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Submitted on 1 Jan 1988

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Angle-resolved photoemission of xenon adsorbed on Pt(111) : commensurate and incommensurate monolayers

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(Reçu le 12 avril 1988, révisé le 9 juin 1988, accepté le 13 juin 1988)

Abstract. — The dispersion curves of the commensurate (~3 x ~3) R30° and the hexagonal compact incommensurate rotated xenon overlayers on Pt(111) are given. Comparison with other angle-resolved photoemission results on copper, palladium, aluminium, silver, platinum and graphite show that the splitting of the 5p3/2 levels is mainly due to the overlap of the 5p orbitals from neighbouring Xe atoms below a minimum distance. It increases only slightly with decreasing distances independently on the substrate nature.

I. Introduction.

Physisorbed layers of rare gases and particularly xenon layers form a hexagonal (or nearly hexagonal) compact structure on most single crystals [1-17]. In some cases, e.g. on Cu(110) [10, 11], Cu(111) [3, 12], Pd(111) [15] and Pt(111) [17], less dense solid layers can also be formed at lower coverages. The Xe/Pt(111) system has been extensively studied in recent years on an almost defect free sample by Kern et al. [18-21] using high resolution helium beam scattering. It appears to be one of the most interesting of quasi-2D systems obtained so far by physisorption of rare gases on single crystal metal surfaces. Indeed, depending on the coverage and temperature, a variety of phases may be formed : a commensurate one (~3 x ~3) R30° (C) stable above 63 K ; a striped incommensurate one (SI) ; a hexagonal incommensurate one (HI) and, a hexagonal incommensurate rotated phase (HIR).

The band structure of xenon layers has been scarcely studied. The 5p levels of the solid phases are the 5p1/2 and two 5p3/2 levels (m_j = ± 1/2, m_j = ± 3/2). It has been demonstrated that the 5p3/2 splitting is mainly due to lateral interactions and direct overlap of the 5p wave functions from neighbouring xenon atoms when the adlayer is sufficiently close-packed in an ordered array [9, 22, 23]. The energy order of the 5p3/2 levels (identified by their angular dependence [9] and using polarized electrons [24, 25]) is such that the lateral interaction model and the crystal field model [26, 27] can only explain the results. However, as pointed out by Antoniewicz [28], the latter requires unreasonably large positive charges on surface atoms to produce the observed splitting. Moreover, there is no splitting for a 2D gas on W(100) [29], Ag(111), Cu(111), Ru(001) [30, 31] and at large distances between xenon atoms in the repulsive Xe/Pd(100) system [22]. The dispersion curves of the xenon incommensurate hcp layer have been determined on Pd(100) [9], on Al(111) [16], on the c(2 x 2) phase and on the almost hexagonal phase on Cu(110) [11] and on the (~3 x ~3) R30° phase on Pt(111) [32]. The general trend of all these results, compared in the last reference, is in agreement with theoretical calculations [33, 34]. One observes an increase in the dispersion for all bands and in the 5p3/2 splitting with decreasing interatomic distances in the xenon layer. At normal emission (\Gamma point), the 5p1/2 binding energy referenced to the vacuum level is almost independent on the substrate nature (for Cu,
Pd, Al and Pt) and equals 11.85 eV, supporting a major effect of the initial state in the photoemission process as demonstrated by Wandelt for several Xe/metal surfaces [35]. As a consequence, for various metal surfaces, photoemission of adsorbed xenon (PAX) in one particular direction of detection and preferably near the normal [32], has been used as a « local work function probe » in order to sample structural defects [36-38], adsorbed species [39-41], and alloys [42-43]. However, it must be mentioned that on Pb, Ga and Ba overlayers [44], distance-dependent shifts are not due to work-function changes induced by the Xe adatom itself but to changes in the final state screening [45].

In this paper, a comparison will be made between the dispersion curves of the commensurate (C) and hexagonal incommensurate rotated (HIR) layer (new results) in the context of the previous angle-resolved photoemission data on other substrates. We will demonstrate that the splitting of the 5p3/2 levels is moderately sensitive to the interatomic distance and relatively insensitive to the nature of the substrate.

2. Experimental.

Most of the experiments were made in an apparatus (Atomic Energy Commission — Service de Physique Atomique des Surfaces, Saclay, France) consisting of a home made ultrahigh-vacuum moveable electron spectrometer (hemispherical, radius = 30 mm) mounted in a two-level chamber equipped with a rare-gas discharge lamp (Leybold), a low-energy diffraction (LEED) optics (Riber), an ion gun (Riber) and electron bombardment for crystal preparation. Pumping is ensured through a cryopump (Air Liquide), an ion pump and/or a trapped oil diffusion pump (Edwards). Base pressures below 10^-10 Pa are obtained after bakeout. Additional results at normal emission were obtained at LURE (Laboratoire d’Utilisation du Rayonnement Electromagnétique, Orsay, France) using synchrotron radiation light between 19.5 and 30 eV and in Nancy with our ESCA equipment (Leybold-Heraeus) and a rare-gas discharge lamp.

The Pt crystal was cut from a single crystal rod of 5N purity (Materials Research) after orientation to within 0.5° and mechanically polished. The Pt sample was preoriented under X-ray back reflection before mounting with the light incidence plane along the ΓM orientation of the Pt(111) crystal. It is clamped onto a tantalum reservoir containing circulating liquid nitrogen. The minimum temperature obtainable on the sample was estimated to 80-85 K (see later). After ion bombardment and annealing around 1 000 K, Auger electron spectroscopy (AES) revealed no impurity (C, Si, Ca, Al) at the detection limit [46, 47] and a sharp diffraction pattern of the clean (1 x 1) surface was observed. The LEED pattern showed a slight misalignment (3-4°) with respect to the ΓM orientation.

Photoelectron spectra were taken with unpolarized He I radiation at an incidence angle equal to 45° with 15 meV steps for the electron kinetic energy. Absolute work function was determined as well as the instrumental resolution (150 meV) at the Fermi edge. At LURE, the resolution was only 220 meV and in Nancy around 300 meV.

3. Results.

3.1 LEED. — At the lowest temperature of the sample, adsorption of xenon at 10^-6 Pa pressure (gauge reading uncorrected) produces the (√3 x √3) R30° pattern (C phase). This structure is easily observed and stable under vacuum. When the pressure is increased up to 10^-4 Pa, an intermediate incommensurate hcp phase (HI) (which like the C phase is rotated with respect to the substrate by 30°) appears transiently and converts readily into an incommensurate rotated phase (HIR) consisting of domains rotated from the common orientation of the C and HI phase by ± 3°. Under vacuum, the reverse sequence of patterns is observed and the C phase is recovered. From the heats of adsorption of the various phases [17], the minimum temperature of the sample can be estimated to be 80-85 K. At this temperature, the phase diagram given by Kern et al. is not clear [18, 21]. However, at 88 K, it was shown in a preceding paper [17] that the HIR phase existed at saturation of the xenon overlayer.

3.2 ARUPS. — We will consider here the C and the HIR overlayers. Dispersion curves were made along the ΓKM direction of the C phase. The LEED pattern of the C layer and the Surface Brillouin Zone (SBZ) are schematically shown in figure 1. The Xe-Xe distances were estimated to be respectively around 4.8 Å and 30 eV and in Nancy with our ESCA equipment (Leybold-Heraeus) and a rare-gas discharge lamp.

![Fig. 1. — Low electron energy diffraction pattern of the (√3 x √3) R30° xenon overlayer. Surface Brillouin zone (SBZ) of xenon.](image-url)
tation of the crystal, we note also \( k_p \) at the H point, viz 0.814 Å\(^{-1}\). The corresponding values for the HIR phase are 0.9558 Å\(^{-1}\) and 1.4378 Å\(^{-1}\). Two domains in the HIR phase coexist in such a way that one domain is almost strictly in the \( \Gamma K MK \) direction while the other one is misoriented by about 6°-7°. As a consequence, dispersion curves of the HIR layer are expected to be less accurate than for the C phase.

The direction of the normal was determined precisely using various methods [32], including the symmetry of the dispersion curve itself. Photoelectron spectra were taken every 4 degrees in order to obtain roughly 0.1 Å\(^{-1}\) variation in \( k_\parallel \), according to

\[
k_\parallel = 0.511 \sqrt{E \sin \theta}
\]

where \( E \) is the kinetic energy (eV) of the electrons leaving the crystal, and \( \theta \) the angle of analysis with respect to the surface normal. Knowing the work function \( \Phi \), \( E \) is given by

\[
E = h \nu - E_F - \Phi
\]

The experimental work function of the clean metal was found to be 5.85 eV. A 0.60 eV decrease was obtained with the C overlayer and slightly more (0.65 eV) with the HIR layer. Values of \( k_\parallel \) were computed taking into account the work function of the covered surface.

Figure 2 gives the photoelectron spectra of the C and HIR phases at the \( \Gamma \) point. Several features should be noted.

(a) The three 5p levels of adsorbed xenon are clearly seen. Their positions are almost the same for the two phases. A similar result was obtained at LURE in the 19.5-20 eV photon energy range and in Nancy using He I radiation (21.21 eV).

(b) On the high binding energy side of the 5p1/2 and 5p3/2 (\( m_j = \pm 1/2 \)) levels extra transitions exist. They do not disperse and were attributed to indirect transitions due to defects in the crystal [32].

(c) After removal of the base line the spectra were decomposed using an optimization routine into five peaks (Gaussian-Lorentzian) [48] to account for the extra transitions. Allowing for an experimental resolution of 150 meV deduced from the Fermi cut-off, the natural width of the lines is around 200 meV at the \( \Gamma \) point for the C layer. The 5p3/2, \( m_j = \pm 3/2 \) level is broader (600 meV) because of the remaining influence of a Pt 5d induced transition. This influence disappears upon analysis away from the surface normal because of a different dispersion behaviour. An example of decomposition of spectra of the C and HIR layers at the \( \Gamma \) point is given in figure 3.

The same decomposition procedure was followed to determine the dispersion curves. Note that off normal direction, the 5p levels of the HIR phase were broader than for the C phase, a fact which is not surprising because of the coexistence of two rotated domains. As expected, the dispersion curves show more scatter for the HIR phase than for the C phase; they are given in figure 4.

4. Discussion.

Qualitative agreement exists between the dispersion curves of figure 4 and other experimental results on different substrates and layers [9, 11, 16, 32]. Despite different accuracies for the two layers examined here, we note the following points:

(a) at the \( \Gamma \) point, the binding energy of all levels are only slightly different for the C and HIR layers in the three apparatus that we have used (see also Fig. 2). This result is at variance with those obtained by Schönhense [24, 25] for the 5p3/2 levels using a
Fig. 4. — Dispersion curves of the 5p xenon levels along $\Gamma K M K$ direction; binding energies are referenced to the Fermi level; incidence angle = 45°: (●, ○) C layer; (▲, △) HIR layer.

In order to assess more clearly the influence of the Xe-Xe lateral interactions on dispersion and splitting, we have recalled in Table I all the photoemission results that we know along with the xenon-xenon distance in the layer. Some of the results have been determined after enlargement of the original figures and may be relatively inaccurate. For Cu(110), the two structures are not strictly hexagonal but uniaxially compressed (along the [110] direction). Contrary to Table II in reference [32] and following a suggestion of Mandel [51] « effective » Xe-Xe distances calculated from the values of the areas for adatom under the assumption of a hexagonal close-packed Xe structure have been used. Some very recent results for xenon monolayers and bilayers on graphite (001) [52] are also included. The corresponding values obtained from differences in threshold positions in the work of Schönhense [24] are such that the separation of the 5p3/2 bands at $\Gamma$ point is smaller for the first layer than for the bilayer. On graphite, depending on temperature (below and above 63 K) the first layer is commensurate or incommensurate with the substrate [53]. In the second case, the xenon-xenon distance varies continuously between 4.51 Å and 4.44 Å. It explains the question mark.

Table I deserves more comments:

(a) the general trend is in agreement with theoretical calculations [33, 34]. With decreasing Xe-Xe distances one observes an increase in the dispersion for all bands and in the 5p3/2 splitting. The variation of the spin-orbit splitting is less obvious. For comparison, the theoretical values of Hermann et al. [33] for an hcp layer (4.48 Å) are 0.38, 0.48 and 0.6 eV for the maximum dispersion of the three bands, 0.43 and 1.32 eV for the 5p3/2 splitting and the spin-orbit splitting. If the interatomic spacings in the adsorbed Xe monolayer are taken into account [51], a relatively good agreement is found for the dispersion of the 5p1/2 level;

(b) a parameter, quite sensitive to the distance, is the 5p3/2 splitting at the $\Gamma$ point. In the case of the repulsive Xe/Pd(100) system, Bradshaw et al. [22] have observed a splitting of these levels at coverages as low as 0.30. This corresponds to a Xe-Xe distance of around 5.4 Å. This system presents the advantage of a continuous variation of the Xe-Xe distance. Unfortunately, the variation of this splitting versus coverage was not recorded in this last work. Results show nevertheless that the 5p orbitals start to overlap when the Xe-Xe distance is close to 5.4 Å;

(c) between the Xe $\sqrt{3} \times \sqrt{3}$ R30°/Pt(111) layer and the hcp layer this splitting varies only between 0.4 and 0.65 eV. For the hcp Xe/Cu(111) layer and the hcp Xe/Ru(001) layer Eder et al. [30, 31] have found splittings respectively equal to 0.3 and 0.2 eV, values much lower than for the hcp
Table I. — Dispersion results.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Xe-Xe distance (Å)</th>
<th>$5p^{1/2}$ dispersion (eV)</th>
<th>$5p^{3/2}$, $m_f = \pm \frac{1}{2}$ dispersion (eV)</th>
<th>$5p^{3/2}$, $m_f = \pm \frac{3}{2}$ dispersion (eV)</th>
<th>Separation of bands at $\Gamma$ point (eV)</th>
<th>$5p^{3/2}$ splitting</th>
<th>spin-orbit splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>4.8 [24]</td>
<td>0.32 0.35</td>
<td>0.35 0.41</td>
<td>0.33 0.65</td>
<td></td>
<td>0.4 1.2</td>
<td>0.45 1.25</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>4.8 [TW1]</td>
<td>0.24 0.36</td>
<td>0.4 0.36 0.44</td>
<td></td>
<td></td>
<td>0.43</td>
<td>0.44 1.24</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>4.8 [TW2]</td>
<td>0.4 0.55 0.60</td>
<td>0.55 0.8</td>
<td></td>
<td>0.57 1.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir(111)</td>
<td>4.7 [24]</td>
<td>0.6 0.51 0.72</td>
<td></td>
<td></td>
<td>0.62 1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(110)</td>
<td>4.6 [11]</td>
<td>0.4 0.35 0.65 0.8</td>
<td></td>
<td>0.5 1.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(110)</td>
<td>4.38 [11]</td>
<td>0.6</td>
<td></td>
<td></td>
<td>0.6 1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd(100)</td>
<td>4.38 [9]</td>
<td>0.45 0.51 0.72</td>
<td></td>
<td></td>
<td>0.62 1.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(111)</td>
<td>4.38 [16]</td>
<td>0.42 0.47 0.55 0.8</td>
<td></td>
<td>0.62 1.28</td>
<td>0.06 1.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(111)</td>
<td>4.38 [12]</td>
<td>0.47 0.55 0.8</td>
<td></td>
<td></td>
<td>0.57 1.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr(111)</td>
<td>4.38 [TW1]</td>
<td>0.35 0.4 0.65 0.95</td>
<td></td>
<td>0.64 1.22</td>
<td>0.04 1.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(111)</td>
<td>4.38 [24]</td>
<td>0.47 0.55 0.95</td>
<td></td>
<td>0.64 1.22</td>
<td>0.04 1.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir(111)</td>
<td>4.38 [24]</td>
<td>0.55 (*)</td>
<td></td>
<td></td>
<td>0.55 1.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag(111)</td>
<td>4.38 [30]</td>
<td></td>
<td></td>
<td></td>
<td>0.64 1.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(111)</td>
<td>4.38 [52]</td>
<td>0.33 0.47 0.55 0.95</td>
<td></td>
<td>0.64 1.22</td>
<td>0.04 1.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(111)</td>
<td>4.26 [52]</td>
<td>0.6</td>
<td></td>
<td></td>
<td>0.57 1.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag(111)</td>
<td>4.38 [24]</td>
<td></td>
<td></td>
<td></td>
<td>0.55 1.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gr(001)</td>
<td>4.38 [52]</td>
<td>0.33 0.47 0.55 0.95</td>
<td></td>
<td>0.64 1.22</td>
<td>0.04 1.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gr(001)</td>
<td>4.26 [52]</td>
<td>0.6</td>
<td></td>
<td></td>
<td>0.57 1.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gr(001)</td>
<td>4.38 [24]</td>
<td>0.64 1.22</td>
<td>0.04 1.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[TW1]: This work - Apparatus in Saclay.
[TW2]: This work - Leybold apparatus in Nancy.
(*) : at M or K point.
(**): bilayer.

Fig. 5. — Separation of the $5p^{3/2}$ levels at the $\Gamma$ point versus the xenon-xenon distance.

Xe/Ag(111) layer (0.5 eV). Accordingly they proposed that the splitting was « mainly caused by lateral interactions and 2D band structure formation and that the size of the splitting could be regarded as a measure of the lateral Xe-Xe attraction ». They added that « this is compatible with the sequence of dipole moments ». However, this attractive explanation is contradicted by the data of table I.

It must be noticed that in Eder's experiments [54] the photoemission spectra are recorded at an angle of about 45° and not in the normal direction. Therefore the emission point in the SBZ depends therefore on the azimuthal orientation of the substrate. Indeed, as it can be seen in figure 6 of reference [11], for Cu(110) the splitting of the $5p^{3/2}$ levels depends on the azimuthal angle for a given detection angle. For instance at 45°, it is smaller in the $\Gamma$KMK direction than in the $\Gamma$MG direction (0.25 eV compared to 0.5 eV). A similar result is found for Xe/graphite (001) [52]. The splitting of the $5p^{3/2}$ levels at 45° is 0.34 in the $\Gamma$KMK direction and 0.65 in the $\Gamma$MG direction. The Ag and Cu films used by Eder et al. were epitaxially grown on Ru(001) [54]. On bulk Cu(111) [12] and Ru(001) [55] the xenon saturated layer is rotated with respect to the substrate; it is aligned to the substrate on Ag(111) [5, 6]. The 30° difference in angle of the overlayer corresponds exactly to a change from the $\Gamma$KMK direction (Cu(111) and Ru(001)) to the $\Gamma$MG direction (Ag(111)). As a consequence, the results of Eder et al., when interpreted self-consistently, do not contradict those presented in table I and do not require a special interpretation.

Therefore it must be concluded that despite differ-
ent adsorption energies and dipole moments for xenon adsorbed on Cu, Al, Pd, Pt, Ag and graphite there is no significant change of the xenon 5p3/2 splitting on different substrates, apart from small variations due to the different xenon-xenon distances.

5. Conclusion.

Like on other metals xenon adsorbed on Pt(111) in 2D dense phases shows marked dispersion effects on its 5p levels. Due to lateral interactions and to the overlap of orbitals, the 5p3/2 levels are split. This splitting appears to be mainly characteristic of the xenon-xenon distance. It varies between approximately 0.45 eV and 0.65 eV for distances between, roughly, 4.8 and 4.3 Å.

Acknowledgements.
The authors would like to thank J. Cousty and R. Riwan (SPAS-Saclay) for fruitful discussions and appreciate the opportunity to have used their angle-resolved equipment.

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