Supplemental Information:

Laboratory X-ray Emission Spectrometer for Phosphorus Kα and Kβ

Study of Air-Sensitive Samples

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Table SI-1 Ni_2P nanophase sample replicate phosphide fraction determined from fitting to reference spectra (Ni_2P-Bulk and $Ni_3(PO_4)_2$), standard deviation and standard error. See Fig. SI-1 for plots of fits.

Replicate 5 Phosphide Fraction	Replicate 6 Phosphide Fraction	Replicate 7 Phosphide Fraction	Standard Deviation	Standard Error
0.93	0.94	0.94	0.010	0.0038
0.88	0.89	0.89	0.011	0.0043
0.83	0.82	0.82	0.0073	0.0028
0.78	0.77	0.77	0.0049	0.0019
0.76	0.74	0.74	0.0083	0.0031
0.72	0.71	0.70	0.0073	0.0028
0.69	0.68	0.67	0.0073	0.0028
0.69	0.66	0.65	0.012	0.0047
0.54	0.52	0.50	0.016	0.0060
0.44	0.41	0.38	0.024	0.0090
0.32	0.28	0.26	0.026	0.0097
0.23	0.20	0.19	0.018	0.0069

Table SI-2 Ni_2P nanophase sample replicate phosphide fraction determined from fitting to 0.2 eV broadened reference spectra (Ni_2P-Bulk and $Ni_3(PO_4)_2$), standard deviation and standard error. See Fig. SI-1 for plots of fits.

Replicate 5 Phosphide Fraction	Replicate 6 Phosphide Fraction	Replicate 7 Phosphide Fraction	Standard Deviation	Standard Error
0.97	0.97	0.96	0.0081	0.0030
0.91	0.91	0.91	0.0088	0.0033
0.85	0.85	0.85	0.0053	0.0020
0.81	0.80	0.79	0.0064	0.0024
0.77	0.76	0.76	0.0070	0.0026
0.74	0.72	0.72	0.0076	0.0029
0.71	0.69	0.68	0.0090	0.0034
0.70	0.67	0.66	0.014	0.0052
0.54	0.52	0.49	0.018	0.0069
0.43	0.40	0.36	0.027	0.010
0.30	0.26	0.24	0.026	0.0097
0.20	0.17	0.16	0.018	0.0069

Figure SI-1: P Kα and Kβ reference spectra, Ni_2P-Bulk and $Ni_3(PO_4)_2$, with Na_2HPO_4 reference spectra. The Na_2HPO_4 spectra was used to set the energy scale, see text for details.

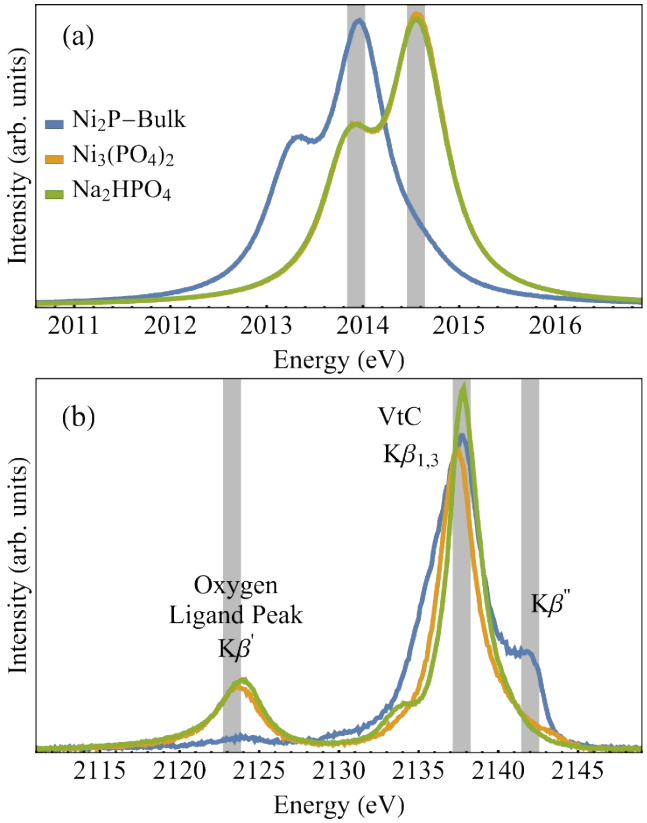
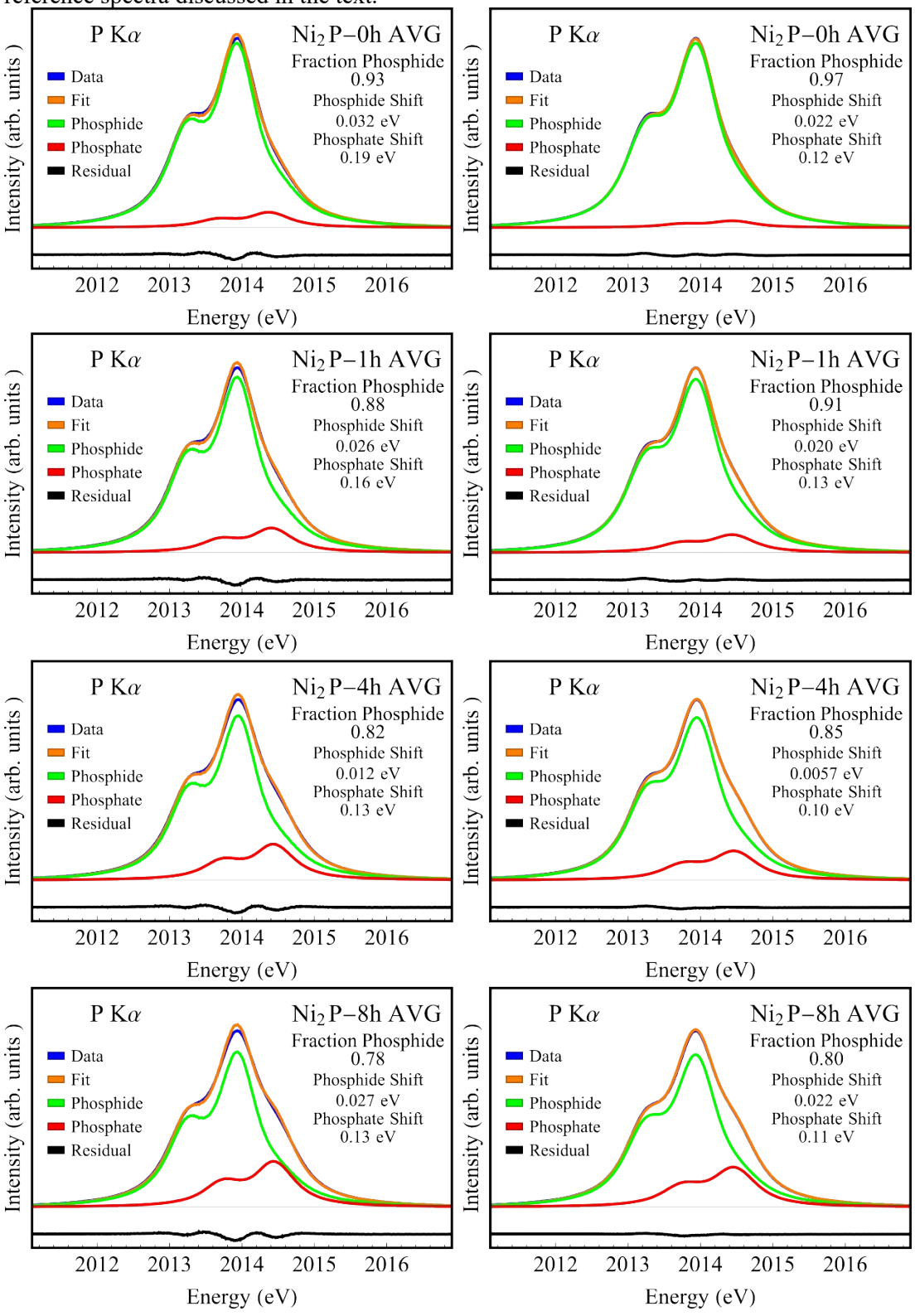
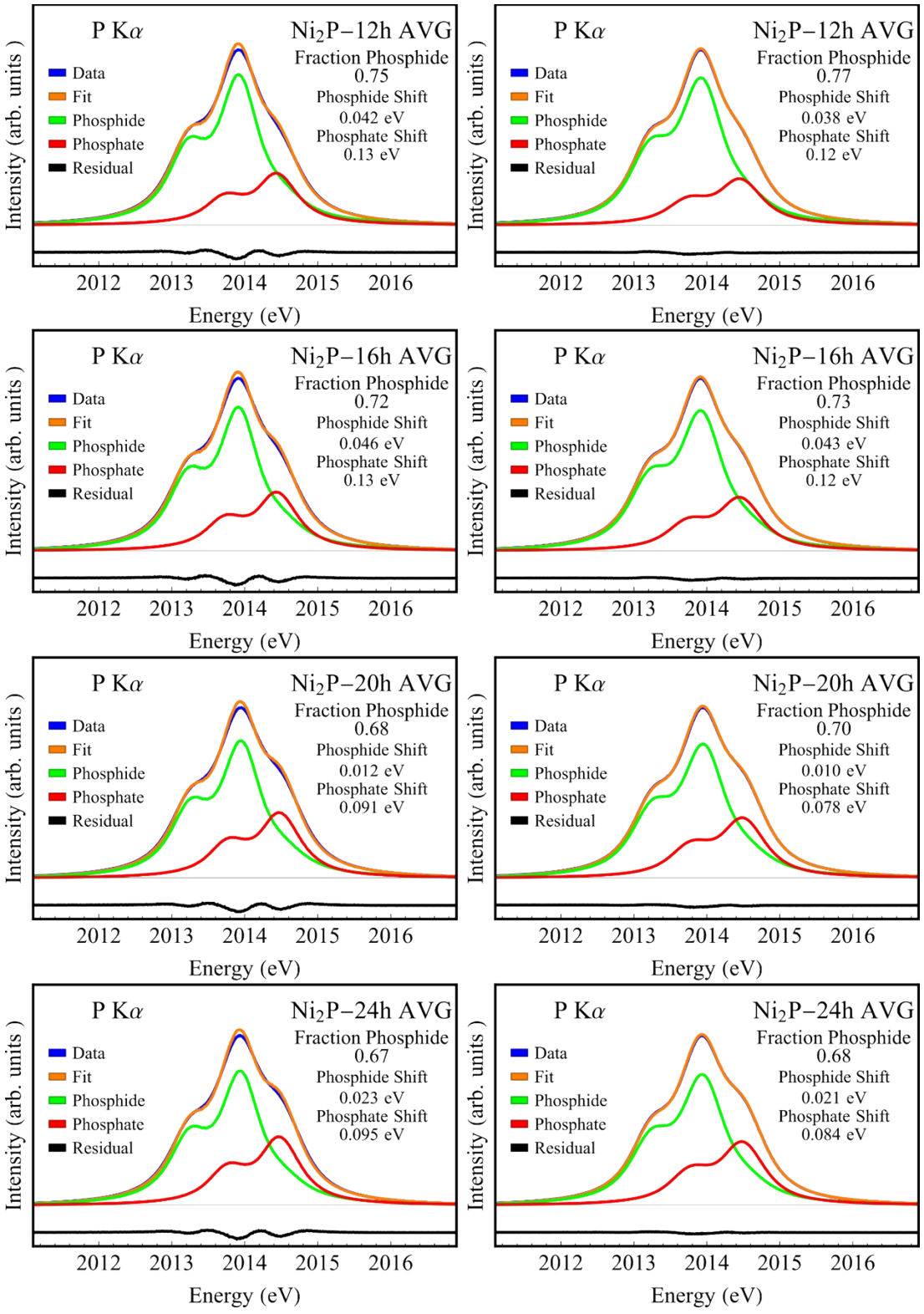


Figure SI-2 (below and following pages): A compendium of P Kα XES results with fits, references, and residuals for all Ni_2P nanophase samples after summing replicate spectra. In each case the left column is the fit with the original, unbroadened references, while the right column uses the slightly broadened reference spectra discussed in the text.




P Kα
Ni2P–12h AVG
Fraction Phosphide
0.75
Phosphide Shift
0.042 eV
Phosphate Shift
0.13 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–12h AVG
Fraction Phosphide
0.77
Phosphide Shift
0.038 eV
Phosphate Shift
0.12 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–16h AVG
Fraction Phosphide
0.72
Phosphide Shift
0.046 eV
Phosphate Shift
0.13 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–16h AVG
Fraction Phosphide
0.73
Phosphide Shift
0.043 eV
Phosphate Shift
0.12 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–20h AVG
Fraction Phosphide
0.68
Phosphide Shift
0.012 eV
Phosphate Shift
0.091 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–20h AVG
Fraction Phosphide
0.70
Phosphide Shift
0.010 eV
Phosphate Shift
0.078 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–24h AVG
Fraction Phosphide
0.67
Phosphide Shift
0.023 eV
Phosphate Shift
0.095 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–24h AVG
Fraction Phosphide
0.68
Phosphide Shift
0.021 eV
Phosphate Shift
0.084 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)

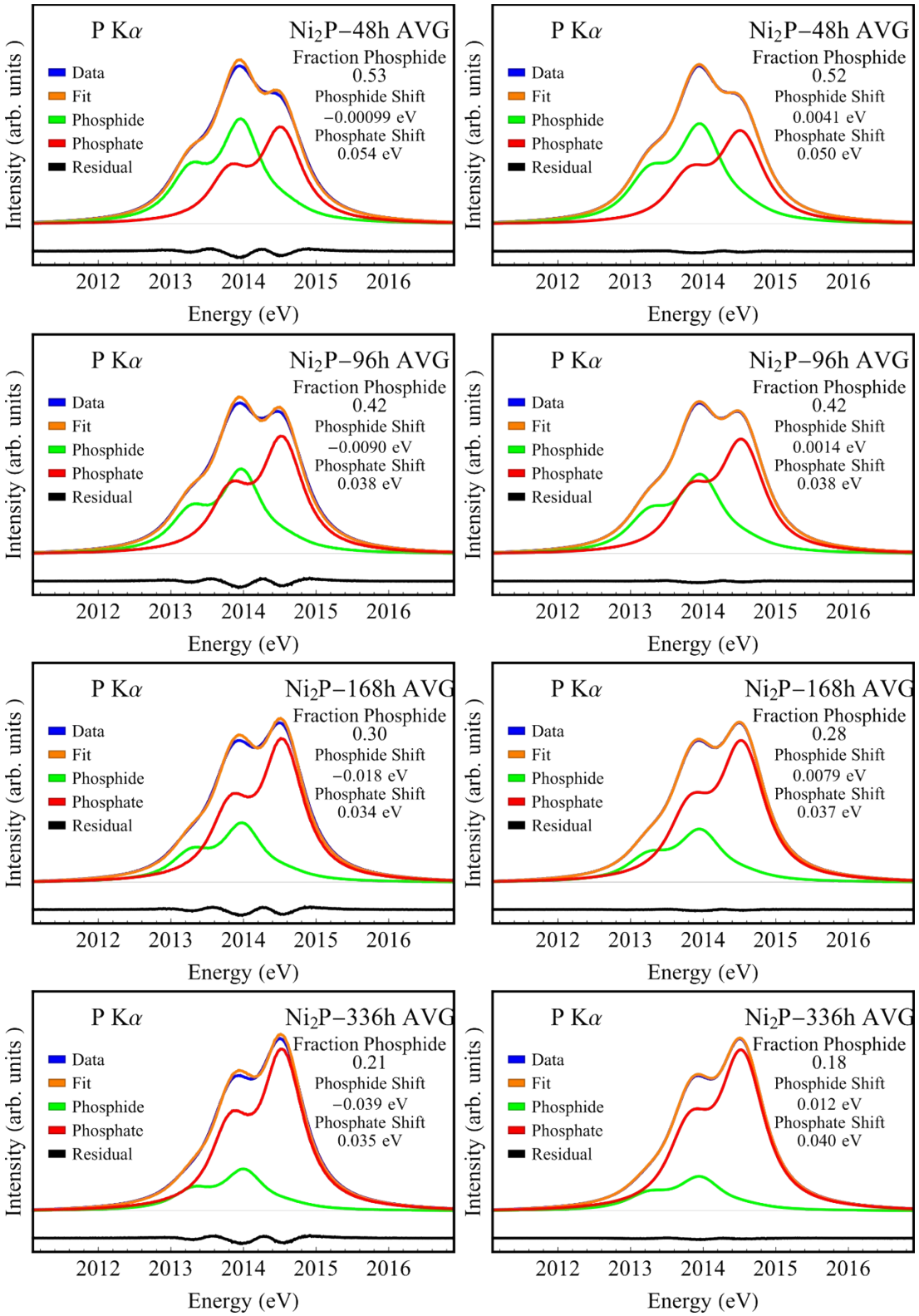

P Kα
Ni2P–48h AVG
Fraction Phosphide
0.53
Phosphide Shift
−0.00099 eV
Phosphate Shift
0.054 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–48h AVG
Fraction Phosphide
0.52
Phosphide Shift
0.0041 eV
Phosphate Shift
0.050 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–96h AVG
Fraction Phosphide
0.42
Phosphide Shift
−0.0090 eV
Phosphate Shift
0.038 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–96h AVG
Fraction Phosphide
0.42
Phosphide Shift
0.0014 eV
Phosphate Shift
0.038 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–168h AVG
Fraction Phosphide
0.30
Phosphide Shift
−0.018 eV
Phosphate Shift
0.034 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–168h AVG
Fraction Phosphide
0.28
Phosphide Shift
0.0079 eV
Phosphate Shift
0.037 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–336h AVG
Fraction Phosphide
0.21
Phosphide Shift
−0.039 eV
Phosphate Shift
0.035 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)
P Kα
Ni2P–336h AVG
Fraction Phosphide
0.18
Phosphide Shift
0.012 eV
Phosphate Shift
0.040 eV
Data
Fit
Phosphide
Phosphate
Residual
Intensity (arb. units)
2012
2013
2014
2015
2016
Energy (eV)

Figure SI-3: Plots showing the absolute divergence from the Bragg energy as a function of distance from the analyzer center for both the P Kα and P Kβ spectrometers. The energy divergence is calculated by Bragg's law using an angular divergence due to the analyzer crystal not lying perfectly on circle, also known as Johann error. The vertical dashed black line corresponds to the masking on the P Kβ analyzer and is used to cap the divergence due to Johann error. The difference in magnitude of divergence for the Kα verses Kβ analyzer is due to the more favorable Bragg angle of the Kα analyzer.

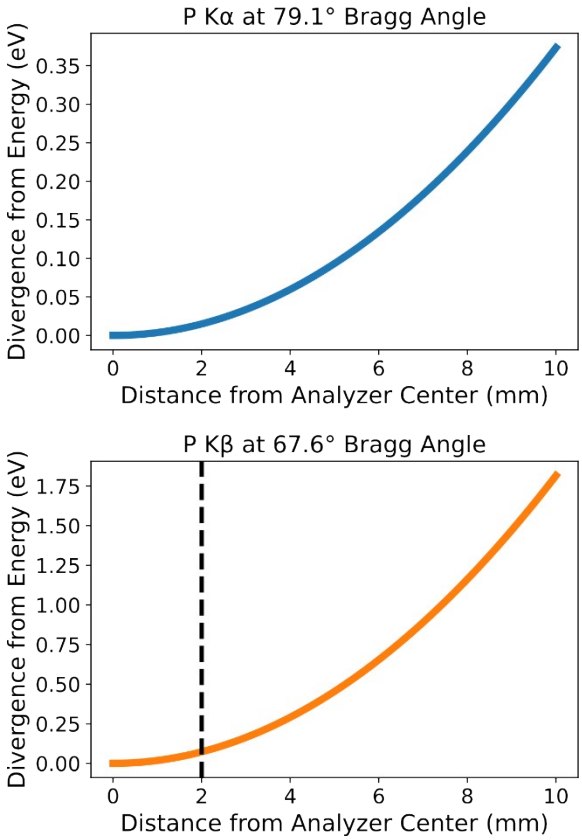


Figure SI-4: Plot showing the fitting of the $Ni_3(PO_4)_2$ reference spectra to two Voigt profiles. The fitting was performed using the `lmfit` package in python. Both profiles use a Gaussian FWHM of 0.29 and a Lorentzian FWHM of 0.53. The Lorentzian component is associated with the energy broadening due to the core hole lifetime of the emission and the Gaussian component is associated with the spectrometer energy broadening. The Lorentzian FWHM of 0.53 is within the range of reported values for the P Kα emission.