Surface deposition of the nanomagnet Ni_{12} on mica: GIXRD studies at BM25-B ESRF

E. Carolina Sañudo

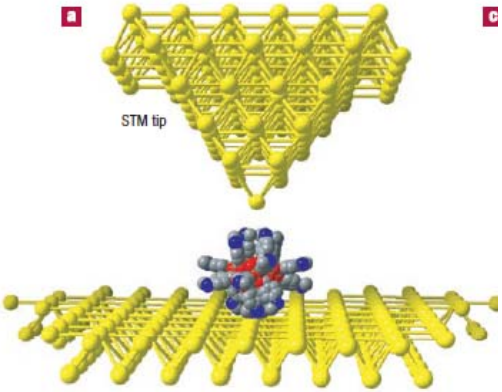
Department of Inorganic Chemistry – IN2UB

HTTP://www.ub.edu/inorgani/recerca/gmmf.htm

http://www.ub.edu/inorgani/recerca/ecsanudo.htm

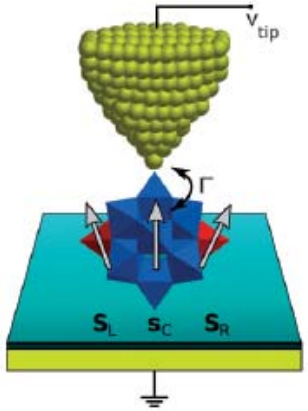
How to manipulate/address one molecule? Nano-structuration : surface deposition

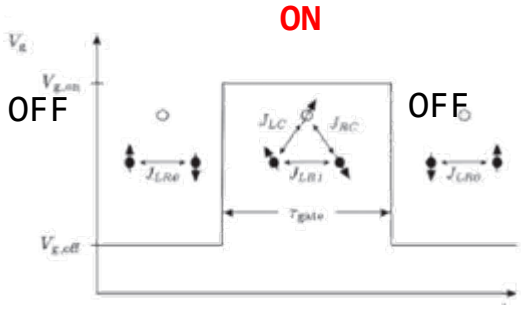
Transport experiments on SMMs using STM



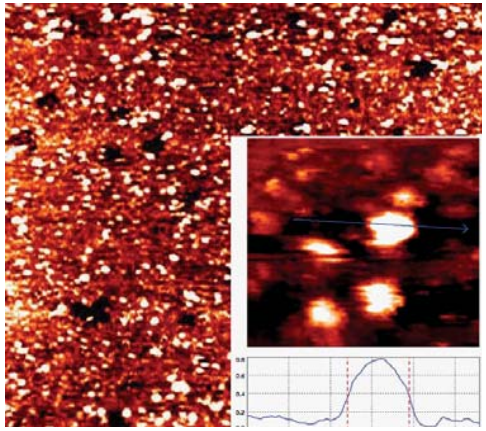
Wernsdorfer *et al*, *Nature materials*. **2008**

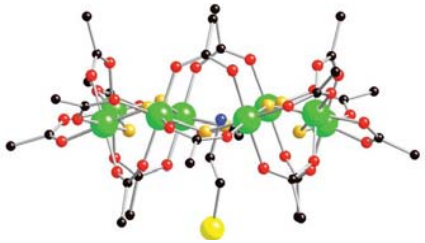
STM, POM and a redox switch





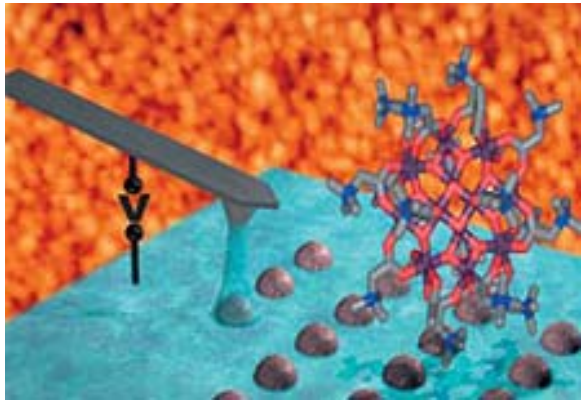
Coronado *et al*. *J. Mat. Chem*. **2009**





STM image of a Cr_7Ni ring on Au(111)

Winpenny, *Dalton Trans*., **2006**, 2810–2817



Coronado *et al*. *Adv. Mater*. **2007**, *19*, 291

Nano-structuration – deposition of Ni_{12} on mica AFM studies

Surface deposition of Ni_{12} on mica

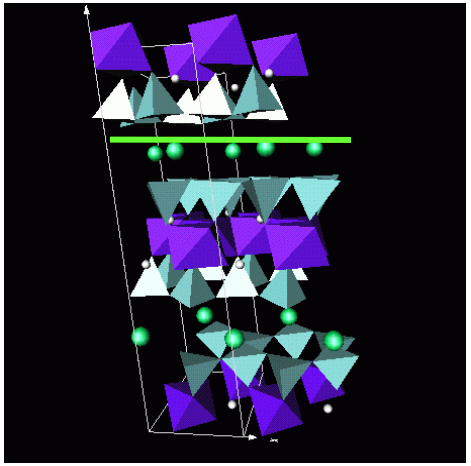
-MICA = muscovite $K_2Al_4Si_6Al_2O_{20}(OH,F)_4$
negatively charged cleaved surface

-**electrostatic interaction** between the Ni_{12} nanocrystals and the surface

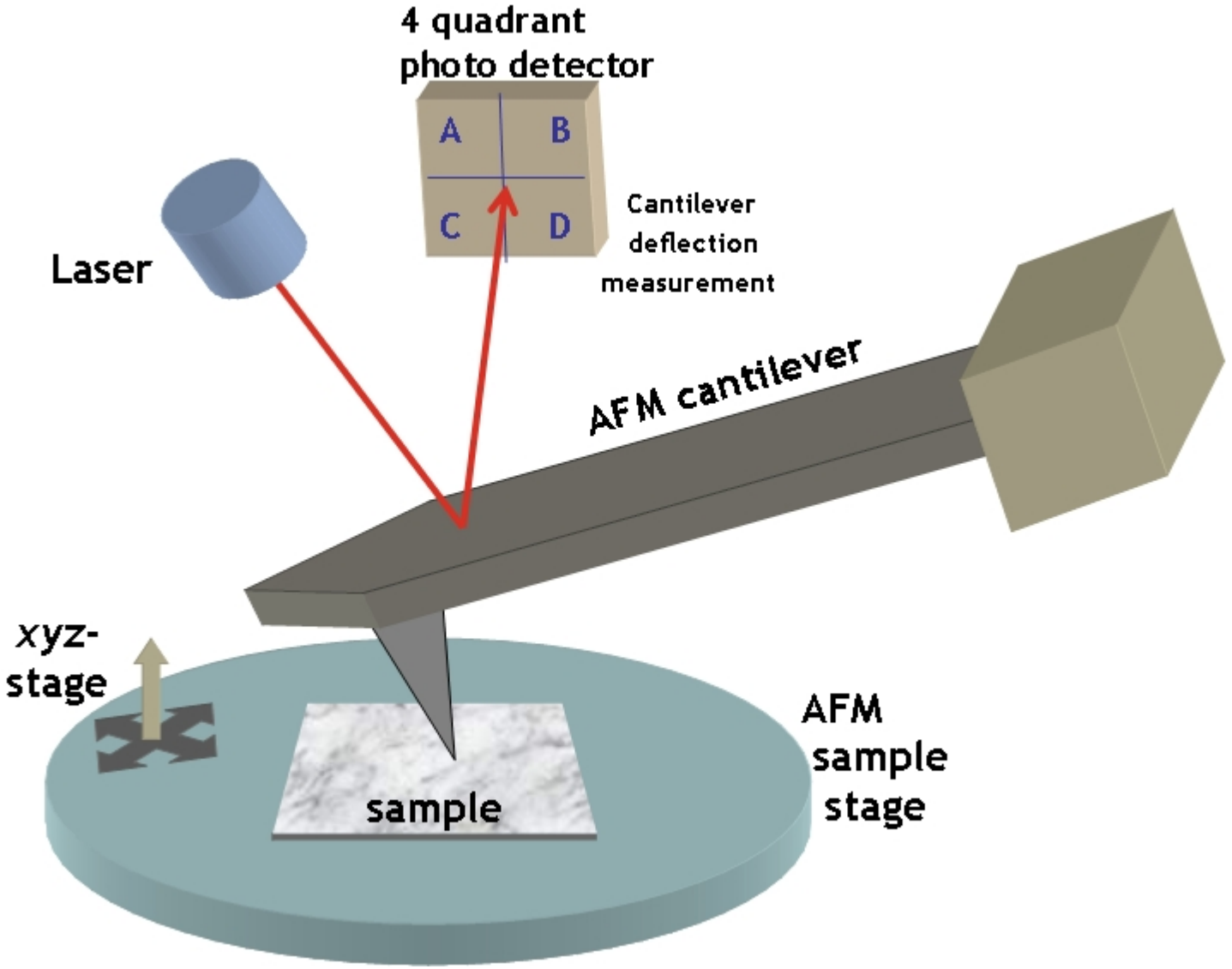
-10^{-6} and 10^{-5} M solutions of Ni_{12} in acetone or CH_2Cl_2

-drop casting, dip coating and spin coating

BEST results obtained by spin coating

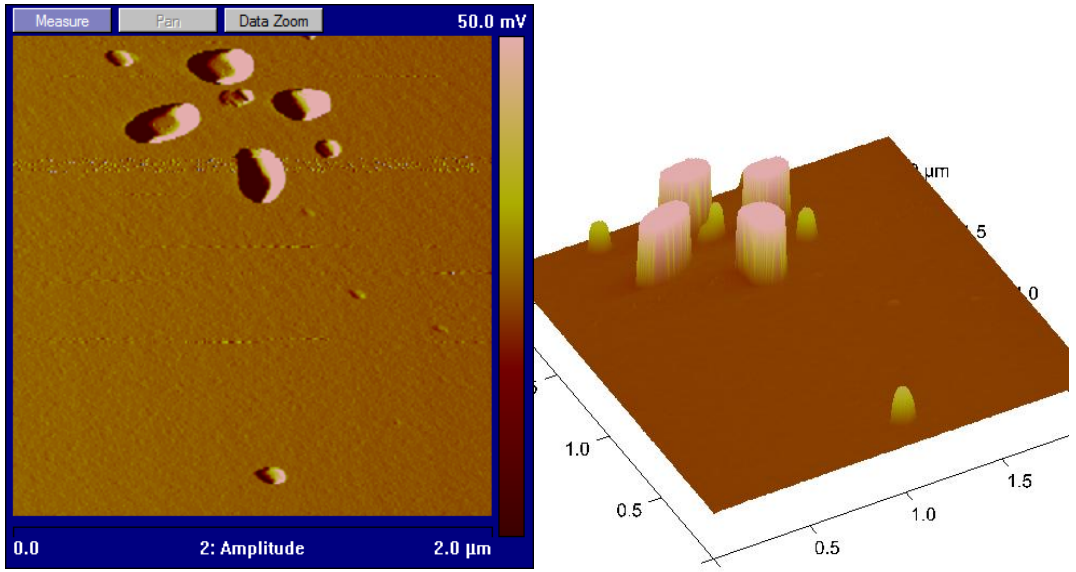


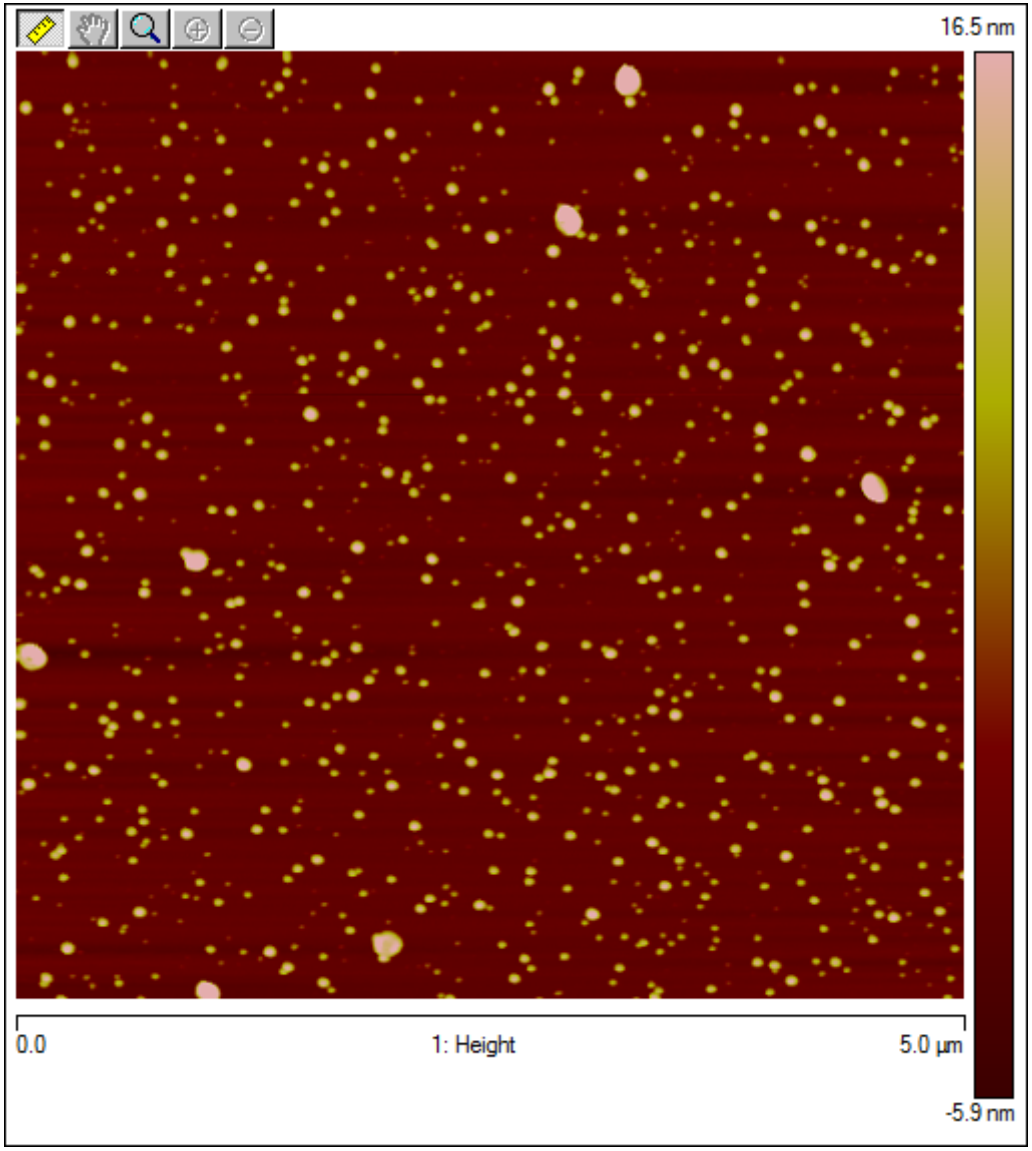
AFM microscopy



Nano-structuration – deposition of Ni_{12} on mica AFM studies

High resolution image of Ni12 on mica (dip coated sample)
Small aggregates with faces: are they crystalline?

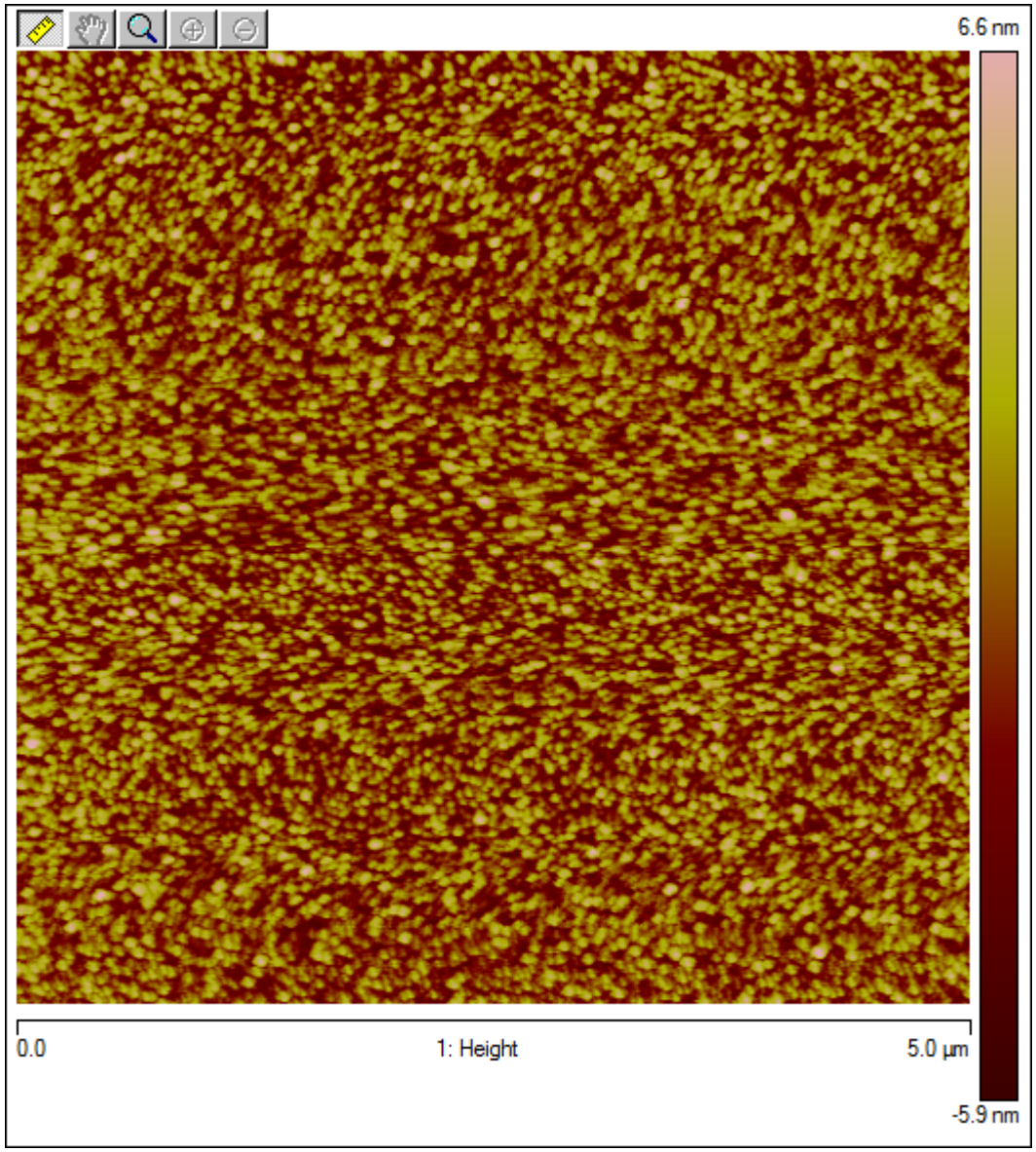




Sample 7

Ni12-Br 10-4 M in MeOH

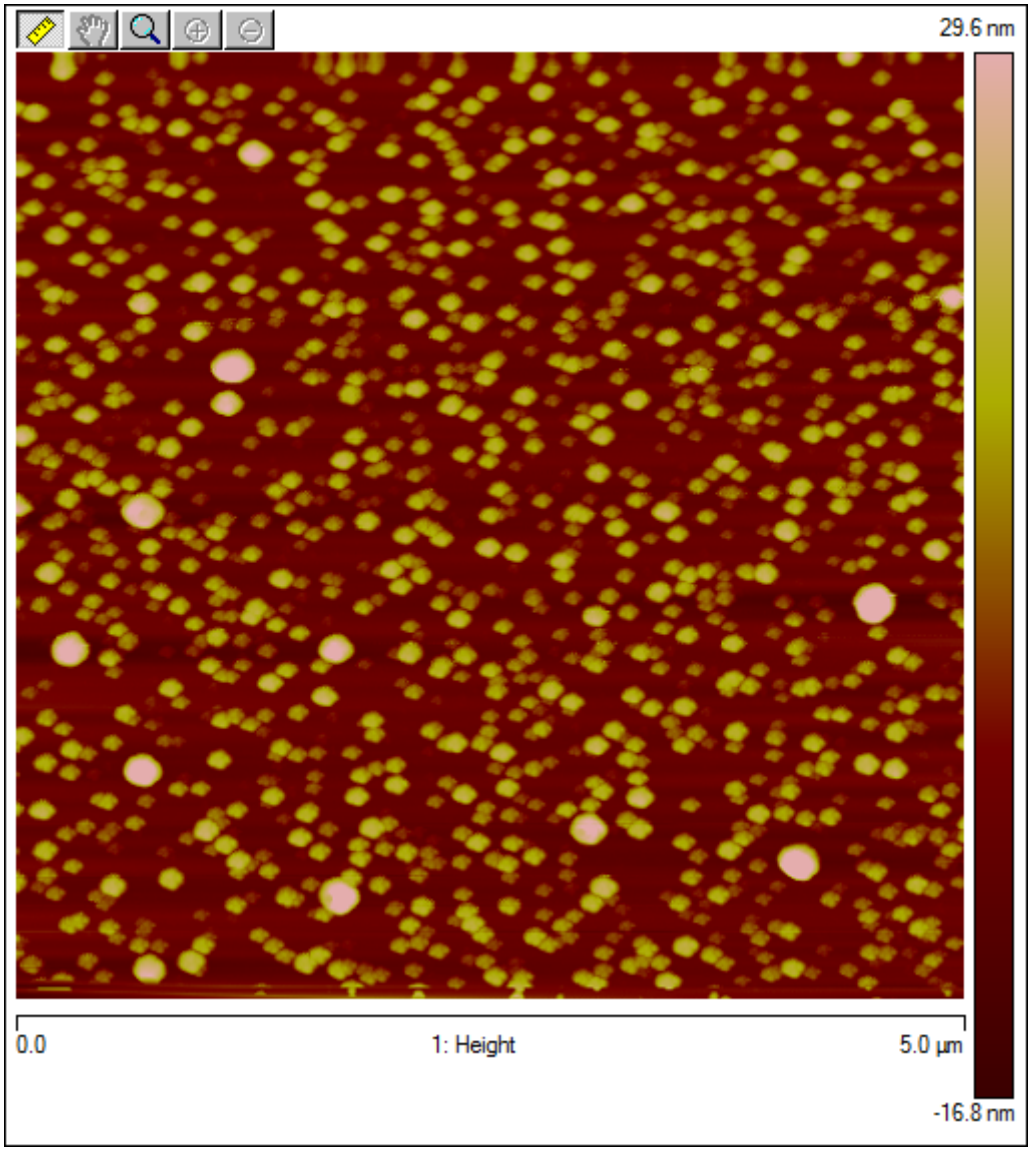
Spin coating 3000 rpm
30 sec



Sample 8

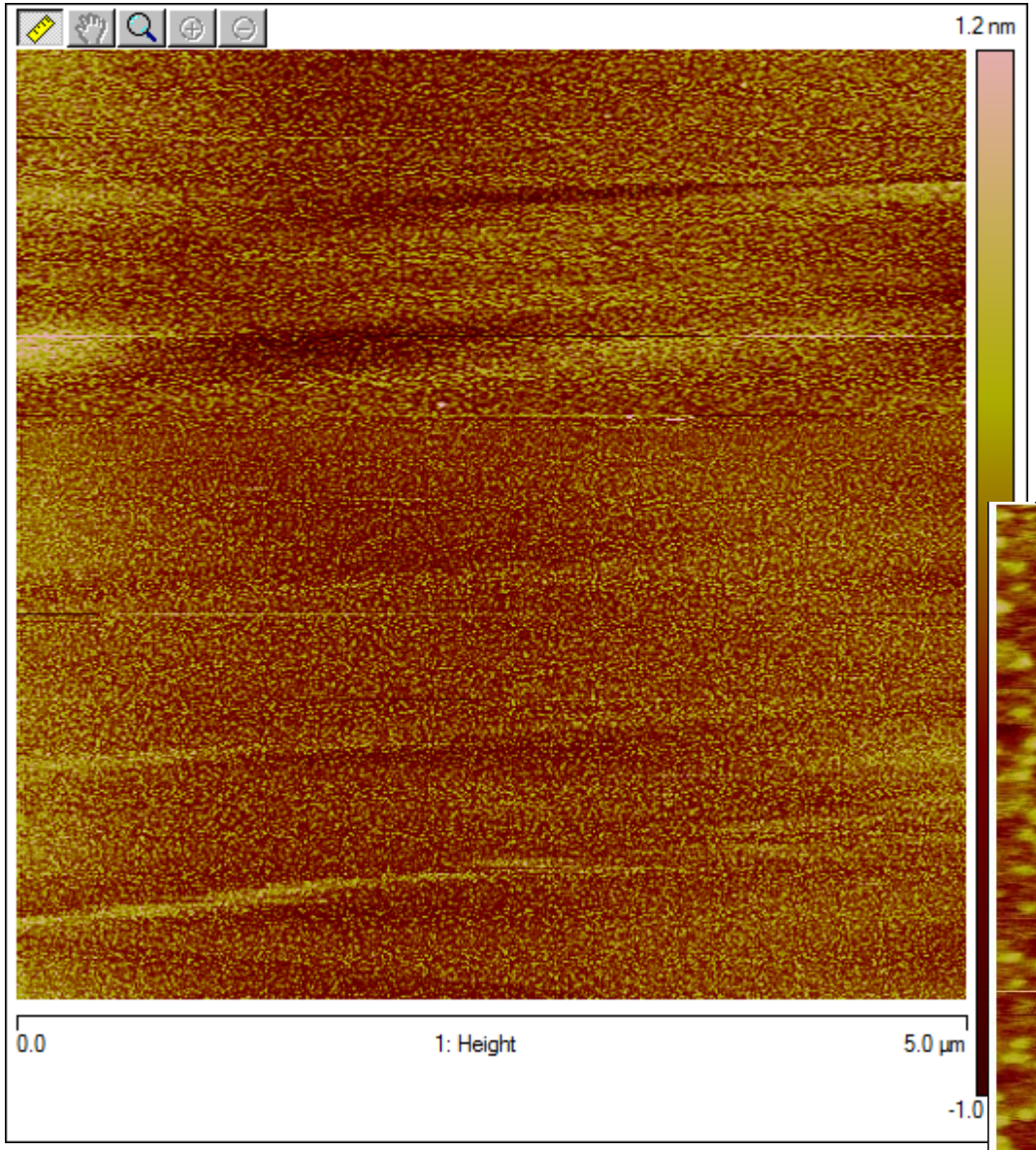
Ni12-Br 10-4 M in MeOH

Spin coating 500 rpm
30 sec



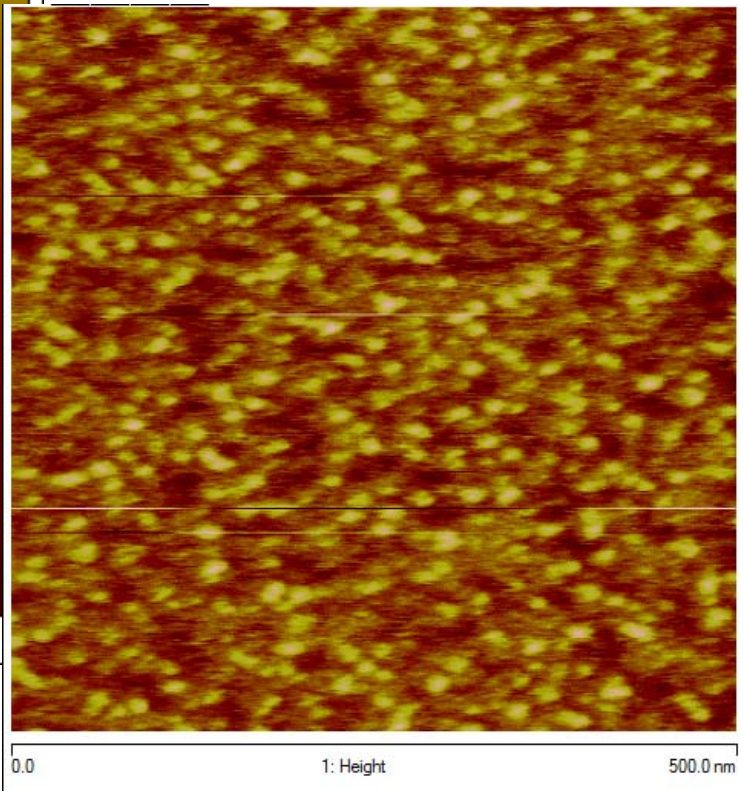
Sample 9
Ni12-Br 10-4 M in MeOH

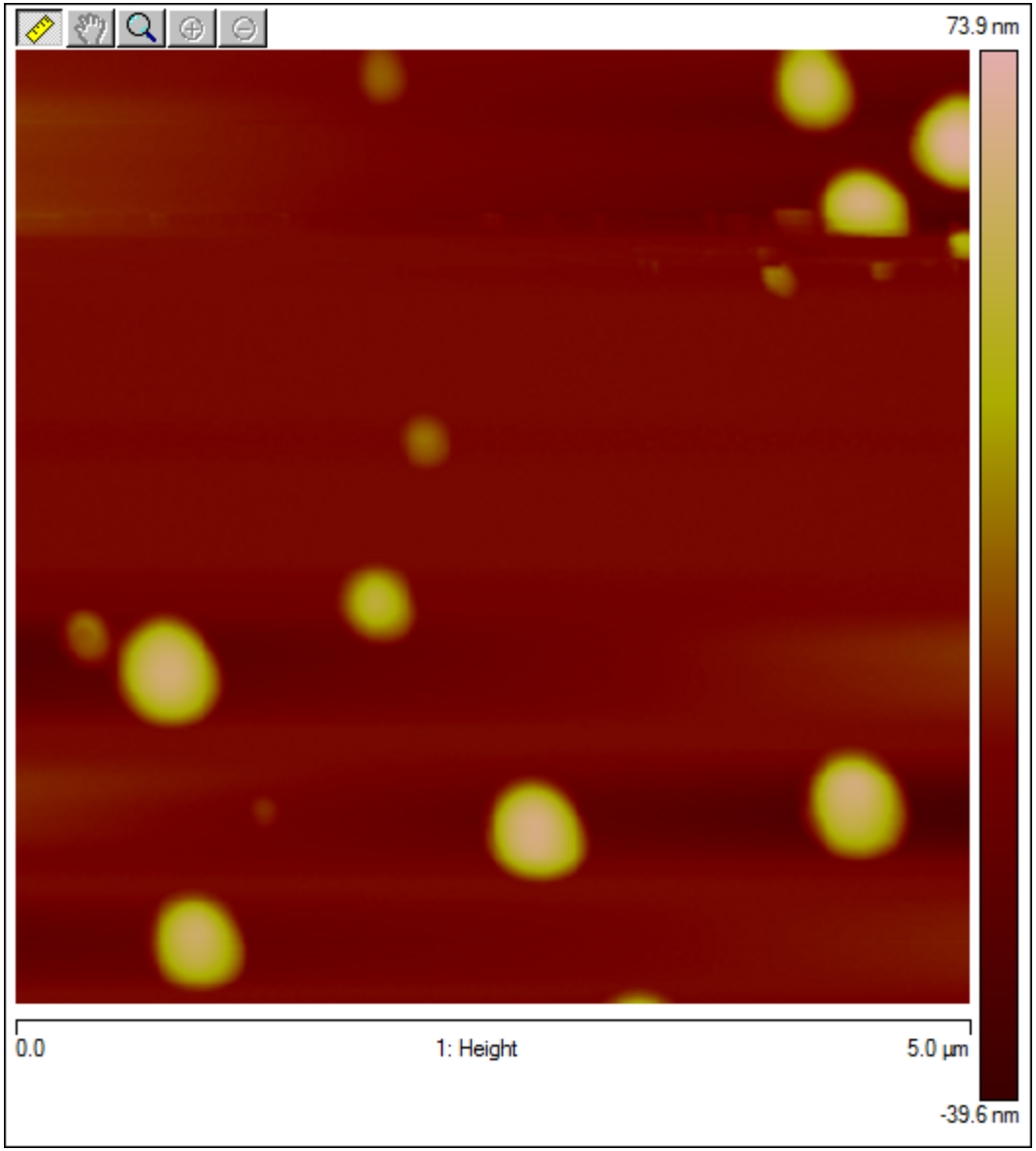
Spin coating 500 rpm 30 sec + spin coating 3000 rpm 30 sec



destroyed..
Ni12-Br 10-4 M in MeOH

Spin coating 3000 rpm
30 sec continuous
input of sample

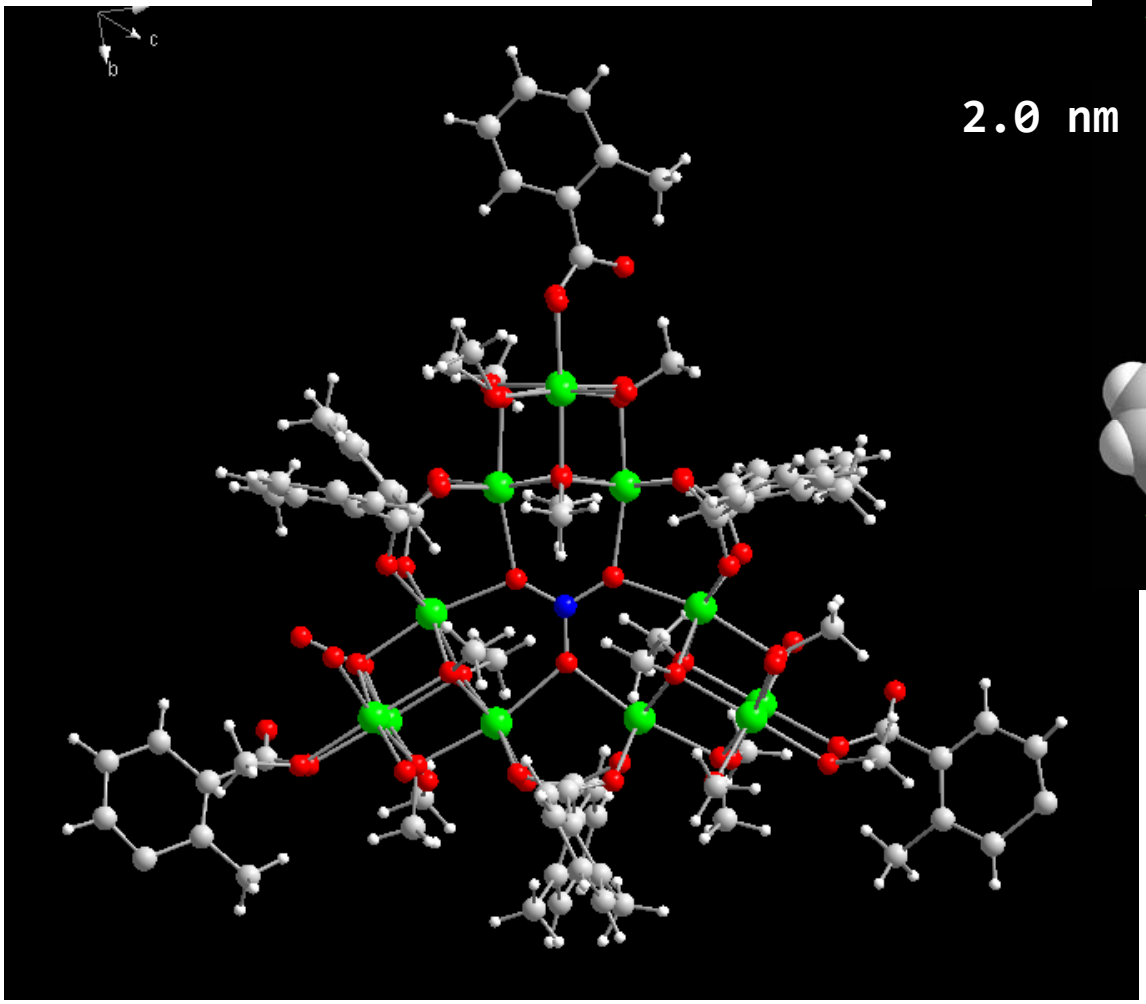


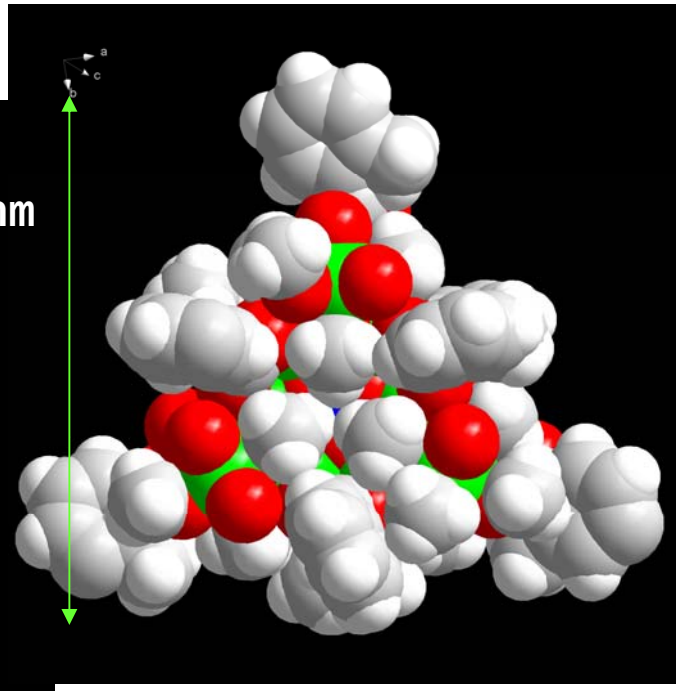


Sample 10

Ni12-Br 10-4 M in MeOH
1 drop, before spinning,
then
spin coating 500 rpm
30 sec

Ni_{12}-NO_3



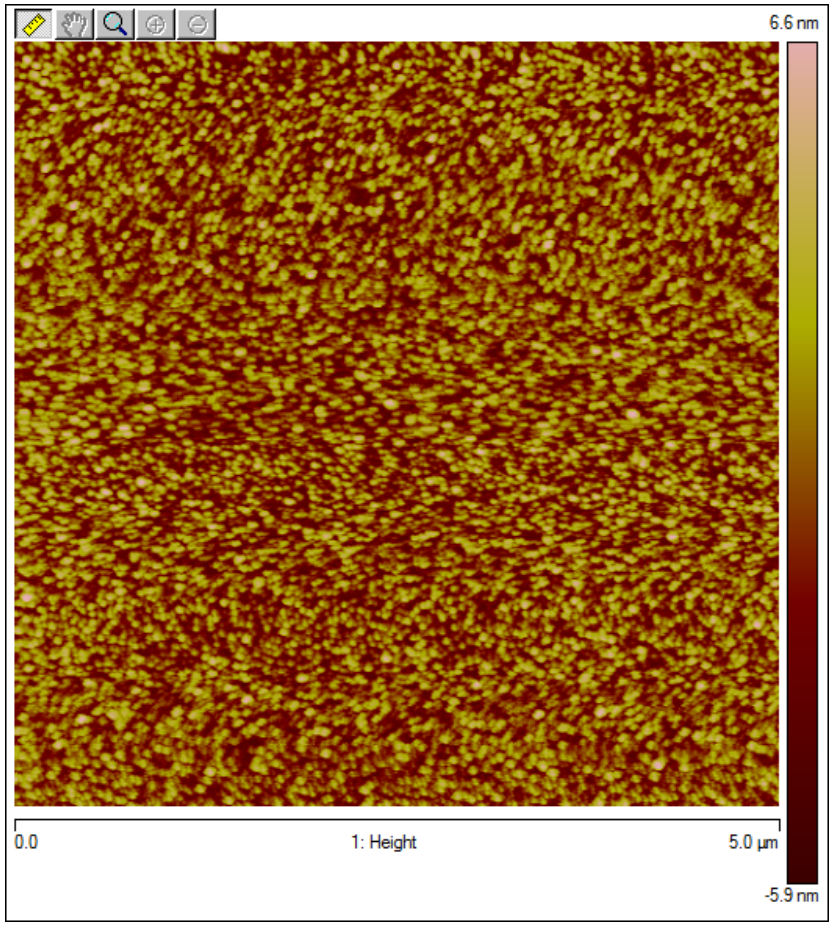


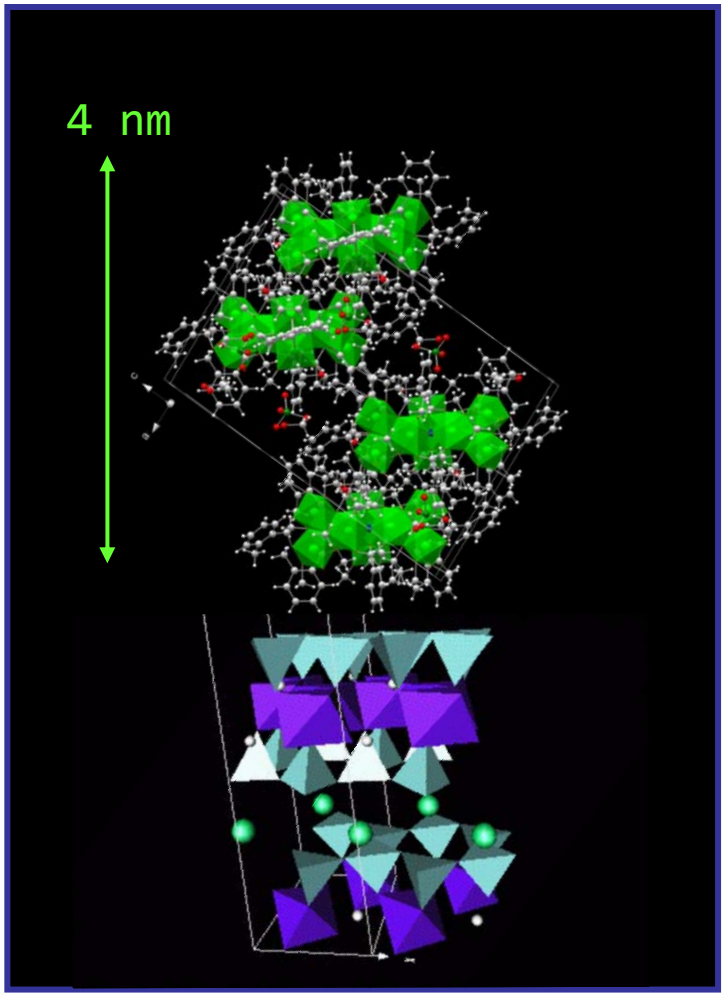
-3 Ni_4O_4 SMMs linked by a central NO_3^- and six carboxylates

-Triclinic P-1

Surface deposition of the nanomagnet Ni_{12} on mica

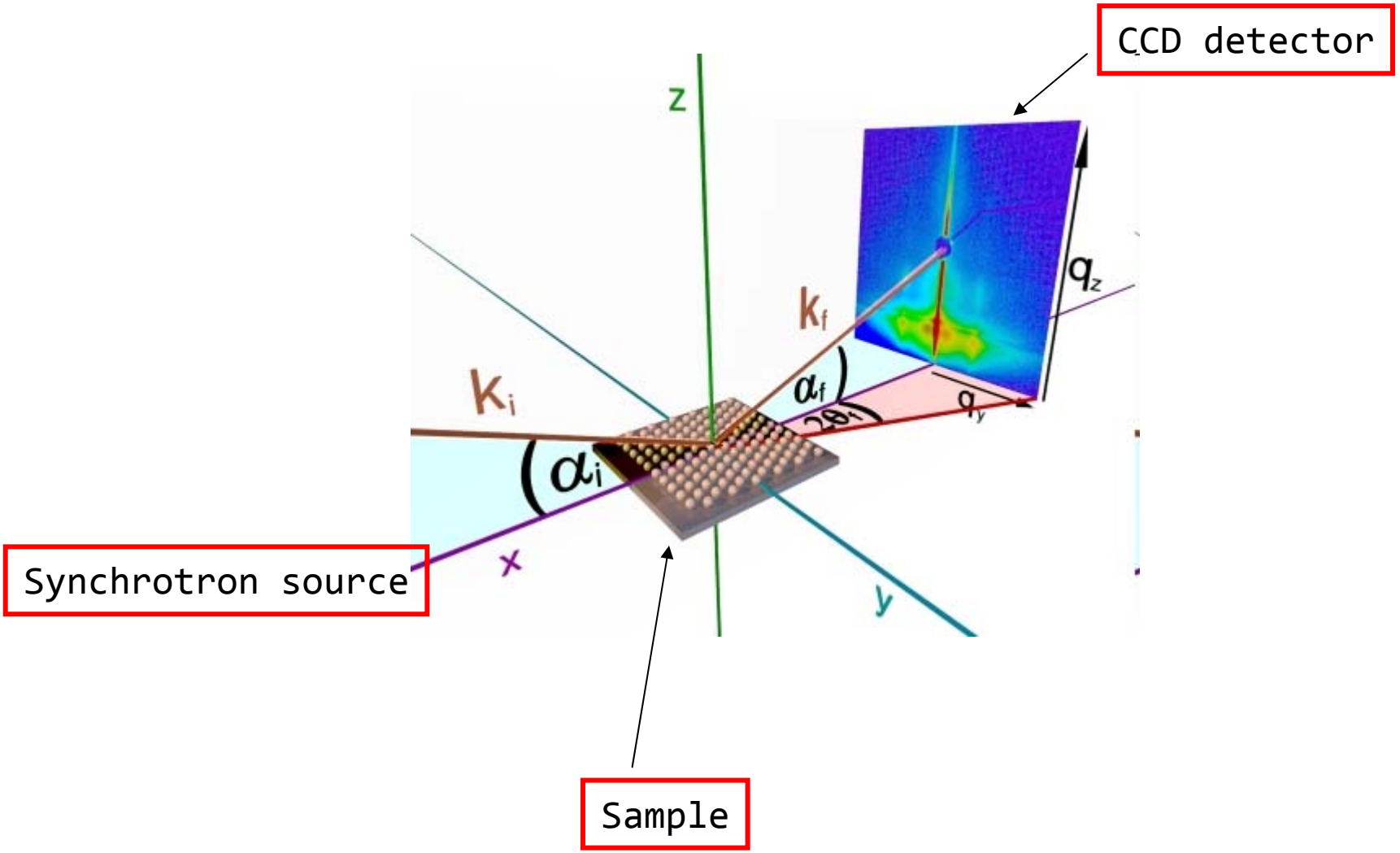
$P2_1/C$, $Z = 4$
$V = 12.51\ nm^3$



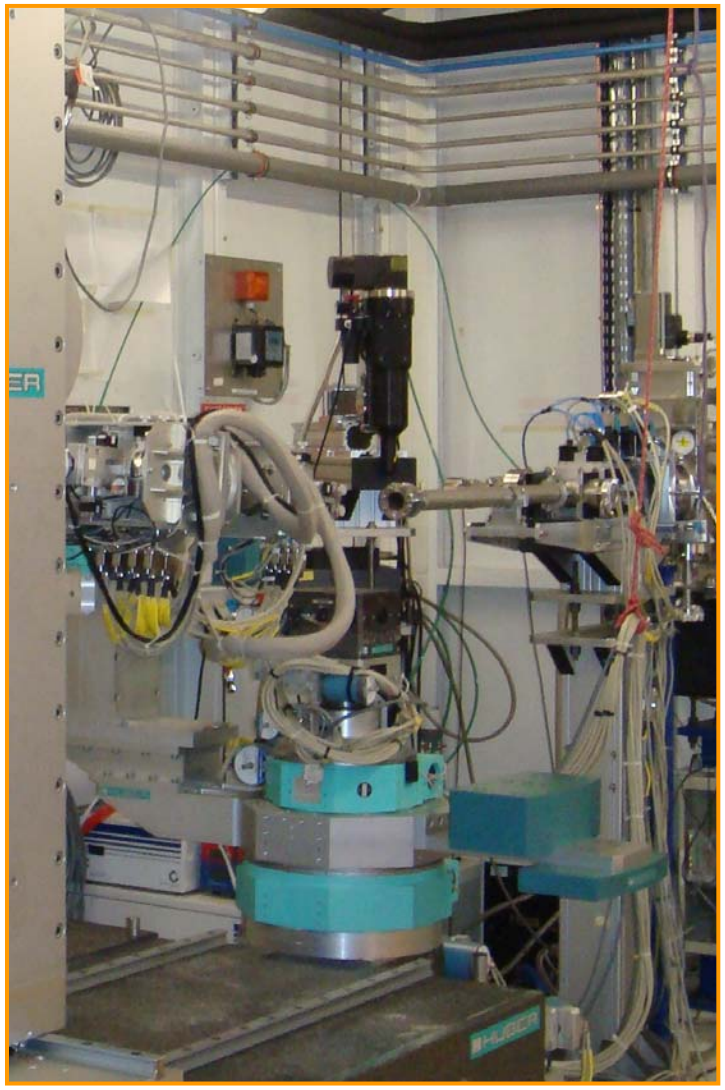


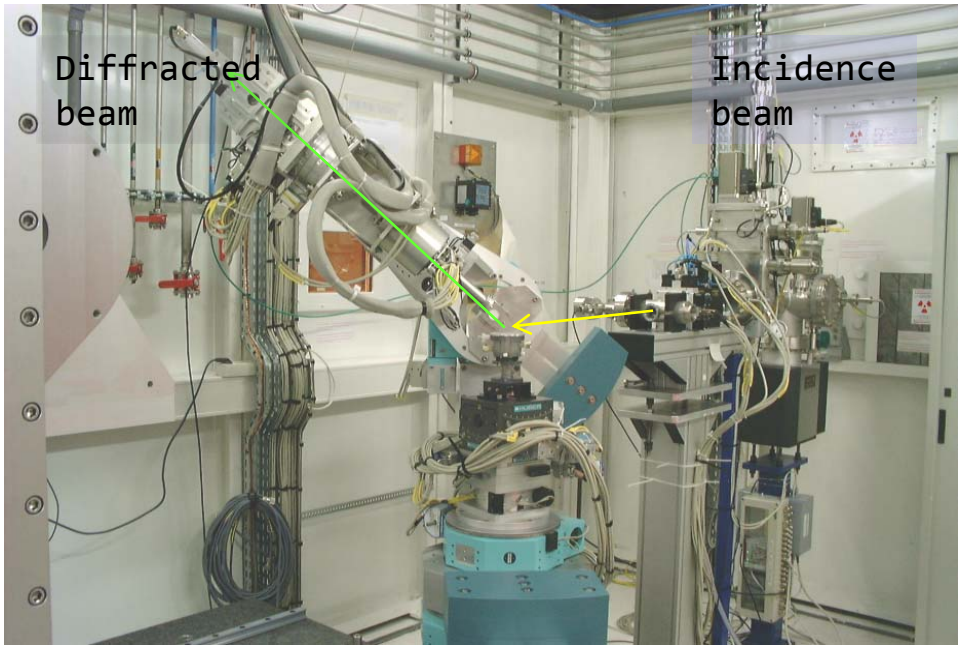
AFM image of a monolayer of Ni_{12} on mica prepared by spin coating

Grazing incidence X-ray diffraction : BM25 ESRF Grenoble



The Beamline

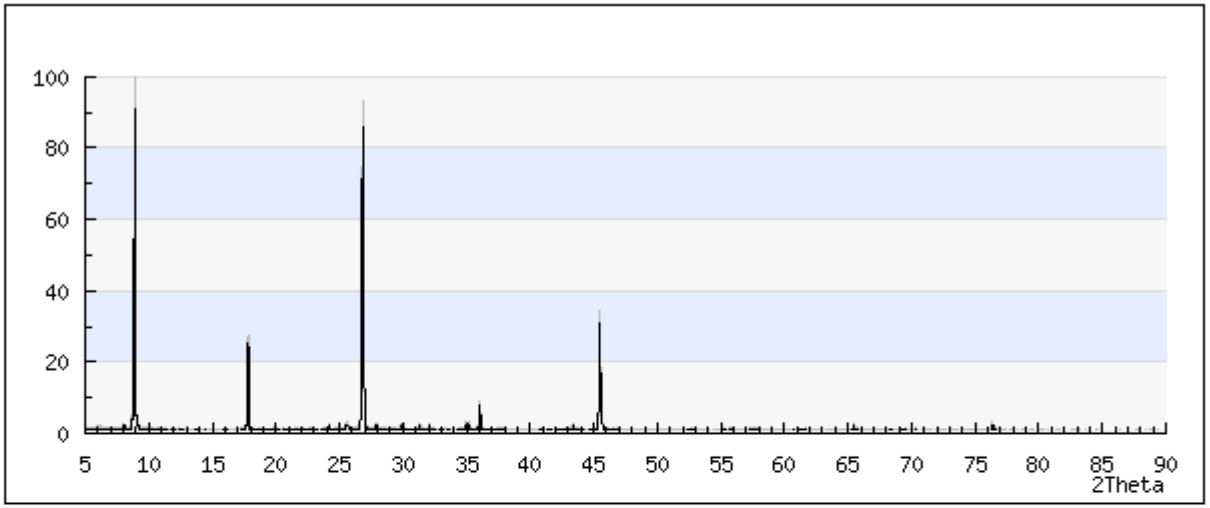




CCD camera
3 x 11 Megapixels
Final image resolution 7651 x 3825 pixels
Pixel size 32.8 microns square
Input active area 250 x 125 mm

Muscovite - mica

X-Ray Powder Diffraction:



Radiation - Copper Kα

Data Set: unknown 274

Horizontal Axis: 5 ° to 90 ° Vertical Axis: 100 % Source Data: ☑ Filtered Data: ☑ Peaks: ☐

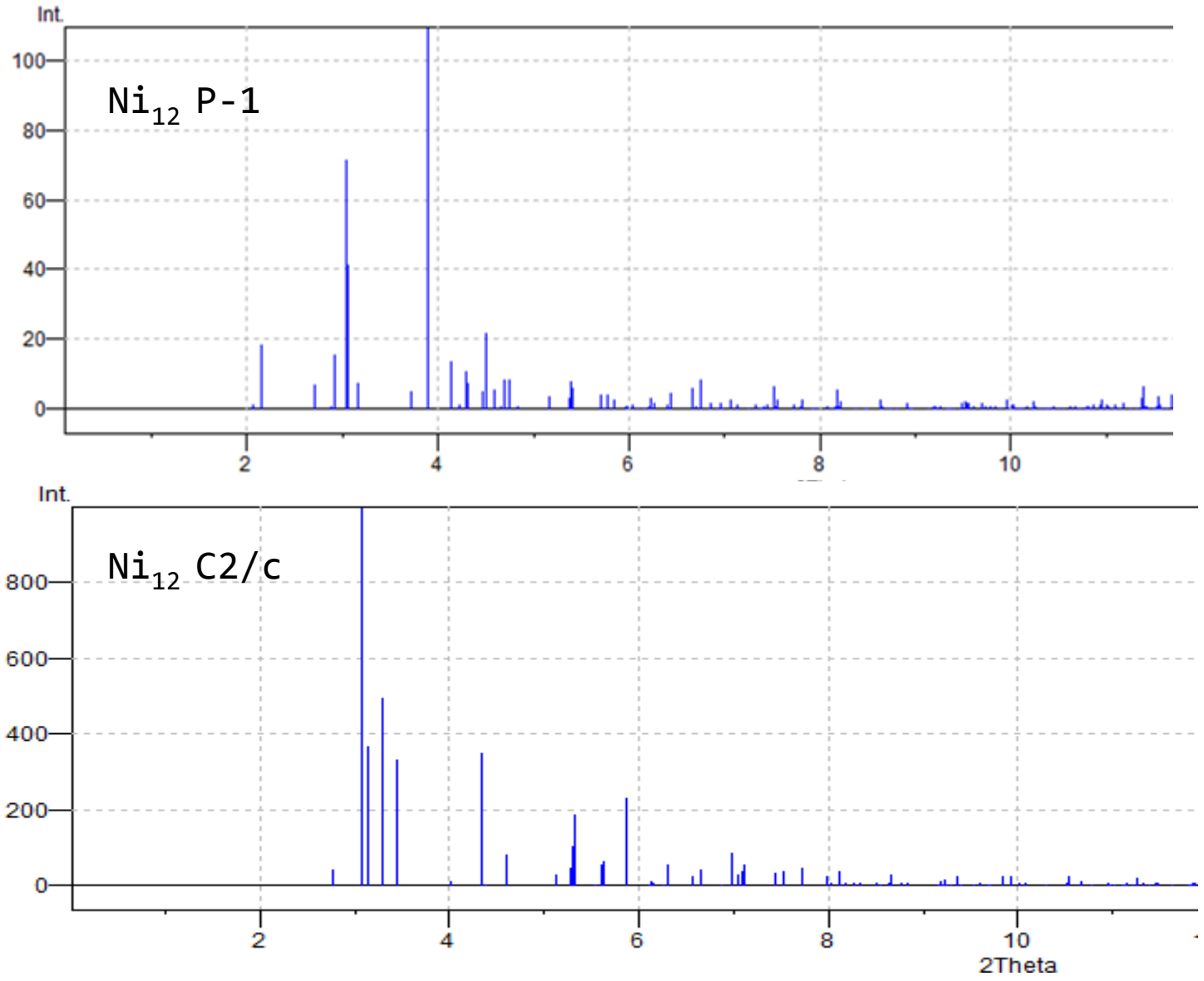
Data courtesy of RRUFF project at University of Arizona, used with permission.

X-Ray Powder Diffraction:

d-spacing	Intensity
10.01	(100)
5.02	(60)
4.48	(60)
4.46	(70)
3.35	(100)
3.21	(50)
2.59	(50)
2.56	(90)

Comments: Data given are for the -2M^1 polytype.

Calculated powder diffraction pattern for Ni_{12}



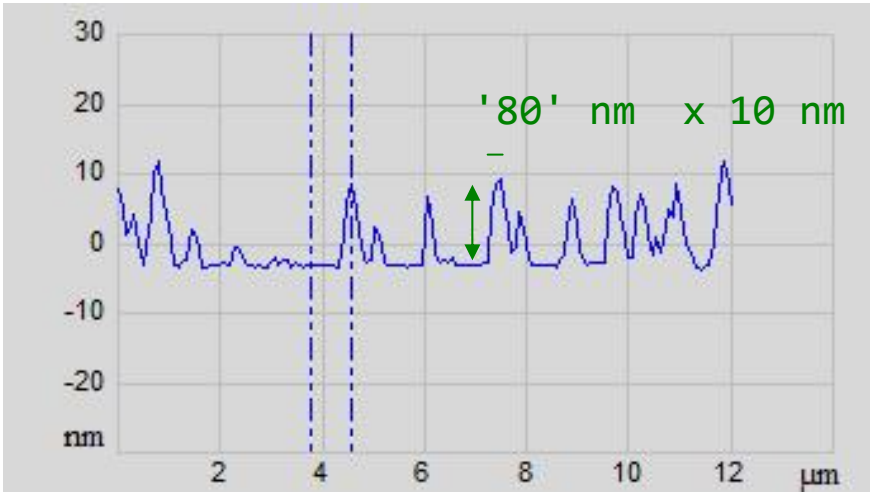
Ni_{12} P-1

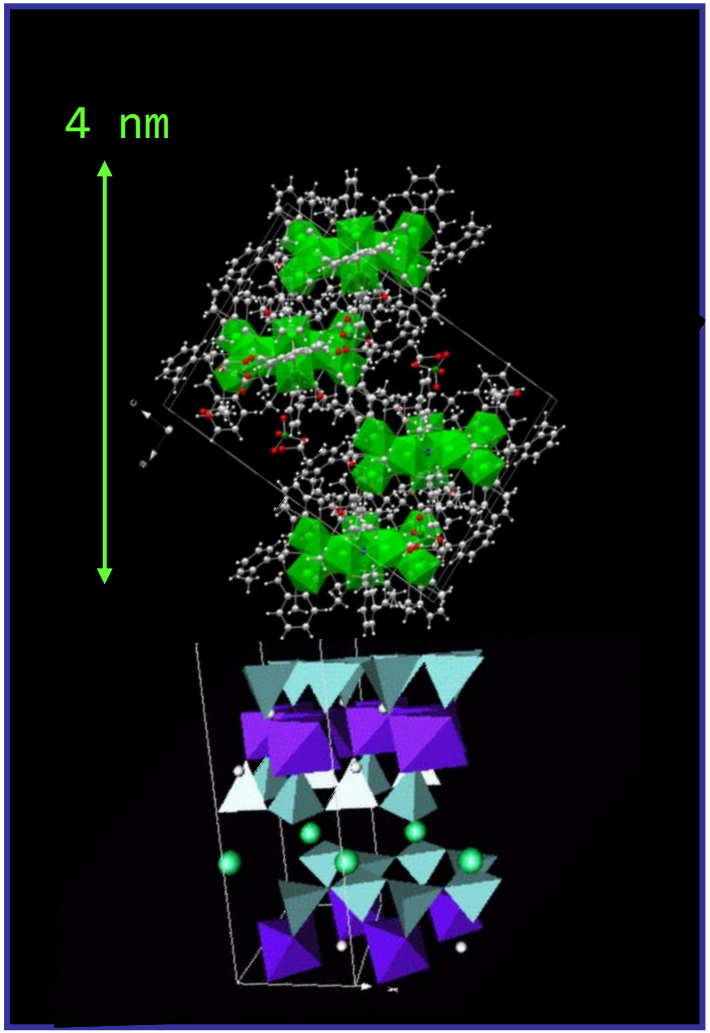
2Theta [°]	d-spacing [Å]	Int.	h	k	l
2.073	19.7223	16946737.45	0	0	1
2.149	19.0303	214284389...	0	1	0
2.706	15.1085	81461970.15	1	0	0
2.890	14.1484	12439108.61	1	1	0
2.927	13.9687	181984640...	0	1	1
3.043	13.4359	833002811...	0	-1	1
3.064	13.3450	482818583...	1	0	1
3.173	12.8857	86929790.02	1	1	1
3.723	10.9841	58743093.20	-1	0	1
3.903	10.4769	127249007...	-1	-1	1
3.941	10.3758	88239.85	-1	1	0
4.147	9.8611	159295915...	0	0	2
4.236	9.6538	17066482.18	1	-1	1
4.298	9.5152	125567472...	0	2	0
4.315	9.4776	89139196.12	1	2	0
4.471	9.1468	3974452.39	1	2	1
4.478	9.1321	58471579.62	1	0	2
4.516	9.0568	257997161...	1	1	2
4.596	8.8980	68216070.08	0	1	2
4.661	8.7743	12744206.69	-1	1	1
4.699	8.7034	98833036.95	0	2	1
4.745	8.6196	99729543.28	0	-1	2
4.844	8.4424	13084279.11	0	-2	1
5.085	8.0439	172940.33	-1	-2	1
5.122	7.9855	1844968.57	2	1	1
5.172	7.9078	43221417.58	2	1	0
5.382	7.5999	917051.11	1	-1	2
5.386	7.5946	39800099.97	-1	0	2
5.399	7.5764	91854499.91	2	0	1
5.414	7.5542	70341301.89	2	0	0

Ni_{12} C2/c

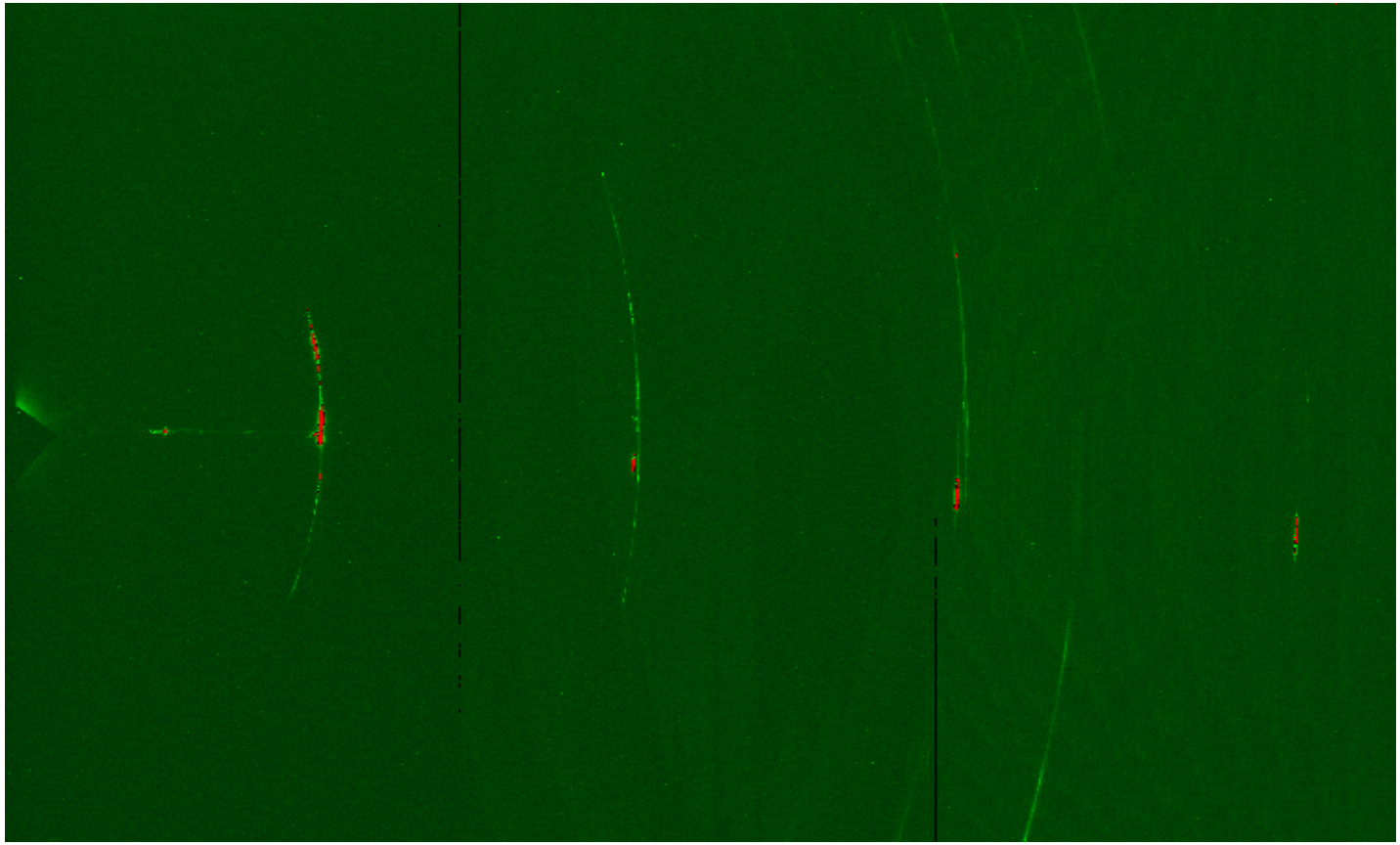
2Theta [°]	d-spacing [Å]	Int.	h	k	l
2.760	14.8161	143046316...	1	1	0
2.760	14.8161	143046331...	-1	1	0
3.051	13.4021	541363.92	0	2	0
3.067	13.3313	641499525...	-1	-1	1
3.126	13.0795	236224429...	0	0	2
3.273	12.4932	159045175...	1	1	1
3.273	12.4932	159045122...	1	-1	1
3.428	11.9278	107880068...	0	2	1
3.428	11.9278	107880063...	0	-2	1
4.011	10.1953	77391564.62	-1	1	2
4.324	9.4571	112857615...	1	1	2
4.324	9.4571	112857597...	1	-1	2
4.369	9.3606	11249460.69	0	2	2
4.369	9.3606	11249434.81	0	-2	2
4.601	8.8895	540996207...	2	0	0
5.123	7.9833	197115533...	1	3	0
5.260	7.7762	299334535...	-1	1	3
5.295	7.7240	679366141...	-1	-3	1
5.323	7.6834	120181725...	-2	0	2
5.417	7.5503	2066540.51	1	3	1
5.417	7.5503	2066533.81	1	-3	1
5.521	7.4080	23242477.48	2	2	0
5.596	7.3089	378182126...	0	2	3
5.620	7.2782	52814720.89	1	1	3
5.624	7.2734	411524353...	-2	-2	1
5.793	7.0604	53904.13	2	0	2
5.851	6.9905	755560987...	2	2	1
5.851	6.9905	755561050...	2	-2	1
5.893	6.9412	2667423.93	-1	3	2
6.104	6.7010	16023040.73	0	4	0
6.111	6.6941	42495727.10	1	3	2
6.111	6.6941	42495829.43	1	-3	2

A model of Ni_{12} on mica. The average height of the aggregates on mica is 5- 10 nm, in agreement with having a stack of 4-10 molecules of Ni_{12}.





We can observe at small MU values peaks from both the sample (Ni_{12} P-1) and the substrate (mica)



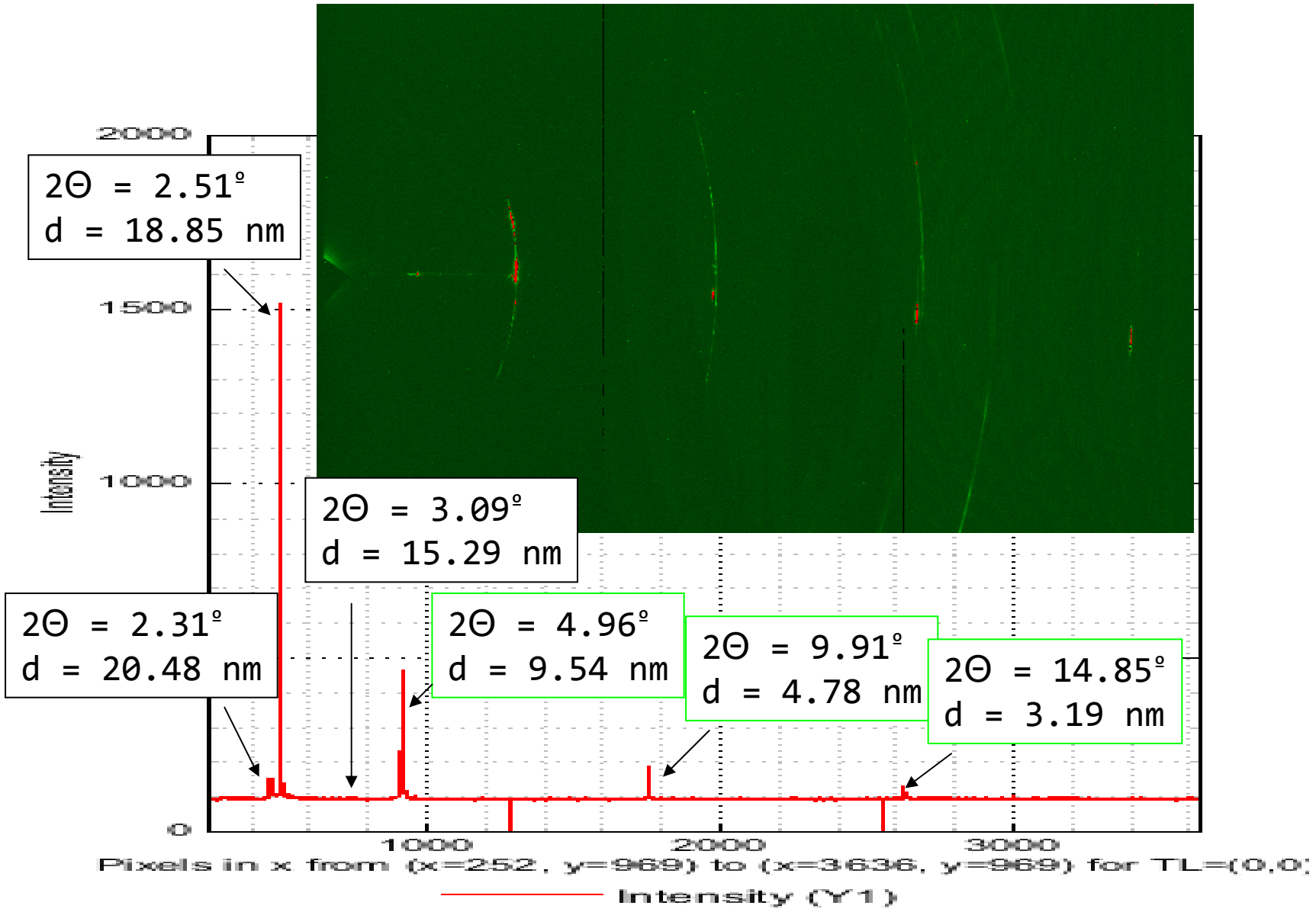


image Ni12Br8B_0059, D 630 mm, MU = 1

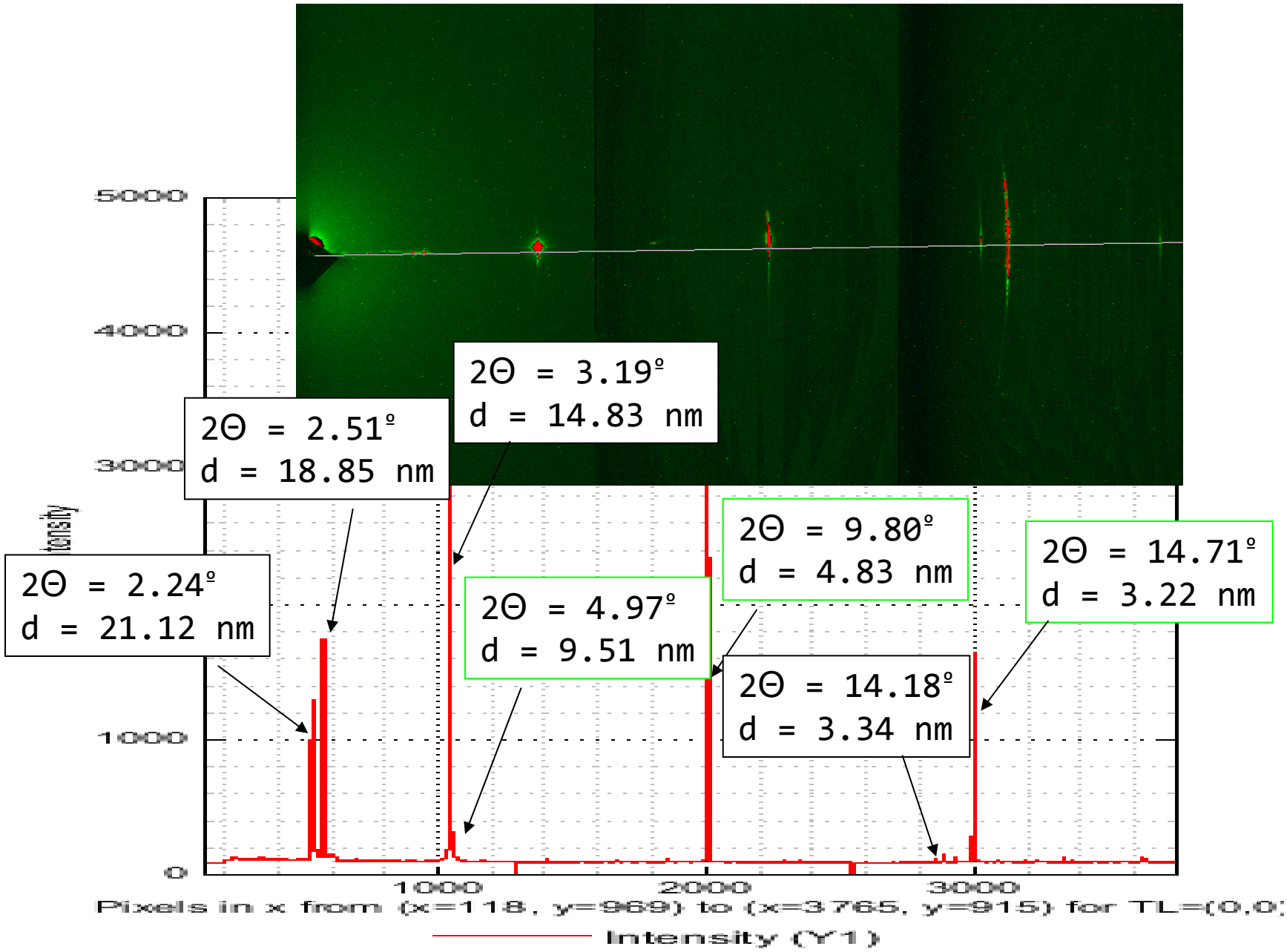
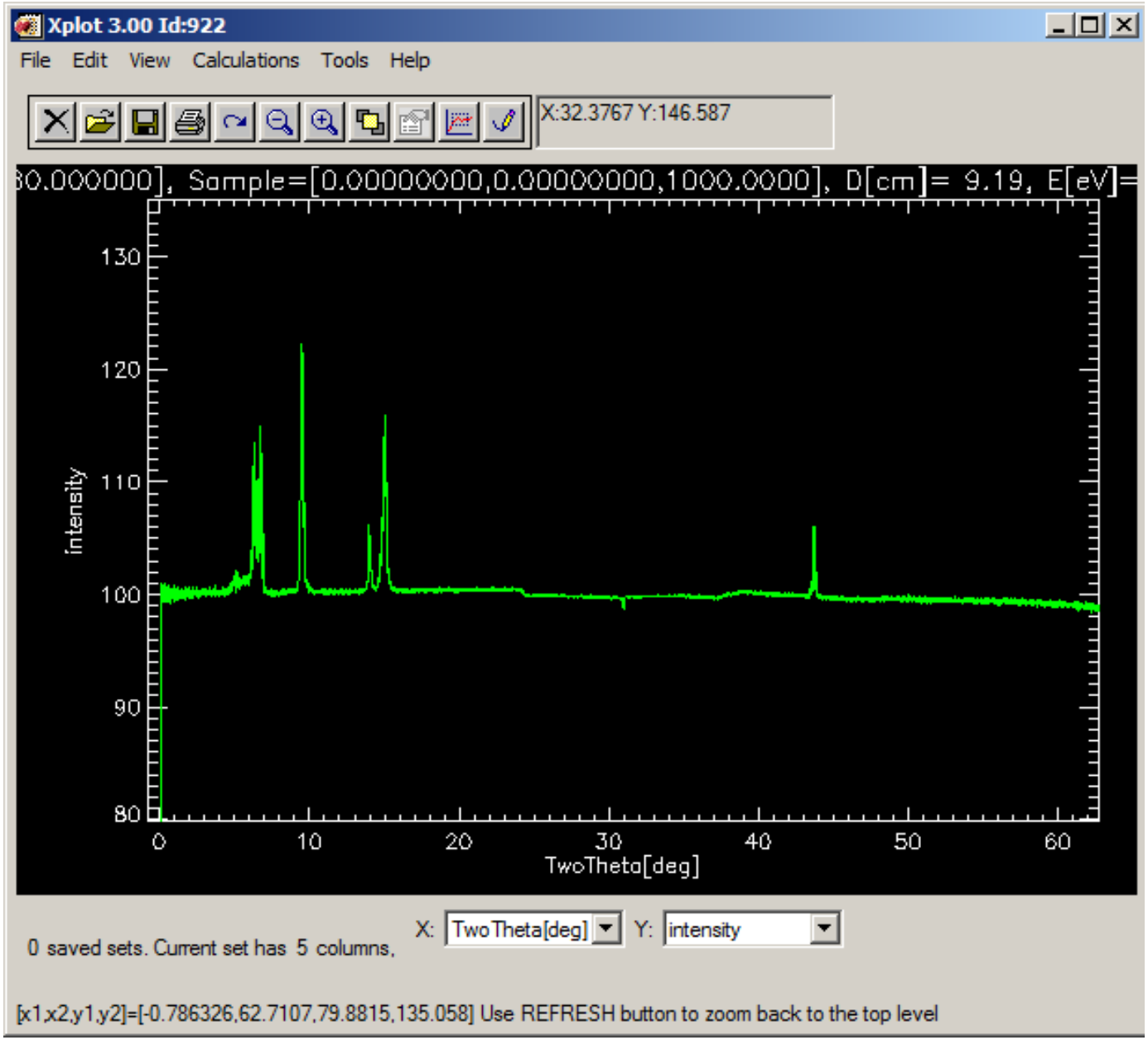
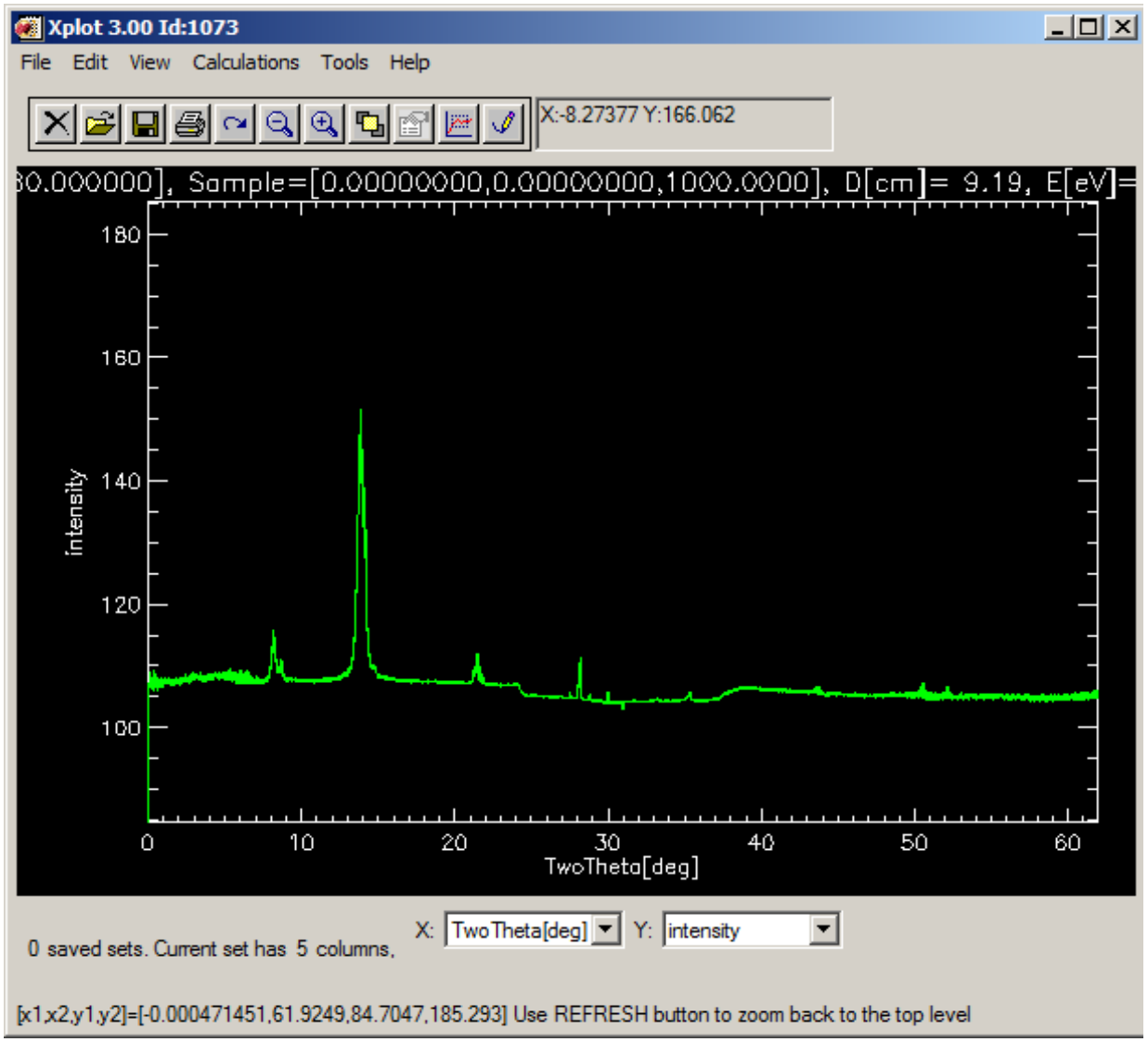


image Ni12Br8B2_00647, D 730 mm, MU = 0.5 TH = 90º

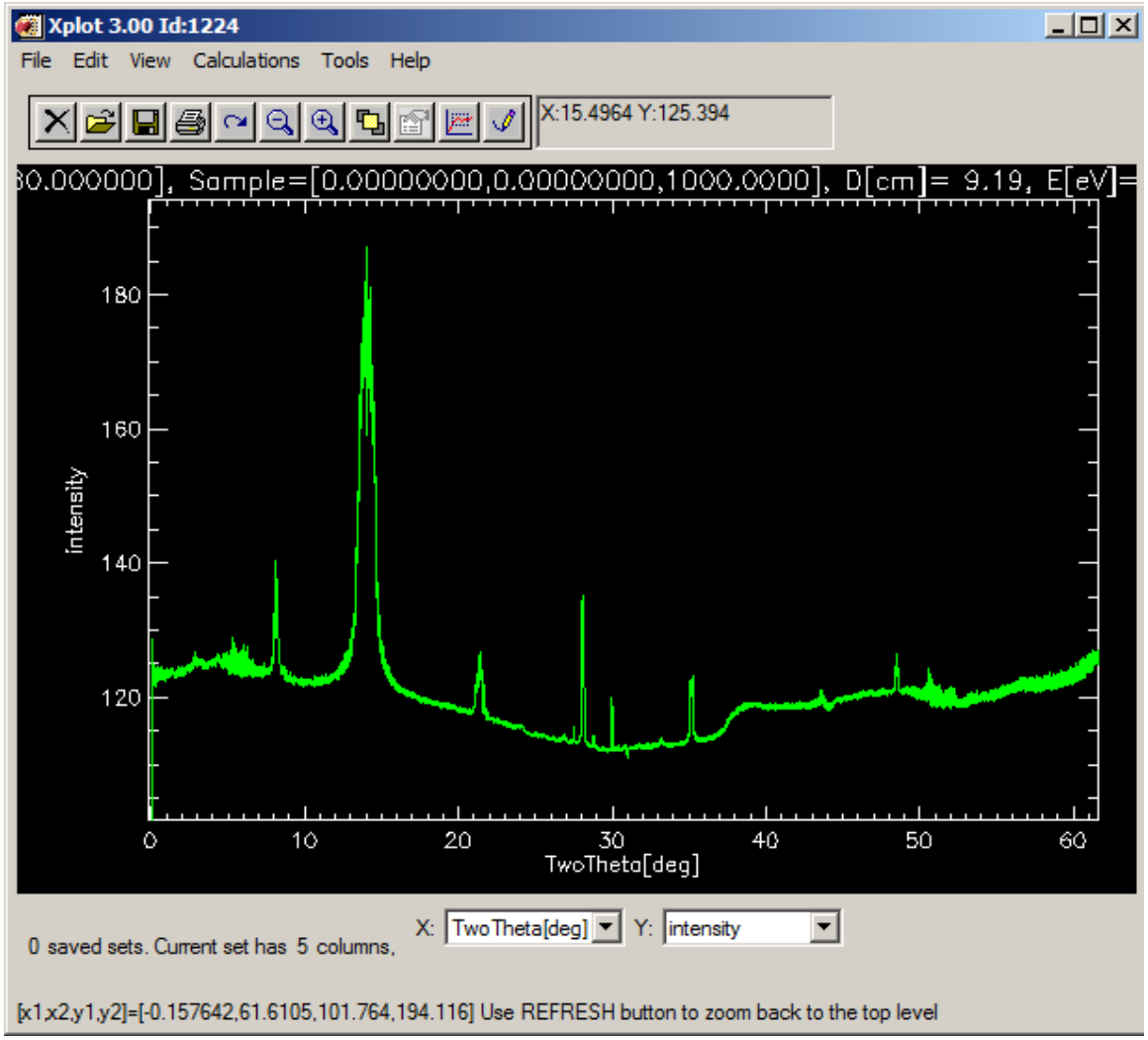
Ni12DP1_0014

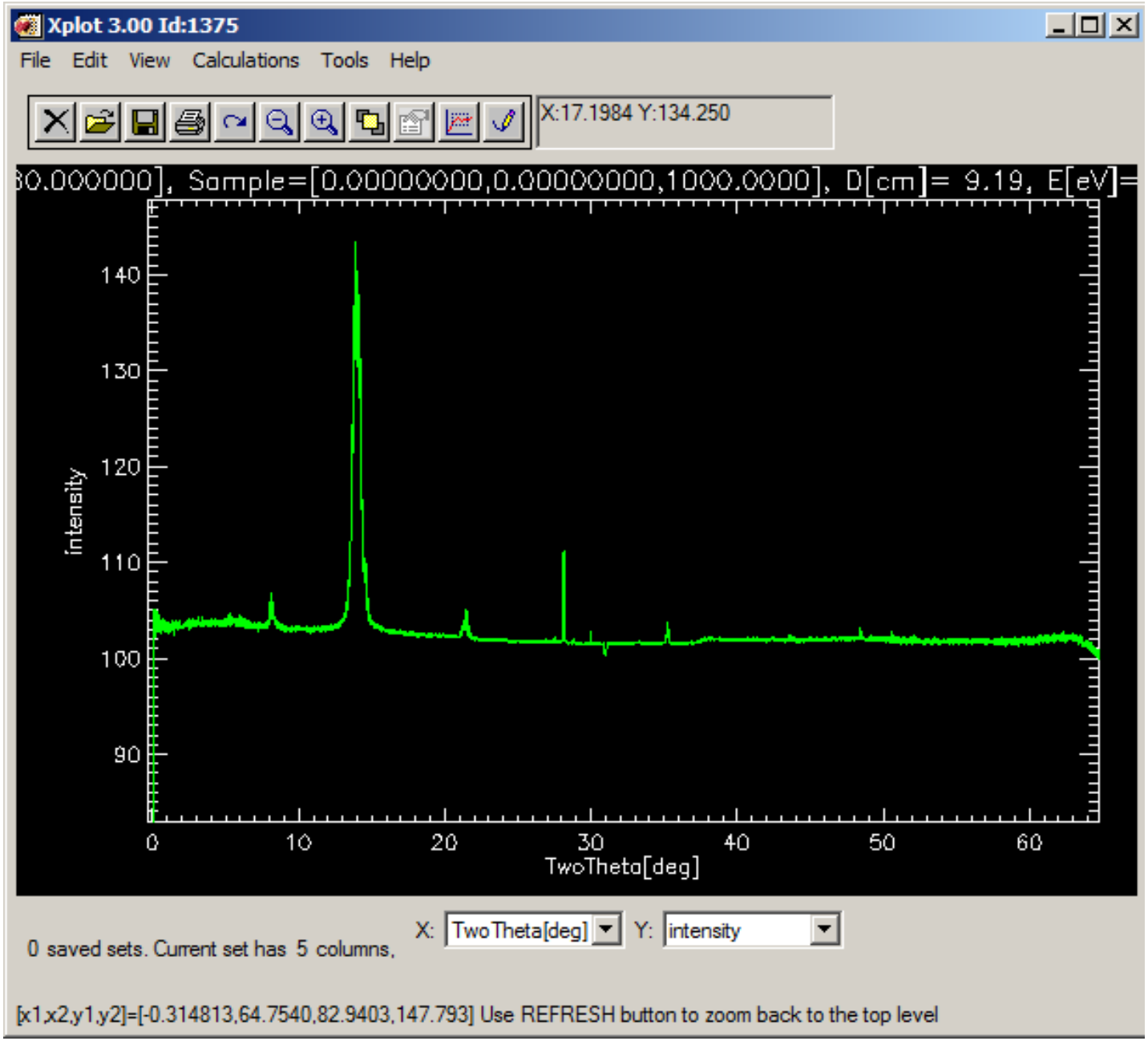


Ni12DP1_0024



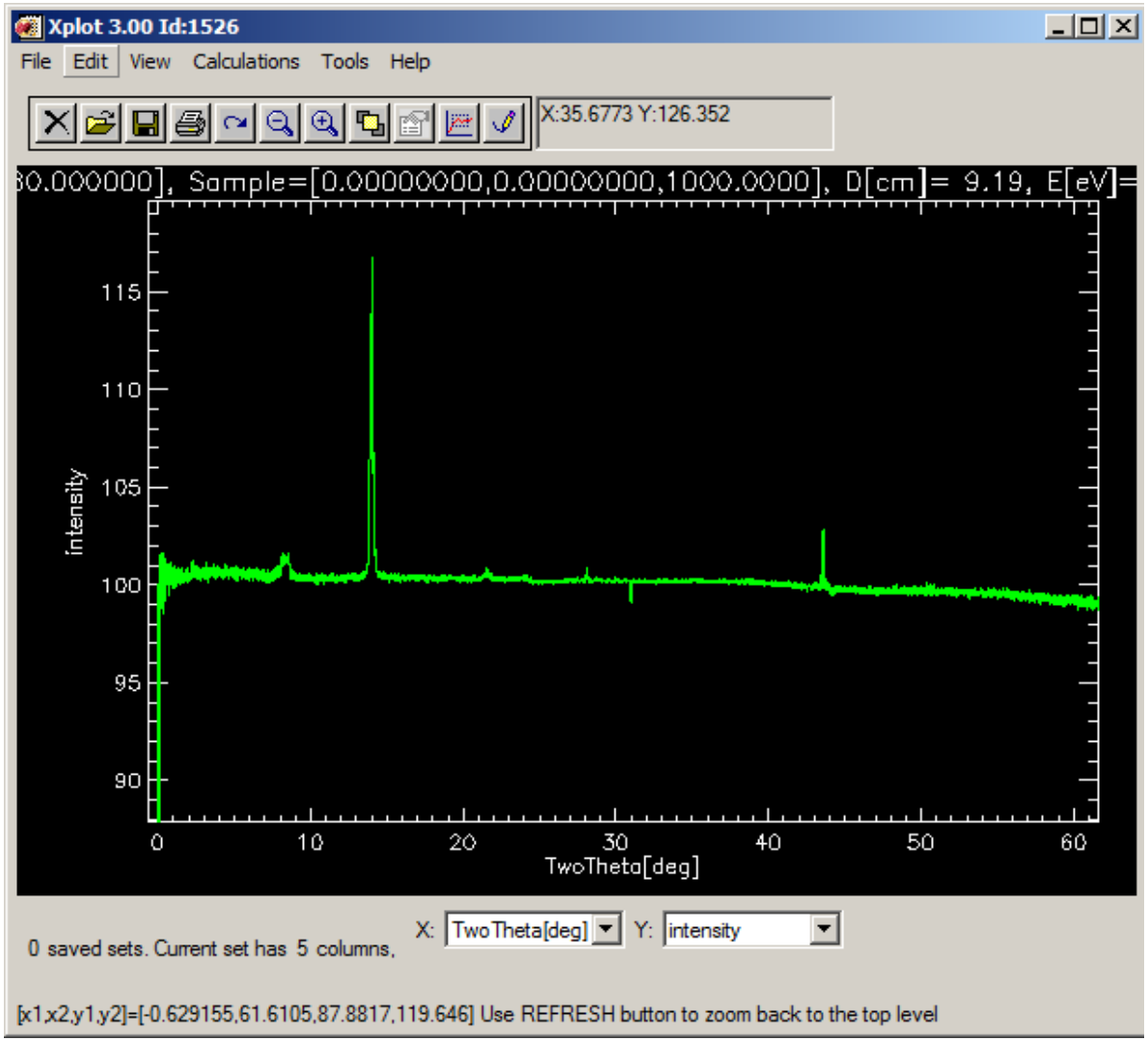
Ni12DP1_0026





Ni12DP1_0047

Ni12DP1_0049



Summary

Ni_{12} complexes can be deposited on mica

The aggregates observed by AFM are between 5 and 10 nm high, in agreement with having stacks of 4 to 10 Ni_{12} molecules

The reflectivity could not be observed by GIXRD. The GIXRD study shows that the aggregates are in fact Ni_{12}. The GIXRD study shows that these aggregates are crystalline. The beamline use was very successful and the results will be published soon.