High Resolution XPS Study of a Thin $Cr_2O_3(111)$ Film Grown on Cr(110)

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Accession #s 00317, 00318
Technique: XPS
Host Material: #00317: Cr metal; #00318: Cr_2O_3
Instrument: Leybold-Heraeus EA 11
Major Elements in Spectrum: Cr, O
Minor Elements in Spectrum: none
Printed Spectra: 6
Spectra in Electronic Record: 6
Spectral Category: comparison
Original Submission: 8/24/95
Accepted for Publication: 6/17/97

Transition metal oxides are important materials in heterogenous catalysis, as supporting materials as well as active components. The catalytic activity of Cr_2O_3 for IE polymerization of olefines or hydrogenation of alkenes is well known and rather high. Therefore, it is important to get information on the surface electronic structure of Cr_2O_3. Here we report high resolution XPS measurements of a thin epitaxial $Cr_2O_3(111)$ film grown on Cr(110). The oxide films have been prepared by *in situ* oxidation of a Cr(110) single crystal disk (12 mm diameter, 1.5 mm thickness, purity $5n$) at elevated temperatures (540 K to 780 K) in an atmosphere of 10^{-6} mbar of O_2. The oxygen doses have been typically in the range of a few thousand Langmuirs. Under these conditions a $Cr_2O_3(111)$ layer [$Cr_2O_3(0001)$ orientation in hexagonal notation] forms on the surface as confirmed via low energy electron diffraction IV analysis. The film thickness ranges from about 2.5 nm to 8.0 nm under the chosen preparation conditions, allowing electron spectroscopy to be performed without charge compensation. The studies of $Cr_2O_3(111)$ have been performed as part of a project aimed at investigating idealized catalytic systems under ultrahigh vacuum conditions. © *1998 American Vacuum Society.* [S1055-5269(96)00303-9]

Keywords: *x-ray photoelectron spectroscopy; oxidation; chromium oxide*

PACS: *79.60.Dp, 82.65.Jv, 81.65.Mq*

SPECIMEN DESCRIPTION (Accession #00317)

Host Material: Cr metal

CAS Registry #: 2440-47-3

Host Material Characteristics: homogeneous; solid; single crystal; conductor; metal; thin film

Chemical Name: chromium

Host Composition: Cr

Form: single crystal

Structure: (110) face centered cubic

As Received Condition: single crystal as grown (12 mm diameter, 1.5 mm thick, purity $5n$)

Analyzed Region: (110) surface

***Ex Situ* Preparation/Mounting:** single crystal cut in (110) direction and polished, then spot-welded to the manipulator

***In Situ* Preparation:** The Cr(110) substrate was cleaned by cycles of neon sputtering ($E = 750$ eV, $T = 780$ K, 2 h) and annealing ($T = 1040$ K, some minutes) until the contaminant concentration (nitrogen) was below 3% according to XPS.

Charge Control: No charge control was necessary, as the host material was metallic.

Temp. During Analysis: 300 K

Pressure During Analysis: $<1\times10^{-7}$ Pa

SPECIMEN DESCRIPTION (Accession #00318)

Host Material: Cr_2O_3

CAS Registry #: 2440-47-3

Host Material Characteristics: homogeneous; solid; single crystal; dielectric; inorganic compound; thin film

Chemical Name: chromium oxide

Host Composition: Cr, O

Form: thin film

Structure: $Cr_2O_3(111)$

History & Significance: Cr_2O_3 has been studied as part of a project aiming at modeling catalysts (especially supported catalysts) under ultrahigh vacuum (UHV) conditions. We have chosen to study a thin $Cr_2O_3(111)$ film instead of a bulk crystal since this allows for electron spectroscopy to be performed without charging of the sample. The substrate for the oxide was a Cr(110) single crystal disk (12 mm diameter, 1.5 mm thick, purity $5n$) with the main contaminant being nitrogen. For this film adsorption data as well as data for the electronic and geometric structure are available (Refs. 1 and 2).

As Received Condition: not specified

Analyzed Region: (111) surface

***Ex Situ* Preparation/Mounting:** no additional preparation after oxidation

***In Situ* Preparation:** Oxidation procedure: 10^{-6} mbar O_2, 1 min annealing at 540 K, followed by 2 min at 780 K, then flash at 1140 K. This was repeated until the low energy electron diffraction (LEED) pattern exhibited sharp spots of $Cr_2O_3(111)$ without visible spots of the Cr(110) substrate.

Charge Control: No charge control was necessary as the host material was metallic, and the oxide film was too thin for charging.

Temp. During Analysis: 300 K

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Pressure During Analysis: $<1\times10^{-7}$ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Leybold-Heraeus EA 11

Analyzer Type: spherical sector

Detector: 2 multichannel plates

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ Spectrometer

Analyzer Mode: constant pass energy

Throughput ($T=E^N$): $N=-1$

Excitation Source Window: 1.5 μm Al window

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 450 W

Analyzer Width: 3000 μm × 3000 μm

Signal Mode: multichannel direct

■ Geometry

Incident Angle: 45°

Source to Analyzer Angle: 45°

Emission Angle: 0°

Specimen Azimuthal Angle: 0°

Acceptance Angle from Analyzer Axis: 1.5°

Analyzer Angular Acceptance Width: 3° × 3°

■ Ion Gun

Manufacturer and Model: Leybold-Heraeus IQE 12/38

Energy: 500 eV

Current: 10 μA

Current Measurement Method: biased stage

Sputtering Species: Ne

Raster Size: 10000 μm × 10000 μm

Incident Angle: 45°

Polar Angle: 45°

Azimuthal Angle: 0°

DATA ANALYSIS METHOD

Energy Scale Correction: energy scale calibration to Fermi level of Cr metal

Quantitation Method: The thickness of the layer has been calculated from the intensity ratio of the Cr $2p_{3/2}$ levels of the Cr(110) substrate with and without oxide film using an empirical mean free path length for the electrons of 1.8 nm. The latter value has been calculated for Cr_2O_3 according to a procedure given by Seah and Dench (Ref. 3). Due to the limited accuracy of this value the error of the estimated layer thickness may be some 10%. Apart from this the film thickness is also strongly dependent on the oxygen dose and the oxidation temperature. Therefore the film thicknesses may vary for different films. For the preparation conditions chosen in our experiments we estimate the film thicknesses to range from about 2.5 nm to 8.0 nm. The equation used for calculating the film thickness was $I1/I2 = \exp(-\delta/\lambda$, where I1 = intensity of the Cr $2p_{3/2}$ level of Cr(110) with oxide, I2 = intensity of the Cr $2p_{3/2}$ level of Cr(110) without oxide, δ = film thickness, and λ = mean free electron path length.

ACKNOWLEDGMENTS

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2. F. Rohr, M. Beumer, H.-J. Freund, J. A. Mejias, V. Staemmler, S. Moeller, L. Hammer, and K. Heinz, Surf. Sci. Lett. **372**, L291 (1997).
3. M. P. Seah and W. A. Dench, Surf. Interface Anal. **1**, 1 (1979).

SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area	Sensitivity Factor	Concen- tration (at. %)	Peak Assignment
00318-02	Cr $2p_{3/2}$	576.6	2.5	...	...	...	Cr_2O_3
00318-02	Cr $2p_{1/2}$	586.5	3.0	...	...	...	Cr_2O_3
00318-02	Cr $2p_{1/2}$	583.1	...	...	...	...	Cr(110) metal (substrate)
00318-02	Cr $2p_{3/2}$	574	...	...	...	...	Cr(110) metal (substrate)
00318-03	O $1s$	530.7	1.1	...	...	...	Cr_2O_3
00318-04	Cr $3s$	75.3	3.3	...	...	...	Cr_2O_3
00318-04	Cr $3p$	43.9	3.0	...	...	...	Cr_2O_3
00318-04	O $2s$	22.9	2.8	...	...	...	Cr_2O_3
00318-04	valence band	4.7	7.0	...	...	...	Cr and O from Cr_2O_3
00318-05	Cr $2s$	698.9	9.5	...	...	...	Cr_2O_3

Footnote to Spectrum 00318-01: oxidized Cr(110) single crystal, Cr 2*p* region, showing structures due to Cr_2O_3(111) and small Cr 2*p* peaks due to the Cr(110) substrate (583.1 eV, 574 eV).

ANALYZER CALIBRATION TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Sensitivity Factor	Concen- tration (at. %)	Peak Assignment
...		...	...	...	...	...

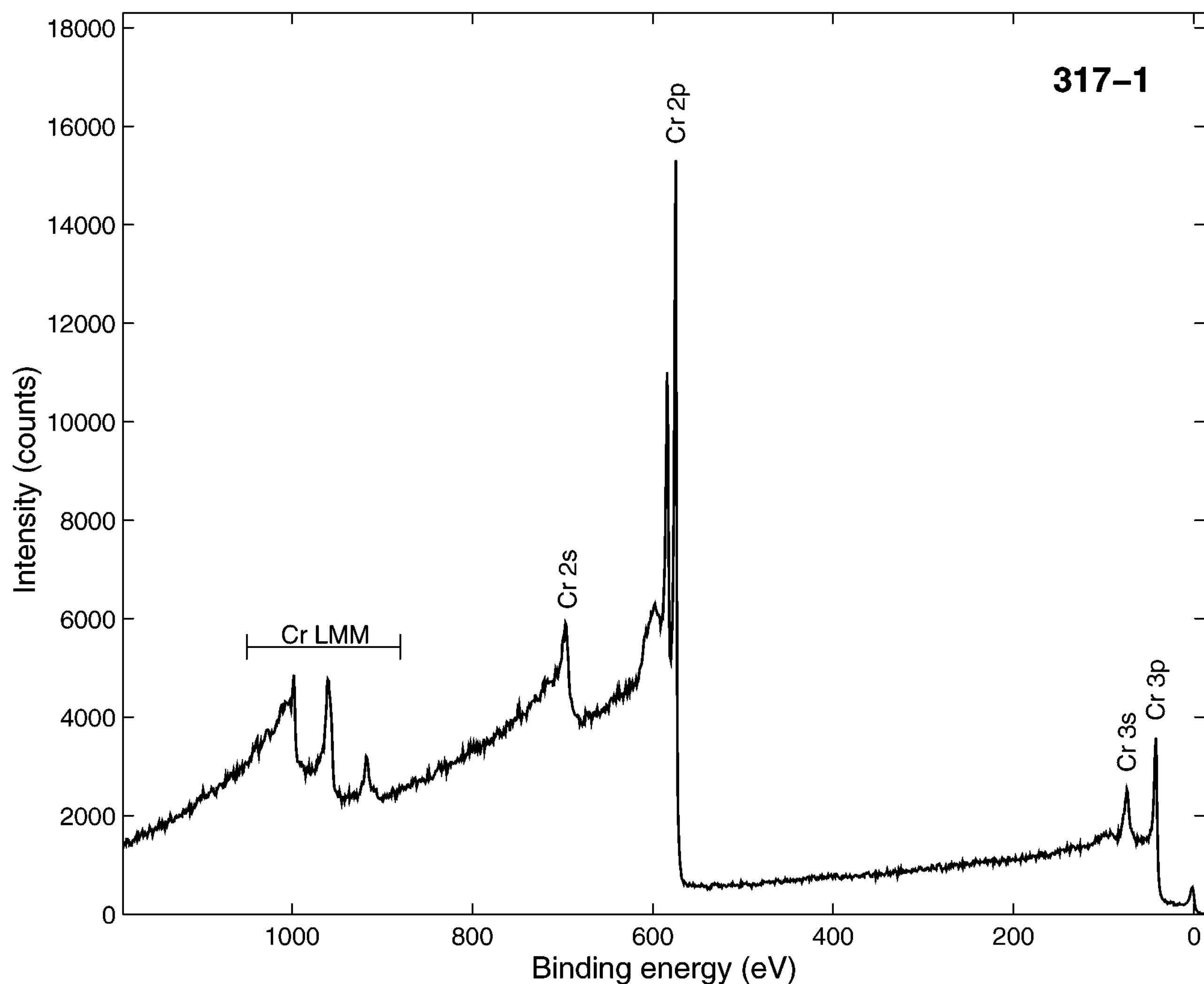
Comment to Analyzer Calibration Table: The energy scale was calibrated by determining the Fermi edge of the Cr(110) substrate.

GUIDE TO FIGURES

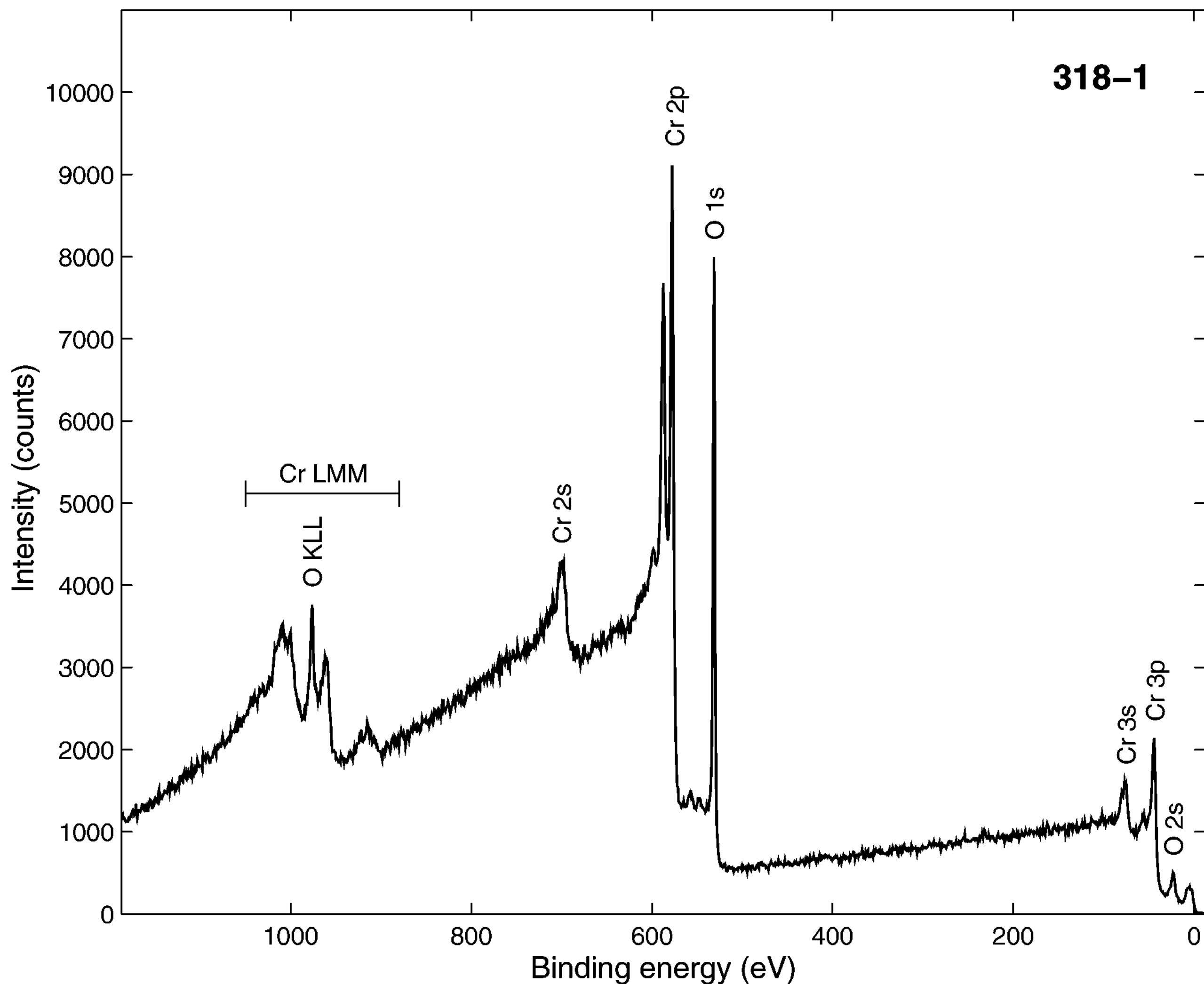
Spectrum (Accession) #	Sample Voltage*	Multiplier	Baseline	Comment #
317-1	0	1.000	0	1
318-1	0	1.000	0	2
318-2	0	1.000	0	2
318-3	0	1.000	0	2
318-4	0	1.000	0	2
318-5	0	1.000	0	2

* Sample voltage due to charging unless otherwise noted.

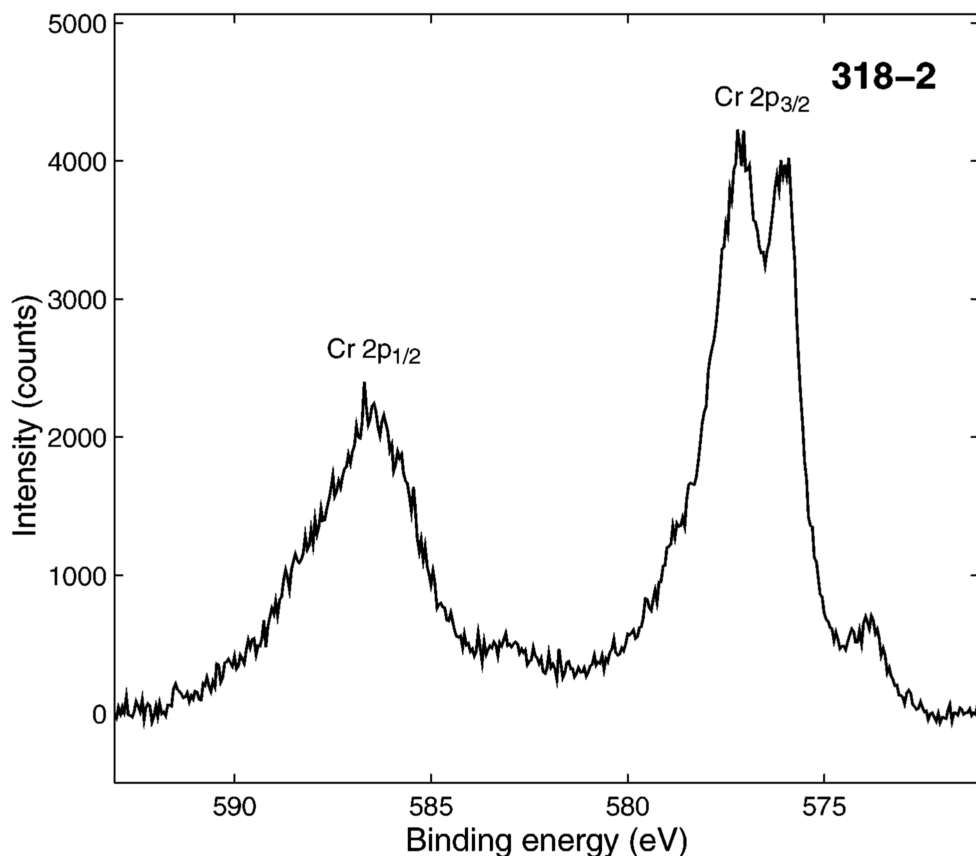
1. Clean Cr.
2. Cr_2O_3 peak energies were referenced to Fermi level of Cr metal which could be measured through thin oxide (see 318-5).



Accession #	00317-01
Host Material	Cr metal
Technique	XPS
Spectral Region	survey
Instrument	Leybold-Heraeus EA 11
Excitation Source	Al K_α monochromatic
Source Energy	1486.6 eV
Source Strength	450 W
Source Size	not specified
Analyzer Type	spherical sector
Incident Angle	45°
Emission Angle	0°
Analyzer Retard Ratio	4
Analyzer Resolution	0.125 eV
Total Signal Accumulation Time	not specified
Total Elapsed Time	330 s
Number of Scans	5
Comment	survey of the clean Cr single crystal



Accession #	00318-01
Host Material	Cr_2O_3
Technique	XPS
Spectral Region	survey
Instrument	Leybold-Heraeus EA 11
Excitation Source	Al K_α monochromatic
Source Energy	1486.6 eV
Source Strength	450 W
Source Size	not specified
Analyzer Type	spherical sector
Incident Angle	45°
Emission Angle	0°
Analyzer Retard Ratio	4
Analyzer Resolution	0.125 eV
Total Signal Accumulation Time	not specified
Total Elapsed Time	330 s
Number of Scans	5
Comment	survey of the oxidized Cr single crystal



- **Accession #:** 00318-02
- **Host Material:** Cr_2O_3
- **Technique:** XPS
- **Spectral Region:** Cr $2p_{1/2}$; Cr $2p_{3/2}$

Instrument: Leybold-Heraeus EA 11

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 450 W

Source Size: not specified

Incident Angle: 45°

Analyzer Type: spherical sector

Analyzer Pass Energy: 12.6 eV

Analyzer Resolution: 0.1 eV

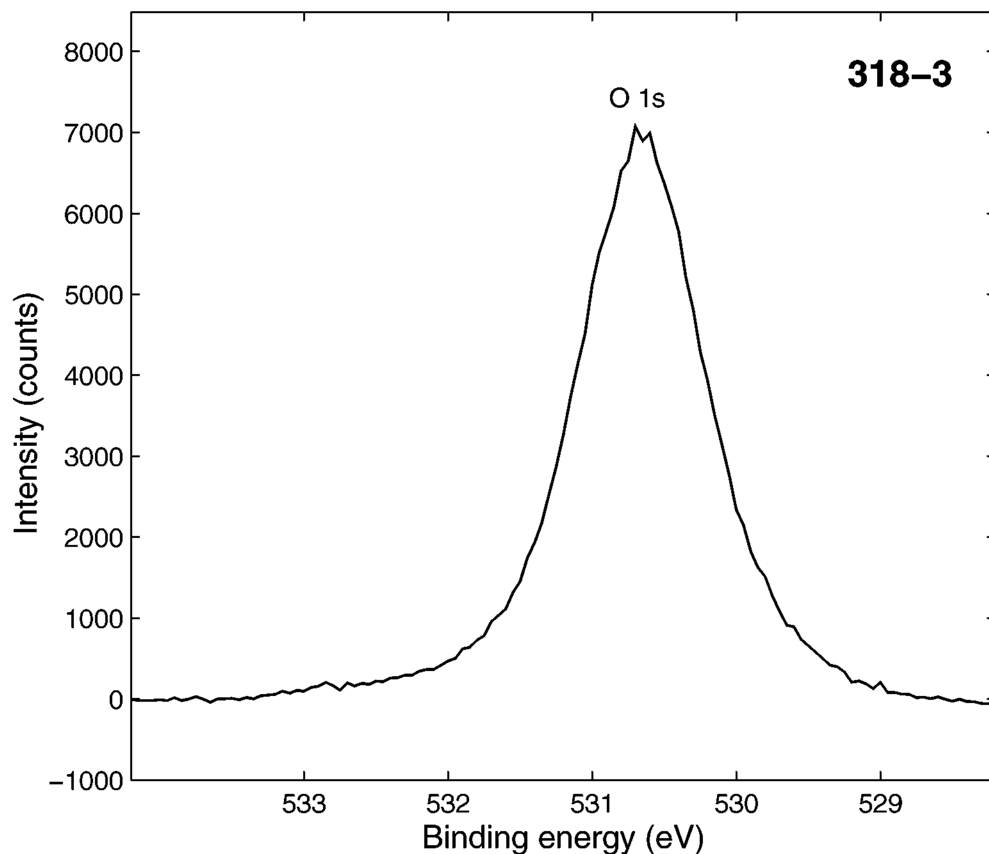
Emission Angle: 0°

Total Signal Accumulation Time: not specified

Total Elapsed Time: 8250 s

Number of Scans: 150

Comment: See footnote below the Spectral Features Table.



- **Accession #:** 00318-03
- **Host Material:** Cr_2O_3
- **Technique:** XPS
- **Spectral Region:** O 1*s*

Instrument: Leybold-Heraeus EA 11

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 450 W

Source Size: not specified

Incident Angle: 45°

Analyzer Type: spherical sector

Analyzer Pass Energy: 25.2 eV

Analyzer Resolution: 0.3 eV

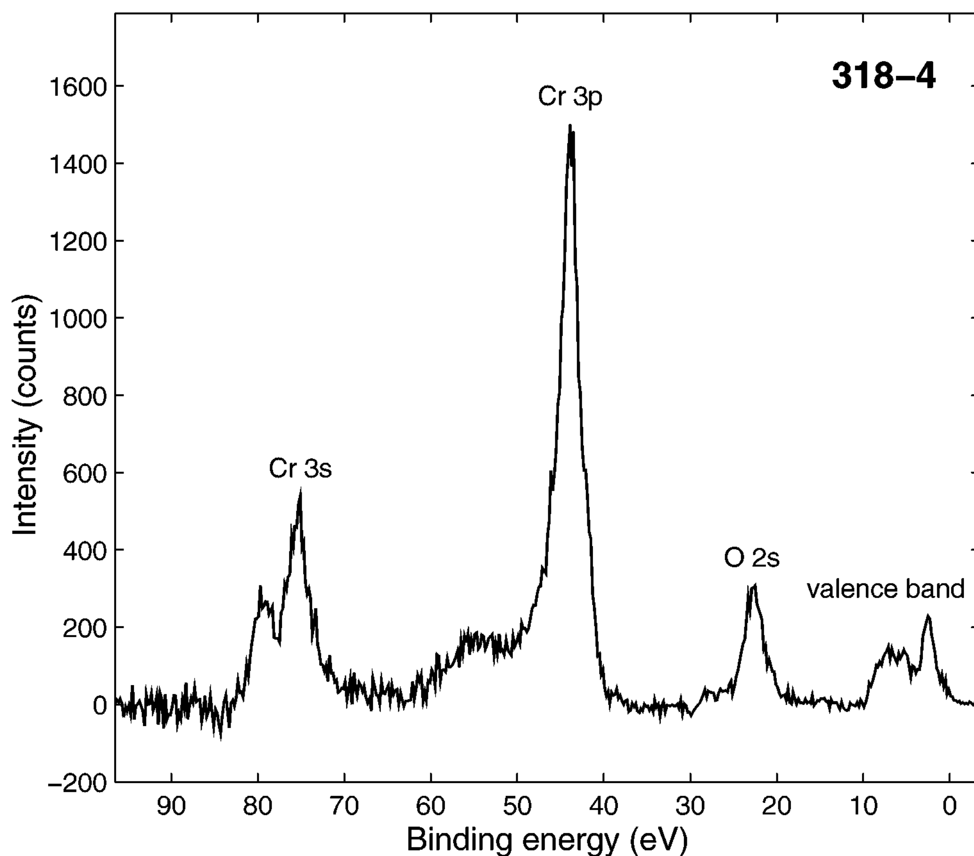
Emission Angle: 0°

Total Signal Accumulation Time: not specified

Total Elapsed Time: 600 s

Number of Scans: 20

Comment: oxidized Cr single crystal



- **Accession #:** 00318-04
- **Host Material:** Cr_2O_3
- **Technique:** XPS
- **Spectral Region:** Cr 3*s*; Cr 3*p*; O 2*s*; Cr/O valence band

Instrument: Leybold-Heraeus EA 11

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 450 W

Source Size: not specified

Incident Angle: 45°

Analyzer Type: spherical sector

Analyzer Pass Energy: 100.8 eV

Analyzer Resolution: 0.77 eV

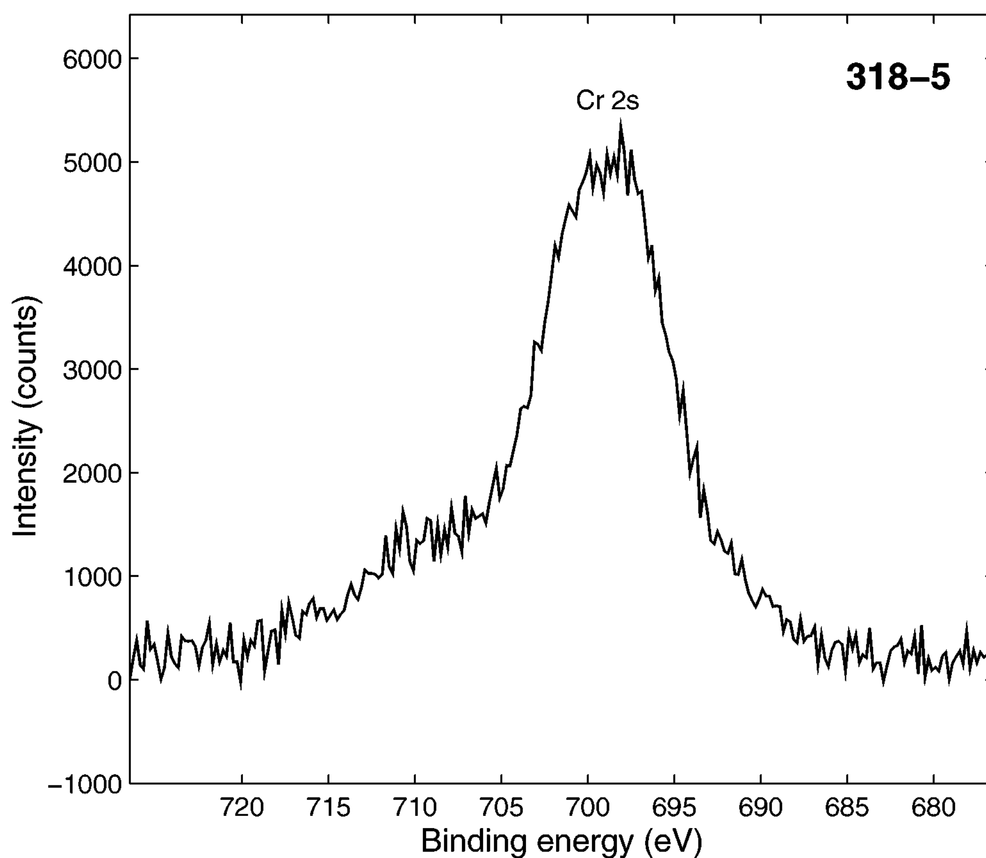
Emission Angle: 0°

Total Signal Accumulation Time: not specified

Total Elapsed Time: 560 s

Number of Scans: 10

Comment: oxidized Cr single crystal



- **Accession #:** 00318-05
- **Host Material:** Cr_2O_3
- **Technique:** XPS
- **Spectral Region:** Cr 2*s*

Instrument: Leybold-Heraeus EA 11

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 450 W

Source Size: not specified

Incident Angle: 45°

Analyzer Type: spherical sector

Analyzer Pass Energy: 100.8 eV

Analyzer Resolution: 0.77 eV

Emission Angle: 0°

Total Signal Accumulation Time: not specified

Total Elapsed Time: 930 s

Number of Scans: 30

Comment: oxidized Cr single crystal