

SURFACE SCIENCE LETTERS

**THERMODYNAMIC MEASUREMENTS OF Xe-ADSORPTION
ON Pt(111)**

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The adsorption of xenon on a nearly defect free Pt(111) surface has been studied by elastic and inelastic He-scattering. With decreasing temperature the sequential of 2D-gas, monolayer, bilayer and multilayer films are observed. The thermodynamic phase diagram and the latent heats of adsorption are determined.

Elastic scattering of thermal He-atoms is a powerful tool to investigate the 2D-dilute-2D-condensed phase transition [1] and the structural properties of the 2D-condensed phases [2] in physisorption systems. We have extended here the capabilities of He-scattering by using time-of-flight (TOF) analysis to characterize the condensation of monolayer, bilayer and bulk Xe on Pt(111).

The UHV He-TOF spectrometer has been described in detail elsewhere [3]; here only the properties pertinent to the present results are reminded. The sample is a high quality Pt(111) surface with a defect density less than 0.1% [4]. The crystal is mounted on a manipulator which allows for short cooling times to temperatures as low as 25 K. The measurements are performed with a liquid nitrogen cooled nozzle, generating a 18 meV He-beam with a velocity spread of $\Delta v/v \approx 0.8\%$. The overall effective energy resolution upon cross correlation analysis of the TOF distributions is about 0.3 meV. Both, the angular spread of the incident beam and the angle subtended by the ionizer opening are equal to 0.2° .

The physisorption of xenon on several single crystal metal surfaces has been studied experimentally [2,5-9] and theoretically [10,11] in the past. The Xe 2D-solid phases may be in or out of registry with the substrate topography, depending on the balance between adsorbate-substrate and adatom-adatom interactions. Several studies have shown that Xe on close packed metal surfaces tend to build a hexagonal close packed overlayer, the dimensions of which are governed by the Xe-Xe lateral interaction rather than by the potential of the substrate underneath. Only few exceptions are known [2,6,8]; among them the very smooth Pt(111) surface seems to be one of the most

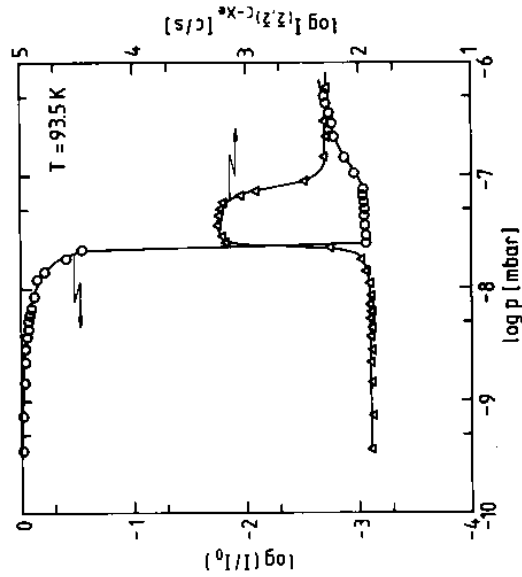


Fig. 1. Adsorption isotherm of Xe on Pt(111), plotted as relative He specular peak height, I/I_0 , versus 3D-Xe pressure, p (O). The triangles (Δ) denote the height of the (2, 2)-He diffraction peak obtained from the commensurate Xe ($\sqrt{3} \times \sqrt{3}$)R30° layer.

interesting representatives. Despite the apparent lateral smoothness of the rare gas/Pt(111) potential, a variety of structural 2D-solid phases are observed [2]: commensurate, incommensurate and incommensurate rotated (Novaco-McTague phase). The commensurate ($\sqrt{3} \times \sqrt{3}$)R30° phase exists in the coverage range $\theta < 0.33$ ($\theta = 1$ corresponds to 1.5×10^{15} Xe-atoms per cm^2) and for temperatures $62 < T < 99$ K. The incommensurate phase is also a R30° phase and exists for $\theta < 0.33$ ($T < 55$ K) and $0.33 < \theta < 0.38$ ($T < 99$ K). The incommensurate rotated phase exists for $\theta > 0.38$; its maximum rotation angle is $\pm 3.3^\circ$.

In the present letter we report on equilibrium measurements (i.e. the 3D-Xe gas is in quasi-equilibrium with the 2D-Xe phases) of the physisorption system Xe/Pt(111) by means of elastic and inelastic He-scattering. The information on the condensation of the monolayer is obtained from isotherms. The adsorption isotherms are measured as follows. After a short flash to desorb residual contaminants (essentially CO and H₂) the crystal is rapidly cooled down to the desired temperature which is then kept constant. The 3D-Xe pressure is increased step by step and the corresponding equilibrium coverage is monitored via the attenuation of the specular He-beam [1]. An example for an isotherm ($T = 93.5$ K) obtained in this way is shown in fig. 1. The relative specular intensity, I/I_0 , is plotted as a function of the 3D-Xe pressure (O).

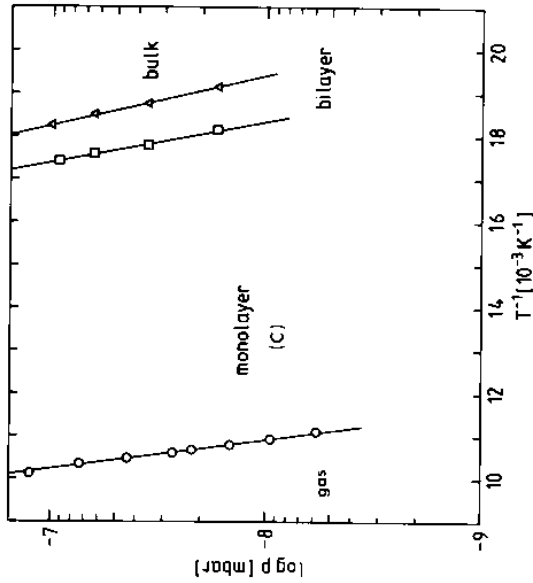


Fig. 2. Thermodynamic phase diagram of xenon adsorption on Pt(111).

This isotherm is typical for an adsorption system undergoing a 2D-gas-2D-solid phase transition. Starting at $\theta = 0$ ($I/I_0 = 1$) the specular intensity drops slowly with increasing Xe coverage. This behavior is characteristic for a 2D-lattice gas (the dependency of the relative intensity I/I_0 on the coverage is given by $I/I_0 = (1 - \theta)^{n^2}$ [1], where Σ is the scattering cross section for diffuse scattering per adatom and n is the number of adsorption sites per unit area). Upon further 3D-Xe pressure increase a sharp drop of the specular intensity is obvious. The intensity drop by more than two orders of magnitude is due to the sudden coverage of the surface with Xe atoms. This marks the condensation of the 2D-dense phase. The condensed phase has been proved to be a commensurate ($\sqrt{3} \times \sqrt{3}$)R30° solid phase ($d_{Xe} = 4.80$ Å) [2]. This is also demonstrated in fig. 1 by plotting the detector counting rate (Δ) for the scattering geometry corresponding to the detection of the (2, 2)_{Xe} diffraction peak of the commensurate ($\sqrt{3} \times \sqrt{3}$)R30° phase. The sharp counting rate increase indicates the formation of the commensurate phase. The coincidence with the 3D-Xe pressure at which the specular intensity suddenly drops is a useful cross-check for the determination of the 3D-vapor pressure of the 2D-Xe commensurate (C) phase at the given temperature. The coincidence for the 2D-gas and 2D-C-solid monolayer obtained by measuring a number of such isotherms at different temperatures is shown in fig. 2.

The (Δ) plot in fig. 1 shows further that after the sharp increase, the counting rate of the (2, 2)_{Xe} peak levels off, and with further 3D-Xe pressure

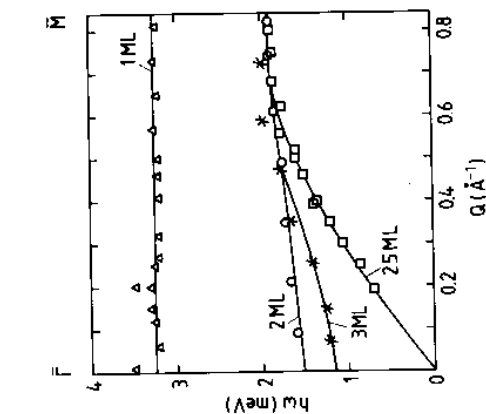


Fig. 3. Measured phonon dispersion of the mono-, bi-, tri- and 25-layer Xe-films on Pt(111).

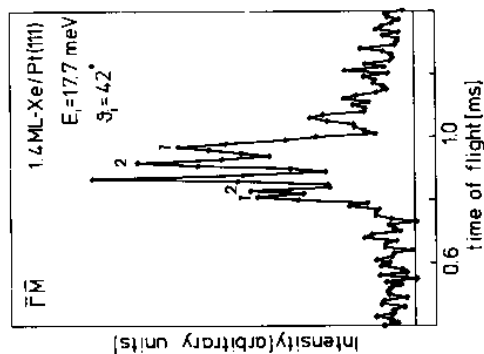


Fig. 4. He TOF spectrum of 1.4 ML xenon adsorbed on Pt(111). The phonon events originating from the Xe monolayer atoms are denoted by (1), those originating from Xe-atoms in the second layer by (2). The spectrum is taken in the $\bar{\Gamma}\bar{M}$ -direction with a beam energy of 17.7 meV, at an incident angle $\theta_i = 42^\circ$, a TOF path of 79 cm and a surface temperature of 25 K.

bilayer with an excellent accuracy. This is exemplified by the TOF spectrum in fig. 4 measured on a 1.4 ML Xe film. The first and second layer phonon energy losses are so well resolved that the appearance of the second layer losses (onset of the bilayer condensation) and the disappearance of the first layer ones (completion of the bilayer) can be monitored within a few percent. The phase boundary for bilayer condensation obtained from TOF spectra taken at different surface temperatures is also plotted in fig. 2 (□). The same procedure can be applied to derive the condensation of multilayers. The scanning curve has only to intersect the dispersion curves in the left part of the Brillouin zone, where the phonon energies of bi-, tri- and multilayers are substantially different. The triangles in fig. 2 are the data for the onset of the condensation of multilayers. The temperature interval between the formation of the third and subsequent layers is too small to be resolved in our experiment. Lattice constants and average domain sizes of the different Xe-films have been deduced recently from high resolution He-diffraction measurements [12]. The data show that the lattice constants of the full monolayer and of the multilayer films are the same within the experimental accuracy (0.01 Å) and that these values ($d_{Xe} = 4.33$ Å) are in excellent agreement with the lattice constant of bulk xenon at the same temperature. The lack of discontinuity at the monolayer-bilayer transition is in good agreement with theoretical expectations [10]. If the second layer grows epitaxially on the monolayer, as is the case for Xe/Pt(111) [12], the chemical potential of the bilayer is minimized when the lattice parameter is very near to its bulk value.

The latent heats of adsorption are defined from the phase diagram (fig. 2) as:

$$q_i = -k_B [\partial(\ln P_i) / \partial(1/T)]_{\text{const}},$$

where the derivative is taken along the i th phase boundary. From the data in fig. 2 the C-monolayer and the bilayer heats are determined to $q_1 = 311 \pm 16$ meV and $q_2 = 205 \pm 12$ meV. The latent heat of bulk sublimation is estimated to $q_b = 171 \pm 12$ meV, in good agreement with the tabulated value of 165 meV [14]. The latent heats along with the previous result [1] for the isosteric (q_{st}) heat of Xe-adsorption on Pt(111) are summarized in table 1. For comparison, this table also includes the corresponding heats of adsorption on Ag(111)

Table 1

Heats of adsorption of Xe on several crystal surfaces in meV/atom (q_1 - monolayer, q_2 - bilayer, q_b - bulk, and q_{st} - isosteric heat of adsorption)

	q_1	q_2	q_b	q_{st}
Pt(111)	311	205	171	277
Ag(111)	225	173		215
Graphite(0001)	239	165		165

increase, decreases. This indicates that the 2D-commensurate-2D-incommensurate phase transition takes place [2]. The relatively smooth counting rate drop suggests a higher order CI-transition [12]. During the solid-solid transition the specular He intensity ((○) in fig. 1) increases by a factor of about two, suggesting that the He/surface potential of the incommensurate Xe-layer is less corrugated, probably because of its higher density.

The phase boundaries for the formation of the bilayer and of the bulk Xe are also shown in fig. 2. The data for these plots have been inferred from inelastic He-scattering by means of a new, somewhat unusual procedure. The lattice dynamics of noble gas films on Ag(111) and Pt(111) has recently been studied by inelastic He-scattering [12,13]. The results show a layer by layer evolution of the surface phonon dispersion with increasing film thickness. This is obvious from fig. 3; the Xe-monolayer possesses a dispersionless mode, corresponding to independent vibrating atoms (Einstein oscillators), the bilayer a slight dispersion at substantial lower energy, whereas the 25-layer film exhibits a typical Rayleigh wave. The large energy difference between first and second Xe-layer phonons makes it easy to determine the condensation of the

[9,16] and graphite(0001) [17]. The difference between latent heat of monolayer condensation and isosteric heat is approximately equal to the lateral adatom interaction energy e^1 [16]. The corresponding value for Xe on Pt(111) resulting from table 1, $e^1 = q_1 - q_{st} = 34 \pm 20$ meV, is consistent with the recently measured (48 meV [1]) and calculated (44.2 meV [15]) values.

In summary, we have shown that by combining elastic and inelastic scattering of thermal He-atoms a full set of thermodynamic parameters of a physisorption system may be inferred. It should be noted that the method is also well suited to characterize the structural properties of the different phases, irrespective of the nature of the substrate and without any damaging.

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