Structure of Xenon Monolayers on Metal Surfaces

By M. A. CHESTERS, M. HUSSAIN, and J. PRITCHARD*
(*Chemistry Department, Queen Mary College, Mile End Road, London* E1 4NS)

Summary Xenon gives hexagonal close-packed monolayers on single-crystal faces of copper and silver at 77 K with a nearly constant cross-sectional area of 17 Å^2 per atom, and in which adsorbate layer is epitaxially related to the substrate but not necessarily in registry with it.

THE structure of the completed monolayer is an important factor in surface area measurements by physical adsorption. The early assumption that the adsorbate packing would resemble that in the liquid or solid state has sometimes conflicted with the monolayer capacities for different gases on the same surface and has led to the concept of site adsorption on metals, particularly for krypton and xenon.[1]

Direct observation by low-energy electron diffraction has revealed[2] a compressed hexagonal xenon layer on graphite, corresponding to site adsorption; but in the only reported structure on a metal surface,[3] Pd(100), the xenon atoms form a hexagonal close-packed layer which is out of registry with the metal lattice. That the latter may be more generally characteristic of xenon adsorption on metals is

suggested by the very similar structures which we have found on Cu(100), Cu(111), Cu(110), and Ag(111) surfaces, in which the xenon–xenon spacing is nearly constant at 4·5 ± 0·1 Å. The diffraction patterns show pronounced double-diffraction features.

The influence of the metal lattice is shown by the epitaxy of the xenon layer but it is not sufficient to cause site adsorption unless the epitaxial misfit is very small. Site adsorption occurs on Cu(111) in a $(\sqrt{3}\times\sqrt{3})R30°$ structure with a xenon–xenon distance of 4·42 Å; but, although the xenon–xenon distance is practically the same on Ag(111), the larger metal atom spacing precludes site adsorption and results in a non-rotated out-of-registry overlayer. On Cu(100) the xenon layer is again out of registry. Two equivalent orthogonal orientations of the monolayer are preferred.

These results, together with the similar xenon–xenon spacing previously reported on Pd(100), suggest that xenon may always tend to form such close-packed layers on the denser planes of metals, and that reasonably accurate surface areas would be obtained from volumetric adsorption measurements on polycrystalline metals by assuming an effective cross-sectional area of 17 Å^2. The suitability of this molecular area for polycrystalline copper surfaces is supported by the xenon monolayer structure on Cu(110). The more open metal structure was expected to influence the monolayer structure, and indeed site adsorption does occur at first to give a $C(2 \times 2)$ structure. The nearest neighbour distance is then 4·42 Å but the xenon atoms are not quite close-packed. As the monolayer is completed the structure is compressed in the $[1\bar{1}0]$ direction until the packing density again corresponds to 17 Å^2 per atom and the xenon layer is nearly hexagonal.

We thank the Science Research Council for financial support.

(*Received, 25th February* 1972; *Com.* 314.)

[1] D. Brennan and M. J. Graham, *Phil. Trans.*, 1965, **258**, 325.
[2] J. Morrison and J. J. Lander, *Surface Sci.*, 1966, **5**, 163.
[3] P. W. Palmberg, *Surface Sci.*, 1971, **25**, 598.