

Spin-Resolved Photoemission from Xe-Adlayers on Pd(111)

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Abstract

Xe-adsorbates on Pd(111) in the coverage region from one layer up to a Xe(111) crystal with first layer Xe–Xe distances comparable to bulk Xe are studied by spin-resolved photoemission. Normally incident circularly polarized synchrotron radiation from BESSY (Berlin) is used and normally emitted electrons are analyzed. No dispersion with photon energy can be found for a system of two Xe-layers. The spin-polarization component measured along the direction of light points to a changing symmetry of the final states. Their symmetry is atom-like for a one-layer system and bulk-like for two and more layers. The initial state symmetry is examined by excitation and decay of excitonic states and is found to be the same for two Xe-layers as for one single Xe-layer. The degeneracy of the valence levels connected with the high symmetry of the Γ -point in bulk Xe can be observed for a system of much more than 5 Xe-layers thickness.

Xe-adsorbates have been studied by different techniques [1]. Spin-resolved photoelectron spectroscopy of Xe-adsorbates using circularly polarized synchrotron radiation has been shown to be a suitable method to get information beyond intensity spectroscopy [2–6]: The lateral Xe–Xe interaction has been found to dominate the splitting of the $|m_j\rangle$ -sublevels of the $p_{3/2}$ -state [5, 6, 23]. The bandstructure of bulk Xe along Λ has been elaborated by symmetry-resolved bandmapping using relativistic dipole selection rules [7, 8]. An emission process via the excitation and decay of an excitonic state has been found at photon energies below the threshold of direct photoemission for Xe-coverages from one Xe-layer to a Xe-crystal [3, 5].

An interesting question is to understand the development of the properties of a three-dimensional Xe-crystal when two-dimensional Xe-layers are stacked. Layer by layer growth of Xe-adsorbates has been intensively studied by spectroscopy of photoelectron intensities. The layer dependent photoemission-peak shifts observed in going from a single adsorbate layer to multilayers have been discussed controversially [9, 10]. Recent experiments with Ar, Kr and Xe on Pb(111) demonstrate that these peak shifts are due to the change of the relaxation of the final-state hole [11]. This interpretation was firstly proposed in Ref. [12] and was used in Ref. [13] to interpret layer-dependent photoemission intensity-spectra from Xe/A1(111). The spectra of the two-layer system have been found to be the sum of two one-layer spectra shifted against each other. The first hints for bulk bands have appeared at about 2.5 layers.

The aim of our experiment is to study the onset of effects of the third dimension in the layer by layer growth of Xe/Pd(111) by spin-resolved photoelectron spectroscopy. The measurements are performed at the 6.5 m NI-monochromator [14] for circularly polarized radiation at BESSY in Berlin. The experimental setup has been previously described [15]. The circularly polarized ($90 \pm 3\%$) synchrotron radiation with energies from 7.8 to 17 eV hits normally the target.

The normally emitted photoelectrons are energy analyzed by a simulated hemispherical-field spectrometer [16]. For electrons with a kinetic energy of 1 eV the angular resolution is ± 7.5 deg [17]. The overall resolution (photons plus electrons) is better than 200 meV. The spin-polarization component P in the direction of light incidence is measured by Mott scattering. Positive P means electron-spin polarization parallel to the photon spin [18]. The experimental results are displayed in the form of partial intensities I_+ and I_- giving the parts of the emitted electrons with expectation value of the polarization operator $+1$ or -1 , respectively. I_+ and I_- result from the total electron intensity I_0 and the spin polarization P by:

$$I_+ = 0.5I_0(1 + P) \quad I_- = 0.5I_0(1 - P). \quad (1)$$

The Pd(111)-substrate crystal can be cooled by liquid helium and is cleaned by Ne-sputtering, heating in oxygen at about 800 K and flashing to about 1300 K. The crystal surface is characterized by LEED, by Auger-spectroscopy and concerning C-contamination by cycles of oxygen adsorption and CO-desorption spectroscopy [19].

The Xe-adsorbate is prepared by cooling the substrate down to temperatures between 100 and 40 K and subsequent Xe deposition via a gas doser. It is controlled by photoemission-peak shifts [9–13] and by LEED. Always a layer with a LEED-pattern showing a hexagonal structure with two domains rotated by 26 ± 2 deg with respect to the substrate has been prepared as a first layer. The Xe–Xe distance within this first layer turns out to be 4.25 ± 0.15 Å and is thus comparable to the bulk Xe–Xe distance of 4.37 Å [20]. A comparable structure with a Xe–Xe distance of 4.33 ± 0.03 Å and a rotation by 26.7 deg has been found for single Xe-layers on nearly defect free Pt(111) and has been interpreted as a high-order commensurate phase: each eleventh Xe-atom is located at a high symmetry site [21, 22]. As the nearest-neighbor distances of Pd and Pt are nearly identical (2.75 Å for Pd and 2.77 Å for Pt [20]), we suppose that the Xe-layer on Pd(111) showing the 26 deg rotation has to be interpreted in a similar way. Due to the better agreement with the bulk Xe–Xe distance this first layer structure seems to be a more suitable basis for a layer by layer growth of a Xe-crystal than the more compressed and more buckled Xe($\sqrt{7} \times \sqrt{7}$) R19, 2° /Pd(111) layer [23]. The Xe-atoms of this adsorbate layer show a distance of 4.2 ± 0.05 Å in the projection to the surface plane which is a lower limit for the Xe–Xe distance in the less compressed first layer of the adsorbates used in the present work. The ± 26 deg rotation of the two Xe-domains has not to be considered because circularly polarized light with normal incidence and normal photoelectron emission has been used.

Figure 1 shows the photoelectron spectra of Xe/Pd(111) for a photon energy of $h\nu = 12.5$ eV and various Xe-coverages.

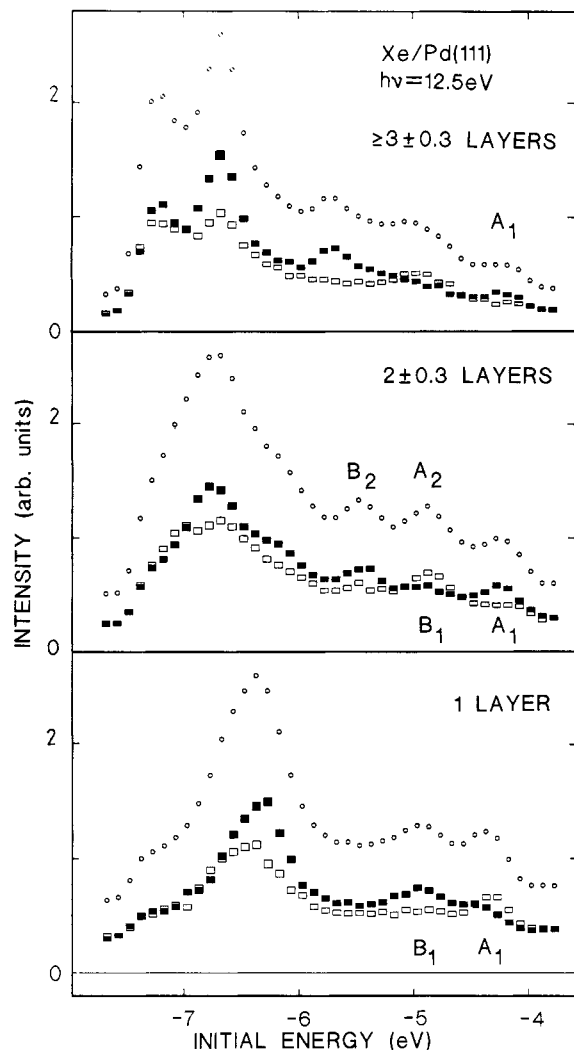


Fig. 1. Spin-resolved photoemission spectra from Xe/Pd(111) at different coverages and $h\nu = 12.5$ eV. (O: total intensity I_0 ; ■: partial intensity I_+ ; □: partial intensity I_-); the heights of the I_+/I_- -symbols represent the uncertainties given by the errors of the total intensity and the polarization. The intensities are normalized to equal height of the largest maxima. The energy refers to the Fermi level of the substrate. The peak assignments are given in the text.

The one Xe-layer spectrum at the bottom of the figure shows three peaks in the total intensities. They correspond to the $p_{1/2}$ - and the two $|m_j|$ -split $p_{3/2}$ -hole states of the Xe-adsorbate which can be seen by comparing the spin-dependent partial intensities I_+ and I_- with the results of Ref. [6] ($p_{1/2}$: peak in I_+ , $p_{3/2}|m_j| = \frac{1}{2}$: peak in I_+ , $p_{3/2}|m_j| = \frac{3}{2}$: peak in I_-). The large I_- -part in the $p_{1/2}$ -peak at about -6.4 eV might be due to a density of states feature and will be not discussed further. We will focus on the ($p_{3/2}$, $|m_j| = \frac{3}{2}$)-peak at -4.3 eV and the ($p_{3/2}$, $|m_j| = \frac{1}{2}$)-peak at -4.9 eV denoted as A_1 and B_1 , respectively. When going to the spectrum of 2 ± 0.3 Xe-layers (Fig. 1, middle panel) the corresponding transitions starting from Xe-atoms of the second layer (denoted by A_2 and B_2) occur at lower initial state energies. The preferential spin direction in the peaks at -4.9 eV and -5.5 eV seems to be dominated by the transitions A_2 and B_2 , respectively. A surprising effect is the change of the spin polarization measured in the peak A_1 (originating from the *first* layer) from dominating partial intensity I_- to dominating partial intensity I_+ when a second layer is adsorbed. If the coverage is increased to more than three Xe-layers (Fig. 1, top panel) peak A_1 still shows positive

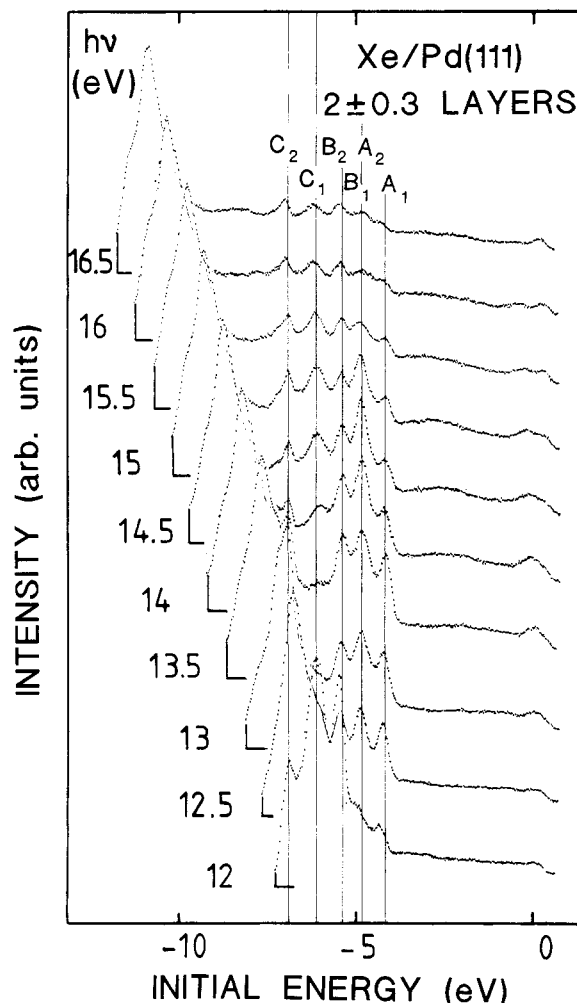


Fig. 2. Total photoemission spectra for a system of 2 ± 0.3 Xe-layers on Pd(111) at varied photon energies. The intensities are normalized to equal height of the largest maxima. (Peak assignments see text.)

spin polarization though the intensity decreases relative to the other peaks. The intensity decrease can be understood by the limited free path of the electrons which are created in the first Xe-layer and which have to cross another two Xe-layers before leaving the adsorbate. The positive spin polarization in peak A_1 at a coverage of 2 Xe-layers can not be understood in a model assuming photoemission from two independent layers with identical symmetry of the electronic states.

Three dimensional systems typically show dispersion of photoemission-intensity peaks when the photon energy is varied (e.g. Ref. [7]). Figure 2 shows the photoelectron-intensity spectra for a system of two Xe-layers on Pd(111) at different photon energies between 12 and 16.5 eV. The large peak at constant kinetic energy near the vacuum edge might be due to a density of states feature [7]. Here this peak will not be discussed in detail. Near E_F some weak features of Pd are visible. The peaks between -4 and -7 eV correspond to photoelectrons from the adsorbate. Going from high to low initial energy they can be assigned as A_1 , B_1/A_2 , B_2 , C_1 , C_2 (C_1 and C_2 denote emission from the $p_{1/2}$ -states of the first and second Xe-layer, respectively). The initial energies do not significantly vary with photon energy: we can not find dispersion for the two Xe-layer system. This behaviour is not very surprising remembering other results from systems of two Xe-layers [9–13].

The symmetries of the initial states can be analyzed by constant final state spectroscopy (CFS): The total intensity I_0

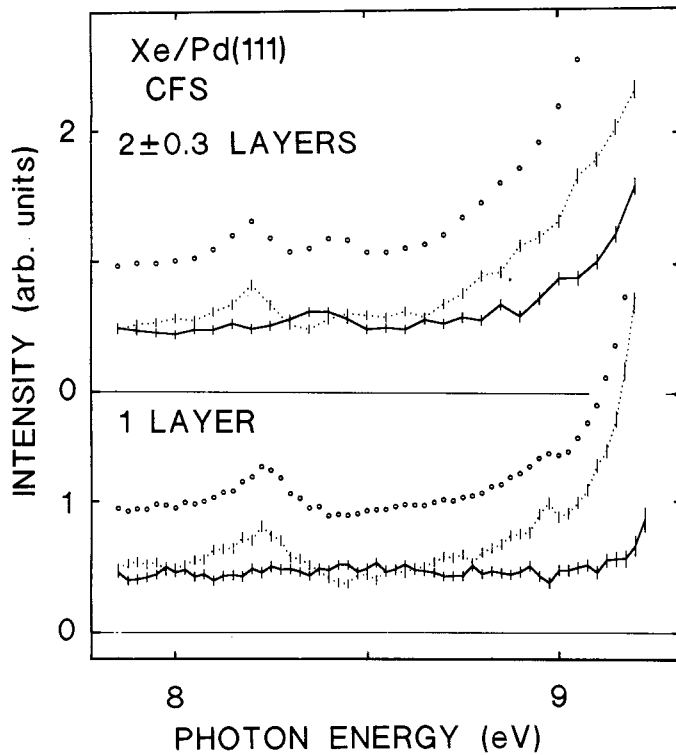


Fig. 3. Spin-resolved constant final state spectra at final state energy $E_f \approx 0.4$ eV with photon energies below the threshold for direct photoemission showing emission via excitonic states at different coverages. (○: I_0 , —: I_+ , ···: I_-). The intensity scales are not comparable.

and the spin polarization P of electrons with a constant kinetic energy of about 0.4 eV are measured under variation of photon energy starting at photon energies below the onset of direct photoemission. Figure 3 shows these CFS-spectra for one Xe-layer (bottom of Fig. 3) and for 2 ± 0.3 Xe-layers (top of Fig. 3) on Pd(111). Above a photon energy of 9 eV the intensity increases dramatically due to the onset of direct photoemission. We will not discuss this region. The feature of main interest in the context of this paper is the peak in the partial intensity I_- at a photon energy of about 8.2 eV which results from the decay of an excited excitonic state of the adsorbate [3, 5]. The exciton belongs to an excited state with symmetry $[5p^5 (^2P_{3/2}|M_J) = \frac{3}{2})6s^0]_1$ [5]. The core of this state has the same symmetry as the initial hole states corresponding to the A_1 -, A_2 -peaks in direct photoemission. In contrast to the results from direct photoemission the peak in the CFS-spectra of Fig. 3 does not change the sign of spin polarization when going from one Xe-layer to two Xe-layers on Pd(111). We conclude therefore that the change of sign observed in direct photoemission is *not* induced by a change in the symmetry of the initial state.

The lack of dispersion for a system of two Xe-layers under variation of the photon energy allows to study the change of the preferential spin direction of peak A_1 by constant initial state spectroscopy (CIS). Figure 4 shows a CIS-spectrum for two Xe-layers with an initial energy of -4.3 eV corresponding to the A_1 initial state. The electron intensities measured are not corrected for the photon flux of the monochromator as the photon flux has been measured to be nearly constant for photon energies between 11 and 15 eV [14]. The decrease of electron intensity at photon energies higher than 15 eV may be caused by the decreasing flux having a minimum at

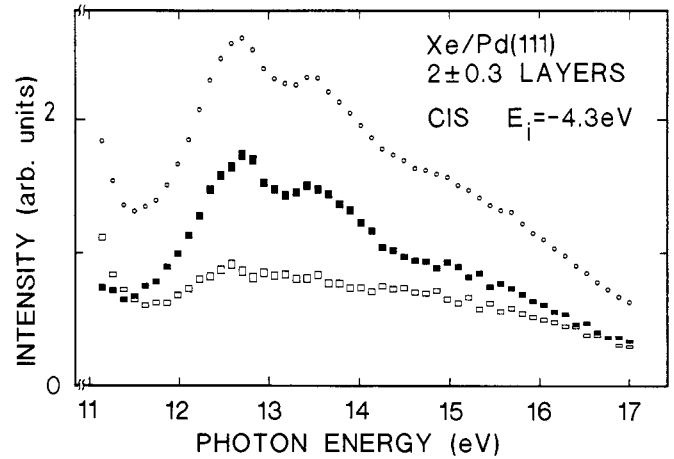


Fig. 4. Spin-resolved constant initial state spectrum at initial state energy of -4.3 eV for 2 ± 0.3 Xe-layers. (○: I_0 , ■: I_+ , □: I_-).

about 20 eV. The partial intensity I_+ dominates for all photon energies measured above about 11.5 eV. This is in accordance with the results from Fig. 1 at $h\nu = 12.5$ eV where the peak A_1 is caused by the partial intensity I_+ for a system of two Xe-layers. However at photon energies below about 11.5 eV the partial intensity I_- dominates in the peak A_1 . We conclude that the symmetry of the final state involved changes and this change causes the positive sign of spin polarization for photon energies above 11.5 eV. The maxima in the partial intensity I_+ at about 12.7 and 13.4 eV may be induced by a high density of final states.

The spin-polarization behavior of peak A_1 can be explained by a comparison with the bandstructure of a Xe-crystal in the Λ -direction [7]. Considering the screening effects induced by the substrate which are highest for the first Xe-layer the A_1 initial state lies 0.7 eV above the valence band maximum (VBM) of solid Xe. This initial energy shows no dispersion, it is flat between Γ and L . The symmetry of the A_1 initial state is purely x, y ($-z$ is the direction of the surface normal) [24] which is mostly comparable to a band which transforms according to $\Lambda_{4,5}^3$ [25]. From the dipole selection rules in the Λ -direction of f.c.c. and b.c.c. crystals [8] it follows that negative and positive spin polarization characterizes transitions from states with symmetry $\Lambda_{4,5}^3$ into empty states of symmetry Λ_6^1 and Λ_6^3 , respectively. Regarding to the bandstructure given in Ref. [7] the lowest lying empty band along Λ transforms as Λ_6^1 . Going to higher energies an energy gap between 11 and 13 eV and two flat hybridized bands with Λ_6^3/Λ_6^1 -symmetry follow at about 13.8 and 14.3 eV above VBM. A CIS-measurement with the initial energy of an ideal flat $\Lambda_{4,5}^3$ -band located 0.7 eV above VBM should therefore result in negative polarized photoelectrons up to a photon energy of 10.3 eV and positive polarized photoelectrons above $h\nu = 12.3$ eV with maximum intensities at 13.1 and 13.6 eV. For photon energies between about 10.3 and 12.3 eV the gap should induce a zone of nearly vanishing electron intensity. A comparison with the CIS-spectrum of Fig. 4 shows a quite good agreement though the gap is strongly weakened and the energies do not coincide exactly. We conclude therefore that the spin-polarization measured for two Xe-layers can roughly be explained by assuming empty states with symmetries corresponding to those of bulk Xe.

An important characteristic of the bandstructure of a three dimensional Xe-crystal is the degeneracy of the two topmost

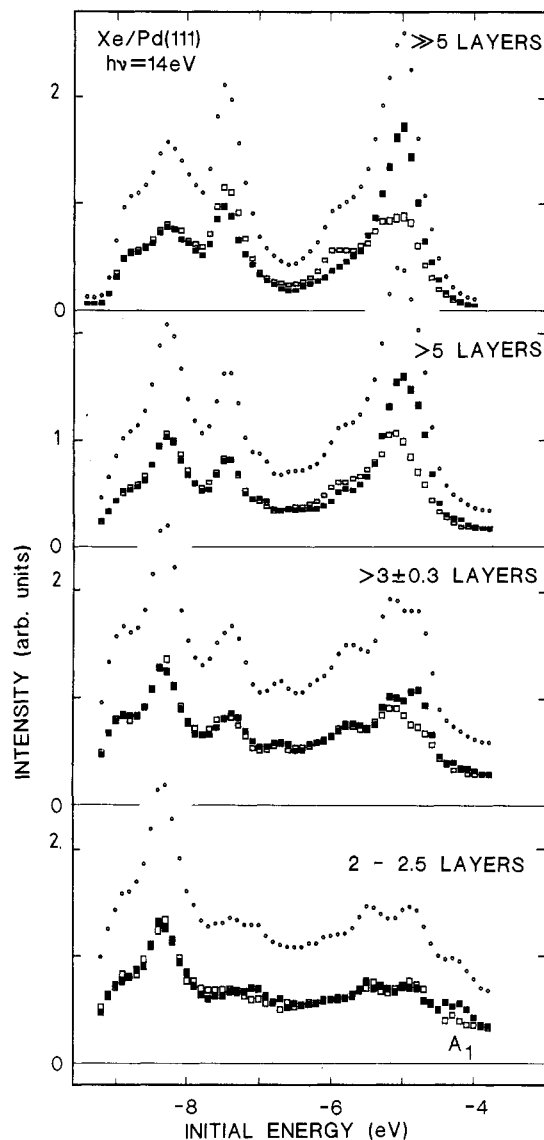


Fig. 5. Spin-resolved photoemission spectra for Xe/Pd(111) at different coverages and $h\nu = 14$ eV. (○: I_0 , ■: I_+ , □: I_- , peak assignments see text).

valence levels at the Γ -point due to the high symmetry of this point. With a Xe-crystal electrons from the Γ -point can be observed at a photon energy of 14 eV. Figure 5 shows photoemission spectra at $h\nu = 14$ eV at various Xe-coverages on a Pd(111)-substrate. We will concentrate on the initial energies from about -4 to -5 eV. At low coverage (2–2.5 Xe-layers, Fig. 5, bottom panel) the total intensity shows discrete peaks. At -4.3 eV peak A_1 can be identified due to its positive spin polarization. With increasing Xe-coverage ($> 3 \pm 0.3$ layers and > 5 layers, Fig. 5) an asymmetric peak at about -5 eV is built up in the total intensity by one peak in the partial intensity I_+ and one slightly shifted peak in the partial intensity I_- . For a system of more than 5 Xe-layers thickness the I_+ -peak and the I_- -peak still show a splitting of at least 0.1 eV. When the coverage is further increased (≥ 5 Xe-layers, Fig. 5, upper panel) we get a three dimensional crystal and the splitting vanishes. The spectrum equals those obtained from Xe(111) on Ir(111) and Pt(111) [7]. The I_+ -peak and the I_- -peak at about -5 eV characterize the VBM of the Xe-crystal where the two topmost valence bands are degenerated. Assuming a transition in an empty band of Λ_6^3/Λ_6^1 -symmetry the I_+ -peak and the I_- -peak originate from

the Λ_4^3 and the Λ_6^1 initial bands, respectively. We conclude that for 5 Xe-layers the band structure of the Xe-crystal is not yet developed which might be due to the lack of degeneracy or to an energy shift of the levels involved.

Summarizing spin resolved photoemission data in normal incidence of circularly polarized synchrotron radiation and normal electron emission from Xe-adsorbates on Pd(111) are presented. The hexagonal adlayer with a Xe–Xe distance comparable to that of bulk Xe growing in two domains rotated by 26 ± 3 deg is supposed to be high-order commensurate and to be an ideal first layer for growing of a Xe-crystal. The symmetry of the initial state corresponding to the atomic $p_{3/2}|m_j| = \frac{3}{2}$ level is the same for one Xe-layer and for two Xe-layers as can be seen by excitation and decay of excitonic states. From spin-resolved photoemission it results that in a system of two Xe-layers the empty electronic states normal to the layer show symmetries comparable to bulk Xe along Λ (Λ_6^1 and Λ_6^3/Λ_6^1), the gaps are weakened. The completely developed bandstructure of solid Xe near Γ can only be observed for a system of much more than 5 Xe-layers.

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