Modification of a Bruker APEX Duo Diffractometer for Variable Temperature, Solvated Powder X-Ray Diffraction and Synchrotron Screening

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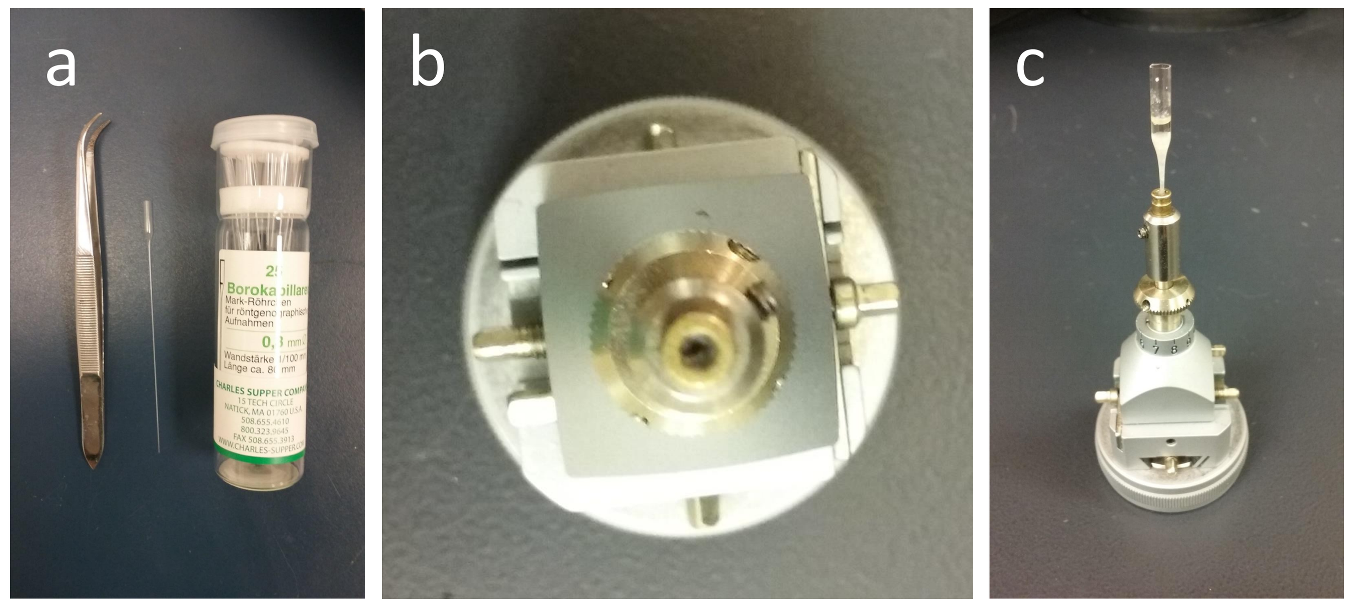
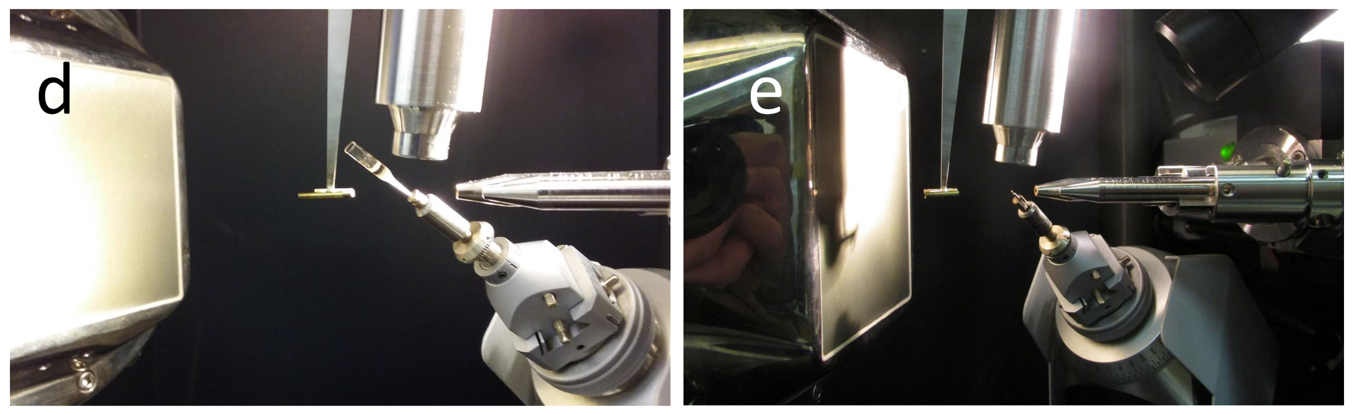
Sample Setup



Polycrystalline powder samples are loaded in sodium borosilicate capillaries through a wide mouth (a). Gentle vibration is applied to the body of the capillary using the side of a pair of tweezers to work the sample to the sealed base of the capillary. The capillary is cropped and loaded into a goniometer containing wax. A soldering iron is used to melt the wax and seal the capillary in place (b).

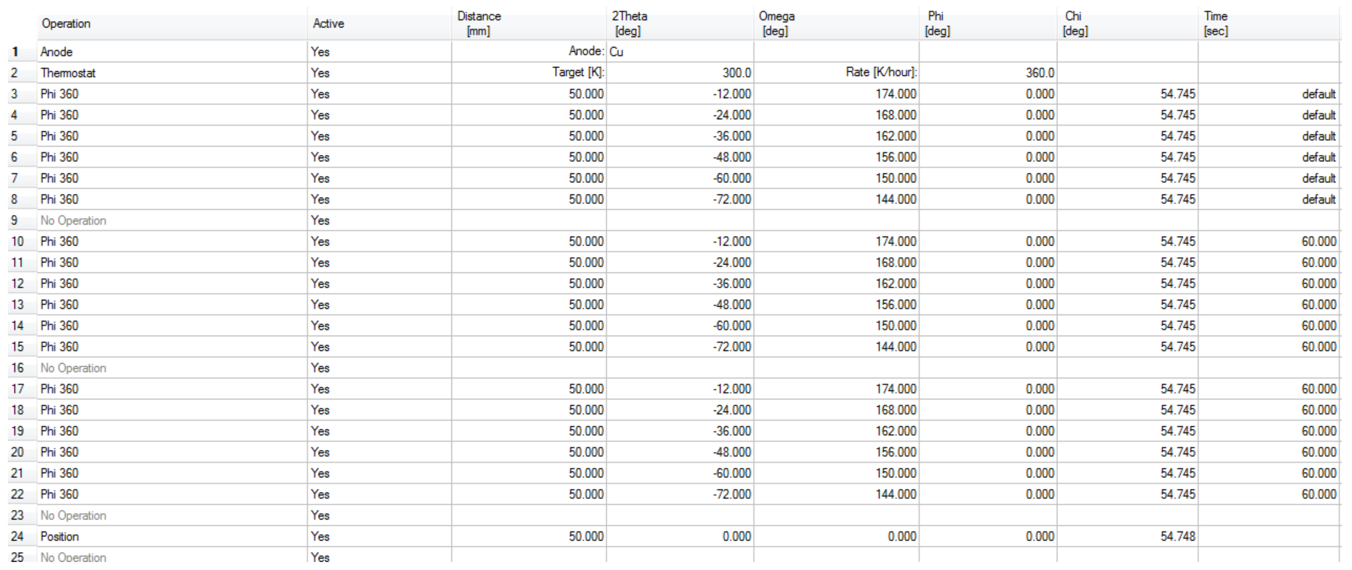
For solvated samples, the capillary is cropped prior to sample loading. The sealed end is removed to retain the wide mouthed end. The new base is sealed using a Bunsen burner before the sample is loaded (c).



A side by side comparison of the goniometer setup is shown for (d) a solvated powder sample and (e) a standard single crystal measurement.

For powder measurements, detector distance is set to 150 mm, detector format is 1024x1024. Cu source is used.

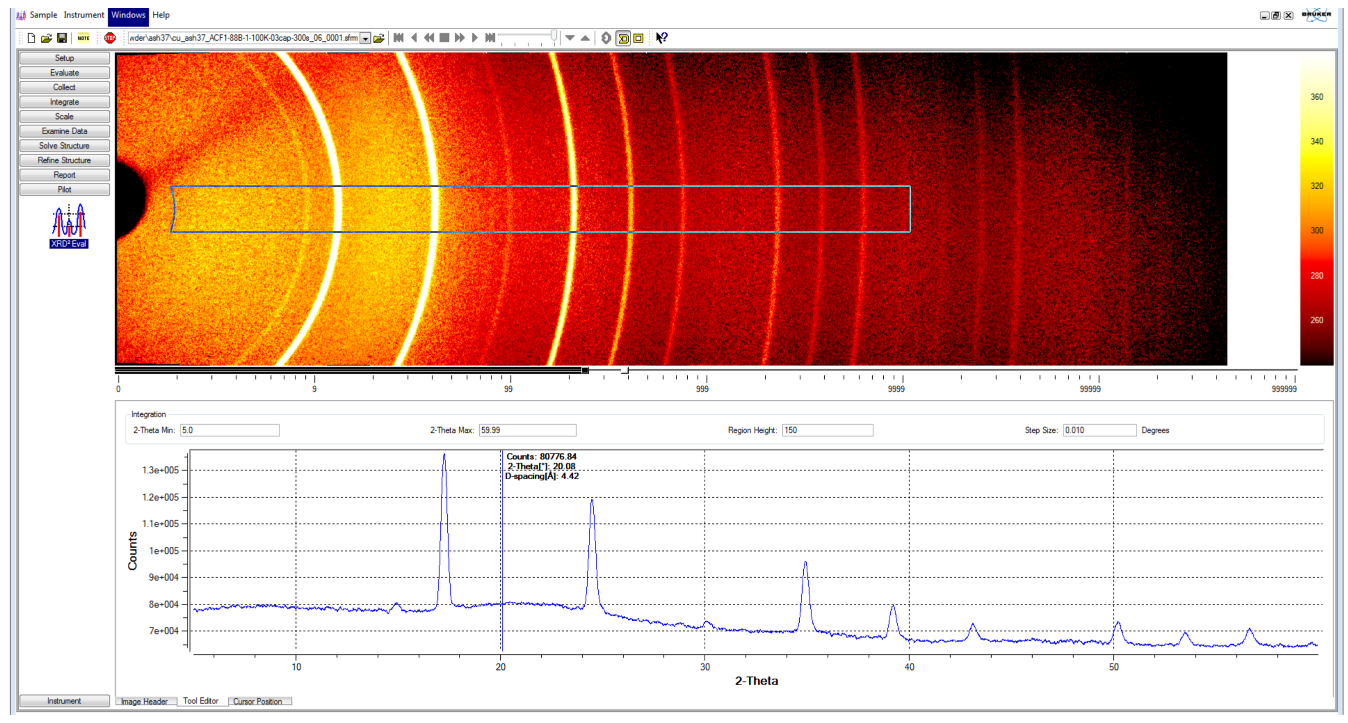
Experimental Setup and Data



	Operation	Active	Distance [mm]	2Theta [deg]	Omega [deg]	Phi [deg]	Chi [deg]	Time [sec]
1	Anode	Yes	Anode:	Cu				
2	Thermostat	Yes	Target [K]:	300.0	Rate [K/hour]:	360.0		
3	Phi 360	Yes	50.000	-12.000	174.000	0.000	54.745	default
4	Phi 360	Yes	50.000	-24.000	168.000	0.000	54.745	default
5	Phi 360	Yes	50.000	-36.000	162.000	0.000	54.745	default
6	Phi 360	Yes	50.000	-48.000	156.000	0.000	54.745	default
7	Phi 360	Yes	50.000	-60.000	150.000	0.000	54.745	default
8	Phi 360	Yes	50.000	-72.000	144.000	0.000	54.745	default
9	No Operation	Yes						
10	Phi 360	Yes	50.000	-12.000	174.000	0.000	54.745	60.000
11	Phi 360	Yes	50.000	-24.000	168.000	0.000	54.745	60.000
12	Phi 360	Yes	50.000	-36.000	162.000	0.000	54.745	60.000
13	Phi 360	Yes	50.000	-48.000	156.000	0.000	54.745	60.000
14	Phi 360	Yes	50.000	-60.000	150.000	0.000	54.745	60.000
15	Phi 360	Yes	50.000	-72.000	144.000	0.000	54.745	60.000
16	No Operation	Yes						
17	Phi 360	Yes	50.000	-12.000	174.000	0.000	54.745	60.000
18	Phi 360	Yes	50.000	-24.000	168.000	0.000	54.745	60.000
19	Phi 360	Yes	50.000	-36.000	162.000	0.000	54.745	60.000
20	Phi 360	Yes	50.000	-48.000	156.000	0.000	54.745	60.000
21	Phi 360	Yes	50.000	-60.000	150.000	0.000	54.745	60.000
22	Phi 360	Yes	50.000	-72.000	144.000	0.000	54.745	60.000
23	No Operation	Yes						
24	Position	Yes	50.000	0.000	0.000	0.000	54.748	
25	No Operation	Yes						

Example of an experiment for a solvated powder sample at room temperature. Phi 360 measurements are utilized for samples which tend towards preferred orientation.

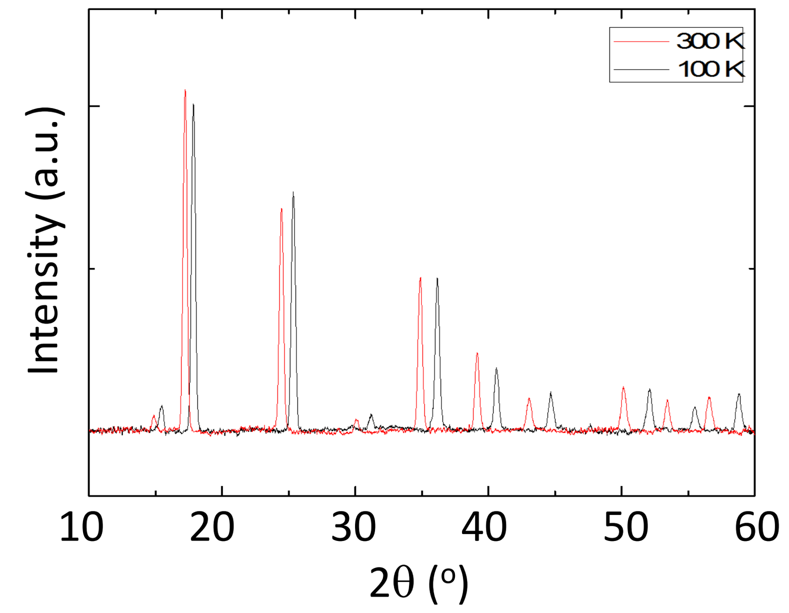
Additional lines may be used to ramp temperature, hold for sample equilibration, or position the sample.

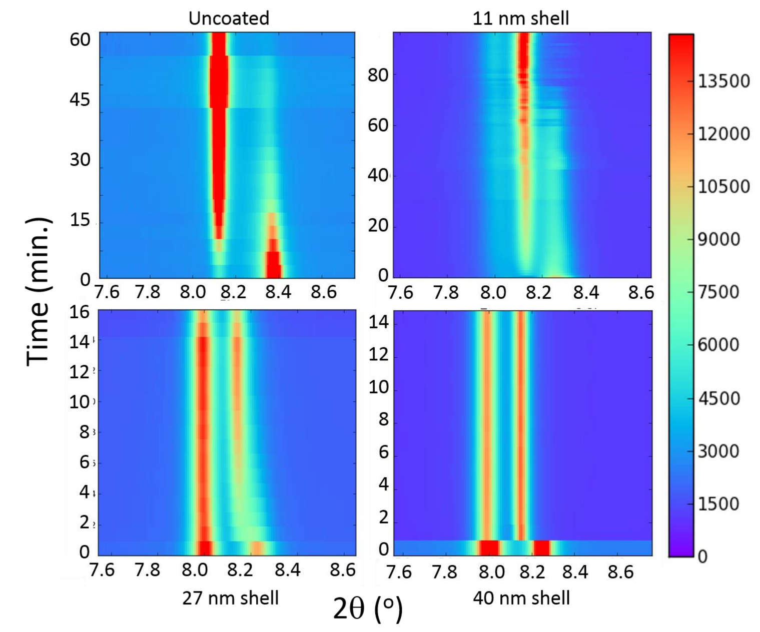


An example of a powder diffraction pattern obtained using the Bruker APEX Duo.

Images are combined using the Pilot portion of APEX II, and then integrated. The files can be saved as .raw files to be handled in other software.

Screening for Synchrotron Experiments



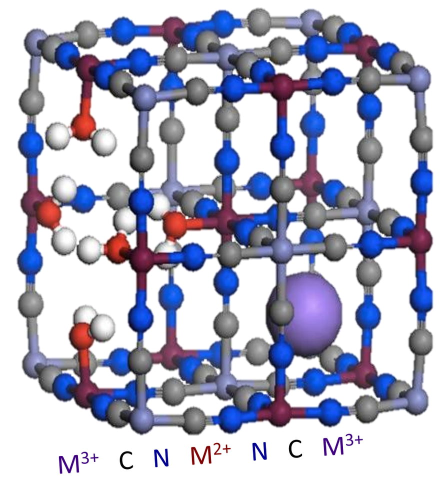


About the Materials

Work performed under the advisement of Dr. Daniel R. Talham.

PBA's

General formula
$\mathbf{A_jM^{II}_k[M'^{III}(CN)_6]_l \cdot nH_2O}$



M^{II} and **M'**^{II} determine the identity of the analogue, referred to as **M M '** - PBA.

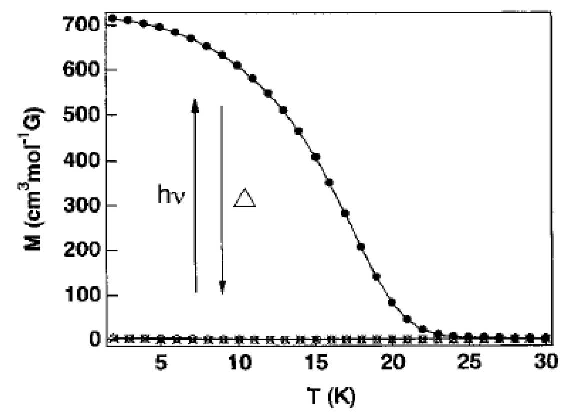
Charge balance necessitates interstitial alkali cations (A) or $[M'(CN)_6]$ vacancies, where water coordinates instead.

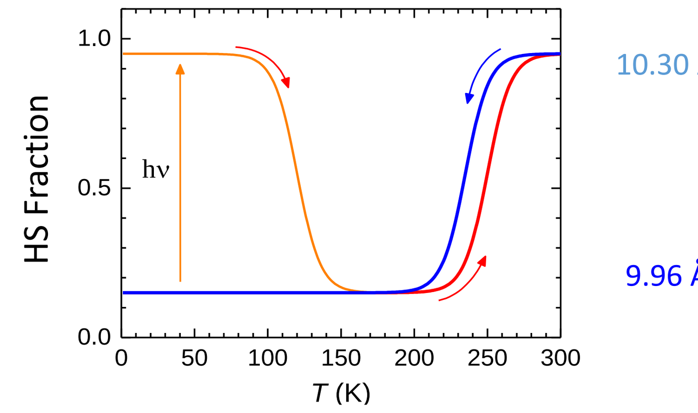
Cobalt Hexacyanoferrate (CoFe-PBA)

CoFe-PBA exhibits a photo-induced (PI) increase in magnetization due to a Charge-Transfer Induced Spin Transition (CTIST), where it is switched between a low-spin (LS) and a high-spin (HS) state:

Co^{III} (LS) – Fe^{II} (LS) ⟷ Co^{II} (HS) – Fe^{III} (LS)

The CTIST of CoFe-PBA is associated with a large change in the cubic unit cell parameter, a, from a_{LS}=9.96 A in the LS state to a_{HS}=10.30 A in the HS state, corresponding to a significant change in volume (~10%).

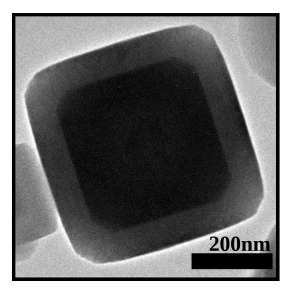


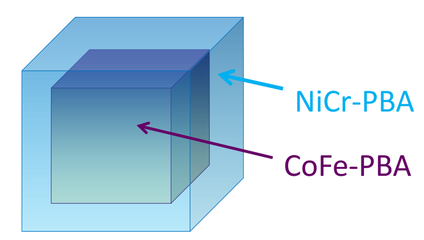


The CTIST can be induced with a variety of stimuli including light, change in temperature, and change in pressure.

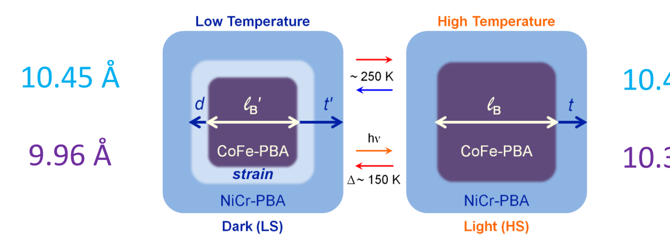
Two PBA's are coupled via an interface in the core-shell architecture. Here, the desirable photoactivity of CoFe-PBA is coupled with the magnetic NiCr-PBA, resulting in a light-sensitive magnetic material.

CoFe@NiCr-PBA

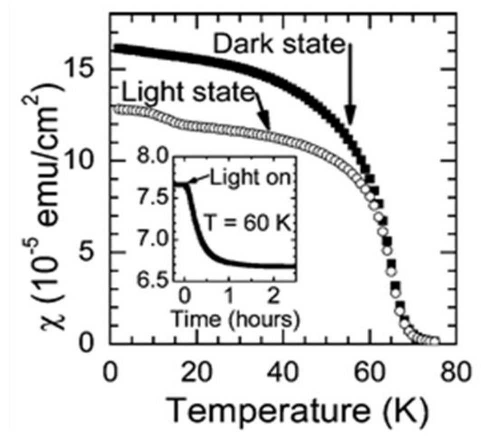


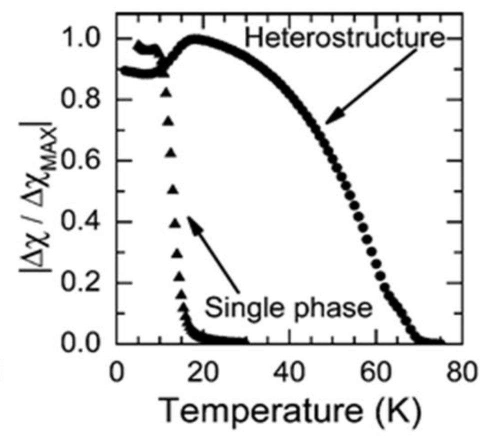


CoFe@NiCr-PBA



Magnetomechanical Effect





In collaboration with Prof. M.W. Meisel, Dept. of Physics

The CoFe@NiCr-PBA heterostructure now exhibits a photo-induced decrease in magnetization through the ordering temperature of the NiCr-PBA component.

This is proposed to be magnetomechanical in origin. The large change in volume of the core exerts a stress in the shell, resulting in strain. This strain prevents some magnetic domains from orienting along their preferred magnetocrystalline axis, until the strain is relieved with light, allowing them to reorient away from the direction of the applied magnetic field.

Our Team / References and Acknowledgements

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Dr. Isabelle Maurin

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