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Structure, Composition, and Chemisorption Studies of Thin Ordered Iron Oxide Films on Platinum (111)

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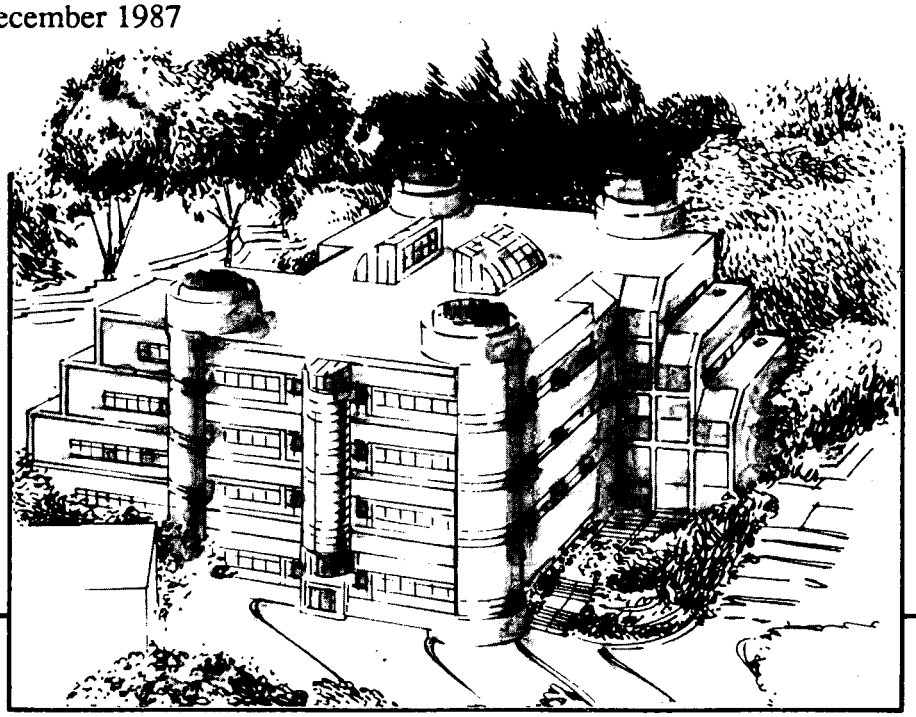

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Structure, Composition and Chemisorption Studies of thin ordered Iron Oxide Films on platinum (111)

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Abstract

We report the epitaxial growth of iron oxide overlayers on a platinum(111) single crystal, in the monolayer and the multilayer regimes. Different LEED structures have been observed for each of these regimes. At one monolayer coverage iron oxide forms an incommensurate overlayer with 10% longer unit cell vectors than those of clean platinum. At coverages of 3 to 10 monolayers, iron oxide forms a new structure, which is (2×2) with respect to that formed at one monolayer. AES and XPS show that the iron in the oxide overlayer is in the 2+ oxidation state and from ISS studies it was determined that both iron and oxygen are present in the outermost atomic layer in about equal amounts. Water adsorption on the iron oxide films was studied by TPD. It was found that the desorption spectrum is very sensitive to the presence of various type of defects on the oxide.

1 Introduction

The surface structure and chemisorption properties of transition metal oxides have been explored to much lesser extent than in the case of transition metals. The reason lies in the difficulties of preparing and cleaning ordered single crystals of oxides and to carry out electron spectroscopy studies on their usually insulating surfaces. In this paper we report a novel method that overcomes these difficulties. We deposit ordered iron oxide films on a platinum(111) single crystal surface by evaporating iron layer by layer and oxidizing it. We investigated the growth behaviour, the stoichiometry, the ordering and the CO and H_2O chemisorption properties of iron oxide films up to 10 monolayers.

We find that the iron oxide grows epitaxially in the first monolayer and there are strong indications for a layer by layer growth mechanism. The first monolayer is specially stable on platinum(111) and orders into an incommensurate structure with (7×7) coincidence periodicity upon heating to 830 K as determined by LEED. In both the monolayer and the multilayer regime the iron oxide is most stable with a stoichiometry in UHV which is close to that of FeO, although it can be oxidized to Fe_2O_3. At high partial pressures of oxygen the ordered oxide is chemically inert, it does not chemisorb CO or H_2O. However in the presence of defects (oxygen vacancies or steps) H_2O chemisorption can be detected.

Surfaces of iron oxides are important for a number of reasons. Firstly iron oxide is a versatile oxidation catalyst [1,2]. Secondly, iron oxide is photochemically active when illuminated with visible light [3,4,5] (α-Fe_2O_3 has a bandgap of 2.2 eV [6]). Thirdly contacts between iron and other metals in the presence of oxygen are of great importance with respect to corrosion and wear studies [7,8]. Studies of the surface composition and surface structure are important in determining the activity and selectivity of the catalyst. Defects on the surface are known to be responsible for the activity of oxidation catalysts [9,10]. Surface science studies should provide information on these surface properties.

2 Experimental

The ultra high vacuum (UHV) studies were performed in a standard system with a base pressure of 1×10^{-10} Torr. Physical Electronics equipment was used for Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), Low energy electron diffraction (LEED) and Argon sputtering. In the AES experiments the modulation voltage was 6 V peak to peak. A primary beam with an energy of 2000 eV was used at approximately normal incidence. Typical crystal currents of 6 μA were used. The XPS spectra were obtained using a Mg K_α x-ray source. Peak positions were assigned by setting the Pt $4f_{5/2}$ and Pt $4f_{7/2}$ peaks to 74.25 eV and 70.9 eV binding energy respectively. Ion scattering spectroscopy (ISS) experiments could be performed by a simple modification of the double pass cylindrical mirror analyzer (CMA). Three quarters of the double pass CMA entrance was closed with tantalum foil, to increase the resolution. The CMA was then operated in constant pass energy and pulse counting mode. In order to be able to detect the ion energy with the CMA, the outer cylinder was kept 300 V positive with respect to the inner cylinder by means of a battery, while the entrance of the channeltron electron multiplier was biased 300 V negative with respect to the inner cylinder. The primary ion beam consisted of 500 eV He^+ ions. The approximate scattering angle was 140°. Under these conditions ISS is only sensitive to the outermost atomic layer. A UTI mass spectrometer was used for the Thermal Programmed Desorption (TPD) studies. The mass spectrometer was encapsulated except for a protruding, 2 mm diameter aperture. Exposures were measured in Langmuirs (1 L = 10^{-6} Torr.s) without corrections for the ion gauge sensitivity. Temperatures were measured using a chromel alumel thermocouple directly spotwelded to the platinum single crystal.

The iron source used in the preparation of the iron oxide films consisted of a 15 mil iron wire wrapped around a 30 mil tungsten filament that was resistively heated. Oxygen and carbon were common contaminants of the iron after evaporation. Thin

iron oxide films, with thickness of up to several monolayers were prepared on a platinum(111) substrate in three steps. First iron was evaporated on the platinum substrate. The second step consisted of the oxidation of the iron with 5×10^{-7} Torr oxygen, which removed the carbon and oxidized the iron. Raising the temperature to 830 K for a few ($\approx$ 3) seconds in the oxygen atmosphere caused the iron oxide to order as confirmed by LEED. At coverages of several monolayers, several ($\approx$ 3) minutes of heating at 830 K were required in order to produce an ordered overlayer. The third step of the preparation, only necessary at coverages below one monolayer (ML), consisted in removing the excess oxygen from the platinum by dosing 1 Langmuir (L) of CO at 300 K, followed by ramping the temperature to 520 K in 30 seconds. This removed the excess CO and the excess oxygen from the platinum as CO_2.

3 Results

3.1 Coverage determination of iron oxide films on platinum(111)

The coverage of iron oxide on platinum was determined by AES. After each minute of iron evaporation the iron was oxidized. In order to determine the monolayer coverage, uptake curves were obtained by measuring the Auger peak to peak intensity as a function of evaporation time. Simultaneously the current between the crystal and ground was measured [11]. The results of these measurements are shown in figure 1. The curves can be interpreted by assuming a Frank- van der Merwe layer by layer growth mechanism. By fitting straight lines we find breaks at 11 and 22 minutes iron evaporation time [12]. The break at 11 minutes iron evaporation time is assigned to the one monolayer coverage. The platinum 237 eV signal is then attenuated by 42% in agreement with typical monolayer attenuation values

[13]. Also the crystal current shows an abrupt change of slope at eleven minutes evaporation time, but a linear decrease is seen after this time. In ISS experiments the platinum signal decreased to zero at the iron oxide coverage corresponding to the 11 minute break, as shown in figure 2, confirming the completion of an iron oxide monolayer [12].

3.2 Stoichiometry of iron oxide films on platinum(111)

When an iron oxide monolayer was prepared in the manner indicated above, the oxygen 510 eV to the iron 651 eV peak to peak ratio (AES oxygen to iron ratio) was constant and equal to 2.4. The oxygen to iron ratio in the ISS spectra (ISS oxygen to iron ratio) was 1.5. Alterations of the preparation procedure would change the AES oxygen to iron ratio. A value of 0.2 could be obtained by omitting the oxidation step and an AES oxygen to iron ratio of 4.3 was reached by oxidizing in 10 Torr of oxygen at 760 K. However the AES oxygen to iron ratio decreased from 4.3 to 2.4, when the iron oxide overlayer were exposed to UHV conditions for 3 hours. If several monolayers ($\approx$ 4 ML) were prepared in UHV, according to the description in the experimental section, the AES oxygen to iron ratio was still 2.4. However the ISS oxygen to iron ratio decreased, with respect the the one monolayer ratio, from 1.5 to 1.0

The Fe $2p_{3/2}$ binding energy of the ordered monolayer as measured by XPS is 709.5 eV, indicating an Fe^{2+} oxidation state [14,15]. Upon oxidation of the monolayer of iron oxide with 10 Torr of oxygen at 760 K, the binding energy changed to 710.6 eV, close to the Fe^{3+} binding energy values [14,15]. Oxidation of several monolayers in 10 Torr of oxygen resulted in a Fe $2p_{3/2}$ binding energy of 710.9 eV. A decrease of the binding energy to 709.5 eV was observed, if the iron oxide overlayer was exposed to UHV for a period of 3 hours.

3.3 Structure of iron oxide films on platinum(111)

Clean platinum(111) gives a LEED pattern corresponding to a (1×1) surface structure, characteristic of the bulk platinum periodicity (see figure 3a). The x-ray diffraction parameter of platinum is 3.91Å. This LEED pattern becomes diffuse after the iron oxide coverage reaches values larger than θ=0.2 ML, as determined by AES. Above 0.8 ML coverage of iron oxide, a new LEED pattern occurs, consisting of a sextet of weak spots around a bright central spot of a hexagonal pattern with the same orientation as the clean platinum. The bright spot in the floret is 10% closer to the (00) beam than in the clean platinum pattern (figure 3b). We will call this structure I. The spots in this structure become sharper upon approaching the one monolayer coverage. A schematic representation of this LEED pattern is shown in figure 3c.

Structure I could also be observed at coverages higher than 1 ML. It was necessary however to heat the iron oxide for several minutes (instead of a few seconds) at 830 K to induce ordering. If an iron oxide film of more than 10 monolayer equivalent was deposited on the platinum surface, followed by heating to 1040 K for 2 minutes, LEED showed a new pattern (structure II), which indicates the presence of a surface structure with a (2×2) periodicity with respect to the monolayer structure. Structure II occured with partial dissolution of the iron oxide in the platinum. Approximately one to two monolayers were dissolved in a minute of heating at 1040 K. If the coverage after partial dissolution approached one monolayer, a mixture of structure I and structure II was observed, i.e. structure I with half order diffraction spots in between the florets.

If heating at 1040 K is continued for several hours, all the iron oxide dissolves into the platinum, except for the last monolayer. Heating to 1100 K and above is necessary to remove this monolayer, indicating that the iron oxide monolayer on platinum is very stable.

Oxidizing the monolayer of iron oxide in 10 Torr of oxygen, resulted in the

dissapearance of the LEED pattern. This is in agreement with studies on the oxidation of iron [16].

3.4 CO and H_2O chemisorption studies on iron oxide on platinum(111)

CO chemisorption was studied in order to monitor the formation of the iron oxide monolayer, since CO does not adsorb in UHV on the iron oxide surface, while it adsorbs on the platinum substrate. The CO TPD curves are shown in figure 4. In these experiments the surface was exposed to 1 Langmuir of CO, which approximately corresponds to half the saturation coverage on the clean platinum. The area under the CO TPD peaks from the platinum substrate decreases with increasing iron oxide coverage. Also a shift in the low temperature onset of the CO TPD peaks towards lower temperature is seen at the lowest iron oxide coverages (in figure 4). The iron oxide surface is inert towards CO adsorption at coverages above 1 monolayer. In contrast to a clean platinum single crystal, the iron oxide covered surface can be left for several days in ultra high vacuum conditions without any detectable buildup of carbon or any other contaminants. From figure 4, it appears that the total amount of CO adsorbed on the platinum surface after exposure to 1 L, does not decrease much with increasing iron oxide coverages from $\theta = 0$ to $\theta = 0.5$ ML. However the onset and the maximum of the CO desorption rate shifts to lower temperatures. The reasons for this will be discussed in the following section.

Water adsorption on the iron oxide covered platinum surface was studied next. The water TPD spectra corresponding to a 1 L exposure at 110 K as function of iron oxide coverage are shown in figure 5. Clean platinum has a sharp water physisorption peak at 171 K [17]. This peak shifts to higher temperature with increasing exposure, indicating that on clean platinum(111) the desorption process is zero order, in agreement with previous studies [17]. With the addition of iron oxide up to the monolayer coverage, the water TPD peak becomes broader. At one monolayer coverage the desorption kinetics is first order, since the maximum in the

desorption rate does not change with exposure from 1 to 3 L. After this exposure, the shift to higher temperatures of the desorption maximum, indicates that the desorption kinetics become zero order. Above the monolayer a shoulder appears on the high temperature side of the physisorbed water peak at 200 K. This shoulder does not disappear at higher oxide coverages. Higher temperature desorption peaks were also obtained, if the iron oxide multilayer is heated to 1040 K, so that structure II is observed, and the ISS oxygen to iron ratio decreases from 1.5 to 1.0. Figure 6 shows the different features in the water TPD observed after heating a 10 monolayer iron oxide overlayer to 1040 K. Two additional peaks are observed at 200 and 220 K respectively, in addition to the physisorbed peak at 173 K. These two peaks correspond to new adsorption sites, that saturate at approximately 0.4 and 0.6 L respectively.

4 Discussion

4.1 Coverage determination of iron oxide on platinum(111)

As described in the experimental section, we monitored the growth of iron oxide on platinum with four different techniques. Using AES [12] a break is observed after the completion of each layer. Also a break is observed in the current between the crystal and ground [11]. ISS can also be utilized because it is only sensitive to the outermost layer under our conditions [18]. Finally CO TPD can be used as a further check, since CO adsorbs only on platinum under our low pressure conditions.

In the AES uptake curves (figure 1) there is a break at eleven minutes evaporation time. This is interpreted by the completion of a two dimensional monolayer before the formation of the second monolayer is started [12]. At this break the platinum Auger 237 eV peak to peak intensity is attenuated 42%.This is in the range expected for monolayer attenuation values [13]. The break at 22 minutes

evaporation time is then interpreted as the completion of the second layer. The platinum signal decreased another 42% at this break, consistent with a Frank- van der Merwe layer by layer growth mechanism for iron oxide on platinum(111).

Based on the observed peak ratios at the monolayer coverage we derive the following expression for submonolayer coverages (θ) of iron oxide on platinum (111) that is a function of the iron and platinum AES peak to peak intensities:

$$\theta = 1.40X - 0.43X^2 \qquad (\pm 0.05ML)$$

where X is the ratio of the iron 651 eV and platinum 237 eV peak to peak AES intensities.

The crystal current is the complement of the backscattered electron flux. At 2 keV primary energy most emitted electrons leave the sample with very low (below 5 eV) energies. These are the so called secondary or cascade electrons. Changes in work function of the surface or changes in the surface structure have a large influence on the number of secondary electrons [11]. After the monolayer coverage is reached the crystal current curve does not show any abrupt change in slope. Therefore it can be concluded that the abrupt change in work function occurring when the monolayer coverage is completed is mostly responsible for the observed break.

The ISS data in figure 2 show that no platinum is visible when the monolayer coverage of iron oxide on platinum(111) is reached. This is another indication for the fact that the first monolayer is completed before the formation of the second monolayer is started.

The interpretation of the monolayer completion is also supported by the simultaneous suppression of the CO (see figure 4). From our CO chemisorption studies, we know that CO adsorbs only on the surface of the platinum, if the iron oxide coverage is lower than 1 ML. This contributes additional evidence for our determination of the absolute monolayer coverage and indirectly supports the two dimensional epitaxial growth of iron oxide on platinum(111), in least at its initial stages.

In conclusion, all techniques used to monitor the iron oxide growth on plat-

inum(111) show that the first monolayer is completed before the formation of the second monolayer is started. It is thus shown that iron oxide grows two dimensionally, for the first layer. The AES data further supports the fact that the layer by layer growth is sustained above the monolayer iron oxide coverage.

4.2 Stoichiometry of iron oxide on platinum(111)

In order to study the stoichiometry and the oxidation state of iron in the iron oxide overlayer formed on the platinum(111) substrate, several techniques were used. ISS and AES were utilized to study the stoichiometry, while XPS was used to determine the oxidation state of iron in the overlayers.

Iron oxide compounds can be formed in a wide range of stoichiometry on a platinum(111) single crystal. This is supported by the different AES oxygen to iron ratios observed in this study, ranging from 0.2 to 4.3. A value of 0.0 should be obtained for clean iron; however due to the reactivity of the iron and the limited vacuum of 1×10^{-9} Torr during evaporation of the iron, the cleanest overlayer obtained in this study had an AES oxygen to iron ratio of 0.2. Also a slight carbon contamination was found in this case, due to the CO residual gas in the vacuum system. The highest AES oxygen to iron ratio that could be obtained was 4.3. This ratio was achieved by oxidizing the iron overlayer in 10 Torr oxygen at 760 K. Langell et al. [16] reported an AES oxygen to iron ratio of 4.3 for Fe_2O_3. Clearly the whole range of existing iron oxygen stoichiometries can be formed, from pure Fe to that of FeO, Fe_3O_4 and Fe_2O_3.

The binding energy of the Fe $2p_{3/2}$ core level for the monolayer prepared in UHV (709.5 eV) is very close to that for Fe^{2+} as reported in literature; namely, 709.7, 709.5 eV [14] and 709.2 eV [15]. Upon oxidation in 10 Torr of oxygen, the binding energy increased to 710.6 eV. The binding energy obtained by oxidation of several monolayers in 10 Torr of oxygen at 760 K was 710.9 eV. This is comparable to the binding energies of 711.2 and 711.0 for Fe^{3+} as reported by Brundle et al. [14] and Asami et al. [15] respectively. The Fe $2p_{3/2}$ binding energy for one monolayer

iron oxide after oxidation in 10 Torr of oxygen at 760 K is slightly lower than the binding energy for several monolayers of iron oxide. This could be due to a slow decomposition of the iron oxide in vacuum, if the iron oxide is in the Fe^{3+} oxidation state. In the course of several hours the oxygen to iron ratio in the heavily oxidized films changes from 4.3 to 2.4, while reducing iron from the Fe^{3+} to the Fe^{2+} state.

At one monolayer iron oxide coverage, the stable layer in UHV has an AES oxygen to iron ratio of 2.4. We propose that this corresponds to the FeO stoichiometry. The 2+ oxidation state of the iron as determined from XPS supports this assignment. Upon oxidation of an overlayer of iron oxide on platinum(111) in 10 Torr of oxygen at 760 K, AES shows that the Fe_2O_3 stoichiometry is reached. The AES oxygen to iron ratio is 4.3. Again this is supported by the XPS results, that indicate a 3+ oxidation state of the iron. However the overlayer with Fe_2O_3 stoichiometry is reduced in a matter of hours to the FeO stoichiometry at room temperature under UHV conditions as indicated by both AES and XPS.

When multilayers of iron oxide are prepared in UHV, there is no change in the AES oxygen to iron ratio with respect to the corresponding ratio for one monolayer (i.e. it remains equal to 2.4). Therefore the decrease in the ISS oxygen to iron ratio in the case of the multilayer indicates a reduction of only the outermost atomic layer, since ISS is only sensitive to this outermost layer, while AES samples several layers (≈ 5) at the oxygen and iron peak energies.

Rao et al. [19,20] reported that the oxidation state of iron in its oxides could be determined by taking the different Fe (LMM) Auger peak ratios. In our case however the different LMM - peak to peak ratios did not change appreciably, when the AES oxygen to iron peak to peak ratio changed from 0.2 to 4.3. The average value for the Fe 651 eV to Fe 703 eV LMM peak to peak ratio was 0.79, which according to this method should correspond to Fe_3O_4. We do not think this method of determining the oxidation state or stoichiometry is accurate in our case, since the value does not change within error upon different treatments, while the AES oxygen to iron ratio, the ISS oxygen to iron ration and the Fe $2p_{3/2}$ binding energy obtained by XPS do show a change due to a change in the altered iron oxidation

state caused by the different treatments.

4.3 Structure of iron oxide on platinum(111)

From the analysis of the LEED structure I (figure 3c) we deduce that the iron oxide overlayer has a 10% larger unit cell than platinum in real space. In figure 3b, corresponding to 40 eV beam energy 6 weak spots show up around the "(0,1)" spots. The bright spots are not the platinum(111) substrate spots, but are 10% closer to the (0,0) beam, as indicated earlier. If double diffraction between the overlayer and the substrate was responsible for this floret of spots, then 3 of those spots should originate from double diffraction from a (0,2) substrate beam. Calculations reveal that electrons of 40 eV energy do not have enough energy to produce a (0,2) diffracted beam (The energy associated with a parallel momentum equal to the (0,2) vector would be 56 eV). Therefore the floret of spots can not be explained as a double diffraction between an overlayer and the substrate.

The pattern can be explained by assuming an incommensurate iron oxide overlayer, that covers the surface in small repeating domains. A domain size consisting of (6×6) iron oxide unit cells covering a (7×7) area of platinum substrate atoms, can explain the observed results. The real periodicity of the lattice (i.e. (7×7)) is obscured by the fact that the structure factor (and therefore the intensity of the spots), according to a kinematic approximation, peaks at 6 times the reciprocal unit cell vector of the overlayer. The width of the structure factor curve is such that the most intense spots are seen at around a distance of 6 times multiple of the overlayer reciprocal lattice vector, with possibly one lower intensity spot from the (7×7) structure around it in each direction.

There are three known crystalline forms of iron oxide [21]. The sodium chloride structure for $Fe_{1-x}O$, the spinel structure for the range of compounds from Fe_3O_4 to γ-Fe_2O_3 and the corundum structure for α-Fe_2O_3. All structures have hexagonal arrangements of iron and oxygen atoms in one or more of their crystal planes. All diffraction parameters of the hexagonal iron oxide structures are slightly larger

than the platinum diffraction parameter, which within our experimental error are compatible with the LEED data. From the XPS and AES information it is known that the oxidation state of the iron is 2+. This suggests that the monolayer structure could be analog to one of the hexagonal planes in the $Fe_{1-x}O$ structure. However the (111) planes of this structure contain either oxygen or iron and ISS shows that both iron and oxygen occur in the outermost atomic layer.

If we consider an hypothetical FeO (210) surface [22], with both iron and oxygen in a near hexagonal symmetry, it consists of parallel chains of FeO structures. Two consecutive chains have oxygen and iron ions in direct opposition. In bulk FeO the repulsive interaction of this configuration is stabilized by the layers below, that are staggered to each other. It is thus unclear, whether this FeO layer can still be stabilized by the platinum(111) substrate or if a different structure is produced, not found in any of the iron oxides.

In FeO multilayers the oxygen atoms in the outermost layers can be removed by heating to 1040 K as indicated by our ISS results, thereby creating vacancies that expose the iron atoms. This causes a change in the LEED pattern due to the formation of a "2×2" surface structure. The disappearance of the sextets of spots can be explained by the fact that the platinum surface is below the probing depth of the low energy electrons and does not contribute to the overall surface periodicity. Also the decrease in the ISS oxygen to iron ratio is not accompanied by any appreciable change in the AES oxygen to iron ratio, indicating a reduction of only the outermost atomic layer. The determination of the iron and oxygen atom positions and a study of the vacancy formation will be performed in the future using a scanning tunneling microscope.

4.4 CO and H_2O chemisorption studies on iron oxide on platinum(111)

The total amount of CO adsorbed on the iron oxide covered surface of platinum does not change very much at iron oxide coverages below half a monolayer. This

indicates that the sticking coefficient for CO does not decrease with increasing iron oxide coverage. The reason for this behaviour is not understood at present. A tentative explanation could be that CO can be weekly bound to FeO for a short time, enough to diffuse to a clean platinum area before desorption. The fact that the onset and the maximum of the CO TPD spectra shifts to lower temperature can be interpreted as due to the repulsive dipole- dipole interactions, indicating that the CO is more closely packed on the surface at higher iron oxide coverages. When the CO exposure is increased on clean platinum(111) similar peak shifts are observed.

Below 1 monolayer of iron oxide coverage on platinum(111) water desorbs in a first order process for exposures up to 3 L and with zero order at higher exposures. Assuming a preexponential factor of 10^{13} [23] the activation energy for desorption is 10 kcal/mol in the low coverage range. It is clear from figure 5 that when the iron oxide coverage is higher than 1 monolayer a shoulder appears on the high temperature side in the water desorption spectrum corresponding to 1 L exposure. Assuming a first order desorption process and a preexponential factor of 10^{13} an activation energy for desorption of 12 kcal/mol is found. This result indicates, that water has a stronger interaction with the iron oxide surface, above one monolayer. This shoulder can be explained by defects on the iron oxide surface. The nature of these defects is not clear, but since the shoulder appears even at iron oxide coverages slightly above one monolayer, we suggest these could be due to imperfections such as steps.

The desorption of water from a multilayer surface that is heated to 1040 K, shows desorption peaks at 200 and 220 K, which we attribute to defects, related to the higher iron concentration of the surface. Assuming a first order desorption process and a preexponential factor of 10^{13} this results in activation energies for desorption of 12 and 13 kcal/mol respectively. The ISS showed a decrease in the iron to oxygen ratio from 1.5 to 1.0, indicating oxygen vacancies on the surface. In these defects water molecules are more strongly bound than on step defects. Water appears to be a very sensitive probe of the different type of defects (steps and oxygen vacancies) occuring on an iron oxide surface.

5 Summary

By studying the Auger uptake and crystal current curves we have shown that iron oxide grows two dimensionally on the platinum(111) crystal surface. The 2-D nature of this overlayer is further demonstrated by the ISS and the CO chemisorption results. The break in the Auger uptake curve occurs at an attenuation of the platinum 237 eV of 42 %. The Fe $2p_{3/2}$ binding energies, determined with XPS, and the Auger oxygen to iron ratio show that the iron is in the 2+ oxidation state. Iron oxide can be prepared in the 3+ oxidation state by oxidizing with 10 Torr of oxygen; however these films are not stable under UHV conditions and the films reduce to a FeO stoichiometry.. From ISS information we determined that oxygen as well as iron are exposed in the outermost atomic layer of the iron oxide. LEED shows that the monolayer is ordered with hexagonal symmetry (Structure I). The two dimensional lattice unit vectors are approximately 10 % longer than the corresponding platinum(111) lattice unit vectors. This could correspond to an ordered overlayer similar to the FeO(210) plane although deviations induced by its interaction with the platinum(111) substrate could be present.

It is shown from water chemisorption studies, that water is a very sensitive probe for defects in the iron oxide structures. These defects can be either steps or oxygen vacancies on the surface. Our results indicate, that the water adsorbs more strongly and preferentially at the defect sites of iron oxide.

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Figure captions

Figure 1. Variation of the crystal current (μA), and of the iron 651 eV and platinum 237 eV AES peak to peak intensities as a function of iron evaporation time. After each minute of iron evaporation the iron was oxidized.

Figure 2. ISS spectra corresponding to clean platinum(111), and to various iron oxide covered platinum surfaces. Each spectrum is normalized with respect to the largest peak in that spectrum. The iron oxide coverage is shown next to the corresponding curve.

Figure 3. a: LEED pattern at 40 eV beam energy of the clean platinum (111) (1×1) structure. b: LEED pattern at 40 eV beam energy corresponding to one monolayer iron oxide coverage. c: A schematic representation of figure 3b.

Figure 4. Thermal desorption spectra of CO after exposure of the partially covered iron oxide surface with 1 langmuir carbon monoxide. The iron oxide coverage is shown next to the corresponding curve.

Figure 5. Thermal desorption spectra of water from iron oxide covered platinum surfaces after exposure to 1 Langmuir water. The iron oxide coverage is shown next to the corresponding curve.

Figure 6. Thermal desorption spectra of water from a multilayer ($\approx$ 10 ML) of iron oxide, that was heated to 1040 K for 1 minute. The water exposures are shown to the right of the corresponding curves. The desorption peak at 250 K is due to a spurious effect, caused by the manipulator.

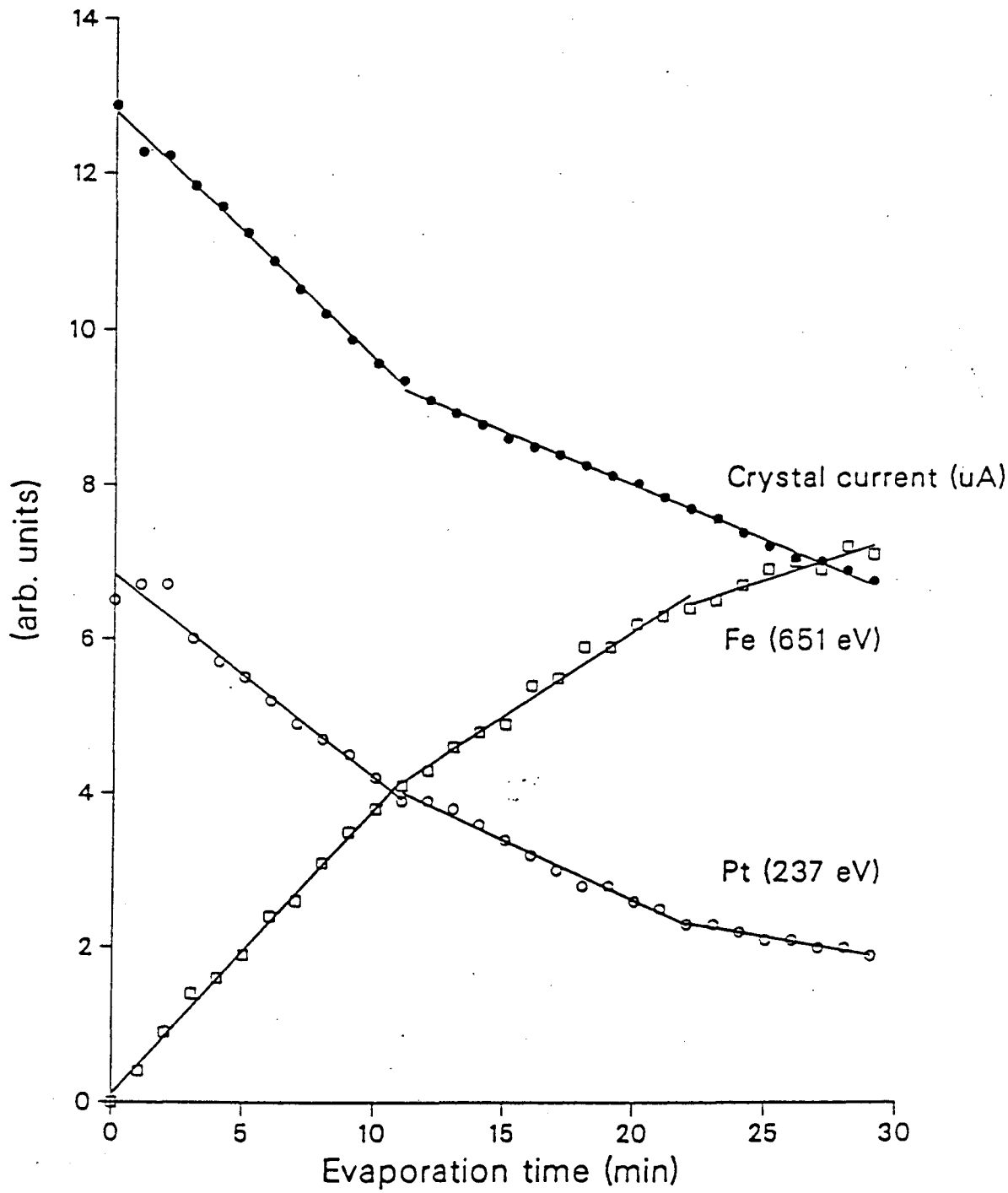

14
12
10
8
6
4
2
0
(arb. units)
0
5
10
15
20
25
30
Evaporation time (min)
Crystal current (uA)
Fe (651 eV)
Pt (237 eV)

Fig. 1

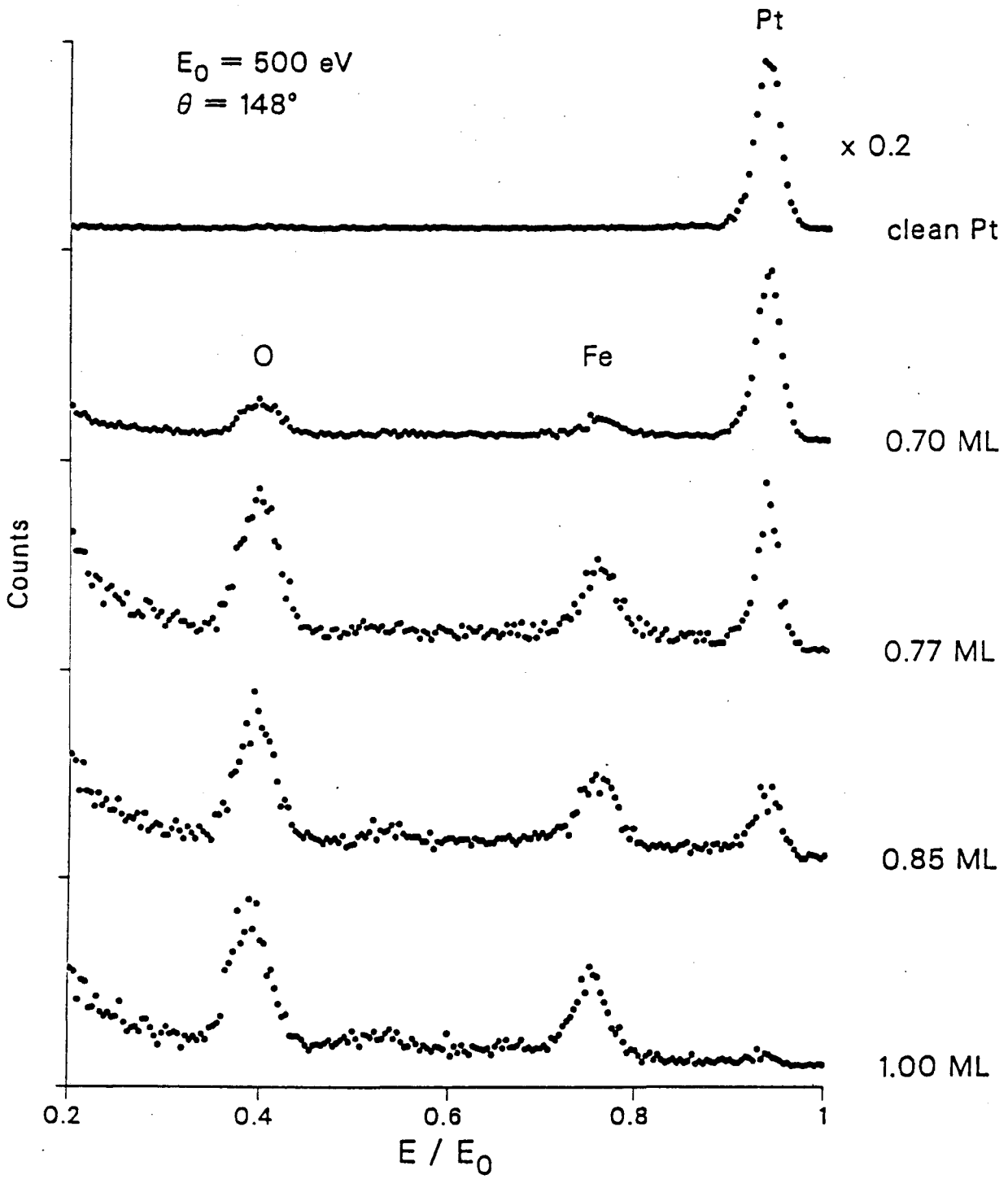
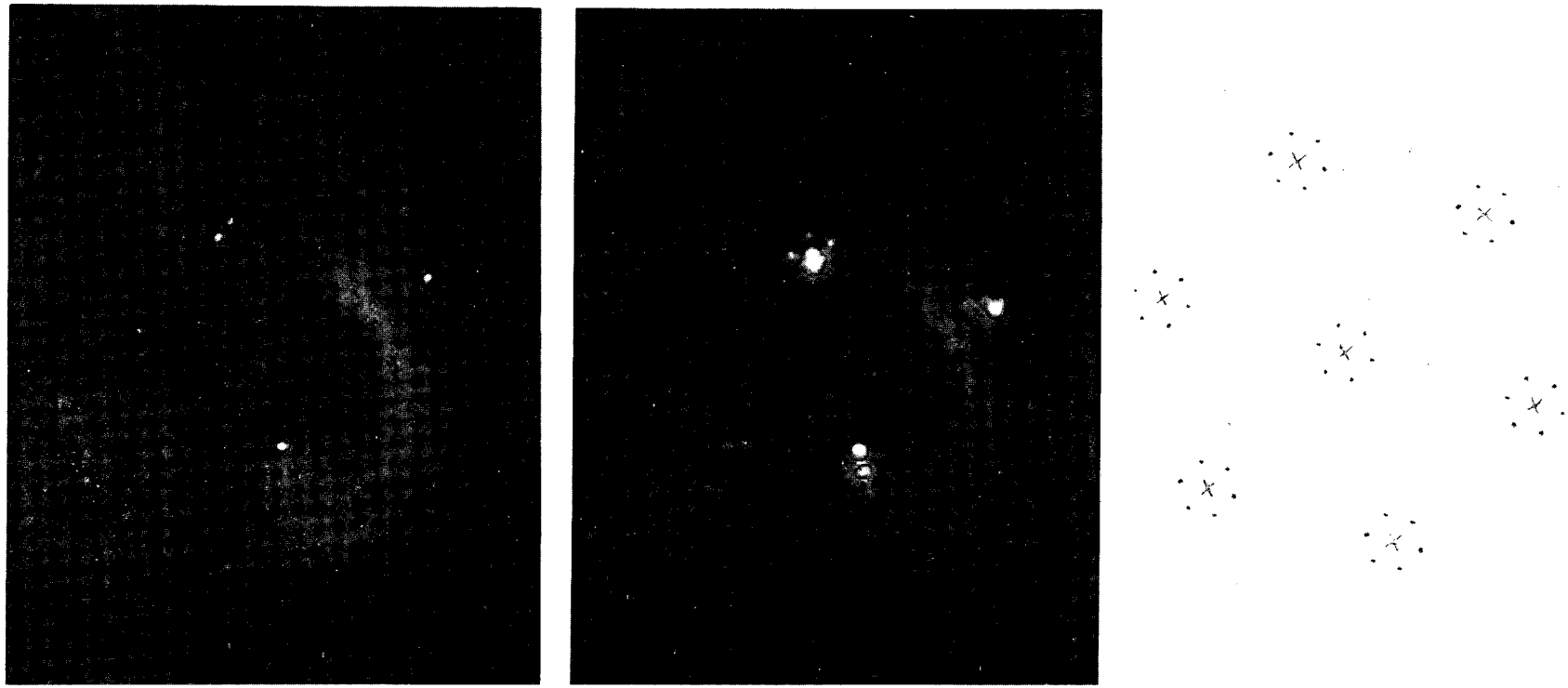

Pt
E_0 = 500 eV
θ = 148°
x 0.2
clean Pt
O
Fe
0.70 ML
Counts
0.77 ML
0.85 ML
1.00 ML
0.2
0.4
0.6
0.8
1
E / E_0

Fig. 2



A B C

Fig. 3

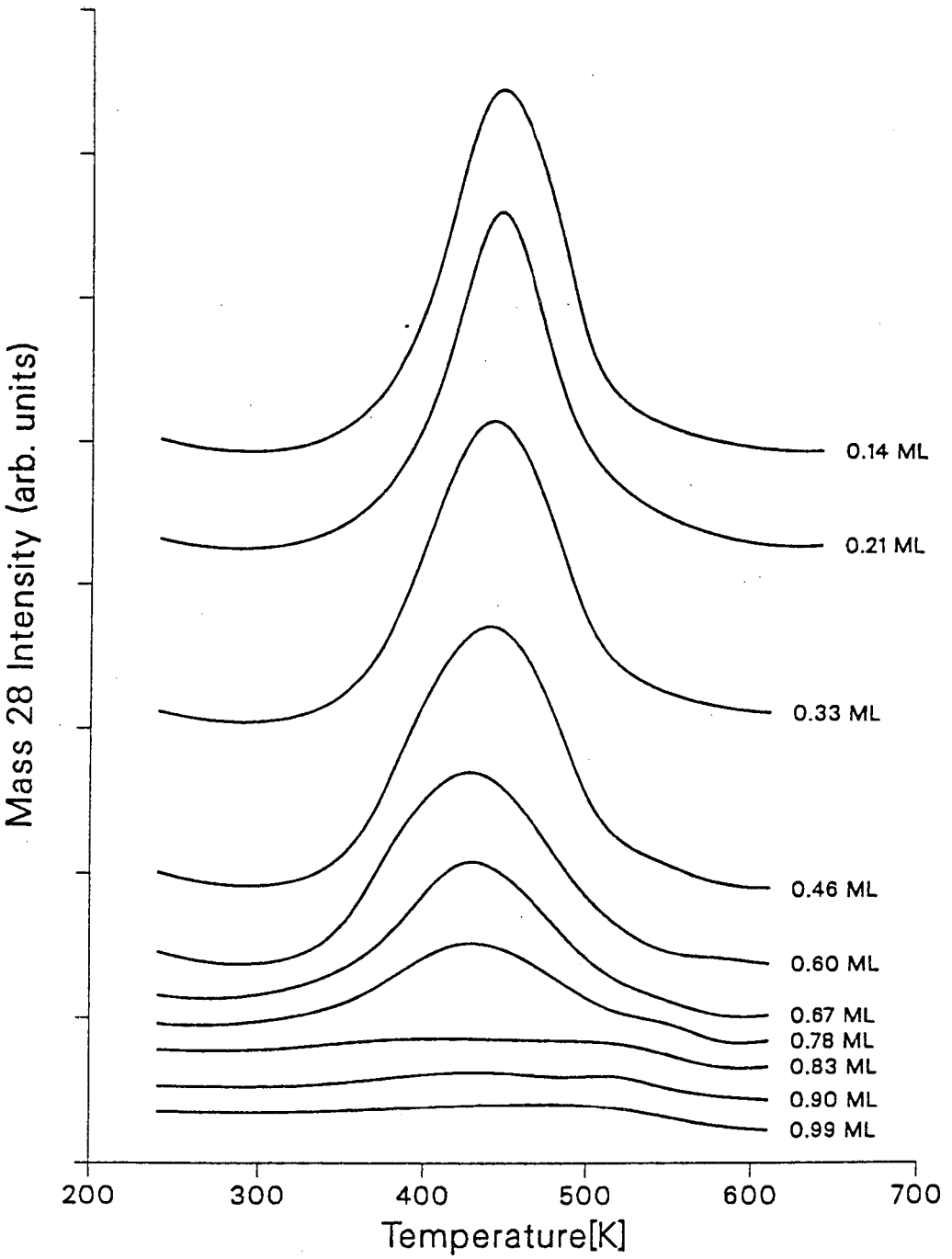

Mass 28 Intensity (arb. units)
0.14 ML
0.21 ML
0.33 ML
0.46 ML
0.60 ML
0.67 ML
0.78 ML
0.83 ML
0.90 ML
0.99 ML
200
300
400
500
600
700
Temperature[K]

Fig. 4

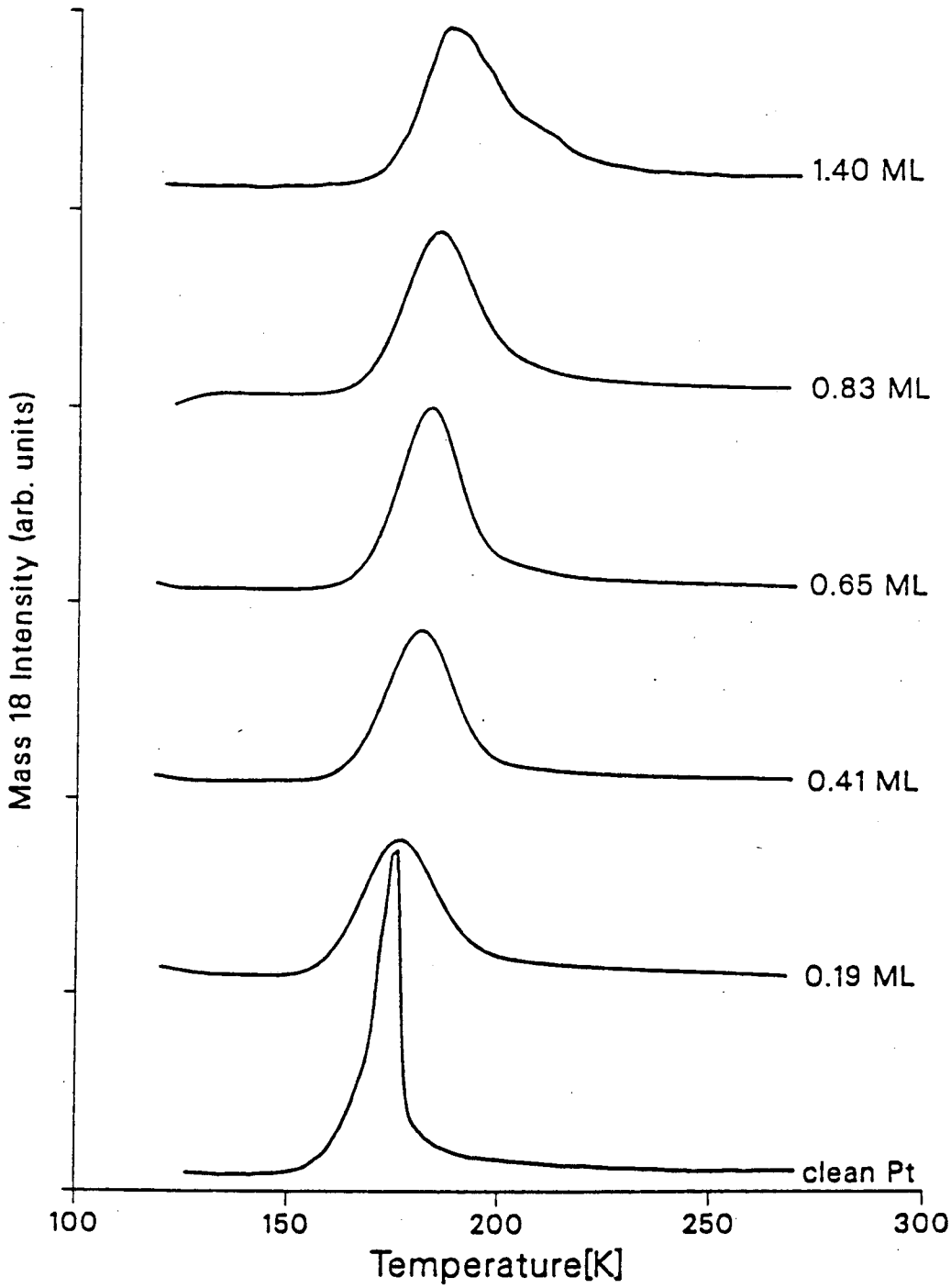

1.40 ML
0.83 ML
0.65 ML
0.41 ML
0.19 ML
clean Pt
Mass 18 Intensity (arb. units)
100
150
200
250
300
Temperature[K]

Fig. 5

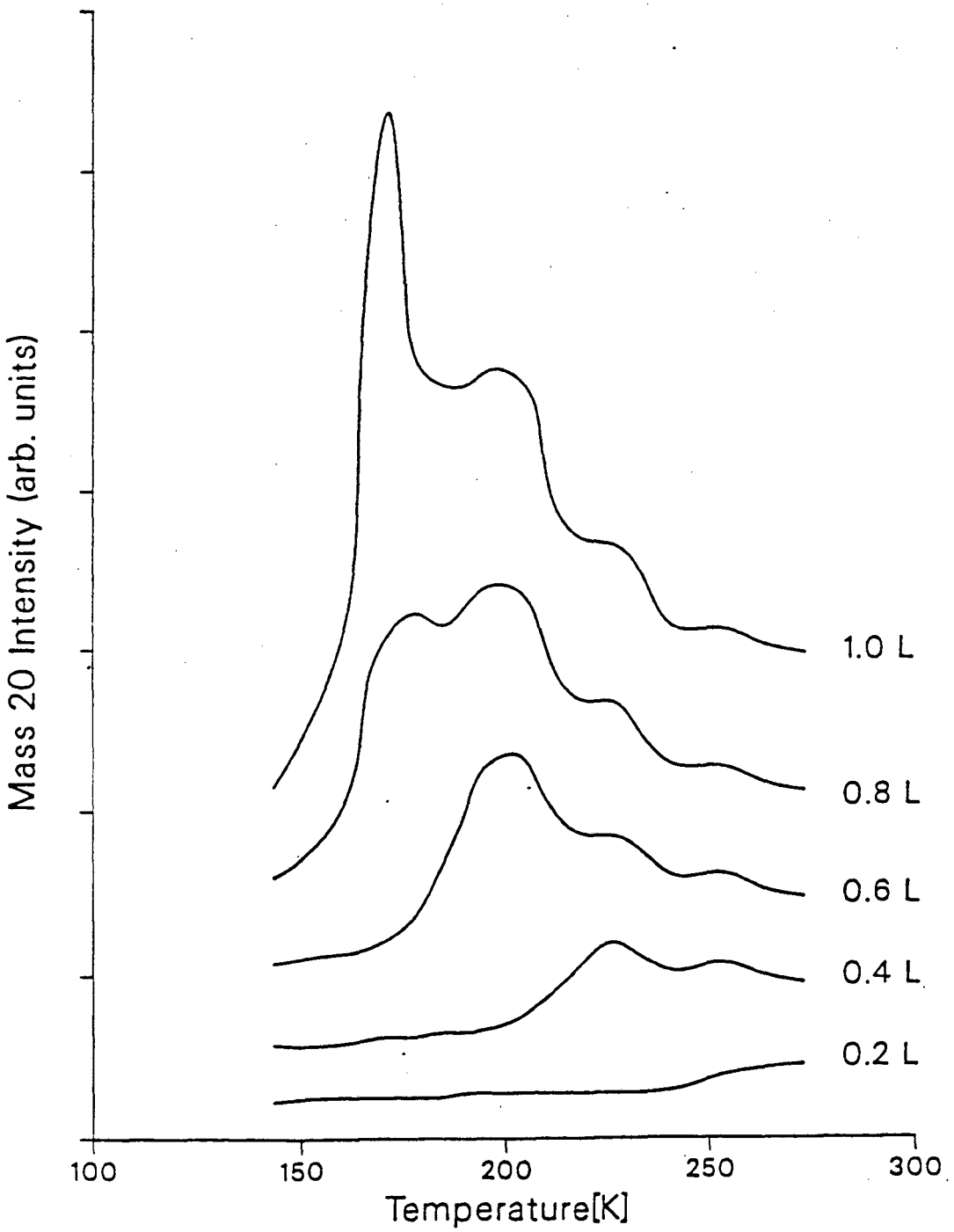

Mass 20 Intensity (arb. units)
1.0 L
0.8 L
0.6 L
0.4 L
0.2 L
100
150
200
250
300
Temperature[K]

Fig. 6

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