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RADIATION DAMAGE STUDIES BY X-RAY PHOTOELEC-TRON SPECTROSCOPY II. ELECTRON IRRADIATED Li<sub>2</sub>CrO<sub>4</sub> AND Li<sub>2</sub>WO<sub>4</sub>

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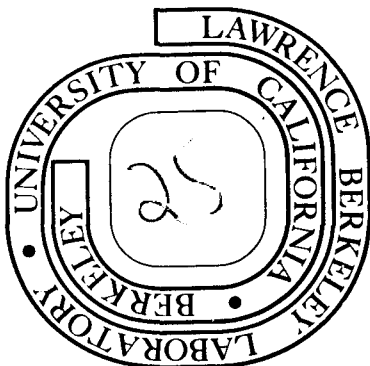
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Radiation Damage Studies by X-ray Photoelectron Spectroscopy  
II. Electron Irradiated  $\text{Li}_2\text{CrO}_4$  and  $\text{Li}_2\text{WO}_4^*$

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ABSTRACT

Single crystals of  $\text{Li}_2\text{CrO}_4$  and  $\text{Li}_2\text{WO}_4$  were irradiated in situ with 0.3 - 1.6 keV electrons in an UHV x-ray photoelectron spectrometer. Chemical shifts of core-level peaks in XPS spectra indicate formation of Cr(III) on the irradiated  $\text{Li}_2\text{CrO}_4$  surface and of W(IV) and W(V) on the irradiated  $\text{Li}_2\text{WO}_4$  surface. Accompanying formation of the reduced species, new peaks attributable to photoelectrons from non-bonding orbitals appear at binding energies just below the respective Fermi levels. A lower limit of the G-value for Cr(III) formation is estimated to be about  $1.3 \times 10^{-2}$  from the differential energy loss of the incident electrons. Comparison of this G-value with previous data determined by ESR suggests that solid surfaces are far more sensitive to radiation damage than the bulk. The irradiation of  $\text{Li}_2\text{WO}_4$  causes a shift in the entire XPS spectrum to lower binding energy, initially ca. 2 eV, which decreases over a 20 hour period until the original peak positions are recovered. This is interpreted in terms of surface charging caused by electron irradiation.

## I. INTRODUCTION

A new approach to radiation damage studies, by means of x-ray photoelectron spectroscopy (XPS), was presented in the previous paper.<sup>1</sup> Not only were the chemical forms of products on the surfaces of electron-irradiated  $\text{LiNO}_3$  and  $\text{Li}_2\text{SO}_4$  determined from chemical shifts in core-level peaks, but the G-values (i.e., the number of molecules produced or decomposed per 100 eV of radiation absorbed) were also estimated from the differential energy losses of the incident electrons. This paper reports the effects of electron irradiation on the XPS spectra of  $\text{Li}_2\text{CrO}_4$  and  $\text{Li}_2\text{WO}_4$  single crystals.

Recent applications of XPS by De Angelis and Schiavello<sup>2,3</sup> provided interesting information about Al  $K\alpha$  x-ray induced reduction on the surfaces of Cr(VI) and W(VI) compounds. From chemical shifts in core-level peaks, the species formed on  $\text{CrO}_3$  and  $\text{K}_2\text{CrO}_4$  surfaces were assigned as being only Cr(III),<sup>2</sup> while reduction products on a  $\text{Na}_{0.547}\text{WO}_3$  surface were identified as W(IV) and W(V).<sup>3</sup> In both cases, however, valence band spectra could yield further interesting information. Cr(III) has three electrons in the 3d shell and W(IV) and W(V) have two and one electrons, respectively, in the 5d or 6s atomic shells; the central atoms of the parent oxyanions have no electrons in these subshells. Because these atomic subshells are non-bonding orbitals, photopeaks from these shells are expected to lie on the low binding energy side of the molecular orbital peaks. In fact, a photopeak in this position was found for an UV-irradiated  $\text{WO}_3$  film by Hollinger, et al.<sup>4</sup>, and was correlated with a blue coloration of the film.

In this paper, spectral changes in the core levels as well as the valence band region are examined. The observations of multiplet splitting in the Cr(3s) peak and of a photopeak attributable to the non-bonding orbital provide further confirmatory evidence of Cr(III) formation on an irradiated  $\text{Li}_2\text{CrO}_4$  surface. The G-value for the Cr(III) formation will be compared with the corresponding bulk data. Time-dependent changes in the XPS spectra of the electron-irradiated  $\text{Li}_2\text{WO}_4$  are reported. In addition, a conclusive assignment will be given for the origin of a satellite on the high binding-energy side of the W(4f) peaks, a subject of some uncertainty.<sup>3</sup> The time dependence of the  $\text{Li}_2\text{WO}_4$  spectra after irradiation is discussed in terms of sample charging and a rather long relaxation time unique to lithium tungstate. In all cases our spectra are explained quite well in terms of the production of reduced species, rather than invoking inelastic electron loss mechanisms<sup>6</sup> or color center formation.<sup>7</sup>

## II. EXPERIMENTAL

The single crystals were grown from their melts. Analytic-reagent grade  $\text{Li}_2\text{CrO}_4$  and  $\text{Li}_2\text{WO}_4$  powders were heated in air to 600°C and 820°C, respectively. The melts were then cooled at ca. 80°C/day. The high-purity single crystals so obtained were kept in a vacuum desiccator until the time of the XPS measurements due to their highly hygroscopic nature.

In situ irradiations were carried out by using 0.3 - 1.6 keV electrons, as reported previously.<sup>1</sup> The XPS spectra were recorded at pressures less than  $1 \times 10^{-9}$  Torr by a Hewlett-Packard 5950A ESCA

spectrometer, which utilizes monochromatized Al  $K\alpha$  x-rays (1486.6 eV). The sample surface was oriented at  $38^\circ$  from the direction of the spectrometer electron energy analyzer. The x-ray source power was 1200 W. The instrumental resolution was such that the measured full-width at half-maximum height (FWHM) of the Au(4f) $_{7/2}$  line of a polycrystalline gold sample was 0.88 eV. Charging effects caused by the source x-rays were minimized by flooding the sample surfaces with low energy electrons. The optimum voltage and filament current of the electron flood gun were determined to be 1.5 V, 0.6 mA for the  $\text{Li}_2\text{CrO}_4$  sample and 4 V, 0.8 mA for the  $\text{Li}_2\text{WO}_4$  sample.

Binding energies were referenced to the Fermi level of the respective solids. Published valence band spectra<sup>8-11</sup> have also been utilized for the confirmation of the binding energies and assignment of the molecular orbitals of  $\text{CrO}_4^{2-}$ . Other aspects of the experimental procedure have been described previously.<sup>1</sup>

### III. RESULTS AND DISCUSSION

#### A. XPS Spectra of Electron-Irradiated $\text{Li}_2\text{CrO}_4$

Irradiation of  $\text{Li}_2\text{CrO}_4$  with 1 keV electrons for 10 minutes at 1 mA electron gun filament current induced considerable changes in both the core-level and valence band spectra, while exposure to source x-rays for as long as 40 hours caused only very small changes. Figure 1 shows the spectral changes in the Cr(2p) region. All spectra were normalized to the intensity of the highest peak, and the total incident charge is indicated by  $I_c$  in units of  $10^{-1}$  Coulomb/cm<sup>2</sup>. As seen in Fig. 1(a), a small feature appears at a binding energy lower by ca. 2.8 eV than

the main peak position of  $\text{Cr}(2p)_{3/2}$ . As this spectrum was recorded after exposure to source x-rays for 24 hours, this feature might be caused by x-ray induced reduction. A similar observation was made for a  $\text{CrO}_3$  sample.<sup>2</sup> This feature is conspicuously enhanced by electron irradiation and about 80% of the  $\text{CrO}_4^{2-}$  within the sampling depth undergoes radiation induced reduction following a total dose equal to  $I_c = 14.3$  of  $1.4$  keV electrons. The oxidation state of the product is inferred to be +3 by comparison of the chemical shift with values reported for various inorganic chromium compounds.<sup>12-15</sup> From our measurements the spin-orbit splittings between  $\text{Cr}(2p)_{1/2}$  and  $\text{Cr}(2p)_{3/2}$  are  $9.1$  eV for  $\text{CrO}_4^{2-}$  and  $9.8$  eV for  $\text{Cr(III)}$ . Such an increase in the splitting energy with a decrease in the oxidation state of chromium has been found in previous work,<sup>12-14</sup>

The assignment of the product is also supported by spectral changes in the  $\text{Cr}(3s)$  region, shown in Fig. 2. In spite of the 80% reduction shown by the  $\text{Cr}(2p)$  lines, Fig. 2(b) appears to show that a considerable amount of  $\text{CrO}_4^{2-}$  remained. This is due to a multiplet splitting in the  $3s$  level, which is well-known for compounds of transition metals possessing unpaired  $3d$  electrons.<sup>16-18</sup>  $\text{Cr(III)}$  has three unpaired electrons in the  $3d$  shell, while  $\text{Cr(VI)}$  in  $\text{CrO}_4^{2-}$  has none. The splitting energy of the  $3s$  level increases with the number of unpaired electrons, and we can expect ca.  $4$  eV for the  $3s$  splitting of  $\text{Cr(III)}$  from an evaluation given by Carver, et al.<sup>16</sup> The splitting of  $3.8$  eV observed here is in good agreement with this expectation and is consistent with the observed values for  $\text{Cr}_2\text{O}_3$ <sup>14</sup> and  $\text{NaCrO}_2$ .<sup>15</sup> Assuming that ionization of the  $3s$  shell results in only one (exchange-split) electron



configuration for the final state, the theoretical intensity ratio of the high-energy triplet peak to the low-energy quintet peak is predicted to be 0.6 from the multiplicity ratio. The observed value of 0.7, which was obtained after correcting for the remaining  $\text{CrO}_4^{2-}$  contribution in the high-energy peak, is consistent with this estimate.

Figure 3 shows spectral evolution in the Cr(3p) region with radiation exposure. The observed chemical shift in the Cr(3p) line of the product, vis. -4.4 eV, corresponds well to the reported difference of -4.5 eV in the Cr(3p) energy between  $\text{NaCrO}_2$  and  $\text{Na}_2\text{CrO}_4$ .<sup>13</sup> Changes in the valence band region are displayed in Fig. 4. The spectral shapes in Fig. 4(a) are analogous to those reported for  $\text{CrO}_4^{2-}$  in previous publications.<sup>8-10</sup> The  $4t_2$  and  $5a_1$  orbitals are mainly O(2s) in character, and the  $1e$  and  $5t_2$  orbitals have O(2p) character. After irradiation, two new peaks (I) and (II) appear at 10.3 and 2.4 eV, respectively. The absolute intensity of peak (I) initially increases with total radiation dose and then decreases under heavy irradiation, while the intensity of peak (II) does not change with respect to the  $1e$ ,  $5t_2$  peak as shown in Figs. 4(b) and 4(c). Peak (I) is assigned to the O(2p)-like bonding orbitals of product molecular oxygen formed in the crystal lattice. The FWHM of this peak is 1.8 eV and is considered too narrow to arise from valence orbital hybridization in a Cr-O bond. Heavy irradiation caused a relative decrease in the intensity of this peak due to thermal transport of the trapped  $\text{O}_2$  to the sample surface and subsequent desorption during electron bombardment. The broadening of the peaks from O(2s)-derived orbitals from 2.7 eV FWHM in Fig. 4(a) to 3.3 eV in Fig. 4(c) is attributable to O(2s)-derived molecular orbitals of the trapped  $\text{O}_2$ .

On the other hand, peak (II) is assigned to the Cr(3d)-derived orbitals of the reduced product. Photopeaks in this position from non-bonding orbitals have been previously observed for both Cr(III) and Cr(IV) compounds.<sup>12,14</sup>

From the above observations we conclude the main products are lithium chromite ( $\text{LiCrO}_2$ ) and molecularly adsorbed oxygen.  $\text{LiCrO}_2$  is expected to be a more stable chemical form than  $\text{Cr}_2\text{O}_3$  in the presence of  $\text{Li}^+$ . This assignment is also based on the observation that neither O(1s) nor Li(1s) attributable to  $\text{Li}_2\text{O}$ , which were observed in irradiated  $\text{LiNO}_3$  and  $\text{Li}_2\text{SO}_4$ ,<sup>1</sup> appear in irradiated  $\text{Li}_2\text{CrO}_4$ . In addition, the production of  $\text{CrO}_2^-$  has been observed in gamma-irradiated  $\text{K}_2\text{CrO}_4$  by ESR studies.<sup>19</sup>

#### B. Determination of Absolute Cr(III) Yield

The importance of the G-value estimated from XPS data was discussed in detail in the previous paper in connection with irradiated  $\text{Li}_2\text{SO}_4$ .<sup>1</sup> The irradiation of  $\text{Li}_2\text{CrO}_4$  does not yield a gaseous chromium containing product, while  $\text{Li}_2\text{SO}_4$  could yield a gaseous product such as  $\text{SO}_2$  that might be lost during electron irradiation. Thus the present case could in principle yield more reliable G-values.

Figure 5 shows the fraction of chromium present as product Cr(III) estimated from the peak intensities of  $\text{Cr}(2p)_{3/2}$  and  $\text{Cr}(3p)$ . The differences in product estimates from the two different core lines indicate the precision of the determination. The initial slope of the curve in Fig. 5 must be employed to estimate the G-value.

A lower limit of the G-value for the differential energy loss can be obtained as previously described:<sup>1</sup>

$$G \approx \frac{A \cdot \rho \cdot \lambda'}{M(E_{e1} - E_{e2})} \frac{P}{C} 1.6 \times 10^{-17} \quad , \quad (1)$$

where A and M are Avogadro's number and the molecular weight of  $\text{Li}_2\text{CrO}_4$ , respectively. The density  $\rho$  is  $2.427 \text{ g/cm}^3$ .<sup>20</sup> P is the fraction of Cr(III) in the layer whose thickness corresponds to  $\lambda'$ , the effective photoelectron sampling depth, and C is the integrated incident charge per unit area of the radiation dose.  $E_{e1}$  and  $E_{e2}$  are the incident electron energy and the average kinetic energy of an electron which has traversed a layer of thickness  $\lambda'$ . To determine  $(E_{e1} - E_{e2})$ , the extrapolated penetration range  $R_e$  was estimated from a semiempirical equation<sup>21</sup> which gives a good fit to experimental data over the range of electron energies from 0.3 keV to 30 MeV. Note that  $(E_{e1} - E_{e2})$  is an upper limit for the amount of energy deposited in the layer of thickness  $\lambda'$ , since secondary electrons may carry energy out of this layer, either into the vacuum or deeper within the crystal.<sup>1</sup> The inelastic collision mean free path  $\lambda_e$  was calculated as a function of energy according to an equation by Penn.<sup>21</sup> Both  $R_e$  and  $\lambda_e$  are shown as a function of electron energy in Fig. 6. From Fig. 6,  $\lambda_e$  for 907 eV kinetic energy photoelectrons from the  $\text{Cr}(2p)_{3/2}$  shell is  $15.6\text{\AA}$ , yielding a <sup>mean</sup> sampling depth  $\lambda'$  of  $9.6\text{\AA}$  for a  $38^\circ$  take-off angle.<sup>1</sup> The amount of energy lost by an electron in the layer  $\lambda'$  for an incident energy of 1 keV can be estimated<sup>1</sup> from the  $R_e$  curve of Fig. 6 to be ca. 19.2 eV. The G-value given by Eq. (1) simplifies to yield:

$$G \approx 9.0 \times 10^{-4} \left( \frac{\Delta P}{\Delta C} \right)_i \quad (2)$$

where  $(\Delta P/\Delta C)_i$  refers to the initial slope of the yield curve in the layer  $\lambda'$ . Thus the lower limit of the G-value for the Cr(III) formation is determined to be  $1.3 \times 10^{-2}$  which is also appropriate for the radiation decomposition of  $\text{Li}_2\text{CrO}_4$ .

It is interesting to compare the present value with related data, obtained by ESR. Apers and co-workers<sup>18</sup> obtained G-values of the order of  $10^{-4}$  for the yield of total radicals including  $\text{CrO}_2^-$ , and of  $2 \times 10^{-5}$  for  $\text{CrO}_3^-$  formation<sup>23</sup> in  $\text{K}_2\text{CrO}_4$  single crystals irradiated with  $^{60}\text{Co}$  gamma-rays at room temperature. These small G-values may indicate that the potassium salt is more resistant to radiation damage than the lithium salt. However, the most important parameter relevant to our studies is the extreme surface sensitivity of the XPS probing technique. Since our surface G-value, which in fact is a lower limit, is two to three orders of magnitude larger than the bulk values, the surface must be far more sensitive to ionizing electron irradiation than the bulk of the crystal. Among the likely causes of this enhanced surface reactivity are surface charging, loss of volatile dissociation products, and hindrance of diffusional recombination by stable or metastable composition and/or charge gradients near the surface. None of these factors could affect radiation damage sensitivity in the bulk.

### C. Charging and Chemical Reduction of the $\text{Li}_2\text{WO}_4$ Surface

Electron irradiation did not cause visible changes in the  $\text{Li}_2\text{WO}_4$  surface. The most evident change in the XPS spectra was a time-dependent shift in the core-level peaks. The spectral changes in the O(1s)

and W(4f) regions of the sample irradiated by 1 keV electrons are shown in Fig. 7. The total incident charge was  $0.51 \text{ Coulomb/cm}^2$ , and the elapsed times after irradiation are given in the rectangles. Just after irradiation the O(1s) and W(4f) regions shift toward lower binding energy by 1.8 and 2.2 eV, respectively. These shifts decrease with the passage of time, and after 20 hours the original peak positions are nearly recovered. Because all the core-level peaks, including  $W(4p)_{3/2}$  ( $E_b \approx 429 \text{ eV}$ ) and  $W(4d)_{5/2}$  ( $E_b \approx 249 \text{ eV}$ ), shift to lower binding energy and require almost the same time for recovery, the phenomena can not be attributed to formation of unstable products.<sup>24</sup>

The direction of the spectral shift means that photoelectrons gain kinetic energy during emission. This can be interpreted in terms of sub-surface charging. Drenckhan, et al.<sup>25</sup> found a high energy tail extending 80 eV in the energy distribution of thermally-stimulated exoelectron emission from an electron-irradiated  $\text{SiO}_2$  surface. They suggested that this high energy electron emission is caused by acceleration arising from the electric field induced between the positively charged sample surface and a negatively charged region around the terminal site of the incident electrons. In the present case, the sample surface relevant to the XPS spectra might be positively charged due to secondary electron emission during irradiation. On the other hand, the terminal region of incident and secondary electrons will be negatively charged until diffusive processes neutralize the excess charge. The electric field generated in this way can accelerate photoelectrons. This would explain a larger binding energy shift for the W(4f) peak than for the O(1s) peak, because photoelectrons from the W(4f) shell have a larger escape depth, corresponding to a longer acceleration distance. The induced

field strength in the surface layer of irradiated  $\text{Li}_2\text{WO}_4$  is estimated to be  $1 \times 10^7$  V/cm from the magnitude of the energy shift and the mean free path of the photoelectrons. The peak broadening of W(4f) in Fig. 7(b) is also presumably due to differences in the acceleration distance along the mean-free path. The spectral evolution in Fig. 7(c) indicates a gradual neutralization of the excess charge, due presumably to electron diffusion and recombination. The observed shift must arise through photoelectron acceleration by a net negative subsurface charge. The limited broadening and considerable peak shifts in Fig. 7 show that the excess negative charge layer lies considerably deeper than the sampling depth. It is also noteworthy that the time-dependent shift is characteristic of only irradiated  $\text{Li}_2\text{WO}_4$ ; such phenomena have not been observed for the other ten oxyanion samples we have examined to date.

A permanent change in the W(4f) region is the broadening with a small shoulder to the low energy side, as seen in Fig. 7(c). Similar trends were also observed for the W(4p) and W(4d) lines. This broadening arises from the formation of reduced tungsten species. The spectral shape of W(4f) in Fig. 7(c) is very similar to the observations of De Angelis, et al.<sup>3</sup> for  $\text{Na}_{0.547}\text{WO}_3$  exposed to Al  $K\alpha$  x-rays for 8 hours. They resolved their spectrum into three chemically inequivalent components: W(IV), W(V), and W(VI). However, it is difficult to draw a definite conclusion for the amount of reduction of the tungsten bronze due to x-ray exposure, since a spectrum of the 4f region for initial x-ray exposure was not given. An analogous spectral feature of W(4f) has been observed for UV colored  $\text{WO}_3$  films by Hollinger, et al.<sup>4</sup> There is only fair agreement between their observed spectrum and a computer fit which included two spin-orbit split doublets due to W(VI) and W(V) and their corresponding plasmon satellites (see Fig. 2 in Ref. 4).

Using only two spin-orbit doublets with no satellite structure, we were unable to obtain a satisfactory fit, especially for the low energy side of the W(4f) region in Fig. 7(c). However, inclusion of a W(IV) component yielded a good fit to our data, shown in Fig. 8. The W(4f) linewidths for W(IV) and W(V) were assumed to be the same as that for W(VI), and the energy separation between W(IV) and W(VI) was taken to be 3.0 eV from the data for tungsten oxides.<sup>26</sup> A slight peak at higher binding energy was not included in the spectral fitting. The fit indicates a 26% transformation of  $\text{WO}_4^{2-}$  within the photoelectron sampling depth into reduced species. While computer fits of partially-resolved spectra are never as satisfying as actually resolving the lines, we note that the  $4f_{7/2}$  peak of W(V) appears as a readily observable shoulder on the W(VI)  $4f_{7/2}$  peak in Fig. 8, and even the weak W(IV)  $4f_{7/2}$  peak gives rise to a visible shoulder.

The W(4f) spectrum obtained by Hollinger, et al.<sup>4</sup> of an UV colored  $\text{WO}_3$  film can be seen from Fig. 1(c) of Ref. 4 to be very similar to the spectrum presented in Fig. 8 of this work. A small but definite shoulder which corresponds well to W(IV) appears at ca. 34 eV  $E_B$ , but was neglected in the spectral fit. The introduction of two extra pairs of Gaussian peaks as plasmon satellites in the spectral fit of Ref. 4 does not appear justified in light of the excellent fits obtained for tungsten oxide films by De Angelis and Schiavello<sup>3</sup> and for  $\text{Li}_2\text{WO}_4$  from this work using only one spin-orbit split doublet for each chemical state of W present. In addition, such intense plasmon satellites required in the fit of Ref. 4 would give rise to a series of multiple loss peaks, which are not observed. The apparent broadening seen in the spectra of the UV colored films must be explained by some other mechanism, such as perhaps an inhomogeneous charging effect induced by

intense UV irradiation similar to that observed for electron bombardment. There is also a striking similarity in the peak positions for the W(VI) and W(V) components of Fig. 8 and the W(4f) spectra of Campagna, et al.<sup>6</sup> and Chazalviel, et al.<sup>27</sup> This correspondence argues strongly in favor of the interpretation of the spectra of the sodium tungsten bronzes  $\text{Na}_x\text{WO}_3$  at least predominantly in terms of mixed valence states of tungsten, rather than collective excitation phenomena. The presence of a small satellite structure such as is observed for the Na(1s) and O(1s) peaks<sup>6</sup> in spectra of  $\text{Na}_x\text{WO}_3$  acts to complicate the spectra but it probably does not contribute a major portion of the W photoemission intensity.

The valence band region, with the Li(1s) line, is shown in Fig. 9. The origin of peak (II) on the high binding energy side of W(4f) in Fig. 9 has been discussed by several workers.<sup>4-6</sup> Considering the observations of this peak in the XPS spectra of metallic tungsten,<sup>5</sup>  $\text{WO}_3$ ,<sup>3,4,28</sup> and  $\text{Na}_x\text{WO}_3$  ( $x = 0.547, 0.620, 0.764, \text{ and } 0.805$ ),<sup>3,6</sup> we infer it is characteristic of tungsten rather than a particular compound. It is associated with another peak (I) located around 55 eV  $E_B$ . We assign these to  $\text{W}(5p)_{3/2}$  and  $\text{W}(5p)_{1/2}$ , respectively. The peak intensity of  $\text{W}(5p)_{3/2}$  is estimated to be approximately 0.15 times that of  $\text{W}(4f)_{7/2}$  from the photoionization cross sections calculated by Scofield.<sup>29</sup> The separation energy observed for the spin-orbit splitting is 13.5 eV, while Lu, et al.<sup>30</sup> estimated a splitting of 10.4 eV.

Electron irradiation brought about the appearance of a new structure at ca. 2 eV below the Fermi level, as seen in Fig. 9(b). Such a low energy photopeak originates from a non-bonding orbital similar to



the one observed for irradiated  $\text{Li}_2\text{CrO}_4$ . Its intensity is about 0.1 times that of the O(2p)-derived orbital (IV). The peak shape and position are very similar to those found for UV colored<sup>4</sup> or electrocolored<sup>31</sup>  $\text{WO}_3$ , and for nonirradiated  $\text{Na}_x\text{WO}_3$ .<sup>6</sup> The lack of coloration of the irradiated  $\text{Li}_2\text{WO}_4$  sample proves conclusively that this feature is not due to emission from a color center, as had been suggested in connection with photoemission from UV and electrocolored films of  $\text{MoO}_3$  by Rabalais.<sup>7</sup> This feature is now well established<sup>3-6</sup> to arise from transitions out of the W(5d)/(6s) non-bonding orbitals (conduction band). That electron irradiation failed to color the  $\text{Li}_2\text{WO}_4$  crystal surface may be due to the extremely clean conditions under which the dosage was applied. Perhaps the final states for the transitions in the red portion of the spectrum of colored  $\text{WO}_3$  or  $\text{MO}_3$  are provided by  $\text{H}^+$  ions in the lattice which originate from water contamination of the sample or are injected into the sample during electrolysis.

Accompanying the spectral changes in the core-level peaks and valence band region, the Li(1s) line was broadened. This suggests formation of other lithium containing compounds. Although definite identification of the chemical forms of these compounds is not feasible,  $\text{Li}_2\text{WO}_3$  is a likely candidate though it can be only a minor constituent as indicated by the weak W(IV) signal observed. We note the absence of an O(1s) line attributable to  $\text{Li}_2\text{O}$ , similar to the situation observed for  $\text{Li}_2\text{CrO}_4$ .

Electron irradiation of anhydrous  $\text{Li}_2\text{CrO}_4$  produces Cr(III) as  $\text{CrO}^-$ , with a G-value of ca.  $1.3 \times 10^{-2}$ . It was clearly shown that the surface of this compound is much more sensitive to long-term electron radiation damage than is the bulk. In irradiated  $\text{Li}_2\text{WO}_4$ , products were identified as W(V) and (with less certainty) W(IV). Further,  $\text{Li}_2\text{WO}_4$  was found to be far more stable than  $\text{Li}_2\text{CrO}_4$  for electron irradiation induced reduction of the central metal in the oxyanion. Occupied non-bonding orbitals were formed in the irradiation products in both cases. Time dependent shifts were observed for  $\text{Li}_2\text{WO}_4$ , with recovery times of ca. 20 hours. These were attributed to subsurface charging. Again XPS has been shown to be a sensitive method for studying in situ chemical changes induced in a crystalline surface layer by electron irradiation.

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FIGURE CAPTIONS

- Fig. 1. Spectral changes in the Cr(2p) region of irradiated  $\text{Li}_2\text{CrO}_4$ . The chromium reduction product is assigned as  $\text{LiCrO}_2$ . The integrated incident charge per unit surface area  $I_c$  is in units of  $10^{-1}$  Coulomb/cm<sup>2</sup> (electron kinetic energy of 1 keV).
- Fig. 2. Spectral changes in the Cr(3s) region of irradiated  $\text{Li}_2\text{CrO}_4$ . In parts (b) and (c), the peak at higher binding energy contains intensity from the 3s level of Cr(VI) and from the higher binding energy component of the exchange split 3s level of Cr(III) (see text).
- Fig. 3. Spectral changes in the Li(1s) and Cr(3p) regions of irradiated  $\text{Li}_2\text{CrO}_4$ . The spin-orbit splitting in the Cr(3p) level is seen as only a small shoulder in the photoemission peaks.
- Fig. 4. Spectral changes in the valence band region of irradiated  $\text{Li}_2\text{CrO}_4$ . Peak I is assigned to (2p)-like levels of molecularly adsorbed oxygen. Peak II is due to transitions from the occupied Cr(3d) levels of the reduction product.
- Fig. 5. The value of  $\text{Cr(III)}/(\text{Cr(III)} + \text{Cr(VI)})$  as a function of the total incident charge. The values were determined from the intensities of the Cr(2p)<sub>3/2</sub> and Cr(3p) peaks.
- Fig. 6. Penetration range  $R_e$  and inelastic collision mean-free path  $\lambda_e$  of electrons in  $\text{Li}_2\text{CrO}_4$ . The semi-empirical equations used for the calculations for  $R_e$  and  $\lambda_e$  are given by Tabata, et al.<sup>20</sup> and Penn,<sup>21</sup> respectively. The dashed extrapolations of these curves represent the expected behavior for very low energy electrons.

Fig. 7. Part (a) shows the O(1s) and W(4f) spectral regions of  $\text{Li}_2\text{WO}_4$  before electron irradiation. Parts (b) and (c) illustrate the time evolution of these spectra after a radiation dose  $I_c = 0.51 \text{ Coulomb/cm}^2$  of 1 keV electrons.

Fig. 8. Deconvolution of the W(4f) region. The spectrum is the same as that shown in Fig. 7(c). The darker line indicates the sum of 6 Gaussians corresponding to  $\text{W}(4f)_{5/2}$  and  $\text{W}(4f)_{7/2}$  for the three likely chemical species present.

Fig. 9. Spectral changes in the valence band region of irradiated  $\text{Li}_2\text{WO}_4$ . The spectrum (b) was recorded 17 hours after irradiation. Peaks (I) and (II) are assigned to  $\text{W}(5p)_{1/2}$  and  $(5p)_{3/2}$ , respectively. Peaks (III) and (IV) are primarily O(2s) and (2p)-derived molecular orbitals. Peak (V) arises due to transitions from the occupied W 5d/6s orbitals of the reduction product.

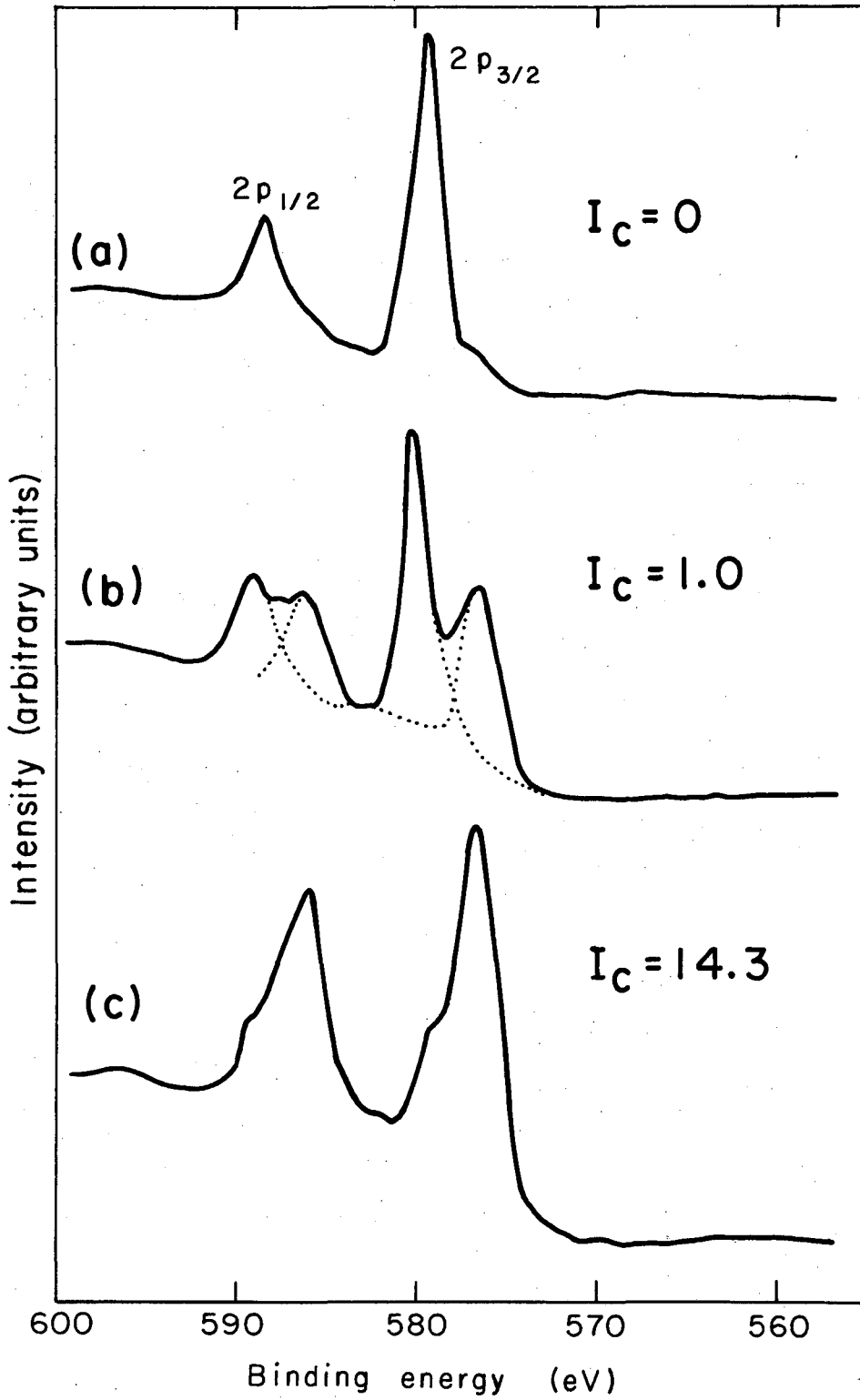


Fig. 1

XBL7612-III57



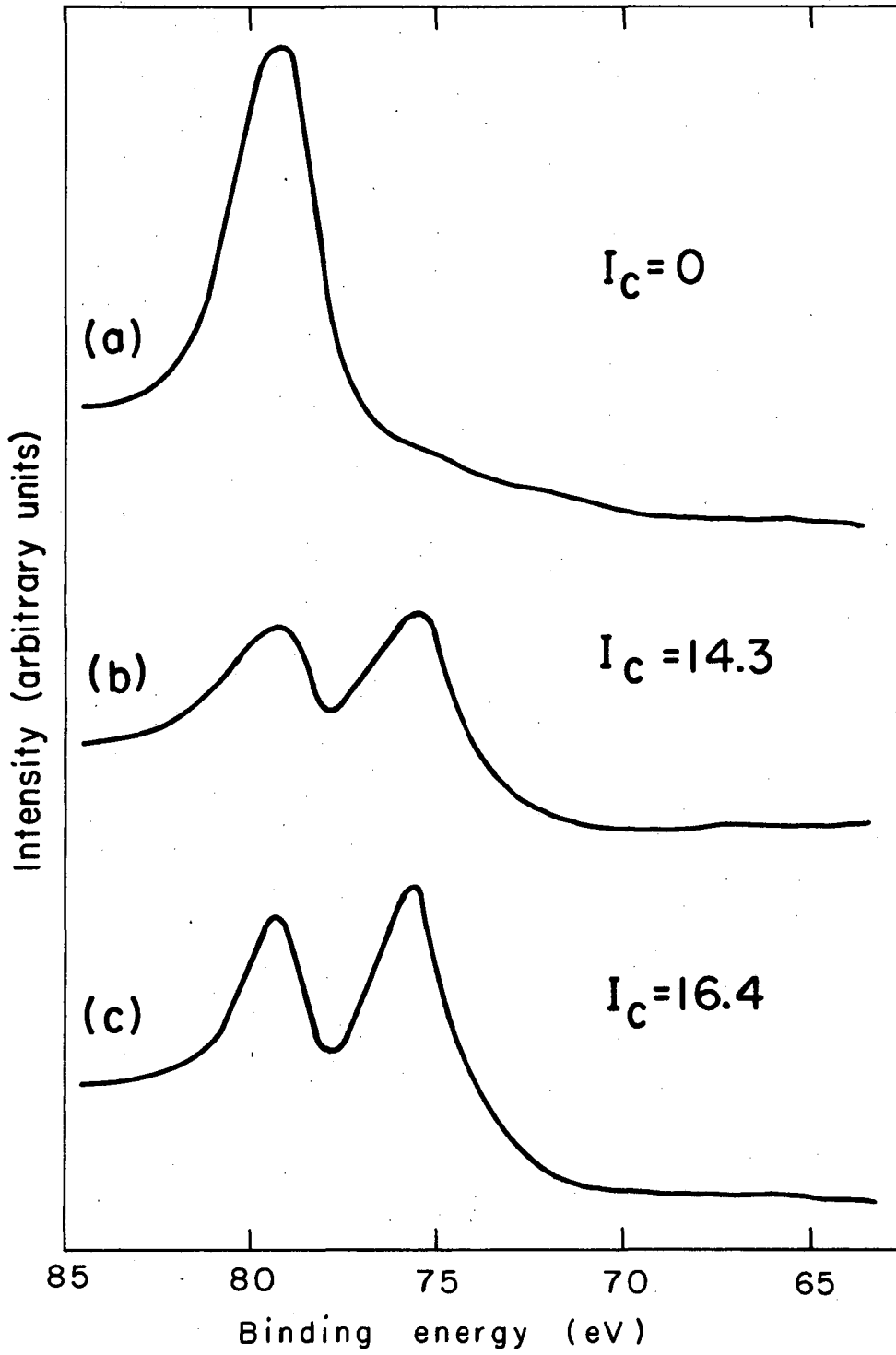


Fig. 2

XBL 7612 - 11153

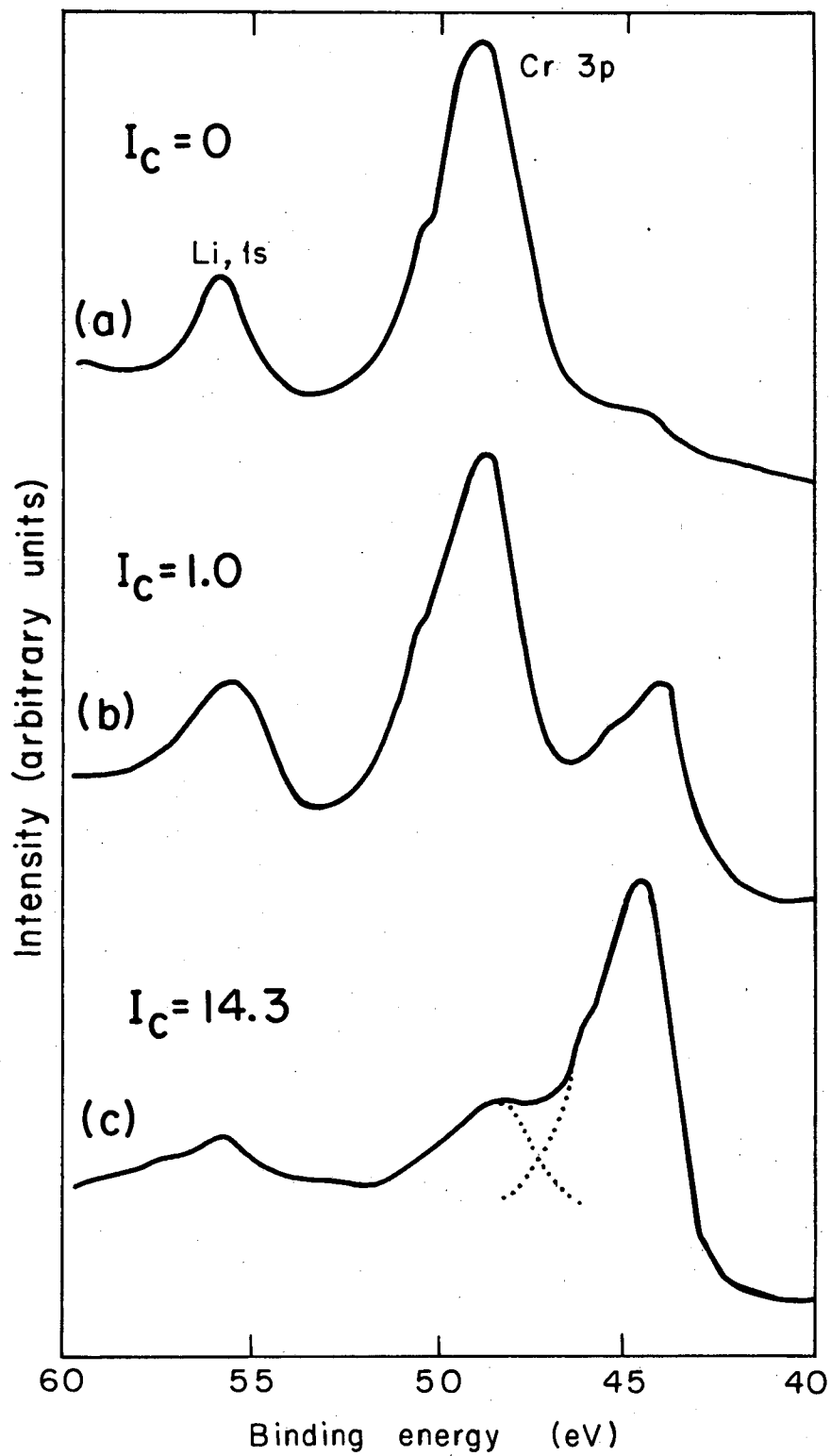


Fig. 3

XBL7612-11163

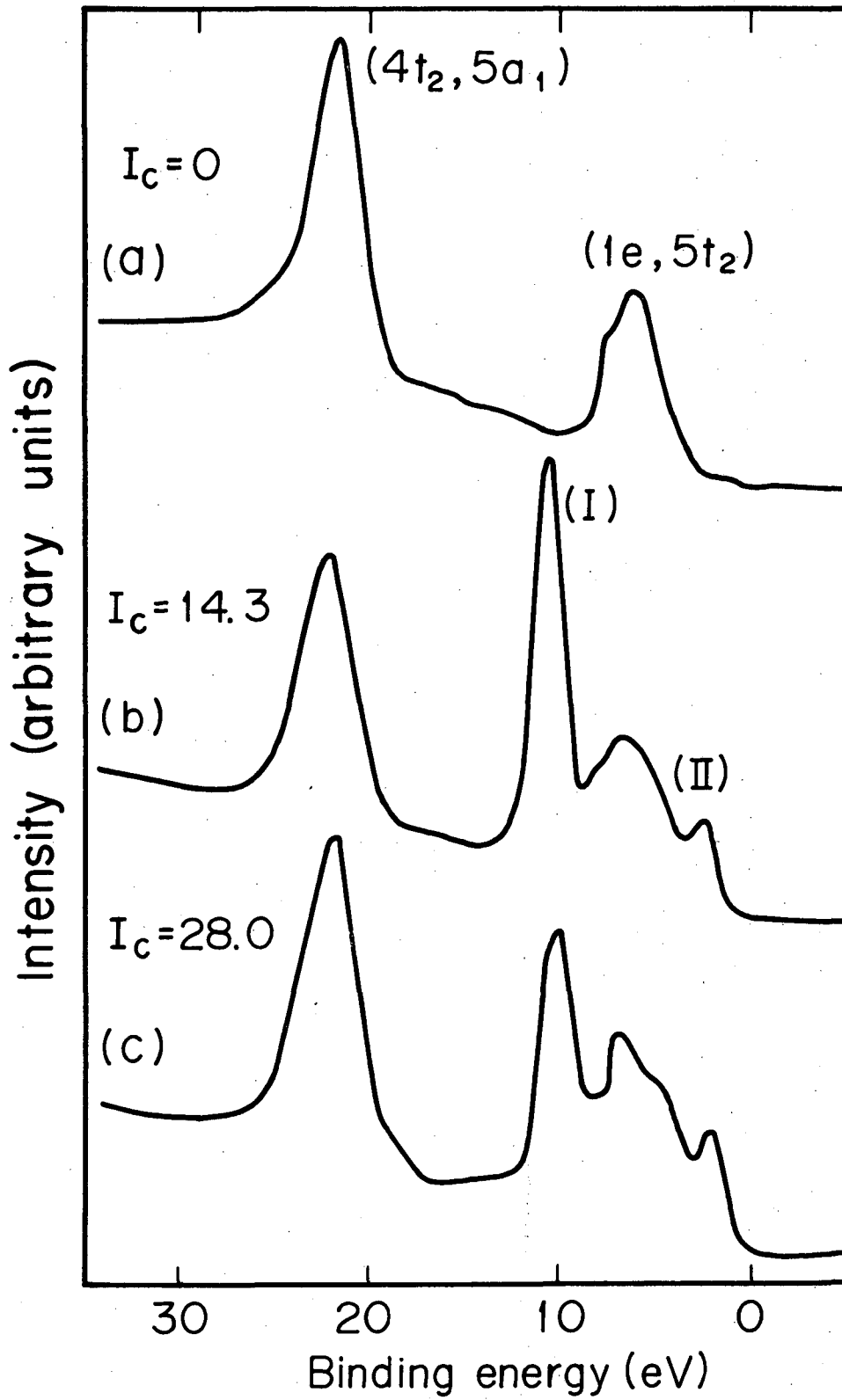


Fig. 4

XBL 7710-6853

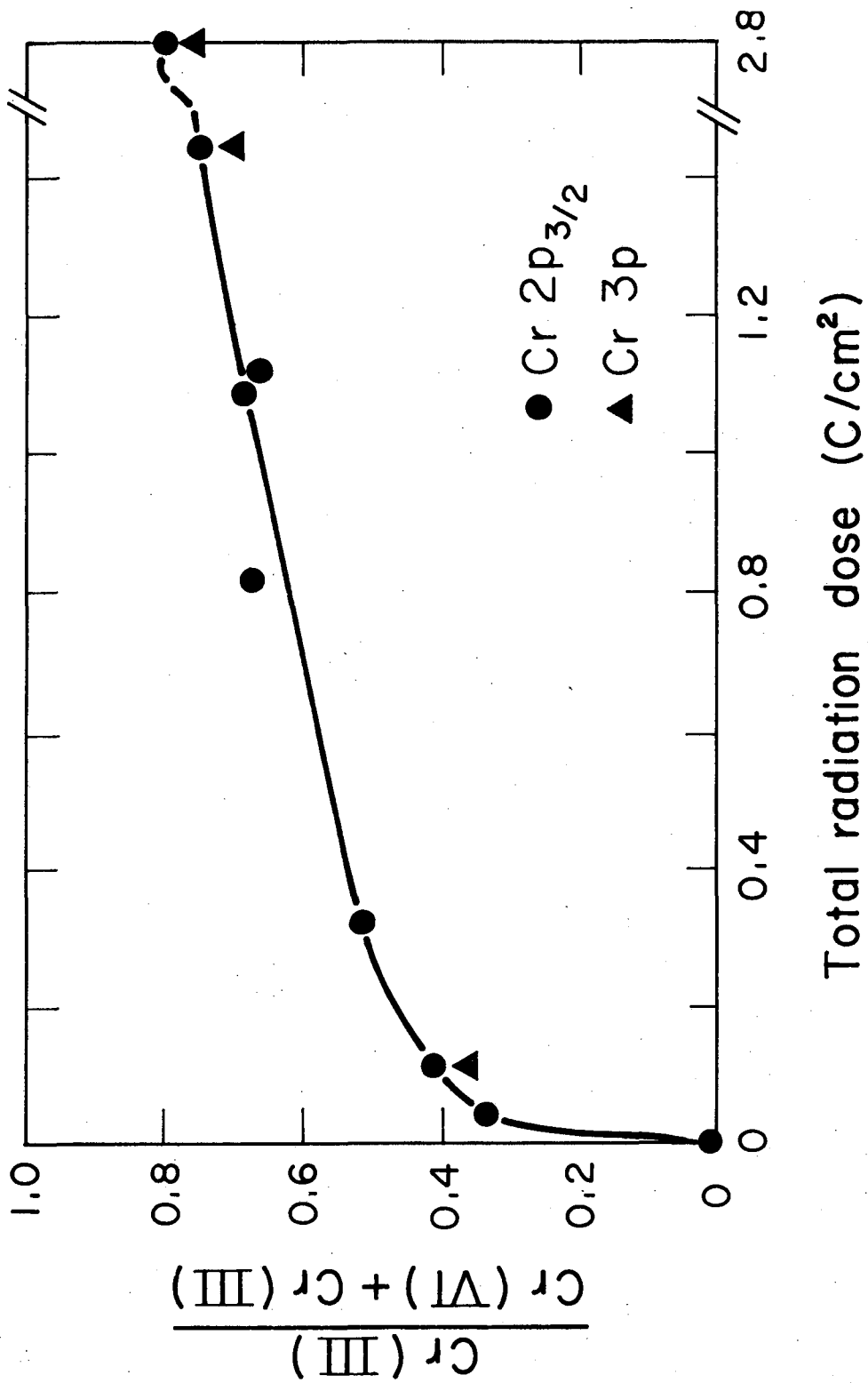


Fig. 5

XBL 777-130

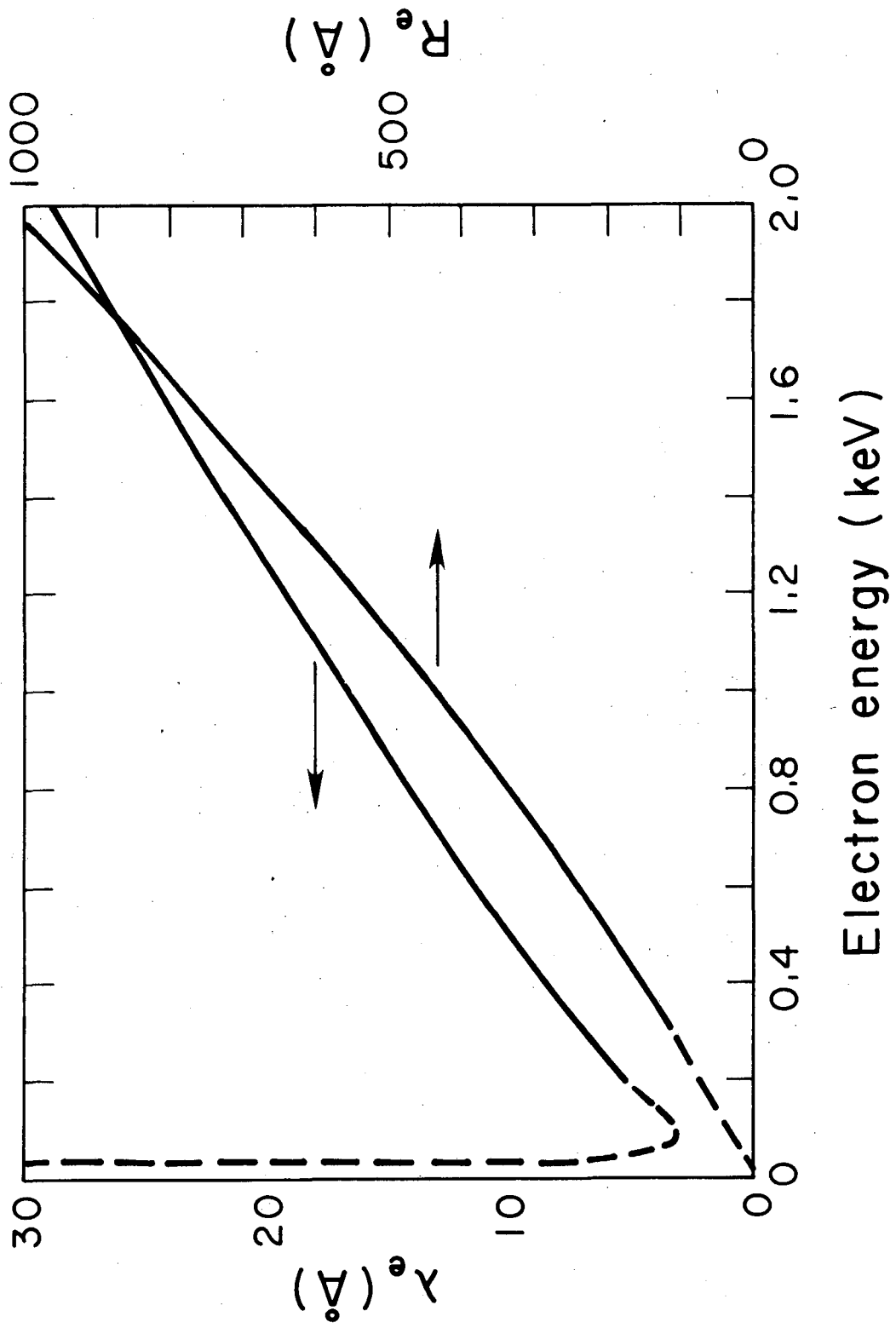


Fig. 6

XBL 777-1303

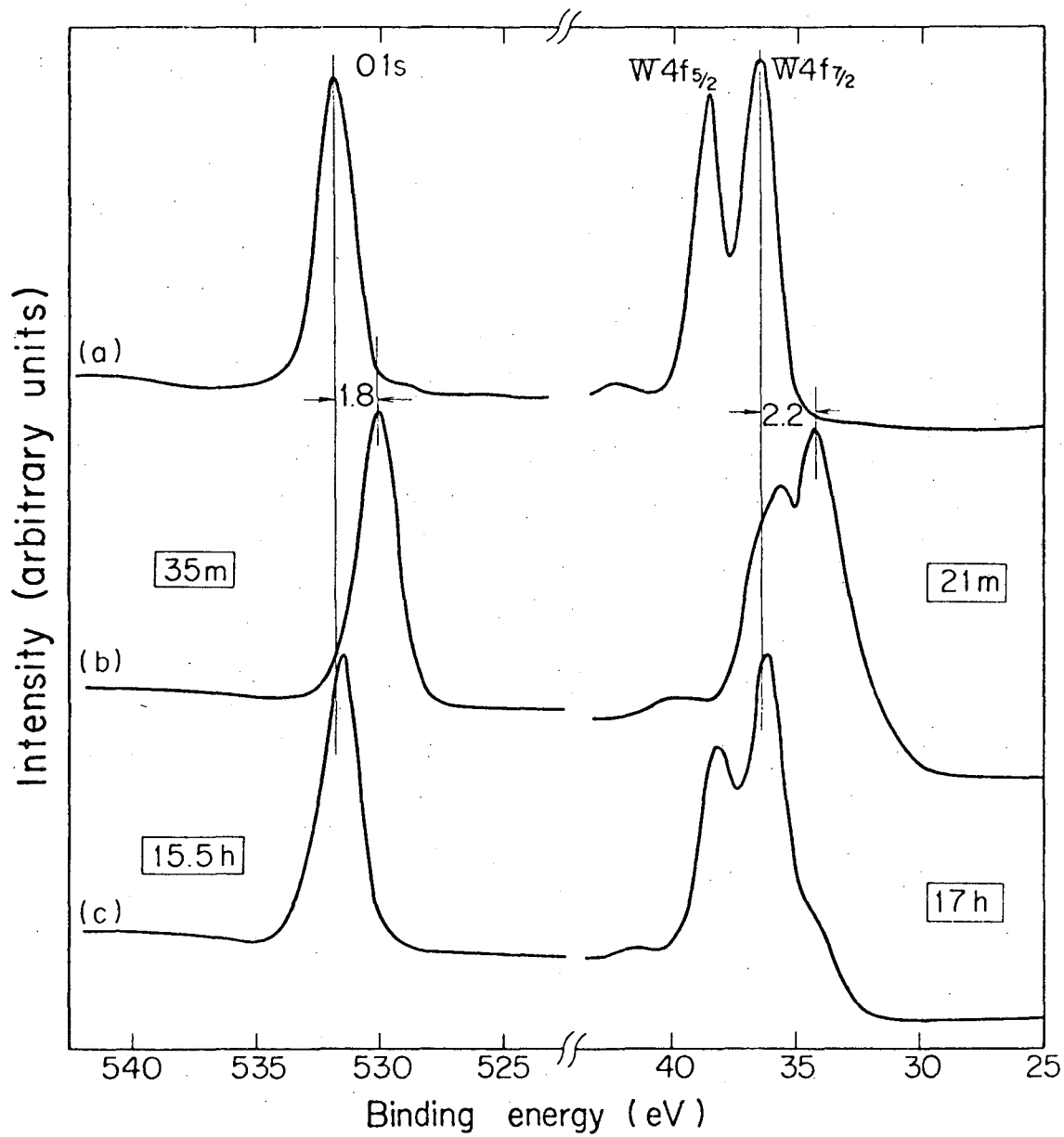


Fig. 7

XBL 7710-6848

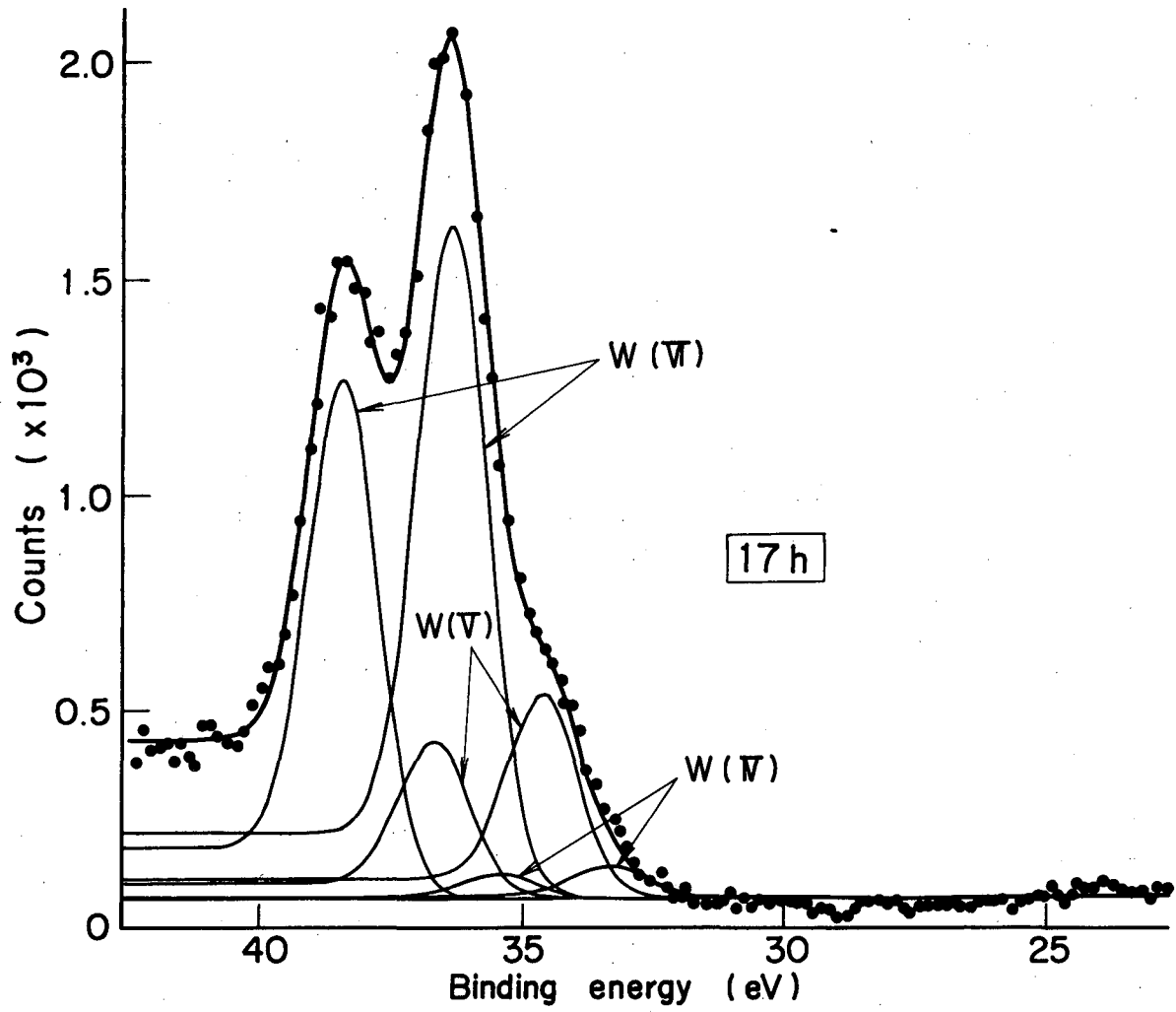


Fig. 8

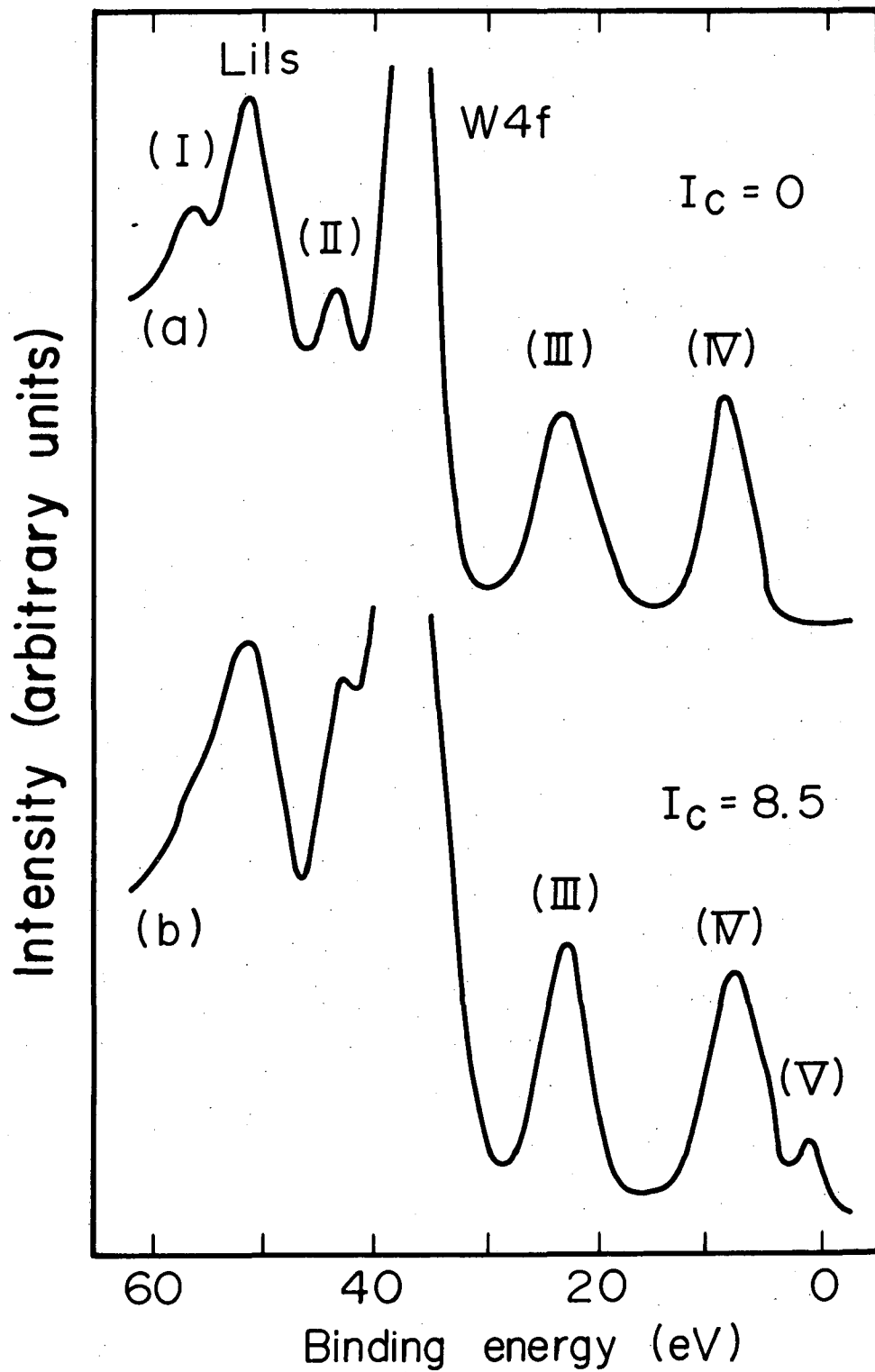


Fig. 9

XBL 7710-6850



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