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Core-level spectra of metallic lanthanides: Dysprosium (Dy)

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ABSTRACT

The core-level spectra for the lanthanide metal, dysprosium, are presented. The spectra exhibit significant multiplet splitting, which must be included for accurate quantification of the metallic state. Within the paper, modified relative sensitivity factors are presented for some regions, together with recommended backgrounds integration limits and types.

Key words: XPS, lanthanide, metal, dysprosium, rare earth

Accession #: 01857
Technique: XPS
Specimen: Dy
Instrument: Thermo K-Alpha$^+$
Major Elements in Spectra: Dy
Minor Elements in Spectra: O
Published Spectra: 7
Spectral Category: Comparison

INTRODUCTION

The rare earth metal dysprosium (Dy) is found in the lanthanide series and has the ground state electronic configuration [Xe] $4f^{10}$ $6s^2$. Since the metallic state of lanthanides is of little use, their surface chemistry is not greatly explored and to date, the published data on heavier lanthanide elements are mostly limited to non-monochromatic sources (Ref. 1). Given that photoemission of low-lying 4*d* orbitals will result in a final state of the form $4d^9 4f^n$, complex multiplet splitting is observed through the coupling of the 4*d* core-hole and the partly filled 4*f* shell and are excellent materials to understand the complex spectra resulting from this phenomenon.

The lanthanide series is a highly distinctive class of elements, with notable electrophilicity and magnetic and electronic properties. However, despite being an uncommon element presented to surface analysts, dysprosium finds many uses in alloys for technological applications such as laser materials (Ref. 2), infrared sources (Ref. 3), and to aid coercivity in neodymium-based magnets in harsh environments (Ref. 4).

Given that lanthanides are electropositive, they have a high affinity for oxygen and halides. Keeping them clean to record core-level spectra is difficult as noted previously (Ref. 5). Within this reference, the spectra for clean Dy are presented, which were obtained by light argon etching (20 s) between acquisitions.

SPECIMEN DESCRIPTION (ACCESSION # 01857

Specimen: Dysprosium, Dy
CAS Registry #: 7429-91-6
Specimen Characteristics: Homogeneous; solid; polycrystalline; conductor; metal; other
Chemical Name: Dysprosium
Source: Alfa Aesar
Composition: Dy
Form: Solid dendrite, approximately 20 × 10 mm^2

Structure: Dy
History and Significance: Distilled dendrites of 99.9% grade material obtained from Alfa Aesar under an argon atmosphere.
As Received Condition: Received as distilled metallic dendrites packaged in an argon atmosphere.
Analyzed Region: Elliptical region within the approximate center of the etched area.
***Ex Situ* Preparation/Mounting:** A suitably sized fragment was wet polished to form a visually flat and smooth surface using isopropyl alcohol and SiC paper (grit size 7 μm). After polishing, the sample was again washed with isopropyl alcohol and dried under a stream of nitrogen. The dry sample was then attached to a conducting sample plate using copper clips. Initial survey scans (not shown) of the polished sample revealed small amounts of Si and Zn and significant amounts of carbon and oxygen.
***In Situ* Preparation:** Argon ion sputtering
Charge Control: None
Temp. During Analysis: 298 K
Pressure During Analysis: 1.33×10^{-6} Pa
Pre-analysis Beam Exposure: 30 s

INSTRUMENT DESCRIPTION

Manufacturer and Model: Thermo Fisher Scientific K-Alpha+
Analyzer Type: Spherical sector
Detector: Multichannel resistive plate
Number of Detector Elements: 128

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

Spectrometer

Analyzer Mode: Constant pass energy
Throughput ($T = E^N$): Calculated from a polynomial fit to a plot of log [peak area/(PE*XSF)] versus log(KE/PE), where PE is the pass energy, KE is the kinetic energy, and XSF is the relative sensitivity factor.
Excitation Source Window: No window
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Beam Size: $600 \times 400\ \mu m^2$
Signal Mode: Multichannel direct

Geometry

Incident Angle: 60°
Source-to-Analyzer Angle: 60°
Emission Angle: 0°
Specimen Azimuthal Angle: 0°
Acceptance Angle from Analyzer Axis: 0°
Analyzer Angular Acceptance Width: 30° × 30°

Ion Gun

Manufacturer and Model: Thermo Scientific MAGCIS
Energy: 4000 eV
Current: 6 mA
Current Measurement Method: Faraday cup
Sputtering Species and Charge: Ar^+
Spot Size (unrastered): 50 μm
Raster Size: $2000 \times 1000\ \mu m^2$
Incident Angle: 58°
Polar Angle: 58°
Azimuthal Angle: 90°
Comment: The ion gun was used to clean the as introduced sample for 300 s and then for 20 s between each region to minimize any adsorption of background gases, which readily oxidize the material during analysis.

DATA ANALYSIS METHOD

Energy Scale Correction: The sample is conductive and mounted on a conductive sample holder using clips, hence no calibration is required.
Recommended Energy Scale Shift: 0
Peak Shape and Background Method: For Dy *4d*, $3d_{5/2}$, and Dy $4p_{3/2}$ regions, a Shirley background is used. For Dy *4s* and Dy $3d_{3/2}$ peaks, a linear background is employed. Recommend background start and end points are (±0.2 eV) as follows:
Dy *4d*: 147–196 eV
Dy $4p_{3/2}$: 283–316 eV
Dy *4s*: 404.5–429.5 eV
Dy $3d_{5/2}$: 1286.5–1319 eV
Dy $3d_{3/2}$: 1329.5–1348 eV
Quantitation Method: Data analysis was performed using CASAXPS performed in CASAXPS V2.3.26 rev1.0N, using a Shirley background unless otherwise specified. Electron escape depth correction was performed using the TPP-2M equation within CASAXPS and peak areas were corrected using Scofield sensitivity factors. Modified sensitivity factors were used for *4p* and *4s* levels as noted in the comments on the spectral features table.

ACKNOWLEDGMENTS

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AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

David Morgan: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Project administration (lead); Writing – original draft (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES

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[3]David R Lide, "Dysprosium," in *CRC Handbook of Chemistry and Physics* (CRC, New York, 2007–2008), Vol. 4, p. 11, ISBN 978-0-8493-0488-0.
[4]X. Fang, Y. Shi, and D. C. Jiles, IEEE Trans. Magn. **34**, 1291 (1998).
[5]M. Engelhard and D. Baer, Surf. Sci. Spectra **7**, 1 (2000).

SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV counts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
01857-01[a]	Dy *4d*	…	…	7 915 350	11.43	100	Dy 4d with multiplet structure
01857-02	Valence	…	…	…	…	…	
01857-03[a]	Dy *4d*	…	…	…	…	…	Dy 4d with multiplet structure
01857-03	Dy $4d_{5/2}$	152.2	0.95	…	…	…	…
01857-04[b]	Dy $4p_{3/2}$	292.7	…	207 603	2.15	…	…
01857-05[c]	Dy *4s*	412.9	5.4	78 776	0.815	…	…
01857-06	O *1s*	…	…	…	…	…	…
01857-07	Dy $3d_{5/2}$	1293.3	…	…	49.42	…	…
01857-07	Dy $3d_{3/2}$	1333.3	…	3 294 451	34.20	…	…

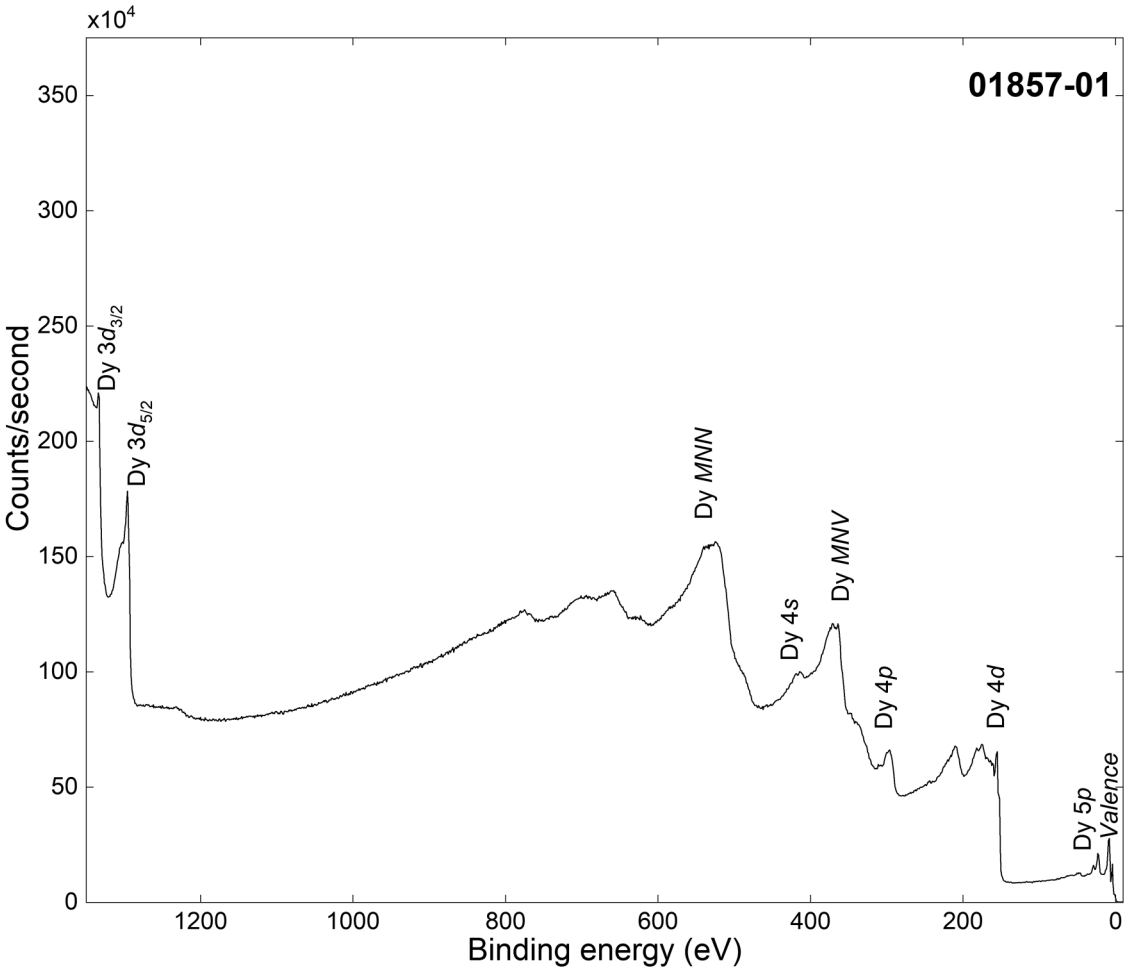
[a]Peak areas include satellite structure and multiplet splitting for correct use of RSF. Peak position and FHWM obtained by peak fit using the line shape of LA(0.8,1,143)
[b]Binding energy measured on peak maximum due to the complex peak structure. A modified sensitivity factor of 2.15 is used.
[c]Binding energy and FWHM measured through fitting of multiplet split structure using a LA(1.53, 243) line shape. A modified sensitivity factor of 0.815 is used.

ANALYZER CALIBRATION TABLE

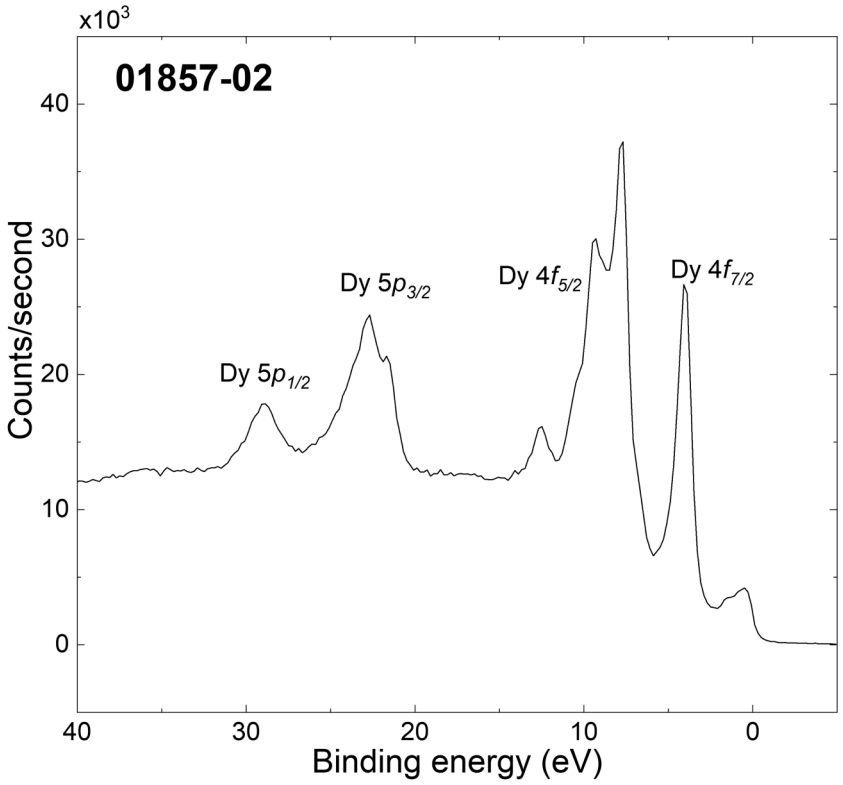
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV counts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
…	Au $4f_{7/2}$	83.99	0.78	1 252 439	9.58	100	Gold metal
…	Ag $3d_{5/2}$	368.28	0.61	1 676 008	7.38	100	Silver metal
…	Cu $2p_{3/2}$	932.67	0.86	2 867 973	16.73	100	Copper metal

GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift	Multiplier	Baseline	Comment #
01857-01	Survey	0	1	0	…
01857-02	Valence	0	1	0	0.2 eV step size
01857-03	Dy *4d*	0	1	0	…
01857-04	Dy $4p_{3/2}$	0	1	0	…
01857-05	Dy *4s*	0	1	0	…
01857-06	O *1s*	0	1	0	…
01857-07	Dy *3d*	0	1	0	…

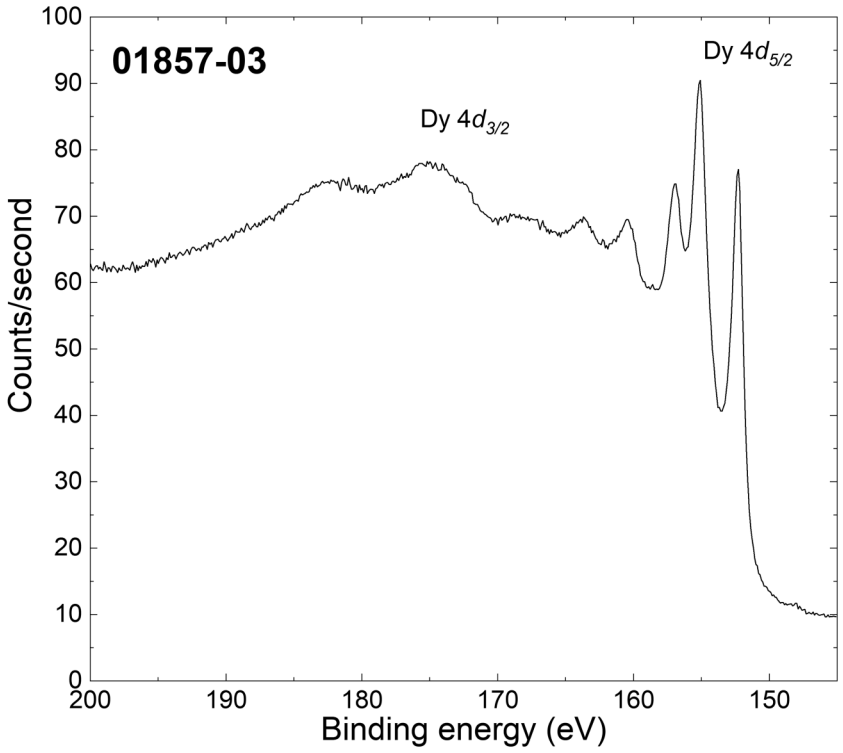


Accession #	01857-01
■ **Specimen**	Dy
■ **Technique**	XPS
■ **Spectral Region**	Survey
Instrument	Thermo Fisher Scientific K-Alpha+
Excitation Source	Al K_α monochromatic
Source Energy	1486.6 eV
Source Strength	72 W
Source Size	0.6 × 0.4 mm^2
Analyzer Type	Spherical sector analyzer
Incident Angle	60°
Emission Angle	0°
Analyzer Pass Energy	150 eV
Analyzer Resolution	1.5 eV
Total Signal Accumulation Time	83 s
Total Elapsed Time	100 s
Number of Scans	6
Effective Detector Width	20.5 eV



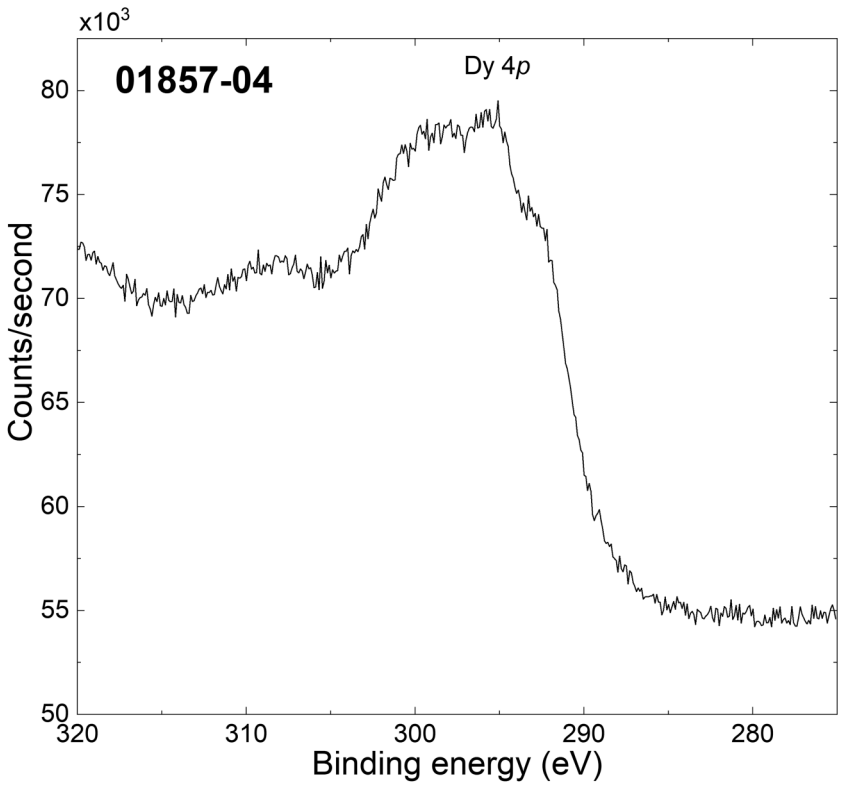
- **Accession #:** 01857-02
- **Specimen:** Dy
- **Technique:** XPS
- **Spectral Region:** Valence

Instrument: Thermo Fisher Scientific K-Alpha+
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 40 eV
Analyzer Resolution: 0.2 eV
Total Signal Accumulation Time: 108 s
Total Elapsed Time: 130 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 20 s etch after collection of the prior spectrum to minimize any oxidation. The *4f* level exhibits a complex multiplet structure.



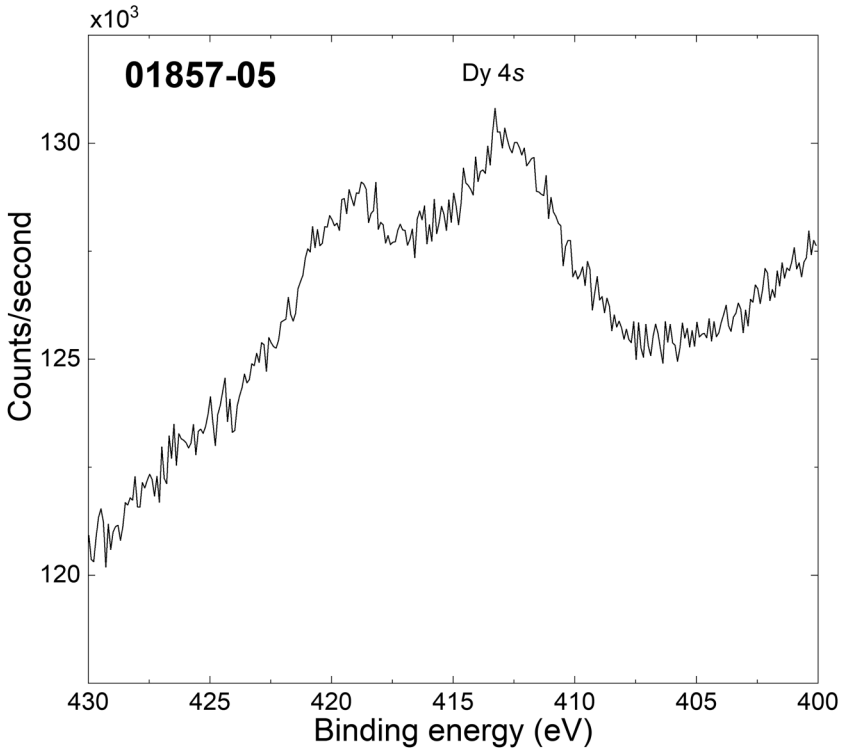
- **Accession #:** 01857-03
- **Specimen:** Dy
- **Technique:** XPS
- **Spectral Region:** Dy *4d*

Instrument: Thermo Fisher Scientific K-Alpha+
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 40 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 277 s
Total Elapsed Time: 300 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 20 s etch after collection of the prior spectrum to minimize any oxidation.



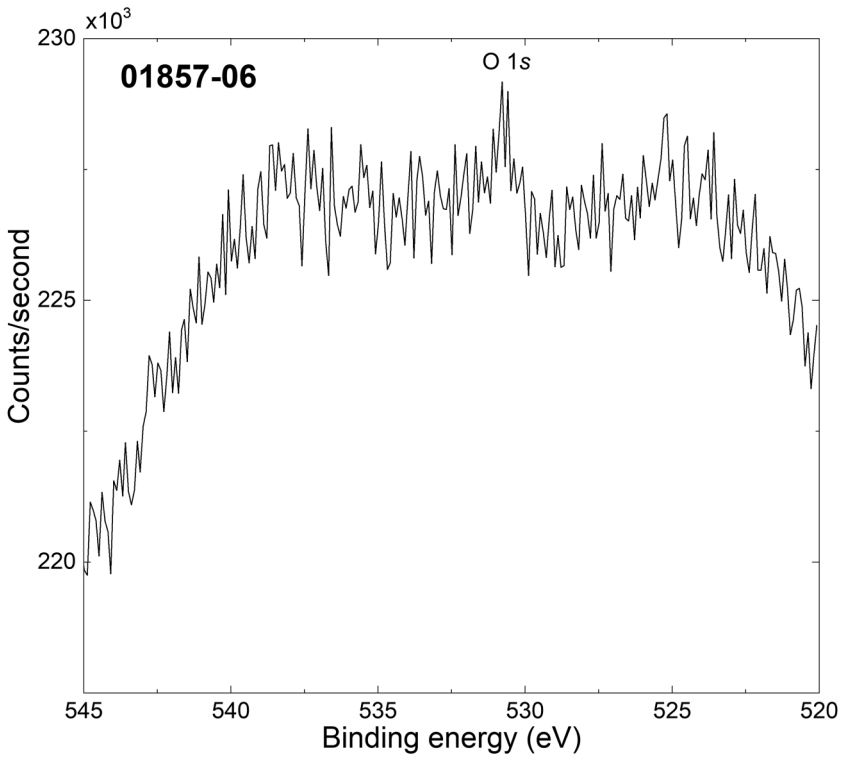
- **Accession #:** 01857-04
- **Specimen:** Dy
- **Technique:** XPS
- **Spectral Region:** Dy $4p_{3/2}$

Instrument: Thermo Fisher Scientific K-Alpha+
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 40 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 227 s
Total Elapsed Time: 300 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 20 s etch after collection of the prior spectrum to minimize any oxidation.



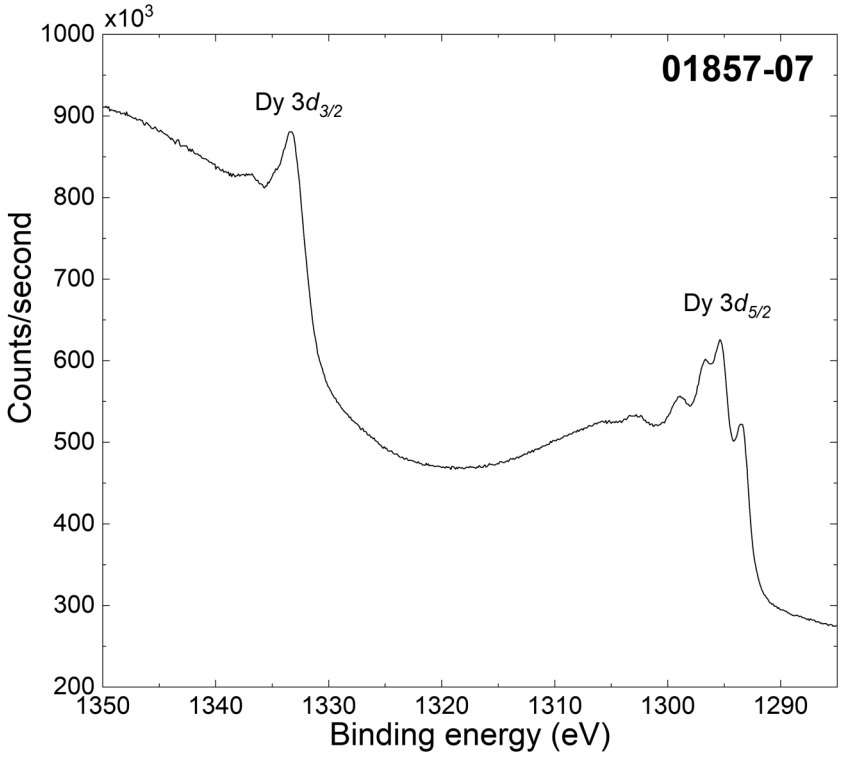
- **Accession #:** 01857-05
- **Specimen:** Dy
- **Technique:** XPS
- **Spectral Region:** Dy *4s*

Instrument: Thermo Fisher Scientific K-Alpha+
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 40 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 300 s
Total Elapsed Time: 330 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 20 s etch after collection of the prior spectrum to minimize any oxidation.



- **Accession #:** 01857-06
- **Specimen:** Dy
- **Technique:** XPS
- **Spectral Region:** O *1s*

Instrument: Thermo Fisher Scientific K-Alpha+
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 40 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 126 s
Total Elapsed Time: 150 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 20 s etch after collection of the prior spectrum to minimize any oxidation.



- **Accession #:** 01857-07
- **Specimen:** Dy
- **Technique:** XPS
- **Spectral Region:** Dy *3d*

Instrument: Thermo Fisher Scientific K-Alpha+
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 40 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 324 s
Total Elapsed Time: 350 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 20 s etch after collection of the prior spectrum to minimize any oxidation.