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E.L. Garfunkel and G.A. Somorjai

August 1981

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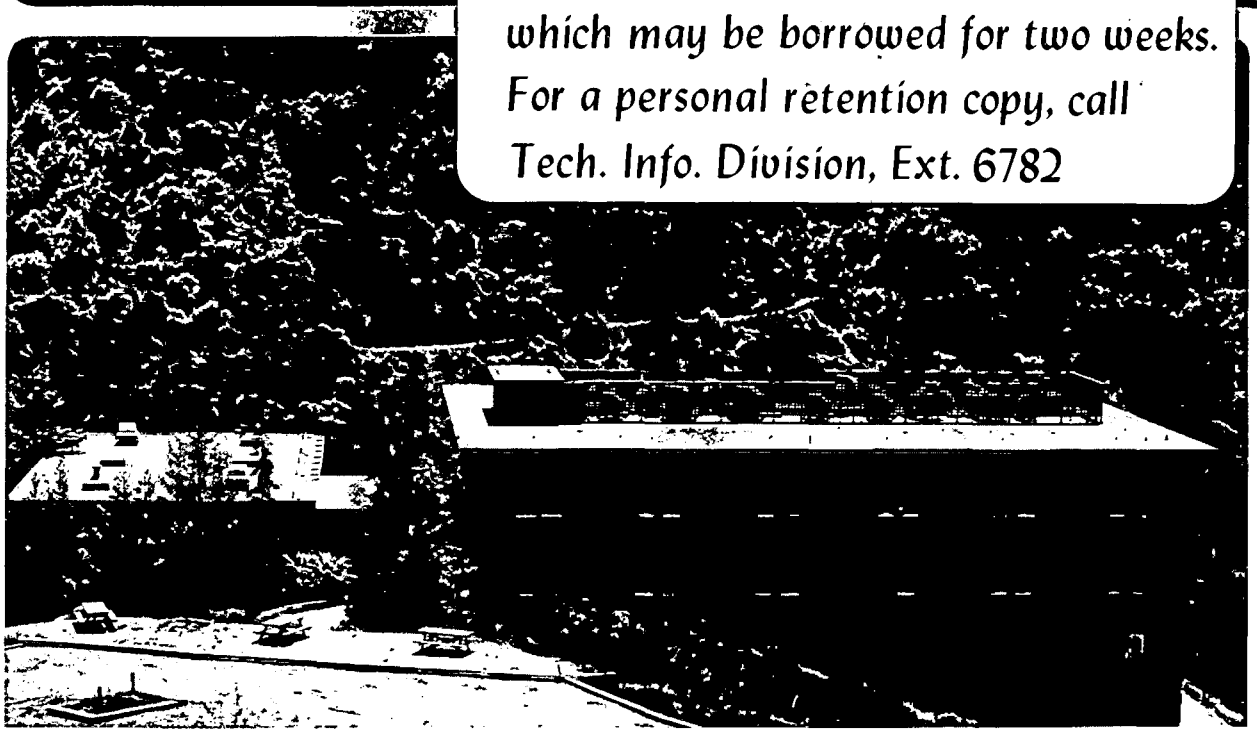

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LBL 13293

POTASSIUM AND POTASSIUM OXIDE MONOLAYERS ON THE PLATINUM (111) AND STEPPED (755) CRYSTAL SURFACES. A LEED, AES, AND TDS STUDY

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Abstract

The adsorption of potassium and the coadsorption of potassium and oxygen on the Pt(111) and stepped Pt(755) crystal surfaces were studied by AES, LEED, and TDS. Pure potassium adlayers were found by LEED to be hexagonally ordered on Pt(111) at coverages of Θ_K=0.9-1. The monolayer coverage was 5.4×10^{14} K atoms/cm^2 (0.36 times the atomic density of the Pt(111) surface). Orientational reordering of the adlayers, similar to the behavior of noble gas phase transitions on metals, was observed. The heat of desorption of K decreased, due to depolarization effects, from 60 kcal/mole at Θ_K<0.1, to 25 kcal/mole at Θ_K=1 on both Pt(111) and Pt(755). Exposure to oxygen thermally stabilizes a potassium monolayer, increasing the heat of desorption from 25 kcal/mole to 50 kcal/mole. Both potassium and oxygen were found to desorb simultaneously indicating strong interactions in the adsorbed overlayer. LEED results on Pt(111) further indicate that a planar K_2O layer may be formed by annealing coadsorbed potassium and oxygen to 750K.

Introduction

The study of alkali metal and alkali oxide adsorption on transition metal surfaces has received considerable attention in the past. As early as 1923, Langmuir[1] showed that adsorbed cesium greatly increased the electron emission from hot tungsten surfaces as a result of the decrease in the metal's work function. This finding had many applications in the design of thermionic and photoelectron emitters[2]. It was also found that the addition of alkali metal oxides and carbonates greatly increased the activity of certain transition metal catalysts[3]. Alkali metal compounds are now routinely used as additives (or promoters) for iron catalysts in both the ammonia synthesis and the hydrogenation of carbon monoxide to hydrocarbons (the Fischer-Tropsch reaction). With the advent of modern ultrahigh vacuum (UHV) techniques, it is now possible to explore the structure, composition and other atomic scale surface properties of alkali metal and alkali oxide monolayers to uncover the reasons for their physical and chemical behavior.

In order to better understand how alkali adlayers impart unique chemical activity to transition metal catalytic surfaces, we have undertaken a systematic study of the chemisorption, the electronic and atomic structure, and the catalytic properties of potassium when adsorbed on platinum crystal surfaces. In this paper we focus on the structure and bonding of potassium and potassium oxide monolayers on the flat Pt(111) and stepped Pt(755) crystal faces. Low energy electron diffraction (LEED) revealed the presence of many different ordered surface structures

as potassium and potassium oxide coverages were changed. Thermal desorption spectroscopy (TDS) of pure potassium adlayers showed a large decrease in the heat of desorption of potassium with increasing coverage. Our results indicate that at coverages below about .4 monolayers either potassium or potassium oxide is bound so strongly to the platinum substrate that it would remain there permanently both under reducing (hydrogen) and oxidizing (oxygen) catalytic reaction conditions.

Experimental

All work was performed in a Varian ultrahigh vacuum (UHV) chamber equipped with a Physical Electronics (PHI) single pass cylindrical mirror analyser (CMA) for Auger electron spectroscopy (AES), a PHI four grid LEED system, and a UTI quadrupole mass spectrometer (QMS) interfaced to a PET computer for thermal desorption spectroscopy (TDS). A 99.998% pure platinum crystal was cut, oriented, and cleaned using standard procedures. The Pt(111) surface was argon ion bombarded at room temperature and 1000K to remove traces of Ca, Mg, and Si, then residual carbon was oxidized off by heating to 800K in 10^{-7} torr O_2 for several minutes followed by a flash to 1400K to remove platinum oxide. Before each experiment the surface was checked by AES and LEED to insure purity.

Atomic potassium was deposited by heating a "Saes Getters" potassium source mounted approximately three centimeters from the sample. Deposition rates were routinely on the order of .2 monolayers/min, with the platinum crystal sample held at room

temperature. Small amounts of hydrogen outgassed from the source but did not appear to significantly affect potassium overlayer surface structures or bonding. The Saes Getters source was found to give off no oxygen, which we found to be a significant contaminant in K-zeolite sources. Recently we have achieved considerable success with a pure potassium ampule source mounted in a differentially pumped evaporation chamber. No contaminants were found to be emitted with deposition rates as high as several monolayers per minute.

Auger calibrations of potassium and potassium oxide were made by using the Pt 64eV and 237eV peaks, the K 252eV peak (superimposed on the Pt 250eV peak), and the oxygen 510eV peak. Thermal desorption spectra were taken with heating rates of about 30 K/sec for both O_2 and K. Potassium oxide was made by either coadsorbing O_2 with the condensing potassium vapor or post-adsorbing O_2 after a potassium monolayer had been deposited. A leak valve connected to a molecular doser was used to introduce oxygen so that the chamber would retain its base pressure of $1x10^{-10}$ torr. Hence all exposures, while reported in units of Langmuirs (1 Langmuir = $1x10^{-6}$ torr sec), are only relative, as accurate pressure measurements at the sample surface could not be taken.

Results and Discussion

Potassium Uptake and Growth Calibration

The potassium Auger signal intensity is plotted against

deposition time on the Pt(111) crystal face in figures 1a and 1b. At platinum crystal temperatures slightly above 350K, (figure 1a), the curve, linear at first, leveled off abruptly to a maximum. The height of the maximum was determined by both the temperature of the crystal and the potassium flux to the surface. At 350K with a potassium flux of about .2 monolayers/min., the potassium adsorption proceeded until the potassium Auger signal was about one half the maximum intensity from a cooled pure potassium multilayer. The growth of multilayer potassium deposits is not observed at these temperatures.

Platinum crystal surfaces cooled below room temperature showed smoother Auger uptake curves, (figure 1b), displaying slight breaks at the positions which corresponded to the first and second layers, as confirmed from TDS and LEED experiments (see below). The deposition is shown in figure 1b as the ratio between the K 252eV and the Pt 64eV Auger peak heights, with the crystal held at 250K. The first break occured when the K(252eV)/Pt(64eV) peak ratio was 1.1 (as monitored by our PHI single pass CMA). This was also the coverage at which the most densely packed potassium monolayer LEED pattern was visible (see below). Therefore, we define this potassium coverage (Θ_K) to be one monolayer; as will be shown below, this corresponds to 5.4×10^{-14} K atoms/cm^2, or 36% of the surface atomic density of the substrate Pt(111) face. The large difference between the potassium and platinum surface density is due to the much larger potassium metallic radius.

Potassium Thermal Desorption

The results for the thermal desorption of potassium from the Pt(111) surface are shown in figure 2. At coverages of less than .1 monolayer, the potassium binds tightly to the surface, desorbing at about 1000K. As the coverage is increased, the temperature at which the desorption rate is at a maximum decreases continuously, and at one monolayer the desorption temperature is at 400K. We believe that this shift is due to repulsive lateral interactions between the (slightly ionized) potassium atoms that weakens their bonding to the platinum surface, similar to the behavior of alkali atoms on other transition metal surfaces[1,4-6]. Assuming first order desorption kinetics and a preexponential factor of $1x10^{13}$ that would be characteristic of a mobile atomic overlayer[7], the variation of the desorption temperature peak with coverage corresponds to a heat of desorption shift from 60 to 20 kcal/mole as Θ_K is increased. The heat of desorption of potassium as a function of coverage thus calculated from the TDS spectra is shown in figure 3.

The large variation in binding energy with coverage of alkali metals adsorbed on transition metals has been observed by others. For example Gerlach and Rhodin[4] showed that the heat of desorption of potassium on Ni(110) drops from 58 to 28 kcal/mole as the potassium coverage is increased from near zero to 0.5 monolayers. All of the models that were proposed assume that the decrease in heat of desorption is due to the depolarization of the surface dipoles at high coverages. The binding energy

shift can be rationalized if one considers an alkali atom adsorption potential having two terms: $\Delta H_{ads} \approx \Delta H_{sub} + P(\Theta)$. ΔH_{sub} is the heat of sublimation of pure potassium ($\approx$20 kcal/mole), while $P(\Theta)$ is a coverage dependent term, related to the Topping formula[8], that takes into account the polarization of the adsorbed potassium. At low coverages the surface dipoles would not affect each other and $P(\Theta)$ would assume a high value, while at high coverages the dipoles would have a significant depolarizing effect on one another, decreasing $P(\Theta)$ and therefore ΔH_{ads} (see figure 3).

LEED Studies of Potassium Monolayers on the Pt(111) Surface

In figures 4a, b, c, & d we show the progression of LEED patterns obtained from the pure potassium overlayers as the coverage is decreased (by thermal desorption). The pattern in figure 4a was obtained by depositing a monolayer of potassium. At higher coverages the LEED patterns became more diffuse.

The inner spots of the LEED pattern of figure 4a are indicative of an incommensurate hexagonally close packed surface structure. Assuming one potassium atom per unit cell, the potassium overlayer is calculated to have a surface density of 5.4×10^{14} atoms/cm^2, in agreement with results found on other surfaces[5]. Others define the overlayer coverage as the adlayer atomic density divided by the substrate surface density; in our case, the coverage with respect to the surface density of the Pt(111) substrate would be 0.36.

From the LEED pattern we see that the overlayer structure has its axes aligned with the substrate but with an interatomic

spacing of 4.6±.1Å , 66% greater than that of the platinum interatomic distance (2.78Å), and slightly smaller than the known metallic potassium interatomic distance (4.70Å). The real space transformation matrix for this structure is $\begin{pmatrix} 1.66 & 0 \\ 0 & 1.66 \end{pmatrix}$.

As the coverage is decreased by desorption, orientational reordering of the overlayer occurs. At first ring-like patterns appeared. Upon desorption, the ring transformed into well defined spot pairs, figures 4b and c (each pair being split about the (1/3, 1/3) spot position). After further desorption by annealing the crystal to 400K and cooling, the split pairs eventually coalesced into the (1/3, 1/3) spot positions, producing a $(\sqrt{3}x\sqrt{3})R30°$ surface structure (figure 4d), at Θ_K=.9. Lower coverages only resulted in the loss of the $(\sqrt{3}x\sqrt{3})R30°$ surface structure and in the appearance of a higher background intensity, indicative of surface disorder. It should be noted that the ordering behavior of the potassium monolayer on Pt(111) is very similar both to weakly adsorbed noble gases on metal and graphite surfaces as predicted by Novaco and McTague[9], and to the ordering behavior of halogen monolayers on metals[10]. In many of these studies the adlayers were found to have hexagonal symmetry at a coverage of one monolayer, regardless of the substrate symmetry.

From the thermal desorption results which indicate a higher degree of polarization at low coverages, we also would expect lateral interactions to favor hexagonal ordering at less than monolayer coverages. Recently Ertl & coworkers[5] showed the existence of a low coverage (3x3) surface structure for potassium on the Fe(111) surface. We do not see any ordered structures

at coverages less than Θ_K=0.9. That these lower coverage, ordered structures were not seen with the crystal held at 250K might be due to a liquid-like mobility of the potassium overlayer in this temperature and coverage region. Previously reported LEED intensity calculations indicate that alkali metal atoms favor three- and four-fold hollow sites[11], where presumably the alkali atom can donate its excess charge more easily to the substrate.

Potassium Oxide Thermal Desorption

Metallic potassium on the Pt(111) surface readily promotes the adsorption of O_2, in sharp contrast to the low, defect-sensitive, sticking coefficient of O_2 on clean Pt(111), estimated[12] to be in the range of $1x10^{-6}$ to $1x10^{-2}$. The potassium oxide overlayer thermal desorption spectra are given in figures 5a and 5b. Potassium desorption, mass 39, is recorded in figure 5a and oxygen desorption in figure 5b. The two thermal desorption spectra overlap indicating simultaneous desorption of potassium and oxygen. While no noticeable desorption of a potassium-oxygen cluster could be detected by the mass spectrometer, it is known that K_2O can exist as a vapor species[13]. Therefore we must consider the possibility that any potassium oxide cluster that may desorb is broken apart by the mass spectrometer ionizer. Our results, however, only give evidence for the simultaneous desorption of K^+ and O_2^+. We cannot say with certainty whether the dissociation occurs at the surface or in the mass spectrometer ionizer.

The potassium thermal desorption spectrum in figure 5a

indicates a slight decrease in heat of desorption as the coverage is increased in the first monolayer. Again, assuming first order desorption kinetics, the change in desorption temperatures correspond to a heat of desorption shift from 60 to 50 kcal/mole as coverage is increased from 0.1 to 3 layers, much less than the shift seen for pure potassium. Here the potassium coverages are reported in units of overlayer coverage (Θ_{KO}), where the K(252eV)/Pt(64eV) Auger monolayer ratio is 1.9, compared to 1.1 for potassium adsorption alone. Thus more potassium fits into a "potassium oxide" monolayer than in a pure potassium monolayer. The desorption temperature for the multilayer remains at about 810K. Comparing the potassium desorption spectra for the pure potassium and potassium oxide overlayers we see that for potassium coverages in excess of 0.2 monolayers, the oxygen in effect thermally stabilizes the potassium overlayer. This factor would likely be of significance under actual catalytic conditions.

The oxygen thermal desorption spectra are shown in figure 5b. After predepositing various amounts of potassium on the Pt(111) crystal face, we exposed the surface to 10 Langmuirs of O_2. The first major peak to develop in the thermal desorption spectrum appeared at 660K. This peak had a long tail and retained its position, shape and intensity, up to potassium coverages in excess of one monolayer. At these high coverages the peak disappeared. The second oxygen peak to develop, as we increased the potassium coverage above Θ_{KO}=0.2, came first at 730K, and moved up to 770K as the potassium coverage was increased to a monolayer. At higher coverages

this peak also disappeared. Next, a third peak developed at 900K appearing at coverages of $\Theta_{KO}>0.5$, which retained its position and size, even in the multilayer. And lastly, a fourth peak appeared at 820K, at the completion of the first monolayer. This was found to be the dominant peak in the multilayer. We also note that at potassium coverages between 0.5 and 1.0 monolayer, a low energy peak appeared at 500K. This might be due to chemisorption of molecular oxygen.

An explanation of this rather complex oxygen thermal desorption behavior is offered in a forthcoming paper where we analyze the vibrational spectra of these adlayers as obtained by high resolution electron energy loss spectroscopy (HREELS)[14]. At present we only wish to note that several forms of oxygen are present on the surface, and that some of the oxygen desorbs simultaneously with the potassium although not necessarily as a potassium oxide cluster.

LEED Studies of Surface Potassium Oxides

Four stable and reproducible ordered potassium oxide surface structures were seen by LEED at specific potassium and oxygen coverages. These structures included three which were commensurate, (4x4), (8x2), and (10x2) overlayer structures (figures 6b-e) and an incommensurate one (figure 6f). The (4x4) surface structure, (figure 6b), was generated by exposing a cooled Pt(111) crystal with $\Theta_K \geq 1.5$ to 10 Langmuirs of O_2, then annealing the crystal at 650K for several seconds, in effect desorbing the oxygen associated with the 650K peak in the TDS spectrum of figure 5b. The pattern was observed over a range of coverages for which

K(252eV)/Pt(64eV) Auger peak ratios of between 1.5 and 2.5 were found. The K(252eV)/O(510eV) peak height ratio was 5±.2 for the (4x4) surface structure, for both relatively high and low total coverages. The fact that the same LEED pattern was observed over a range of "potassium oxide" total coverages, but where the potassium to oxygen stoichiometry stayed constant, is indicative of ordered domains on the surface at less than monolayer coverages.

After annealing to 700K and cooling to room temperature an (8x2) overlayer structure developed, (figure 6c). One of the most stable structures was the (10x2), (figure 6d), generated by annealing the sample at 750K for several seconds. This pattern was visible with K(252eV)/Pt(64eV) Auger peak ratios of 1.25-1.6 and with a K(252eV)/O(510eV) peak ratio of 7.3±.3. As is seen in figure 6e, the (10x2) surface structure could be induced to form one domain. This was accomplished by ion bombarding the surface at a slight angle (about 5 degrees) away from the surface normal. The single domain pattern is then readily analyzed to yield the (10x2) surface structure.

The pattern in figure 6f was also generated by heating the crystal to 750K, but appeared to have slightly less oxygen incorporated into the surface oxide than the (10x2) structure. The K(252eV)/O(510eV) Auger peak ratio was found to be 7.7±.3. Upon close examination of the LEED pattern in figure 6e one sees that the most intense of the inner spots is not located in the exact half order spot locations, which would imply a (2x2) surface structure, but rather are shifted slightly outward indicative of an incommensurate overlayer. Their deviation

from the half order spot position and hence the deviation from a (2x2) overlayer structure is readily calculated from the positions of the double diffraction spots. The extra spots yield a hexagonal overlayer unit cell lattice constant of 4.71Å, a 15% contraction from a (2x2) structure.

A likely stoichiometry that could account for this structure is K_2O, in which each oxygen is hexagonally surrounded by 6 coplanar potassium atoms and each potassium by 3 oxygen and 3 potassium atoms. Using the average ionic crystal radii[15] for K^+ (1.33Å) and O^{2-} (1.4Å) the K_2O unit cell lattice parameter should be 4.69Å, very close to the value derived from the LEED pattern. To confirm this model a more exact LEED intensity analysis will have to be made of the overlayer, and combined with HREELS and photoelectron results. Double layer models have been proposed[6] for alkali oxide overlayers, and cannot be ruled out.

Platinum Stepped Surfaces

We have also carried out the experiments described above on the stepped Pt(755) [or 6(111)x(100)] surface and found only a few minor differences. The thermal desorption of both potassium and potassium oxide were very similar to that of the flat Pt(111) surface. The LEED patterns of pure potassium monolayers were not visible, but single domain patterns of (4x2), (8x2), and (10x2) potassium oxide structures were all seen. As will be described in an upcoming paper[16], potassium was found to be distributed evenly among step and terrace sites when titrated with CO.

Conclusion

The adsorption of potassium on the Pt(111) and stepped Pt(755) crystal faces is similar to the behavior exhibited by most pure alkali metal monolayers on other transition metal surfaces. At low coverages ($\Theta_K<0.1$) the potassium atoms are tightly bound with heats of desorption of about 60 kcal/mole. As the potassium coverage is increased, the heat of desorption decreases, due to depolarization effects, approaching the heat of sublimation (20 kcal/mole) in the second monolayer of potassium. We have observed ordered LEED patterns, corresponding to close-packed hexagonal overlayers, at coverages of $.9\leq\theta_k\leq1$. This surface structure behavior is similar to surface phase transitions of noble gas monolayers[9]. The most densely packed overlayer at which a LEED pattern was recognizable, was defined as a monolayer and yielded a coverage of 5.4×10^{14} atoms/cm^2. Although no overlayer surface structures were visible by LEED for the stepped Pt(755) surface, the TDS results indicated very similar adsorption energetics.

Our coadsorption studies of potassium and oxygen show a strong interaction between the oxygen and potassium at all coverages. The potassium became thermally stabilized by coadsorbed oxygen and its heat of adsorption at $\Theta_K=1$ increased from about 25 kcal/mole for pure potassium to 50 kcal/mole in the presence of oxygen. Molecular oxygen and atomic potassium were found to desorb simultanesouly when coadsorbed, and very little of the substrate platinum was left oxidized. In addition,

some weakly bound oxygen was found to be adsorbed at low potassium coverages.

A series of stable surface structures appeared on the Pt(111) surface which had been annealed after exposure to potassium and oxygen. The structures, as determined by their LEED patterns, were quite distinct from either the pure oxygen or pure potassium adlayer surface structures. It was also shown that the surface stoichiometry changed, and the LEED patterns transformed, as the sample was annealed. An incommensurate K_2O surface structure has been proposed for one of the LEED patterns (fig. 6e) from geometrical arguments. In this model the potassium and oxygen are coplanar and assume standard ionic radii[15] given for K^+(≈1.33Å) and O^{2-}(≈1.4Å). The incommensurate K_2O overlayer implies that lateral interactions between potassium and oxygen dominate over substrate induced forces in determining adlayer structure. Of course the image charges in the substrate induced by a surface alkali oxide would tend to stabilize the adlayer in the direction perpendicular to the surface. The presence of sharp LEED patterns at low coverages implies the existence of isolated potassium oxide domains.

There has been some disagreement in the literature on the existence of surface alkali oxides. Lindgren and Walden[17] conclude that surface cesium oxide exists on the Cu(111) crystal face. On the other hand Broden et al[6], in their XPS and UPS studies on both the Fe(110) and Pt(111) surfaces, conclude that potassium oxide does not exist at monolayer coverages.

Instead they argue that oxygen is present in two forms: (a) chemisorbed to the substrate, and (b) either as a substrate-metal oxide, or incorporated in the substrate lattice. Although we cannot prove that oxygen and potassium have formal charges of -2 and +1 respectively when coadsorbed in the first monolayer, we tend to agree with the model of Lindgren and Walden in which the alkali metal and oxygen do interact strongly with one another when coadsorbed. Our LEED results further imply that a coplanar potassium oxide might exist on the Pt(111) surface. Other models[6], such as a double layer where the potassium atoms are situated above the oxygen atoms, are not ruled out.

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Figure Captions:

1. Potassium Auger uptake curves on Pt(111) surface.
   a) K(252eV) peak intensity vs. deposition time with the crystal held at 360K.
   b) K(252eV)/Pt(64eV) peak ratio vs. deposition time with the crystal held at 250K. Inset figure is the Auger signal after 7 minutes and corresponds to 1 monolayer.

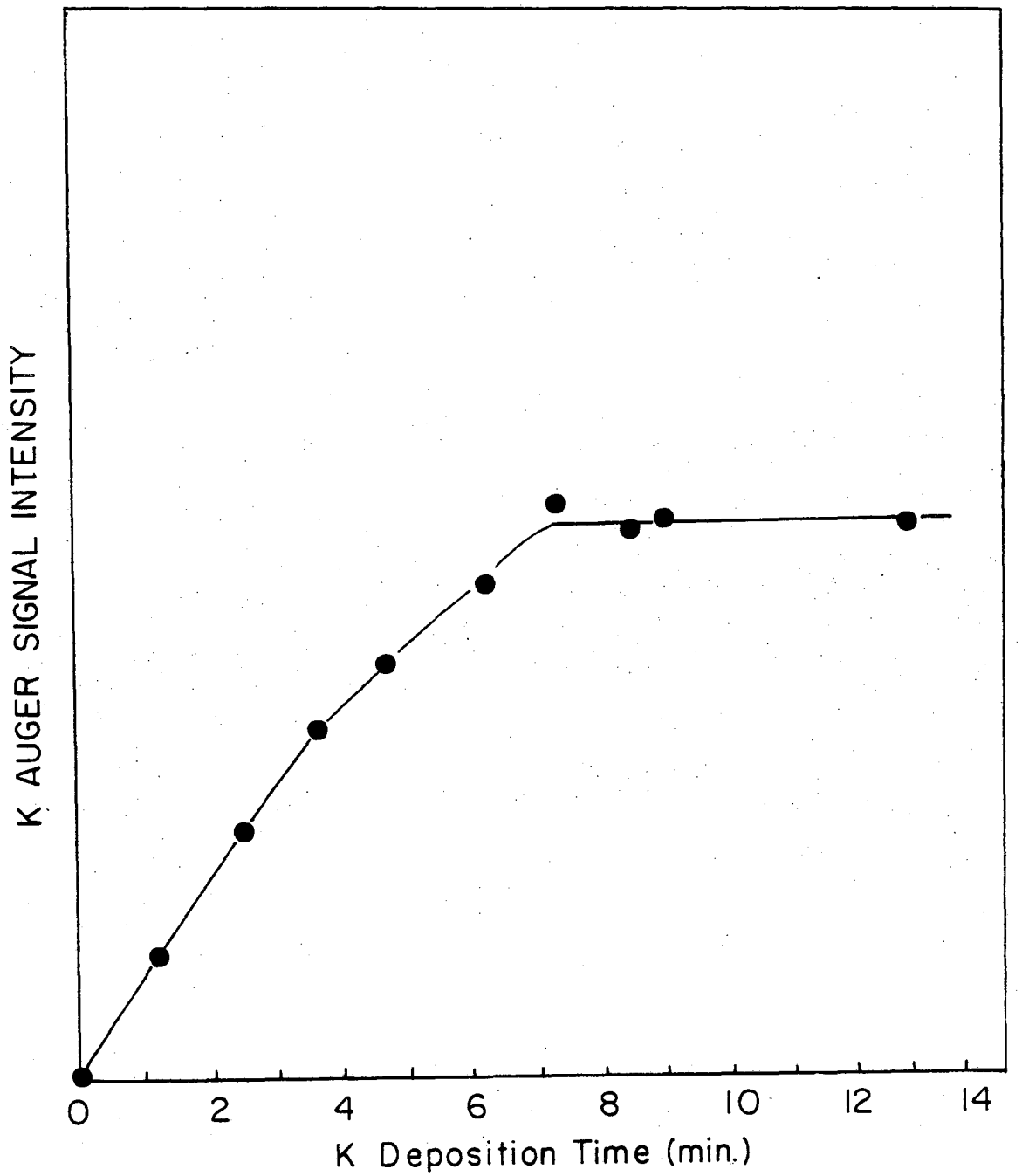
2. Potassium thermal desorption spectrum from Pt(111) surface. The coverages are calibrated from peak areas and Auger signal intensities. The heating rate was 30 K/sec.

3. The heat of adsorption of potassium vs. coverage on Pt(111)

4. Sequence of LEED patterns obtained for K on Pt(111) at 58eV; crystal temperature 250-270K at time of exposure.
   a) One monolayer, 5.4×10^{14} K atoms/cm^2
   b) After (a) was annealed to 330K, Θ_K=0.95, and
   c) 350K, Θ_K=0.94.
   d) After the crystal was annealed to 400K, Θ_K=0.9.
   Further annealing caused a loss of overlayer patterns, and a diffuse background.

5. The thermal desorption spectra for (a) K and (b) O_2 from coadsorbed potassium and oxygen on Pt(111). Here one monolayer, Θ_{KO}, is defined as K(252eV)/Pt(64eV)=1.9, compared to 1.1 for a pure potassium monolayer.

6. LEED patterns of "potassium oxide" monolayers on Pt(111).
   a) Clean Pt(111).
   b) The (4x4) overlayer structure formed after Θ_K=2, 10L O_2 then annealing to 650K.
   c) Subsequent annealing to 700K resulted in a (8x2) overlayer structure.
   d) After annealing to 750K, a (10x2) overlayer structure develops.
   e) One domain of the (10x2) surface structure.
   f) Incommensurate overlayer, similar to the (10x2) structure in preparation, but with a slightly different surface stoichiometry.



XBL 818-6283

Fig.1a

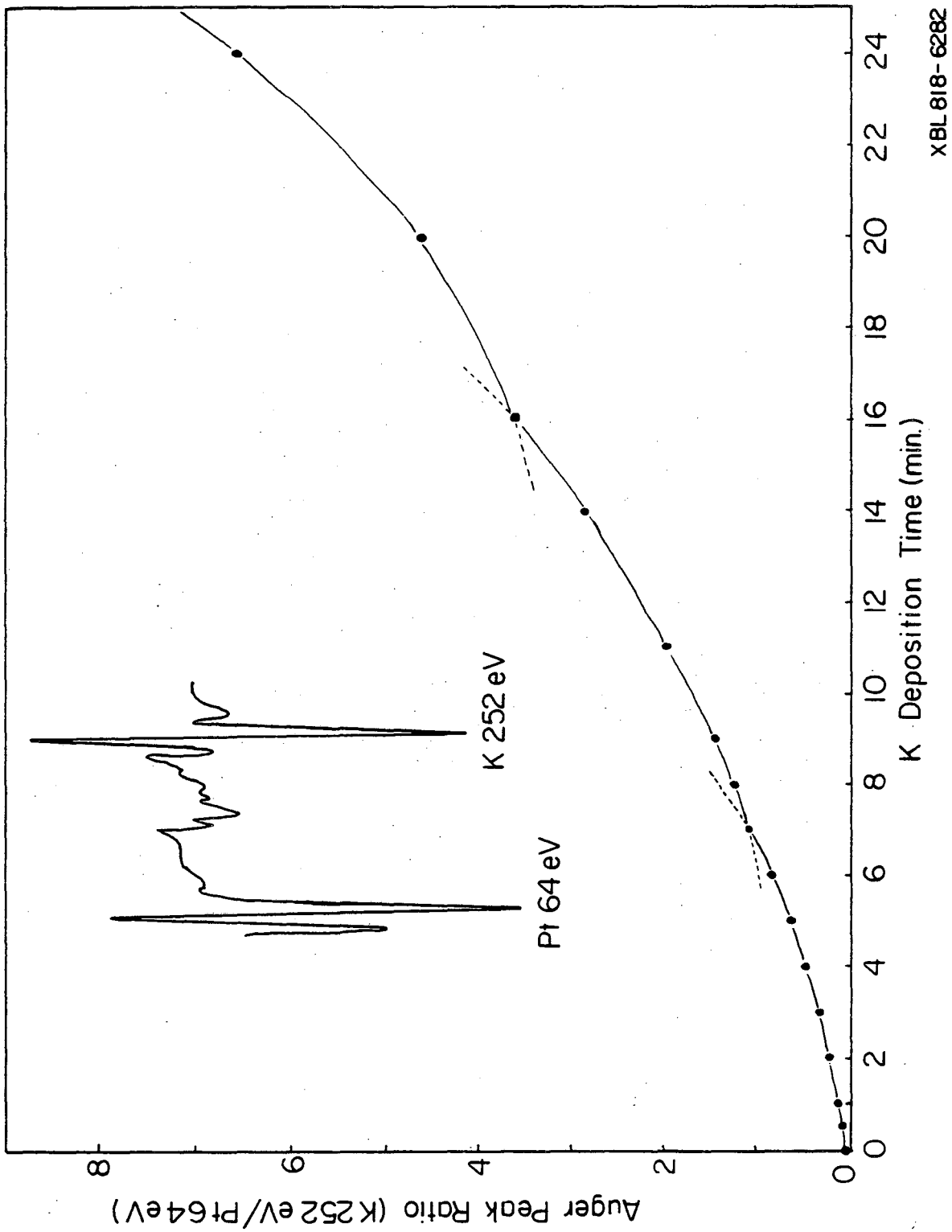
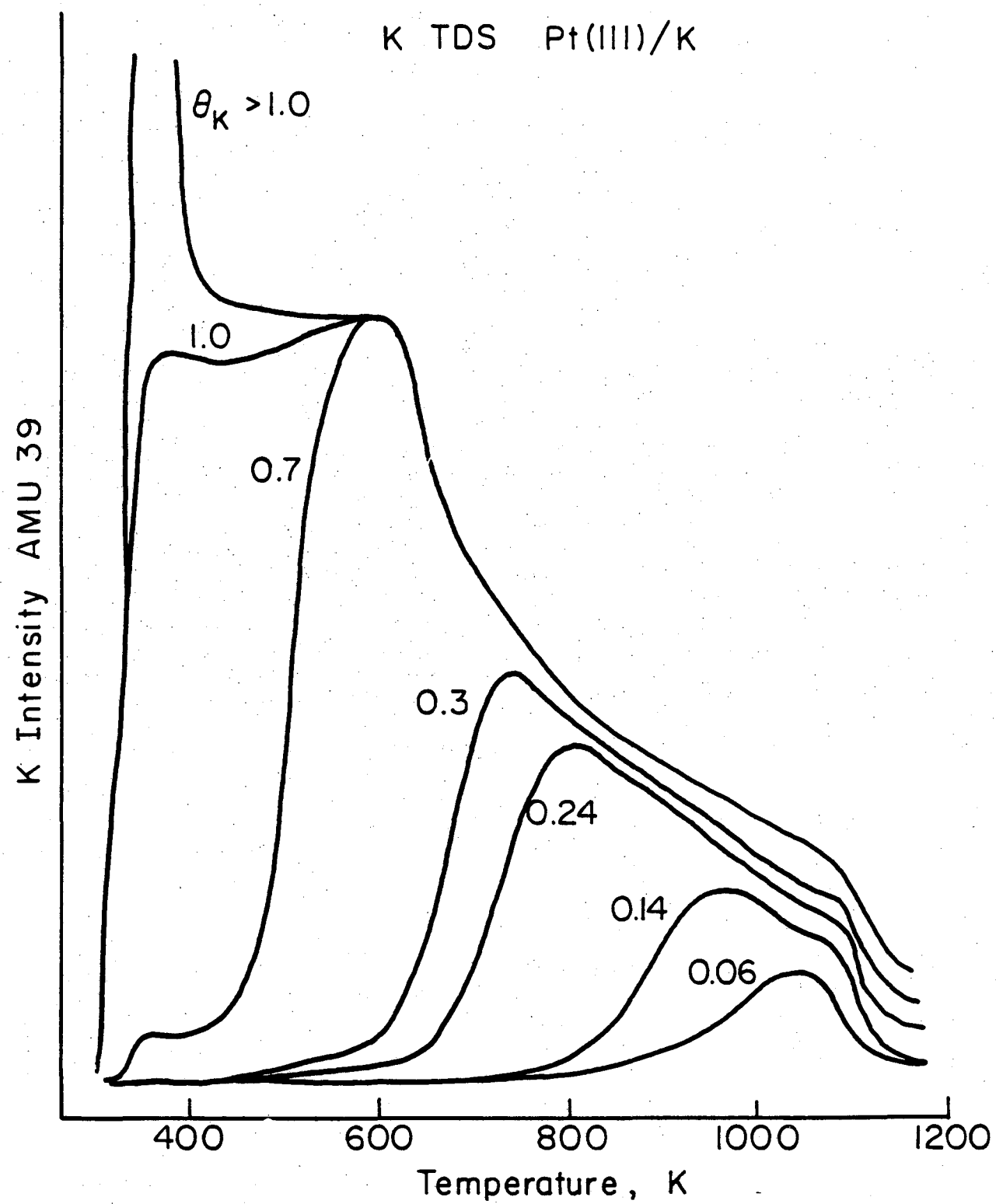

Auger Peak Ratio (K 252 eV/Pt 64 eV)
0
2
4
6
8
K Deposition Time (min.)
0
2
4
6
8
10
12
14
16
18
20
22
24
Pt 64 eV
K 252 eV
XBL 818-6282

Fig.1b



XBL 816-5909

Fig.2

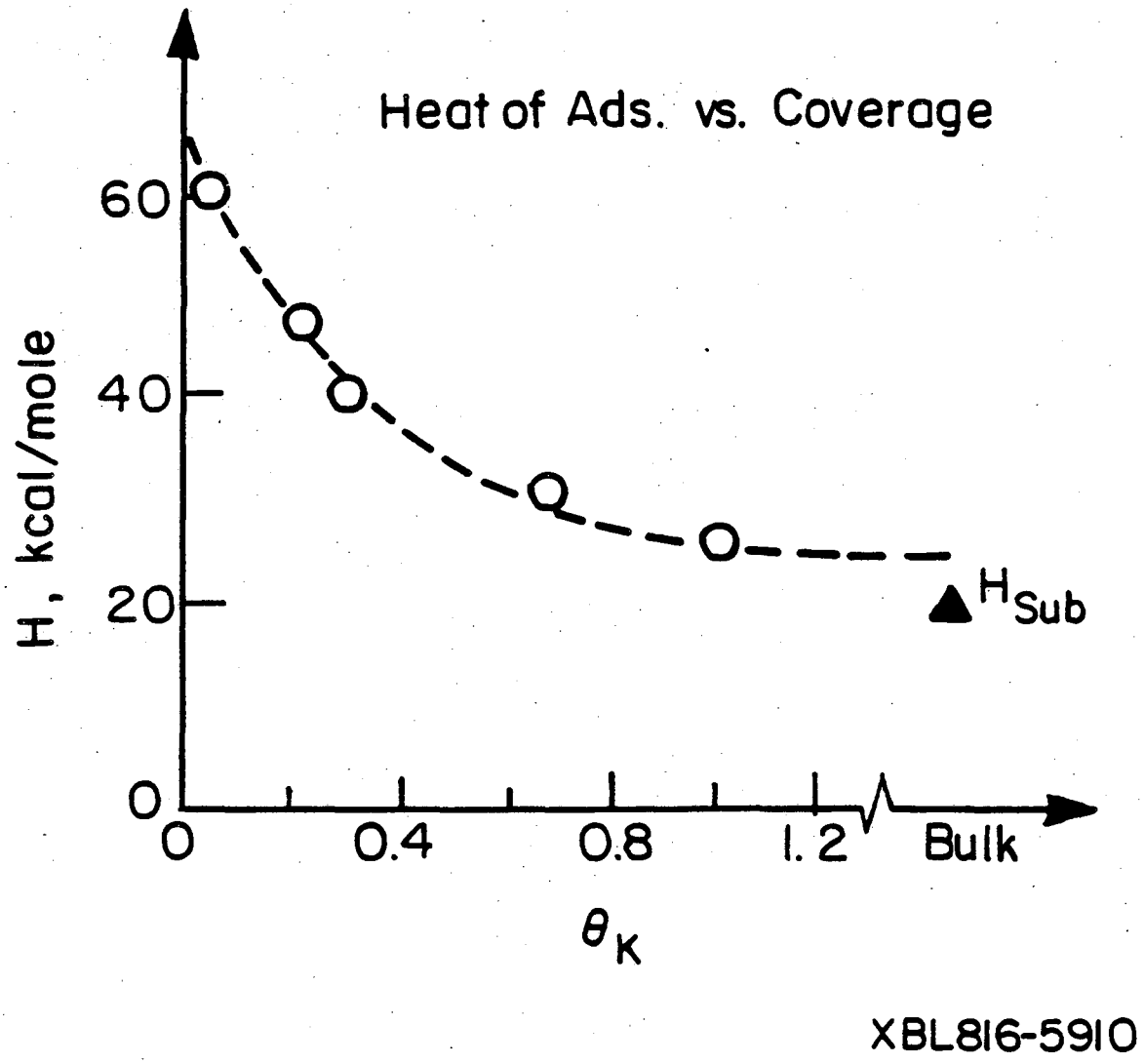
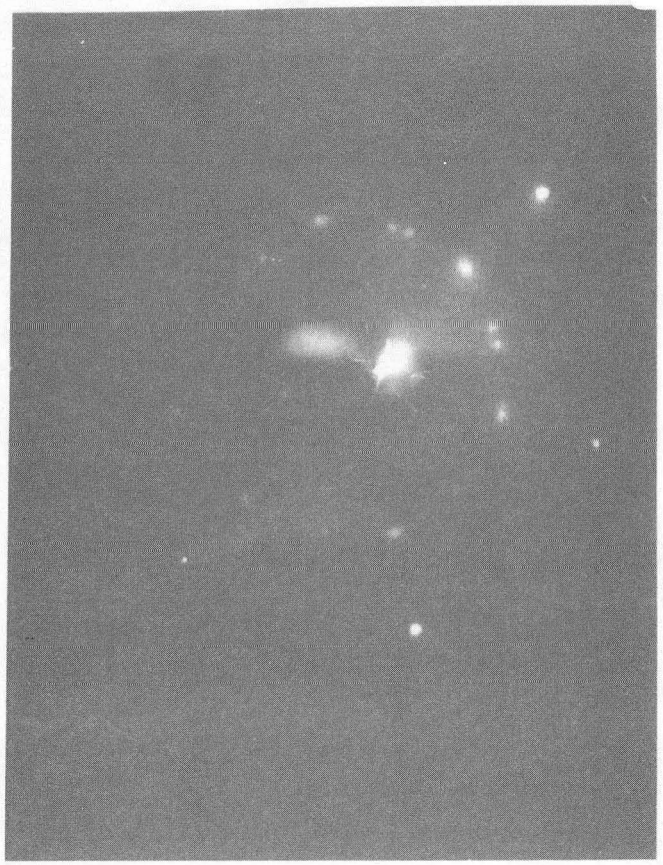

Heat of Ads. vs. Coverage
H, kcal/mole
60
40
20
0
0
0.4
0.8
1.2
Bulk
θ_K
H_{Sub}
XBL816-5910

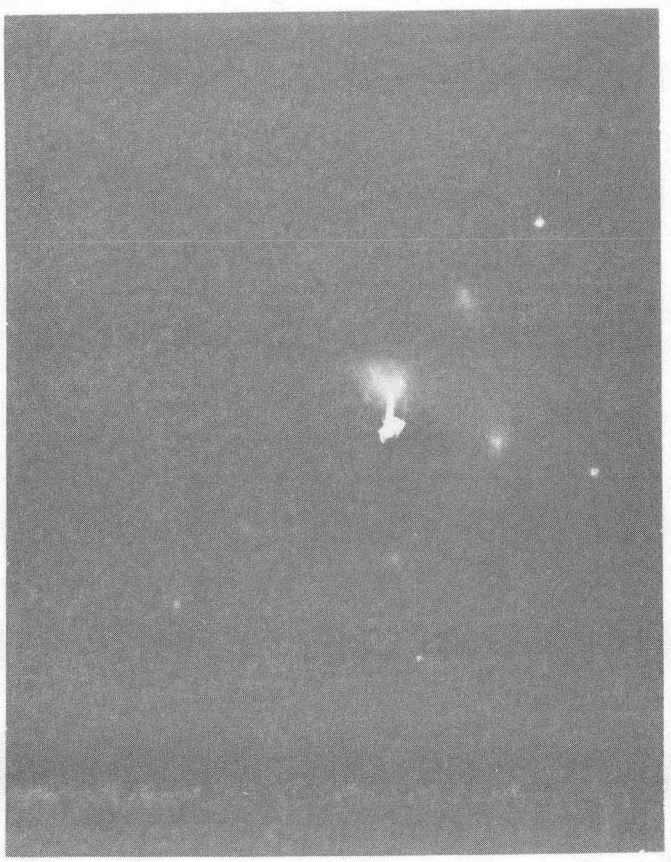
Fig.3



b

d

Fig.4



a

c

XBB815-4642

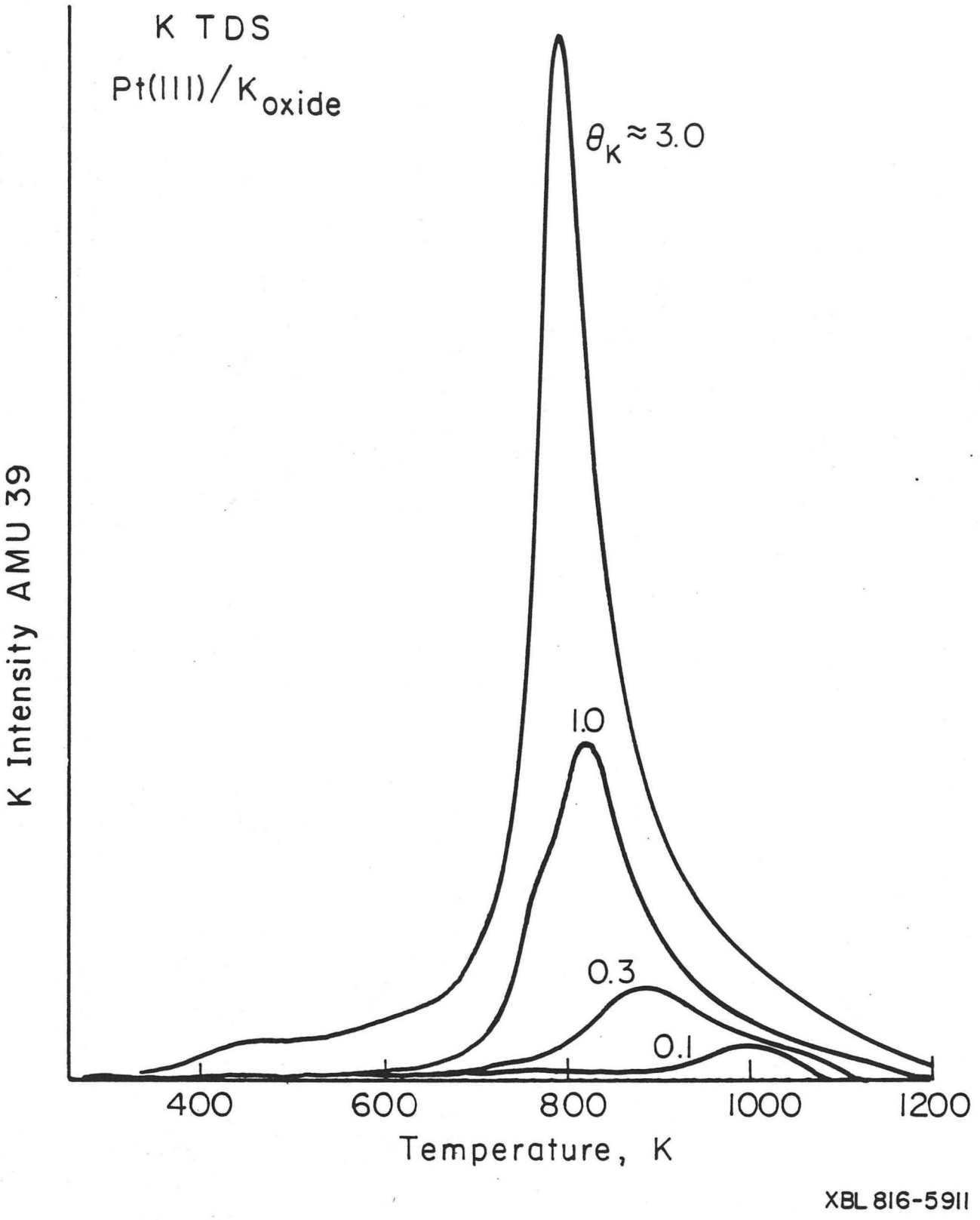
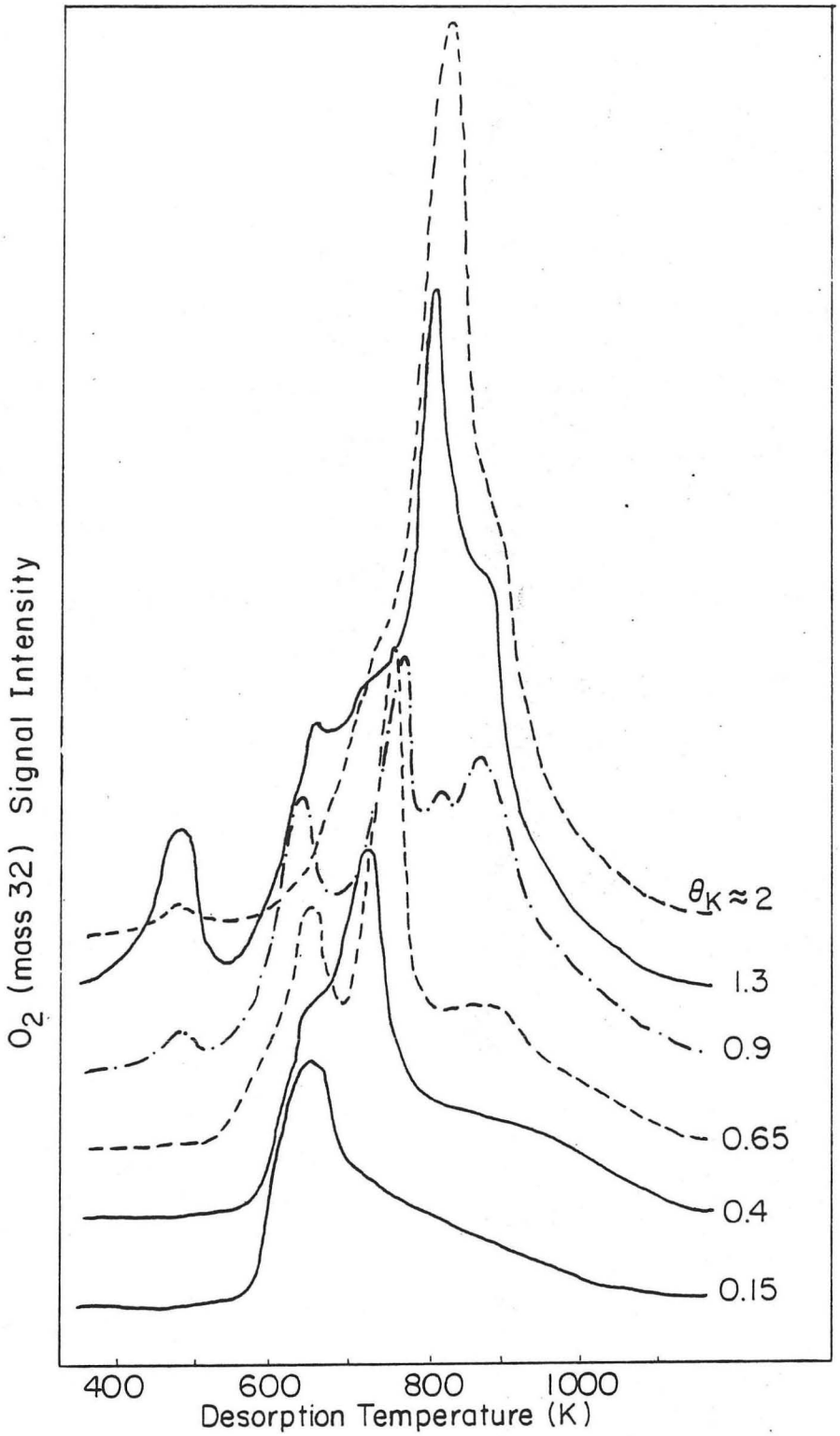
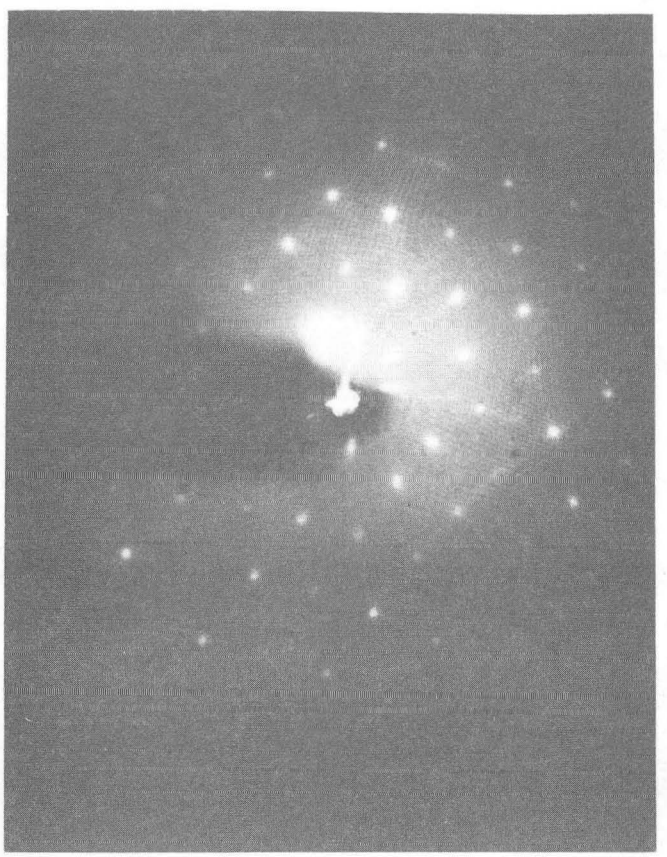

K TDS
Pt(111)/K oxide
θK ≈ 3.0
1.0
0.3
0.1
K Intensity AMU 39
400
600
800
1000
1200
Temperature, K
XBL 816-5911

Fig.5a

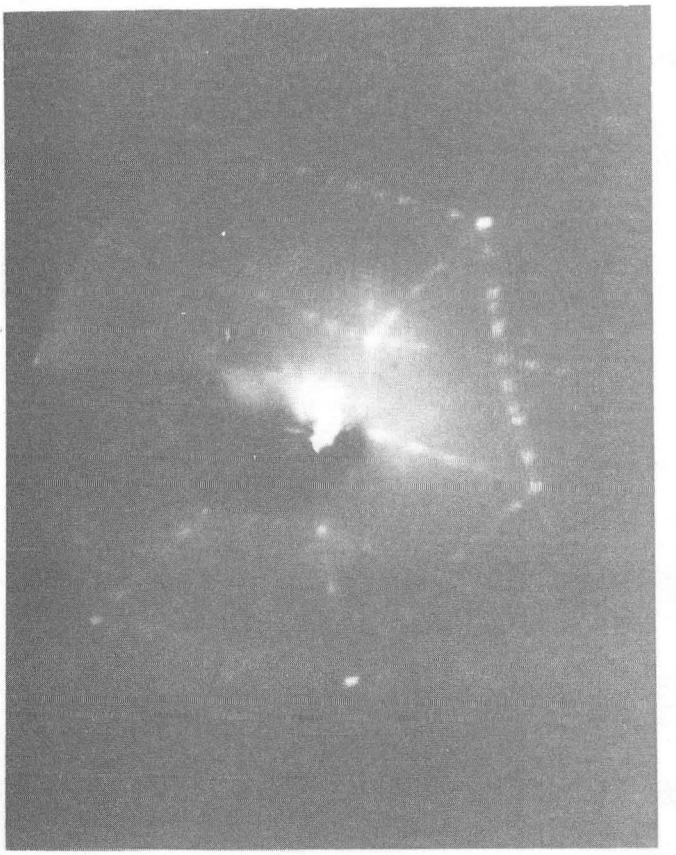


XBL818-6285

Fig. 5b

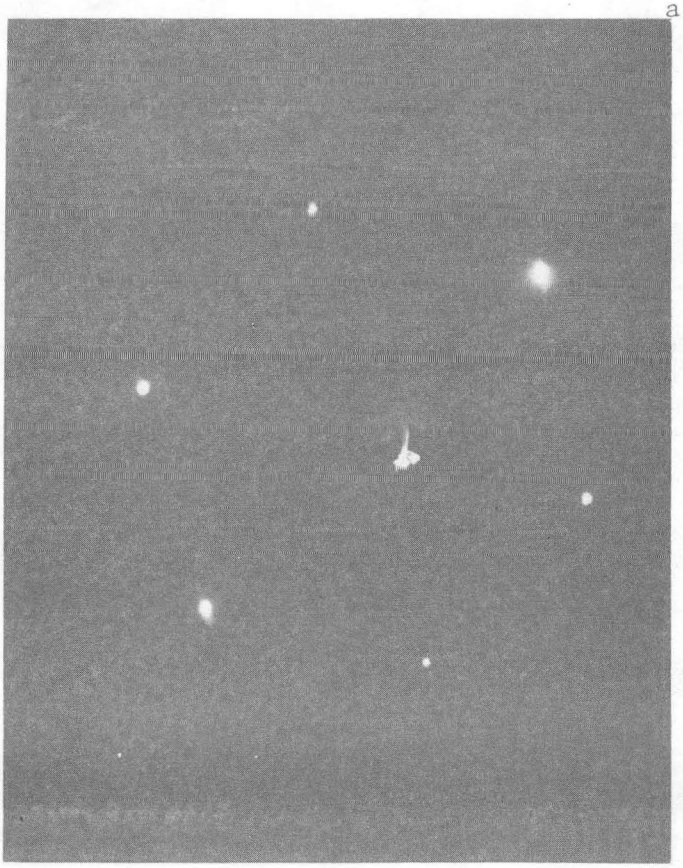


b

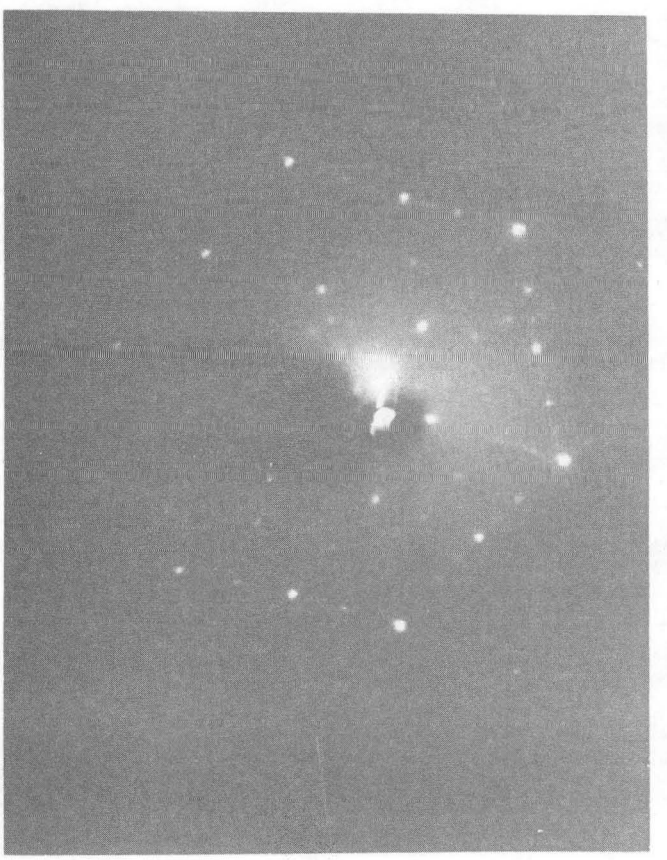


d

Fig.6
a.b.c.d

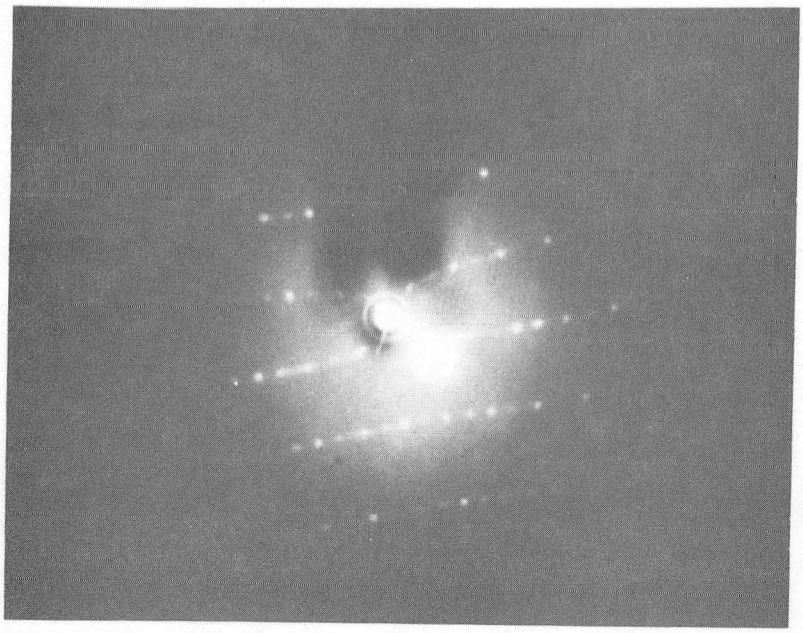


a



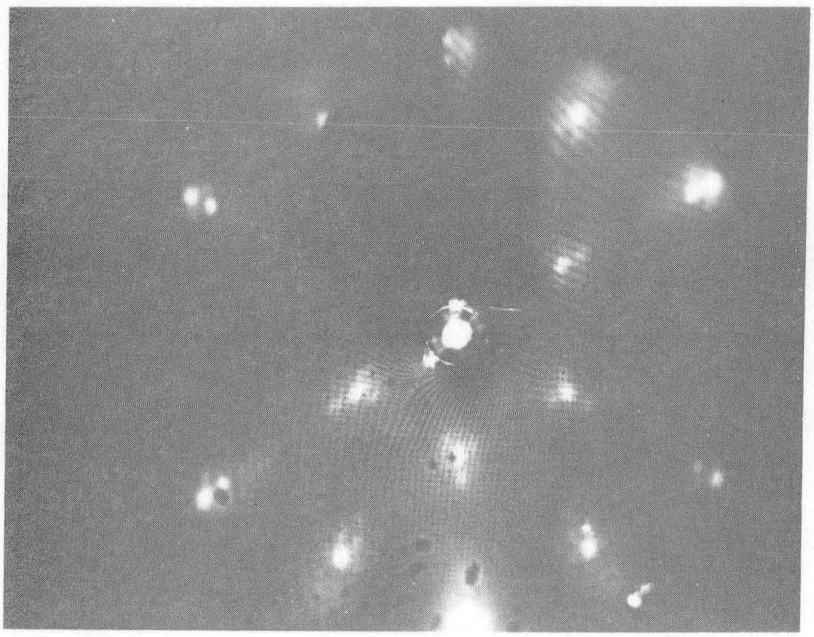
c

XBB815-4641



XBB800-12546

Fig.6
e,f



XBB818-7675

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