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### Author

Baca, A.G. K.

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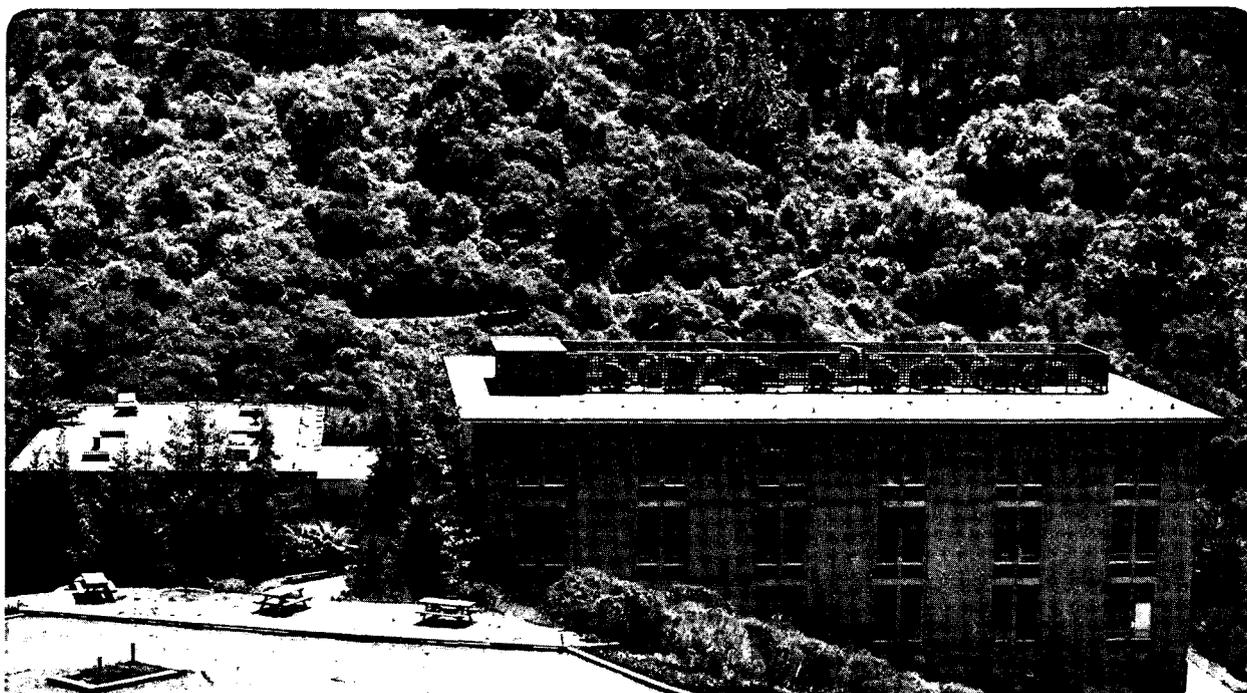
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A.G. Baca, L.E. Klebanoff, M.A. Schulz,  
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Dissociative Adsorption of CO and O<sub>2</sub> on Cr(100), Cr(110),  
and Cr(111) in the Temperature Range 300-1175 K

A.G. Baca,\* L.E. Klebanoff,\*\* M.A. Schulz,  
E. Paparazzo,† and D.A. Shirley

Materials and Molecular Research Division  
Lawrence Berkeley Laboratory  
and  
Department of Chemistry  
University of California  
Berkeley, California 94720

ABSTRACT

Electron energy loss spectroscopy (EELS), low energy electron diffraction (LEED), and Auger spectroscopy have been used to characterize the adsorption of CO and O<sub>2</sub> on Cr(100), Cr(110), and Cr(111) at 300 K and above. No evidence of molecular CO or O<sub>2</sub> was observed on these surfaces at any coverage. For each surface, the vibrational spectra for dissociated CO and oxygen are very similar. Broader EEL spectra are observed on Cr(111) than on Cr(110) or Cr(100), indicative of multiple sites on the very open (111) surface. For O<sub>2</sub> exposures on Cr(110) and at low coverages on Cr(111), similar Cr-O stretching frequencies at ~ 560-580 cm<sup>-1</sup> and at ~ 420-440 cm<sup>-1</sup> are suggestive of similar adsorption sites for oxygen on the two surfaces. These sites are proposed to be the long bridge and 3-fold sites on (110) planes of the two surfaces. A 4-fold hollow site is consistent with the Cr-O stretching frequency at 520 cm<sup>-1</sup> for low coverages of oxygen on Cr(100). Adsorption sites for carbon are the

same. Frequency shifts with coverage and temperature are reported for both chemisorption systems. A (6x1) LEED pattern is observed after an 825 K anneal for a 0.75 L exposure of CO/Cr(110) and a model consistent with the LEED pattern and sites based on EELS data is presented.

\*Present address: AT&T Bell Laboratories, Murray Hill, NJ 07974.

\*\*Present address: National Bureau of Standards, Gaithersburg, MD 20899.

†Permanent address: Istituto di Teoria e Struttura, Elettronica, CNR, 00016 Monterotondo, Roma, Italy.

## 1. INTRODUCTION

Brodén et al. reviewed the adsorption of CO on a number of transition metal surfaces and found a correlation between the energy difference  $\Delta$  of the  $4\sigma$  and  $1\pi$  orbitals of the adsorbed CO and the tendency of CO to dissociate [1]. The parameter  $\Delta(1\pi-4\sigma)$ , larger for surfaces with a greater tendency to dissociate CO, varies in a systematic way across the Periodic Table. Elements further left and higher up the transition metal series dissociate CO more readily than those to the right or bottom [1]. The results from the review, which are summarized below, apply to the low-index surfaces at 300 K. CO completely dissociates on Mo, partly dissociates on W and Fe, and is completely molecular on Ru, Ir, Ni, Pd, and Pt [1]. Results published since then on Re [2], Rh [3], and Co [4] have been largely in agreement with the trends found by Brodén et al.

Amongst the many investigations of CO on transition metal surfaces there are few studies of chromium surfaces. Shinn and Madey [5] recently observed molecular CO at 120 K on Cr(110). Kato et al., using low resolution (electronic transitions) EELS [6], found that CO dissociates on Cr(110) at 300 K and that dissociated CO gives the same spectrum as chemisorbed oxygen. Unfortunately, the electronic EELS study used an electron beam with primary energies (60-250 eV) and currents ( $.4 \mu\text{A}/\text{mm}^2$ ) sufficient to induce dissociation and/or desorption of molecular CO. Vibrational EELS does not suffer from these drawbacks and can in addition provide information about adsorption sites. We report the results of a study using vibrational

EELS, LEED, and Auger for CO and O<sub>2</sub> adsorption on Cr(100), Cr(111), and Cr(110) between 300 K and 900 K. Our results lend support to the above mentioned conclusions of Kato et al. [6]. In fact, the results show complete dissociation of CO on all three low-index surfaces of Cr at room temperature and above, in agreement with the trend proposed by Brodén et al. The dissociative adsorption of CO and oxygen are fully characterized in this study and are presented together because the results show great similarities which aid the interpretation of both systems.

## 2. EXPERIMENTAL

Our sample was a high-purity chromium single crystal that was cut and polished by standard methods. As in a previous study [14], our sample was precleaned by argon-ion bombardment ( $5 \times 10^{-5}$  Torr, 1.5 kV) with high temperature (1120 K) cycling for three weeks to remove bulk nitrogen as detected by Auger. The crystal then displayed a very sharp, low-background (1x1) LEED pattern. No impurities were detectable by Auger, or by vibrational EELS. Oxygen and CO adlayers were removed by the same procedure with shorter sputtering times.

The Cr surfaces were exposed to CO by ambient dosing and to O<sub>2</sub> by effusive beam dosing. When effusive beam dosing was used, approximate values of the exposures in langmuirs (L) were estimated using Auger intensities. LEED and Auger measurements, made with LEED optics, were taken after EEL spectra, so as not to induce dissociation. Some surfaces were annealed to a given temperature for approximately five minutes using electron beam heating, and temperatures were calibrated with an infrared pyrometer. The EEL

spectrometer has been described previously [7,8]. A double pass monochromator and a single pass analyzer, rotatable about a solid angle of  $2\pi$ , were employed. Both are based on hemispherical dispersing elements. All EEL spectra were taken at 300 K. Impact energies  $E_0$  as well as angles of incidence  $\theta_i$  and reflection  $\theta_r$  are given in each figure. The impact energies ranged between 2.0 and 2.5 eV, while the incident current was  $\sim 2 \times 10^{-11}$  amps. Linewidths based on the full width at half maximum (FWHM) are reported for spectra in Table 1.

### 3. OXYGEN ADSORPTION

Oxygen chemisorption results on the (110) and (111) surfaces of Cr are presented first. A chemisorption study of O/Cr(100) will be reported separately. The stretching frequencies from that work are summarized in Table 1 along with those from the present work in order to provide convenient comparison between both studies. The oxygen adsorption data are needed to assign the spectra for the dissociative adsorption of CO on the (100), (110), and (111) surfaces. Because of the similarities in the results for both oxygen and CO adsorption on all three surfaces, the discussion of the site assignments will be presented together in section 5.

#### 3.1. O/Cr(110)

The coverage-dependent spectra for O/Cr(110) at 300 K are shown in Fig. 1. At low coverages ( $\sim 1.6$  L), a Cr-O stretching frequency is observed at  $555 \text{ cm}^{-1}$ . The width of the peak is  $\sim 90 \text{ cm}^{-1}$  FWHM. As more  $\text{O}_2$  is added the frequency shifts upward to  $570 \text{ cm}^{-1}$  and

then to  $585\text{ cm}^{-1}$  for  $\sim 3\text{ L}$  and  $\sim 4\text{ L}$  exposures, respectively. No evidence for molecular  $\text{O}_2$  is observed at any coverage. A small unidentified feature at  $1205\text{ cm}^{-1}$  is observed in the highest exposure spectrum in Fig. 1. The upward shift of  $30\text{ cm}^{-1}$  in the Cr-O stretch contrasts with behavior observed for Cr(100) where the initial Cr-O frequency at  $545\text{ cm}^{-1}$  appears to shift downward with coverage [9]. The spectra are broadened beyond instrumental resolution, but not in the way that was observed on Cr(100), where asymmetric broadening due to the onset of oxidation became apparent during the completion of the chemisorption phase [9]. On Cr(110), all Cr-O stretches are symmetrically broadened up to  $4\text{ L}$  exposure, which corresponds to  $\sim 0.6$  monolayer.

When the lowest-coverage surface ( $1.6\text{ L}$ ) is heated to  $825\text{ K}$  (Fig. 2), the Cr-O stretching intensity becomes stronger but no shift in frequency is observed. For the highest coverage ( $4\text{ L}$ ) surface (Fig. 3), an  $825\text{ K}$  anneal, again, does not result in a shift of the Cr-O frequency. The absence of a shift is in contrast to the  $25\text{ cm}^{-1}$  downward shift on Cr(100) for a  $625\text{ K}$  anneal [9]. At this coverage, the feature at  $440\text{ cm}^{-1}$  is enhanced after annealing, but the  $1205\text{ cm}^{-1}$  peak has disappeared.

### 3.2. $\text{O}/\text{Cr}(111)$

Oxygen adsorption on Cr(111) leads to considerably broader features, as can be seen in Fig. 4. At an exposure of  $\sim 0.6\text{ L}$ , trace (b), there is a peak at  $\sim 580\text{ cm}^{-1}$  and a broad envelope of peaks

centered at  $440\text{ cm}^{-1}$ . Heating to 625 K, trace (c), yields essentially the same spectrum as trace (b). Further addition of  $\sim 0.9\text{ L}$  of  $\text{O}_2$ , trace (d), smears out the spectra. Annealing to 625 K and 1175 K, (e-f), broadens the peaks even more. A (1x1) LEED pattern is observed at all coverages and temperatures. In contrast to  $\text{O/Cr(100)}$  [9] and  $\text{O/Cr(110)}$ , temperature treatments do not lead to greater order. The highest coverage studied here is  $\sim 0.8$  monolayer. The sticking coefficient is much larger for  $\text{Cr(111)}$  than for the other two surfaces, in agreement with previous reports [10,11]

#### 4. CO ADSORPTION

##### 4.1. $\text{CO/Cr(100)}$

The coverage dependence of CO adsorption on  $\text{Cr(100)}$  at 300 K is shown by the EEL spectra in Fig. 5. One stretching frequency at  $520\text{ cm}^{-1}$  is observed which does not shift appreciably in any of the spectra shown. The width of this peak is narrow,  $\sim 55\text{ cm}^{-1}$ , at  $0.2\text{ L}$  and broadens to  $\sim 90\text{ cm}^{-1}$  at  $1.0\text{ L}$ . At  $0.2\text{ L}$ , a  $c(2\times 2)$  LEED pattern is observed, but a (1x1) LEED pattern is reestablished by  $1.0\text{ L}$ . Further increases in CO exposure above  $1.0\text{ L}$  do not lead to further changes in the EEL spectra. The absence of a feature in the range  $1700\text{--}2100\text{ cm}^{-1}$ , indicative of molecular CO, contrasts with CO adsorption on  $\text{W(100)}$  [12], where molecular adsorption is observed at the highest coverages at 300 K and dissociation occurs at lower coverages. A small peak at  $930\text{ cm}^{-1}$  is similar in intensity to a peak at  $960\text{ cm}^{-1}$  for  $\text{O/Cr(100)}$  which was assigned to subsurface

oxygen [9]. The  $30 \text{ cm}^{-1}$  shift of this peak is probably due to the influence of coadsorbed carbon.

Annealing the CO covered sample (Fig. 5) to 825 K leads to large intensity changes in the EEL spectra. Typical of these anneals is the 0.2 L CO exposure, shown in Fig. 6. The increase in intensity after the 825 K anneal is probably due to an increase in the surface order since a  $c(2 \times 2)$  LEED pattern, observed for the 0.2 L exposure, becomes much sharper on annealing. A small downward frequency shift from  $520 \text{ cm}^{-1}$  to  $505 \text{ cm}^{-1}$  is observed with annealing. Annealing after 0.5 L and 1.0 L exposures shows the same frequency shift but less dramatic intensity increases. The peak at  $930 \text{ cm}^{-1}$  disappears with annealing. Finally, a nearly clean spectrum is observed after flashing to  $\sim 1175 \text{ K}$ , as observed in previous work on W(100) [12] where TDS has shown CO desorption at high temperatures due to recombination of adsorbed carbon and oxygen.

The EEL spectra of CO/Cr(100) are similar to those of low coverages of O/Cr(100) [9]. The room temperature frequency is  $545\text{--}520 \text{ cm}^{-1}$  for oxygen and  $520 \text{ cm}^{-1}$  for dissociated CO. Annealing to higher temperatures shifts the frequency to  $495 \text{ cm}^{-1}$  for oxygen and  $505 \text{ cm}^{-1}$  for dissociated CO. One might conclude that the two samples are nearly identical, but this is not the case, as is shown by the presence of C in the Auger spectra of the CO-exposed surface and not the oxygen-exposed surface, and the observation that flashing to 1175 K cleans the CO-exposed surface but not the oxygen-covered surface. In a separate study, we have shown that

Cr-O and Cr-C frequencies are nearly degenerate on Cr(100) [13]. The spectral broadening at the 1.0 L exposure is probably due to different coverage dependences of coadsorbed carbon and oxygen stretching frequencies. The narrow peak at 0.2 L exposure, coupled with the small peak at  $930\text{ cm}^{-1}$ , may indicate that some oxygen initially assumes subsurface sites in the presence of carbon.

#### 4.2. CO/Cr(110)

The coverage dependence of CO adsorption at 300 K on the Cr(110) surface is shown in Fig. 7. For a 0.2 L exposure, a loss is observed at  $560\text{ cm}^{-1}$ . At 0.5 L and 0.75 L a second loss is seen at  $420\text{ cm}^{-1}$ . The higher energy feature shifts upward in frequency, from 560 to  $590\text{ cm}^{-1}$ , with increasing coverage, while the lower energy feature does not appear to shift. For all three coverages shown in Fig. 7, a (1x1) LEED pattern is observed. Again, no evidence for molecular CO is observed.

Figure 8 shows the effect of annealing the 0.75 L exposure to 825 K. Some differences in intensity are observed, as was the case on Cr(100). Annealing the 0.2 L and 0.5 L samples produces similar results. The high energy peak becomes more intense after an 825 K anneal at 0.5 L and 0.75 L, while the low energy peak decreases in intensity. Furthermore, the high energy peak is shifted back to  $560\text{ cm}^{-1}$  at all coverages. On Cr(110), after an 825 K anneal, the 0.5 L and 0.75 L exposures show spectra with a  $55\text{ cm}^{-1}$  FWHM, essentially instrumental resolution. Auger spectra show no

substantial decrease in carbon or oxygen signal after either anneal.

Similarities to O/Cr(110) are apparent, though differences are present. The coverage dependence of the high frequency peak is virtually identical in the two cases. However, when the dissociated CO overlayer is annealed, the frequency shifts back to  $560\text{ cm}^{-1}$ , and its FWHM narrows. When the oxygen overlayer is annealed, no shift occurs and no narrowing occurs. When dissociated CO is annealed, the  $420\text{ cm}^{-1}$  peak decreases, but when the  $4\text{ L O}_2$  exposed surface is annealed, a  $440\text{ cm}^{-1}$  peak appears.

There is a quite dramatic effect on the LEED patterns after an 825 K anneal. These are shown schematically in Fig. 9. At 0.2 L streaks begin to appear in one direction. At 0.5 L spots appear on either side of the (1x1) spots. By 0.75 L a (6x1) LEED pattern is observed. These LEED patterns correspond to EEL spectra where sharp features are observed at  $560\text{ cm}^{-1}$  for both 0.5 L and 0.75 L exposures. They will be discussed further in section 5.2.

#### 4.3. CO/Cr(111)

The coverage-dependent spectra of CO/Cr(111) at 300 K are shown in Fig. 10. In contrast with the other two surfaces, but similar to oxygen adsorption on Cr(111), the spectra here are extremely broad. Two stretching frequencies are observed, at  $565$  and  $440\text{ cm}^{-1}$ . The peak at  $440\text{ cm}^{-1}$  is especially broad and may correspond to more than one mode. The absence of a higher frequency peak indicates that CO

dissociates on Cr(111). Both frequencies are very nearly the same as those observed on Cr(110), suggesting that similar sites are being populated on each surface. For the 1.0 L exposure, annealing to 625 K and 825 K sharpens up the spectra somewhat (Fig. 11), but no appreciable changes are observed in the frequencies. For the 0.5 L exposure, annealing to 625 K and 825 K gives qualitatively similar results, but the spectra are broader than in Fig. 11. When the surface is heated to 1175 K, over 90% of the carbon and oxygen atoms are removed, as is observed on Cr(100) and Cr(110).

#### 4.4. Comparison Between Surfaces

We note several similarities and trends common to these three chromium surfaces. It is found that CO dissociates at room temperature on all three surfaces, and that the spectra on all three surfaces resemble those for the oxygen-covered surfaces. In section 4.1, it was noted that Cr-O and Cr-C stretching frequencies on Cr(100) are nearly degenerate, and they are also of comparable intensity [13]. This was determined by comparing the adsorption systems CO/Cr(100), N/Cr(100), and CH<sub>3</sub>NH<sub>2</sub>/Cr(100) (partly dissociated) [13]. A similar conclusion holds for Cr(111) and Cr(110) [14].

## 5. DISCUSSION

### 5.1. Site Assignments

It was noted above that Cr-O and Cr-C stretching frequencies which we have observed on these surfaces are nearly degenerate. This

conclusion forms the basis for the ensuing discussion, where it will be argued that different peaks correspond to separate adsorption sites and not to different atomic species. This assertion is supported by the similar frequencies but different intensity variations with temperature for CO/Cr(110) and O/Cr(110). The intensity variations are most easily explained as differences in site populations as a function of temperature. The site population distributions are slightly different for CO and O<sub>2</sub> adsorption.

A discussion of the sites responsible for the Cr-O and Cr-C stretching frequencies on the three surfaces, illustrated in Fig. 12, will now be made. The (100) surface has 4-fold symmetry. A hollow site on this surface does not have the same meaning as it would on a more densely packed face-centered cubic (fcc) surface with 4-fold symmetry. On the body-centered cubic (bcc) surface, the spacing between the chromium atoms is so large that a 4-fold coordinated site in the hollow with Cr-O or Cr-C bond lengths typical of known compounds cannot be attained. For an adatom in the hollow, 5-fold coordination occurs and the bond to the second layer Cr atom can be .1-.2Å shorter than the other bonds. In keeping with the convention established by previous workers, this site will be referred to as the 4-fold hollow site, rather than atop to the second layer, even though the greatest bond strength may come from the second layer Cr atom. It is also possible for the adatom to bond to two first layer Cr atoms and one second layer atom in a 3-fold coordinated site on a (110) plane of the (100) surface. The sites we need to consider are atop to

the first layer, bridge, 3-fold, or the 4-fold hollow. On the (110) surface, the possible sites are atop, short bridge, long bridge, or 3-fold. The (111) surface (Fig. 12c), the least densely packed, has three layers of chromium atoms exposed. Each surface chromium atom is the peak of an isolated hill and three neighboring surface atoms define a "pocket" where most of the available adsorption sites exist. The possible sites are: atop to the first, second, and third layer atoms, bridge between first and second layer atoms (short bridge), between first and third layer atoms (long bridge), and between second and third layer atoms (short bridge), and 3-fold to a first, second, and third layer atom. In all, there are seven standard adsorption sites on Cr(111). This plethora of sites may explain why the spectra are so broad on Cr(111) for both oxygen and CO adsorption.

A comparison of the sites available on these three surfaces show some interesting similarities. The three Cr atoms which comprise the 3-fold sites define (110) planes, irrespective of the surface. The only difference among the sites is the coordination number of the oxygen-bonded chromium atoms, i.e., the number of chromium nearest neighbors. The bridge sites available on Cr(111) and Cr(110) are the long and short bridge sites on the (110) plane.

The low-coverage frequency of the Cr-O stretch is 560 and 580  $\text{cm}^{-1}$  at 300 K on the (110) and (111) surfaces, respectively. The similarity in frequencies suggests that the site for this peak is the same on both surfaces, allowing for differences in average chromium coordination number. A second peak near 420-440  $\text{cm}^{-1}$  is

observed on Cr(110) and Cr(111) surfaces. Again, the similar frequencies suggest that a similar site on each surface is being occupied. The lower frequency suggests a higher-coordinated site. The assignments of a 3-fold site for the peaks at 420-440  $\text{cm}^{-1}$  and a long bridge site for the 560-580  $\text{cm}^{-1}$  peaks are favored. Analogous assignments were made using EELS for O/W(110) [15], where vibrational frequencies at 580 and 380  $\text{cm}^{-1}$  were observed. An assignment of long and short bridge sites for the low and high frequency peaks, respectively, would not allow the formation of the (6x1) LEED pattern at  $\theta=1$  and will be discussed further in section 5.2.

On Cr(100), vibrational frequencies between 520 and 545  $\text{cm}^{-1}$  are observed [9]. These frequencies are too low for bridge or atop sites and are higher than would be expected for a 4-fold hollow site where no bonding to second layer atoms can occur, e.g., in (100) surfaces of fcc metals. For bcc metals, bonding to the second layer is likely to be stronger than bonding to the first layer. Bonding to second layer atoms will raise the vibrational frequency by an indeterminate amount since it is not known a priori what the relative strengths of the first layer and second layer bonds are. The EELS data alone cannot distinguish between 3-fold and 4-fold hollow sites on Cr(100), but there are structural measurements on Mo(100) and W(100) which bear on this question [16-18]. None of the structural measurements have found dissociated CO, O, or N to occupy 3-fold sites on Mo(100) [16] or W(100) [17,18], and we are hesitant to make such an assignment on Cr(100) based on vibrational frequencies alone.

## 5.2. Cr(110) LEED Patterns

The LEED patterns that result from high temperature (875 K) anneals of CO/Cr(110) are shown in Fig. 9. For a 0.2 L CO exposure, streaks are apparent along the [10] direction. The streaks are probably caused by both a mixture of unit cells such as (5,1), (6,1), (7,1), etc. and a small domain size associated with low coverage, which will cause uncertainty broadening of the spots. Two extra spots equally spaced about the (1x1) spots emerge for the 0.5 L exposure. A mixture of unit cells can adequately explain the patterns since the first extra spots at the ends are less affected than spots in the middle: e.g. 1/5 is very close to 1/6 and 4/5 to 5/6, but 1/3, 2/5, and 1/2 are further apart. At 0.75 L, the full (6x1) LEED pattern becomes very sharp. A model of the surface consistent with the 3-fold and long bridge sites proposed in section 5.1 is shown in Fig. 13. It should be noted that a (1x6) domain is inequivalent on the (110) surface and is not observed. We emphasize that this model is not necessarily unique and that the population ratios of the suggested sites are not known. It may be possible to propose incommensurate overlayers which are consistent with the EELS data. Such a model would require that the EELS frequencies do not shift with the ordering that occurs after an 825 K anneal and that the  $560\text{ cm}^{-1}$  peak be narrower after the anneal. Long rows in the [01] direction would also have to be retained.

Another possibility to explain the LEED data is surface reconstruction. Compression of the outer layer of Cr atoms to form a

close-packed layer would eliminate the long bridge site and affect the EEL spectra, but other types of reconstructions may be possible. One type that is common to Cr(110) surfaces, faceting, can be ruled out. Faceting is known to occur at high temperature in the presence of oxygen and is evidenced by streaks along one direction and by the presence of rectangular spots due to (100) planes [19-21]. The streaks we observe disappear when the (6x1) LEED pattern is fully developed and no evidence of (100) spots is present.

We believe that the saturation coverage is approximately one monolayer of carbon and oxygen atoms ( $\theta \sim 0.5$  for oxygen and  $\theta \sim 0.5$  for carbon), and we have used this assumption to quantify Auger spectra taken during a study of the oxidation of Cr(100) [9]. A saturation coverage of  $\theta \sim 0.83$  (a missing row or incommensurate adlayer to explain the (6x1) LEED pattern) would not significantly affect the results. If the model of Fig. 13 is not correct, any other explanation would involve adlayer interactions suggestive of a crowded surface.

An assignment of long and short bridge sites for the low and high frequency EELS peaks, respectively, would not allow the formation of an unreconstructed (6x1) LEED pattern at  $\theta=1$ . One would be left proposing  $\theta=.83$  or less in order to make every sixth row different.

## 6. SUMMARY

Dissociative chemisorption of  $O_2$  and CO has been characterized on Cr(100), Cr(110), and Cr(111). No evidence of molecular CO was

observed on any of the surfaces studied at 300 K and above. Dissociated CO and O give very similar EEL spectra on all surfaces. The EEL spectra are broader on Cr(111) than on Cr(100) or Cr(110), indicative of multiple sites on this very open surface. For O<sub>2</sub> exposures on Cr(110) and at low coverages on Cr(111), similar Cr-O stretching frequencies at ~ 560-580 cm<sup>-1</sup> and 420-440 cm<sup>-1</sup> are suggestive of similar sites for both surfaces. These sites are proposed to be the long bridge and 3-fold sites on (110) planes of the two surfaces. No site determinations based on EELS frequencies can be made for the Cr(100) surface, although a 4-fold hollow site is a likely candidate and is consistent with the EELS data. Both O/Cr(110) and CO/Cr(110) show an increase in frequency with coverage at 300 K, but no change in frequency with coverage is observed for CO/Cr(100). High temperature anneals of CO/Cr(110), CO/Cr(100), and O/Cr(100) result in downward shifts in EELS frequencies, but no shifts for O/Cr(110). A (6x1) LEED pattern is observed after an 825 K anneal for a 0.75 L exposure of CO/Cr(110) and a model consistent with the LEED pattern and sites based on EELS data is presented. A summary of all frequencies and linewidths is reported in Table 1.

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Table 1

A summary of all vibrational frequencies (in  $\text{cm}^{-1}$ ) for the dissociative adsorption of CO and  $\text{O}_2$  on Cr(100), Cr(110), and Cr(111) from this work and ref. [9]. Where available, the linewidths in  $\text{cm}^{-1}$  are given in parenthesis.

	Exposure	<u>Anneal To:</u>			
		300 K	625 K	825 K	1175 K
O/Cr(100) <sup>1</sup>	0.75 L	545(60)	-	-	-
	5 L	520(150)	-	-	-
	8 L	(520,635)(~ 170)	-	-	-
	60 L	520,625(85),1250	-	-	-
	3 L	-	495(90)	-	495(90)
	4 L	-	495,630,755,960	-	495,960
	5 L	-	495,630,755,960	-	495,960
O/Cr(110)	1.6 L	555(90)	-	555(80)	-
	3 L	570(80)	-	-	-
	4 L	585(80),1205	-	440,585(80)	-
O/Cr(111)	0.6-1.5 L	440,580(55)	440,580	-	440,580(v. broad)

Table 1 (continued)

	Exposure	300 K	625 K	Anneal To:	
				825 K	1175 K
CO/Cr(100)	0.2 L	520(55),930	-	505(90)	-
	1.0 L	520(90),930	-	510(160)	-
	2.0 L	520(80),930	-	-	-
CO/Cr(110)	0.2 L	420,560(95)	-	555(75)	-
	0.5 L	420,585(80)	-	555(55)	-
	0.75 L	420,590(75)	-	425,560(55)	-
CO/Cr(111)	0.2-1.0 L	440,565(v. broad)	440,560	440,570	-

1. From reference [9].

FIGURE CAPTIONS

- Figure 1. Coverage dependence of EEL spectra for  $O_2$  exposed to Cr(110) at 300 K.  $E_0 = 2.50$  eV.  $\theta_i = \theta_r = 55^\circ$ .
- Figure 2. EEL spectra of the 1.6 L  $O_2$  exposure to Cr(110) annealed to 825 K for 5 min. The lowest spectrum is of the clean surface. Spectra were collected at 300 K.  $E_0 = 2.50$  eV.  $\theta_i = \theta_r = 55^\circ$ .
- Figure 3. EEL spectra of the 4 L  $O_2$  exposure to Cr(110) annealed to 825 K for 5 min. The lowest spectrum is of the clean surface. Spectra were collected at 300 K.  $E_0 = 2.50$  eV.  $\theta_i = \theta_r = 55^\circ$ .
- Figure 4. EEL spectra of  $O_2$  exposed to the Cr(111) surface taken after the following treatments: (b) A 0.6 L exposure at 300 K, (c) annealing to 625 K for 5 min., (d) further addition of 0.9 L at 300 K, (e) annealing to 625 K for 5 min., and (f) annealing to 825 K for 5 min.  $E_0 = 2.20$  eV.  $\theta_i = \theta_r = 55^\circ$ .
- Figure 5. Coverage dependence of EEL spectra for CO exposed to clean Cr(100) at 300 K.  $E_0 = 2.20$  eV.  $\theta_i = \theta_r = 55^\circ$ .
- Figure 6. EEL spectra of the 0.2 L exposure of CO to Cr(100) annealed to 825 K for 5 min. The lowest spectrum is of the clean surface. Spectra were collected at 300 K.  $E_0 = 2.20$  eV.  $\theta_i = \theta_r = 55^\circ$ .
- Figure 7. Coverage dependence of EEL spectra for CO exposed to Cr(110) at 300 K.  $E_0 = 2.20$  eV.  $\theta_i = \theta_r = 55^\circ$ .

Figure 8. EEL spectra of the 0.75 L exposure of CO to Cr(110) annealed to 825 K for 5 min. The lowest spectrum is of the clean surface. Spectra were collected at 300 K.  $E_0 = 2.20$  eV.  $\theta_i = \theta_r = 55^\circ$ .

Figure 9. LEED patterns observed for CO exposures to Cr(110) after anneals to 825 K for 5 min. (x) denotes the substrate spots and (●) denotes the overlayer spots. For the 0.2 L and 0.5 L exposures, streaks are observed in the [10] direction.

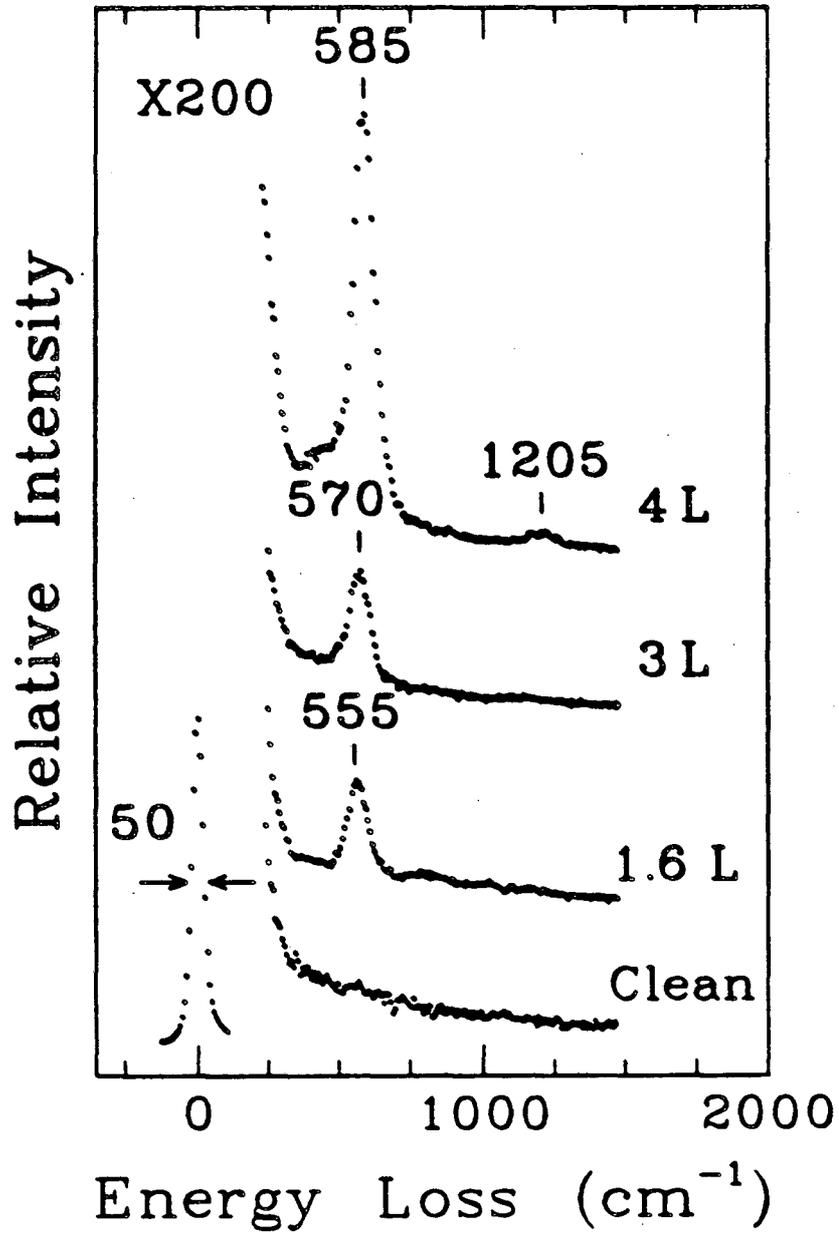
Figure 10. Coverage dependence of EEL spectra for CO exposed to Cr(111) at 300 K.  $E_0 = 2.20$  eV.  $\theta_i = \theta_r = 55^\circ$ .

Figure 11. EEL spectra of the 1.0 L exposure of CO to Cr(111) annealed to 625 K and 825 K for 5 min. The lowest spectrum is of the clean surface. Spectra were collected at 300 K.  $E_0 = 2.20$  eV.  $\theta_i = \theta_r = 55^\circ$ .

Figure 12. Models of the Cr surfaces. (a) Cr(100). Dotted circles are the second layer atoms. (b) Cr(110). (c) Cr(111). Three layers of atoms are exposed in this very open surface.

Figure 13. A model of the Cr(110) surface consistent with both the (6x1) LEED pattern and the EELS data. The LEED pattern is observed after annealing a 0.75 L CO exposure to 825 K for 5 min. The filled circles and the dashed circles may be either carbon or oxygen atoms. Cr atoms are shown as unshaded circles.

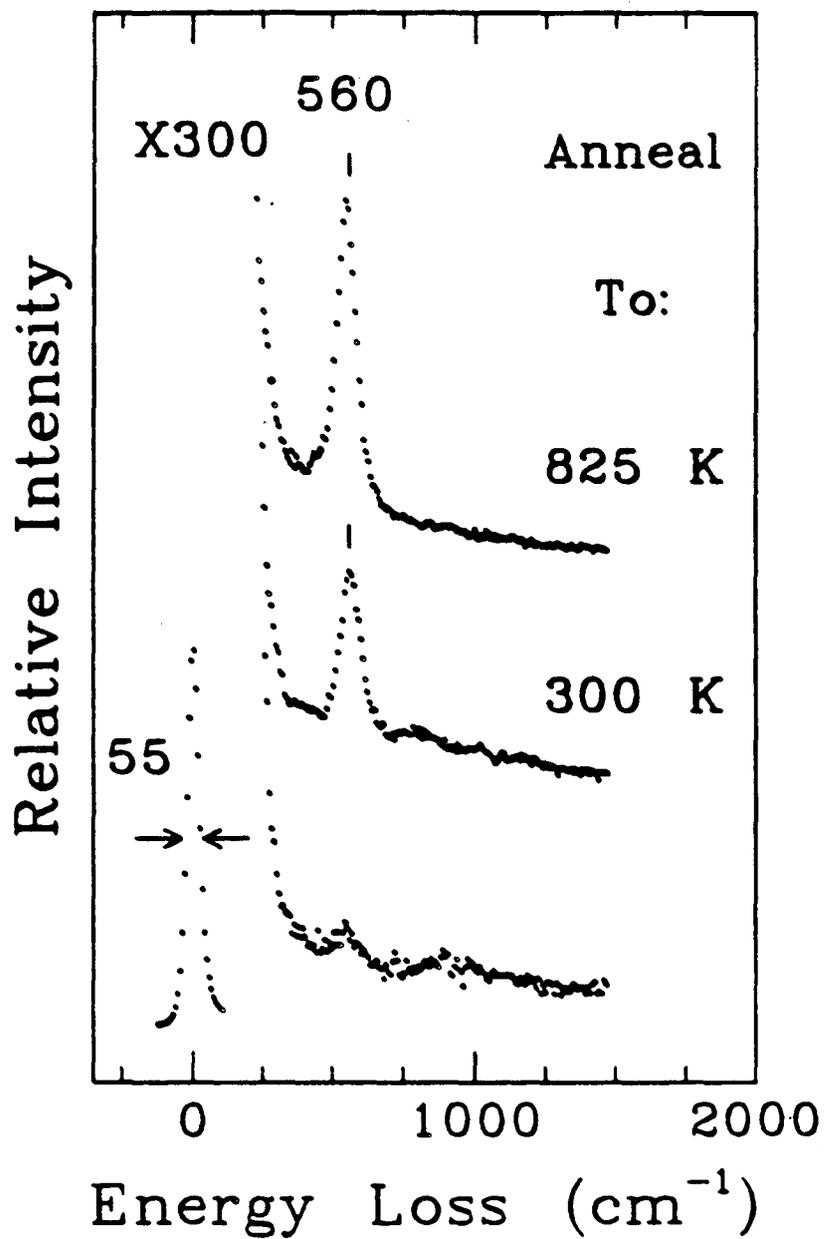
O/Cr(110) 300 K



XBL 851-821

Figure 1

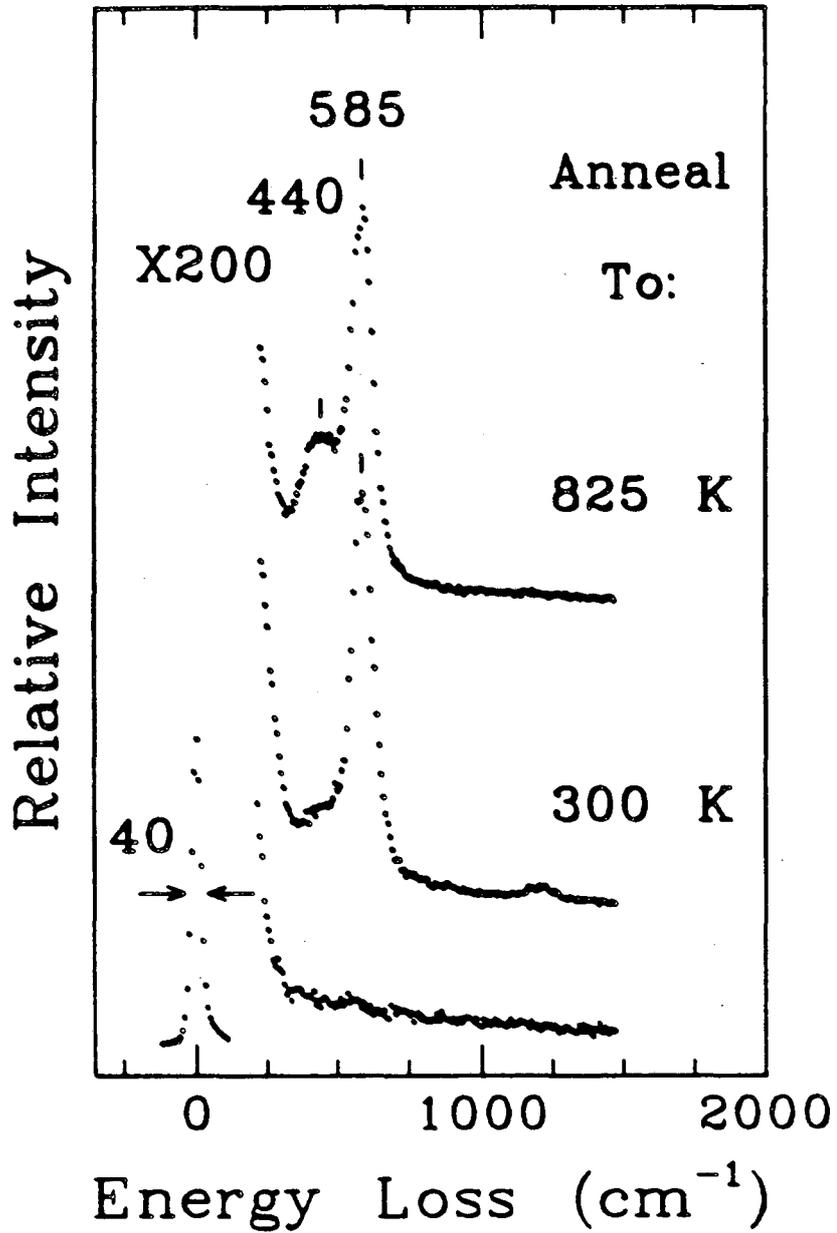
# O/Cr(110) Low Coverage



XBL 851-888

Figure 2

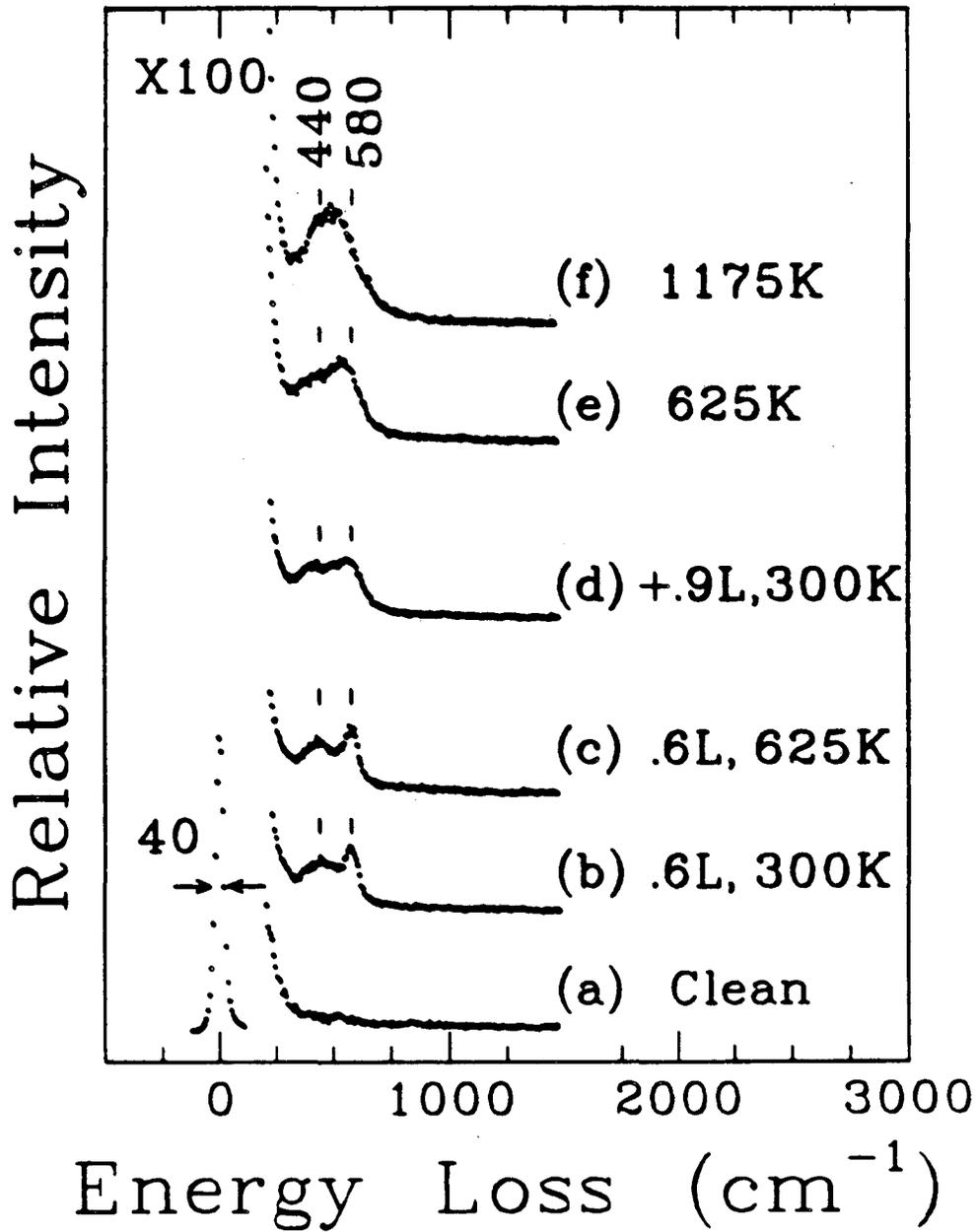
# O/Cr(110) High Coverage



XBL 851-822

Figure 3

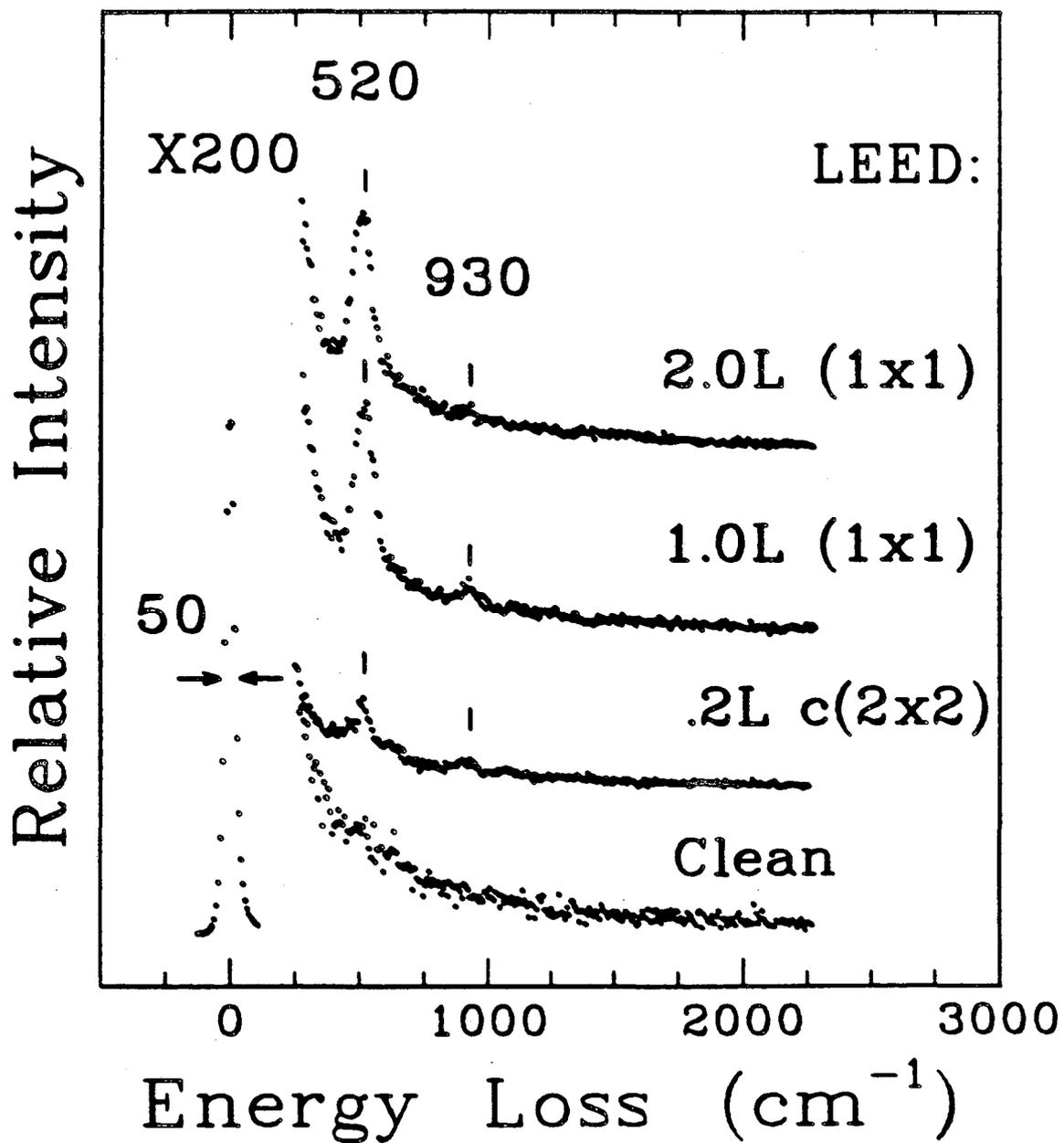
# O/Cr(111)



XBL 851-820

Figure 4

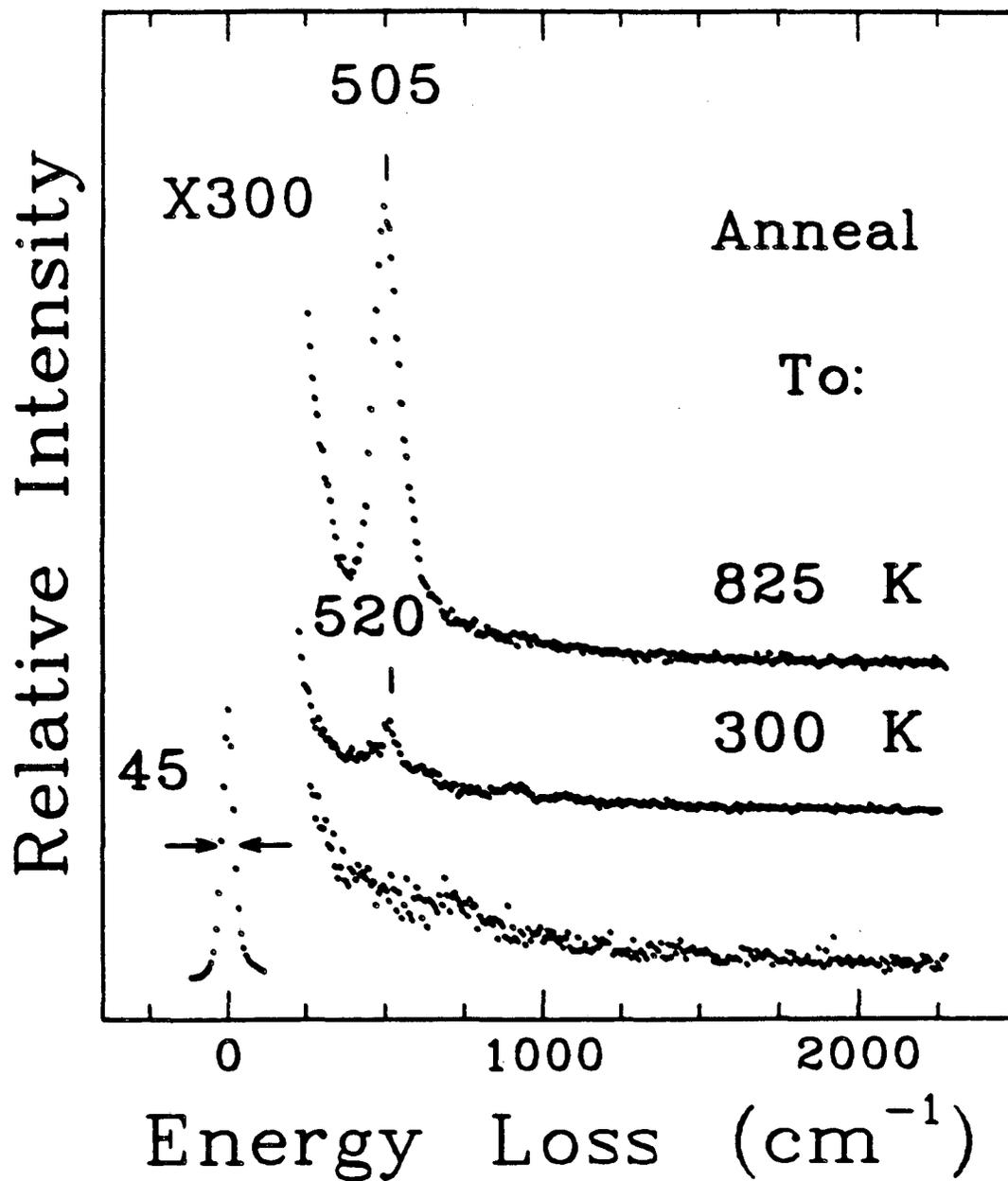
# CO/Cr(100) 300 K



XBL 8412-5466

Figure 5

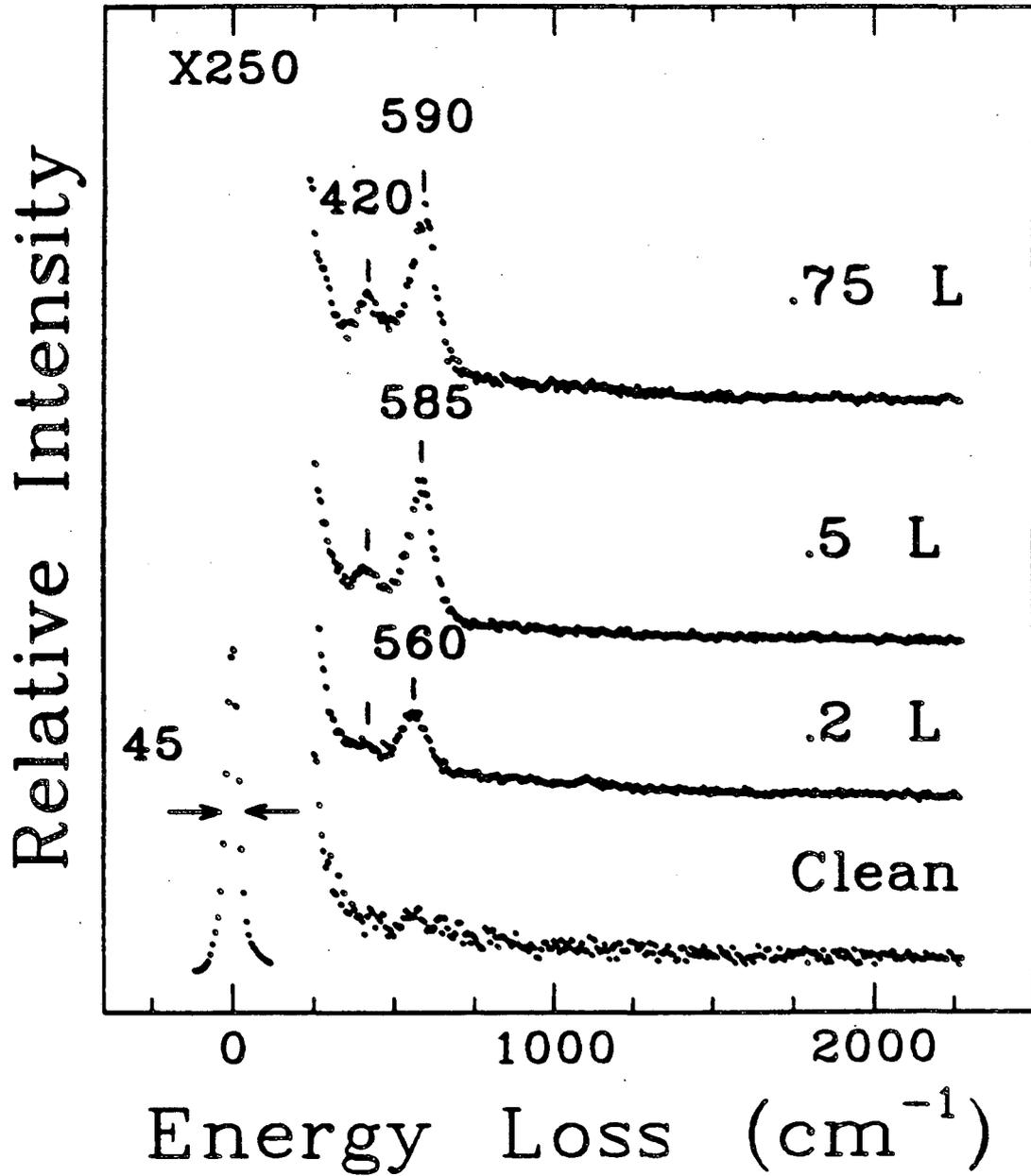
CO/Cr(100) 0.2 L



XBL 8412-5463

Figure 6

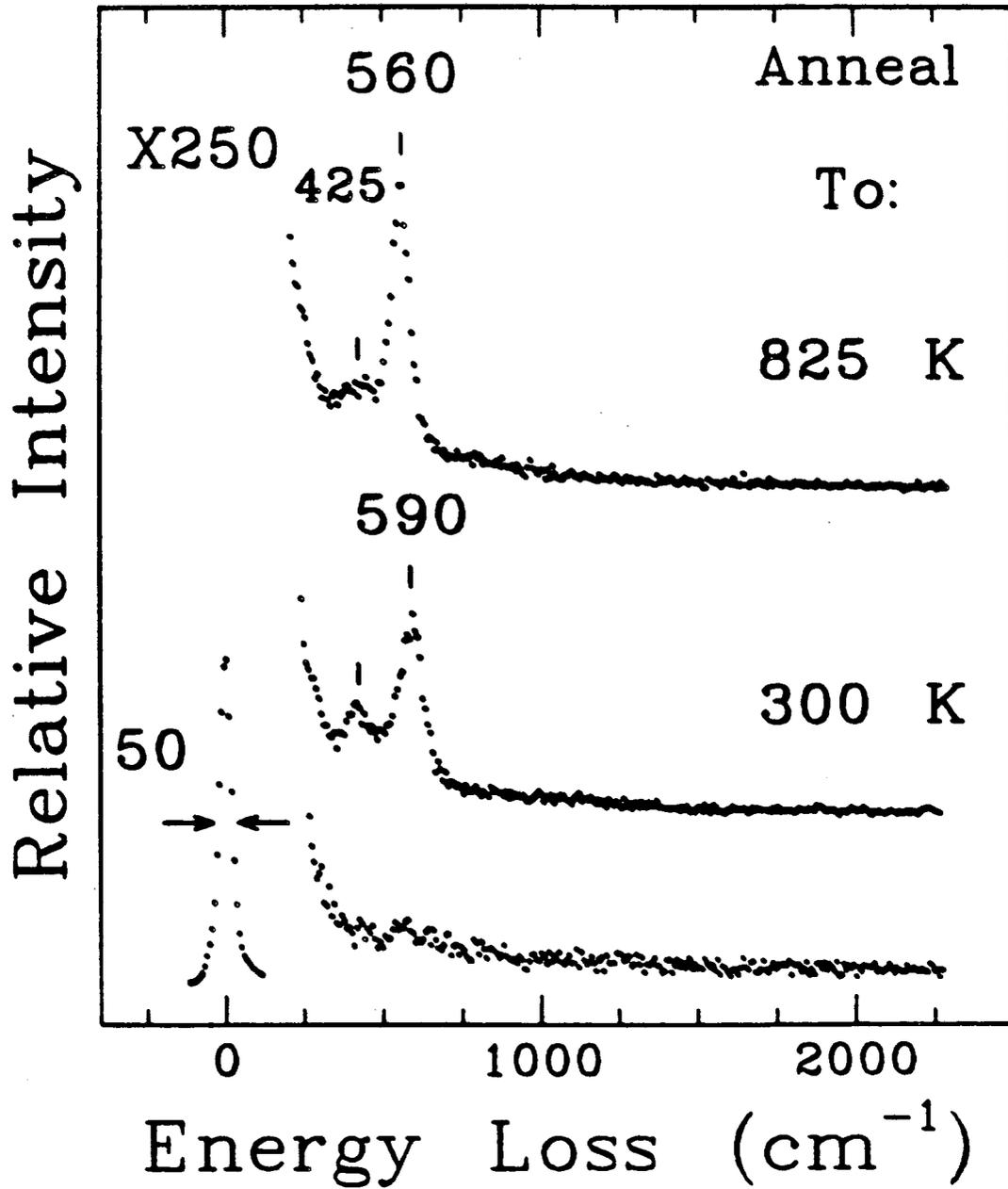
CO/Cr(110) 300 K



XBL 8412-5473

Figure 7

CO/Cr(110) 0.75 L



XBL 8412-5462

Figure 8

x

x-----x (a) 0.2 L

x

x

• x •-----• x • (b) 0.5 L

x

x

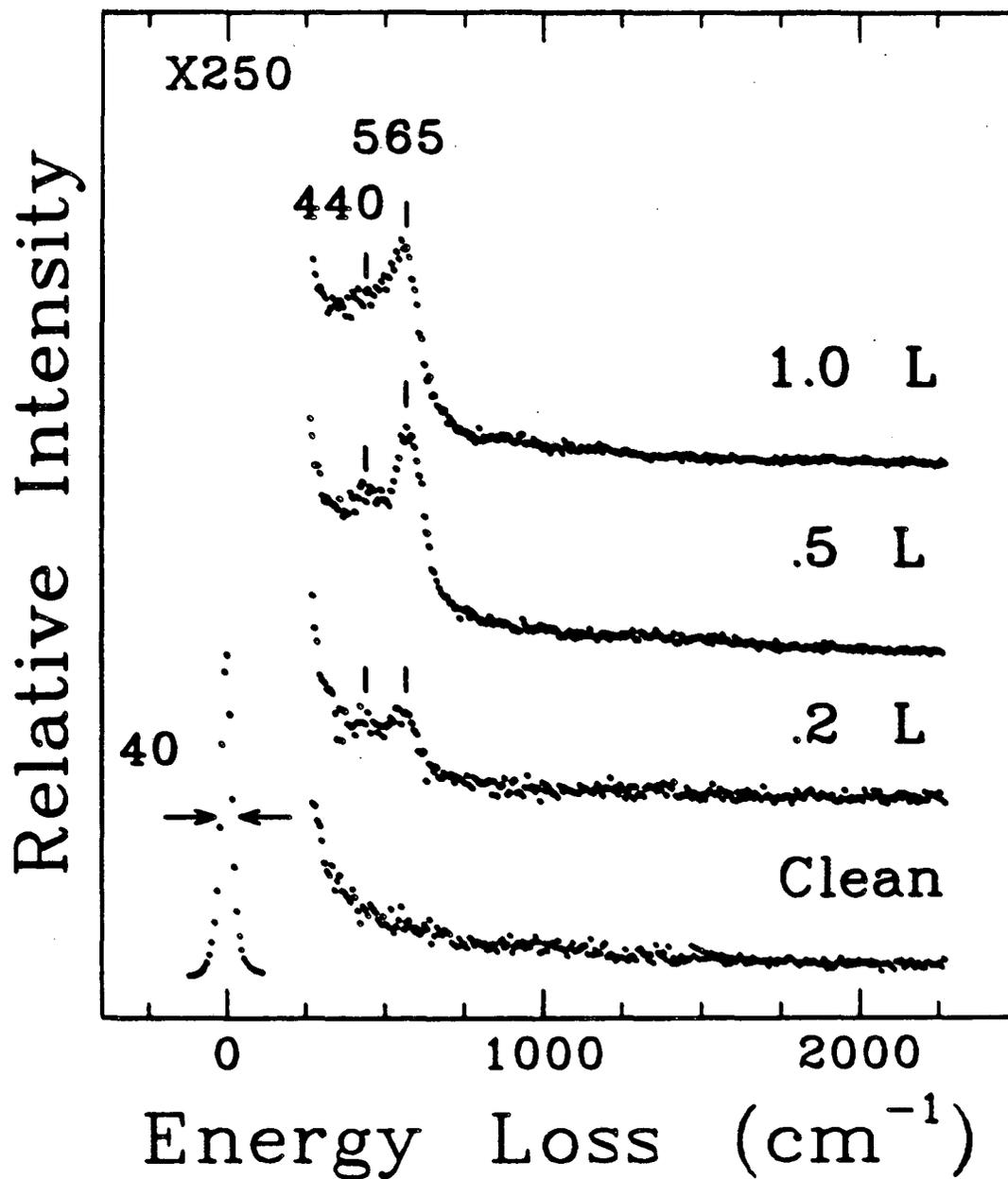
x • • • • • x (c) 0.75 L

x

XBL 851-777

Figure 9

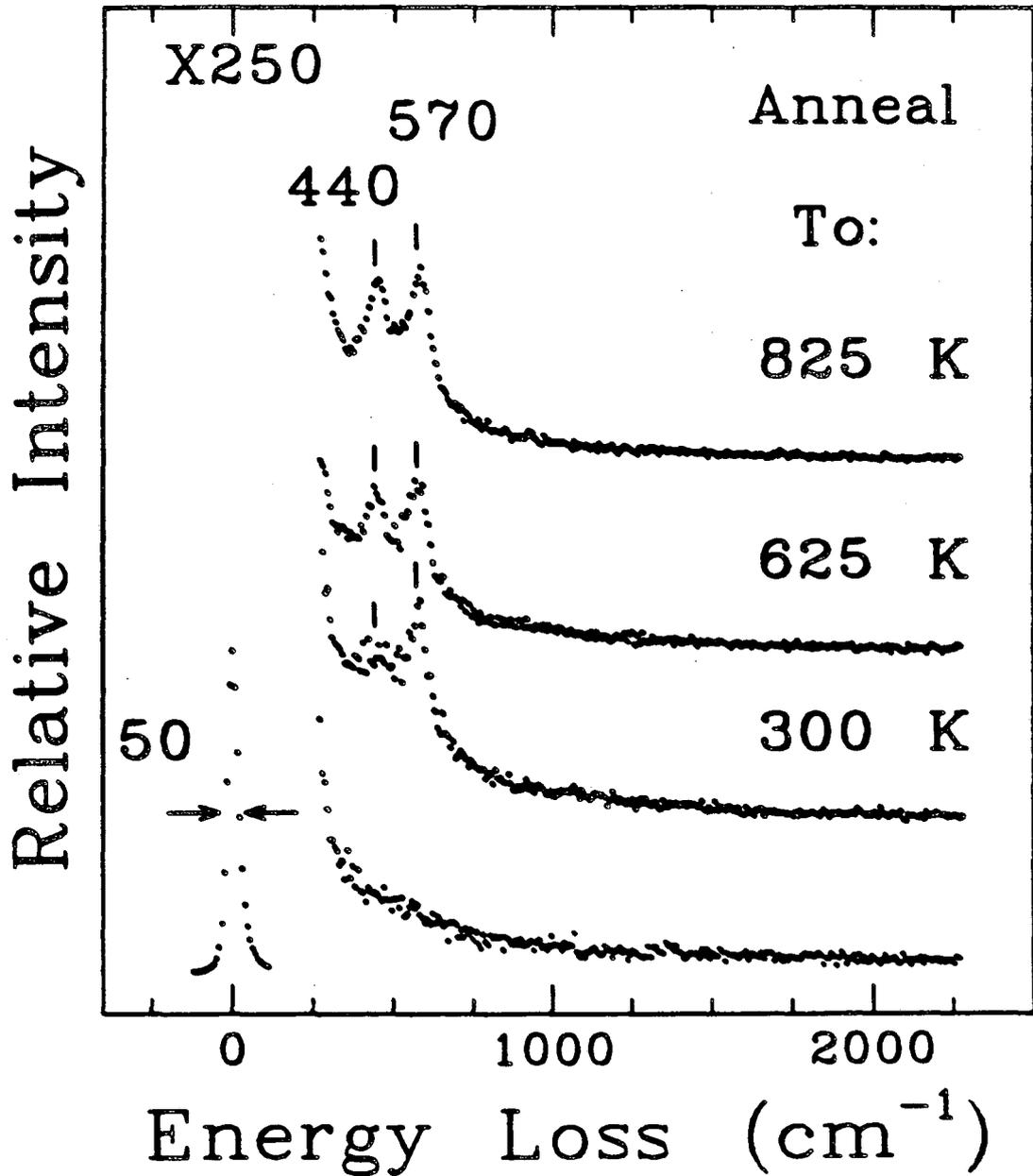
# CO/Cr(111) 300 K



XBL 8412-5474

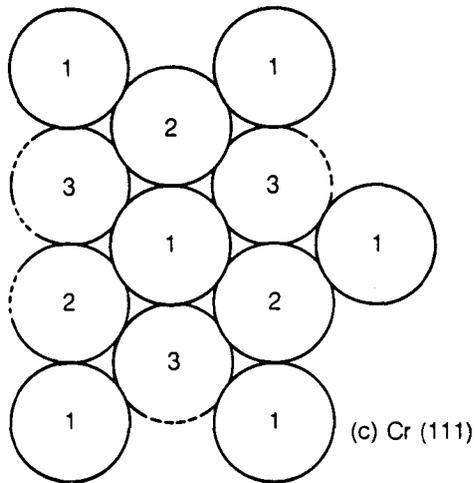
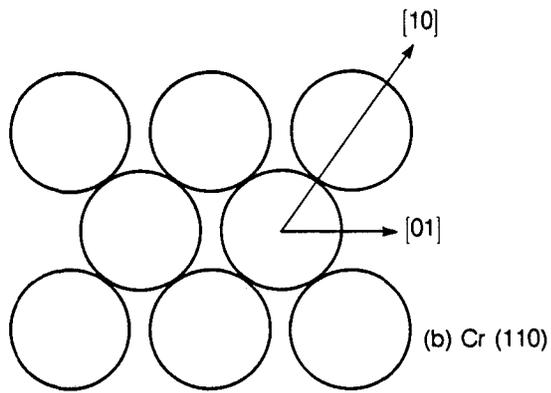
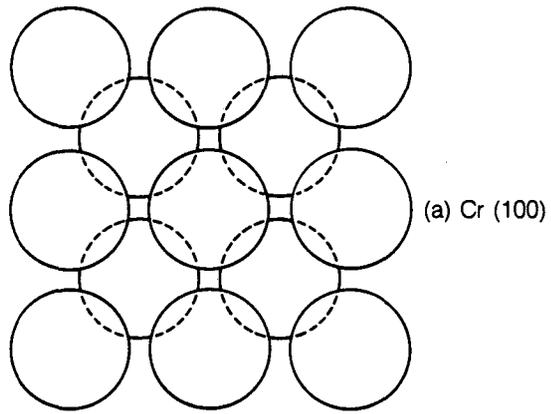
Figure 10

CO/Cr(111) 1.0 L



XBL 8412-5469

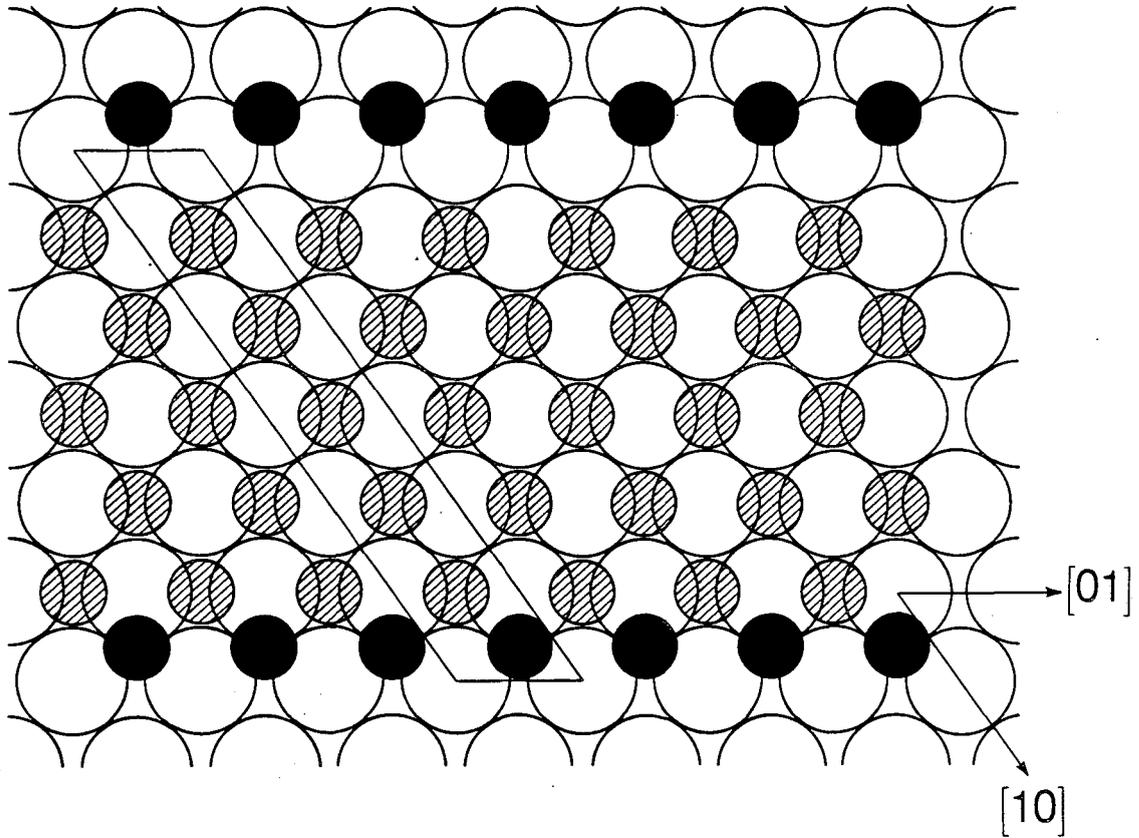
Figure 11



XBL 851-773

Figure 12

CO/Cr(110) 825K Anneal



XBL 851-774

Figure 13

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*LAWRENCE BERKELEY LABORATORY  
TECHNICAL INFORMATION DEPARTMENT  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720*