# The surface phases of mercury on Ni{111}

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**Abstract.** LEED, AES and UPS have been used to characterise the equilibrium and non-equilibrium phases formed by Hg adsorbed on Ni{111} in the temperature range $222 < T < 473$ K, with an applied pressure of $2 \times 10^{-8}$ mbar. Structures are proposed for these surface phases, and their interconversion and stabilities are discussed.

Mercury is a large absorbate (Hg–Hg = 2.99 Å in $\alpha$-Hg [1]) which exhibits strong lateral interactions ($\Delta H_{vap} = 61$ kJ mol$^{-1}$ [2]). When adsorbed onto clean surface meshes of approximately the same size as itself (W{100} [3], Fe{100} [4], Ag{100} [5], Cu$_3$Au{100} [6]), the adlayer is dominated by the corrugation of the substrate–adatom interaction, giving $(1 \times 1)$ structures. For slightly smaller substrate meshes, $c(2 \times 2)$ structures occur at lower coverages (Ni{100} [7], Cu{100} [6]) and complex structures occur at high coverages [7]. In this study we investigate adsorption onto Ni{111} which has a particularly smooth corrugation due to its small unit mesh and hexagonal close-packed structure, and which shows surface structures that are dominated by the Hg–Hg interaction. A full description of this system is given elsewhere [8].

We distinguish two types of chemisorbed mercury phases: those in thermodynamic equilibrium with an applied pressure of mercury, and those formed during adsorption, which are not at thermodynamic equilibrium.

For non-equilibrium adsorption on clean Ni{111} for $T < 290$ K, Hg forms islands, over a wide range of coverage (0.2–0.6 ML), consisting of coincident pseudo-square adlayers of Hg with Hg–Hg distances of 2.99 Å. These islands may be described using the matrix notation

$$\frac{1}{1 - 2x} \begin{bmatrix} 1 - x & -x \\ -x & 1 - x \end{bmatrix}$$

where $x = 0.2$. The island formation, the Hg–Hg distance (compare with $\alpha$-Hg) and the square structure [9] are directly attributable to attractive adatom–adatom interactions.

For non-equilibrium adsorption at $310 < T < 351$ K, the $x = 0.2$ structure is not observed by LEED, but characteristic shifts in the Hg UPS $^2D_{5/2}$ peak strongly suggest that the structure still exists on the surface. We suggest that the smooth corrugation of the substrate–Hg interaction allows the Hg islands to rotate freely to any orientation at these higher temperatures (thus explaining the lack of a LEED structure). For $T > 350$ K, UPS indicates evaporation of the islands into a two-dimensional dispersed phase.

For non-equilibrium coverages between 0.6 and 0.64 ML the pseudo-square adlayer becomes semi-periodic and compresses ($x = 0.2 \rightarrow 0.18$) along a direction perpendicular to the periodic direction and parallel to a substrate direction of closest packing. When the Hg–Hg distance reaches 2.90 Å, (compare with 2.83 Å for $\beta$-Hg [1]), a phase change occurs in which the pseudo-square adlayer converts to a hexagonal layer of 0.75 ML having an Hg–Hg distance of 2.87 Å, which forms a p($2 \times 2$) coincident structure. This phase change is thought to be driven by the density of states at the Fermi level [9].

The p($2 \times 2$)–0.75 ML is an equilibrium structure and is thought to have 0.5 ML of Hg in threefold hollow sites, and 0.25 ML in atop sites. As the equilibrium coverage is reduced, first the phase change, then the compression structure (expanding now) and finally the saturated (0.6 ML) $x = 0.2$ structure are observed. At 0.5 ML another equilibrium p($2 \times 2$) structure is observed, which is thought to consist of open hexagons of Hg formed, in principle, by removing the 0.25 ML of Hg from the atop sites of the higher-coverage p($2 \times 2$). At $\frac{1}{3}$ ML and for an Hg–Hg distance of 4.31 Å, a ($\sqrt{3} \times \sqrt{3}$) R30° equilibrium structure was observed, which was shown to exhibit attractive Hg–Hg interactions by using equilibrium adsorption isotherms. This interaction must be caused by a through-substrate interaction as direct through-space orbital overlap is not possible at this distance.

## References

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