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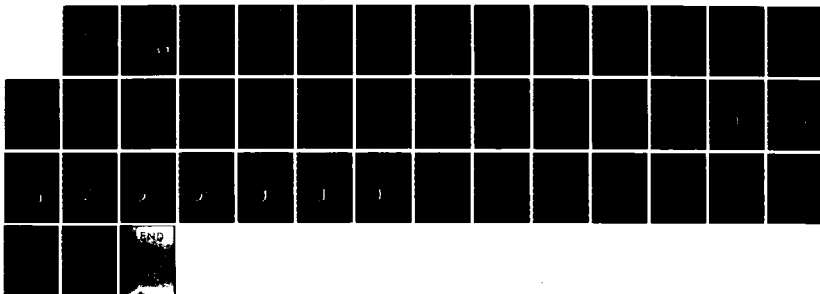
THE ADSORPTION OF CO AND OXYGEN ON CU LAYERS ON A
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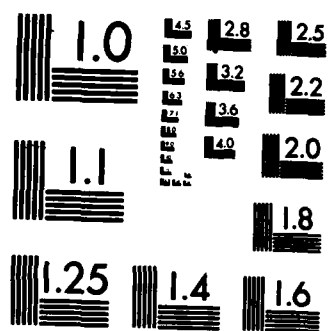
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The adsorption of CO, and to a lesser extent that of oxygen on Cu layers deposited on a W(110) surface has been investigated by thermal desorption, Auger, and XPS measurements. For CO the amount adsorbed decreases monotonically with Cu thickness from 1-5 layers. For O there is a slight increase for 1 layer, followed by a steep decrease up to 4 Cu layers where the amount adsorbed levels off. CO adsorption shifts the core levels of Cu (observed for 1 layer of Cu) to higher binding energy by 0.4 eV; the O 1s level of CO is also shifted to higher binding energy by 1.5 eV, relative to CO/W(110) suggesting that electron transfer from CO occurs

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Thermal desorption of CO at saturation coverage from Cu₁/W(110) shows desorption peaks at 195, 227, and 266 K, as well as small peaks associated with CO desorption from clean W, namely a peak at 363 K and beta-desorption peaks at 1080 and 1180 K. As CO coverage is decreased the 195 and 227 K peaks disappear successively; the W-like peaks remain unchanged in intensity. It is argued that the latter may be due to adsorption on bare W at domain boundaries of the Cu overlayer, while 190-266 K peaks are associated with adsorption on Cu, but probably involve reconstruction of the Cu layer. For n = 2-8 a single but composite peak is seen, shifting from 180 K to 150 K as Cu thickness increases as well as a minor peak at 278 K, which virtually vanishes on annealing the Cu deposit at 850 K.

The effect of tungsten electronic structure on the behavior of adsorbates on the Cu overlayers, as well as similar effects in other sandwich systems are discussed.

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The Adsorption of CO and Oxygen on Cu Layers
on a W(110) Surface

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The effect of tungsten electronic structure on the behavior of adsorbates on the Cu overlayers, as well as similar effects in other sandwich systems are discussed.

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I. INTRODUCTION

The properties of thin (≤ 1 to > 2 atomic layers) of metals deposited on more refractory substrate metals have recently attracted some attention, because of the relevance of such experiments to bimetallic catalysts. The adsorption of CO and O₂ on Pd adsorbed on W(110) surfaces has recently been reported by Prigge, Schlenk, and Bauer [1] and the adsorption of CO on ≤ 1 -2 atomic layers of Cu on Pt(111) has been studied by Shek, Stefan, Lindau, and Spicer [2]. Vickerman, Christmann, and Ertl [3] have studied CO adsorption on Cu overlayers on Ru(0001) surfaces and Yeates and Somorjai [4] the adsorption of CO on Cu adsorbed on and alloyed with Pt(111). Prigge et al. [1] find a decrease in chemisorption of CO for < 1 layer of Pd with a subsequent rise for thicker Pd deposits. They also find a relatively simple single-peaked CO thermal desorption spectrum, although peak position shifts with coverage. Shek et al. [2] concentrate mostly on the electronic properties of the Cu layers as affected by CO and find among other things that CO adsorption shifts the Cu core levels to higher binding energy. They also see relatively simple thermal desorption spectra. Vickerman, Christmann, and Ertl [3] find that Cu reduces the amount of strongly bound CO in the submonolayer regime and that for more than 1 Cu layer some high temperature desorption peaks remain. Most of their work focusses on the submonolayer regime, however. Yeates and Somorjai [4] conclude that epitaxial Cu atoms block CO adsorption without affecting CO desorption energy, but that alloying reduces CO binding energy by as much as 5 Kcal/mole.

These investigations represent bimetallic systems in which either fcc metals are deposited on fcc substrates, or in which, (in the case of Prigge, Schlenk and Bauer's work) an fcc transition metal is deposited on a bcc transition metal substrate. It appeared interesting to adsorb Cu, which has a filled d-band on a bcc transition metal substrate, namely W, to see if the

resultant sandwich layers had different electronic properties. Cu does not alloy with W, and its behavior on W(110) is known from the work of Bauer, Poppa, Todd, and Bonczek [5]: The first Cu layer is adsorbed epitaxially; a second layer shows strained Cu (111) structure. Adsorption of a third layer at 300 K also leads to a strained Cu (111) structure. Higher layers lead to spontaneous formation of 3-dimensional (111) oriented Cu crystallites, and heating to 800 K also converts the third layer to minicrystallites. Thus adsorption on 1 and 2 layers of Cu promised to prove particularly interesting. CO was chosen as the main adsorbate since its behavior on W(110) is well known [6,7]: For $T \leq 350$ K molecular, so called virgin-CO is adsorbed followed at ≥ 350 K by some desorption and conversion of the remainder to dissociated β -CO. The study of CO on Cu/W(110) was initiated some time ago, with preliminary unpublished measurements by L. Richter, R. Opila, and R. Gomer indicating, as expected, much more complex thermal desorption behavior than seen either on bulk Cu or on bulk W(110). The present work has pursued these clues in more detail and also reports some XPS and Auger measurements.

II. EXPERIMENTAL

The apparatus used has been described previously [8]. The feature of particular importance here is the cryoshielded effusion source which makes it possible to dose with CO or O₂ only the central portion of the front surface of the W(110) crystal, previously covered over its entire front surface with Cu layers of desired thickness. The Cu source consisted of a small Ta cylinder, ca. 2.5 cm long and 0.3 cm in I.D. constructed by spotwelding from a strip of 0.0025 cm thick Ta foil. 0.9 mm Ta wires spotwelded to the cylinder at the open and closed ends served as electrical lead-ins. After outgassing in vacuum the cylinder was filled with 1 cm long segments of high

purity 0.127 mm diameter Cu wires and again outgassed in an auxiliary vacuum system. After filling, the crucible was only heated to below the melting point of Cu to prevent wetting of the entire Ta surface by Cu. In this way reproducible doses could be obtained over long periods of time. The source produced pure Cu and after some initial outgassing no oxygen or other contaminants. The W crystal could be rotated in front of the Cu source and was at a distance of 5.5 cm from the latter. It could be shown by Auger profiling that the Cu deposit was uniform to within 5-10% over the entire surface of the W crystal. Dosing was accomplished by heating the Ta crucible electrically with a very stable programmable power supply. The Cu source was so located that the constancy of the Cu flux could be monitored with the quadrupole mass analyzer contained in the apparatus. The initial calibration of Cu doses was done by depositing submonolayer amounts and looking for breaks in the intensity of the Cu LVV peak at ~ 920 eV kinetic energy. These breaks were identical to those reported previously by Bauer et al. [5] and correspond to completion of individual layers as shown by temperature programmed thermal desorption: distinct peaks were seen for the first and second layers. Higher layers lead merely to increases in the lower temperature peak, without affecting that of the first layer; this behavior is identical to that reported by Bauer et al. [5]. The time required to produce a full first layer desorption peak was then used to control doses, the flux being monitored with the mass spectrometer.

The procedure used in these experiments was to clean the W crystal by heating in 10^{-7} torr of O_2 at 1500-1700 K for several hours, and to deposit Cu layers at 300 K after flashing the substrate to 2300-2500 K. After the desired Cu thickness was obtained the crystal was cooled to 80 K, rotated in front of the effusion source and dosed with either O_2 or CO to near saturation. The crystal was then rotated in front of the mass spectrometer

for thermal desorption measurements or in front of the CMA for Auger or XPS measurements. The latter employed a Mg K α source. Binding energies will be reported relative to the Fermi energy, E_F ; the collector work function had been determined previously to be stable and to have a value of 5.25 eV [8].

No attempt to carry out several adsorption measurements on a given Cu layer was made, i.e. fresh Cu deposits were used for each CO or O adsorption experiment.

III. RESULTS

A. Coverage of CO and O

Initial coverages at 80 K were obtained by measurements of the O KLL Auger intensity, using 0.4 μ incident beam current to minimize electron stimulated desorption. The results are shown in Fig. 1. For CO the amount adsorbed decreases, apparently stepwise, with increasing number of Cu monolayers. Annealing even 1 layer of Cu at 850 K before CO adsorption increases the amount adsorbed. Somewhat similar results were found for oxygen, except that a single monolayer of Cu seems to increase the amount of adsorbed O very slightly. Again the amount adsorbed on annealed Cu layers is greater than on unannealed ones. It was possible, in the case of oxygen, to prove that the smallness of the signal, relative to clean W is not the result of O diffusion underneath the Cu layer. Figure 2 shows the result of saturating a clean W surface with oxygen and then depositing increasing thicknesses of Cu on top of this. An O KLL signal is still seen for 8 Cu monolayers with 2000 eV primary electron energy. Similar results for XPS measurements of the O 1s spectrum are also shown up to 4 Cu layers. If as much O as is adsorbed on clean W moved underneath the Cu layer(s) the signal for O/Cu₁/W should be smaller than observed and the signal for O/Cu_n/W for n = 3-8,

larger than observed.

B. Thermal Desorption of CO

Temperature programmed desorption spectra for CO adsorbed at 90 K to saturation coverage on $\text{Cu}_n/\text{W}(110)$ for $n = 0, 0.5, 1, 2, 3, 4$, and 8 are shown in Figs. 3-9. The spectrum on clean W shows the behavior found previously, namely a virgin desorption peak at ~ 400 K (somewhat higher than in the step desorption work of Leung, Vass, and Gomer [6] or Kohrt and Gomer [7] because of the faster heating rate used here) and β -CO peaks at ~ 980 and 1180 K.

For a single Cu layer, $n = 1$, a very complex spectrum is seen. Its most striking feature is that there are still peaks associated with CO on clean W, namely a virgin desorption peak at 363 K and β -like peaks at 1080 and 1180 K. The latter occur at slightly higher temperatures than seen on clean W. In addition there are 3 low temperature peaks at 195, 227, and 266 K. The high temperature peaks are not artifacts since they would be seen on thicker Cu deposits if they resulted from adsorption on the crystal leads or the back of the crystal. They could possibly correspond to holes in the Cu deposit, but even this seems unlikely. When more than 1 layer of Cu was deposited and the crystal then heated to desorb the partial second layer, the 363 K and β -desorption peaks were still seen, although with slightly diminished intensity.

For $n = 2$ most of the structure seen for $n = 1$ has disappeared, with a main but obviously composite peak at ~ 180 K, and a much smaller one at 278 K. There is still some evidence of a residual peak at 376 K. For $n \geq 3$ the main peak is diminished. There is still a trace of desorption at 378 K for $n = 3$. For $n > 2$ the main peak seems unaffected (except in intensity) but the peak originally seen at 278 K moves to slightly lower temperature. Annealing at

850 K for 30 seconds reduces this last peak to almost negligible intensity, suggesting that it is associated with strained or high index regions of the Cu crystallites. Preadsorption of oxygen on 4 Cu layers before CO adsorption also reduced the 278 K peak and shifted it to slightly lower temperature. Oxygen also reduced and broadened the main peak at 150 K.

The amount of CO in each peak could be roughly estimated from the area under each peak; since desorption products are effectively beamed into the mass spectrometer, which therefore measures the desorbing flux rather than a system pressure, an exact determination requires knowledge of the velocities of molecules entering the instrument. Since this depends on desorption temperature but in an unknown way there is some error associated with this method. However, results obtained by Auger determinations of the amount of oxygen remaining after each peak was desorbed give very similar results, listed for $n = 1$ in Table I.

Results for $\text{CO}/\text{Cu}_{0.5}/\text{W}$ are similar to those for $\text{CO}/\text{Cu}_1/\text{W}$ except the intensities of the 195, 227, 266 K peaks are diminished and those of the "W-like" peaks increased. The latter also appear more nearly at the temperatures found for clean W. The total amount of CO adsorbed for $n = 0.5$ is 0.8 of that for $n = 1$ but the amount in Cu-like peaks is 5.2 times that in W-like peaks. Further, the total amount of CO in W-like peaks is only 0.1 of that on clean W(110).

Some experiments were also carried out for submonolayer CO coverages on Cu_1/W . The resulting thermal desorption spectra are shown in Figs. 10 and 11. As the initial CO deposit is decreased the 195 K and 220 K peaks vanish in order, leaving only the 263 K and the higher temperature peaks. The peak seen at 363 K on the full CO layer seems to shift to slightly lower temperature, 344 K. The β -like peaks are still intact. All the "tungsten like" peaks at $T \geq 363$ K have virtually the same intensity for $\theta_{\text{CO}} = 0.25, 0.5$ and 1.

TABLE I

Relative Amounts of CO
in Desorption Peaks
for CO/Cu₁/W(110)

<u>Peak Temperature (K)</u>	<u>Relative Amount</u>
195	15
227	27.4
266	45
363	6.3
1080 + 1182	(6)

Values were determined by measurements of the O KLL Auger intensity differences after desorption of various peaks.

C. XPS Measurements

XPS measurements for CO adsorbed on 0-4 monolayers of Cu on W(110) are shown in Figs. 12-15. For clean W the results obtained previously, namely an O 1s peak at 531.5 eV (relative to E_F) with little structure was found (Fig. 12). For $n = 1$ the main peak has shifted from 531.5 eV on clean W to 533 eV, where it remains for $n > 1$. This value agrees with that seen by Norton on bulk Cu [9]. For $n = 2$ and 4 a distinct broadening on the high binding energy side is noticeable well as a shakeoff peak at 542 eV, in agreement with that seen by Norton [9]. Partial desorption by heating diminished the intensity of the peaks but, within the resolution of our measurements, did not shift them.

A spectrum for oxygen on clean W is shown in Fig. 16. The binding energy, 530.5 eV agrees with previous measurements. The corresponding peak for O/Cu₁/W(110) is shown in Fig. 17. There is virtually no shift, relative to clean W.

Figure 18 shows a Cu 2p_{3/2} peak for Cu₁/W(110), with a binding energy of 932.8 eV. For Cu₄/W the binding energy is 933 eV. It was possible to detect shifts in binding energy of the Cu 2p_{3/2} peak caused by CO and O adsorption. Figure 19 shows the spectrum for CO/Cu₁/W(110). The Cu 2p_{3/2} peak now appears at 933.2 eV, i.e. is shifted to higher binding energy by 0.4 eV. O adsorption raises the binding energy very slightly, to 933.0 eV, i.e. by 0.2 eV (Fig. 20).

IV. DISCUSSION

A. Desorption of CO

The most striking feature of the present experiments is the appearance of quite new desorption peaks for CO on Cu₁/W(110), and the sharp break in behavior between 1 and 2 layers of Cu. It seems fairly clear that for $n \geq 3$

the substrate seems very Cu-like, and almost so for $n = 2$. For $n = 1$, however, the situation is obviously affected very strongly by the underlying W lattice. It seems probable that the desorption spectrum corresponds to distinct binding states, but it is not clear whether these correspond to intrinsically different binding sites which could be occupied at any coverage, to different adsorbate configurations, i.e. to linear vs. bridged CO, or to substrate reconstruction. The results for partial CO coverages do not answer this question. The fact that low temperature peaks are not seen at low CO coverages means either that intrinsically different binding states are filled sequentially with the tightest binding filled first, or that they are created sequentially. If intrinsically different states existed and were filled randomly at 80 K, CO mobility at the temperatures of desorption is apparently sufficient to allow all CO molecules to find the most tightly binding sites available instead of desorbing from weakly binding ones. Given the relatively closepacked structure of the bcc (110) plane and the fact that the first Cu layer is epitaxially adsorbed it seems somewhat unlikely that a large adsorbate like CO would find 3 distinct intrinsic binding sites, all leading to desorption below 300 K on a rigid substrate. It is possible that the 3 peaks, at 195, 227, and 266 K correspond to different bridge or linearly bonded CO species; however, the fact that the 227 and 266 K peaks are still seen for $\theta_{\text{CO}} = 0.5$ argues against a "crowding" mechanism. In view of the fact that $r_{\text{Cu}} = 1.28 \text{ \AA}$ (in a Cu lattice) as compared to $r_{\text{W}} = 1.37 \text{ \AA}$, so that $r_{\text{Cu}}/r_{\text{W}} = 0.93$, it seems more likely that reconstruction of the Cu layer occurs rather easily during CO adsorption. The various desorption peaks then could correspond to various stages of de-reconstruction during desorption. It is possible that LEED measurements, which are planned, will throw some light on this question.

The "tungsten-like" peaks at 363 and 1081 and 1182 K may correspond to extremes of such reconstruction, in which CO molecules displace Cu atoms sufficiently to make contact with bare W. The fact that the first of these peaks occurs at lower temperature, while the last two at higher temperature than on clean W, (or even when $\theta_{\text{Cu}} = 0.5$) suggests that additional Cu displacement may be involved during desorption. The obvious candidates for bare W sites would be boundaries between domains of Cu atoms adsorbed in either of the two sets of (chemically nearly identical) asymmetric bridge sites at each end of the hourglass wells on W(110).

The question remains to what extent the considerably higher binding energies, (judging from the peak temperatures) even for the "Cu-like" states on Cu_1/W are the result of the geometry of this layer relative to bulk Cu(111) and to what extent they are due to modifications of its electronic properties by W. Preliminary isothermal measurements indicate that the desorption kinetics in each peak are complex, corresponding to more than a single activation energy. For this reason we do not attempt here to deduce actual binding energies from peak temperatures. It is probable that both factors are important. For Cu_n/W with $n \geq 2$ there are still considerable strains in the layer but binding energies become progressively closer to those on bulk Cu. Thus it seems likely that electronic factors, an imprinting of W local density of d-states on Cu plays an important role. At the same time the distortion forced by epitaxy for $n = 1$ will also affect the electronic properties of the first Cu layer, in fact reinforcing the W d-state contribution, so that the two factors, geometry and electronic properties are closely related. As n increases the electronic influence of W must decrease, and this is quite clearly demonstrated in the reduction in desorption temperatures as n increases. Since for $n = 2, 3$ there is still effectively equal strain in the top Cu layer this effect must be electronic.

The importance of electronic effects can also be seen From Fig. 1 which shows the effect of layer thickness on the amount of CO and O adsorbed. These decrease monotonically for CO for $n \geq 1$ and monotonically for $n \geq 2$ for oxygen. This strongly suggests that some effect of the W d-band persists. The fact that annealing the layers increases the amounts of CO and O adsorbed probably means that Cu atoms randomly adsorbed on top of rather than incorporated into layers 1 and 2 bind adsorbates less strongly so that coverage increases after they have been incorporated in the layers by anneal. For $n \geq 2$ the effect probably has to do with Cu crystallite growth which locally thins the deposit, thereby making for more and stronger adsorption. The decrease in adsorption with Cu thickness cannot be blamed on geometry since CO (at finite pressure) can become closepacked on Cu assuming gas phase van der Waals dimensions [10], and slightly more than closepacked on the more tightly binding clean W surface [11].

The results for $n < 1$ are also interesting. It was pointed out that the total amount of CO bound for $n = 0.5$ is only slightly less than that on a full Cu monolayer, but that the amount bound on W is only 10%, not 50% of that on clean W. These facts suggest that submonolayer amounts of Cu at 300 K are at least partially adsorbed as isolated atoms or very small islands and that these make adsorption in their vicinity Cu-like, thereby increasing the amount of "Cu-like" CO and decreasing the "W-like" CO.

B. XPS Results

We shall discuss first the behavior of the Cu $2p_{3/2}$ level on clean W. For thick layers, Bauer et al. [5] find $\Delta\phi = -0.52$ eV; taking $\phi = 5.30$ eV as the work function of clean W(110) this gives $\phi_{\text{Cu}} = 4.78$ eV, i.e. slightly higher than the value 4.55 eV observed on polycrystalline Cu [12]. For this

quasi-(111) Cu surface the $2p_{3/2}$ peak appears at $E_b = 933$ eV, and this provides a reference level. For a single Cu layer $\Delta\phi = -0.75$ eV, relative to clean W(110) [5] and thus there is some electron depletion from Cu and one would expect a shift of core levels to higher binding energy. The opposite in fact was seen here, a small decrease by 0.2 eV. The reason for this must lie in the fact that the Cu atoms experience a potential close to that of a clean W surface ~ 5.3 eV above E_F , rather than 4.55 eV which they would see if the full $\Delta\phi$ were effective. For an effective potential of 5.3 eV the $2p_{3/2}$ level would appear at 932.5 eV, if there were no chemical shift. The difference between this value and what is seen, 932.8 eV, thus results from charge depletion and/or a partial contribution from $\Delta\phi$. The effect of CO adsorption is similar to that reported by Shek et al. [2], namely a shift of the Cu peak to higher binding energies. Since CO is adsorbed on bulk Cu with a positive dipole moment [13], i.e. negative $\Delta\phi$, this means either that $\Delta\phi$ is positive when CO is adsorbed on a single Cu layer, leading to electron depletion of Cu or that the electron drain from CO is passed on to the W substrate. A definitive answer must await work function measurements, which are planned in conjunction with UPS experiments, although the position of the O 1s level for CO on Cu/W(110) suggests that there is electron drain from CO. In the case of O adsorption there is no question that there is electron transfer to O. Nevertheless, the Cu binding energy shifts only very slightly to higher values, namely by 0.2 eV for Cu_1/W . Since much larger Cu first layer shifts are seen on bulk Cu, [14], this strongly suggests that the electron drain from Cu is made up by electron transfer from W to Cu.

For O adsorption there is very little shift of the O 1s peak from clean W to Cu_1/W . This suggests that the small O atoms also do not see the full $\Delta\phi$ resulting from Cu adsorption, or that the decrease in effective potential at the O atom is compensated by the work function increase resulting from O

adsorption.

The shifts of the O 1s peak of molecularly adsorbed CO on Cu₁/W relative to clean W can be explained reasonably well by assuming that CO sees the full $\Delta\phi$ resulting from Cu adsorption as well as an additional decrease resulting from its own adsorption. Alternately the increased binding energy of 1.3 eV relative to adsorption on clean W could arise from a combination of the $\Delta\phi$ of Cu and charge transfer from CO to W. It is interesting that the shakeup and the shakeoff peaks seen on bulk Cu begin to appear already for 2 Cu layers, in line with the fact the desorption behavior is already very Cu-like on 2 layers.

V. COMPARISON WITH RELATED WORK

The results found for CO adsorption on the Cu/W(110) system differ markedly in some respects from adsorption on other bimetallic systems. We find a monotonic decrease in CO adsorption with Cu layer thickness while Prigge, Schlenk, and Bauer [1] find that a layer of Pd totally suppresses CO, but not O adsorption. For thicker Pd layers CO adsorption apparently then gets stronger again, reflecting the fact that CO on bulk Pd is reasonably strongly adsorbed. Thus there seems to be destructive interference between Pd and W d-orbitals, as far as CO adsorption is concerned. This could arise from an effective filling of Pd 4d-bands, via tungsten induced rearrangement of Pd 5s and 4d electrons, with some back donation of 5s electrons to W compensated by 5d-4d interactions, making the Pd monolayer relatively inert. For O adsorption the high electronegativity of O is apparently able to break this W-Pd interaction. For Cu on W(110) the only electronic effect possible would be to impose some d-character on the Cu layer, thereby enhancing the adsorption, relative to pure Cu (although decreasing it, relative to pure W).

Submonolayer amounts of Pd apparently suppress CO adsorption, which fits with the above hypothesis. As far as one can tell from Fig. 1 of Ref. 1 the

effect seems linear. For Cu on W(110) on the other hand submonolayer amounts of Cu suppress CO adsorption more strongly as already noted. It is not entirely clear why there should be this difference between Cu and Pd, but it is possible that it is connected with larger island sizes for Pd than for Cu.

Vickerman, Christmann, and Ertl [3] find that Cu reduces the amount of strongly bound CO on Ru(0001) as one would expect, but also that isolated Cu atoms seem to form $\text{Cu}(\text{CO})_2$ complexes, or at least that at low θ_{Cu} the amount of CO adsorbed is twice that on clean Ru(0001), if weakly bonded CO i.e. that adsorbed at 150 K is included. They invoke electron transfer from Ru to Cu for increasing the ease of back-donation bonding to CO for this effect. Since W and Ru have nearly equally filled d-bands, the differences between W and Ru must in some way result from the fact that Ru is a 4d, and W a 5d metal. The fact that 4d and 5s orbitals are probably more tightly bound in Ru than the corresponding 5d and 6s ones in W argues somewhat against the charge transfer mechanism invoked by Vickerman et al. [3]. It seems more probable, in view of the weak CO binding attributable to Cu atoms on Ru that binding on Cu leads to charge transfer in the opposite direction, as also suggested by the sign of the work function change of CO adsorbed on Cu (on Cu/Ru surfaces).

For Cu on Pt Yeates and Somorjai [4] seem to find only that Cu blocks Pt sites without affecting the latter in other ways. Presumably this is due to the already weak adsorption of CO on Pt with its nearly full 5d band, which is not appreciably perturbed by Cu.

VI. CONCLUSION

The results available so far for various bimetallic sandwich systems suggest that interactions with adsorbates depend on a variety of factors, electronic and structural. The former seem to depend rather subtly on the electronic structure of substrate and overlayer metals, with charge self-

consistency probably playing an important role. It seems fairly clear, however, that the electronic properties of a substrate like W strongly affect the first, and to a lesser extent even the second layer of an adsorbed metal like Cu. The structural factors cannot be completely divorced from electronic effects, but, in the case of Cu on W(110) the smaller size of Cu seems to make reconstruction of the epitaxially adsorbed first Cu layer a reasonable explanation for the multiplicity of desorption peaks observed for CO/Cu₁W(110).

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FIGURE CAPTIONS

1. Saturation coverage of CO and O adsorbed on copper layers on W(110), relative to coverage on clean W vs. copper thickness in monolayers. Conditions as on figure. TPD refers to values obtained from temperature programmed desorption.
2. Intensities of O 1s photoelectron intensity (XPS) and KLL Auger electron intensity (Auger) for oxygen adsorbed on a W(110) surface and subsequently covered by varying thicknesses of Cu at 300 K as function of Cu thickness in monolayers.
3. Temperature programmed desorption (TPD) spectrum of CO adsorbed at 90 K on a clean W(110) surface to saturation coverage. Sweep rate ~ 4.4 K/sec.
4. TPD spectrum of CO adsorbed at 90 K to saturation on W(110) surface on which 0.5 monolayers of Cu were first adsorbed at 300 K. Sweep rate ~ 4.4 K/sec.
5. TPD spectrum of CO adsorbed to saturation at 90 K on 1 monolayer of Cu, adsorbed at 300 K on a W(110) surface. Sweep rate ~ 4.4 K/sec.
6. TPD spectrum of CO adsorbed to saturation at 90 K on 2 monolayers of Cu, adsorbed at 300 K on a W(110) surface. Sweep rate ~ 4.4 K/sec.
7. TPD spectrum of CO adsorbed to saturation at 90 K on 3 monolayers of Cu, adsorbed at 300 K on a W(110) surface. Sweep rate ~ 4.4 K/sec.
8. TPD spectrum of CO adsorbed to saturation at 90 K on 4 monolayers of Cu, adsorbed at 300 K on a W(110) surface. Sweep rate ~ 4.4 K/sec.
9. TPD spectrum of CO adsorbed to saturation at 90 K on 8 monolayers of Cu, adsorbed at 300 K on a W(110) surface. Sweep rate ~ 4.4 K/sec.

10. TPD spectrum of 0.25 monolayers of CO adsorbed at 90 K on 1 monolayer of Cu previously adsorbed on W(110) at 300 K. Sweep rate ~ 4.4 K/sec.
11. TPD spectrum of 0.5 monolayers of CO adsorbed at 90 K on 1 monolayer of Cu previously adsorbed on W(110) at 300 K. Sweep rate ~ 4.4 K/sec.
12. O 1s photoelectron spectrum for CO adsorbed to saturation at 90 K on a clean W(110) surface. Binding energy refers to Fermi energy. The background for clean W has been subtracted. Mg K α radiation.
13. O 1s photoelectron spectrum for CO adsorbed to saturation at 90 K on 1 monolayer of Cu previously adsorbed at 300 K on W(110). The Cu₁/W(110) spectrum has been subtracted. Mg K α radiation.
14. O 1s photoelectron spectrum for CO adsorbed at 90 K to saturation on 2 monolayers of Cu adsorbed at 300 K on W(110). Cu₂/W(110) spectrum has been subtracted. Mg K α radiation.
15. O 1s photoelectron spectrum for CO adsorbed to saturation on 4 monolayers of Cu adsorbed at 300 K on W(110). Cu₄/W(110) spectrum has been subtracted. Mg K α radiation.
16. O 1s photoelectron spectrum for oxygen adsorbed to saturation on a clean W(110) surface at 90 K. W(110) spectrum has been subtracted. Mg K α radiation.
17. O 1s spectrum of oxygen adsorbed at 90 K on 1 monolayer of Cu adsorbed at 300 K on W(110). Cu₁/W(110) spectrum has been subtracted. Mg K α radiation.
18. Cu 2p_{3/2} photoelectron spectrum for 1 monolayer of Cu adsorbed at 300 K on W(110). Spectrum taken at 90 K. Mg K α radiation.

19. Cu $2p_{3/2}$ photoelectron spectrum for CO adsorbed to saturation at 90 K on a monolayer of Cu adsorbed on W(110) at 300 K. Mg K α radiation.
20. Cu $2p_{3/2}$ spectrum for oxygen adsorbed to saturation at 90 K on 1 monolayer of Cu adsorbed on W(110) at 300 K. Mg K α radiation.

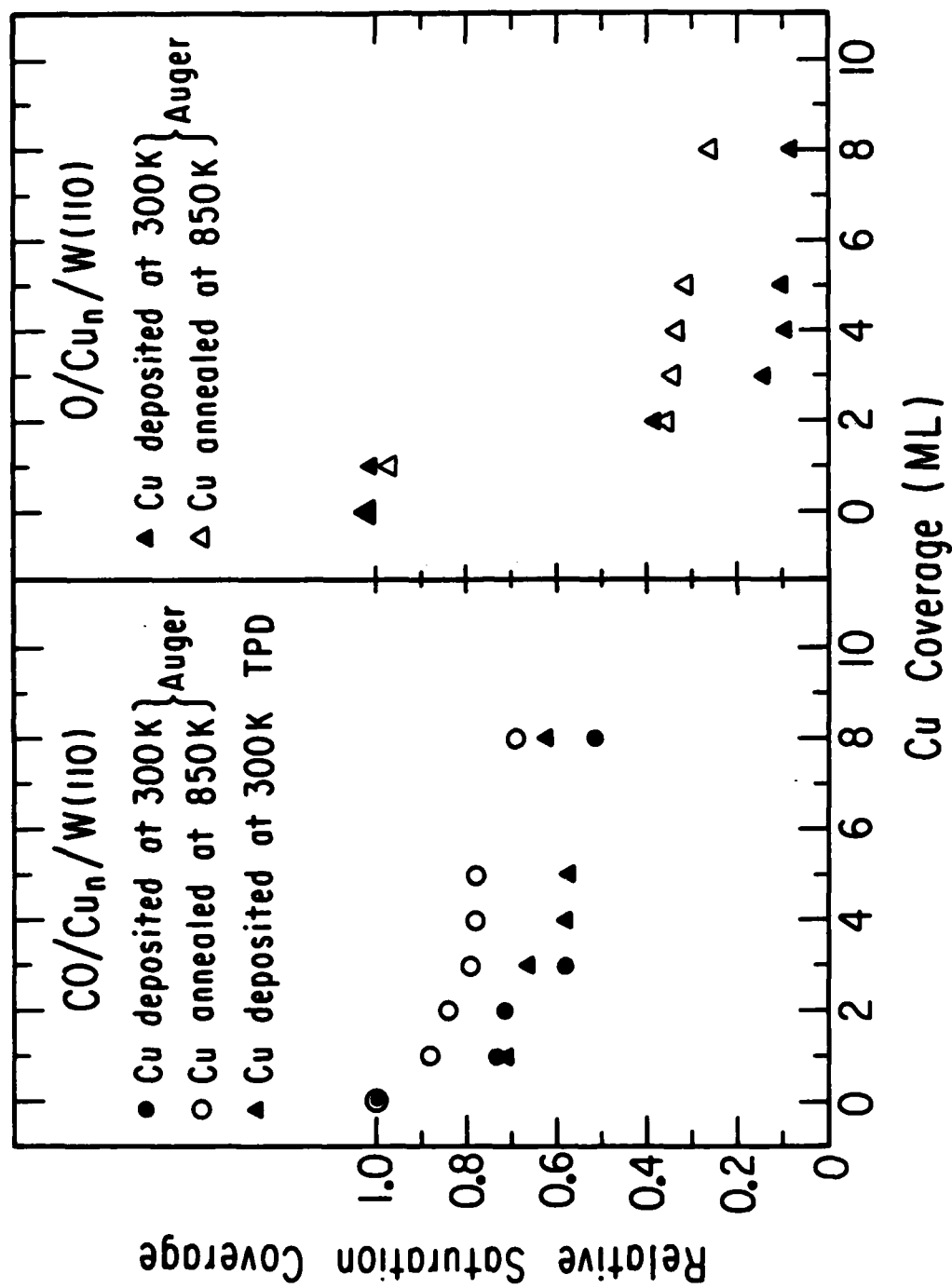


Fig.1

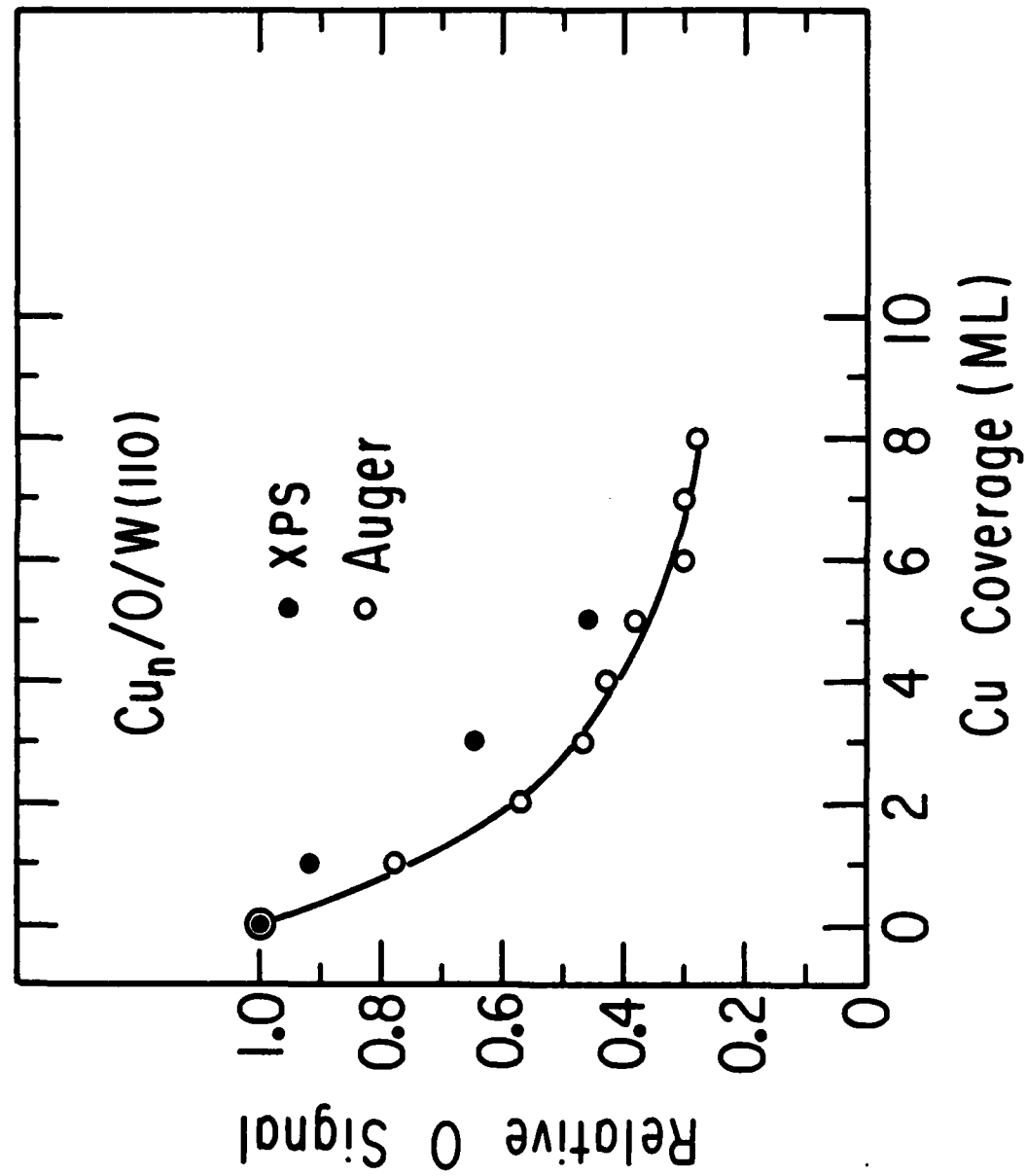


Fig.2

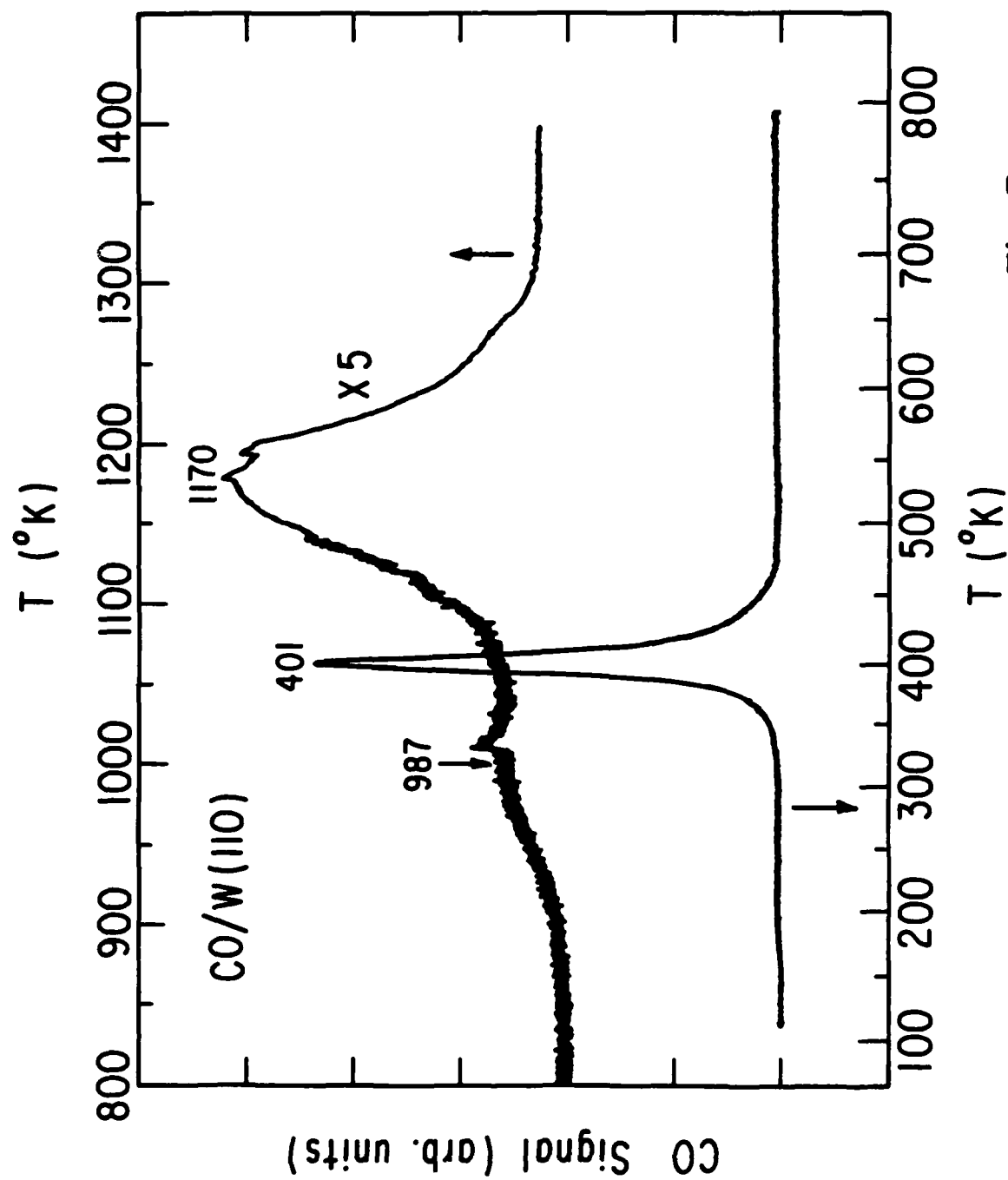


Fig.3

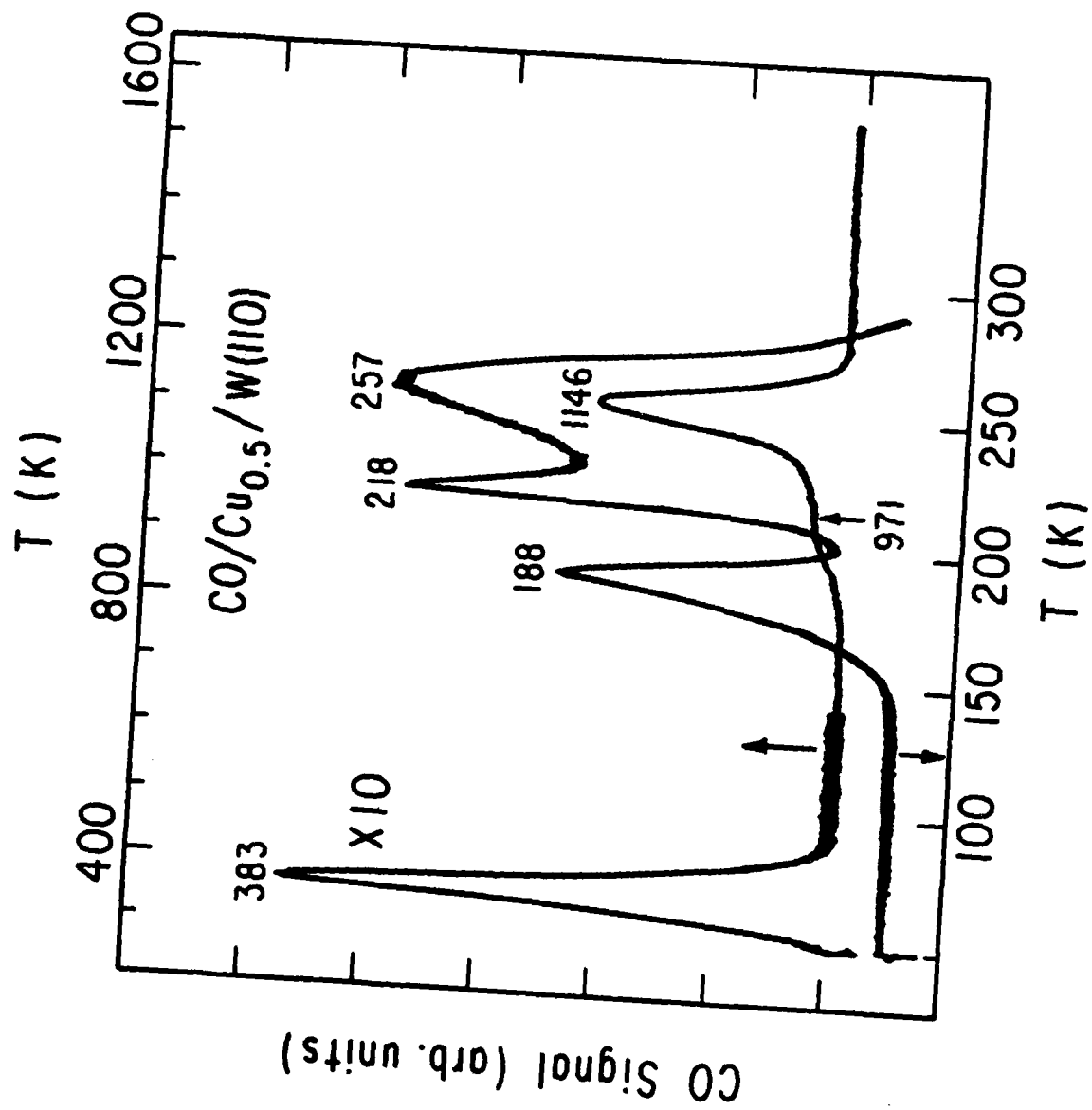


Fig.4

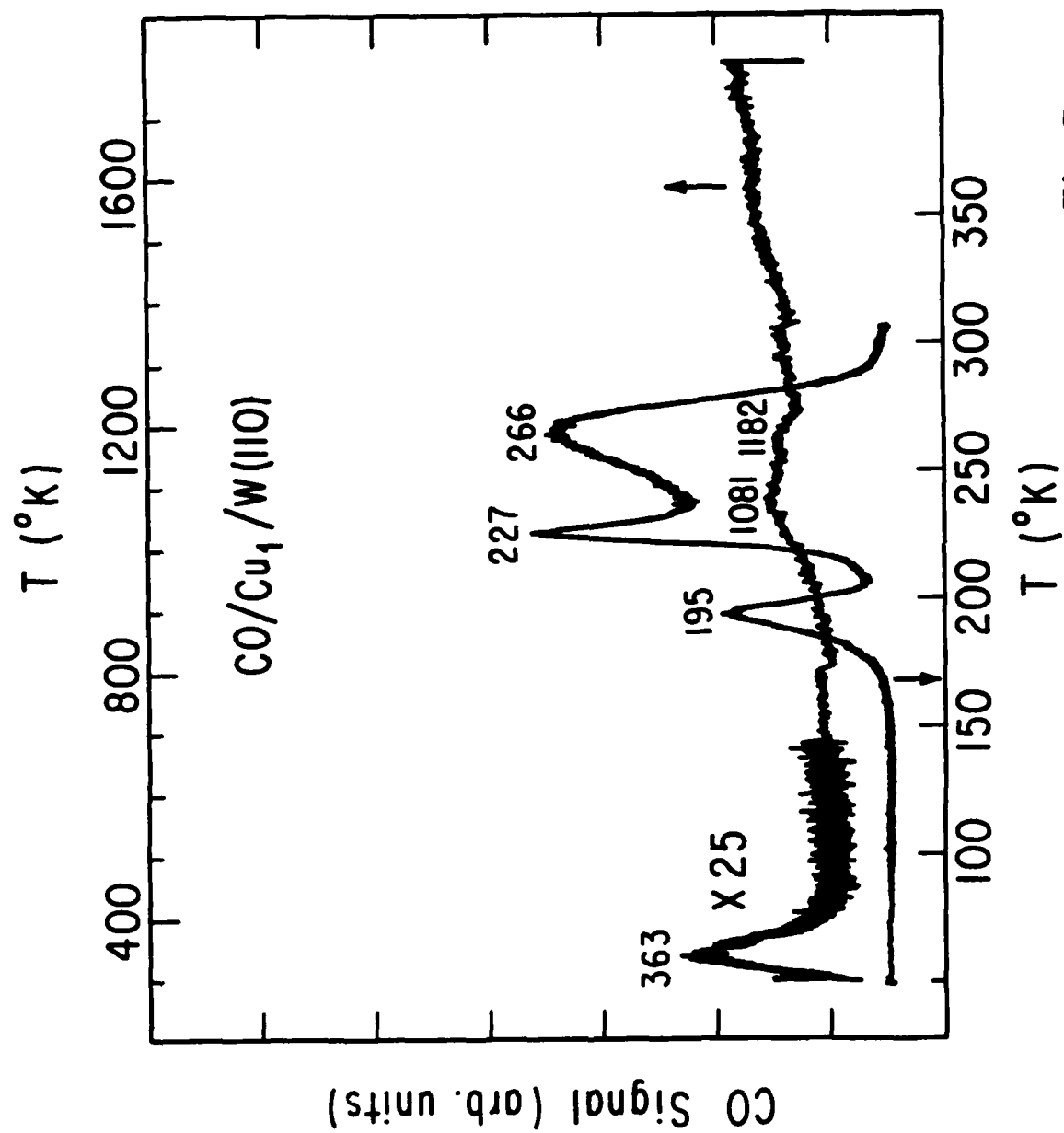


Fig.5

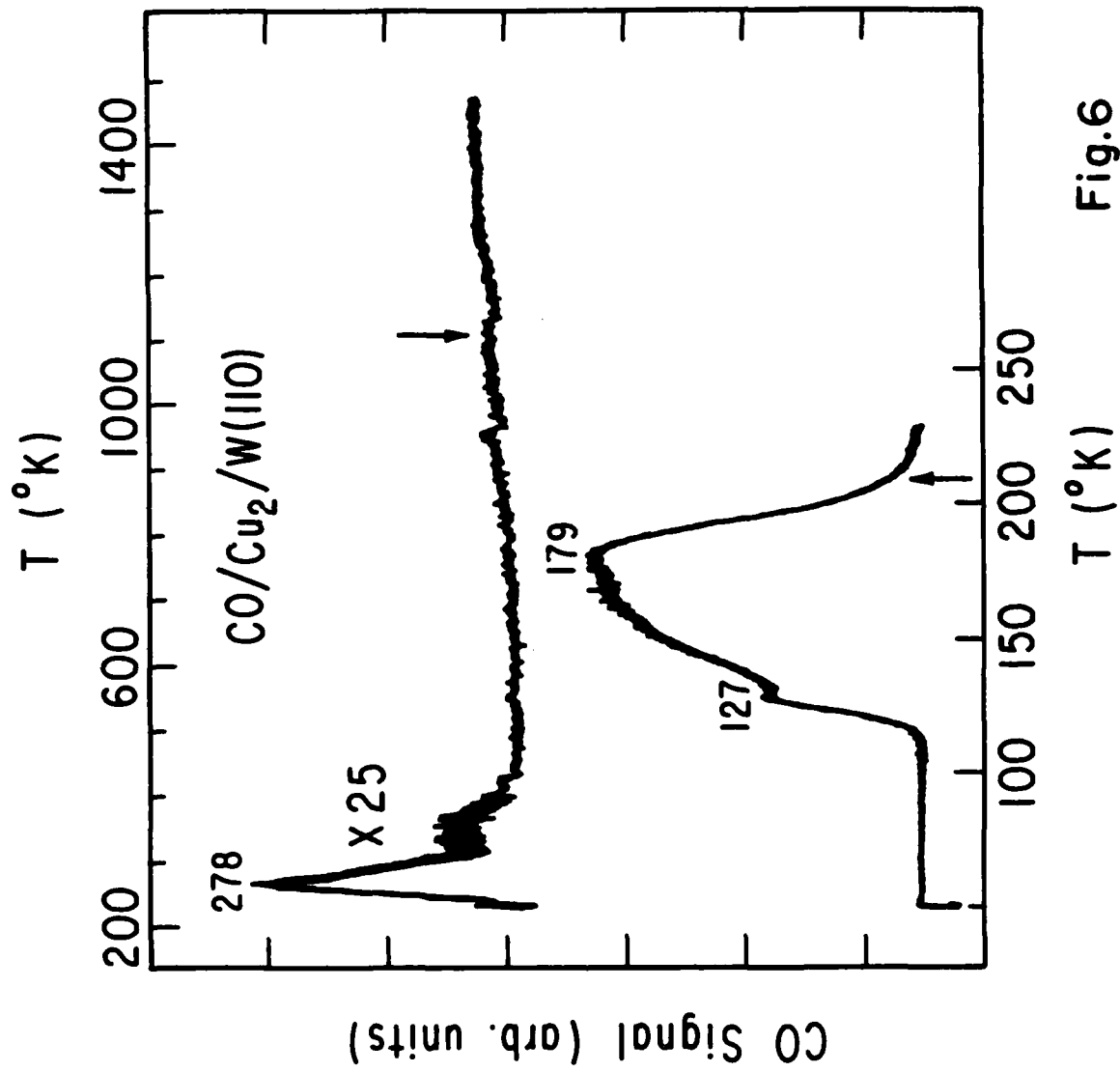


Fig.6

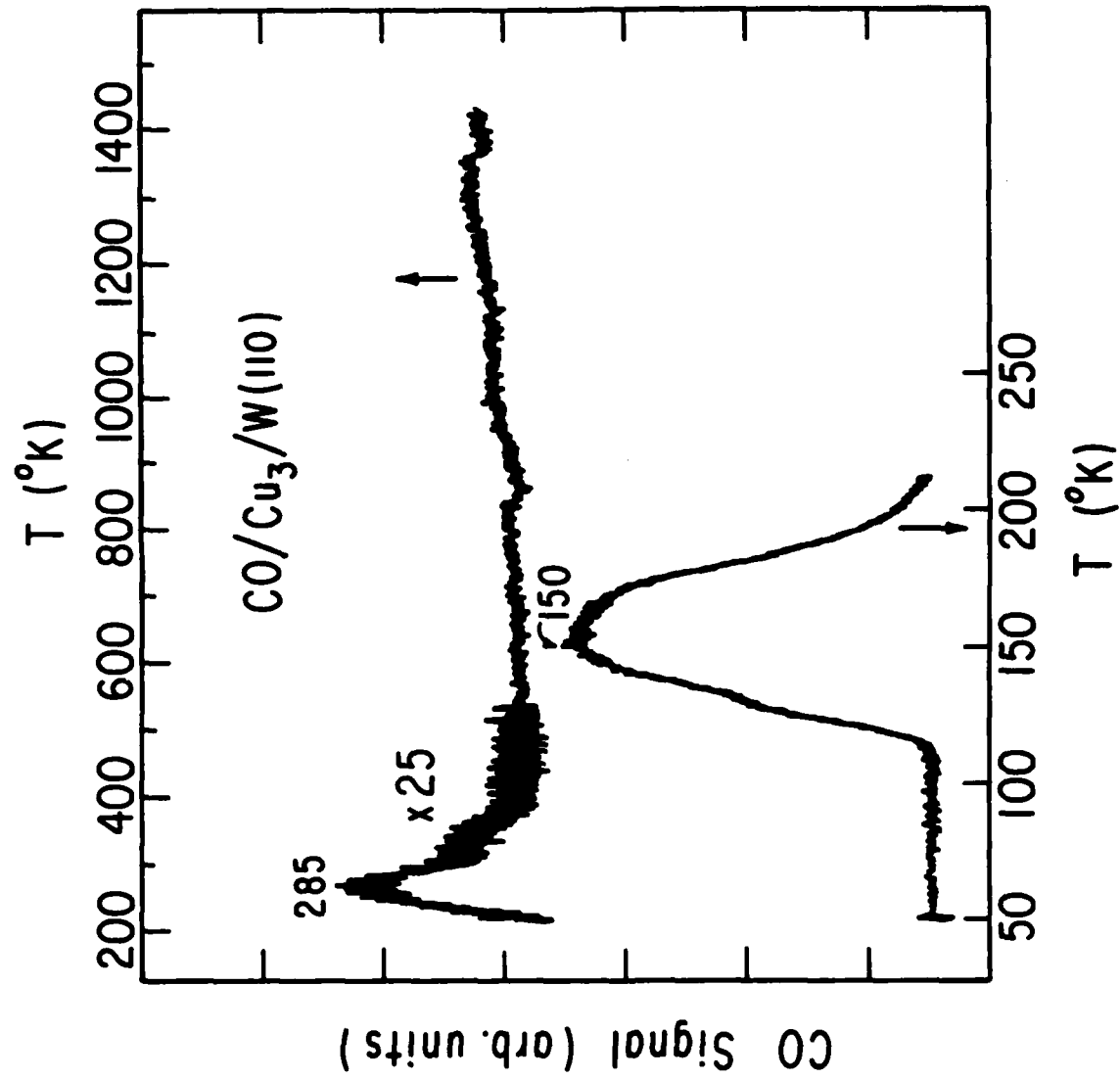


Fig.7

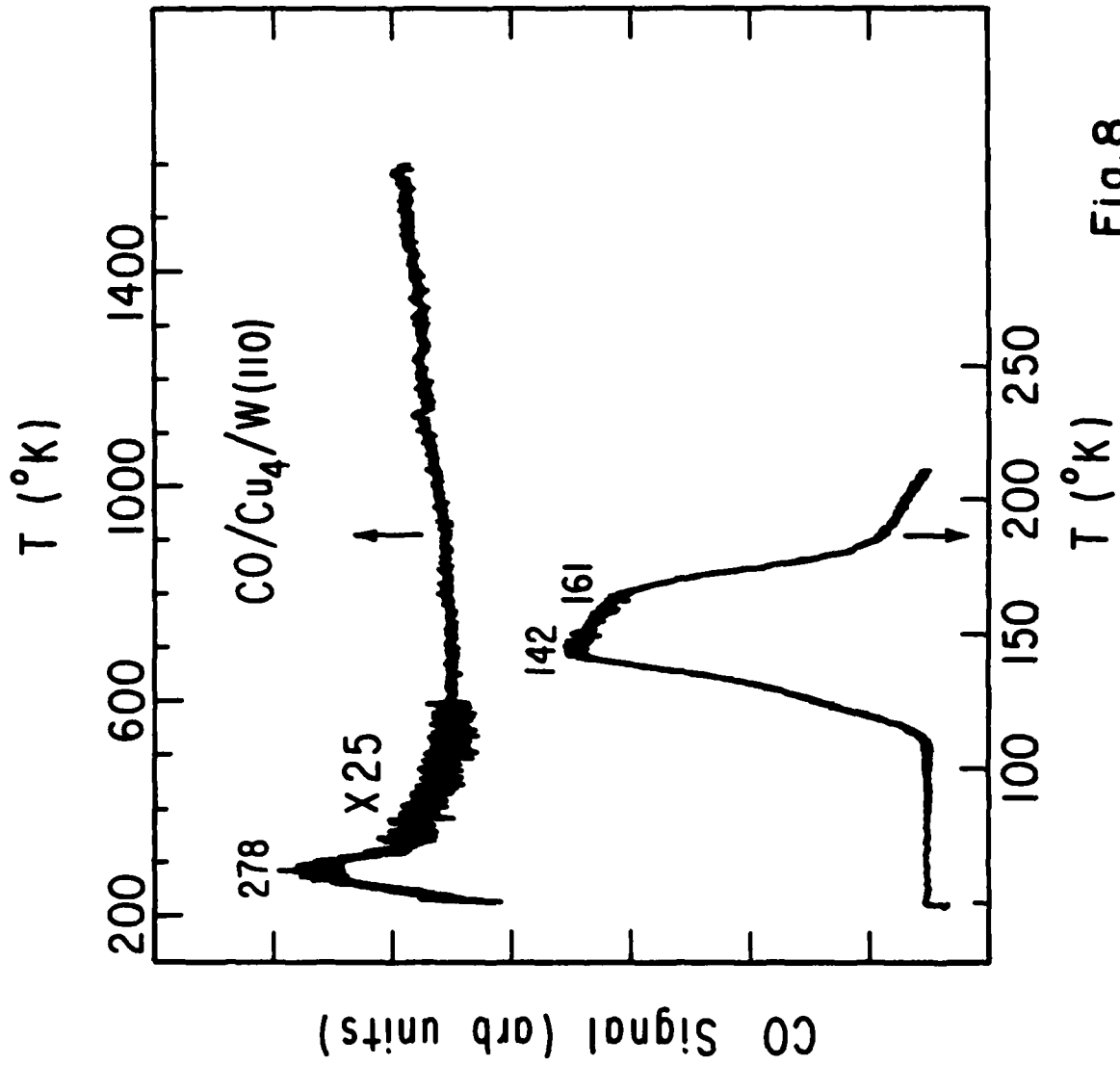


Fig.8

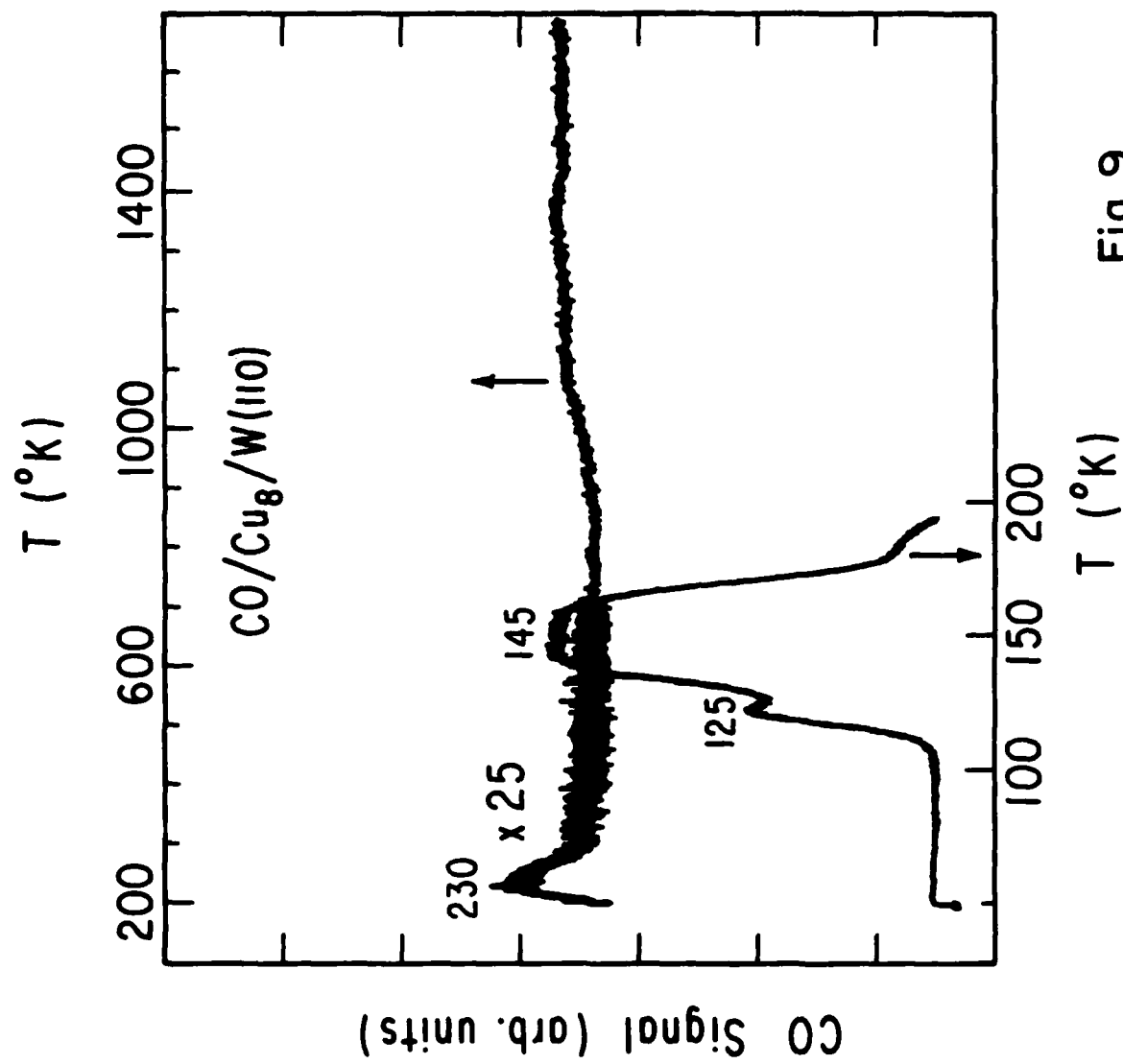


Fig. 9

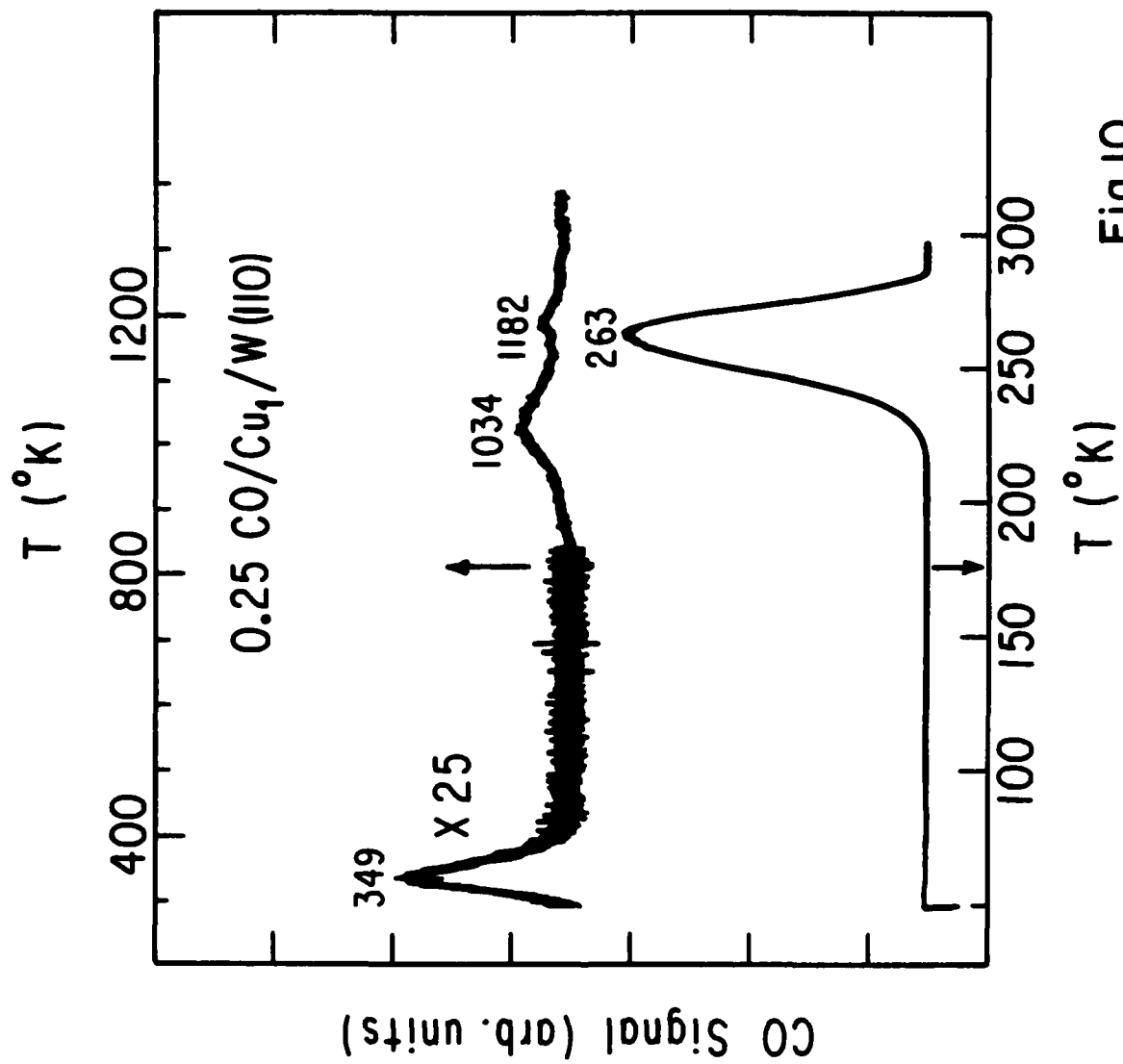


Fig.10

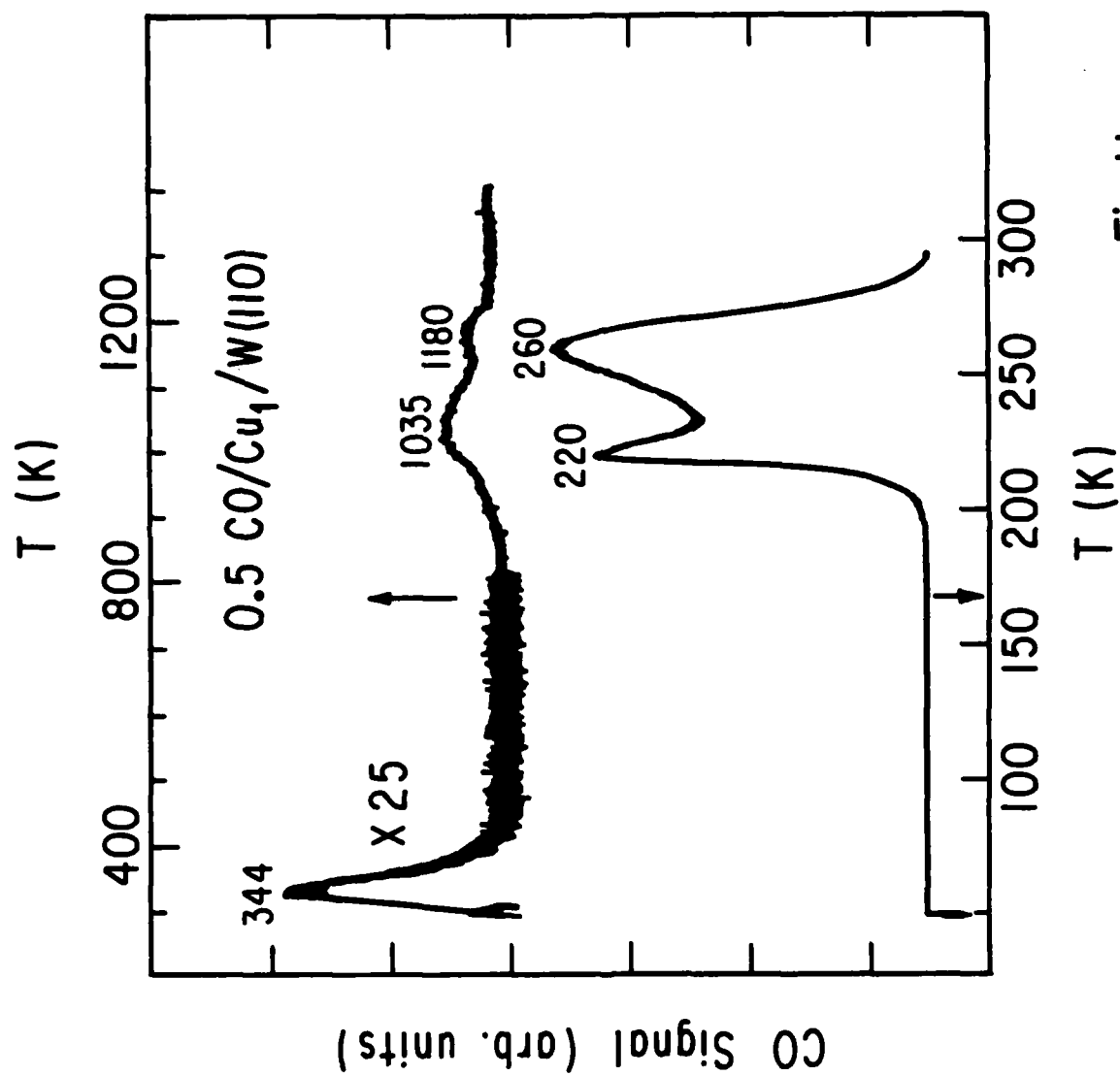
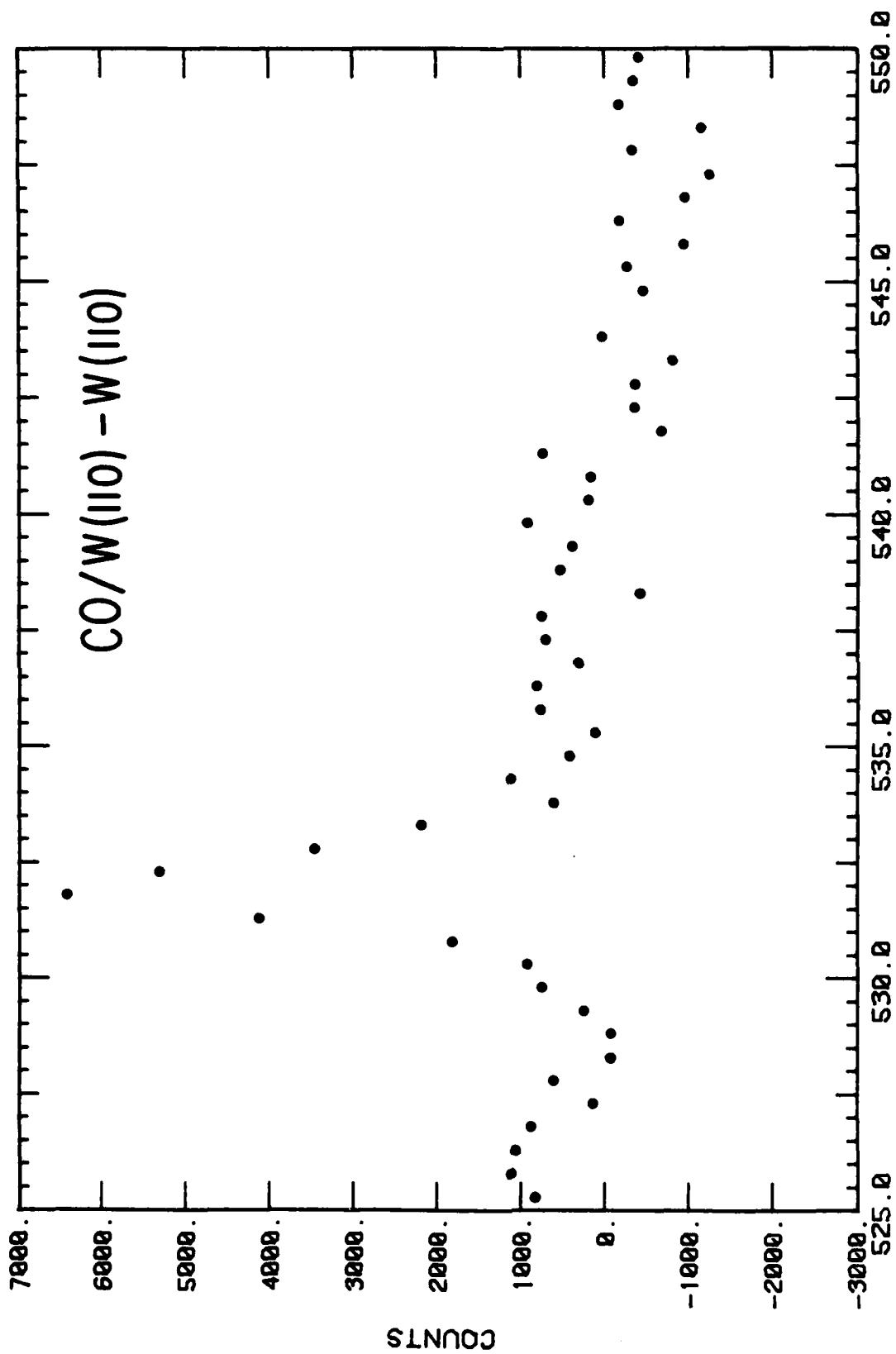
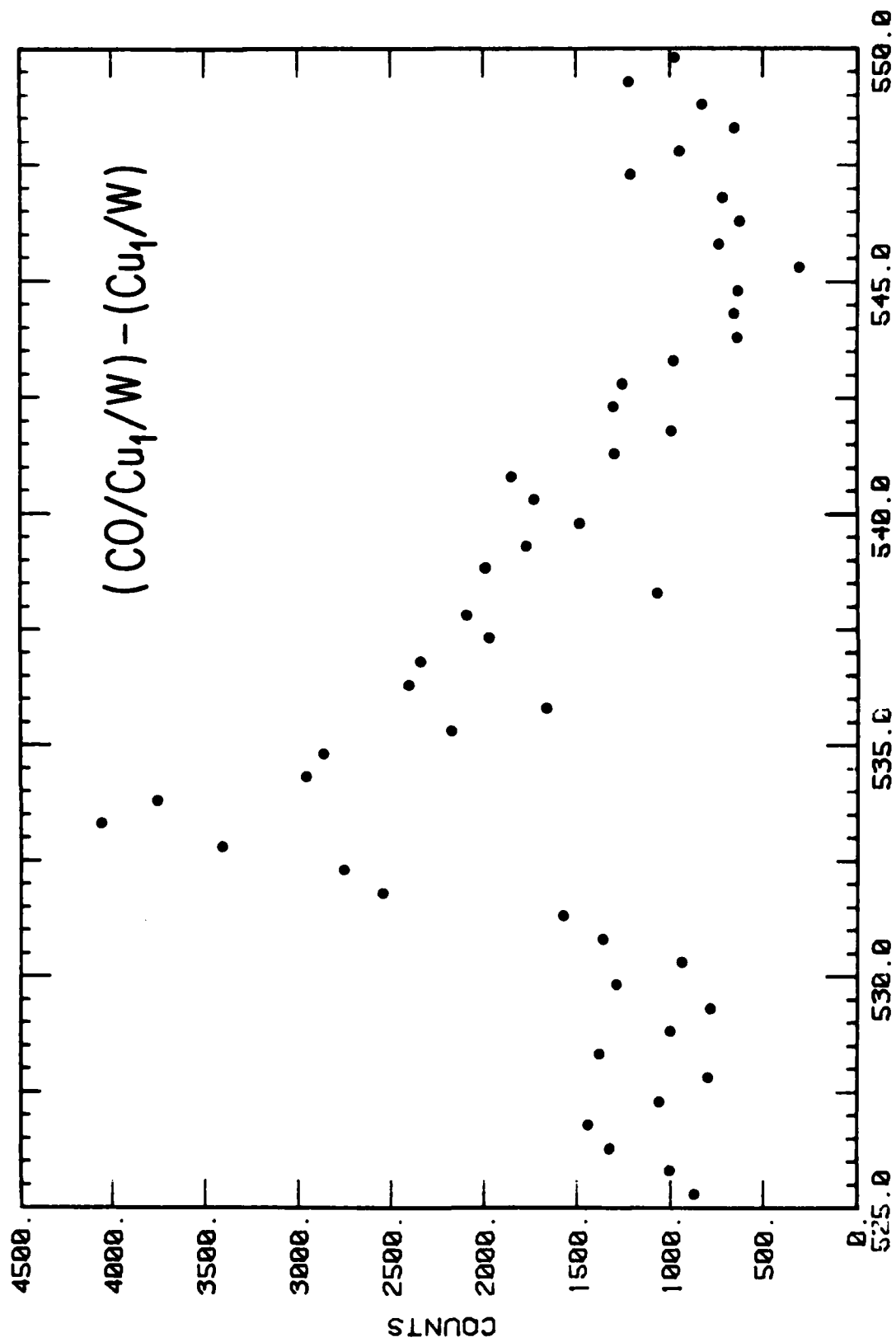


Fig.11



Binding Energy (rel. to E_F), eV

Fig.12



Binding Energy (rel. to E_F), eV

Fig.13

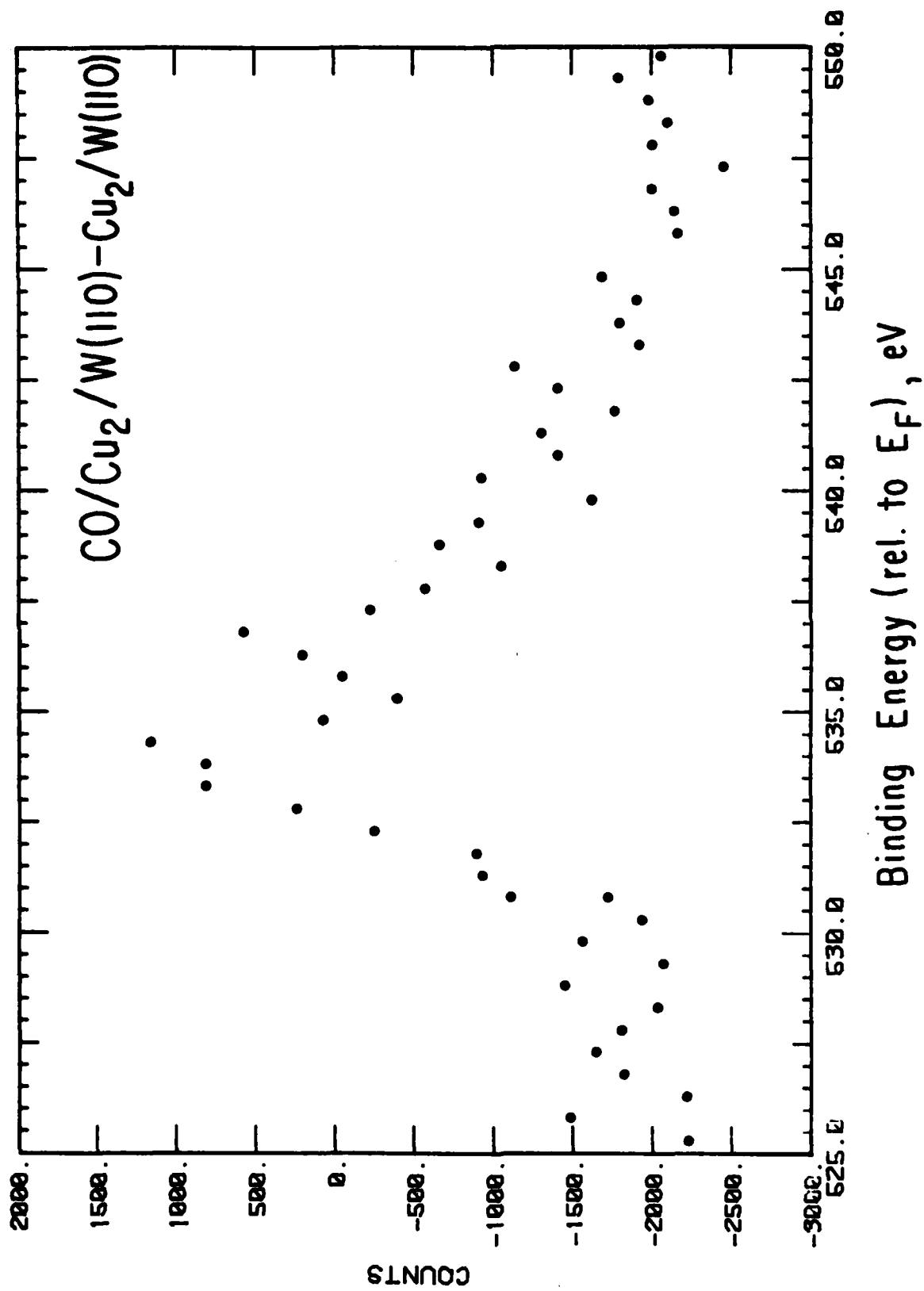


Fig.14

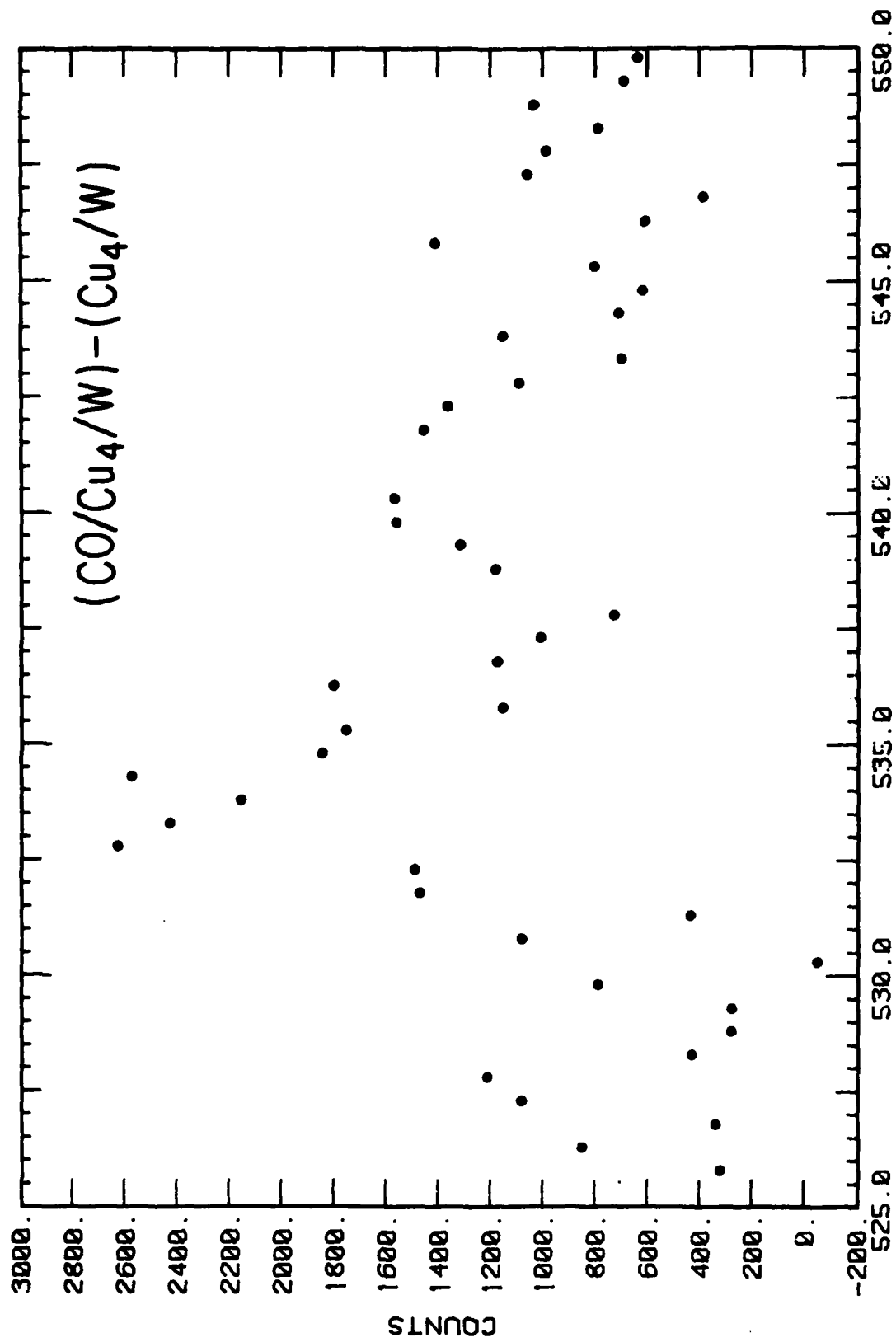


Fig.15

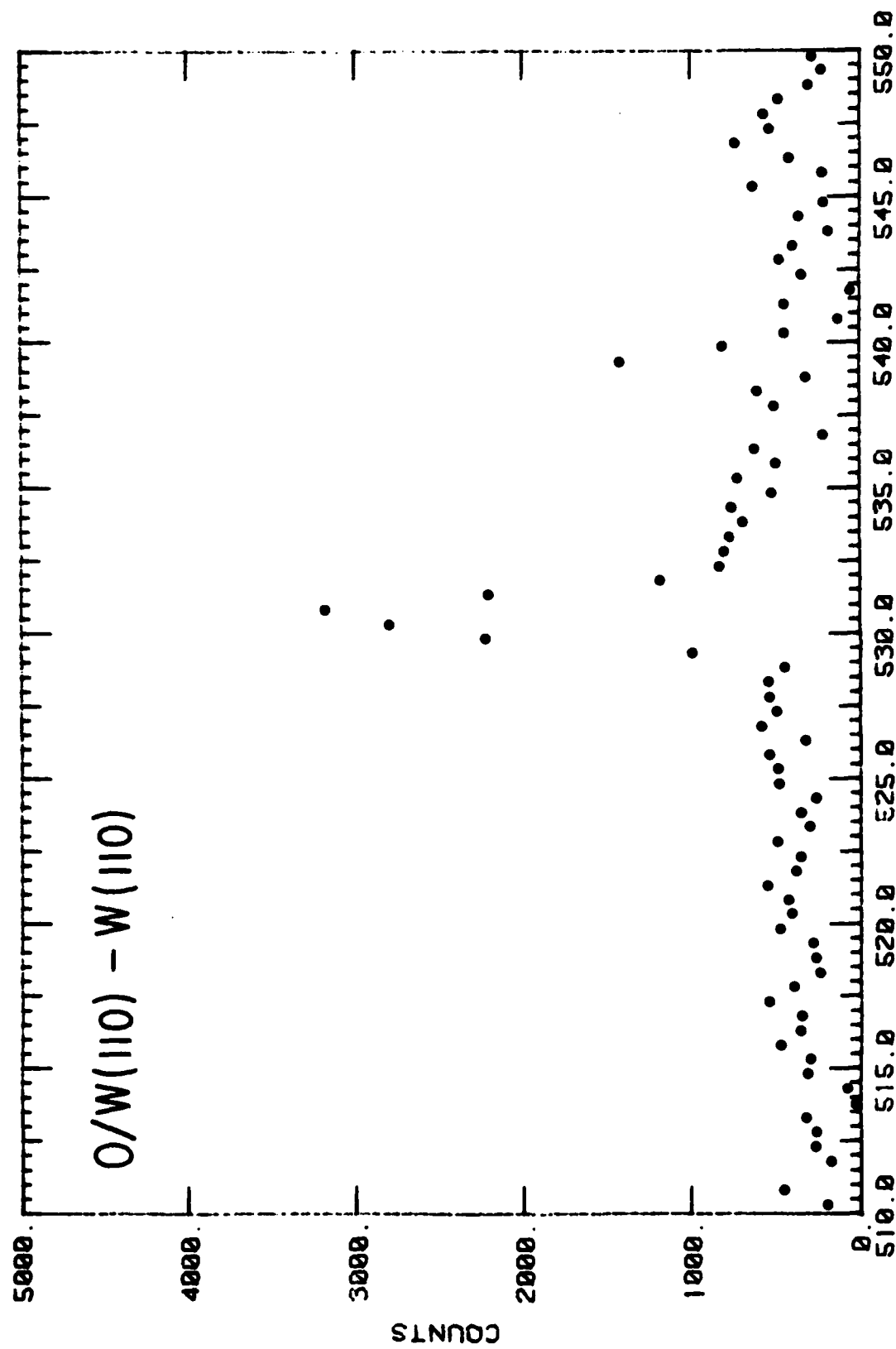


Fig.16

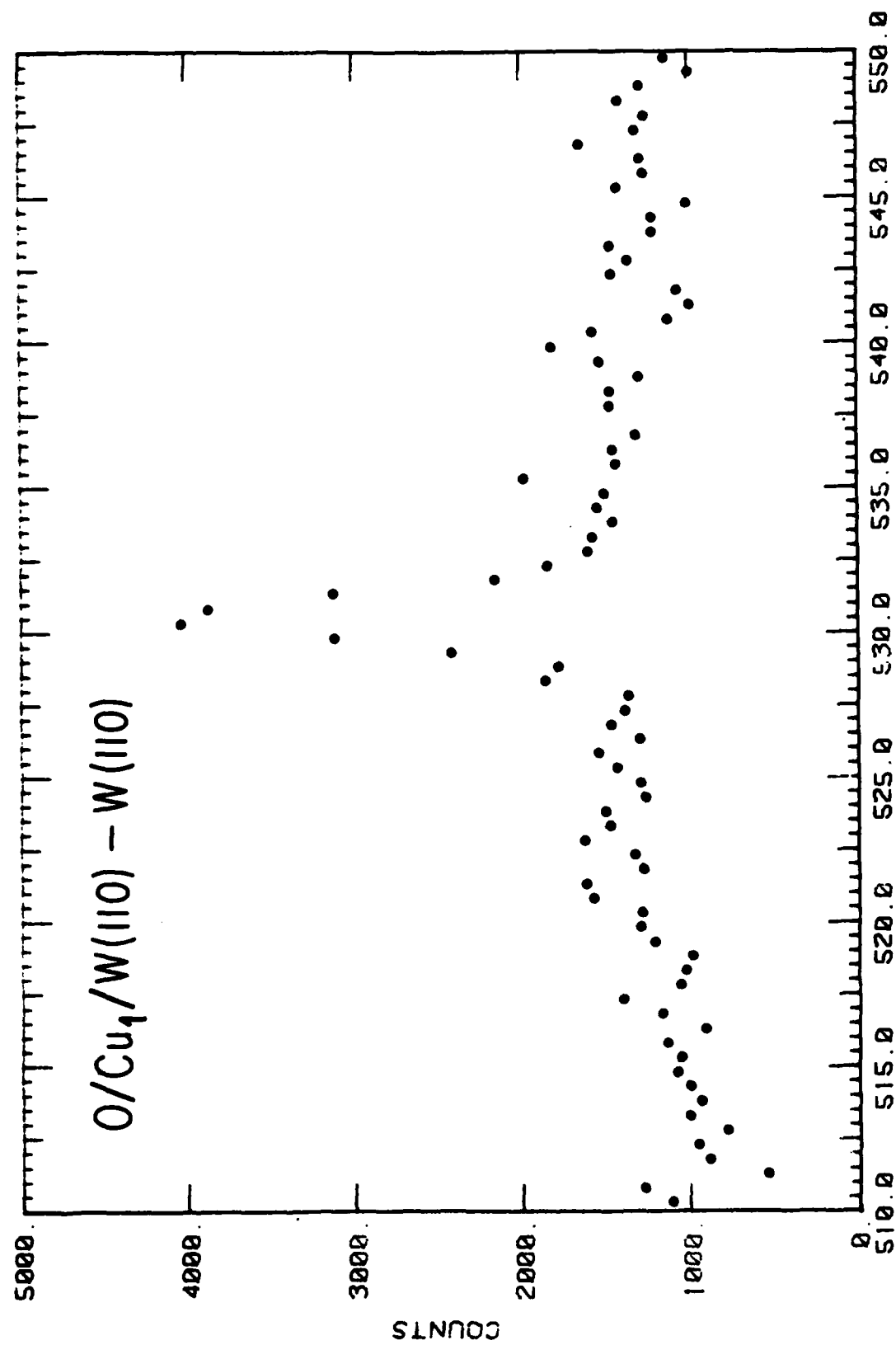


Fig.17

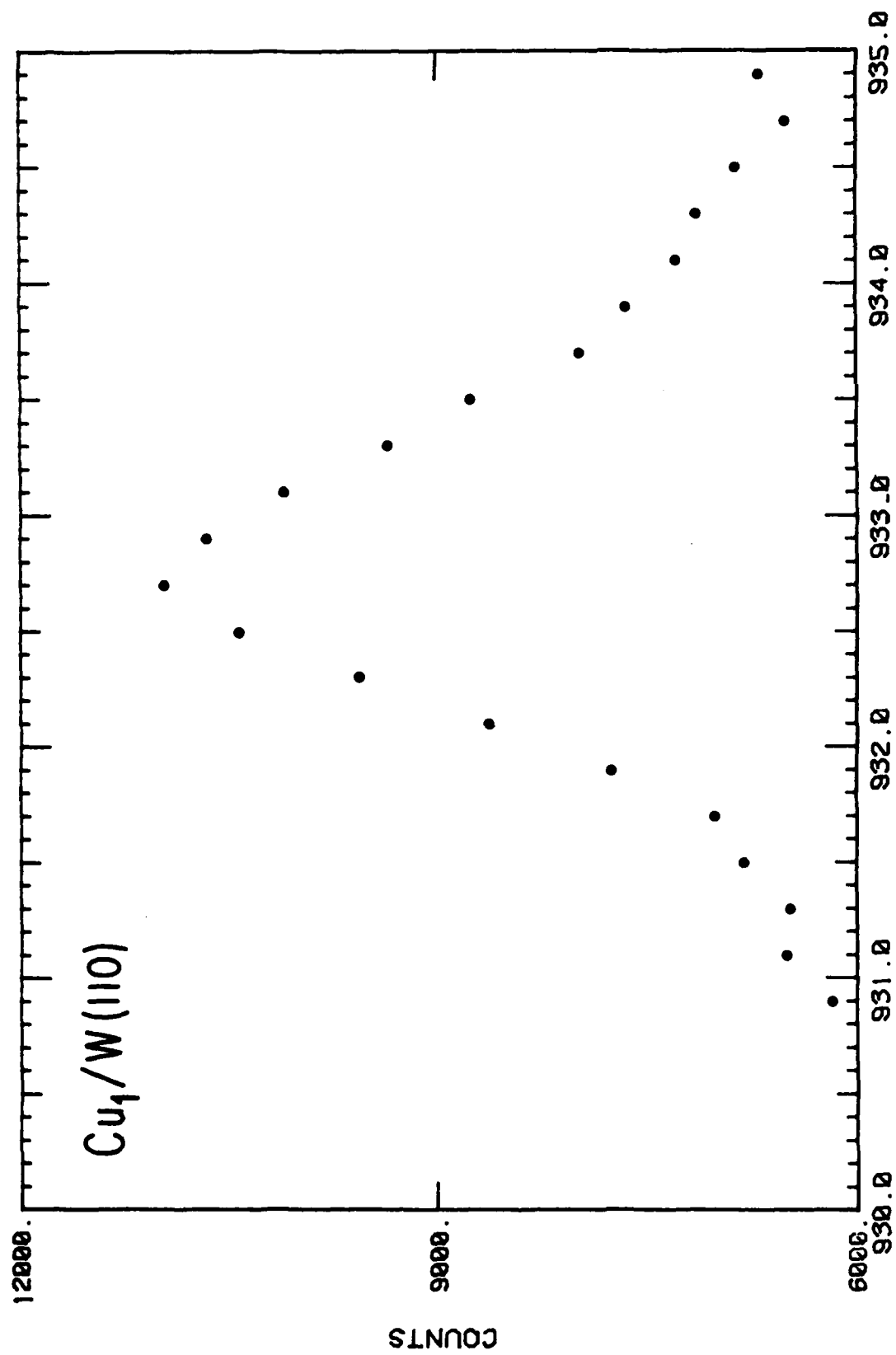


Fig.18

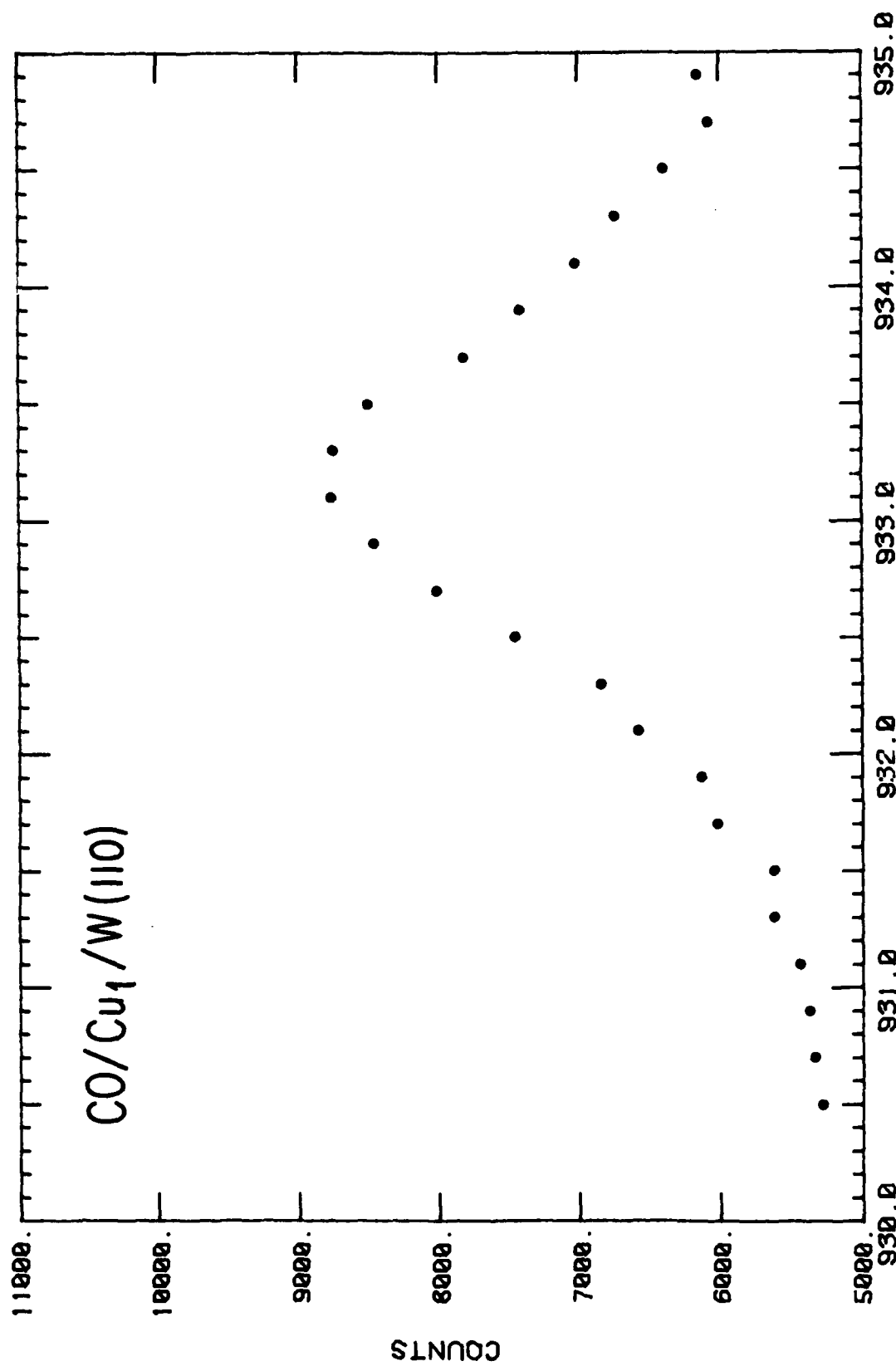


Fig.19

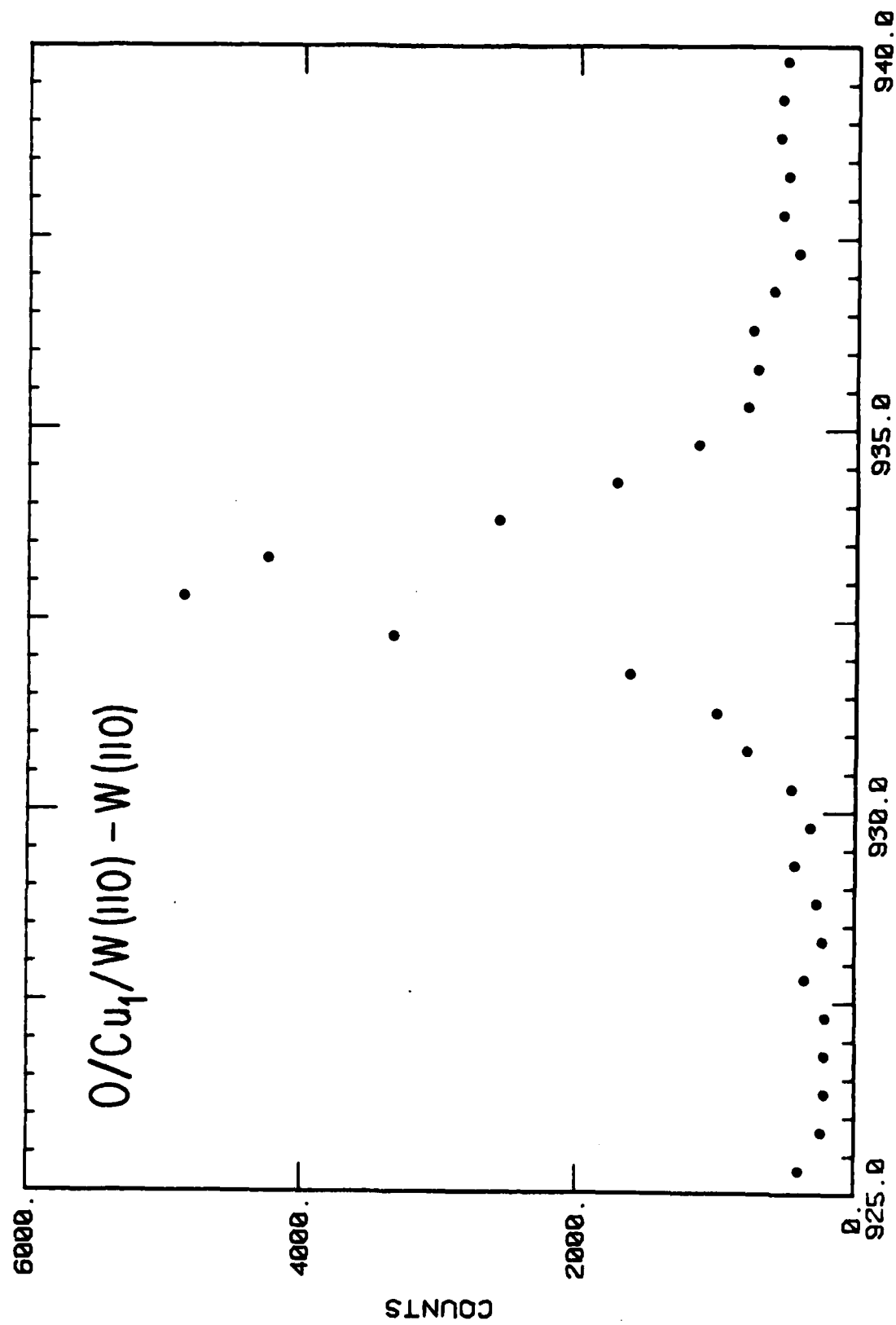


Fig.20

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