

Structural investigations on Xe/Pd(111) with spin-polarized LEED

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$(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Xe/Pd(111)}$ and the dilute phase of Xe/Pd(111) were investigated with spin-polarized low-energy electron diffraction (SPLEED). In the experiment spin-polarized electrons from a GaAs source were scattered and the spin-dependent intensities were measured. Comparative calculations were carried out by means of a relativistic LEED program. The structure determination of $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Xe/Pd(111)}$ yields a layer distance of $3.5 \pm 0.1 \text{ \AA}$, the Xe atoms being adsorbed in hollow sites. In the dilute phase of Xe/Pd(111) the adsorbed Xe atoms occupy on-top sites with a Xe–Pd distance of $4.0 \pm 0.1 \text{ \AA}$ without two-dimensional periodicity.

Spin-polarized LEED (SPLEED) has proven to be a method for studying surface structures with a high sensitivity to structural parameters [1,2]. Thereby SPLEED is especially sensitive to local order, as spin-dependent effects originate from spin–orbit interaction within the single- and multiple-scattering processes at the ion cores of the target. Due to the limited mean-free path of the electrons this scattering is restricted to limited areas of multiple-scattering attached to each surface-lattice point [3]. Using these areas of multiple-scattering as if they were scattering centres the diffraction process can be described in a pseudo-kinematic model. The (long-range) order of the areas of multiple-scattering will determine the lattice factor of the intensity only. As spin-dependent effects are measured normalized to the intensity, they are determined alone by the scattering inside the areas of multiple scattering and therefore by the local order [4]. This sensitivity to local order is similar to the behaviour of the logarithmic derivative of the intensity used in diffuse LEED [5,6]. Compared to diffuse LEED, SPLEED has the advantage that data are accessible via spin-dependent measurements at one fixed

energy. Using diffuse LEED, however, for each data point measurements at two different energies with different multiple-scattering conditions are necessary.

The sensitivity to local order qualifies SPLEED especially to study systems with structural disorder, e.g. surface structures with small domains, and lattice-gas systems on surfaces without long-range order. Thereby calculations for well-ordered systems can be directly used to determine local structural parameters (adsorption sites, distances) in disturbed layers. Only a homogeneous background resulting from the diffuse scattering caused by the disorder has to be considered. Xe/Pd(111) is an adsorbate system showing a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure well ordered in domains and a dilute phase without long-range order. SPLEED is just the method to study this system.

The $(\sqrt{3} \times \sqrt{3})R30^\circ$ and the dilute phase of Xe/Pd(111) are prepared on the clean Pd(111) surface cooled by liquid He to temperatures of 70 and of about 55 K, respectively. The SPLEED measurements are performed using a NEA-GaAs photoemission source of spin-polarized electrons [7,8] and recording the spin-dependent intensities of the scattered electrons. The spin polarization of the GaAs source was $0.255 + 0.032/-0.019$.

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The surface normal is chosen to be in the scattering plane defined by the incoming and the outgoing beam. The spin-polarization vector \mathbf{P} of the incident electron beam is aligned normal to the scattering plane. \mathbf{P} is switched between the two normal directions (+, -) by switching the helicity of the circularly polarized light incident on the GaAs crystal. The spin-dependent intensities $I(+)$, $I(-)$ yield the asymmetry A ,

$$A := \frac{1}{|\mathbf{P}|} \frac{I(+)-I(-)}{I(+)+I(-)}, \quad (1)$$

which per definition is intensity normalized and represents the data determined by local order.

The target crystal can be rotated about its surface normal and about a polar axis lying in the surface. The asymmetry profiles were measured as a function of the scattering angle Θ , which is the angle between the incoming beam and the momentum of the outgoing scattered electrons. The intensities of the scattered electrons were measured by a movable collector system with retarding grids to suppress inelastically scattered electrons. For $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Xe/Pd(111)}$ a Faraday cup was used as collector, for the dilute phase a channel electron multiplier had to be used because of the low backscattered intensity.

The measurements on the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure are performed in the adsorbate-induced $(\frac{1}{3}, \frac{1}{3})$ -beam at a scattering energy of 68 eV. On the dilute phase they were carried out in the same position. The measured data then can be compared with results calculated for an ordered $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Xe/Pd(111)}$ system. Again the scattering energy was chosen to be 68 eV.

The structure determination is performed comparing the measured angle-dependent asymmetry profiles $A(\Theta)$ with corresponding calculations under variation of non-structural and structural parameters. The SPLEED program used for the calculations is described in ref. [9]. To evaluate the agreement, metric r -factors R similar to those described in ref. [10] are applied:

$$R = \frac{1}{N} \sum_n |A_n^{\text{exp}} - A_n^{\text{calc}}|, \quad N = \sum_n |A_n^{\text{exp}}|,$$

with A_n^{exp} and A_n^{calc} being the measured and

calculated data points, respectively. To overcome defect-induced diffuse scattering, a homogeneous spin-independent background was subtracted from $I(+)$ and $I(-)$. The following fixed parameters are used for the structure determination:

- nearest-neighbour distance of the Xe atoms in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -adatom layer: 4.76 Å [11];
- nearest-neighbour distance of the Pd atoms: 2.75 Å [12];
- inner potential of the Pd substrate: $V_{\text{or}} = 10$ eV, $V_{\text{oi}} = 4$ eV [13].

What remains to be determined are the adsorption sites, the distance between the adsorbed Xe atoms and the Pd atoms in the surface and the inner potential of the adsorbate.

$(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Xe/Pd(111)}$

Fig. 1 shows the direct comparison between the measured data (middle panel) and selected

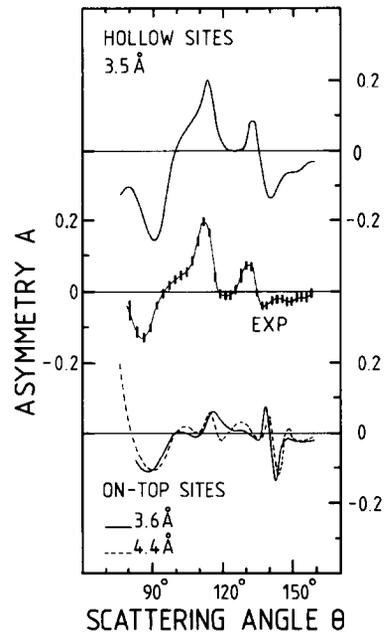


Fig. 1. Measured and calculated asymmetry profiles $A(\Theta)$ for $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-Xe/Pd(111)}$ at scattering energy 68 eV. In the measured data the bar length represents the statistical errors. In addition, a scaling error due to the uncertainty of the spin-polarization \mathbf{P} of the primary beam has to be taken into account. For further details, see text.

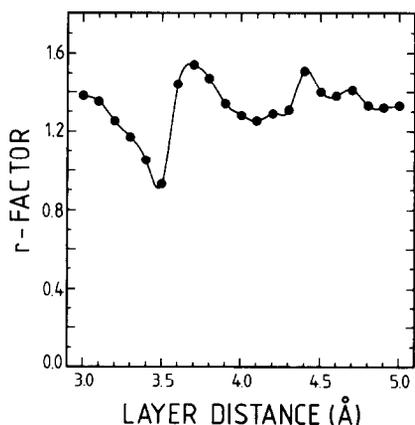


Fig. 2. Metric r -factor of the asymmetry as a function of the layer spacing (inner potential $V_{0r} = 8$ eV, $V_{0i} = 2.5$ eV). Series of measurements and calculations at 68 eV and at 60 eV are averaged.

calculated data. The upper panel presents the calculated asymmetry profile showing the best agreement with the measurements by visual inspection and r -factor analysis as well. This profile is calculated assuming domains of fcc- and hcp-hollow sites with identical domain size probability and random distribution of the domains. The layer spacing is taken to be 3.5 Å (see fig. 2), the inner potential of the adsorbate layer $V_{0r} = 8$ eV and $V_{0i} = 2.5$ eV. The lower panel of fig. 1 shows asymmetry profiles which are calculated assuming on-top adsorption sites and yielding the minimum r -factors for these adsorption sites. The comparison shows a much better agreement for the hollow sites.

Dilute phase of Xe / Pd(111)

Fig. 3 again shows the direct comparison between data measured at the dilute phase in the middle panel and data calculated for an ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Xe layer. The measured data given here are recorded at about 55 K for a coverage of 0.3 (relating to a Pd(111) surface layer). They are only weakly affected by raising the temperature to 85 K and lowering the coverage to 0.15. They differ significantly from the data for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure measured at the identical energy and in the identical angu-

lar positions (see fig. 1). The asymmetry profile in the upper panel again is the calculated profile with the best agreement to the measurements. In contrast to the results in fig. 1 on-top adsorption sites with a Xe-Pd distance of 4.0 Å (see fig. 4) have to be used to get the good agreement. The inner potential used here is $V_{0r} = 4$ eV and $V_{0i} = 2.5$ eV. In the lower panel of fig. 3 corresponding calculations for hollow sites are displayed. These calculations significantly disagree with the measured data.

In conclusion we find the Xe atoms occupy hollow sites in the case of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and on-top sites in the case of the dilute phase of Xe/Pd(111). The change of the adsorption site is connected with a change of the Xe-Pd distance from 3.85 ± 0.1 Å (equivalent to a layer spacing of 3.5 ± 0.1 Å) to 4.0 ± 0.1 Å and with a change of the real part of the inner potential of the Xe adlayer from $V_{0r} = 8 \pm 1$ eV to 4 ± 1 eV.

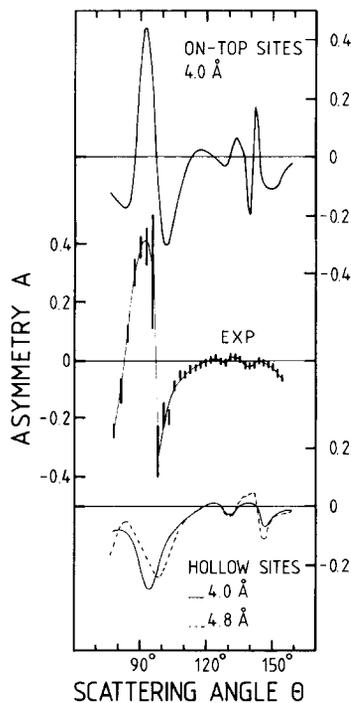


Fig. 3. Measured profiles $A(\theta)$ for the dilute phase of Xe/Pd(111) in comparison with asymmetry profiles calculated for $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Xe/Pd(111) at scattering energy 68 eV.

Experimental errors see fig. 1. Further details, see text.

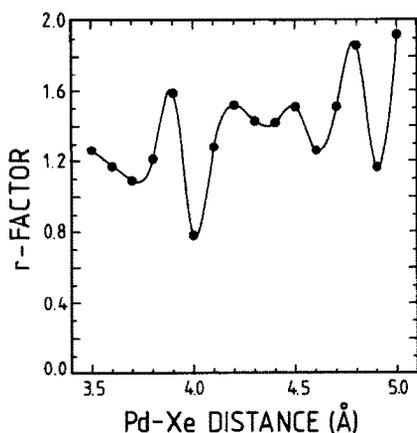


Fig. 4. Metric r -factor of the asymmetry as a function of the Xe-Pd distance evaluated from measurements and calculations for 68 eV (inner potential $V_{or} = 4$ eV, $V_{oi} = 2.5$ eV).

The imaginary part of the inner potential is $V_{oi} = 2.5 \pm 0.5$ eV for both systems. The two different adsorption sites found appear to correspond with the results of spin-resolved photoemission [14]: for the dilute phase no lateral Xe-Xe interaction was found whilst for a $(\sqrt{3} \times \sqrt{3})R30^\circ$ layer this interaction was found to be present.

Generally our investigations show SPLEED to be a well-suited method for studying adatom systems with and without long-range order.

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References

- [1] R. Feder, H. Pleyer, P. Bauer and N. Müller, *Surf. Sci.* 109 (1981) 419.
- [2] R. Feder and J. Kirschner, *Surf. Sci.* 103 (1981) 75.
- [3] The concept of areas of multiple scattering was firstly used in LEED theory for diffuse intensities by H. Jagodzinski, W. Moritz and D. Wolf, *Surf. Sci.* 77 (1978) 233.
- [4] N. Müller, IPP-Report 9/23, MPI für Plasmaphysik, Garching bei München (1979); see also: N. Müller, Thesis, Ludwig-Maximilian-Universität, München, 1977.
- [5] J.B. Pendry and D.K. Saldin, *Surf. Sci.* 145 (1984) 33.
- [6] D.K. Saldin, J.B. Pendry, M.A. Van Hove and G.A. Somorjai, *Phys. Rev. B* 31 (1985) 1216.
- [7] D.T. Pierce and F. Meier, *Phys. Rev. B* 13 (1976) 5484.
- [8] D.T. Pierce, R.J. Celotta, G.-C. Wang, W.N. Unertl, A. Galejs, C.E. Kuyatt and S.R. Mielczarek, *Rev. Sci. Instrum.* 51 (1980) 478.
- [9] G. Hilgers, M. Potthoff, S. Wirth, N. Müller, U. Heinzmann, L. Haunert, J. Braun and G. Borstel, *Surf. Sci.* 251/252 (1991) 612.
- [10] G. Kleinle, W. Moritz and G. Ertl, *Surf. Sci.* 238 (1990) 119.
- [11] K. Wandelt and J.E. Hulse, *J. Chem. Phys.* 80 (1984) 1340.
- [12] R.W.G. Wyckoff, *Crystal Structures II* (Interscience, New York, 1964).
- [13] F. Maca, M. Scheffler and W. Berndt, *Surf. Sci.* 160 (1985) 467.
- [14] B. Vogt, B. Kessler, N. Müller, G. Schönhense, B. Schmiedeskamp and U. Heinzmann, *Phys. Rev. Lett.* 67 (1991) 1318.