, but difference spectra are likely to be of little value in our case because of the presence of the intrinsic surface resonance peak contribution to the clean Cu(100) surface spectrum.

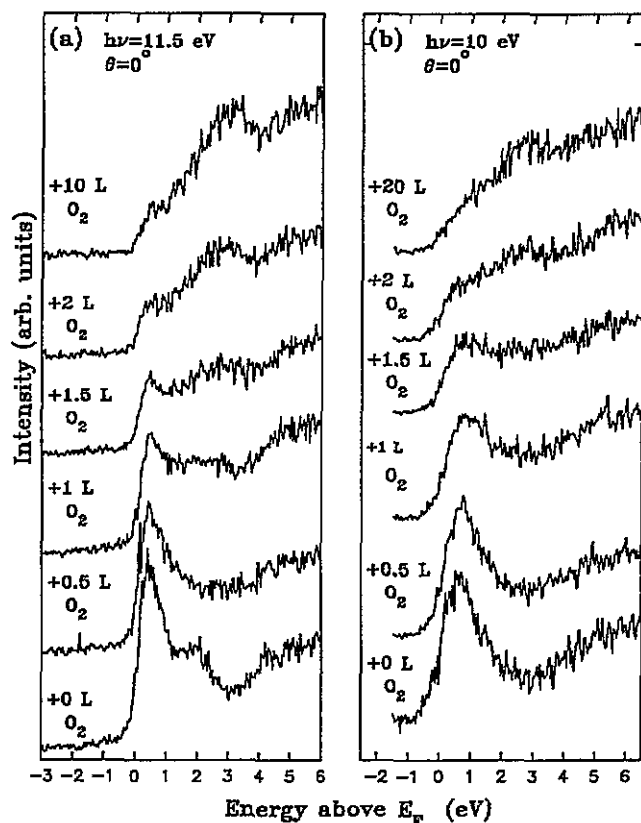


Figure 4. Normal-incidence KRIPES isochromat spectra taken from a Cu(100)c(2 × 2)-Mn surface after various exposures to oxygen.

3.2. Oxidation behaviour

A further interesting feature of the Cu(100)c(2 × 2)-Mn surface is revealed by the influence of oxygen exposure on the normal-incidence KRIPES, as seen in figure 4. The very

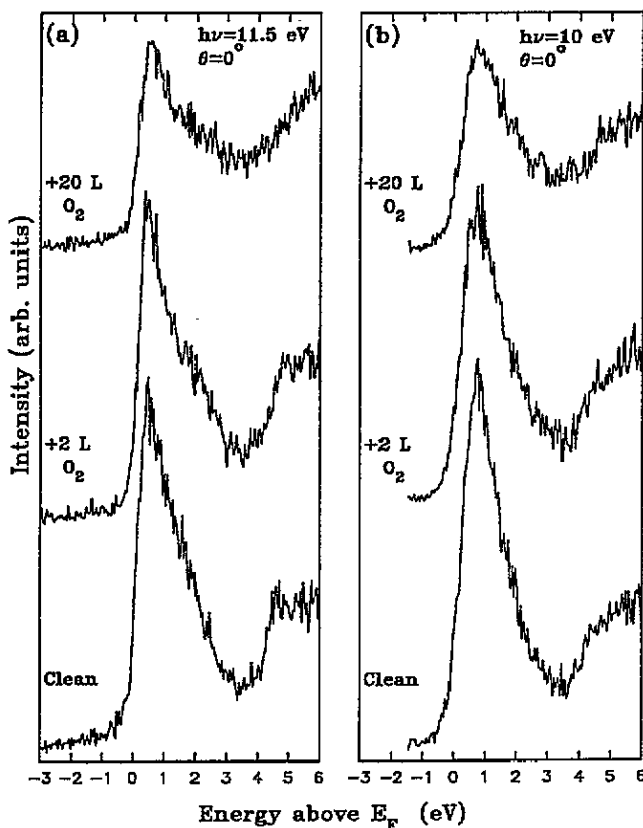


Figure 5. Normal-incidence KRIPES isochromat spectra taken from $\text{Cu}(100)$ after various exposures to oxygen.

pronounced change in the spectra induced by an exposure of only 1 L is in sharp contrast to the effect seen of similar exposures of oxygen to spectra from a clean $\text{Cu}(100)$ surface (see figure 5). On $\text{Cu}(100)$ at room temperature, it appears not to be possible to produce any true three-dimensional oxide of Cu, although a missing-row reconstruction of the surface is effected by chemisorbed oxygen [18]. Typically exposures of several hundred langmuir are required to effect this transition at room temperature. By contrast, the KRIPES data from the $c(2 \times 2)\text{-Mn}$ alloy surface show very major disruption of the surface by an exposure of only 10 L. Indeed, the 11.5 eV isochromat after 10 L exposure shows strong suppression of all emission near the Fermi level and the appearance of a peak or edge at approximately 3 eV above the Fermi level, suggestive of the growth of several layers of bulk-like oxide on the surface showing a band gap around the Fermi level [19]. Similar behaviour at even lower exposure is seen in KRIPES from a multilayer Mn film (figure 6), but in this case the peak which may be assigned to the upper band edge is some 1 eV higher in energy. Valence band spectroscopy is not, of course, the most natural vehicle for the study of such large-scale chemical reactions at surfaces, but these data strongly suggest that the presence of the $c(2 \times 2)\text{-Mn}$ alloy surface catalyses the oxygen dissociation and subsequent oxidation of the underlying Cu. Somewhat similar measurements on the (111) surface of an Ag/15% Mn alloy showed rather modest changes in the KRIPES data even after 100 L exposure of oxygen [16]. The Mn surface concentration in this case is unknown, however, so the

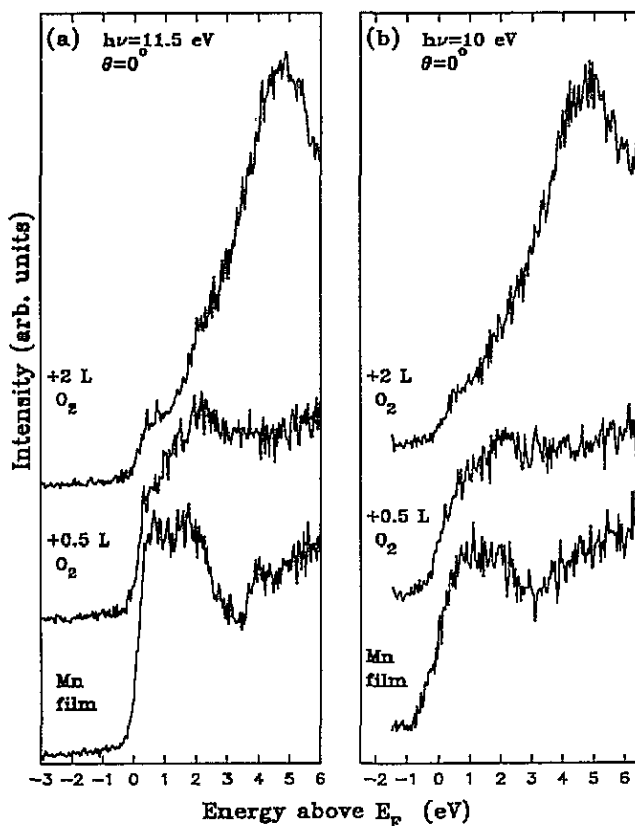


Figure 6. Normal-incidence KRIPES isochromat spectra taken from a multilayer Mn film grown on Cu(100) after various exposures to oxygen.

difference may not only be related to the particularly low reactivity of clean Ag surfaces to oxygen. On Cu, the role of the surface Mn appears to be more typical of that seen in adsorbed alkali metal or rare-earth overlayers on metal (e.g. Al [20]) and semiconductor (especially Si [21]); the presence of these highly reactive atomic species on the surface can lead to strong enhancement of both oxygen dissociation rates, and the rate of formation of surface oxide phases as opposed to simple chemisorbed oxygen overlayers.

4. Conclusions

The KRIPES data recorded from the Cu(100) $c(2 \times 2)$ -Mn surface phase show clearly that an unoccupied Mn 3d state exists some 2.0 eV above the Fermi level and shows no evidence of dispersion for either perpendicular or parallel electron momentum. Such a conclusion is consistent with an essentially atomic state, and while we cannot exclude the possibility that a weak 2D d-band formation occurs, for which the dispersion could be very weak, the location of this well-resolved state is consistent with the high-spin ground state characteristic of the free atom, and quite unlike the Mn in thicker 'bulk' films. These conclusions are consistent with other experimental evidence and with the theoretical considerations of this phase.

Oxygen exposure experiments reveal that the alloy surface is far more highly reactive than the clean Cu(100) surface, and the presence of the more reactive Mn atoms appears to catalyse a true oxidation of the Cu surface not achievable under similar conditions of temperature and pressure for clean Cu surfaces.

Acknowledgments

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