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The structure of the Ni(100)c(2 × 2)Hg surface

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Abstract. The structure of the Ni(100)c(2 × 2)Hg phase has been studied by soft x-ray methods. Delayed onset of photo-ionisation above the Hg M_V and M_{IV} edges prevented SEXAFS being used, but normal-incidence standing x-ray wavefield absorption at the (200) Bragg condition yields a Hg to Ni lattice plane spacing of 0.6 ± 0.1 Å. This is consistent with bridge site adsorption and a Ni–Hg bond length characteristic of either the metallic radii or the NiHg compound. The alternative hollow site can only be reconciled with the data if the surface Ni–Hg bond length is significantly longer, probably accompanied by some top Ni layer relaxation.

1. Introduction

The adsorption of mercury on transition metal surfaces produces an interesting set of weak chemisorption systems in which there can be a delicate balance of adsorbate–substrate and adsorbate–adsorbate interactions. The diameter of the mercury atom (3 Å) is larger than the unit mesh size of many clean metal surfaces, while its closed-shell configuration might be expected to lead to non-directional bonding and low isosteric heats of adsorption. As a result we might expect weak corrugation in the mercury–substrate interaction energy (as a function of lateral position). At the same time, sizeable adsorbate–adsorbate interactions are to be expected as the boiling point of mercury (357 °C) indicates relatively strong bonding in the pure element.

These considerations would lead us to expect that at high coverages on small unit mesh surfaces one would observe incommensurate structures, although at lower coverages or on large unit metal surfaces, commensurate phases should form. Qualitative low-energy electron diffraction (LEED) and thermal desorption experiments support these ideas on W(100) (Jones and Perry 1978), Fe(100) (Jones and Perry 1981), Ni(100) (Jones and Tong 1987), Ni(111) (Singh and Jones 1988, 1989), Ag(100) (Dowben *et al* 1987) and Cu(100) (Onellion *et al* 1987). None of these previous studies has involved a quantitative structural analysis, and typically the mercury is assumed to occupy the highest coordinated hollow site on each surface in the commensurate structures.

In this short paper we present the results of a limited quantitative structural study of one of these commensurate phases, the Ni(100)c(2 × 2)Hg structure, using in particular standing x-ray wavefield absorption (sxw). We have recently shown that this technique can be applied successfully to standard crystal surfaces (Woodruff *et al* 1987, 1988) and

not only the ultrahigh perfection crystals usually associated with the method. The information given by the method is an adsorbate–substrate layer spacing, and in order to infer an adsorption site from this parameter some additional information, such as the adsorbate–substrate nearest-neighbour distance, is needed. Surface-extended x-ray absorption fine structure (SEXAFS) is one method of obtaining this additional information and we have shown that the complementary use of SXW and SEXAFS can be rather effective (Woodruff *et al* 1987, 1988, Prince *et al* 1989). In the present case the application of SEXAFS has some problems and as a result our structural analysis does contain some ambiguity. In particular, while the data are most obviously consistent with the rather surprising conclusion that the mercury atoms bridge-bond to the nickel surface, other interpretations are possible.

2. Experimental details and results

The experiments were conducted at the Science and Engineering Research Council's Daresbury Laboratory, taking x-rays from the Synchrotron Radiation Source on a beam-line originally constructed specifically for SEXAFS studies and equipped with an ultrahigh-vacuum (UHV) double crystal monochromator (McDowell *et al* 1986). The Ni(100) crystal, having been prepared by the usual methods of x-ray Laue alignment, spark machining and mechanical polishing, was cleaned *in situ* in the UHV spectrometer chamber by cycles of argon ion bombardment and annealing until sharp (1×1) LEED patterns were seen and Auger electron spectroscopy showed no surface contamination. Mercury adsorption was effected from an SAES 'getter' source, avoiding the problems of contamination of the vacuum system. LEED observations confirmed the $c(2 \times 2)$ unit mesh previously characterised by Jones and Tong (1987).

The sxw experiment involves the measurement of the x-ray absorption at the adsorbate and substrate sites in the vicinity of a Bragg scattering condition. Our version of the experiment makes use of the insensitivity of the Bragg condition to the exact incidence angle (and thus to crystal mosaicity) at normal incidence. In the present case, the (200) Bragg reflection at normal incidence to the surface at 3522 eV was used, and the absorption in the Ni and Hg atoms respectively monitored by measuring the Ni $L_{III}VV$ (848 eV) and Hg $M_V NN$ (2073 eV) Auger electron peaks with a double-pass cylindrical mirror analyser. The Auger emissions, resulting from the decay of core holes in the Ni L_{III} and Hg M_V levels, have a yield proportional to the photo-ionisation of these levels. The results of the sxw experiment are shown in figure 1, together with curves computed for different possible structures discussed in the next section.

Attempts to measure SEXAFS from this system at the Hg M_V edge (2390 eV) proved unsuccessful. Figure 2 shows the yield of Hg $M_V NN$ Auger electrons as a function of photon energy in the vicinity of the M_V and M_{IV} edges of Hg, the nominal energies of these edges being marked. Evidently the photo-ionisation cross sections at threshold (governing the absorption edge 'jump') is small compared with the strong rise of cross-section some 50 eV above the edge. This behaviour is characteristic of the delayed onset of photo-ionisation cross-section seen for high angular momentum initial states due to the effect of the 'centrifugal barrier' (Fano and Cooper 1968). In this case, the delayed onset is followed by a resonance in the $3d-f$ excitation channel. Clearly the atomic effects are far too strong to allow EXAFS to be measured over the short energy range between these M edges. It is possible that measurements near the M_{III} , M_{II} or M_I edges may be more successful, but the cross-sections for these edges are much lower. On our

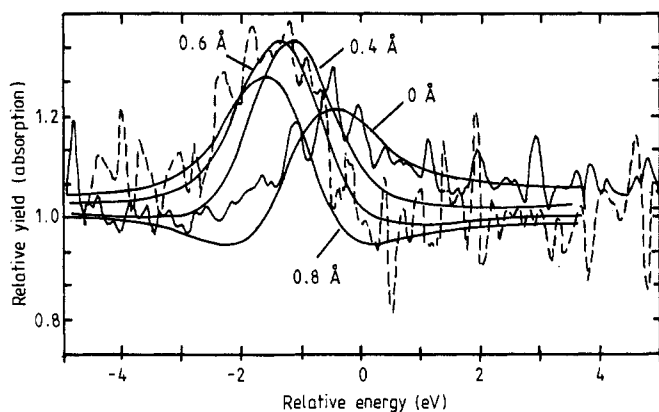


Figure 1. Results of the standing x-ray wavefield absorption experiment for the Ni(100)c(2 × 2)-Hg surface showing the normalised Auger electron yield from Ni (full curves) and Hg (broken curves) as a function of energy around the normal incidence (200) Bragg reflection. Also shown are the results of model calculations described in the text.

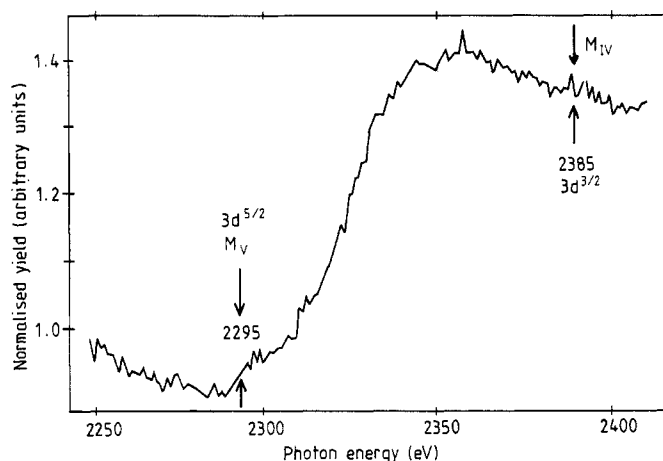


Figure 2. Hg M_V NN Auger yield from the Ni(100)c(2 × 2)-Hg surface as a function of photon energy in the range of the Hg M_V and M_{IV} photo-ionisation thresholds.

instrument, at least, the deeper L edges are not accessible. We were therefore unable to measure SEXAFS and concentrate on the interpretation of the SXW measurement in figure 1.

3. Computational results and discussion

Analysis of the SXW results was conducted by the same method we have used for our earlier studies of Cl and CH₃S on Cu(111) (Woodruff *et al* 1987, 1988, Prince *et al* 1989). In particular, non-structural parameters in the theory-experiment comparison, including the monochromator resolution and the absolute energy scale, were optimised by fitting the substrate absorption signal for which the structure is known. The adsorbate

signal was then fitted by varying the structural parameters only (notably the adsorbate–substrate layer spacing). As may be seen from figure 1, the best fit is given for a Hg–Ni layer spacing of 0.6 Å, but the rather poor signal-to-noise ratio of the data leads to an imprecision in the result of approximately 0.1 Å (clearly the curves for 0.4 Å and 0.8 Å layer spacing lie outside the range of reasonable error bars).

In the absence of an experimental value for Hg–Ni nearest-neighbour bond length for the chemisorption system, a reasonable starting point to the interpretation of this layer spacing is to take the Hg–Ni distance of 2.63 Å found for the compound NiHg (Puselj and Ban 1977). Using this value, we can calculate the Hg–Ni top-layer spacing for the principal high-symmetry adsorption sites. The values are hollow: 1.95 Å (0.19 Å), bridge; 2.31 Å (0.55 Å), atop; 2.63 Å (0.87 Å). The values in parentheses in each case are obtained by subtracting the bulk substrate layer spacing. The sxw technique involves establishing a standing x-ray wavefield with the periodicity of the substrate layer spacing, which extends beyond the surface, so the experimental value is always referenced to the nearest (extended) substrate lattice plane below. Evidently our experimental result fits the bridge site well (experiment 0.6 ± 0.1 Å, theory 0.55 Å), and is inconsistent with either of the other sites.

The apparent occupation of bridge sites of the adsorbed Hg atoms would certainly be rather interesting. We might have expected that the form of the adsorbate–substrate bonding would be metallic and thus non-directional, favouring the highest coordinated hollow sites. Bridge bonding, on the other hand, for a simple commensurate $c(2 \times 2)$ overlayer, implies substantially covalent bonding. However, this structural assignment must be treated with some caution as two ambiguities are present in deducing the structure from the sxw layer spacing. Firstly, of course, our assignment is based on an assumed Hg–Ni bond length of 2.63 Å, taken from the results for a bulk NiHg phase. This bond length is also rather close to the value (2.66 Å) obtained from summing the metallic radii of Ni (1.25 Å) and β -Hg (1.41 Å). A longer value could be reconciled with hollow site adsorption, although the value consistent with the sxw layer spacing is large ($\approx 2.95 \pm 0.10$ Å). In fact the appropriate bond length for metallic overlayers is far from certain. The use of the metallic radius from α -Hg (1.49 Å) leads to a slightly longer predicted Hg–Ni bond length (2.74 Å), but this would still favour the bridge site. Campbell (1986), on the other hand, has argued that the Zachariasen radius (Zachariasen 1973) is more appropriate than a value obtained from the true nearest-neighbour distance in the appropriate elemental solid. This radius is obtained by assuming that the actual solid density is derived from a close packed structure (leading to larger radii for open structures). In the case of α Hg and β Hg the Zachariasen radii are 1.62 Å and 1.58 Å respectively, just large enough to reconcile our data with the hollow site within our quoted errors. Campbell's preference for this radii, however, is based on nearest-neighbour adsorbate–adsorbate distances in the range of metallic overlayers; these overlayers are mainly commensurate with their substrates (often (1×1)) and will therefore tend to give slightly high values to the radii favouring the Zachariasen value. In the present case we feel that the known NiHg amalgam structure value clearly leads us to favour the short bond length and thus bridge site occupation.

One further possibility, however, is that there is some expansion of the top substrate layer spacing(s). The sxw technique measures the adsorbate layer spacing relative to the extension of the bulk lattice planes, so if the top Ni atom layer is displaced Δz above its bulk position, the sxw technique will measure not the true Hg–top Ni layer spacing z but a larger value of $z + \Delta z$. Although surface layer expansions of the order of 0.1 Å are well known for many clean metal surfaces, far less information is available regarding

the substrate layer spacing in the presence of adsorbates which will clearly influence the electronic structure in the near surface region. On the other hand, an expansion of 0.4 Å, needed to reconcile the results with hollow site adsorption and a Hg–Ni distance of 2.63 Å, is unreasonably large. We cannot, however, exclude some combination of expanded layer spacing and longer Hg–Ni distance (with hollow site adsorption) as an alternative to the more straight forward interpretation of bridge site occupation. Further measurements using SEXAFS at another edge, SXW at a different Bragg condition, or some other technique, are clearly required to provide a totally conclusive and unambiguous structural assignment.

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