Applications for X-Ray Spectroscopy

Jordan Planillo

Rensselaer Polytechnic Institute

Dr. Jerry Seidler

University of Washington

Abstract

X-ray crystallography via X-ray diffraction has been a reliable method method for determining crystal structure and composition. For complex crystals, as in the case of metalloproteins, X-ray diffraction fails to provide such information. X-ray spectroscopy gives better insight to the structure and composition of such complex crystal. The metalloprotein of interest is nitrogenase, the enzyme that allows for nitrogen fixation in plants and bacteria. This report details the experimental procedures for analyzing nitrogenase, specifically: experimental apparatus, simulation of nitrogenase with Fe(VI)N, and data analysis.

Introduction

With respect to metalloproteins, one of the hardest technical issues is to identify the existence and species of light elements bonded to catalytically active metal sites. X-ray diffraction cannot be used to obtain such information due to practical and experimental limitations. In terms of practical limitations, large amounts of high quality crystallized material are required. Such large crystals place experimental limitations such as crystal defects and the inability to detect light elements due to the presence of heavier elements.

Nitrogenase is one such metalloprotein of scientific interest as it is the only know method for nitrogen fixation and the exact details as to how nitrogenase performs this function are still unknown. The understanding of this function will allow for the efficient production of man-made fertilizers. The following chemical reaction details nitrogen fixation:

$N_2 + 8 H^+ + 8 e^- + 16 ATP \rightarrow 2 NH_3 + H_2 + 16 ADP + 16 P_i$

Although the reaction of $N_2 + H_2 \rightarrow NH_3$ is energetically favorable, the N_2 triple bond must first be broken. The Mo-Fe co-factor in nitrogenase is the active catalytic site which strips electrons one at a time from N2, thus allowing it to dissociate and react with H2 to form NH3. Einsle, et al, Science (2002) (Fig.1), proposes a new model for the structure of the catalyticallyactive Mo-Fe cofactor where there is a light atom (C, N, O, or S) in a central cavity of the metal cluster, it is suspected to be nitrogen as it can play the role of a charge reservoir.



X-ray spectroscopy is the method of choice for studying metalloproteins because the xray emission spectra from metal atoms allow for the identification of light ligands. The emission of interest is when semicore electrons of the ligand fill in the 1s hole in the metal- the K β '' emission. The K β '' emission energy is directly correlated to the chemical species of the light ligand, however it is very hard to detect (Fig. 2).





Fig.2

Experimental Setup

Before any measurements can be taken, calculations must first be made. One critical calculation is determining the correct crystal for the photon emission energy of interest. This is obtained using Bragg's law:

$$2dsin(\theta) = n\lambda$$

From this, a table relating emission energies to analyzer crystals was compiled (Table 1). For the case of nitrogenase, the emission energy of Fe K β is 7057.980 eV with the corresponding crystal of Ge(620).

Another critical piece of experimental hardware that I was heavily involved in, was the sample box. Special design considerations included the ability for the sample box to contain a He gas environment and accommodate a homologated sample holder. The sample box was manufactured by milling aluminum square tubing.



Fig. 3: Sample box (Design and Construction)

Additional preparation (assembly/sample preparation/sealing/sheilding)took place on-site at the Advanced Photon Source at Argonne National Laboratory.

Fig.4: Spectrometer Assembly



Fig. 5:Noise Reduction

He gas environment in the spectrometer (left), in sample box (center), Lead shield (right)







Fig. 6: Raw Spectrometer data

Fe Elastic scattering lines (bottom) and fluorescence lines (top)



Fig. 7: Calibriation Matrix

Using the elastic scattering lines, the energies associated with each pixel can be assigned



Fig. 8: Nitrogenase Simulation with Fe(VI)N

The purpose of this measurement is to observe the Fe K β '' in a sample similar to nitrogenase and determine systematic considerations for nitrogenase in future experiments.

The initial plot (blue line) is the initial 30s exposure.







Analysis

Fig. 8 shows that each subsequent exposure to the beam changes the Fe(IV)N spectrum. This is most evident in the Fe $3p \rightarrow 1s$ transition, where there is a large increase in Fe spin. This spin is likely explained by spin trapping (Vanko, et al, Angew. Chem. Int. Ed. 2007), where high energy excitations cause a cascade of ionization in the sample. As the cascades settle down, the valence electrons are captured in a high spin state.



Fig. 10: Spin trapping

Fig. 9 provides additional detail on the effects of beam exposure on the sample, specifically, on the presence of the K β '' emission. The 10 minute exposure clearly shows the K β '', but not so much on the shorter exposures. The dramatic change in spectra indicates that beam damage is evident and should be taken into consideration during future experiments.

Conclusions

The study of nitrogenase has been greatly aided by experimenting on. Fe(VI)N. Most important is the indication of beam damage on the Fe(IV)N. Additionally, it was possible to observe the faint emission of K β '', giving further insight as to what might be contained in nitrogenase's MoFe cofactor. For future experiments, one must take beam damage countermeasures. Such countermeasures could include cooling the sample to counter act small damages and possibly sweeping the beam over the sample to prevent large scale damage from prolonged exposure.

Sc Kα 4090.600 4065.600 4105.600 Ge (311) 62.2765 63.3691 62.8224 Sc Kβ 4460.500 4105.600 S(311) 67.237 68.6204 67.9283 Sc Kβ 4460.500 4415.500 Ge (400) 78.3384 83.0596 Ti Kα 4510.800 4455.800 Ge (400) 75.5749 77.7173 76.6467 Ti Kβ 4931.810 4886.810 4967.200 Ge (331) 74.9677 75.7878 74.9277 V Kα 4952.200 4927.200 967.200 Ge (331) 74.0677 75.7878 74.9277 V Kβ 5427.700 5829.700 5429.700 Ge (511).(333) 72.7593 74.7479 73.753 Cr Kβ 5946.710 5901.710 5961.710 Ge (511).(333) 74.3258 75.7825 75.05411 Mn Kα 5898.750 5873.750 5923.750 Ge (511).(333) 74.3258 75.7825 75.05412	Element	Emission Line	Emission line Energy	Low E	High E	Crystal	Low θ	High 0	Average angle
Sc Kα 4090.600 6055.600 4105.600 51311 67.237 68.6204 67.9283 Sc Kβ 4460.500 4415.500 4475.500 6E (400) 78.3384 83.0569 80.6976 TI Kα 4510.800 4485.800 4525.800 6E (400) 75.5749 77.7173 76.6463 TI Kα 4933.810 4886.810 4946.810 6E (311) 74.0677 75.7878 74.9277 V Kα 4952.200 4927.200 6947.200 6E (422) 80.532 88.8537 83.1944 Cr Kα 5346.710 5301.710 5961.710.510 6E (511),(333) 77.7479 73.753 Cr Kβ 5346.710 5901.710 5961.710 5(511),(333) 74.3258 75.787 75.787 75.787 Mn Kα 5946.710 5901.710 5961.710 5(511),(333) 74.3258 75.787 75.787 Mn Kα 5988.750 5873.750 5923.750	Sc	Κα	4090.600	4065.600	4105.600	Ge(311)	62.2765	63.3691	62.8228
Sc Kβ 4460.500 4415.500 6e (400) 78.3384 83.0569 80.69763 TI Kβ 4460.500 4485.800 4525.800 Ge (400) 75.5749 77.717 76.6467 TI Kβ 4931.810 4886.810 4946.810 Ge (311) 74.9171 77.971 76.3572 V Kβ 5427.200 4967.200 Ge (422) 80.5352 85.8537 74.9277 V Kβ 5414.700 5389.700 5429.700 Ge (422) 81.3685 84.809 83.1247 Cr Kβ 5946.710 5901.710 5961.710 S(11),(333) 72.7593 74.7479 73.7537 Cr Kβ 5946.710 5901.710 5961.710 S(11),(333) 74.3258 75.0527 75.05411 Mn Kα 5898.750 5873.750 5923.750 Ge (511),(333) 74.3258 75.6512 Mn Kβ 6490.450 6458.450 6505.450 Ge (531) 85.2091 90 <	Sc	Κα	4090.600	4065.600	4105.600	Si(311)	67.237	68.6204	67.9287
κα 451.0.800 4485.800 4525.800 Ge(400) 75.5749 77.173 76.6467 ΤΙ κβ 4931.810 4886.810 4946.810 Ge(311) 74.9171 77.7971 76.357 V κα 4952.200 4957.200 6e(331) 74.0677 75.7878 74.92773 V κβ 5427.200 5382.290 5442.290 Ge(422) 81.3685 84.8809 83.1247 Cr κα 5946.710 5901.710 5961.710 Ge(511),(333) 74.3279 77.3570 Cr κβ 5946.710 5901.710 5961.710 Ge(511),(333) 74.3258 75.05370 Cr κβ 5946.710 5901.710 5961.710 S(422) 70.171 71.357 70.5370 Mn κα 5898.750 5873.750 5923.750 6e(511),(333) 74.3258 75.7825 75.05413 Mn κβ 6490.450 6458.450 6505.450 Ge(531) 85.2091 90 87.60453	Sc	κβ	4460.500	4415.500	4475.500	Ge (400)	78.3384	83.0569	80.69765
11 Kβ 4931.800 4943.800 4946.810 Ge(311) 74.9171 77.797 76.357 V Kβ 4952.200 4927.200 4967.200 Ge(311) 74.0677 75.7878 74.9277 V Kβ 5427.290 5382.290 Ge(422) 80.5352 85.8537 83.1944 Cr Kα 5946.710 5901.710 5961.710 G(511),(333) 72.7593 74.7479 73.753 Cr Kβ 5946.710 5901.710 5961.710 S(6122) 81.3685 84.8809 83.1243 Cr Kβ 5946.710 5901.710 5961.710 S(1422) 69.7171 71.337 70.5370 Cr Kβ 5946.710 5901.710 5961.710 S(1422) 71.0142 72.1831 71.5986 Mn Kα 5898.750 5873.750 5923.750 S(1422) 71.0142 72.1831 71.5986 Mn Kβ 6490.450 6458.450 6505.450 S(1440) 83.0123 88.8416 85.5269 Mn Kβ 6490.430 66453.4	ті	Ka	4510 800	1185 800	4525 800	Ge(400)	75 57/0	77 7172	76 6461
Ν Ν	ті	KB	4910.800	4405.000	4929.800	Ge(400)	7/ 0171	77 7071	76 3571
V Kα 4952.200 4927.200 4967.200 Ge (331) 74.0677 75.7878 74.92773 V Kβ 5427.290 5382.290 5442.290 Ge (422) 80.5352 85.8537 83.1944 Cr Kα 5414.700 5389.700 5429.700 Ge (422) 81.3685 84.8809 83.1241 Cr Kβ 5946.710 5901.710 5961.710 Ge (511),(333) 72.7593 74.7479 73.7536 Cr Kβ 5946.710 5901.710 5961.710 Si(511),(333) 84.2059 90 87.10293 Mn Kα 5898.750 5873.750 5923.750 Ge (511),(333) 74.3258 75.7825 75.05413 Mn Kβ 6490.450 6458.450 6505.450 Ge (511) 83.10123 88.8416 85.92691 Mn Kβ 6490.450 6458.450 6505.450 Ge (521) 76.3513 775.65127 Fe Kα 6403.800 6378.800 6418.800 Ge (440)		кр	4931.810	4880.810	4940.810	00(311)	74.9171	77.7371	/0.55/1
V Kβ 5427.290 5382.290 5442.290 Ge(422) 80.5352 85.8537 83.1944 Cr Kα 5414.700 5389.700 5429.700 Ge(422) 81.3668 84.8809 83.124 Cr Kβ 5946.710 5901.710 5961.710 Ge(511),(333) 72.7593 74.7479 73.753 Cr Kβ 5946.710 5901.710 5961.710 Si(422) 69.7171 71.357 70.5370 Cr Kβ 5946.710 5901.710 Si(422) 71.0142 72.1831 71.5986 Mn Kα 5898.750 5873.750 5923.750 Si(422) 71.0142 72.1831 71.5986 Mn Kβ 6490.450 6458.450 6505.450 Ge(531) 83.1291 90 87.6045 Mn Kβ 6493.300 6378.800 6418.800 Ge(440) 74.9512 76.3513 75.6512 Fe Kα 6493.300 6905.300 61453.30 707.280 71.4583	V	Κα	4952.200	4927.200	4967.200	Ge(331)	74.0677	75.7878	74.92775
Cr Kα 5414.700 5389.700 5429.700 Ge(422) 81.3668 84.8809 83.124 Cr Kβ 5946.710 5901.710 5961.710 Ge(511),(333) 72.7593 74.7479 73.753 Cr Kβ 5946.710 5901.710 5961.710 Sigl.710 Sigl.720 69.7171 71.357 70.53702 Cr Kβ 5946.710 5901.710 Sigl.710 Sigl.710 Sigl.710 Sigl.720 69.7171 71.357 70.53702 Cr Kβ 5946.710 5901.710 Sigl.710 Sigl.720 69.7171 71.357 70.53702 Mn Kα 5898.750 5873.750 5923.750 Ge(511),(333) 74.3258 75.7825 75.56413 Mn Kβ 6490.450 6458.450 6505.450 Ge(531) 83.1024 88.8416 85.96695 Mn Kβ 6493.300 6378.800 6418.800 Ge(420) 74.7953 77.565123 Fe Kα 6493.30	V	Κβ	5427.290	5382.290	5442.290	Ge(422)	80.5352	85.8537	83.19445
Cr Kβ 5946.710 5961.710 5961.710 Ge(511),(333) 72.7593 74.7479 73.7536 Cr Kβ 5946.710 5901.710 5961.710 Si(422) 69.7171 71.357 70.53705 Cr Kβ 5946.710 5901.710 5961.710 Si(1511),(333) 84.2059 90 87.10295 Mn Kα 5898.750 5873.750 5923.750 Ge(511),(333) 74.3258 75.7825 75.05411 Mn Kα 5898.750 5873.750 5923.750 Ge(511),(333) 74.3258 75.7825 75.05411 Mn Kβ 6490.450 6458.450 6505.450 Ge(531) 83.0123 88.8416 85.92691 Mn Kβ 6490.450 6458.450 6505.450 Ge(620) 78.4729 81.1944 79.83365 Fe Kα 6403.800 6378.800 6418.800 Ge(440) 74.9512 76.3513 75.65122 Fe Kβ 7057.980 7012.980 7072.980 Ge(620) 78.4729 81.1944 79.83365 Co <t< td=""><td>Cr</td><td>Κα</td><td>5414.700</td><td>5389.700</td><td>5429.700</td><td>Ge(422)</td><td>81.3685</td><td>84.8809</td><td>83.1247</td></t<>	Cr	Κα	5414.700	5389.700	5429.700	Ge(422)	81.3685	84.8809	83.1247
Cr Kβ 5946.710 5961.710 5961.710 Sid(422) 69.7171 71.357 70.53703 Cr Kβ 5946.710 5901.710 Sid(511),(333) 84.2059 90 87.10293 Mn Kα 5898.750 5873.750 5923.750 Ge(511),(333) 74.328 75.7825 75.05413 Mn Kα 5898.750 5873.750 5923.750 Ge(511),(333) 74.328 75.7825 75.05413 Mn Kβ 6490.450 6458.450 6505.450 Ge(531) 83.0123 88.8416 85.92693 Mn Kβ 6490.450 6458.450 6505.450 Ge(531) 85.2091 90 87.60453 Fe Kα 6403.800 6378.800 6418.800 Ge(440) 74.9512 76.5313 75.6512 Fe Kβ 7057.980 7012.980 702.980 Ge(620) 78.4729 81.1944 79.83363 Co Kα 6930.300 6905.300 Gi(533) 73.525 <t< td=""><td>Cr</td><td>Кβ</td><td>5946.710</td><td>5901.710</td><td>5961.710</td><td>Ge(511),(333)</td><td>72.7593</td><td>74.7479</td><td>73.7536</td></t<>	Cr	Кβ	5946.710	5901.710	5961.710	Ge(511),(333)	72.7593	74.7479	73.7536
Cr Kβ 5946.710 5901.710 5961.710 Si(511),(333) 84.2059 90 87.10295 Mn Kα 5898.750 5873.750 5923.750 Ge(511),(333) 74.3258 75.7825 75.05411 Mn Kα 5898.750 5923.750 Ge(511),(333) 74.3258 75.7825 75.05411 Mn Kβ 6490.450 6458.450 6505.450 Ge(531) 83.0123 88.8416 85.9269 Mn Kβ 6490.450 6458.450 6505.450 Ge(531) 85.2091 90 87.60455 Fe Kα 6403.800 6378.800 6418.800 Ge(440) 74.9512 76.3513 75.65125 Fe Kβ 7057.980 7012.980 Ge(440) 74.3252 86.6954 84.4003 Co Kα 6930.300 6945.300 Si(531) 76.4868 77.9453 77.2160 Co Kβ 7649.430 7664.430 Si(533) 73.525 74.5989 74.06195	Cr	κβ	5946.710	5901.710	5961.710	Si(422)	69.7171	71.357	70.53705
Mn Kα 5898.750 5873.750 5923.750 6e(511),(333) 74.3258 75.7825 75.0541 Mn Kα 5898.750 5973.750 5923.750 Si(422) 71.0142 72.1831 71.59863 Mn Kβ 6490.450 6458.450 6505.450 Si(440) 83.0123 88.8416 85.9269 Mn Kβ 6490.450 6458.450 6505.450 Ge(531) 85.2091 90 87.60453 Mn Kβ 6403.800 6378.800 6418.800 Ge(440) 74.9512 76.3513 75.6512 Fe Kβ 7057.980 7012.980 7072.980 Ge(440) 74.9512 76.3513 77.2160 Co Kα 6930.300 6905.300 Ge(533) 77.522 79.8372 78.709 Co Kβ 7649.430 7664.430 Si(531) 76.4868 77.9453 77.2160 Co Kβ 7478.150 7453.150 7493.150 Ge(533) 73.525 74.5989 <td>Cr</td> <td>κβ</td> <td>5946.710</td> <td>5901.710</td> <td>5961.710</td> <td>Si(511),(333)</td> <td>84.2059</td> <td>90</td> <td>87.10295</td>	Cr	κβ	5946.710	5901.710	5961.710	Si(511),(333)	84.2059	90	87.10295
Nin Kα 3383.730 3923.730 593.737 75.721603 593.772.721603 593.772.721603 593.772.721603 593.772.721603 593.777.522 79.8372 78.794061 71.01603 593.775.52 79.	Mp	Ka	E909 7E0	E972 7E0	E022 7E0	Co(E11) (222)	74 2250	75 7025	75 05/15
Nin Kα 3938.730 3923.772.730.7721.773.7721.773.7	Mp	Ka	5090.730	5073.750	5925.750	Ge(311),(333)	74.5230	73.7623	73.03413
NmKβG490.450G450.450G50.450G6(410)G30.120G30.120MmKβG400.450G458.450G505.450Ge(531)85.20919087.6045FeKαG403.800G378.800G418.800Ge(440)74.951276.351375.6512FeKβ7057.9807012.9807072.980Ge(620)78.472981.194479.83365CoKαG930.3006905.3006945.300Si(531)76.486877.945377.21600CoKβ7649.4307664.430Ge(444)82.105286.695484.4003CoKβ7649.4307664.430Ge(533)77.58279.837278.7096NiKα7478.1507453.1507493.150Si(520)74.461875.609175.03545NiKα7478.1507453.1507493.150Si(533)87.34729088.6736NiKβ8264.6608219.6608279.660Ge(642)82.04986.04384.046NiKβ8264.6608219.6608279.660Si(711),(551)79.914882.628681.271CuKα8047.8008022.8008062.800Ge(731),(553)76.558377.72177.13965CuKβ8905.2908860.2908920.290Ge(800)79.336381.644380.490.522CuKβ8905.290866.2908920.290Ge(731),(553)76.558377.72177.13965ZnKα8638.	Mn	KB	6/90 /50	6458 450	6505 450	Si(422)	83 0123	88 8/16	85 92695
κμ κμ 6430.430 6438.430 6403.430 64(13) 6418.800 6e(13) 74.9512 76.3513 75.6512 Fe Kβ 7057.980 7012.980 6e(20) 78.4729 81.1944 79.8336 Co Kα 6930.300 6905.300 6945.300 Si(531) 76.4868 77.9453 77.2160 Co Kβ 7649.430 7664.430 7664.430 Ge(444) 82.1052 86.6954 84.400 Co Kβ 7649.430 7664.430 7664.430 Si(533) 77.582 79.8372 78.7096 Ni Kα 7478.150 7453.150 7493.150 Ge(533) 73.525 74.5989 74.06199 Ni Kα 7478.150 7453.150 7493.150 Si(620) 74.4618 75.6091 75.03545 Ni Kα 7478.150 7453.150 7493.150 Si(533) 87.3472 90 88.6736 Ni Kβ 8264.660 8219.660 8279.660	Mp	кв	6490,450	6458 450	6505 450	Go(521)	85 2001	01+0.00	87.60455
FeKα6403.8006378.8006418.800Ge(440)74.951276.351375.65129FeKβ7057.9807012.9807072.980Ge(620)78.472981.194479.83369CoKα6930.3006905.3006945.300Si(531)76.486877.945377.21609CoKβ7649.4307604.4307664.430Ge(444)82.105286.695484.4003CoKβ7649.4307604.4307664.430Si(533)77.58279.837278.7096NiKα7478.1507453.1507493.150Ge(533)73.52574.598974.06199NiKα7478.1507453.1507493.150Ge(642)82.04986.04384.0403NiKα7478.1507453.1507493.150Si(620)74.461875.09175.03543NiKα7478.1507453.1507493.150Si(620)74.461875.609175.03543NiKβ8264.6608219.6608279.660Ge(642)82.04986.04384.0403NiKβ8264.6608219.6608279.660Ge(642)82.04986.04384.0403NiKβ8264.6608219.6608279.660Ge(642)82.04986.04384.0404NiKβ8264.6608219.6608279.660Ge(711),(551)76.062877.264876.6638CuKα8047.8008022.8008062.800Ge(731),(553)79.390681.71480.		кр	0490.430	0438.430	0303.430	06(331)	85.2091		87.00433
Fe Kβ 7057.980 7012.980 7072.980 Ge (620) 78.4729 81.1944 79.83365 Co Kα 6930.300 6905.300 6945.300 Si(531) 76.4868 77.9453 77.21605 Co Kβ 7649.430 7604.430 7664.430 Ge (444) 82.1052 86.6954 84.4003 Co Kβ 7649.430 7604.430 7664.430 Si (533) 77.582 79.8372 78.7096 Ni Kα 7478.150 7453.150 7493.150 Ge (533) 73.525 74.5989 74.0619 Ni Kα 7478.150 7453.150 7493.150 Si (620) 74.4618 75.03545 Ni Kα 7478.150 7453.150 7493.150 Si (620) 74.4618 75.03545 Ni Kβ 8264.660 8219.660 8279.660 Ge (642) 82.049 86.043 84.046 Ni Kβ 8264.660 8219.660 8279.660 Si (711), (551) 76.6628	Fe	Κα	6403.800	6378.800	6418.800	Ge(440)	74.9512	76.3513	75.65125
Co Kα 6930.300 6905.300 6945.300 Si(531) 76.4868 77.9453 77.2160 Co Kβ 7649.430 7604.430 7664.430 Ge(444) 82.1052 86.6954 84.4003 Co Kβ 7478.150 7453.150 7664.430 Si(533) 77.582 79.8372 78.7096 Ni Kα 7478.150 7453.150 7493.150 Ge(533) 73.525 74.5989 74.0619 Ni Kα 7478.150 7453.150 7493.150 Ge(533) 73.525 74.5989 74.0619 Ni Kα 7478.150 7453.150 7493.150 Si(620) 74.4618 75.6091 75.0354 Ni Kα 7478.150 7453.150 7493.150 Si(533) 87.3472 90 88.6736 Ni Kβ 8264.660 8219.660 8279.660 Ge(642) 82.049 86.043 84.046 Ni Kβ 82047.800 8022.800 8062.800 Ge(711),(551)	Fe	Κβ	7057.980	7012.980	7072.980	Ge(620)	78.4729	81.1944	79.83365
CoKβ7649.4307604.4307664.430Ge(444)82.105286.695484.4003CoKβ7649.4307604.4307664.430Si(533)77.58279.837278.7096NiKα7478.1507453.1507493.150Ge(533)73.52574.598974.06195NiKα7478.1507453.1507493.150Si(620)74.461875.609175.03545NiKα7478.1507453.1507493.150Si(620)74.461875.609175.03545NiKα7478.1507453.1507493.150Si(620)74.461875.609175.03545NiKβ8264.6608219.6608279.660Ge(642)82.04986.04384.046NiKβ8264.6608219.6608279.660Ge(711),(551)79.914882.628681.2717CuKα8047.8008022.8008062.800Ge(711),(551)77.66880.3179.538CuKα8047.8008022.8008662.800Si(444)78.766880.3179.538CuKβ8905.2908860.2908920.290Si(731),(553)76.558377.72177.13965ZnKα8638.9008613.9008653.900Ge(731),(553)76.558377.72177.13965ZnKα8638.9008613.9008653.900Ge(731),(553)76.558377.72177.13965ZnKα8638.9008613.9008653.900Ge(731),(553)76.5583<	Со	Κα	6930.300	6905.300	6945.300	Si(531)	76.4868	77.9453	77.21605
Co Kβ 7649.430 7604.430 7664.430 Si (533) 77.582 79.8372 78.709 Ni Kα 7478.150 7453.150 7493.150 Ge(533) 73.525 74.5989 74.0619 Ni Kα 7478.150 7453.150 7493.150 Ge(533) 73.525 74.5989 74.0619 Ni Kα 7478.150 7453.150 7493.150 Si(620) 74.4618 75.6091 75.03545 Ni Kα 7478.150 7453.150 7493.150 Si(533) 87.3472 90 88.6736 Ni Kβ 8264.660 8219.660 8279.660 Ge(642) 82.049 86.043 84.046 Ni Kβ 8264.660 8219.660 8279.660 Si(711),(551) 79.9148 82.6286 81.2717 Cu Kα 8047.800 8022.800 8062.800 Ge(711),(551) 76.0628 77.2648 76.6638 Cu Kβ 8905.290 8860.290 8920.290 Ge(800	Со	Кβ	7649.430	7604.430	7664.430	Ge(444)	82.1052	86.6954	84.4003
NiKα7478.1507493.1507493.150Ge(533)73.52574.598974.06199NiKα7478.1507453.1507493.150Si(620)74.461875.609175.03545NiKα7478.1507453.1507493.150Si(533)87.34729088.6736NiKβ8264.6608219.6608279.660Ge(642)82.04986.04384.046NiKβ8264.6608219.6608279.660Si(711),(551)79.914882.628681.2717CuKα8047.8008022.8008062.800Ge(711),(551)76.062877.264876.6638CuKα8047.8008022.8008062.800Si(444)78.766880.3179.5384CuKβ8905.2908860.2908920.290Ge(800)79.336381.644380.4903CuKβ8905.2908860.2908920.290Si(731),(553)76.558377.72177.13965ZnKα8638.9008613.9008653.900Ge(751),(553)76.558377.412276.6543ZnKβ9572.0009527.0009587.000Ge(751),(550)77.412276.6543ZnKβ9572.0009527.0009587.000Ge(751),(550)81.831484.30483.3805	Со	κβ	7649.430	7604.430	7664.430	Si(533)	77.582	79.8372	78.7096
Ni Kα 7478.150 7453.150 7493.150 Ge(533) 73.525 74.5989 74.06195 Ni Kα 7478.150 7453.150 7493.150 Si(620) 74.4618 75.6091 75.03545 Ni Kα 7478.150 7453.150 7493.150 Si(620) 74.4618 75.6091 75.03545 Ni Kβ 8264.660 8219.660 8279.660 Ge(642) 82.049 86.043 84.046 Ni Kβ 8264.660 8219.660 8279.660 Si(711),(551) 79.9148 82.6286 81.2717 Cu Kα 8047.800 8022.800 8062.800 Ge(711),(551) 76.0628 77.2648 76.6638 Cu Kα 8047.800 8022.800 8062.800 Ge(800) 79.3363 81.6443 80.4903 Cu Kβ 8905.290 8860.290 8920.290 Ge(800) 79.3363 81.6443 80.4903 Cu Kβ 8905.290 8860.290 8920.290 Si(731),(553) 76.5583 77.721 77.13965 Zn Kα						- ()			
NiKα7478.1507453.1507493.150Si(620)74.461875.609175.03545NiKα7478.1507453.1507493.150Si(533)87.34729088.6736NiKβ8264.6608219.6608279.660Ge(642)82.04986.04384.046NiKβ8264.6608219.6608279.660Si(711),(551)79.914882.628681.2717CuKα8047.8008022.8008062.800Ge(711),(551)76.062877.264876.6638CuKα8047.8008022.8008062.800Si(444)78.766880.3179.5384CuKβ8905.2908860.2908920.290Ge(800)79.336381.644380.4903CuKβ8905.2908860.2908920.290Si(731),(553)79.390681.71480.5523ZnKα8638.9008613.9008653.900Ge(731),(553)76.558377.72177.13965ZnKβ9572.0009527.0009587.000Ge(822),(660)75.89677.412276.6543ZnKβ9572.0009527.0009587.000Ge(751),(555)81.831484.930483.3805ZnKβ9572.0009527.0009587.000Ge(751),(555)81.831484.930483.3805	Ni	Κα	7478.150	7453.150	7493.150	Ge(533)	73.525	74.5989	74.06195
NiKα7478.1507453.1507493.15051(533)87.34729088.6730NiKβ8264.6608219.6608279.660Ge(642)82.04986.04384.046NiKβ8264.6608219.6608279.660Si(711),(551)79.914882.628681.2717CuKα8047.8008022.8008062.800Ge(711),(551)76.062877.264876.6638CuKα8047.8008022.8008062.800Ge(711),(551)76.062877.264876.6638CuKβ8905.2908860.2908920.290Ge(800)79.336381.644380.4903CuKβ8905.2908860.2908920.290Ge(800)79.336381.71480.5523CuKβ8905.2908860.2908920.290Si(731),(553)76.558377.72177.13965ZnKα8638.9008613.9008653.900Ge(731),(553)76.558377.72177.13965ZnKβ9572.0009527.0009587.000Ge(822),(660)75.89677.412276.6543ZnKβ9572.0009527.0009587.000Ge(751),(555)81.831484.930483.3805ZnKβ9572.0009527.0009587.000Ge(751),(555)81.831484.930483.3805ZnKβ9572.0009527.0009587.000Ge(751),(555)81.831484.930483.3805	NI	Κα	/4/8.150	7453.150	7493.150	SI(620)	/4.4618	/5.6091	/5.03545
NiKβ8264.6608219.6608279.660Ge(642)82.04986.04384.046NiKβ8264.6608219.6608279.660Si(711),(551)79.914882.628681.2717CuKα8047.8008022.8008062.800Ge(711),(551)76.062877.264876.6638CuKα8047.8008022.8008062.800Ge(711),(551)76.062877.264876.6638CuKβ8095.2908860.2908920.290Ge(800)79.336381.644380.4903CuKβ8905.2908860.2908920.290Ge(800)79.336381.71480.5523CuKβ8905.2908860.2908920.290Si(731),(553)79.390681.71480.5523ZnKα8638.9008613.9008653.900Ge(731),(553)76.558377.72177.13965ZnKβ9572.0009527.0009587.000Ge(751),(555)81.831484.930483.3809ZnKβ9572.0009527.0009587.000Ge(751),(555)81.831484.930483.3809	NI	κα	/4/8.150	7453.150	7493.150	SI(533)	87.3472	90	88.6736
ΝΙ κβ 8264.660 8219.660 8279.660 81(711),(551) 79.9148 82.6286 81.271 Cu Kα 8047.800 8022.800 8062.800 Ge(711),(551) 76.0628 77.2648 76.6638 Cu Kα 8047.800 8022.800 8062.800 Ge(711),(551) 76.0628 77.2648 76.6638 Cu Kβ 8905.290 8860.290 8920.290 Ge(800) 79.3363 81.6443 80.4903 Cu Kβ 8905.290 8860.290 8920.290 Ge(800) 79.3906 81.714 80.5523 Cu Kβ 8905.290 8860.290 8920.290 Si(731),(553) 76.5583 77.721 77.13965 Zn Kα 8638.900 8613.900 8653.900 Ge(731),(553) 76.5583 77.721 77.13965 Zn Kα 8638.900 8613.900 8653.900 Ge(731),(553) 76.5583 77.4122 76.6541 Zn Kβ 9572.000 9587.000		КВ	8264.660	8219.660	8279.660	Ge(642)	82.049	86.043	84.046
CuKα8047.8008022.8008062.800Ge(711),(551)76.062877.264876.6638CuKα8047.8008022.8008062.800Si(444)78.766880.3179.5384CuKβ8905.2908860.2908920.290Ge(800)79.336381.644380.4903CuKβ8905.2908860.2908920.290Si(731),(553)79.390681.71480.5523CuKβ8638.9008613.9008653.900Ge(731),(553)76.558377.72177.13965ZnKα8638.9008613.9008653.900Si(642)80.775382.590981.6833ZnKβ9572.0009527.0009587.000Ge(751),(555)81.831484.930483.3805ZnKβ9572.0009527.0009587.000Ge(751),(555)81.831484.930483.3805	NI	κβ	8264.660	8219.660	8279.660	SI(711),(551)	79.9148	82.6286	81.2/1/
Cu Kα 8047.800 8022.800 8062.800 Si(444) 78.7668 80.31 79.5384 Cu Kβ 8905.290 8860.290 8920.290 Ge(800) 79.3363 81.6443 80.4903 Cu Kβ 8905.290 8860.290 8920.290 Si(731),(553) 79.3906 81.714 80.5523 Cu Kβ 8638.900 8613.900 8653.900 Ge(731),(553) 76.5583 77.721 77.13963 Zn Kα 8638.900 8613.900 8653.900 Ge(731),(553) 76.5583 77.721 77.13963 Zn Kβ 9572.000 9587.000 Ge(822),(660) 75.896 77.4122 76.6543 Zn Kβ 9572.000 9587.000 Ge(751),(555) 81.8314 84.9304 83.3800	Cu	Κα	8047.800	8022.800	8062.800	Ge(711),(551)	76.0628	77.2648	76.6638
Cu Kβ 8905.290 8860.290 8920.290 Ge (800) 79.3363 81.6443 80.4903 Cu Kβ 8905.290 8860.290 8920.290 Si(731),(553) 79.3906 81.714 80.5523 Cu Kα 8638.900 8613.900 8653.900 Ge (731),(553) 76.5583 77.721 77.13965 Zn Kα 8638.900 8613.900 8653.900 Ge (822),(660) 75.896 77.4122 76.6543 Zn Kβ 9572.000 9527.000 9587.000 Ge (751),(555) 81.8314 84.9304 83.3800 Zn Kβ 9572.000 9527.000 9587.000 Ge (751),(555) 81.8314 84.9304 83.3800	Cu	Κα	8047.800	8022.800	8062.800	Si(444)	78.7668	80.31	79.5384
Cu Kβ 8905.290 8860.290 8920.290 Si(731),(553) 79.3906 81.714 80.5523 Zn Kα 8638.900 8613.900 8653.900 Ge(731),(553) 76.5583 77.721 77.13965 Zn Kα 8638.900 8613.900 8653.900 Ge(731),(553) 76.5583 77.721 77.13965 Zn Kα 8638.900 8613.900 8653.900 Ge(731),(553) 76.5583 77.721 77.13965 Zn Kβ 9572.000 9587.000 Ge(822),(660) 75.896 77.4122 76.6543 Zn Kβ 9572.000 9587.000 Ge(751),(555) 81.8314 84.9304 83.3809 Zn Kβ 9572.000 9587.000 Ge(751),(555) 81.8314 84.9304 83.3809	Cu	κβ	8905.290	8860.290	8920.290	Ge(800)	79.3363	81.6443	80.4903
Zn Kα 8638.900 8613.900 8653.900 Ge(731),(553) 76.5583 77.721 77.13965 Zn Kα 8638.900 8613.900 8653.900 Ge(731),(553) 76.5583 77.721 77.13965 Zn Kα 8638.900 8613.900 8653.900 Si(642) 80.7753 82.5909 81.6831 Zn Kβ 9572.000 9527.000 9587.000 Ge(822),(660) 75.896 77.4122 76.6541 Zn Kβ 9572.000 9527.000 9587.000 Ge(751),(555) 81.8314 84.9304 83.3809	Cu	Κβ	8905.290	8860.290	8920.290	Si(731),(553)	79.3906	81.714	80.5523
Zn Kα 8638.900 8613.900 8653.900 Si(642) 80.7753 82.5909 81.6831 Zn Kβ 9572.000 9527.000 9587.000 Ge(822),(660) 75.896 77.4122 76.6541 Zn Kβ 9572.000 9527.000 Ge(751),(555) 81.8314 84.9304 83.3809	Zn	Κα	8638.900	8613.900	8653.900	Ge(731).(553)	76.5583	77.721	77,13965
Zn Kβ 9572.000 9527.000 9587.000 Ge(822),(660) 75.896 77.4122 76.6541 Zn Kβ 9572.000 9527.000 Ge(751),(555) 81.8314 84.9304 83.3805	Zn	Κα	8638 900	8613 900	8653 900	Si(642)	80 7753	82 5909	81 6831
Zn Kβ 9572.000 9527.000 9587.000 Ge(751),(555) 81.8314 84.9304 83.3809	Zn	КВ	9572.000	9527.000	9587.000	Ge(822).(660)	75.896	77.4122	76.6541
	Zn	Кβ	9572.000	9527.000	9587.000	Ge(751).(555)	81.8314	84.9304	83.3809
jzn κρ 95/2.000/952/.000/958/.000/SI(/33) //.0546//8./313 //.89295	Zn	Kβ	9572.000	9527.000	9587.000	SI(733)	77.0546	78.7313	77.89295

Table 1: Emission line energy and corresponding crystals

Ce	Κα	4650.970	4619.230	4665.970	Si(400)	78.1111	81.2836	79.69735
Pr	Κα	5033 700	4998 500	5048 700	Si(331)	80 235	84 5078	82 3714
<u> </u>	Ku	5055.700	4558.500	5048.700	51(551)	00.235	04.3070	02.3714
Nd	Κα	5230.400	5192.700	5245.400	Si(331)	71.5419	73.3719	72.4569
Pm	Κα	5432.500	5392.800	5447.500	Ge(422)	80.212	84.5256	82.3688
Sm	Κα	5636.100	5594.000	5651.100	Ge(422)	71.794	73.6654	72.7297
Sm	Κα	5636.100	5594.000	5651.100	Si(422)	81.7091	88.4827	85.0959
Eu	Κα	5845.700	5801.600	5860.700	Ge(511),(333)	76.2951	78.9396	77.61735
Eu	Κα	5845.700	5801.600	5860.700	Si(422)	72.5844	74.5533	73.56885
Gd	Ka	6057 200	6010 000	6072 200	Ge(511) (333)	69 6671	71 3320	70 5
Gd	Ka	6057.200	6010.000	6072.200	Ge(511),(555)	77 6200	20 71/7	70.3
u	ĸu	0037.200	0010.000	0072.200	51(511),(555)	77.0309	80.7147	79.1720
Tb	Κα	6272.800	6223.000	6287.800	Ge(440)	80.3412	84.9315	82.63635
Tb	Κα	6272.800	6223.000	6287.800	Si(511),(333)	70.6125	72.3862	71.49935
Dy	Κα	6495.200	6442.700	6510.200	Ge(440)	72.2033	74.1799	73.1916
Dy	Κα	6495.200	6442.700	6510.200	Ge(531)	84.7338	90	87.3669
Dy	Κα	6495.200	6442.700	6510.200	Si(440)	82.6792	90	86.3396
Но	Ka	6719 800	6664 500	6734 800	Go(521)	74 2744	76 5972	75 /208
Но	Κα	6719 800	6664 500	673/ 800	Si(440)	73 /1001	75 6696	74 57985
	Ku	0715.800	0004.300	0754.000	51(440)	73.4301	75.0050	74.37303
Er	Κα	6948.700	6890.000	6963.700	Ge(620)	84.3878	90	87.1939
Er	Κα	6948.700	6890.000	6963.700	Ge(531)	68.5803	70.2013	69.3908
Er	Κα	6948.700	6890.000	6963.700	Si(440)	68.011	69.5823	68.79665
Er	Κα	6948.700	6890.000	6963.700	Si(531)	75.8707	78.5563	77.2135
Tm	Κα	7179.900	7118.100	7194.900	Ge(620)	74.4137	76.8102	75.61195
Tm	Κα	7179.900	7118.100	7194.900	Ge(533)	87.0723	90	88.53615
Tm	Κα	7179.900	7118.100	7194.900	Si(531)	69.8153	71.5703	70.6928
Yh	Κα	7415 600	7352 300	7430 600	Ge(620)	68 8554	70 4939	69 67465
Yb	Κα	7415.600	7352.300	7430.600	Ge(533)	75,2433	77.7725	76,5079
Yb	Κα	7415.600	7352.300	7430.600	Si(620)	76.3032	79.085	77.6941
Lu	Κα	7655.500	7589.900	7670.500	Ge(533)	69.5163	71.2126	70.36445
Lu	Κα	7655.500	7589.900	7670.500	Ge(444)	81.7847	90	85.89235
Lu	Κα	7655.500	7589.900	7670.500	Si(620)	70.25	72.0212	71.1356
Lu	Κα	7655.500	7589.900	7670.500	Si(533)	77.3778	80.4685	78.92315

References

Oliver Einsle, F. Akif Tezcan, Susana L. A. Andrade, Benedikt Schmid, Mika Yoshida, James B. Howard, Douglas C. Rees. 6 SEPTEMBER 2002 VOL 297 SCIENCE. P1696-1699

G. T. Seidler, "Design Considerations for Short Working Distance Multiple Crystal X-ray Spectrometers," submitted, Rev. Sci. Instrum., 2009.

P. Glatzel, U. Bergmann, Coordination Chemistry Reviews 249 (2005) 65-95

U. Bergmann, C.R. Horne, T.J. Collins, J.M. Workman, S.P. Cramer, Chem. Phys. Lett. 302 (1999) 119.

Gyorgy Vanko, Franz Renz, Gabor Molnar, Thomas Neisius, and Szilvia Karpati. Angew. Chem. Int. Ed. 2007

Aknowledgements

I would like to thank Jerry Seidler and his students Ken Nagle, Brian Mattern, and Joe Pacold for the opportunity to work with them and learn from them, for being very helpful and motivating.

I would like the thank Ron Musgrave from the UW Physics machine shop for teaching the machine shop course and assisting me in machining the sample box – a critical apparatus.

I would like to thank the REU coordinators Deep Gupta and Alejandro Garcia for coordinating REU activities and lecture series.

I would like to thank Linda and Janine for their hard work and support for many important nonphysics related issues.

I would finally like to thank the University of Washington for hosting the REU program and the encouraging research environment.