Surface Structure Analysis of Cs/Pt(100) by LEED

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The intensity spectra of the platinum(100) surface covered with cesium have been analysed by means of a dynamical calculation (RFS) of the diffraction processes using a simplified model of the adsorbate layer. Convergence problems were introduced by the relatively large size of the cesium atoms and the superstructure unit mesh. Yet the agreement between theory and experiment allows to determine a spacing of 4.25 ± 0.1 Å between the bulk crystal and the overlayer. According to the model most cesium atoms occupy hollow positions on the topmost (100) bulk layer of platinum. However, there is also a considerable amount of bridge positions giving a mixture of sites, which is responsible for the streaking of special spots observed in experiment.

1. The Superstructure of Cesium on Platinum (100)

The complicated LEED-pattern of the clean platinum(100) surface is now understood almost perfectly in terms of a double diffraction model [1–4]. Yet the detailed structure of the reconstructed surface is not fully known, because at the present stage of theory and computation techniques a dynamical calculation of diffraction intensities [$I(E)$-spectra] is essentially impossible due to the large size of the superstructure unit mesh. However, the surface becomes less complicated when cesium is adsorbed. We suggest that the analysis of the corresponding superstructure may be a first step towards a better insight into the complex features of the Pt(100) surface.

The diffraction pattern which is observed, when an ordered monolayer of cesium atoms is adsorbed on Pt(100) is shown schematically in Fig. 1a for one of two orthogonal domains. Original patterns and their detailed interpretation were given in a recent paper [2], from which the main points will be briefly repeated here. The extra superstructure spots which are typical for the clean surface arising from a hexagonally structured first platinum layer have completely disappeared. Apparently the adsorption of cesium atoms (as well as other species) causes this topmost platinum layer to take again the ideal quadratic bulk structure. The new pattern mainly consists of spots created by a $c(4 \times 2)$ superstructure which is shown in the upper half of Fig. 1b for the considered domain. However, the spots inside the unit mesh are considerably streaked, which is caused by a possible shifting of neighboured chains of cesium atoms parallel to each other, as indicated in the lower half of Figure 1b. The formation of chains is assumed to be stabilized by a slight overlap of outer orbitals of the big cesium atoms (in horizontal direction for the considered domain). The model is consistent with the measured Cs coverage of about $4 \cdot 10^{14}$ Cs-atoms/cm^2.

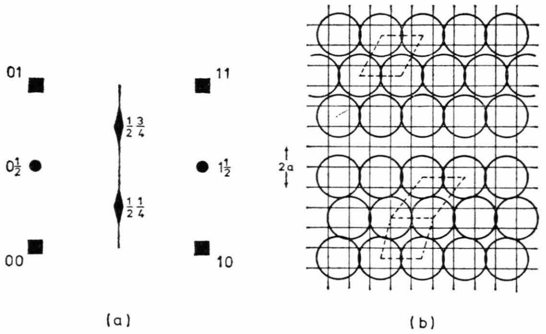

Fig. 1. Adsorption of Cs on Pt(100): (a) Unit mesh of the observed diffraction pattern for one of two orthogonal domains. The spots inside the unit mesh show considerable streaking. (b) Model of the adsorption layer for one domain: There are linear chains of cesium atoms which may form a $c(4 \times 2)$ superstructure if they arrange like in the upper part. Continuous shifting of the chains parallel to each other, as indicated in the lower part, causes streaking of the spots inside the unit mesh.

2. Calculation of Intensities

The interpretation of the LEED pattern can give no information about adsorption sites, neither about the actual distance of the cesium layer from the sub-

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strate nor about the lateral position of cesium atoms with respect to the platinum unit cell. Therefore, the intensities have to bee investigated. However, as may be seen from Fig. 1, the reciprocal lattice vectors of the bulk do not coincide with those of the adsorbate because of streaking. Since non coinciding lattices introduce additional severe problems to computation, we have decided to try a first structure determination by only calculating the intensity spectra of the $c(4\times 2)$ superstructure. This approximation should be remembered if misfits between calculations and measurements arise. The intensities were measured by a method described earlier [5].

For calculation of LEED-intensities the RFS formalism (*R*enormalised *F*orward *S*cattering) was used as described by Pendry [6]. Moreover principle parts of the computer program given in [7] could be applied. A slight modification was introduced with respect to the selection of beams. In order to achieve sufficient convergence with the least efforts for computation, an energy dependent number of beams was used as originally proposed by Rundgren and Salwén [8]. Due to the size of the adsorbate layer unit mesh [(4×2) with respect to that of the substrate] at least 91 beams are involved in the interlayer scattering and have to be taken into account at $E=95$ eV and oblique incidence for sufficient convergence. Because of the limited computer core size restriction to normal incidence of the primary beam was accepted reducing the maximum number of involved beams to 27 by symmetry. Therefore the 00-beam is missing in the structure analysis. Energies exceeding $E=95$ eV were also left out of consideration because they again increase the number of necessary beams. Unfortunately this restriction with respect to energy rules out the spectrum of the 11-beam because it appears at the LEED-screen only above $E=70$ eV. Moreover $\frac{1}{2}\frac{1}{4}$- and $\frac{1}{2}\frac{3}{4}$-spectra could not be used because the intensities are considerably influenced by streaking. Additionally the spectra of the 01- and 10-beams appeared to be equivalent for normal incidence according to the existence of two equally weighted but orthogonal overlayer domains.

The crystal scattering potential was approximated by the usual muffin-tin potential. The muffin-tin radius of platinum was calculated from the bulk lattice constant to be $R_{\mathrm{Pt}}=1.39$ Å. The corresponding value for cesium given in literature differ from 2.7 Å [9] to 3.025 Å [10]. According to the interpretation of the diffraction pattern [2], we took a value which is slightly larger than the platinum next nearest neighbour distance, $R_{\mathrm{Cs}}=2.89$ Å. Phase shifts for the atomic scattering of both atoms were calculated from a self consistent Hartree-Fock potential using atomic wave functions taken from [11]. Overlapping atomic orbitals were cut off at the muffin-tin radius and renormalized inside the muffin-tin sphere to give again a neutral atom. In the energy range below $E=95$ eV, it proved to be sufficient to use 5 phase shifts for the platinum ($l_{\max}=4$) and, according to its larger size, 7 phase shifts for the cesium atom ($l_{\max}=6$). The resulting convergence accurracy with respect to peak positions in the intensity spectra was found to be better than $\Delta E=0.5$ eV. The same tolerance could be maintained by summing up 400 atoms at maximum to calculate the intralayer scattering. Correspondingly the RFS formalism was stopped when two succeeding orders of approximation differed relatively only by 10^{-3}.

A reliable value for the real part of the inner potential was obtained in the following manner. Fitting our calculations to the $I(E)$ spectra of the platinum(111) surface given by Stair et al.[12] yielded $V_{\mathrm{or}}=-16.5$ eV. This value is given with respect to the vacuum level. As the measurements refer to the difference of Fermi-energies between cathode and sample it has to be corrected by their work function difference which is about 4 eV. Consequently we used an inner potential of -12.5 eV for the interpretation of our experimental spectra. The inelastic damping was taken into account by an imaginary part of the inner potential $V_{\mathrm{oi}}=-4.0$ eV. The potential step at the surface was treated in the nonreflecting approximation and always situated in front of the layer of adsorbed Cs-atoms.

Finally, we have neglected all effects caused by lattice vibrations. Due to the large atomic masses of platinum and cesium, the corresponding corrections are considered to be rather small in the relevant energy range.

3. Determination of the Cesium Adsorption Sites

Most of the recent surface structure determinations have made use of the insensitivity of the 00-beam to lateral shifts of the adsorbate layer. As it was pointed out we have unfortunately not been able to include the 00-beam into our structure analysis. Yet we have found that the $0\frac{1}{2}$-beam behaves rather similar to the 00-beam. This is demonstrated in Fig. 2 by comparison with the behaviour of the 01-beam spectrum in a test calculation. So it is possible to proceed in the usual way: We first fit the $I(E)$ spectrum of the $0\frac{1}{2}$-beam by adjusting the interlayer spacing between the top layer of the ideal crystal and the adsorbate layer. Then the spectra of the 10- and $1\frac{1}{2}$-beam are fitted by adjusting the lateral position of the overlayer with respect to the substrate.

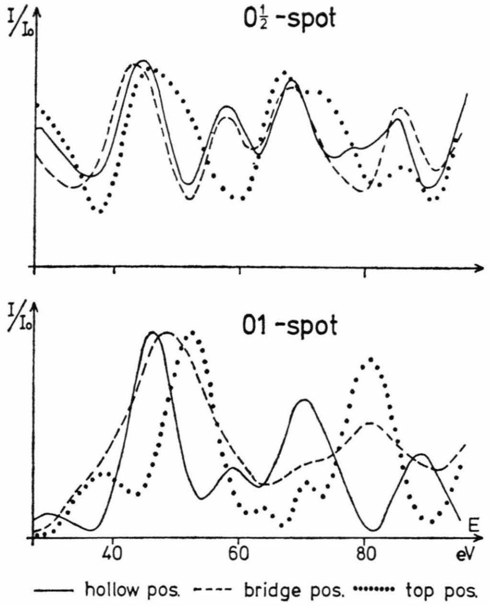

Fig. 2. Sensitivity of the $0\frac{1}{2}$- and 01-beam spectra with respect to overlayer shifts. Top-, bridge- and hollow sites of Cs-atoms are tested with the same value $d = 4.25$ Å for the cesium layer-substrate distance.

In Fig. 3 we present the experimental and the calculated $I(E)$ spectrum of the $0\frac{1}{2}$-beam for three different spacings between overlayer and bulk. The adsorption sites are chosen to be hollows of the bulk surface, but the calculated spectrum of the $0\frac{1}{2}$-beam is rather insensitive to this choice. Nearly perfect agreement between theory and experiment is achieved for a spacing of $d = 4.25$ Å. Only the peak at $E = 30$ eV in the experimental spectrum is not reproduced accurately by the calculation.

For the determination of the actual adsorption site we first consider the $1\frac{1}{2}$-beam (Figure 4). While the calculations for the hollow position reproduce

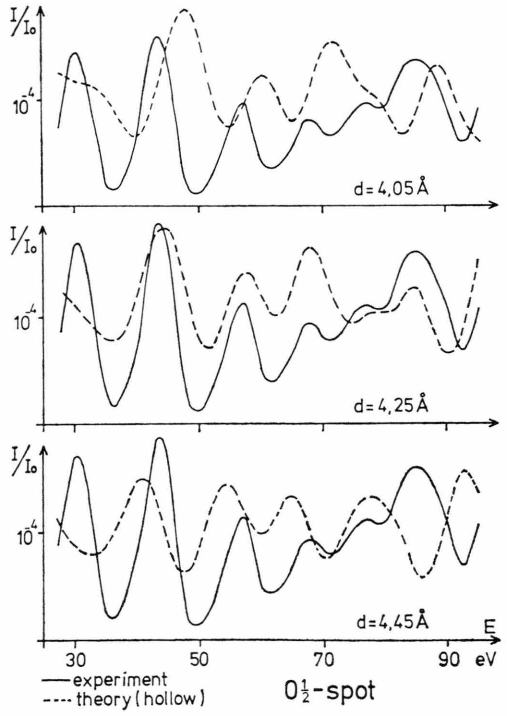

Fig. 3. Variation of the spectrum of the $0\frac{1}{2}$-beam for different values d of the distance between the cesium layer and the platinum substrate. The cesium atoms are assumed to be hollow sited.

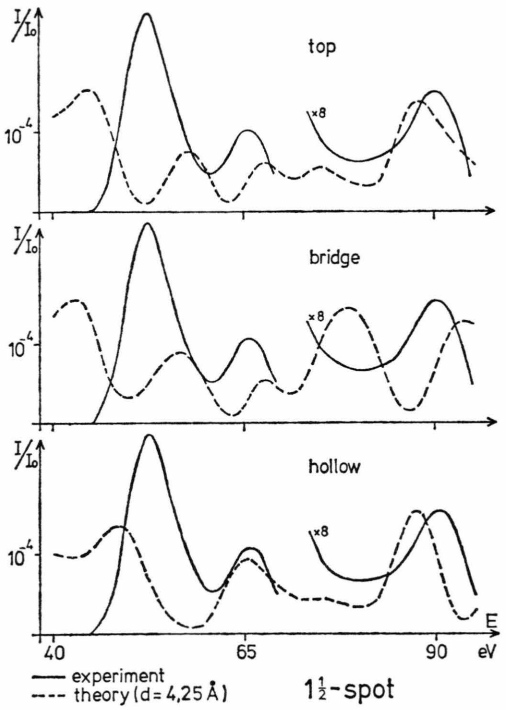

Fig. 4. Variation of the spectrum of the $1\frac{1}{2}$-beam for different lateral adsorption sites, namely top-, bridge- and hollow-position. The value $d = 4.25$ Å fitting the spectrum in Fig. 3 is used as cesium layer-substrate distance.

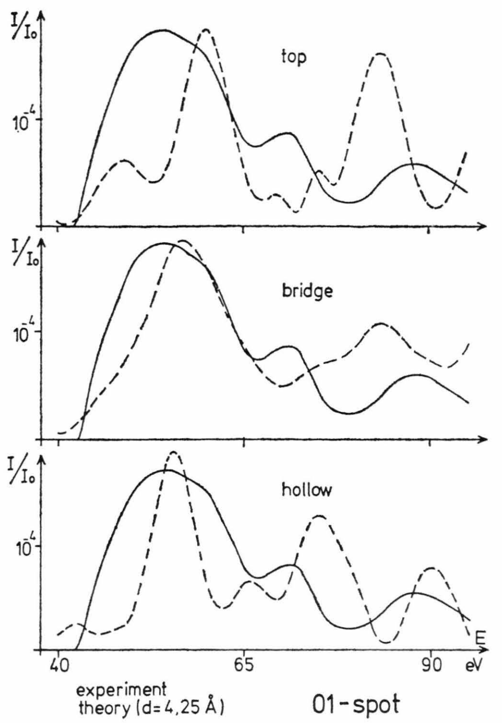

Fig. 5. Variation of the spectrum of the 01-beam for top-, bridge- and hollow-adsorption sites. Again $d=4.25$ Å is used for the cesium layer-substrate distance.

the peaks of the experimental $I(E)$ spectra to within 2.5 eV, the agreement is less satisfactory for the bridge and top positions. Especially the strong peak at $E=52$ eV would not show up if the cesium atoms would accupy the top position.

Additionally the 01-spectrum is tested with respect to the three different adsorption sites (Figure 5). There is no real coincidence, however, the maximum misfit again occurs for the top position. It should be pointed out, that the large width of the measured peak at $E=54$ eV shows up in the case of bridge position only.

4. Discussion

Due to the insensitivity of the $0\frac{1}{2}$-spectrum with respect to the lateral position of the cesium atoms, a definite value for the distance of the cesium layer to the substrate $d=4.25$ Å, could be deduced. Concerning the different approximations made together with the remaining misfit an error of about 0.1 Å is possible. However, a clear decision for the lateral adsorption sites could not be made. Nevertheless the calculations show that the adsorption sites on top of platinum atoms can be excluded. Moreover there seems to be a preference for hollow positions, though a considerable component of bridge positions must be accepted. This is consistent with the recently proposed adsorption model[2] assuming linear chains of cesium atoms which can shift parallel to each other. Because of this linear mobility a mixture of hollow and bridge sites is probable, including the whole spectrum of sites in between. Moreover this is consistent with the relative large value of d, which exceeds that expected from hollow sites by 12%. This rather unlikely amount can be understood in terms of the mixture described.

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[1] A. E. Morgan and G. A. Somorjai, Surf. Sci. **12**, 405 [1968].

[2] K. Müller, P. Heilmann, K. Heinz, and G. G. Waldecker, Vak. Technik **25**, 227 [1976].

[3] K. Heinz, N. Lieske, and K. Müller, Z. Naturforsch. **31 a**, 1520 [1976].

[4] K. Heinz, P. Heilmann, and K. Müller, Z. Naturforsch. **32 a**, 28 [1977].

[5] P. Heilmann, E. Lang, K. Heinz, and K. Müller, Appl. Phys. **9**, 247 [1976].

[6] J. B. Pendry, J. Phys. C **4**, 3095 [1971].

[7] J. B. Pendry, Low Energy Electron Diffraction, Academic Press, London 1974.

[8] J. Rundgren and A. Salwén, J. Phys. C **7**, 4247 [1974].

[9] American Institute of Physics Handbook, New York (1972).

[10] Handbook of Chemistry and Physics, Ohio (1966).

[11] F. Herman and S. Skillman, Atomic Structure Calculations, Prentice Hall, New Jersey (1963).

[12] P. C. Stair, T. J. Kaminska, L. L. Kesmodel, and G. A. Somorjai, Phys. Rev. B **11**, 623 [1975].