Suppression of Magnetism in $La_{1-x}Sr_xCoO_3$ Nanoparticles

David P. Belanger
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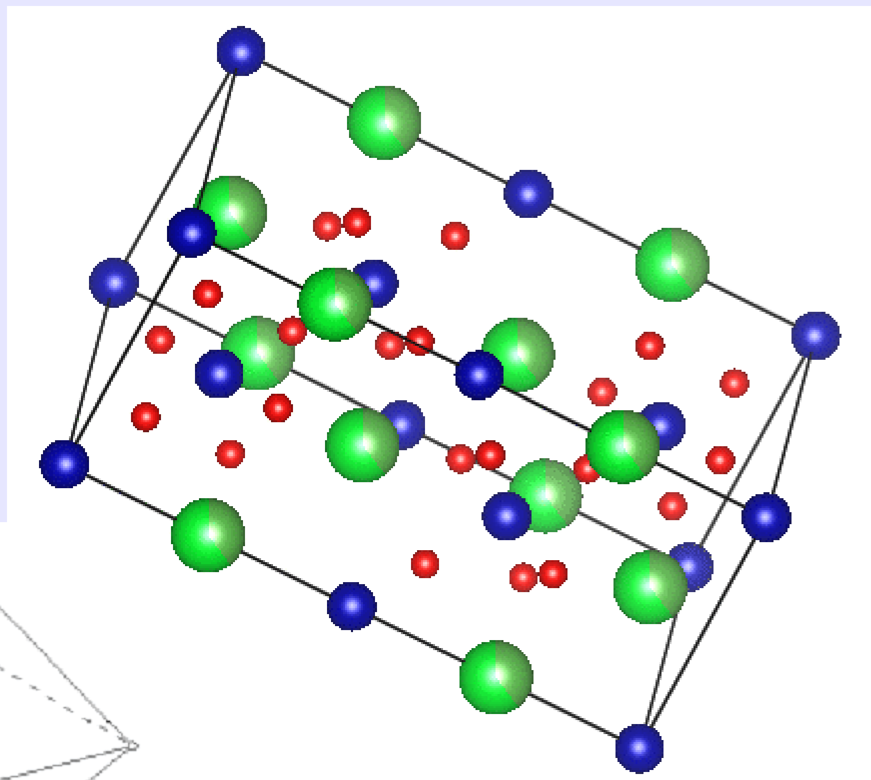

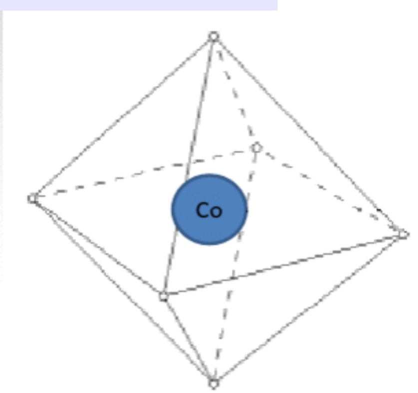

- Bulk system has been studied since the 1950's and yet it is not well understood.
- Nanoparticles of this system have significant practical importance, but the effect of reducing to nanometer sizes is poorly understood.
- Nanoscale particles can be used to probe the physics.

Main Collaborators and Acknowledgments outside ORNL

- Alice Durand – UCSC
- Nalini Sundaram – UCSC
- Ingrid Anderson – UCSC
- Andrew Elvin - UCSC
- Meghana Bhat – UCSC, Castilleja School, Palo Alto, CA
- Yu Jiang – UCSC
- Frank (Bud) Bridges – UCSC
- Gey-Hong Gweon - UCSC
- Corwin Booth – Lawrence Berkeley National Lab
- Thomas Proffen – LANL, now ORNL
- Shaowei Chen – UCSC

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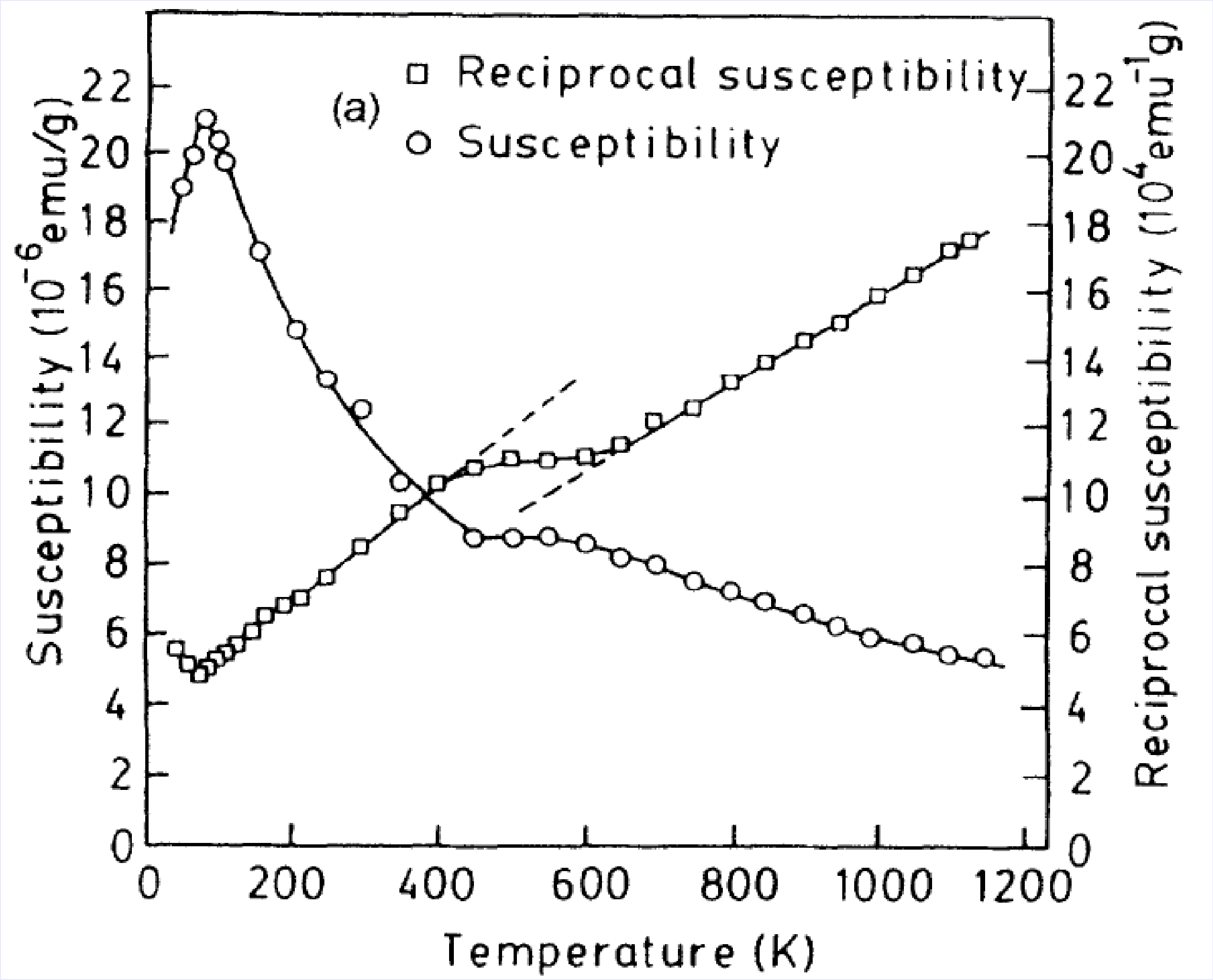
- Jane Howe
- Clarina de la Cruz
- Ashfia Huq
- Songxue Chi
- Andrey Podlesnyak
- Kai Xiao
- Tao Hong
- Andrew Payzant

Susceptibility of LCO – motivation for the LS, IS and HS states in the localized spin picture



Two transitions are clearly visible, one near 90K and the other near 500K. For decades, the prevalent model included three spin states, LS for T<90K, IS For 90K<T<500K, and HS For T>500K. Koritin, et al. argued that the IS is a result of a Jahn-Teller distortion.

K. Asai, et al. Phys. Rev. B 40, 10982, (1989); M. A. Korotin, et al. Phys. Rev. B 54, 5309 (1996),

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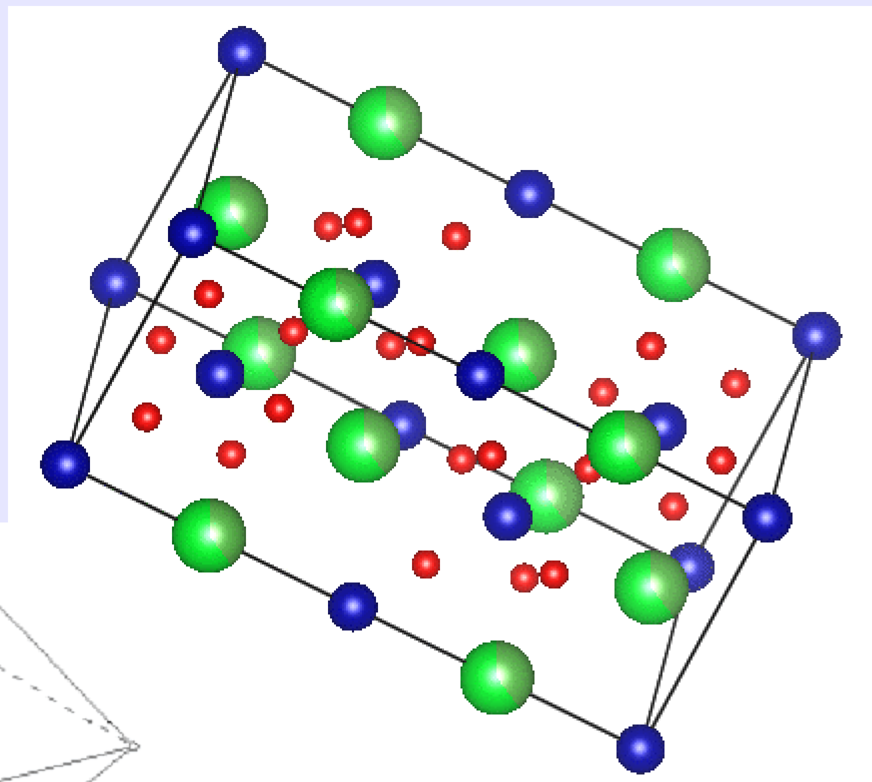

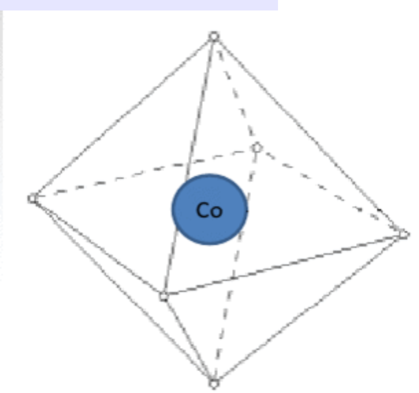

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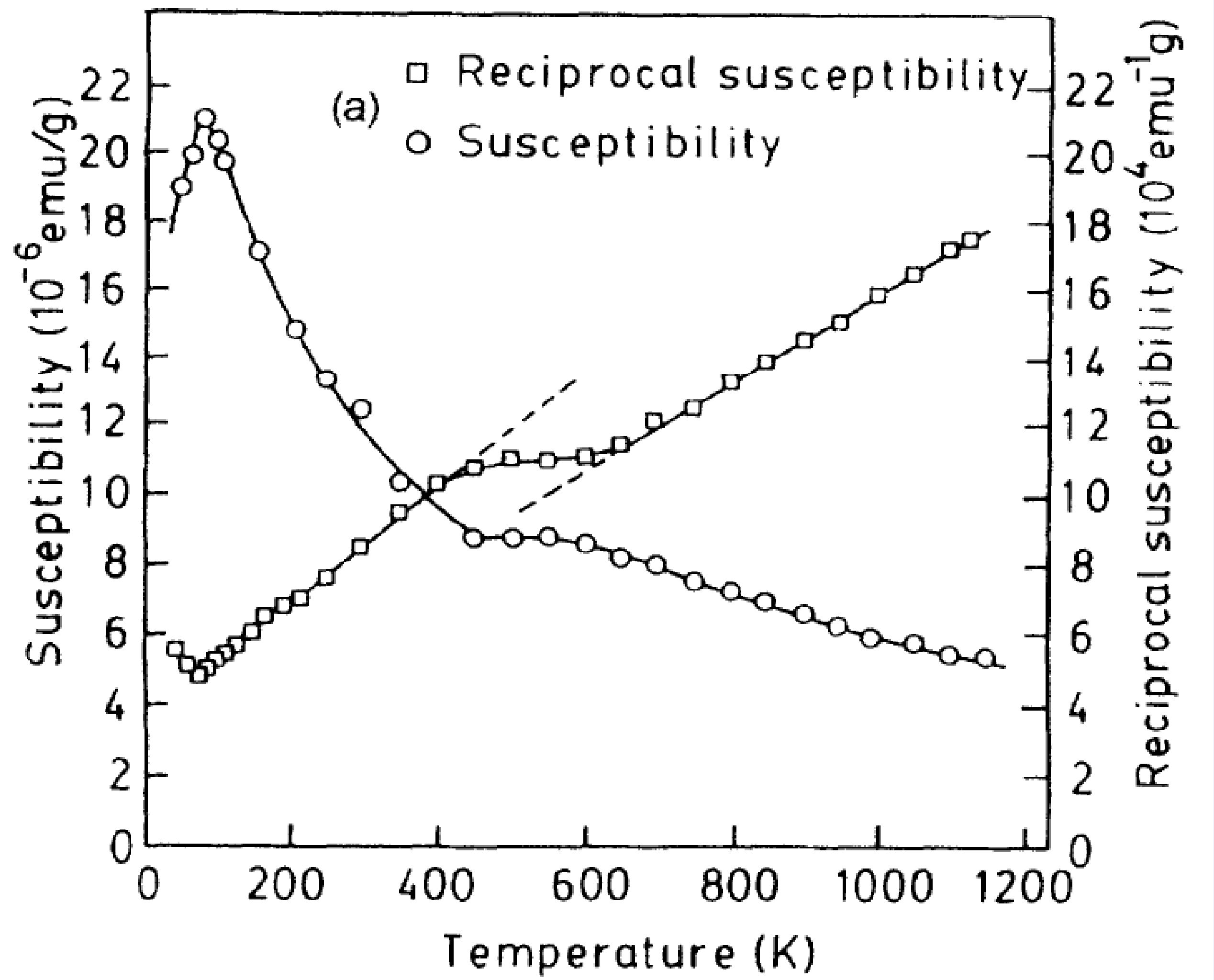
Susceptibility of LCO – motivation for the LS, IS and HS states in the localized spin picture



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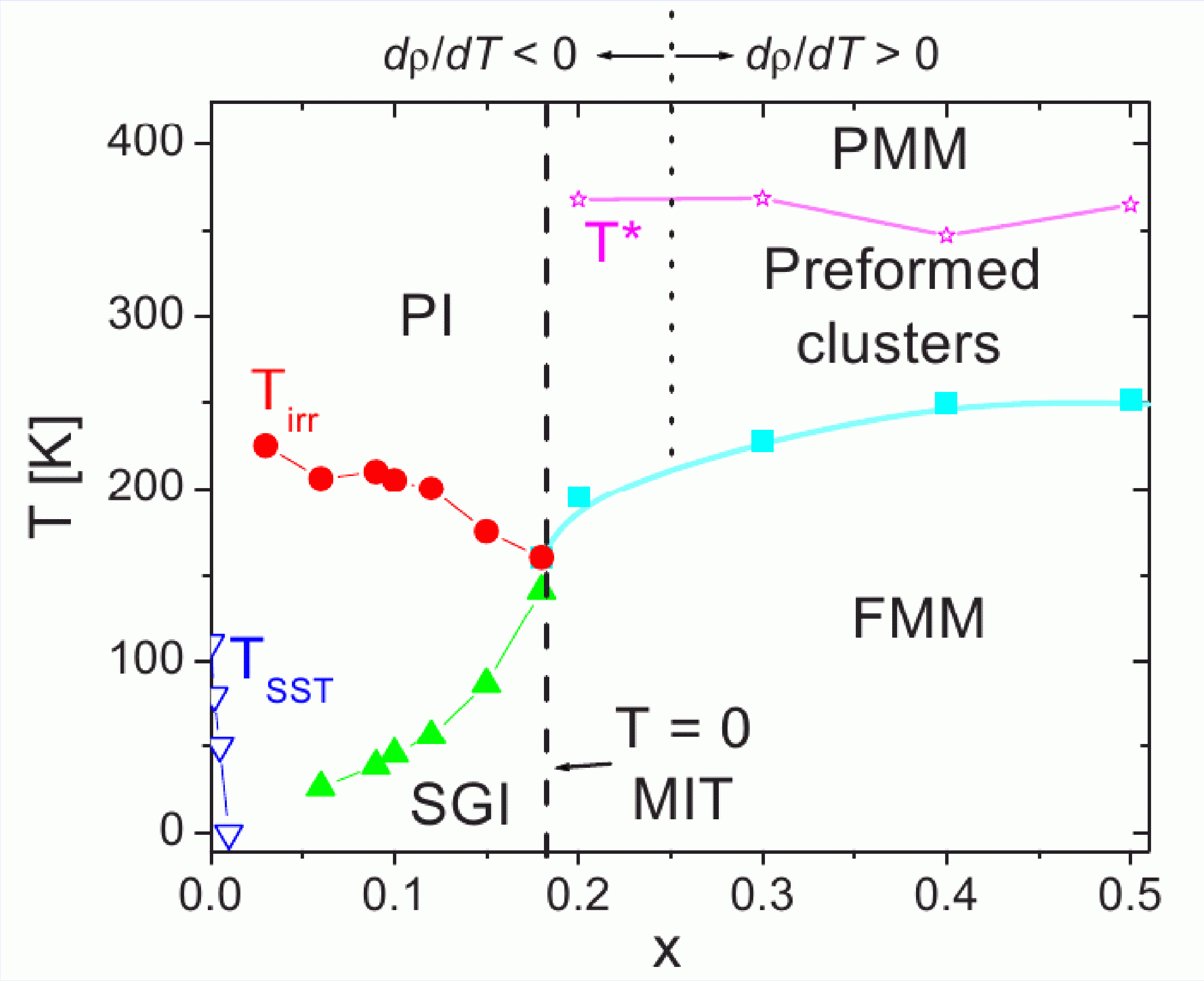
K. Asai, et al. Phys. Rev. B 40, 10982, (1989); M. A. Korotin, et al. Phys. Rev. B 54, 5309 (1996),

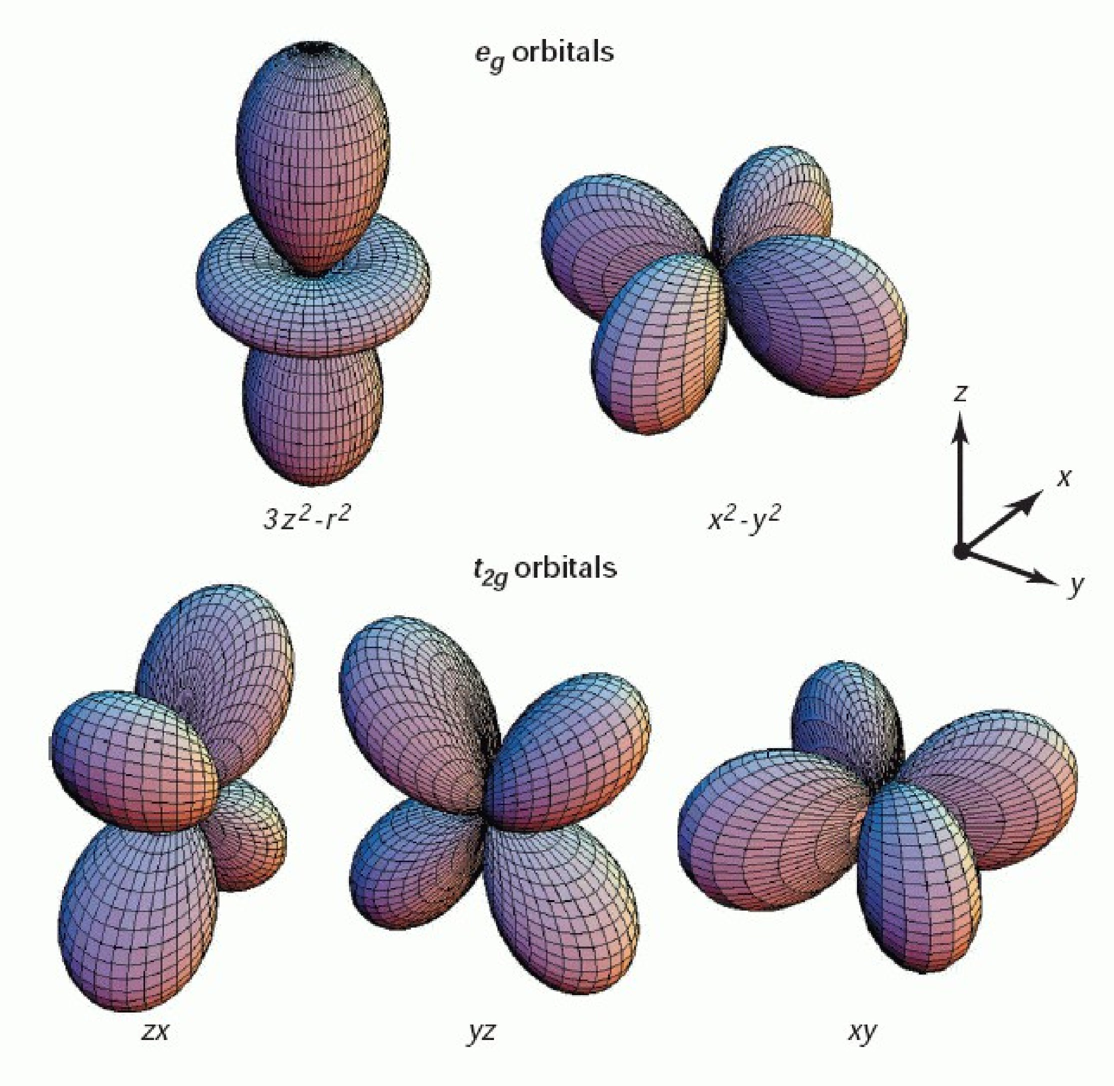
Phase Diagram LSCO bulk

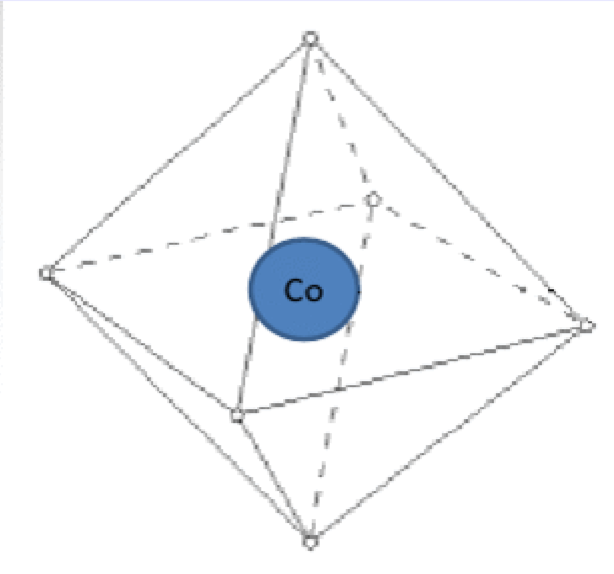


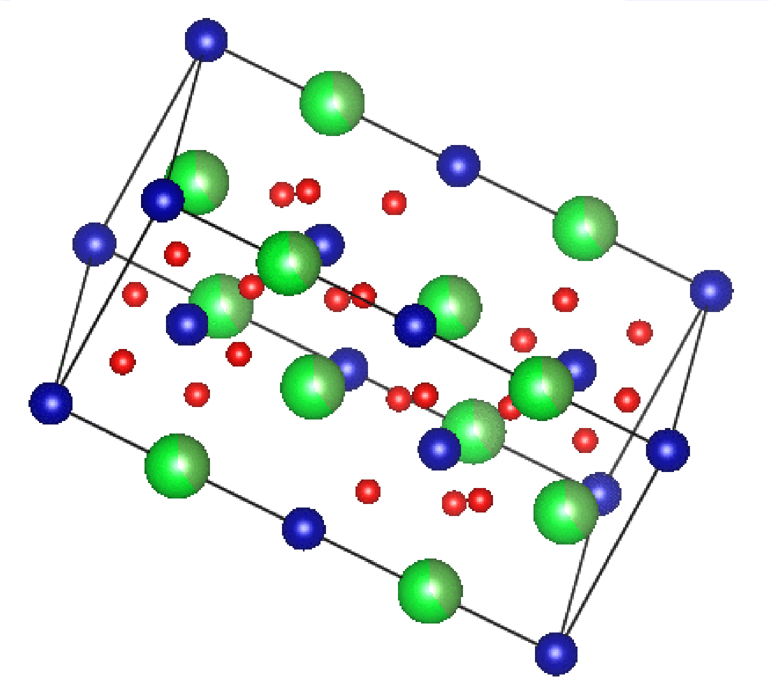
C. He, M. A. Torija, J. Wu, J. W. Lynn, H. Zheng, J. F. Mitchell, and C. Leighton, Phys. Rev. B **76**, 014401 (2007).

e_g and t_{2g} orbitals

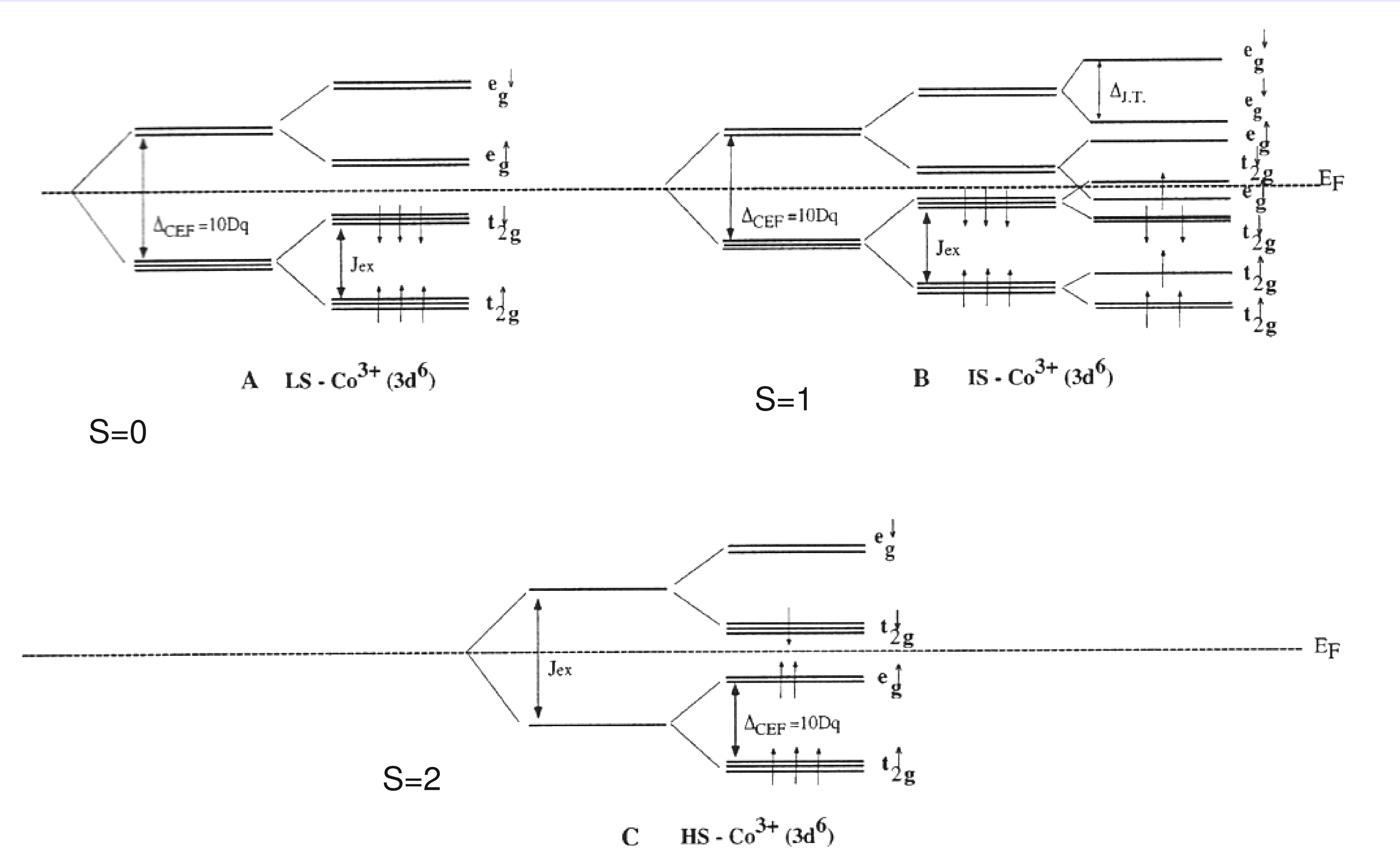
- Y. Tokura and N. Nagaosa, Science **288**, 462 (2008).







Possible Local Co Spin States in $LaCoO_3$ Toulemonde, et al., J. Solid St. Chem. **158**, 208 (2001)



nanoparticle growth

Nalini Sundaram, Alice Durand, Ingrid Anderson, Meghana Bhat
UCSC

$0.75La(NO_3)_3{*}6H_2O + 0.25Sr(NO_3)_2 + Co(NO_3)_2{*}6H_2O + 6H_2O + 4.75NaOH^-$

$\rightarrow 0.75La(OH)_3 + 0.25Sr(OH)_2 + Co(OH)_2 + 12H_2O + 4.75NaNO_3$

adding DTPA $C_{14}H_{23}N_3O_{10}$

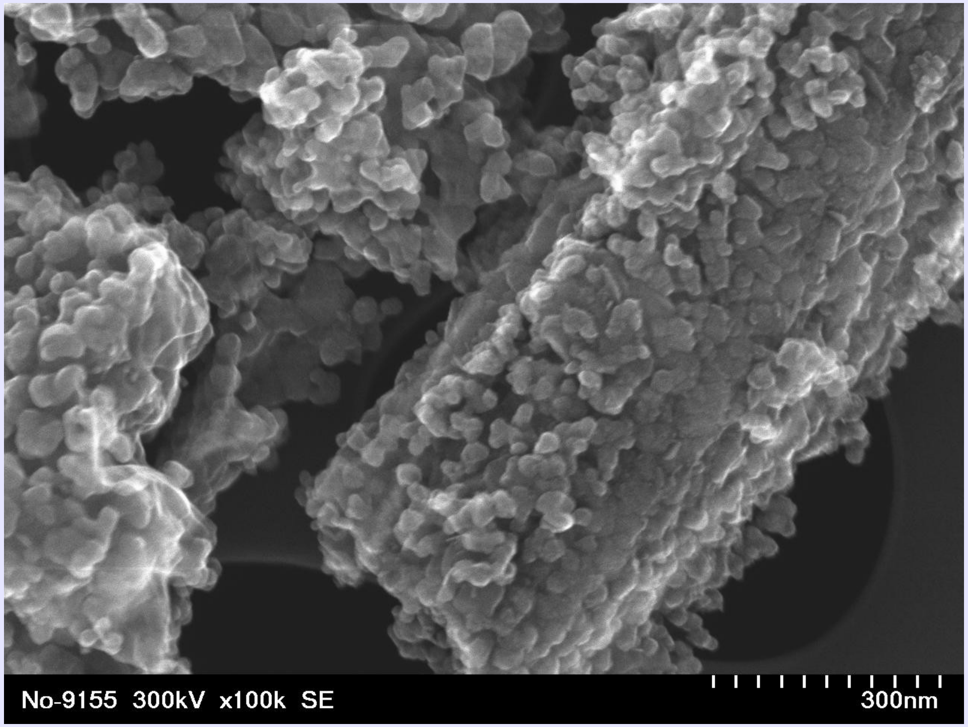
$0.75La(OH)_3 + 0.25Sr(OH)_2 + Co(OH)_2 + 0.95H_5DTPA^-$

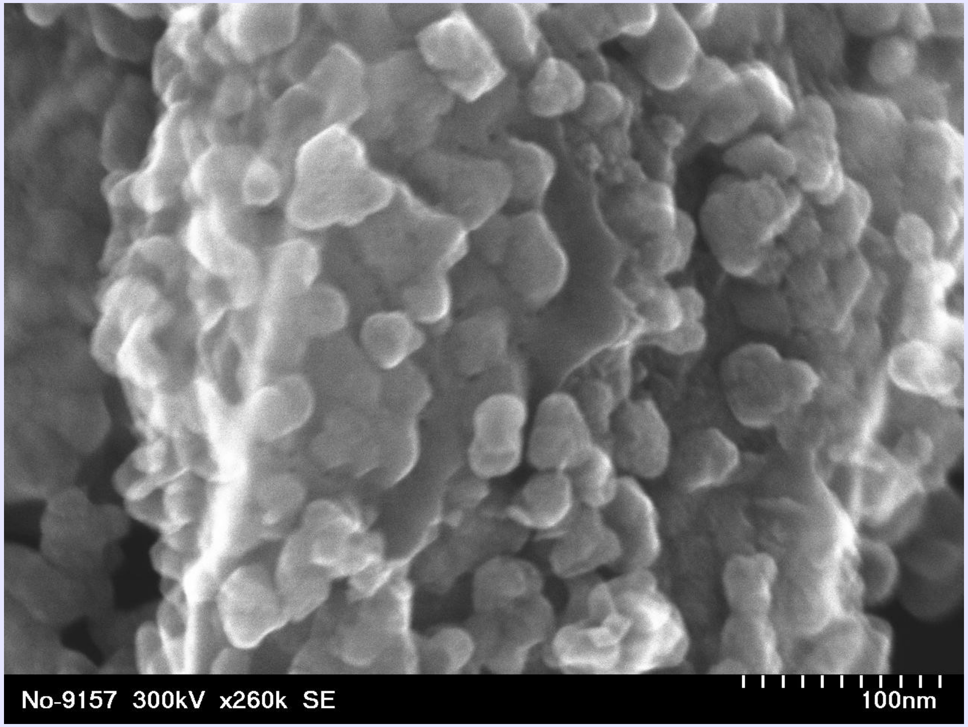
$\rightarrow La_{0.75}Sr_{0.25}CoO_?DTPA_{0.95}$ + (excess)DTPA + $4.75H_2O$

DTPA is removed by heating at 350^oC for 4 hours. Nanoparticles are formed in a tube furnace for 8 hours at calcination temperatures from 620^oC to 1100^oC.

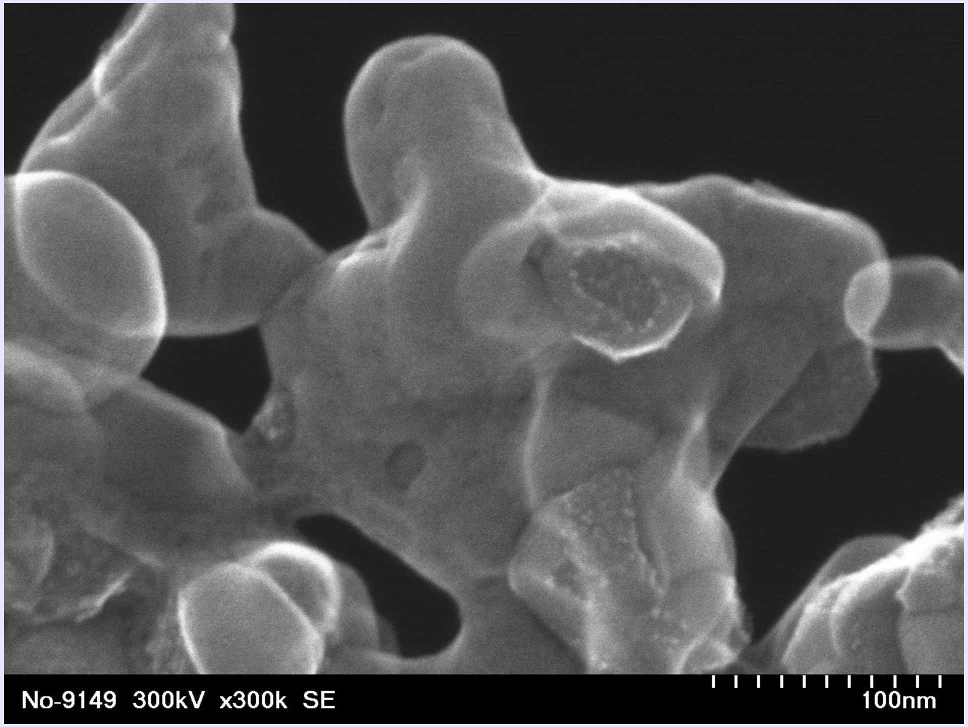
The particles are some of the older ones grown by Sundaram and Anderson that were used in the neutron PDF studies, to be discussed later in the talk. Note that the particles sizes are of order 20nm.

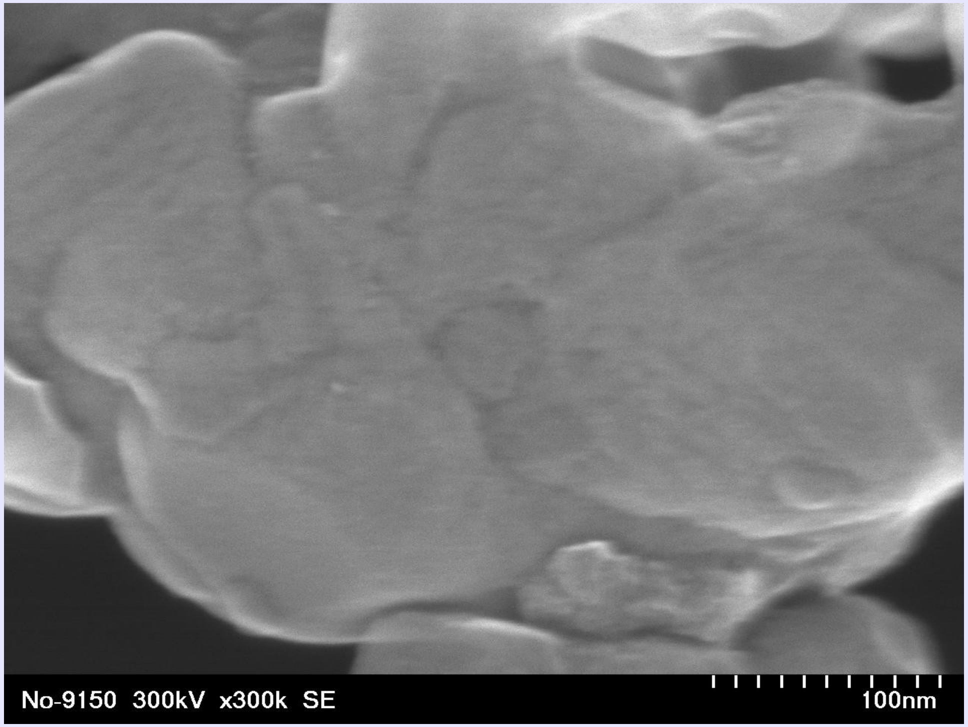
All of these images were made by Jane Howe, ORNL, using the Hitachi HF-3300 Electron microscope.

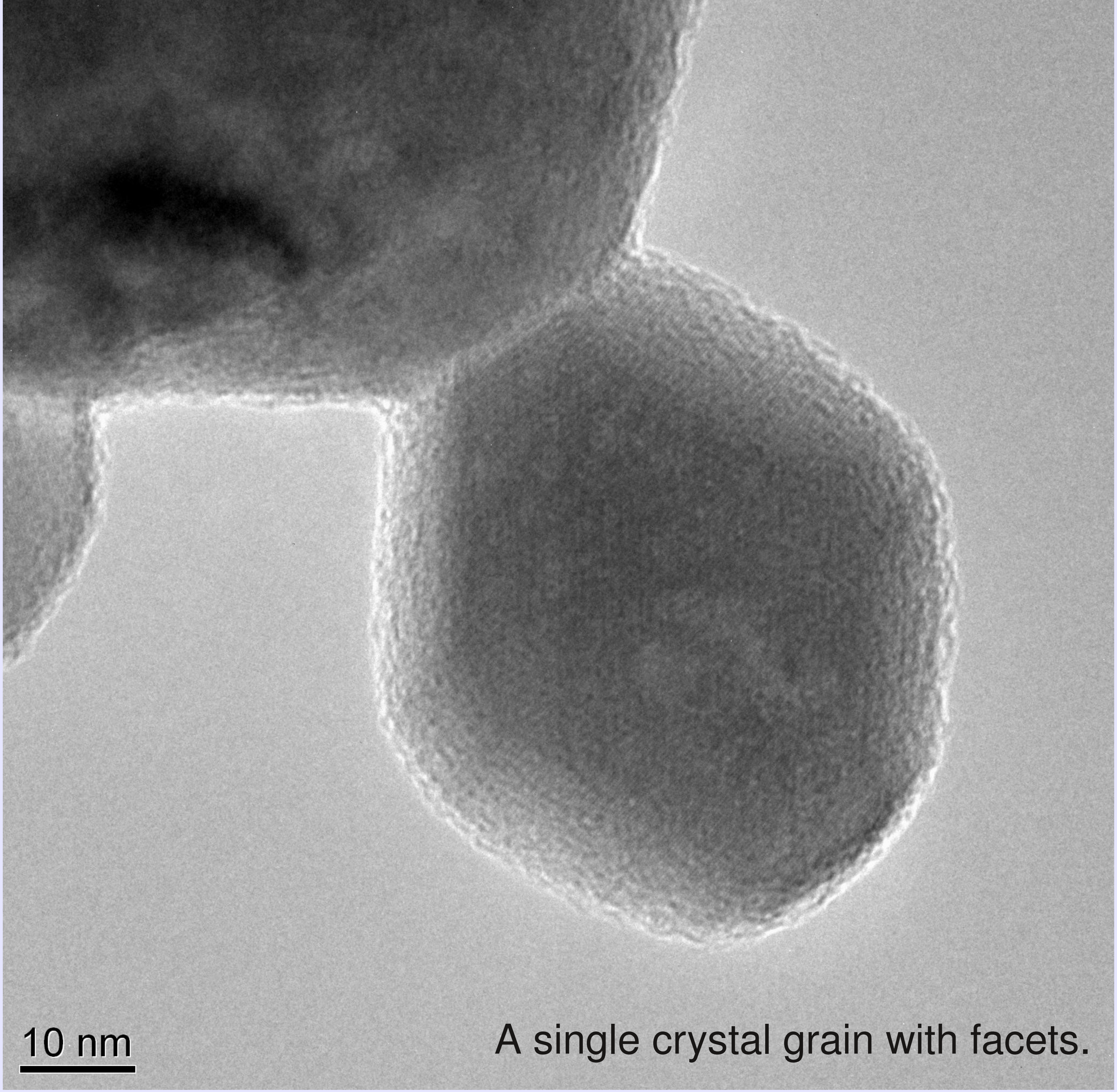


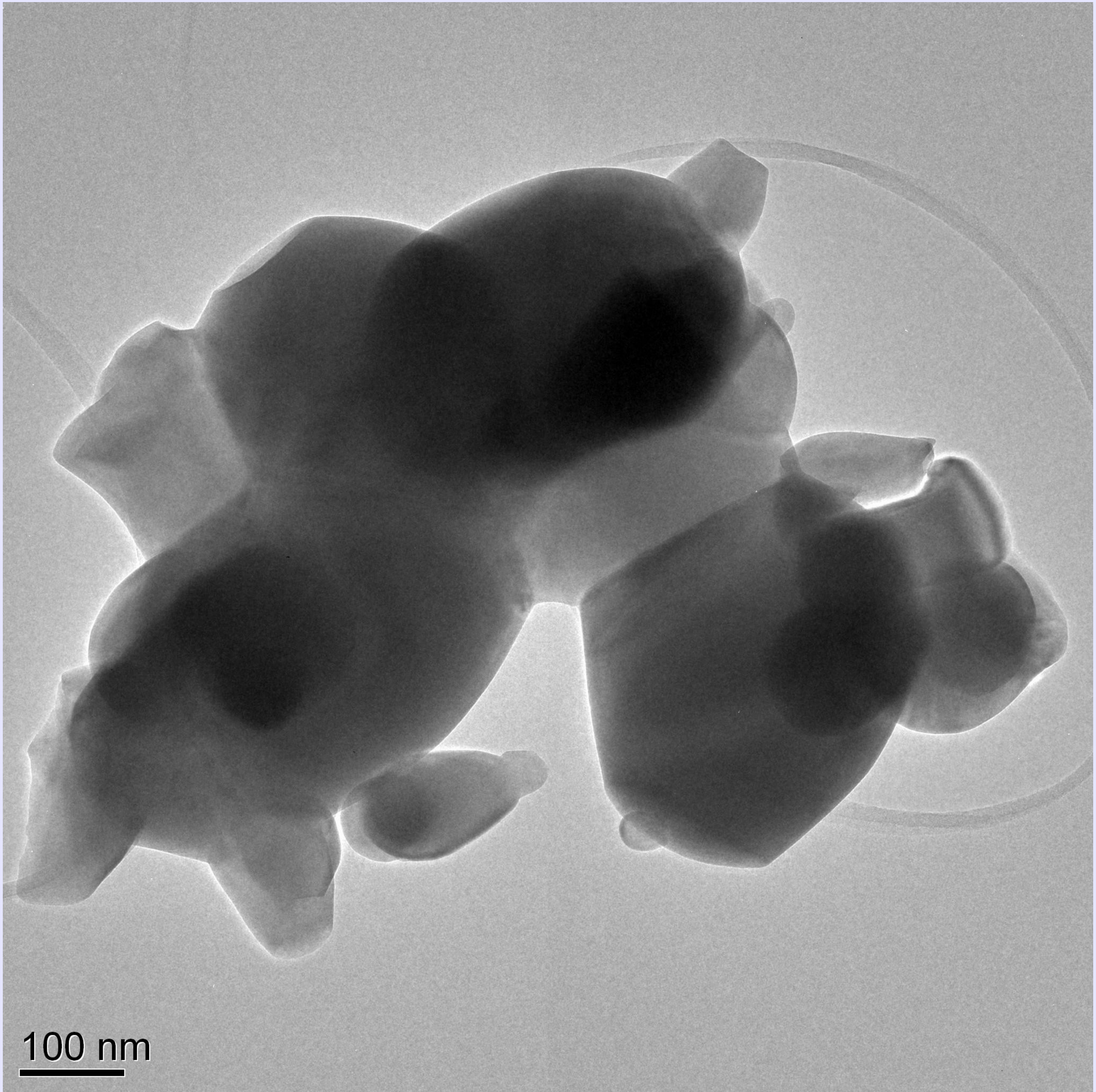


These particles were grown by Durand and Bhat this summer. Note that the particles can be nearly isolated or they can be imbedded. The very act of choosing particles to look at can distort the actual average particle property observations.

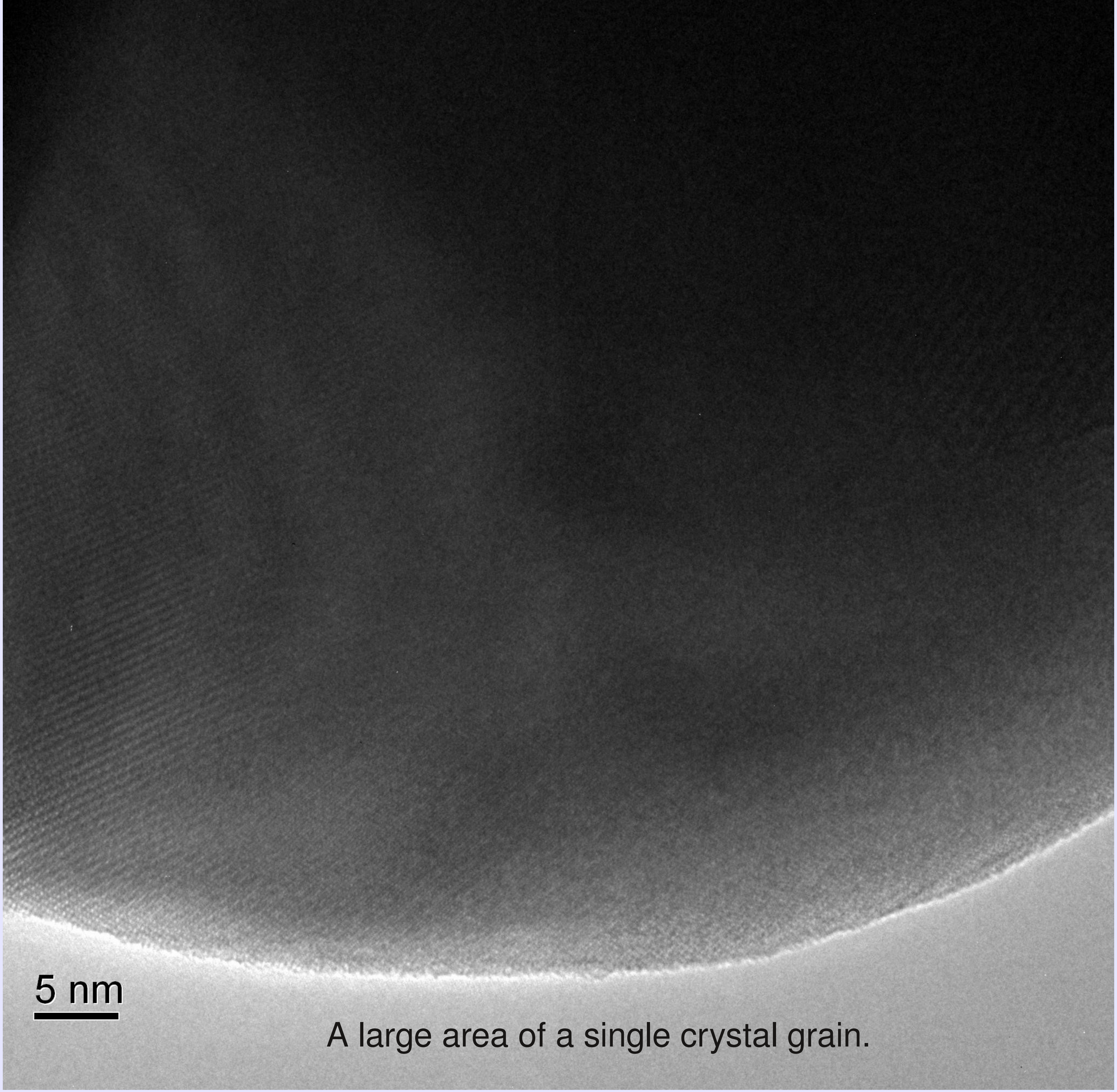




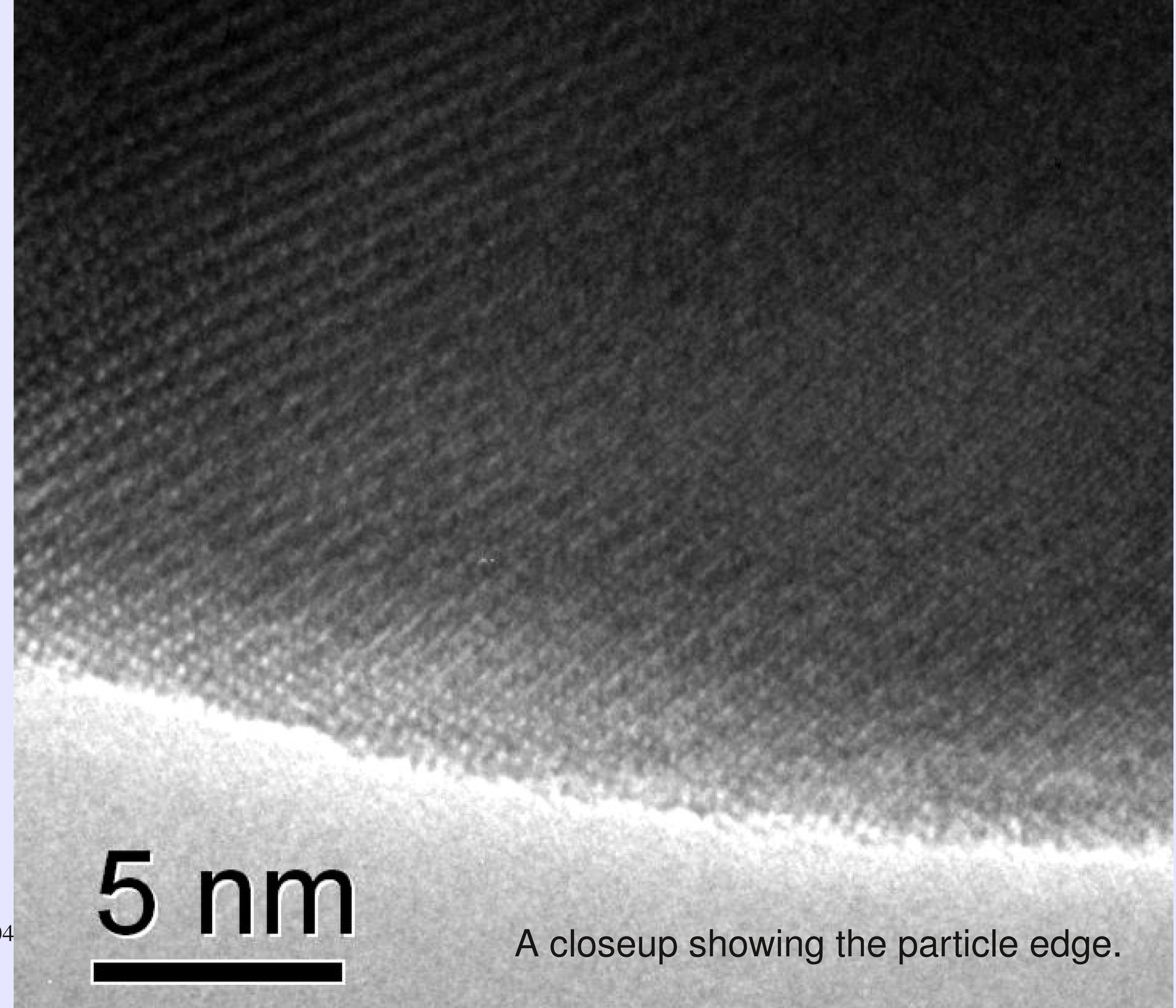

10 nm
A single crystal grain with facets.



03/04/12



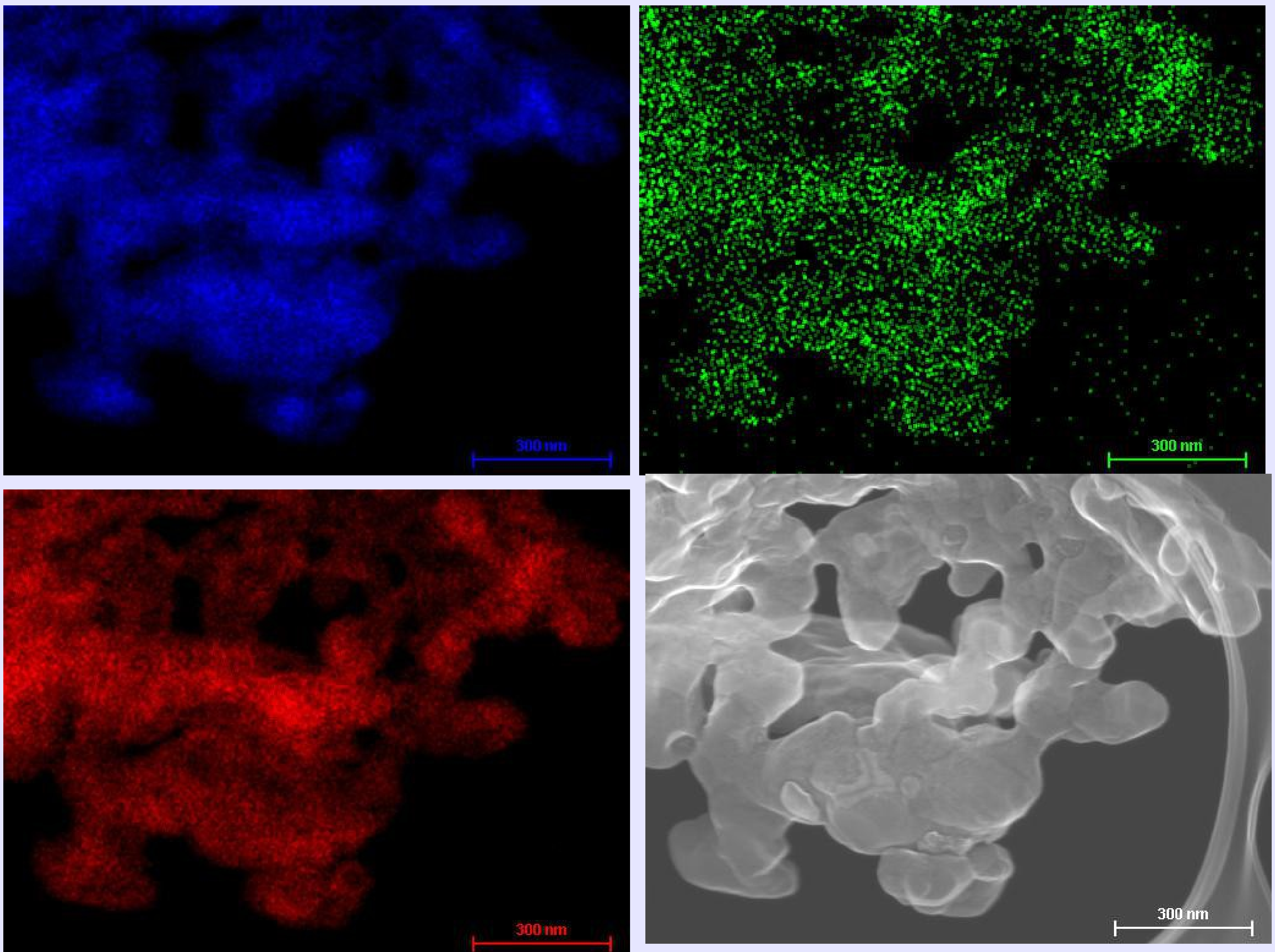
A large area of a single crystal grain.



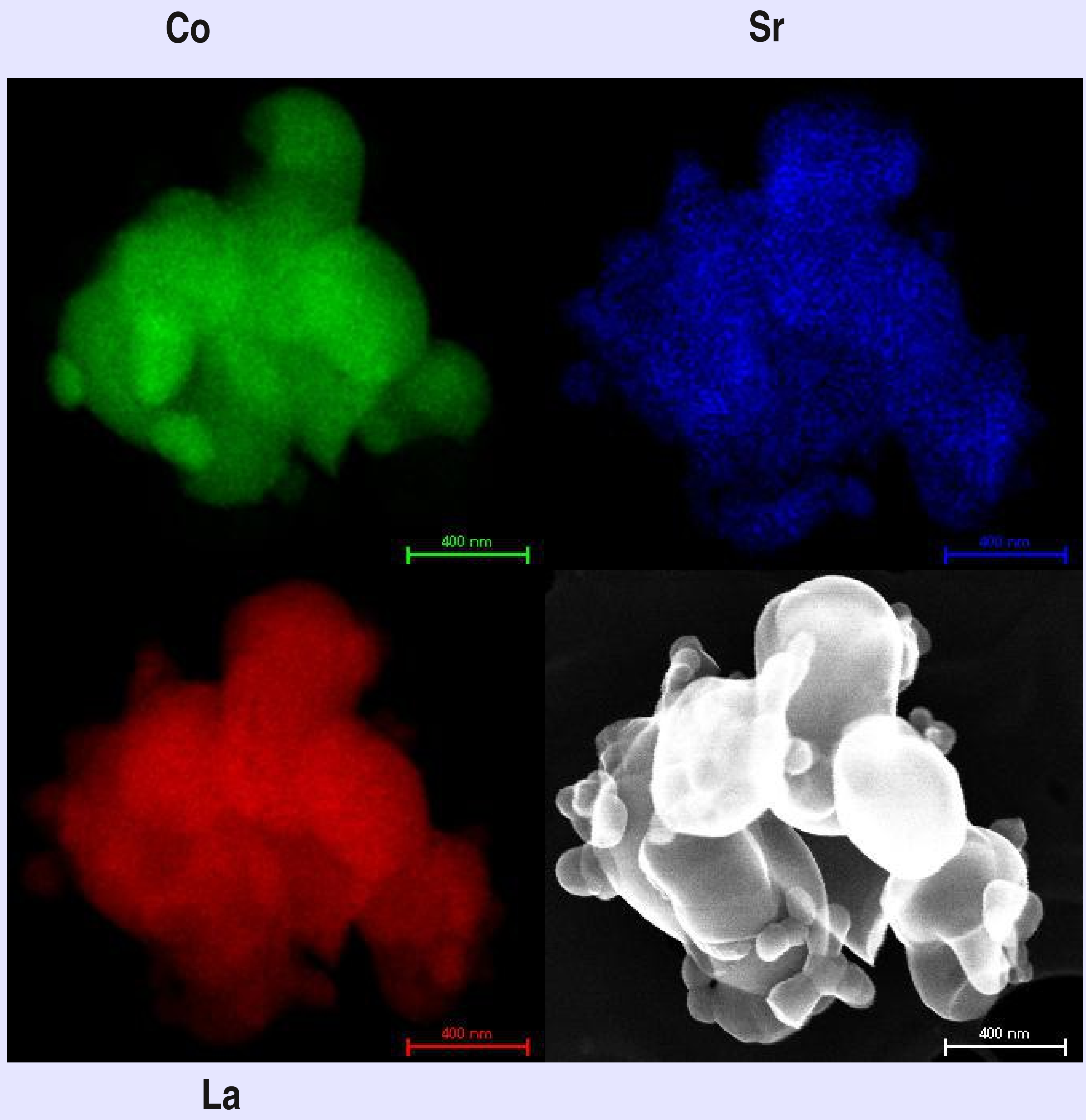
A closeup showing the particle edge.

Co

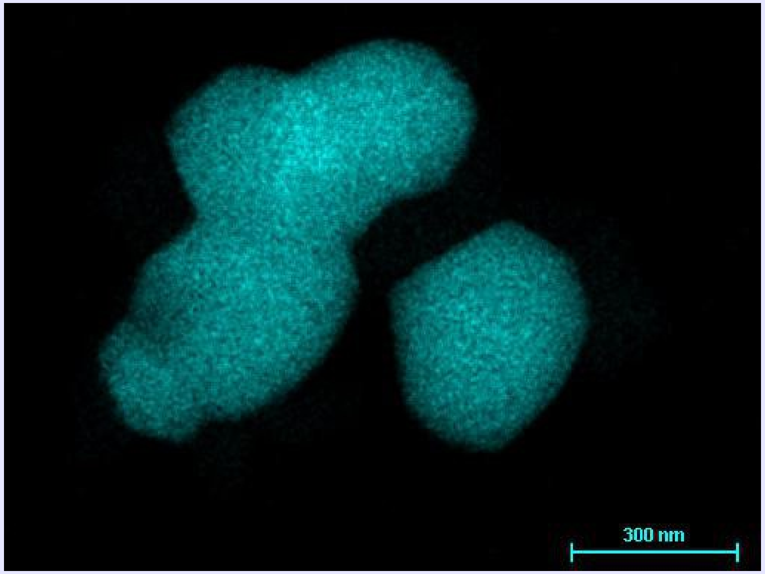
Sr



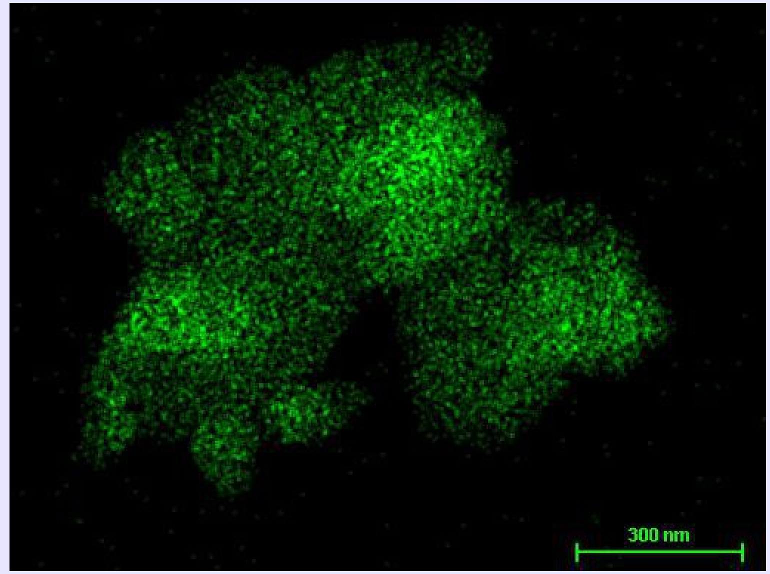
La

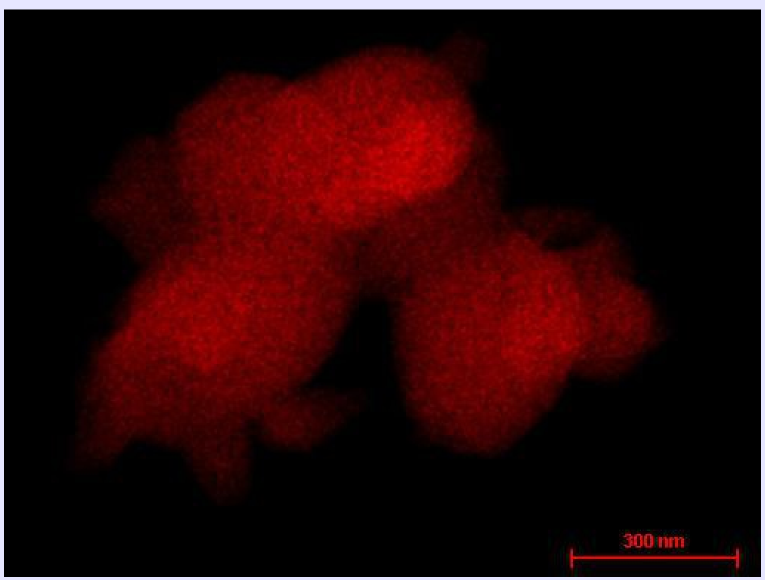

Co
Sr
400 nm
400 nm
400 nm
400 nm
La

Co

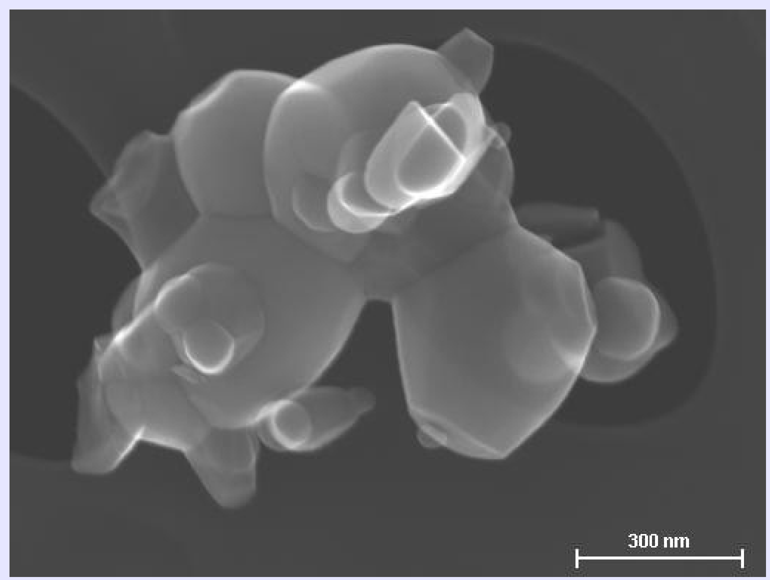


Sr

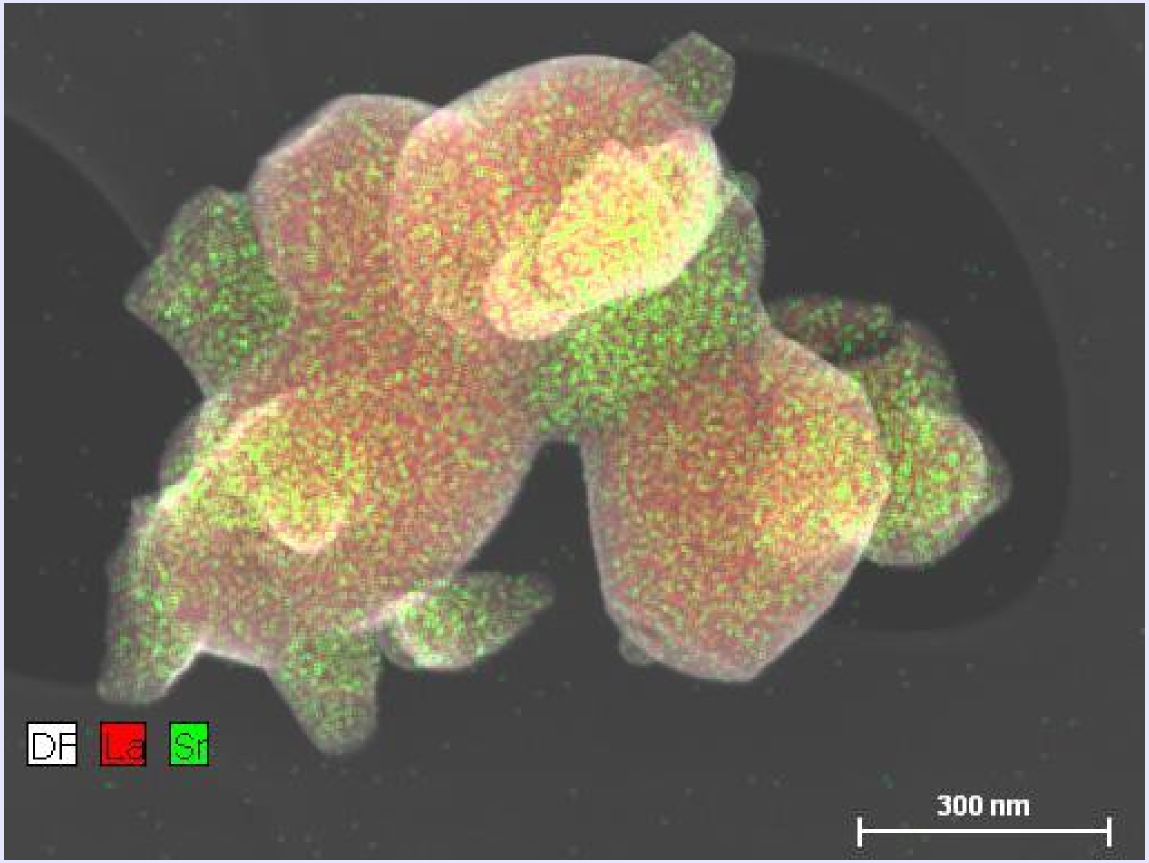




La



When there are impurities, they tend to form their own particles that may be attached to the LSCO particles. We are still working to find the best particle growth techniques to minimize impurities and yield the most uniform particles in size and Sr concentration.



pair distribution function

atomic pair distribution function (PDF)

$$\rho(r) = \rho_0 g(r) = \frac{1}{4\pi N r} \sum_\nu \sum_\mu \delta(r - r_{\nu\mu})$$

ν, μ indicate individual atoms

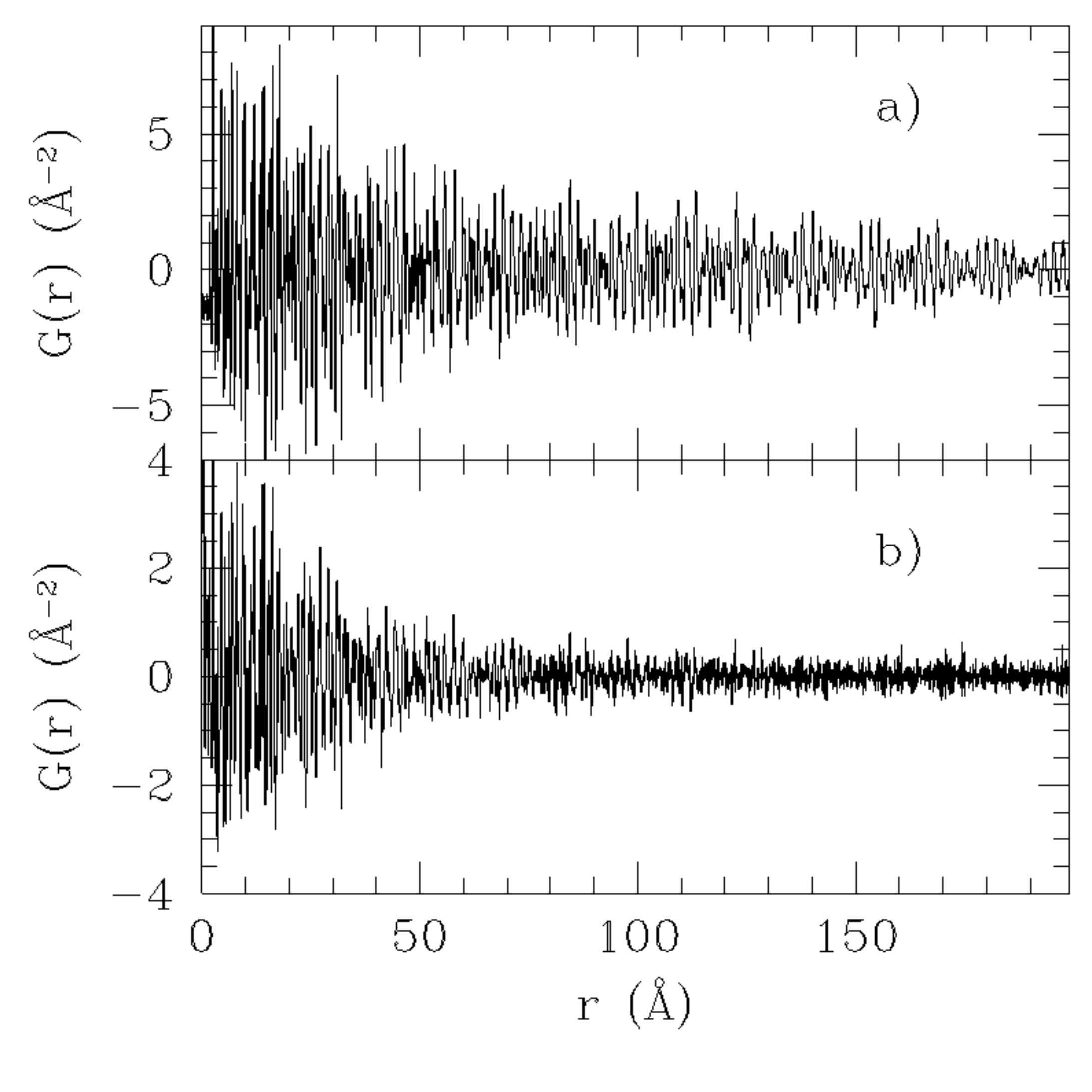
ρ_0 is number density of atoms

$$G(r) = 4\pi\rho_0(g(r) - 1)$$

$$G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ$$

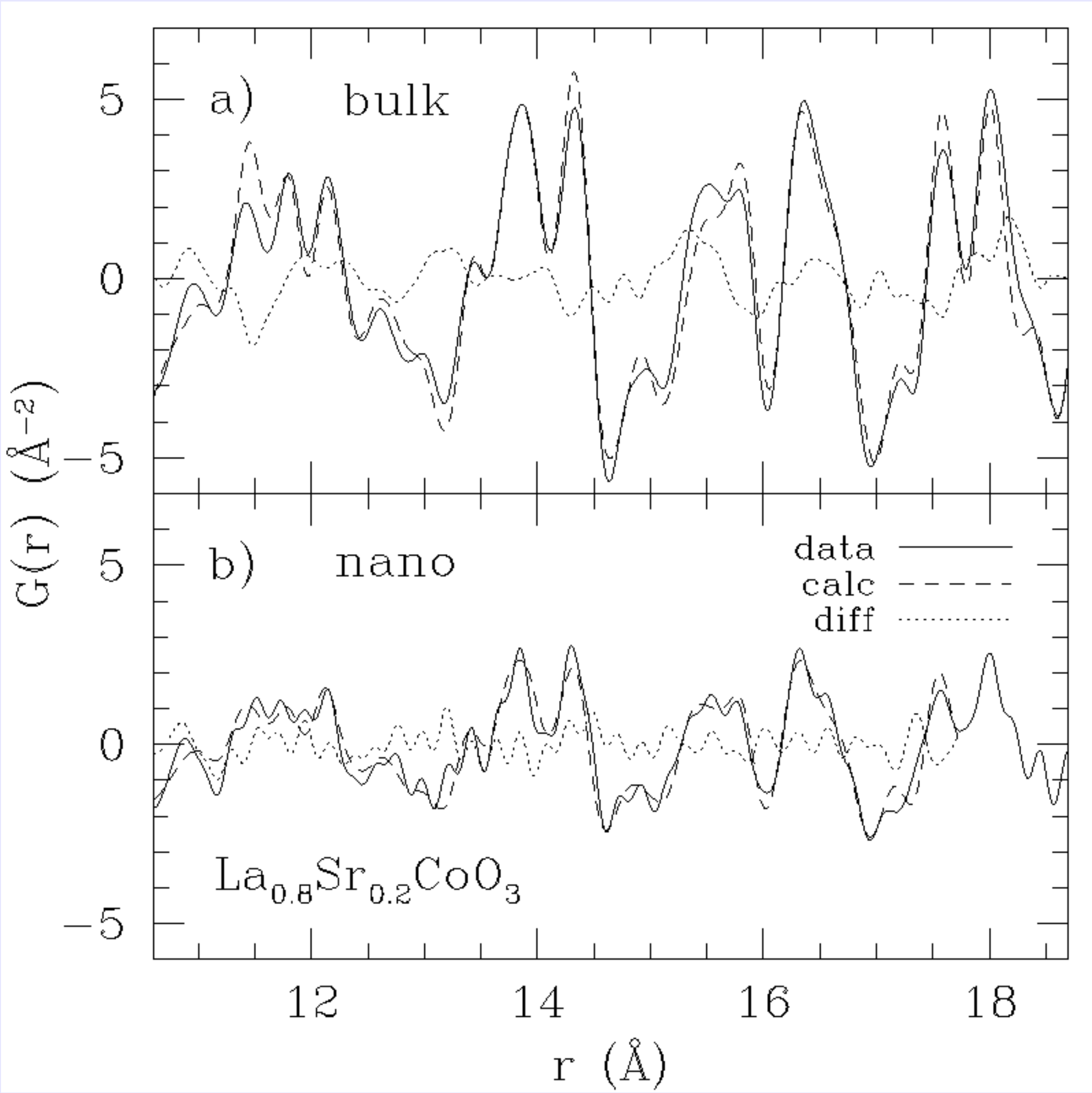
$S(Q)$ is the scattering intensity, structure factor

PDF of bulk and nanoparticle powders



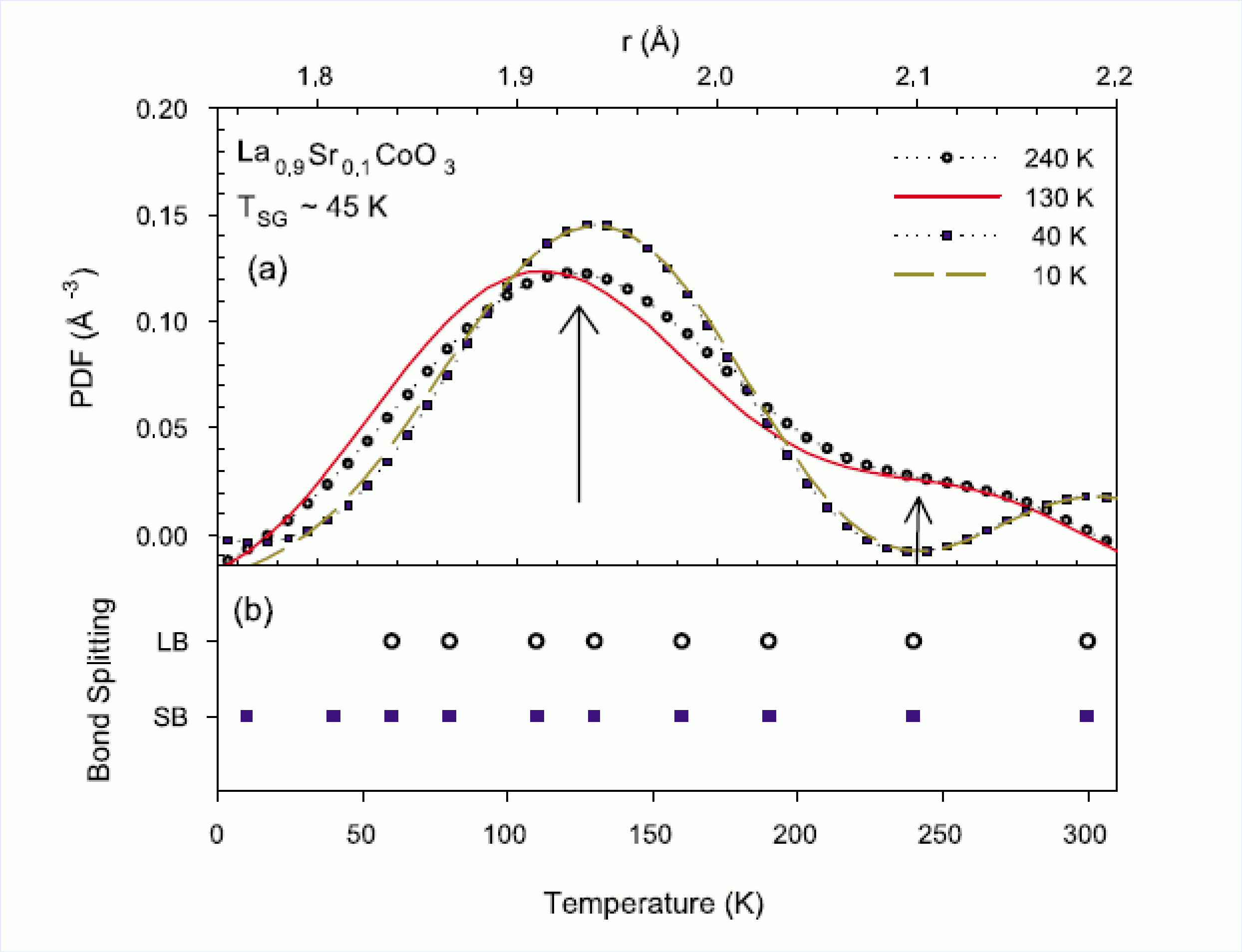
- *G(r)* in $La_{0.8}Sr_{0.2}CoO_3$ bulk powder sample.
- *G(r)* in $La_{0.8}Sr_{0.2}CoO_3$ nanoparticle powder sample. Correlations drop off as the particle size is approached, as expected.

PDF of bulk and nanoparticle powders



- *G(r)* in $La_{0.8}Sr_{0.2}CoO_3$ bulk powder sample at intermediate length scales.
- *G(r)* in $La_{0.8}Sr_{0.2}CoO_3$ nanoparticle powder sample. Correlations show the same structure as the bulk at least out to about 15nm.

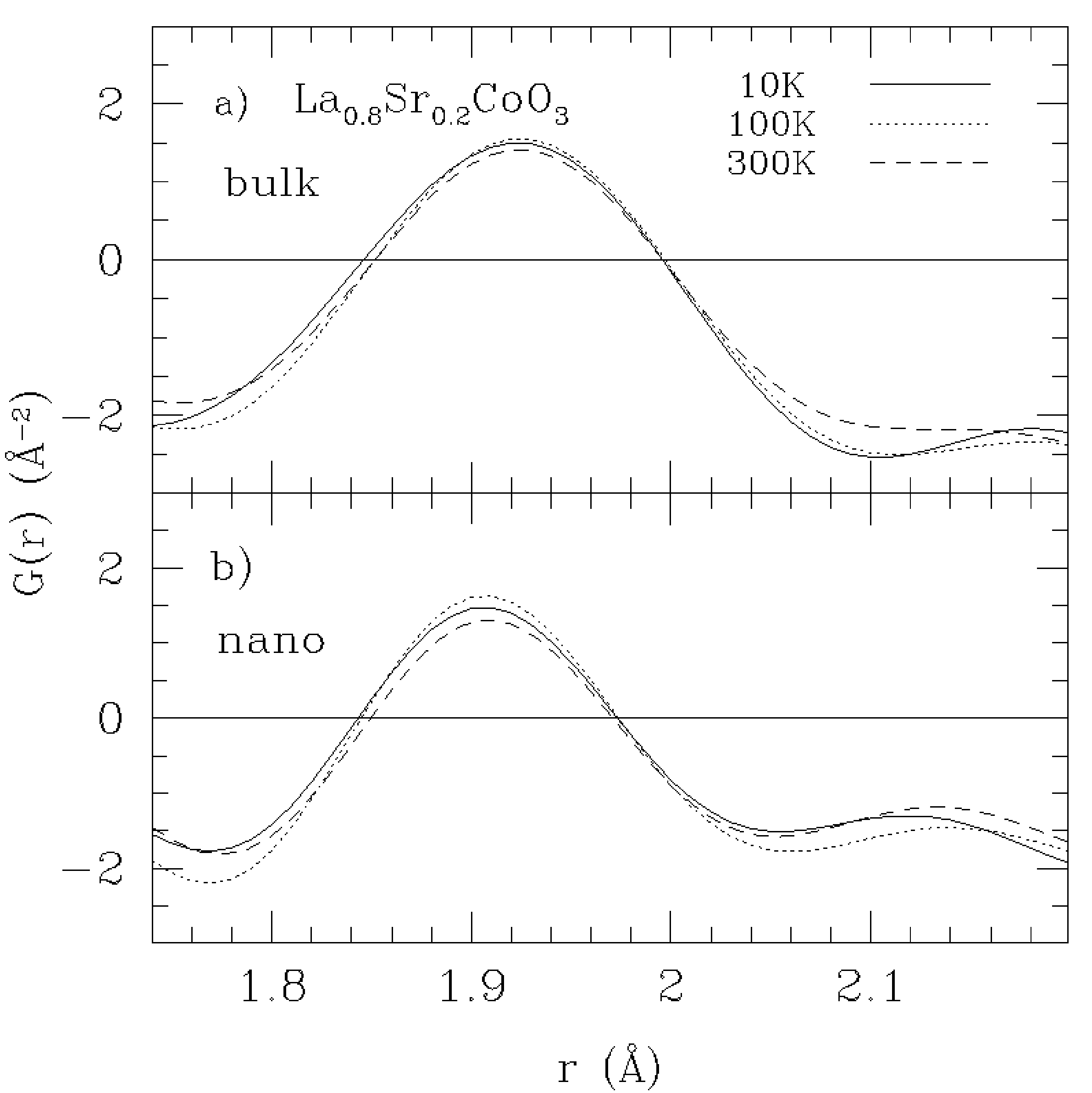
Previous Data of Jahn-Teller Distortion in Cobaltite



A previous neutron PDF study indicated a large J-T distortion, with the second peak at 2.1 Å only for temperatures of 50K or higher, but not at very low temperature. D. Louca and J.L. Sarrao, Phys. Rev. Lett. **91**, 155501 (2003). Many different experimental techniques indicated this as well.

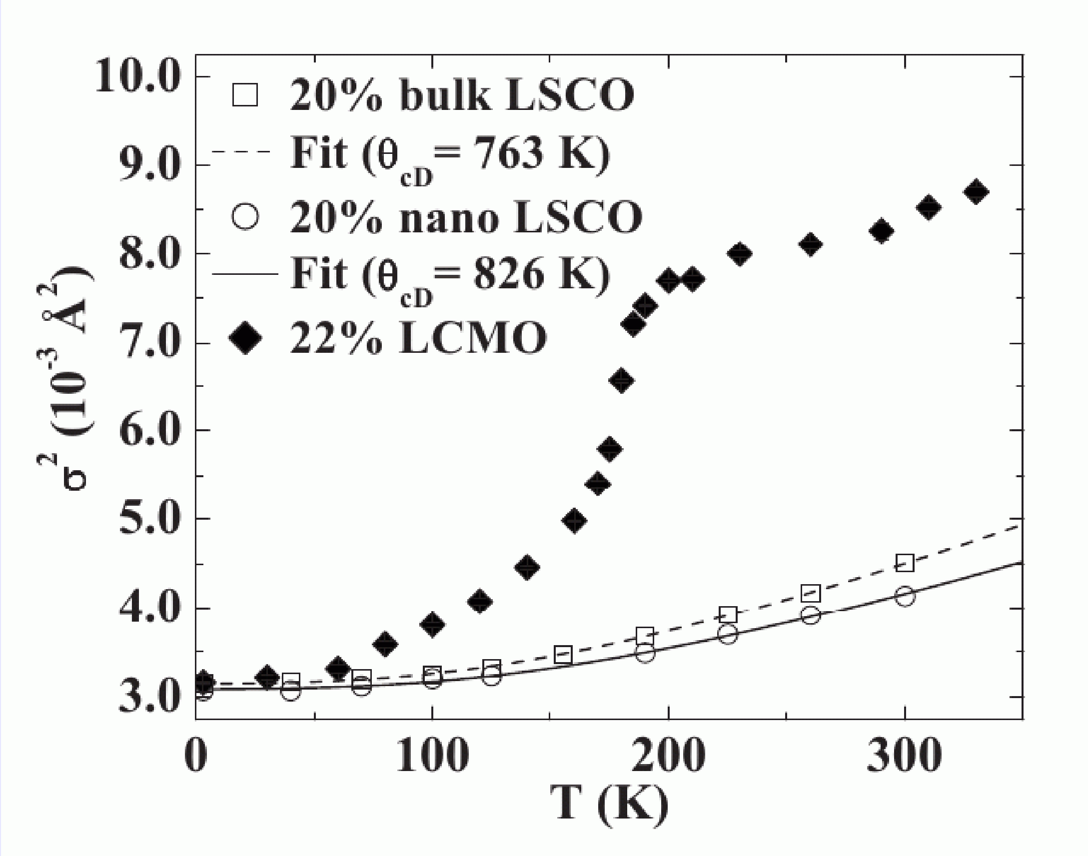
However, in our studies, we observed the distortion in neither bulk nor nanoparticle LSCO.

No J-T distortion in either bulk or nanoparticle powders



- The Co-O bond length shows no evidence for a distortion. The small peak is a result of the Fourier transform.
- There could be a very small distortion, or it could be only on a few sites.

EXAFS evidence against a large local Jahn-Teller distortion in the cobaltites

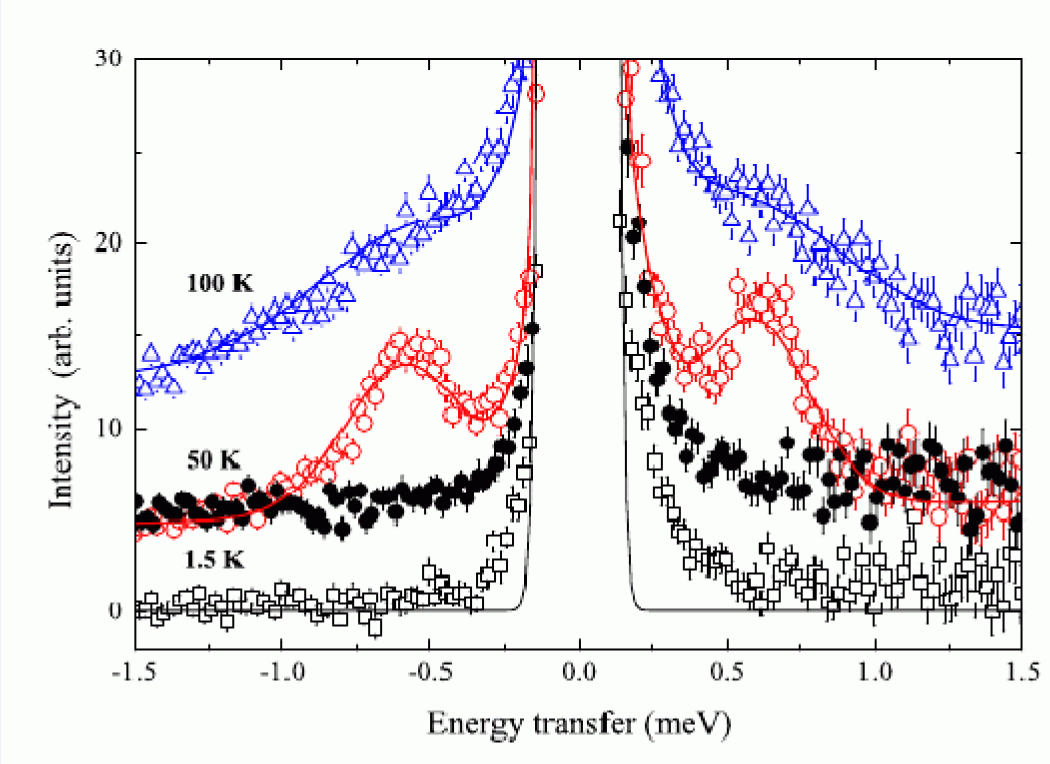


$\sigma^2 = \sigma_{static}^2 + \sigma_{phonon}^2 + \sigma_{J\text{-}T}^2$

The mangantites show a Clear J-T distortion below 200K.

The cobaltite bulk and nanoparticle systems show no J-T distortion, meaning it is either non-existent, or represents a very small distortion or few sites.

Excitations in bulk LCO

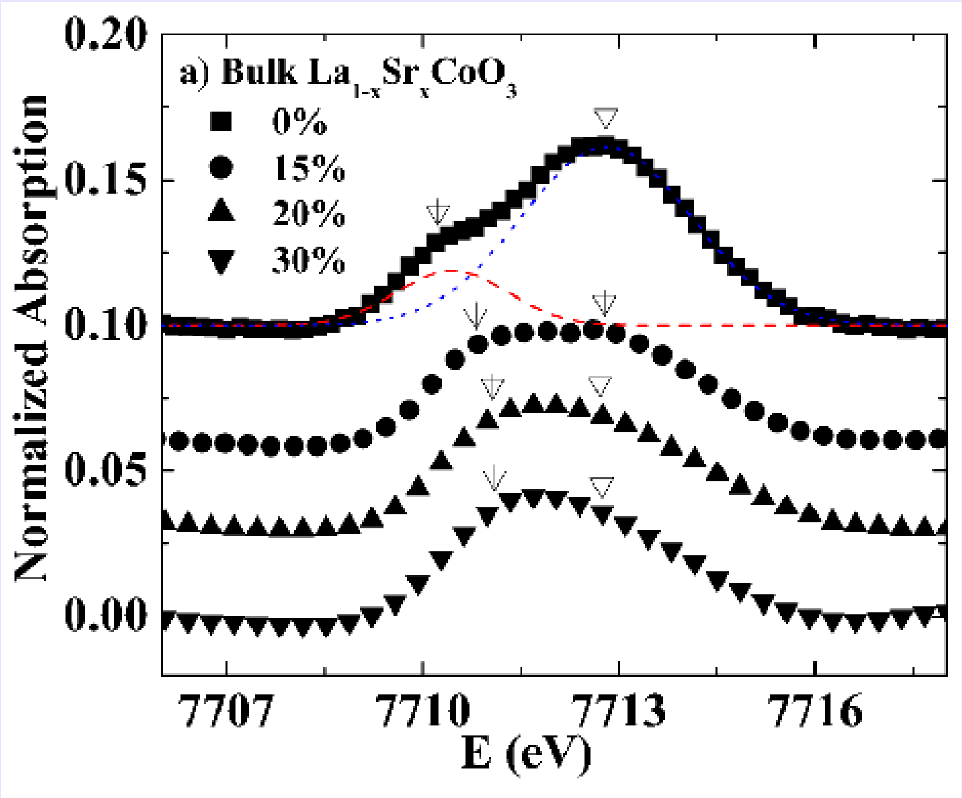


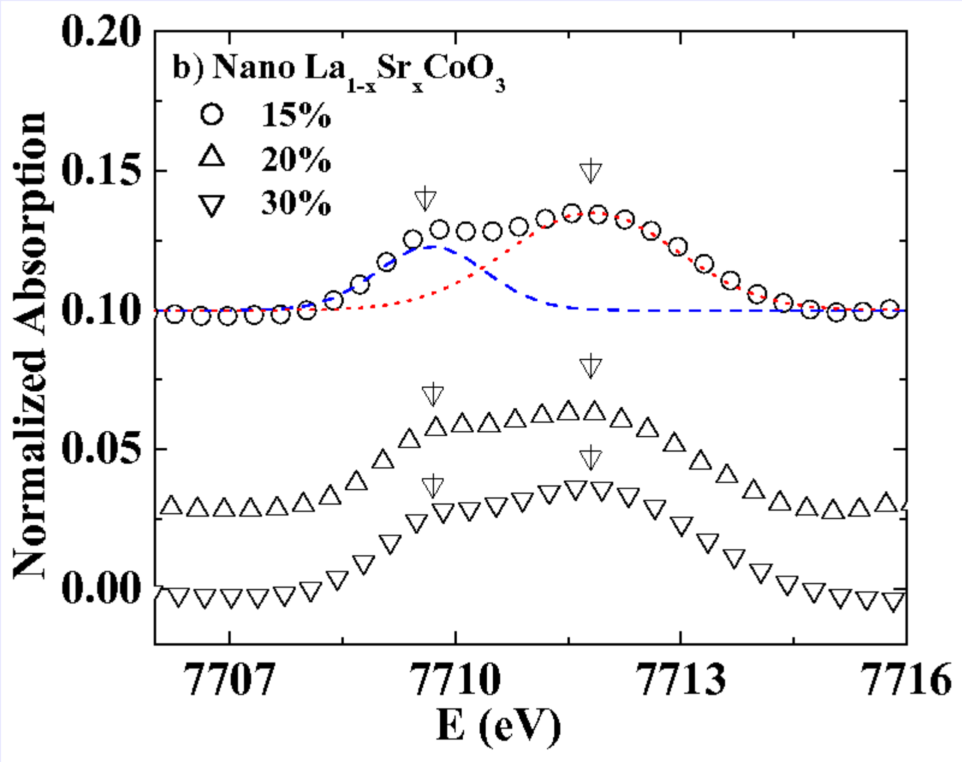
Podlesnyak, et al. were among the first to show experimentally that the transition at 90K was to the HS and not the IS, based on the observed excitations and the value of g ~3, compatible with 3.35 < g < 3.55 obtained by Noguchi, et al. The IS state would require g=2.

A. Podlesnyak, S. Streule, J. Mesot, M. Medarde, E. Pomjakushina, K. Condor, A. Tanaka, M. W. Haverkort, and D. I. Khomskii, Phys. Rev. Lett. 97, 247208 (2006)

S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, Phys. Rev. B 66, 094404 (2002).

X-ray absorption pre-edge peaks

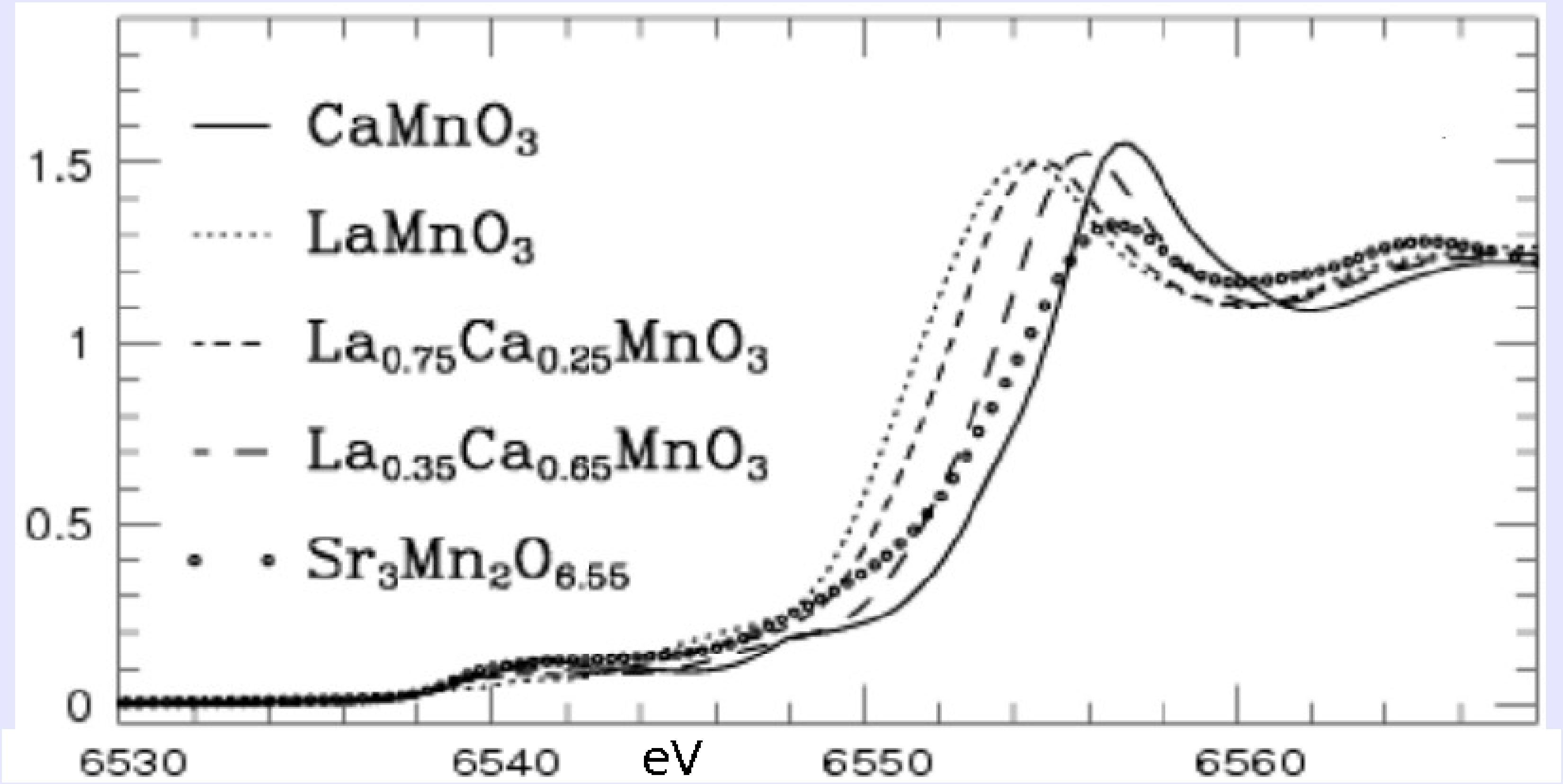




The main edge is 1s4p dipolar, the lower pre-edge is 1s3d quadrupolar and the upper pre-edge is a non-local 1s3d mediated by O and 4p/3d hybridization and has slightly less core screening (Vanko, et al. ArXiv:0802.2744v1)

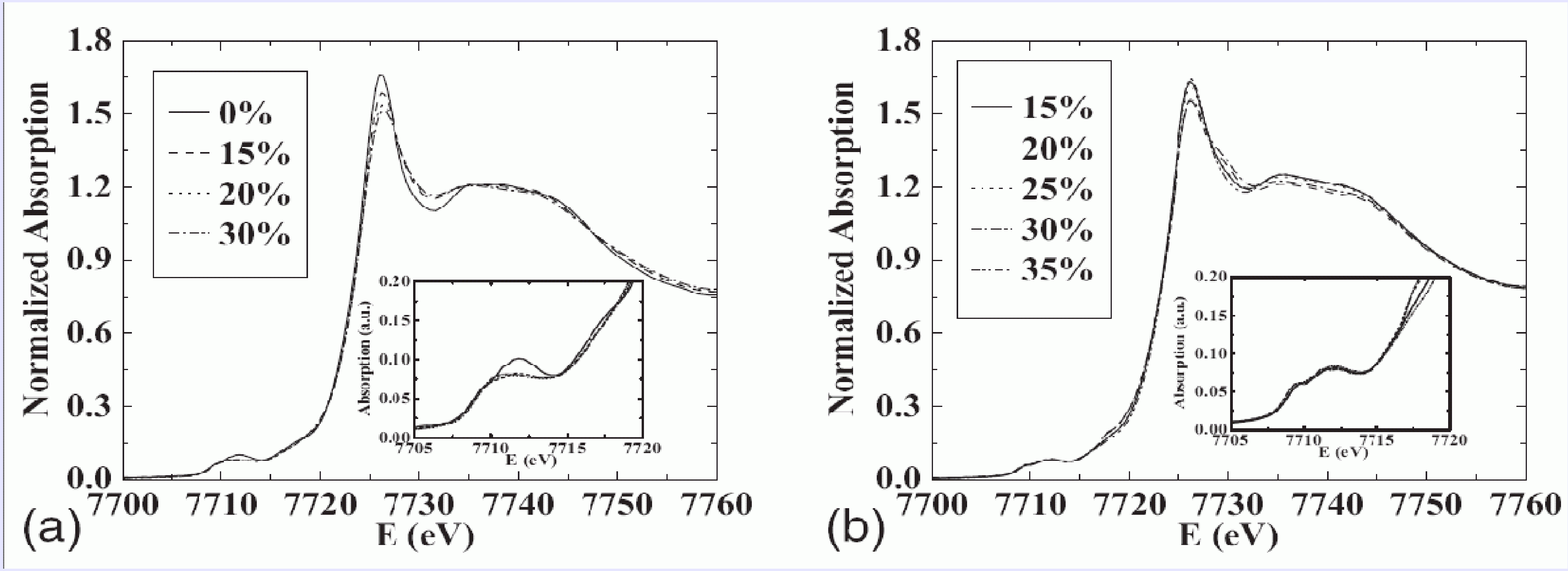
Bulk particles show a merging of the pre-edge peaks, but not the nanoparticles.

Typical shift in the x-ray absorption edge with doping



A typical shift in the edge with doping, in this case a manganite system. The shift is approximately 3eV/valence unity as Mn^{+3} changes to Mn^{+4}.
F. Bridges, et al., Phys. Rev. B 63, 214405 (2001).

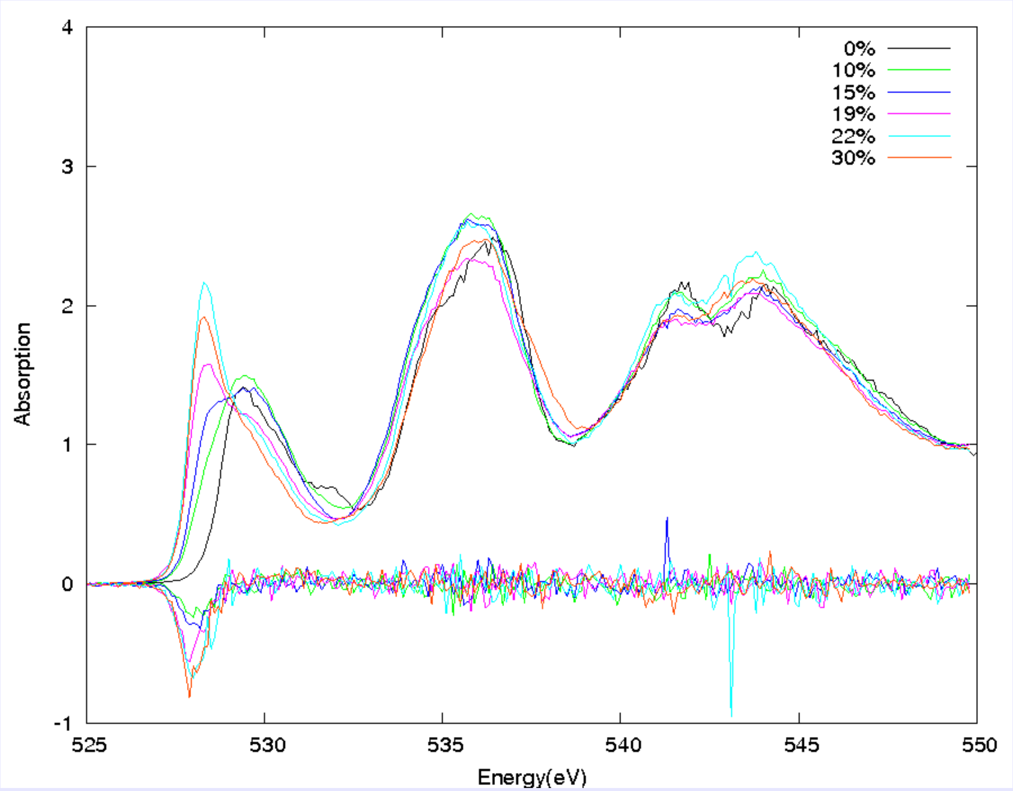
Lack of a shift in the x-ray absorption edge with Sr doping



The Co-K edge hardly shifts with Sr doping in either the bulk or nanoparticle Powders, which is not typical.

This indicates that the Co ions remain Co^{+3}, which suggests that holes are associated with the O ions, consistent with the observed small change in Co-O bond lengths.

X-ray magnetic dichroism: O K-edge for x ranging from 0 to 0.30

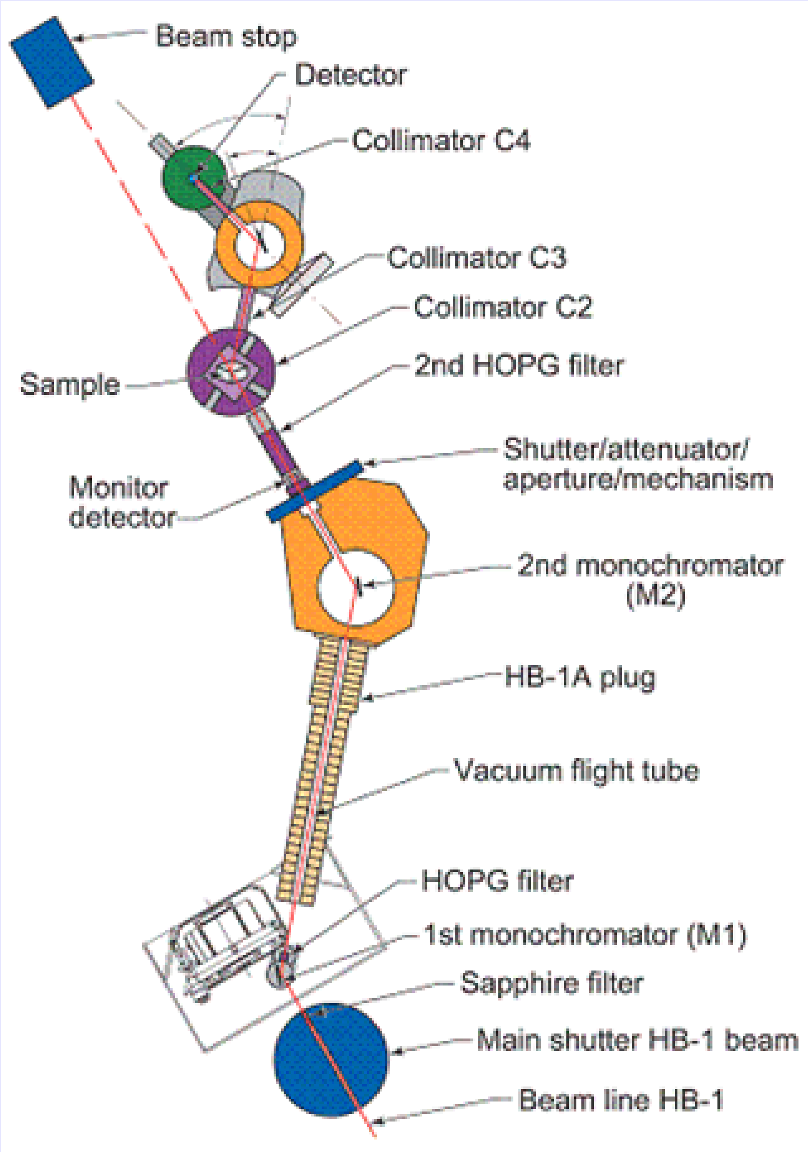


XAS in upper part, XMCD in lower part

Oxygen K-edge magnetic signal indicates magnetism and, therefore, holes are associated with the O sites

S. Medling, F. Bridges, J. W. Freeland, J. Mitchell, and H. Zheng (2010)

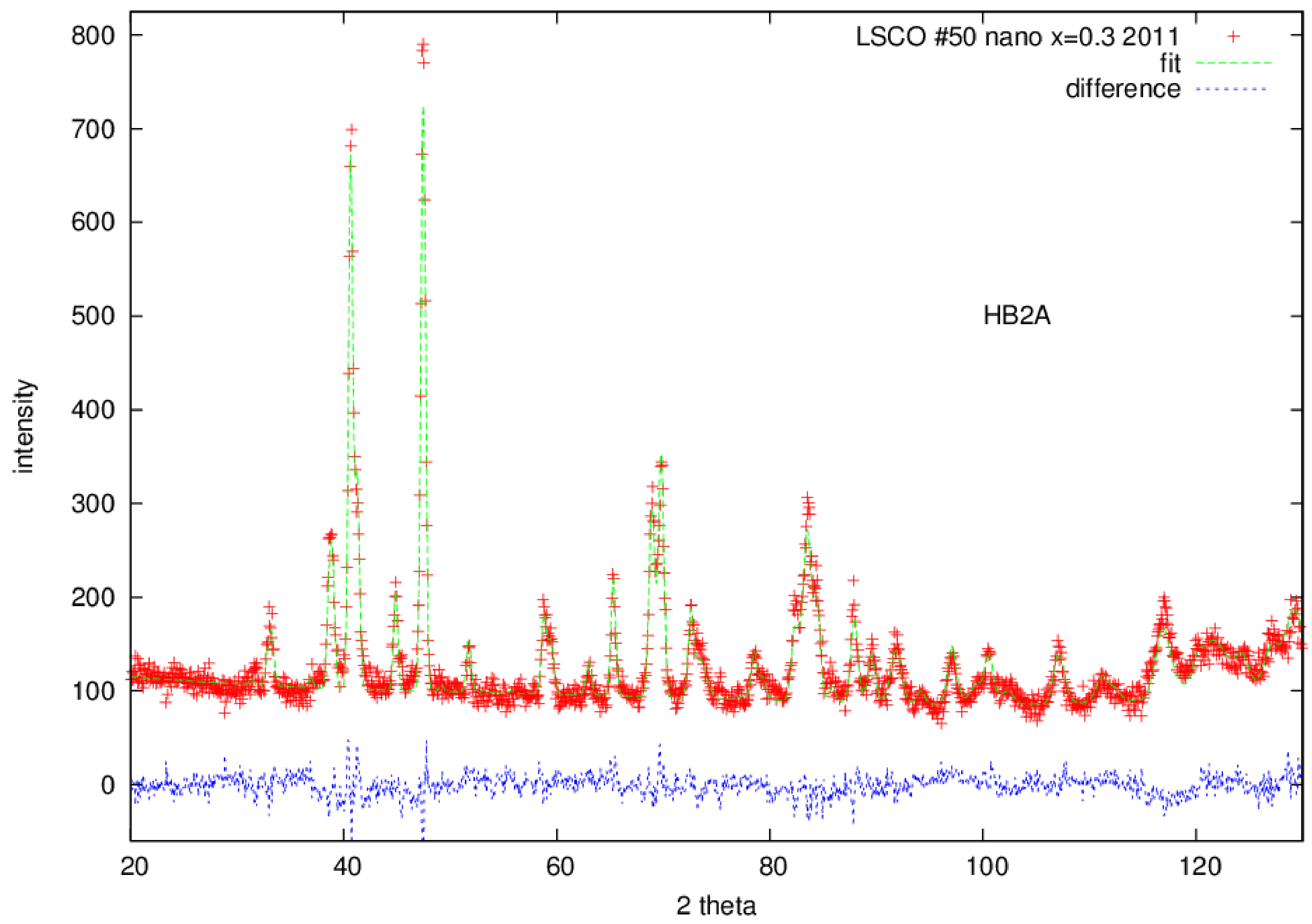
High Flux Isotope Reactor – Oak Ridge National Laboratory



HB-!A triple axis spectrometer at HFIR Oak Ridge National Laboratory

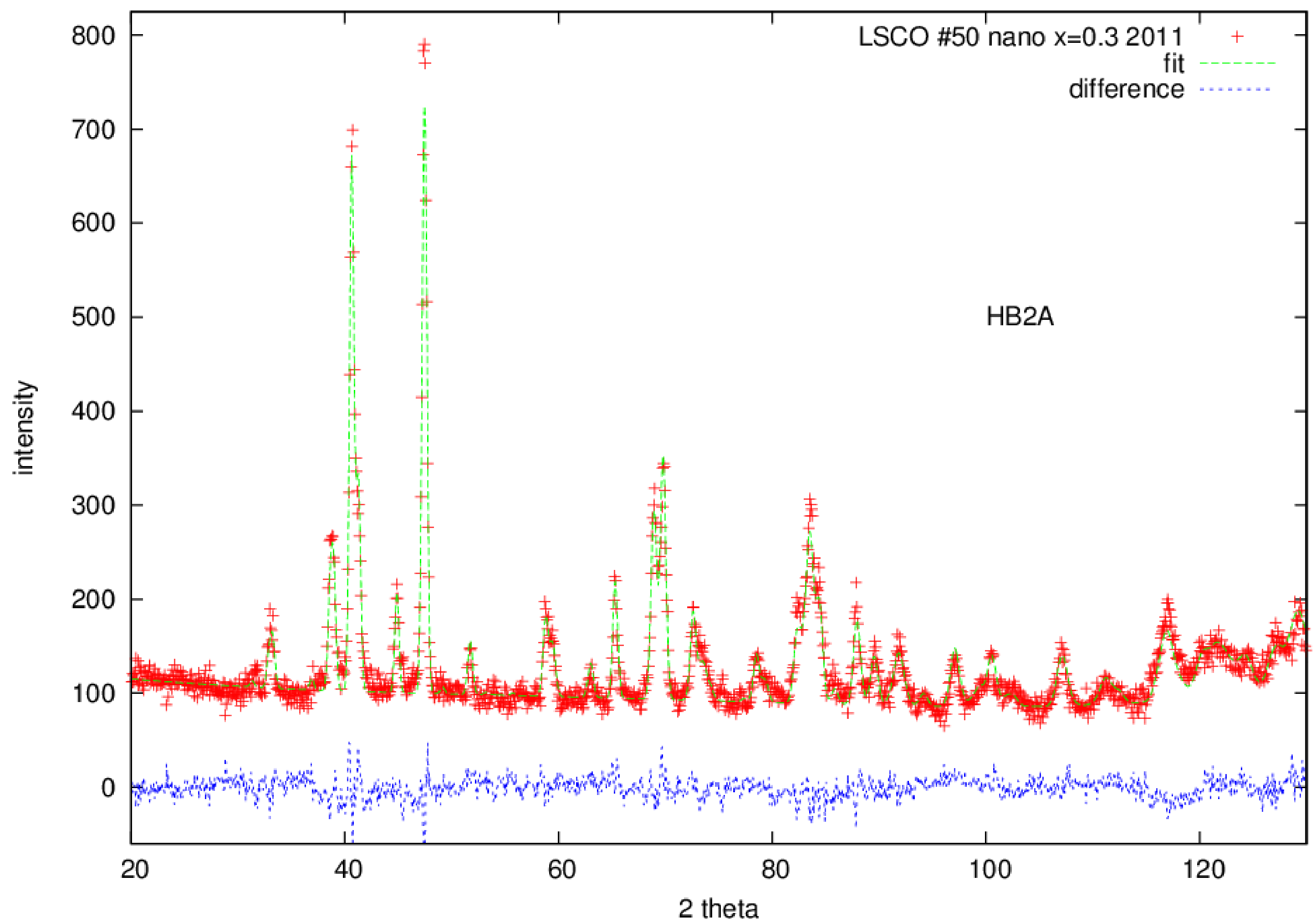
Spallation Neutron Source – Oak Ridge National Laboratory

Average structure of the nanoparticle powders



Average particle size ~19nm for this sample, but with a fairly wide range

Average structure of the nanoparticle powders



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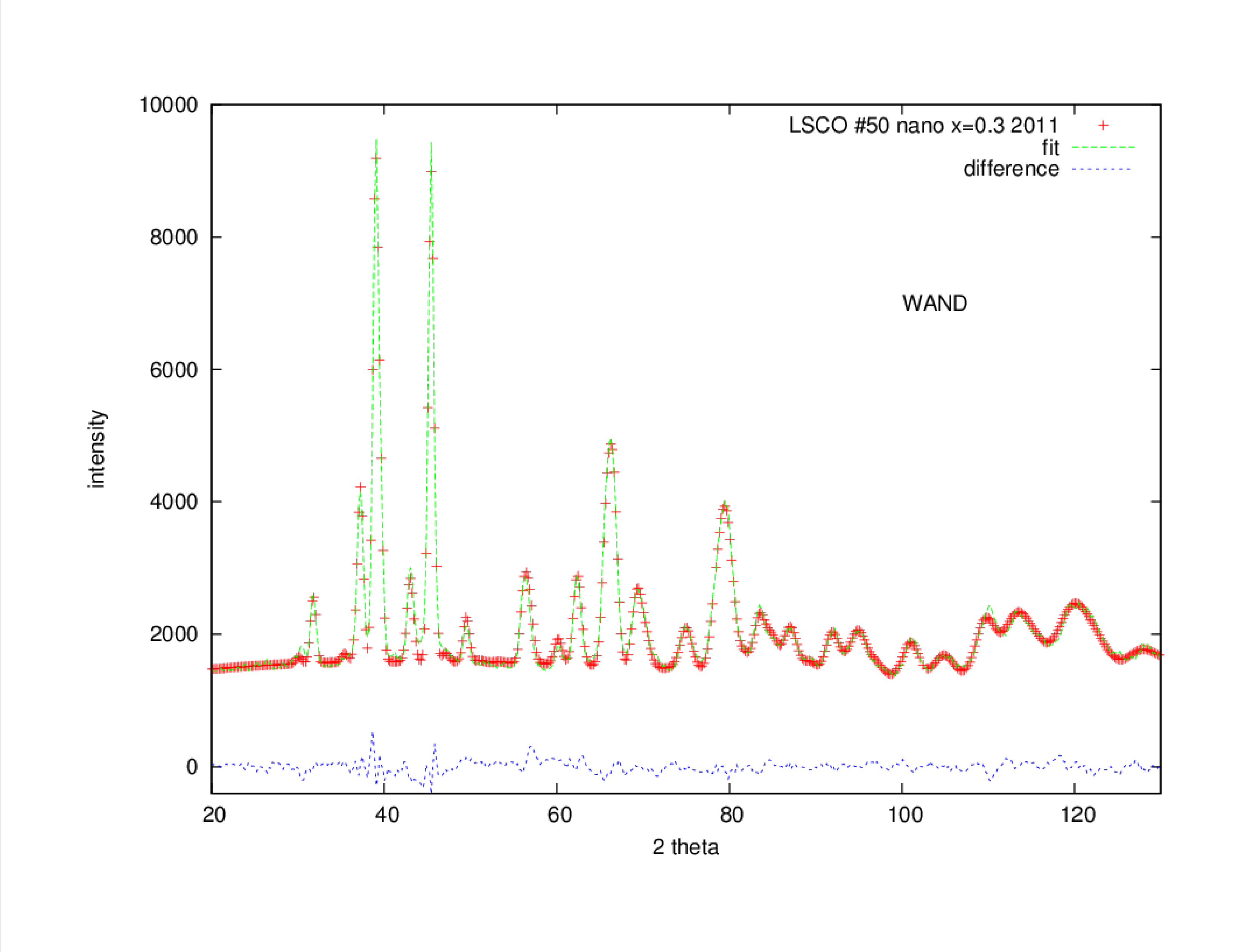
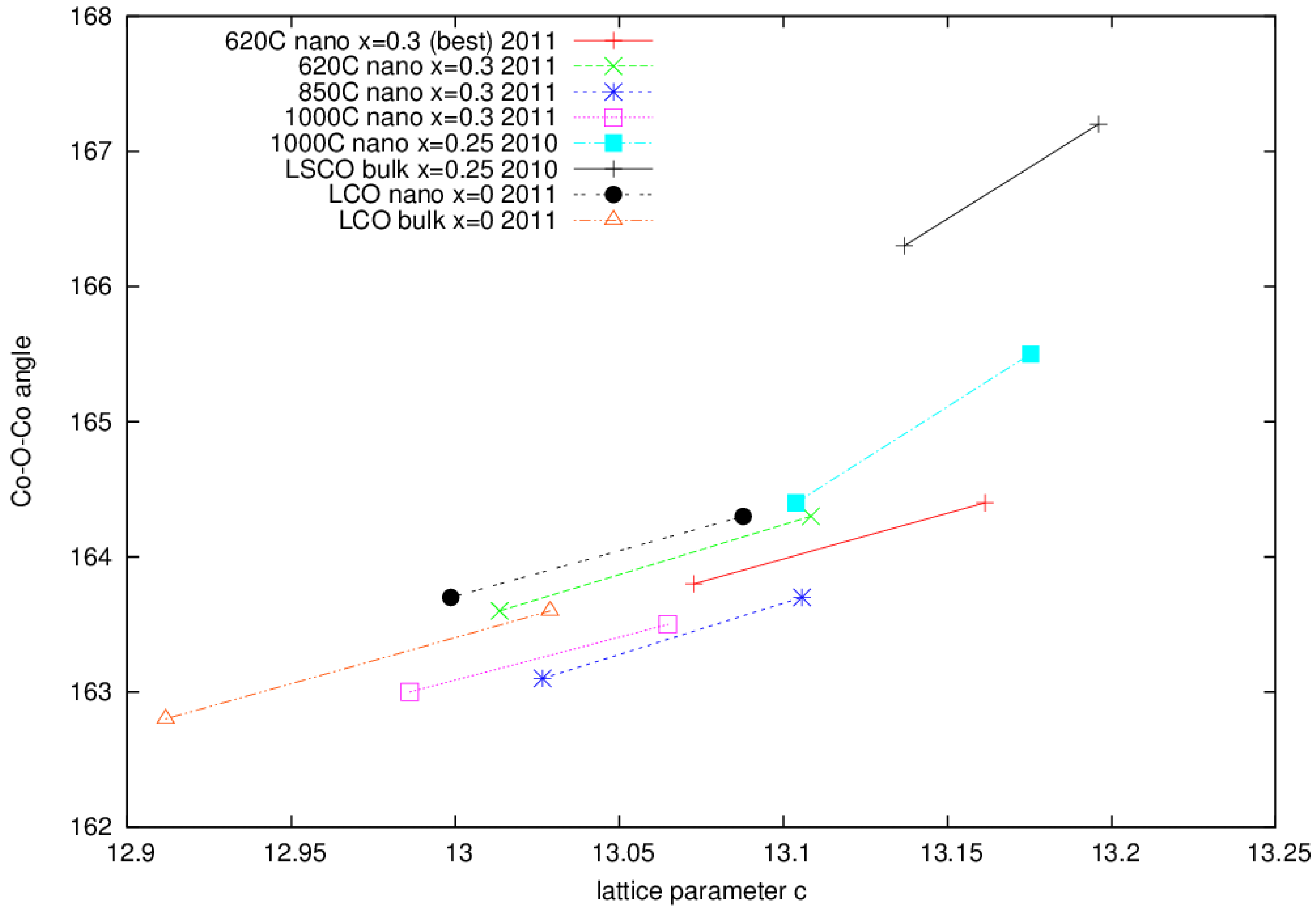
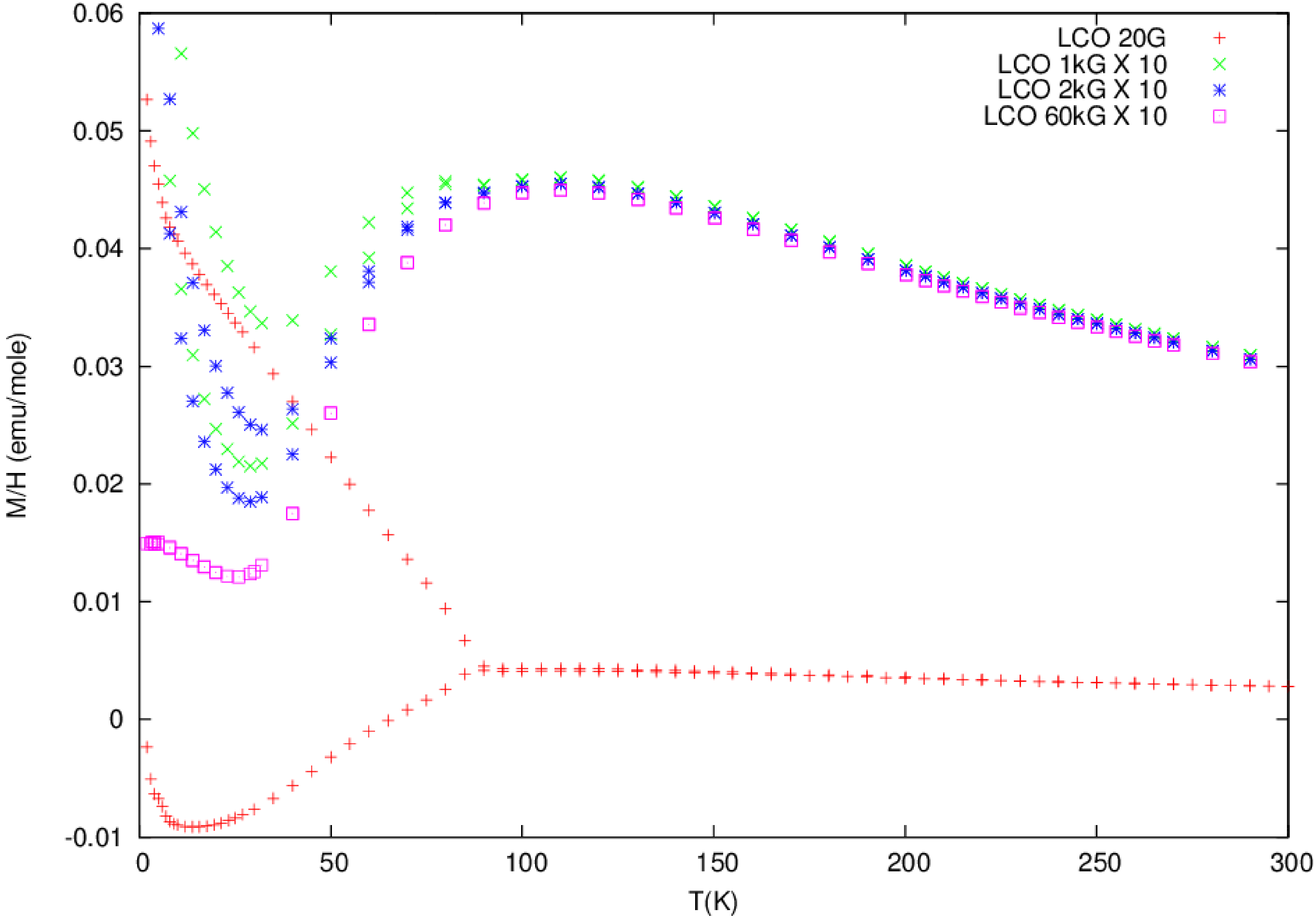
Average structure of the nanoparticle powders

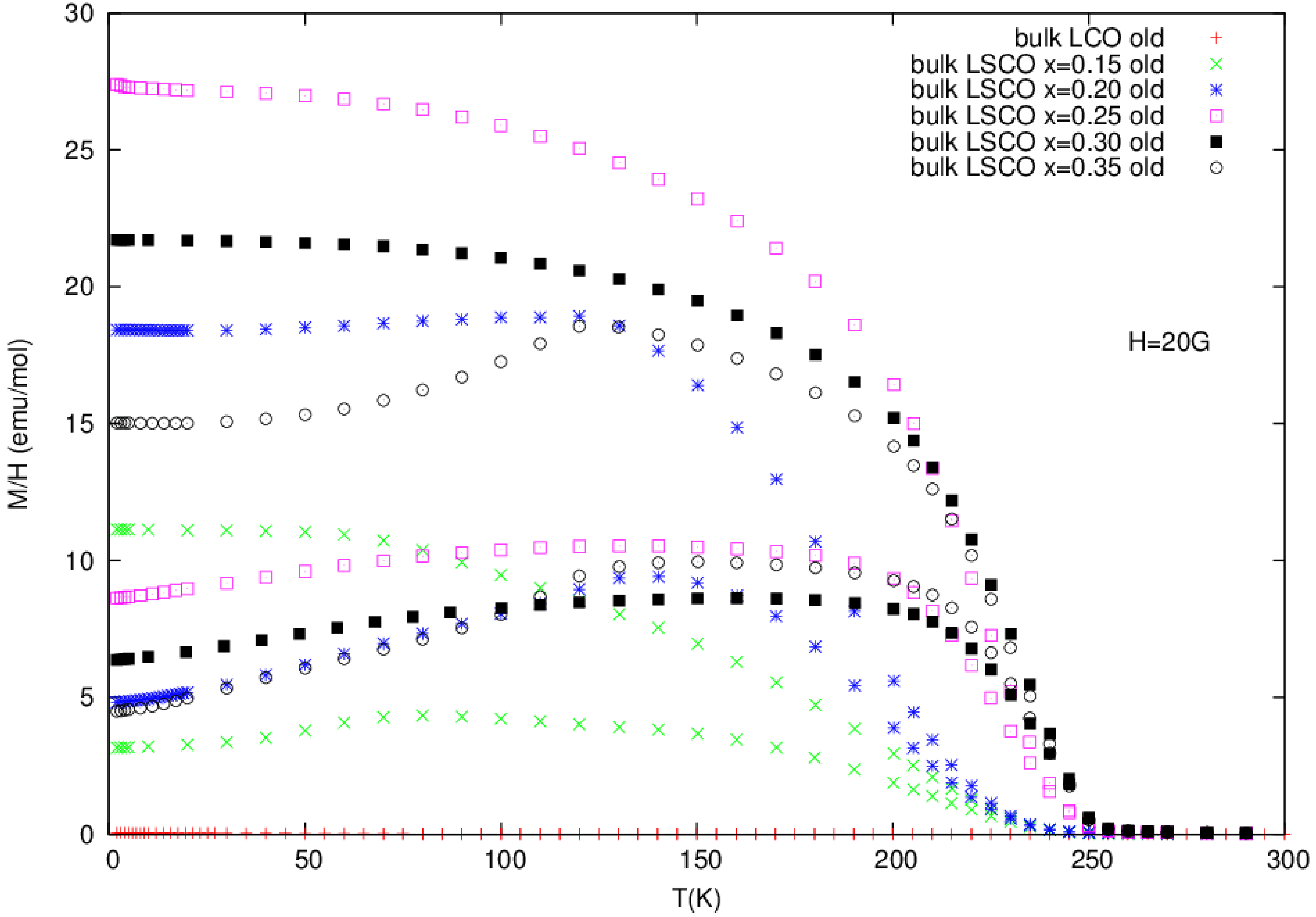


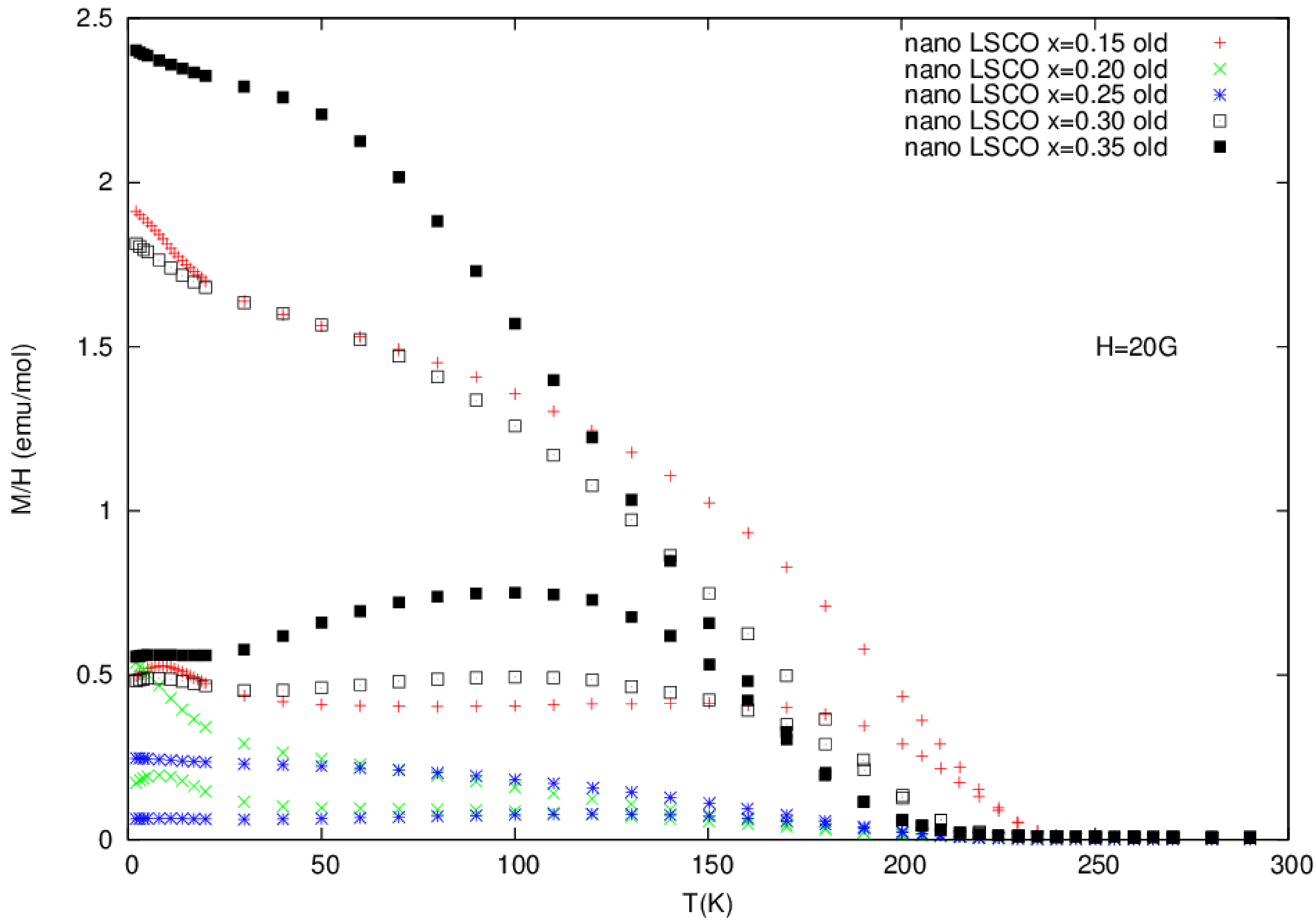


620C nano x=0.3 (best) 2011
620C nano x=0.3 2011
850C nano x=0.3 2011
1000C nano x=0.3 2011
1000C nano x=0.25 2010
LSCO bulk x=0.25 2010
LCO nano x=0 2011
LCO bulk x=0 2011
Co-O-Co angle
lattice parameter c
168
167
166
165
164
163
162
12.9
12.95
13
13.05
13.1
13.15
13.2
13.25

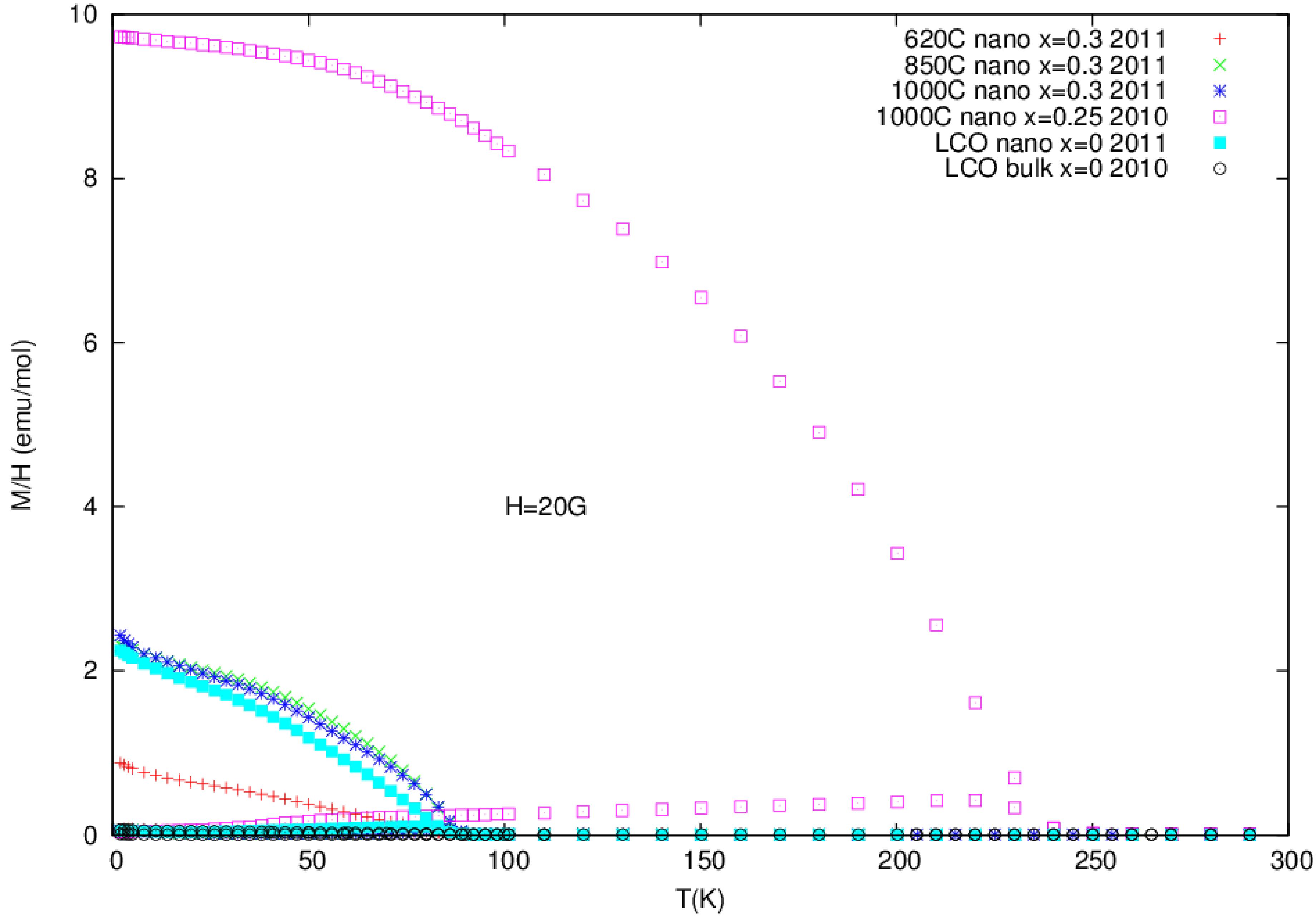


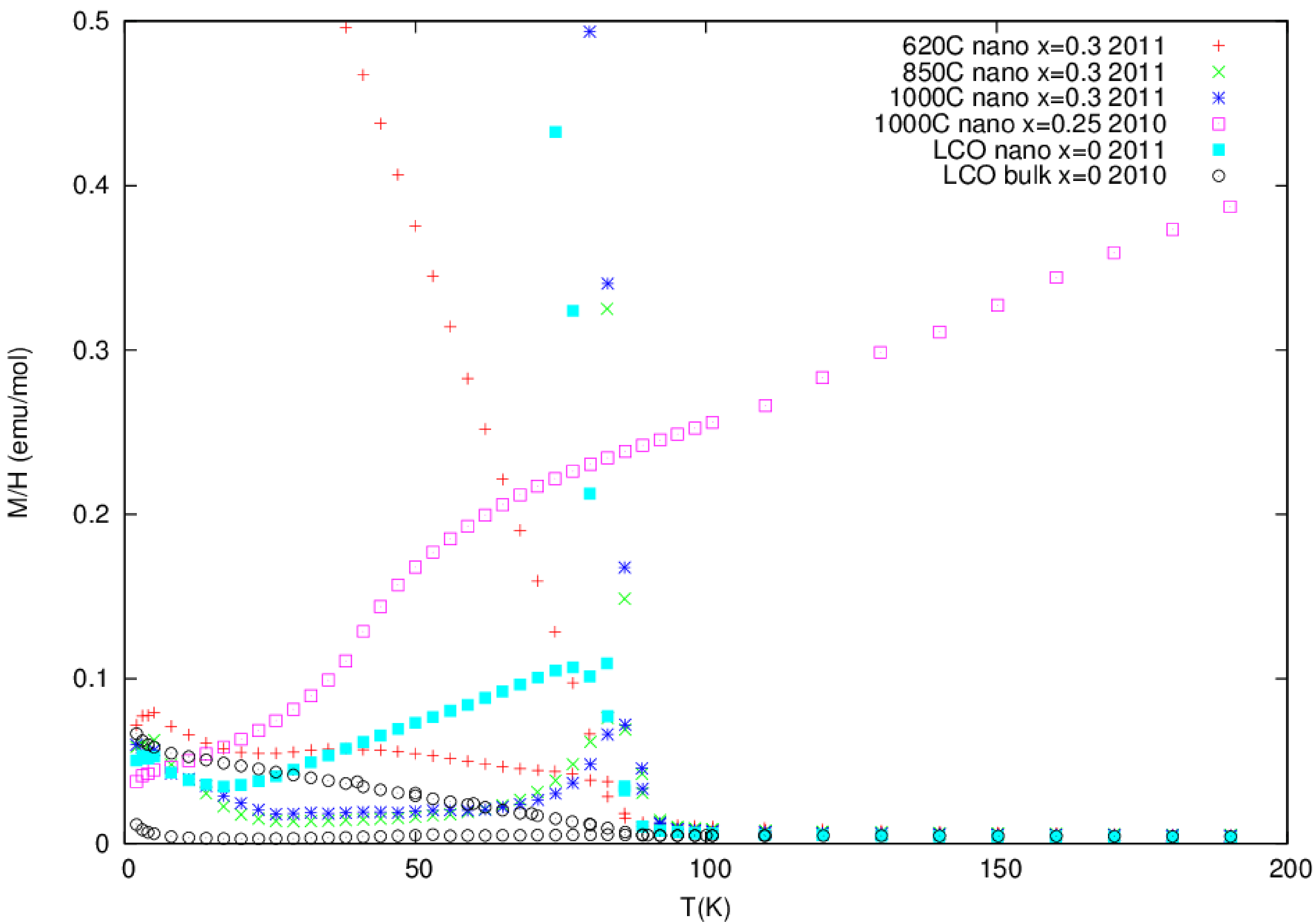
LCO 20G
LCO 1kG X 10
LCO 2kG X 10
LCO 60kG X 10
M/H (emu/mole)
T(K)
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
0
50
100
150
200
250
300


bulk LCO old
bulk LSCO x=0.15 old
bulk LSCO x=0.20 old
bulk LSCO x=0.25 old
bulk LSCO x=0.30 old
bulk LSCO x=0.35 old
H=20G
M/H (emu/mol)
T(K)
0
5
10
15
20
25
30
0
50
100
150
200
250
300



nano LSCO x=0.15 old
nano LSCO x=0.20 old
nano LSCO x=0.25 old
nano LSCO x=0.30 old
nano LSCO x=0.35 old
H=20G
M/H (emu/mol)
T(K)
0
0.5
1
1.5
2
2.5
0
50
100
150
200
250
300


10
8
6
4
2
0
0
50
100
150
200
250
300
M/H (emu/mol)
T(K)
H=20G
620C nano x=0.3 2011
850C nano x=0.3 2011
1000C nano x=0.3 2011
1000C nano x=0.25 2010
LCO nano x=0 2011
LCO bulk x=0 2010



620C nano x=0.3 2011
850C nano x=0.3 2011
1000C nano x=0.3 2011
1000C nano x=0.25 2010
LCO nano x=0 2011
LCO bulk x=0 2010
M/H (emu/mol)
T(K)
0.5
0.4
0.3
0.2
0.1
0
0
50
100
150
200

Conclusions

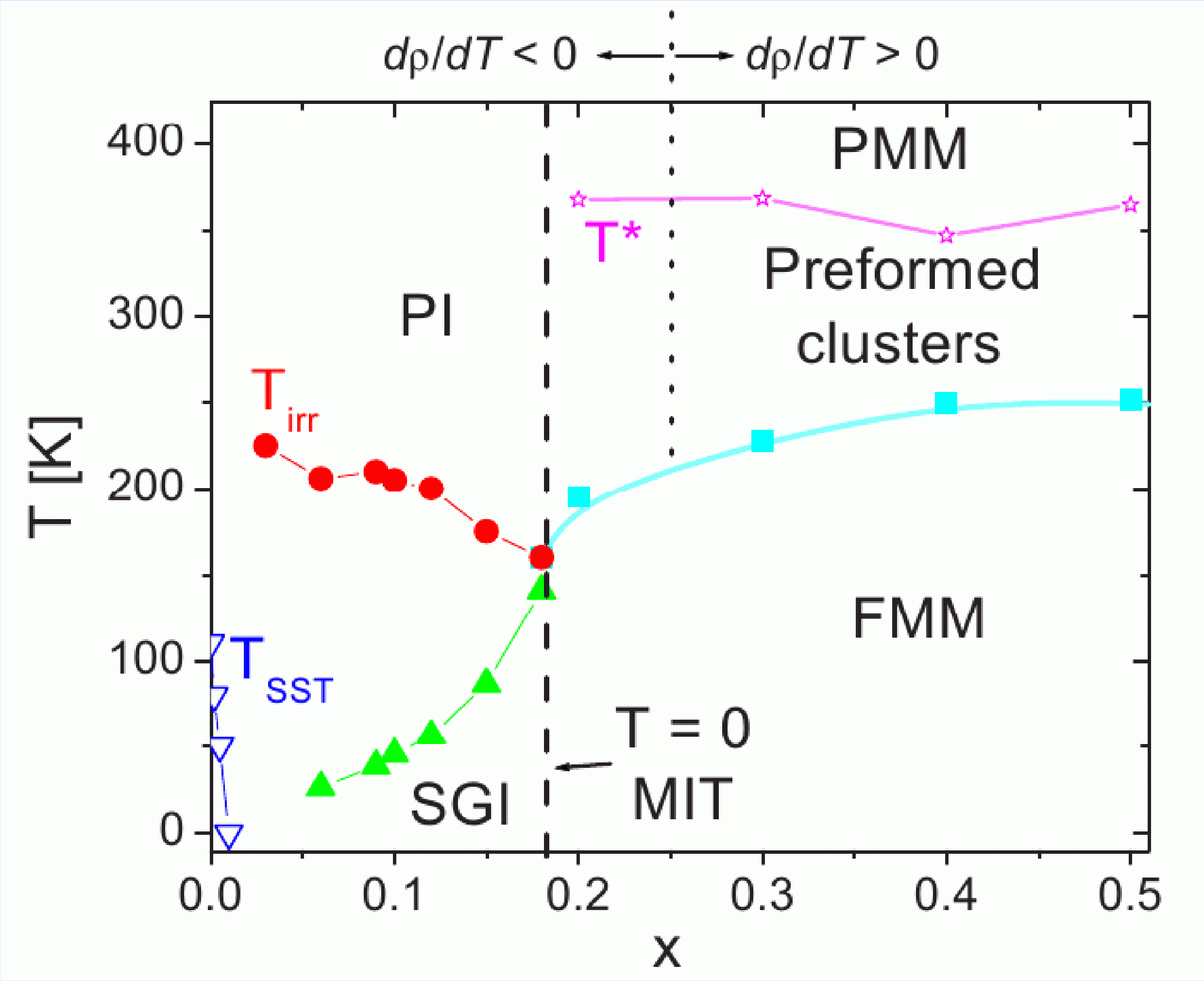
- Nanoparticles of $La_{1-x}Sr_xCoO_3$ are grown and characterized, with sizes 20 to 300nm.
- The neutron, X-ray and magnetometry techniques in bulk and nanoparticle powders cast doubt on intermediate state interpretations of the LSCO system and point instead to correlated electron effects. Holes from Sr doping are not on the Co sites, which remain Co^{+3}, but rather are associated with the O sites.
- Nanoparticles show very little magnetism and this correlates very strongly with the Co-O-Co bond angles as well as the pre-edge behavior in X-ray absorption studies.
- Convincing theoretical models are being developed that take into account the band structure and oxygen holes.
- The different behaviors in nanoparticles that depend on the growth technique need to be understood.

Thank you!

Early work supported by the DOE

Work for past two years supported by the ORNL Summer Visitor’s Program

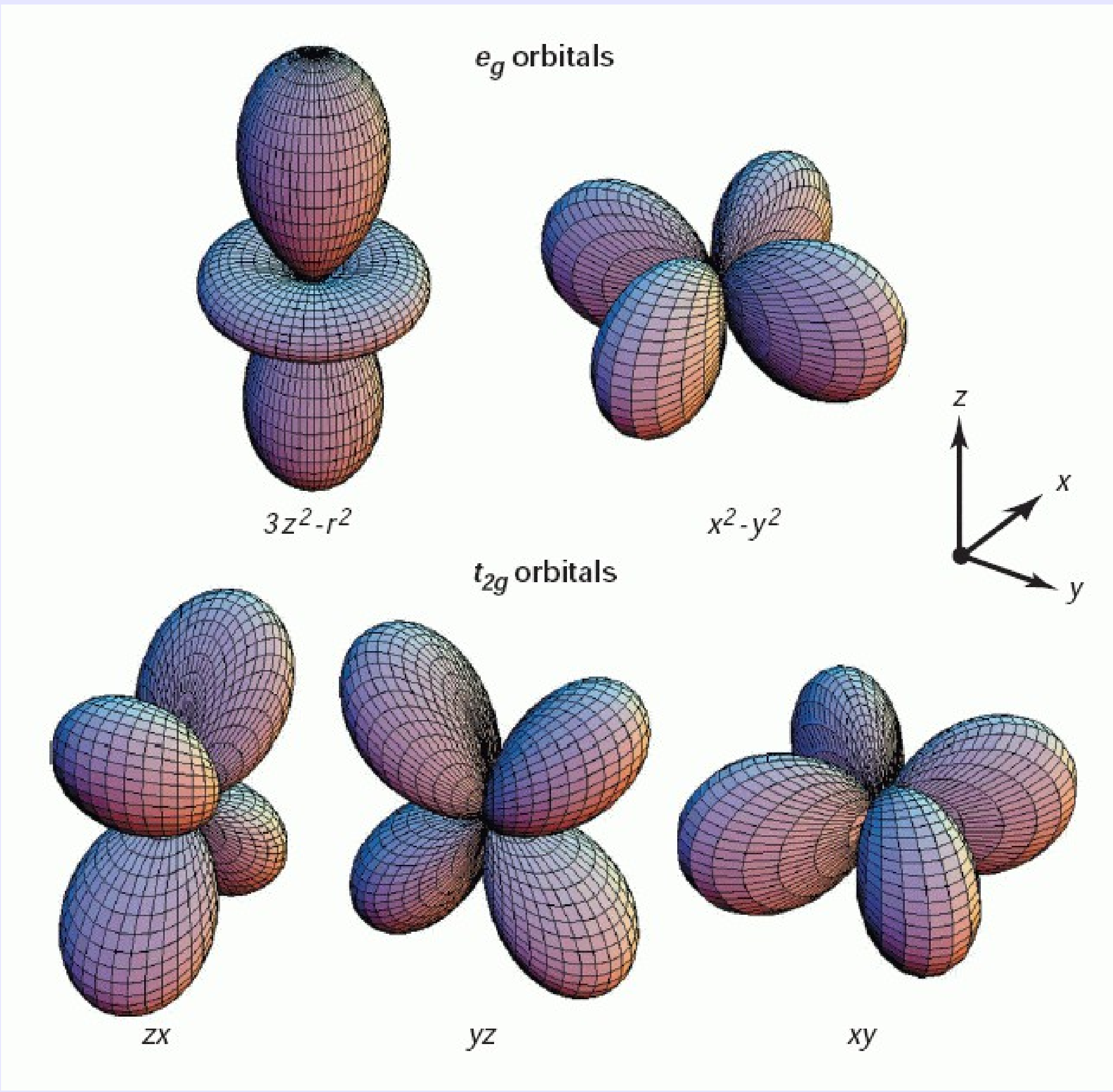
Phase Diagram LSCO bulk

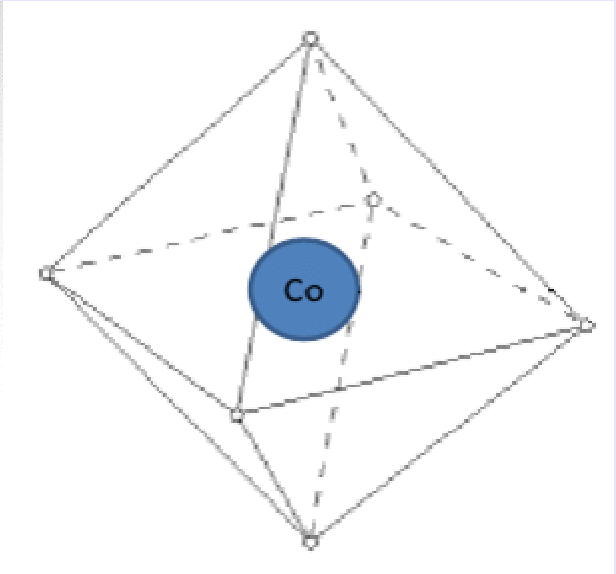


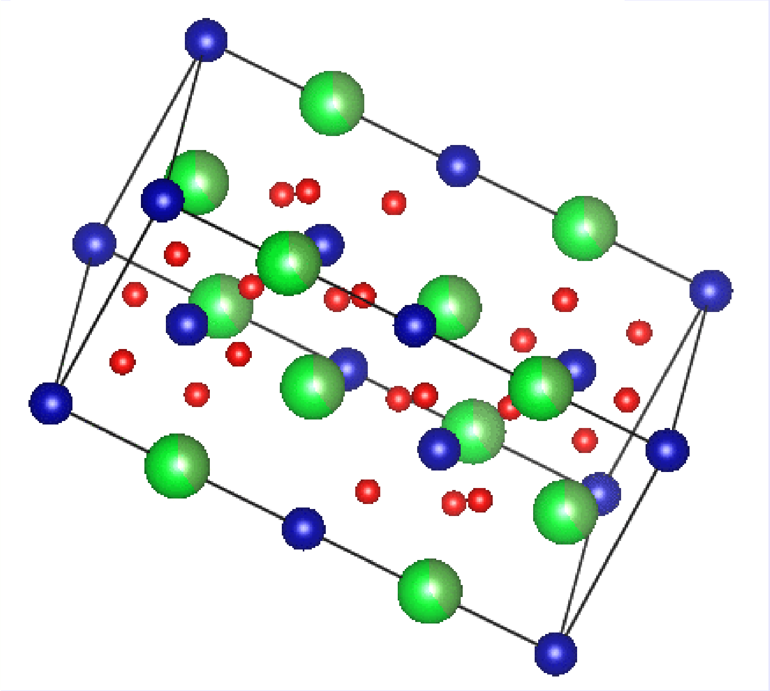
C. He, M. A. Torija, J. Wu, J. W. Lynn, H. Zheng, J. F. Mitchell, and C. Leighton, Phys. Rev. B **76**, 014401 (2007).

e_g and t_{2g} orbitals

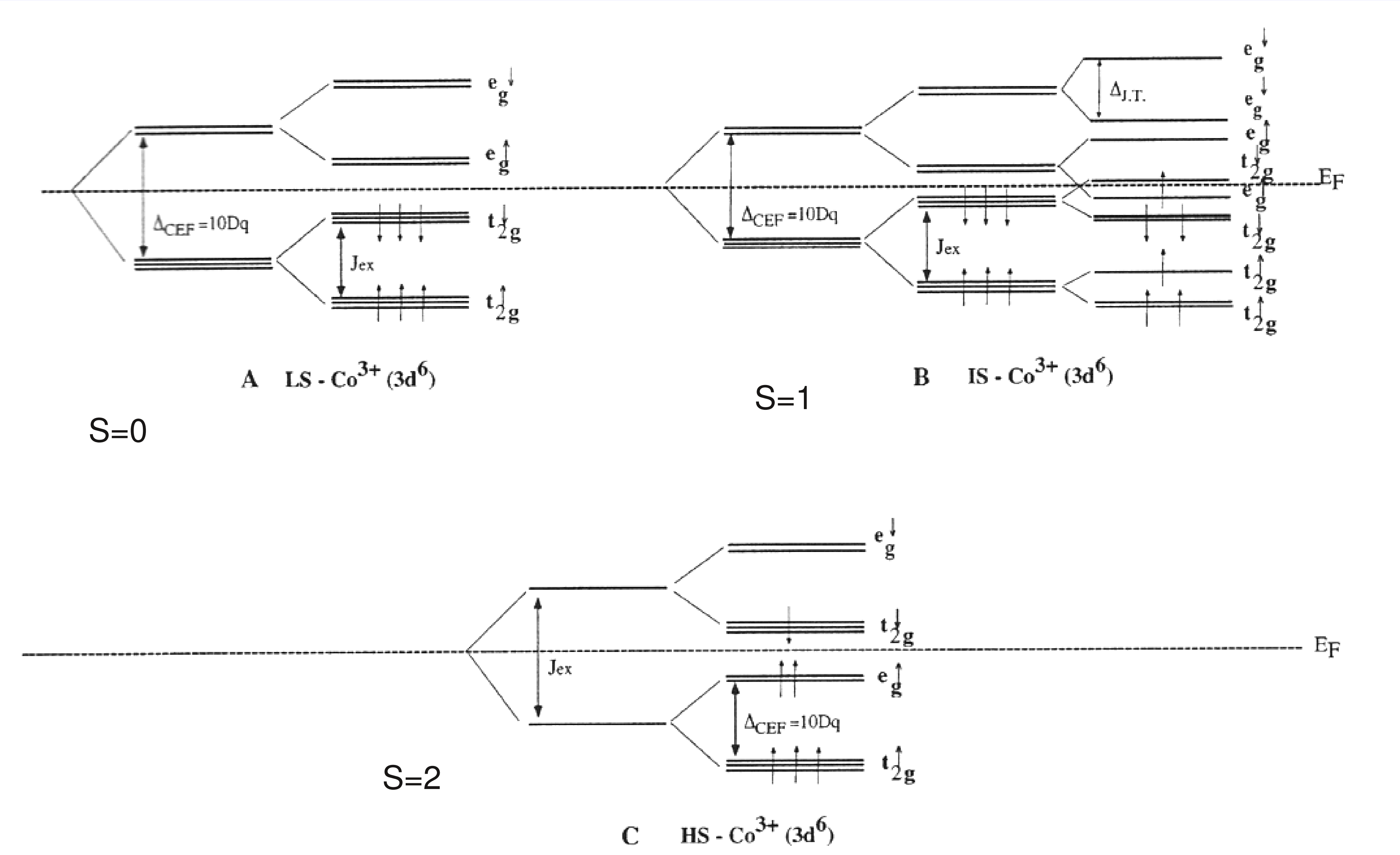
- Y. Tokura and N. Nagaosa, Science **288**, 462 (2008).







Possible Local Co Spin States in $LaCoO_3$ Toulemonde, et al., J. Solid St. Chem. **158**, 208 (2001)



nanoparticle growth

Nalini Sundaram, Alice Durand, Ingrid Anderson, Meghana Bhat
UCSC

$0.75La(NO_3)_3{*}6H_2O + 0.25Sr(NO_3)_2 + Co(NO_3)_2{*}6H_2O + 6H_2O + 4.75NaOH^-$

$\rightarrow 0.75La(OH)_3 + 0.25Sr(OH)_2 + Co(OH)_2 + 12H_2O + 4.75NaNO_3$

adding DTPA $C_{14}H_{23}N_3O_{10}$

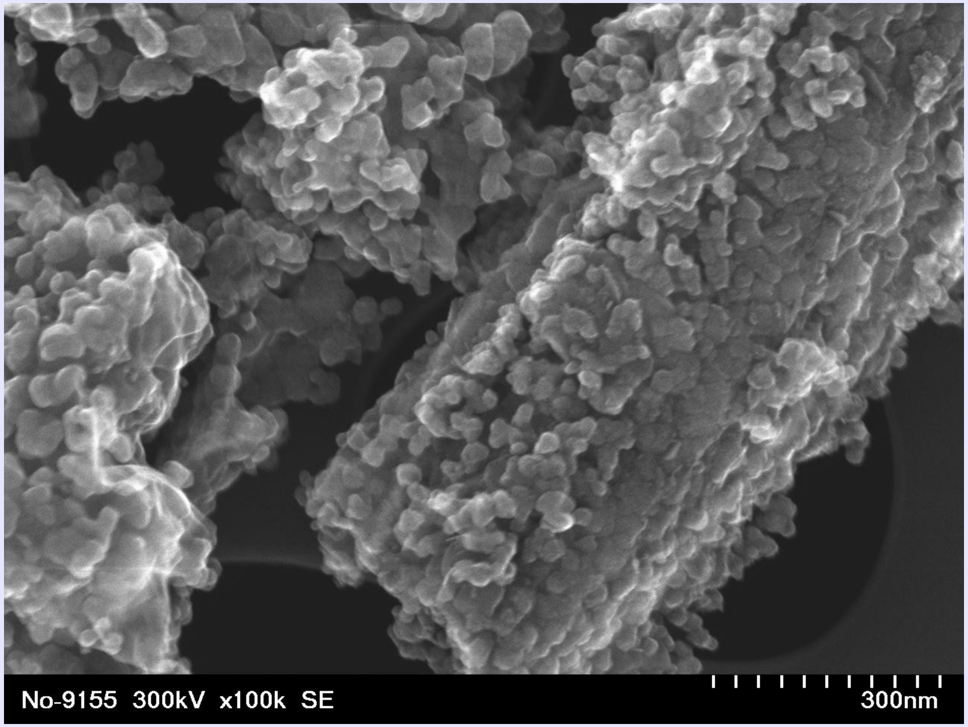
$0.75La(OH)_3 + 0.25Sr(OH)_2 + Co(OH)_2 + 0.95H_5DTPA^-$

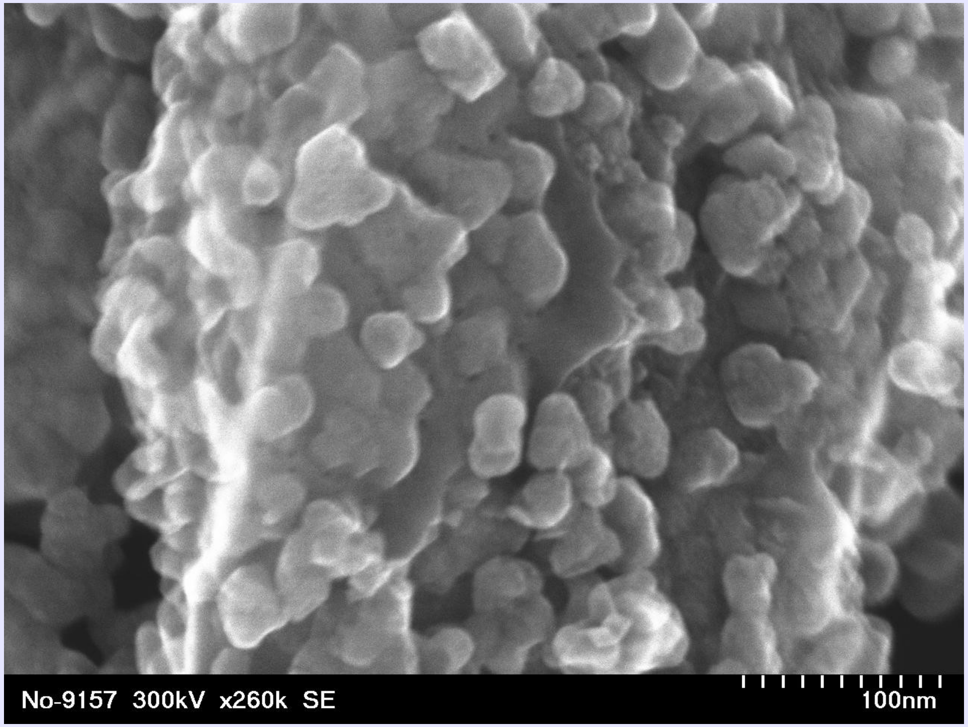
$\rightarrow La_{0.75}Sr_{0.25}CoO_?DTPA_{0.95}$ + (excess)DTPA + $4.75H_2O$

DTPA is removed by heating at 350^{o}C for 4 hours. Nanoparticles are formed in a tube furnace for 8 hours at calcination temperatures from 620^{o}C to 1100^{o}C.

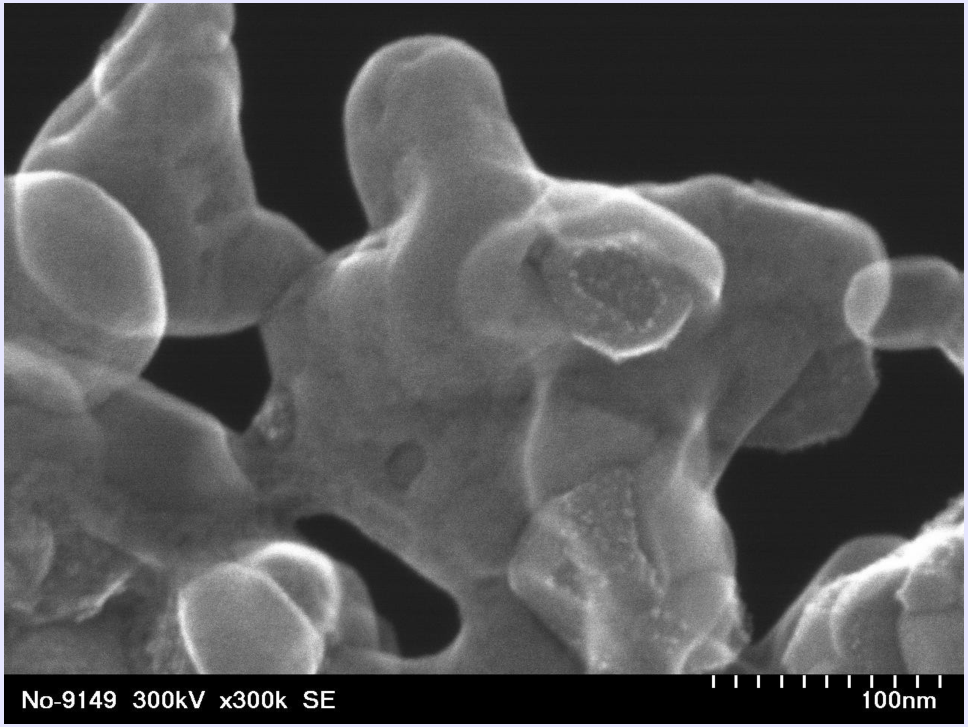
The particles are some of the older ones grown by Sundaram and Anderson that were used in the neutron PDF studies, to be discussed later in the talk. Note that the particles sizes are of order 20nm.

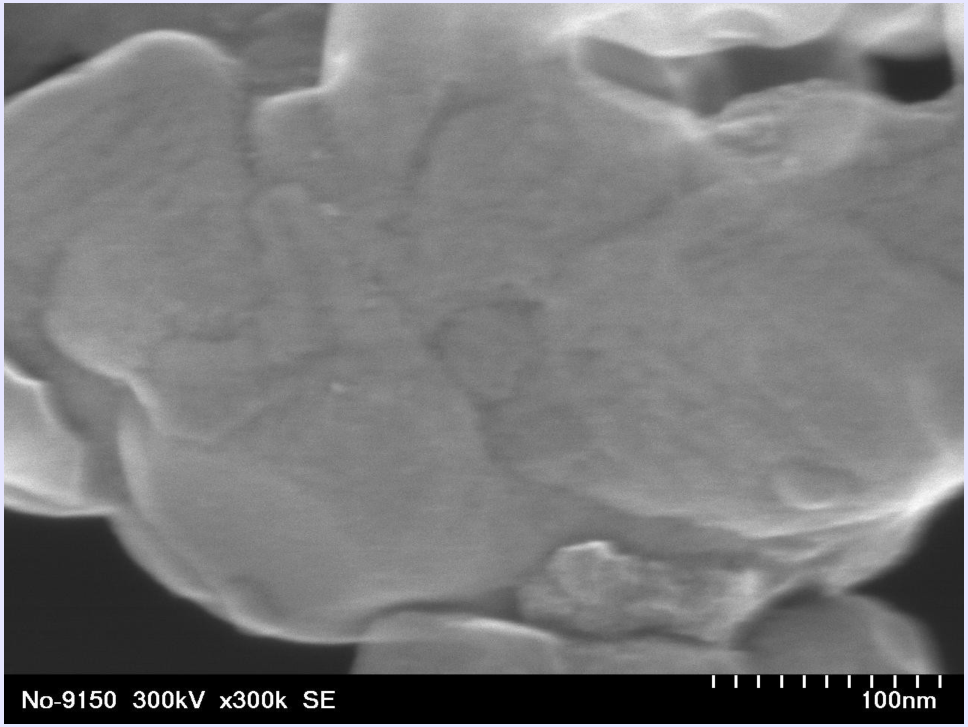
All of these images were made by Jane Howe, ORNL, using the Hitachi HF-3300 Electron microscope.

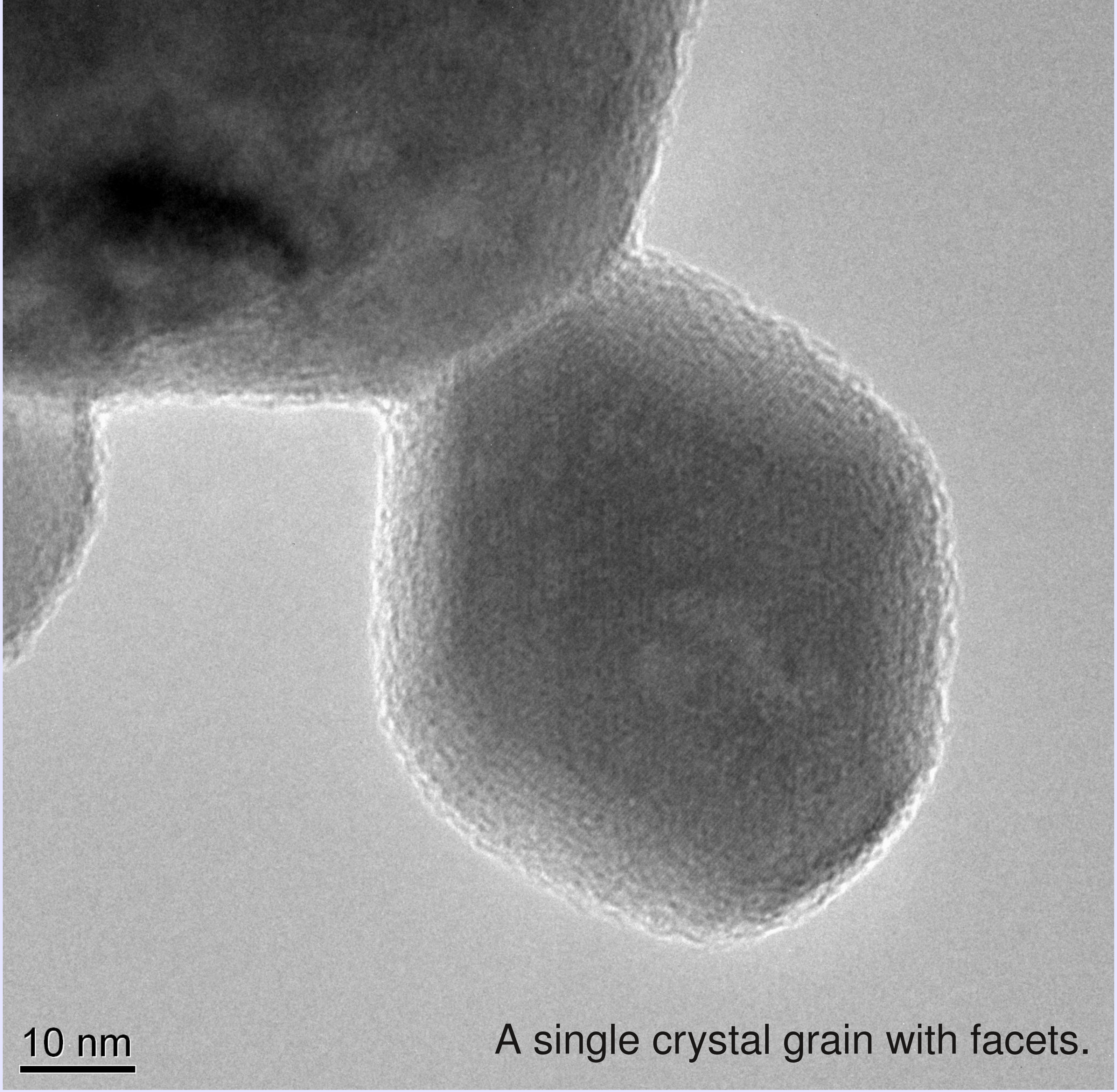




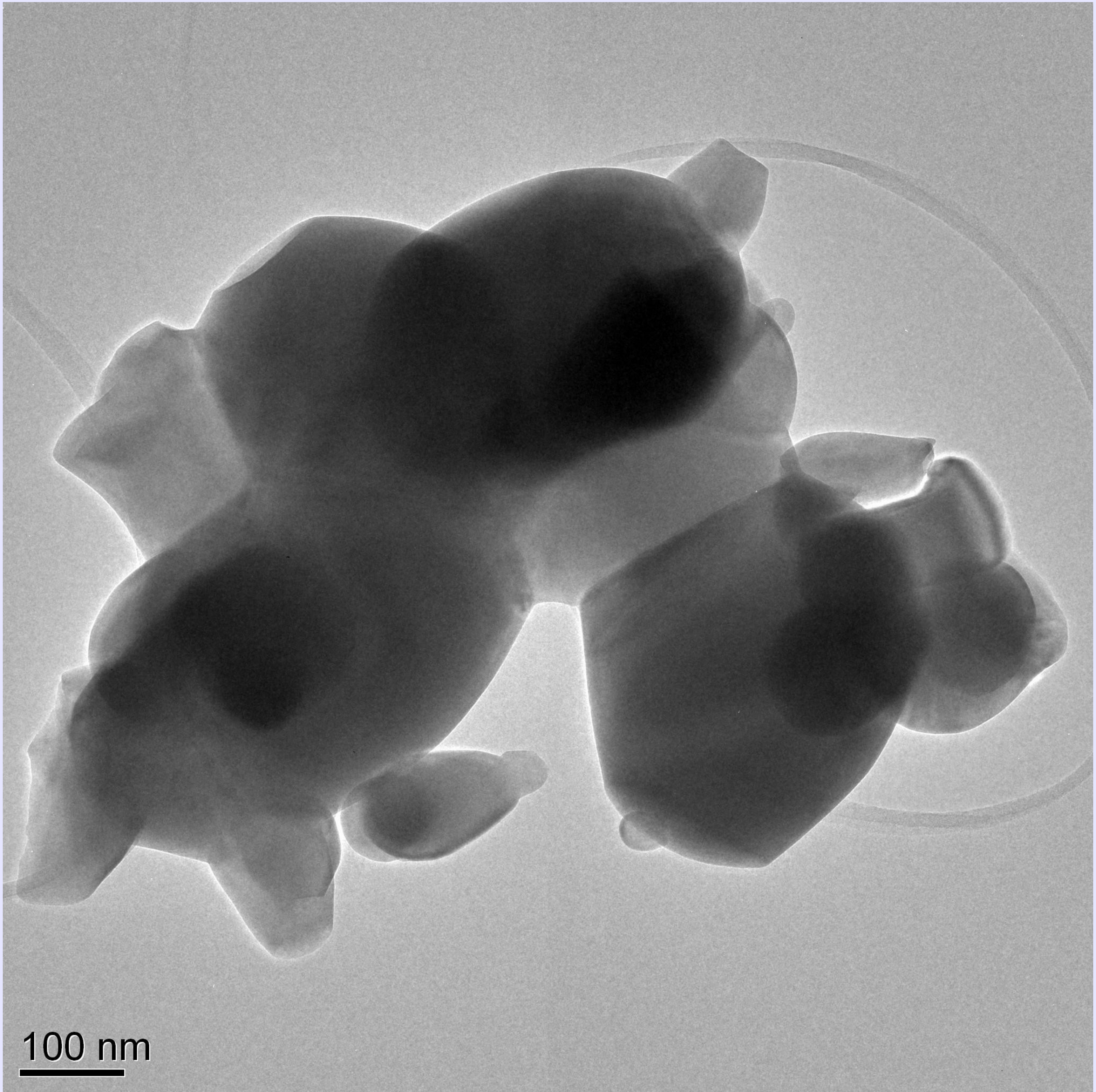
These particles were grown by Durand and Bhat this summer. Note that the particles can be nearly isolated or they can be imbedded. The very act of choosing particles to look at can distort the actual average particle property observations.



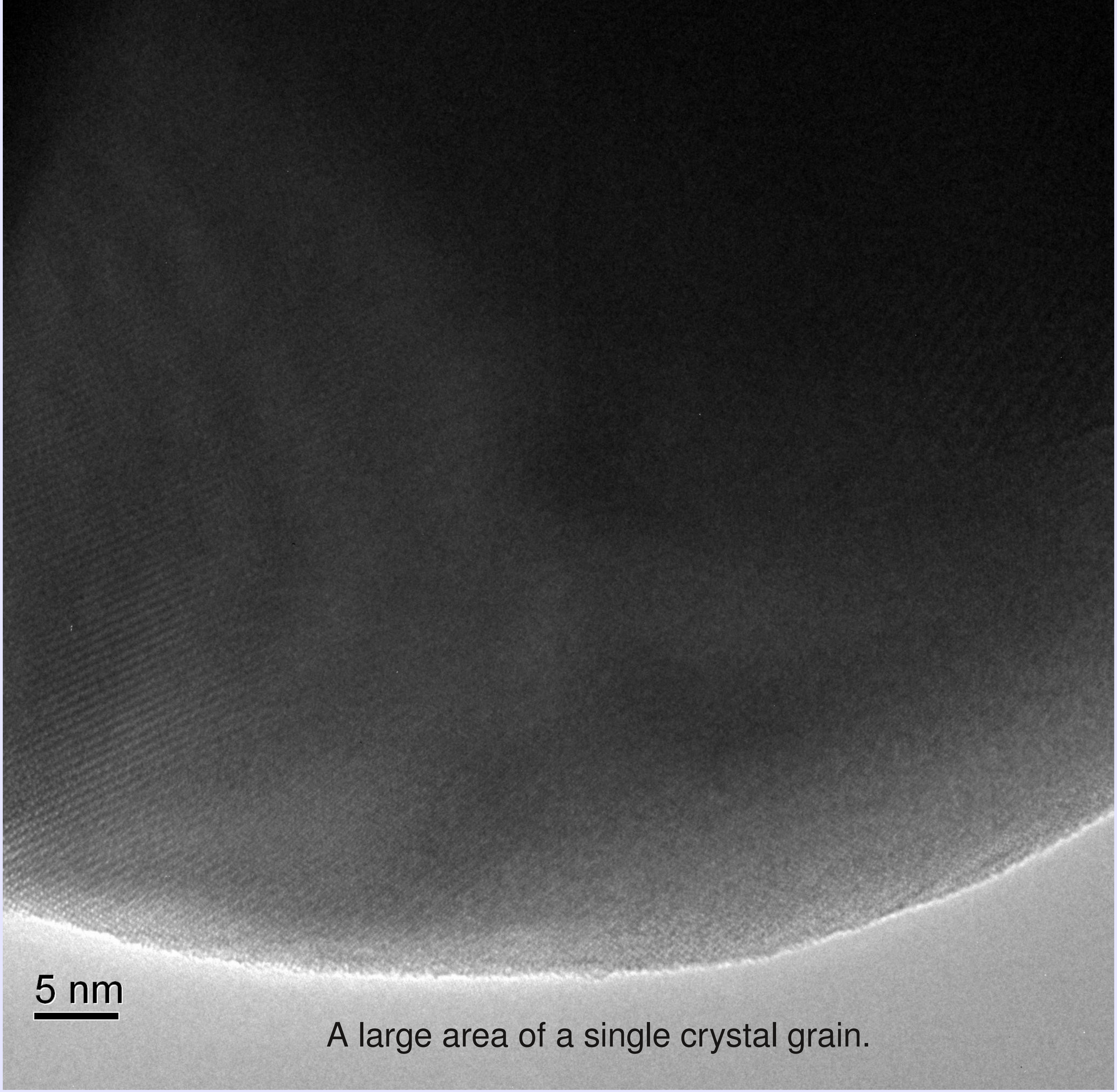




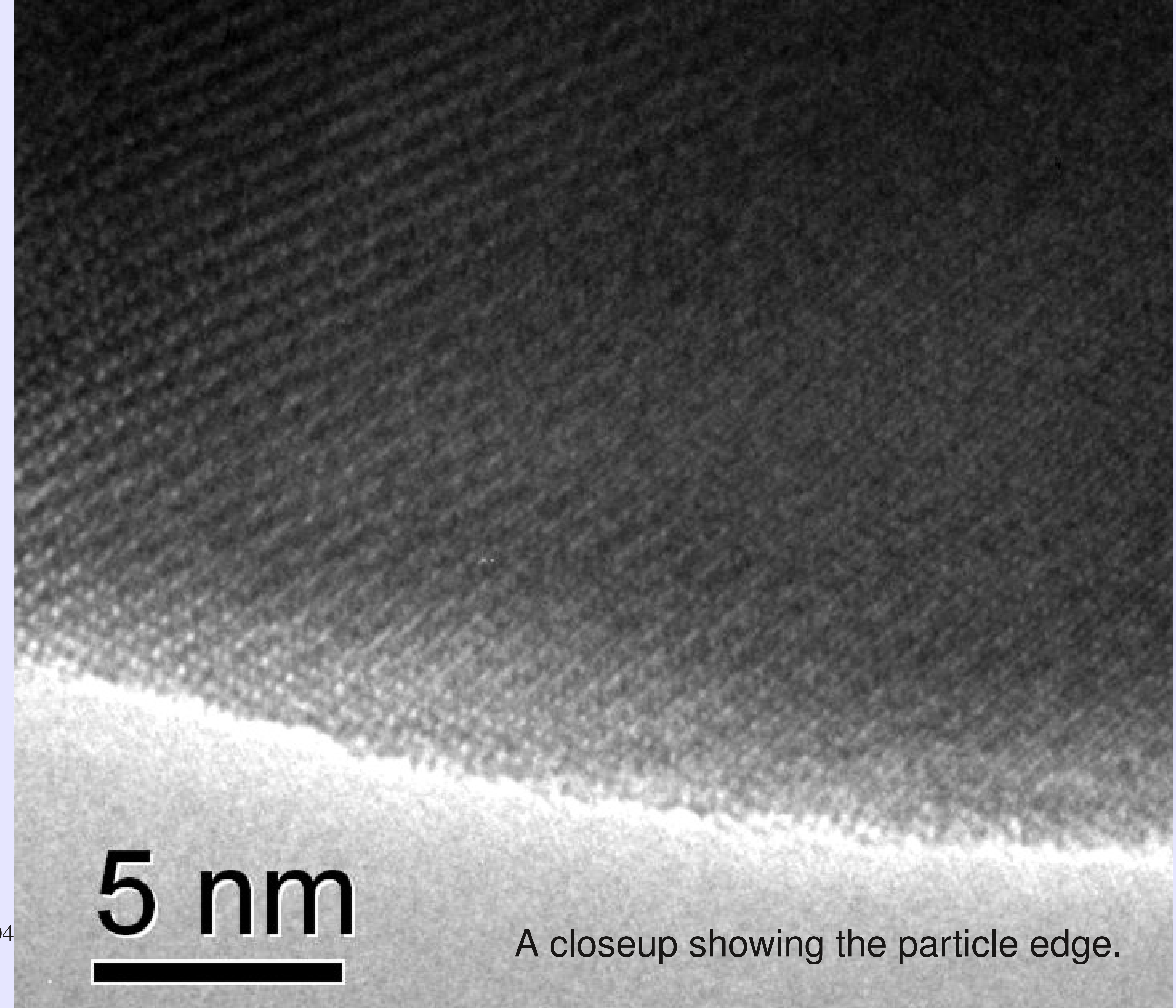
A single crystal grain with facets.



03/04/12

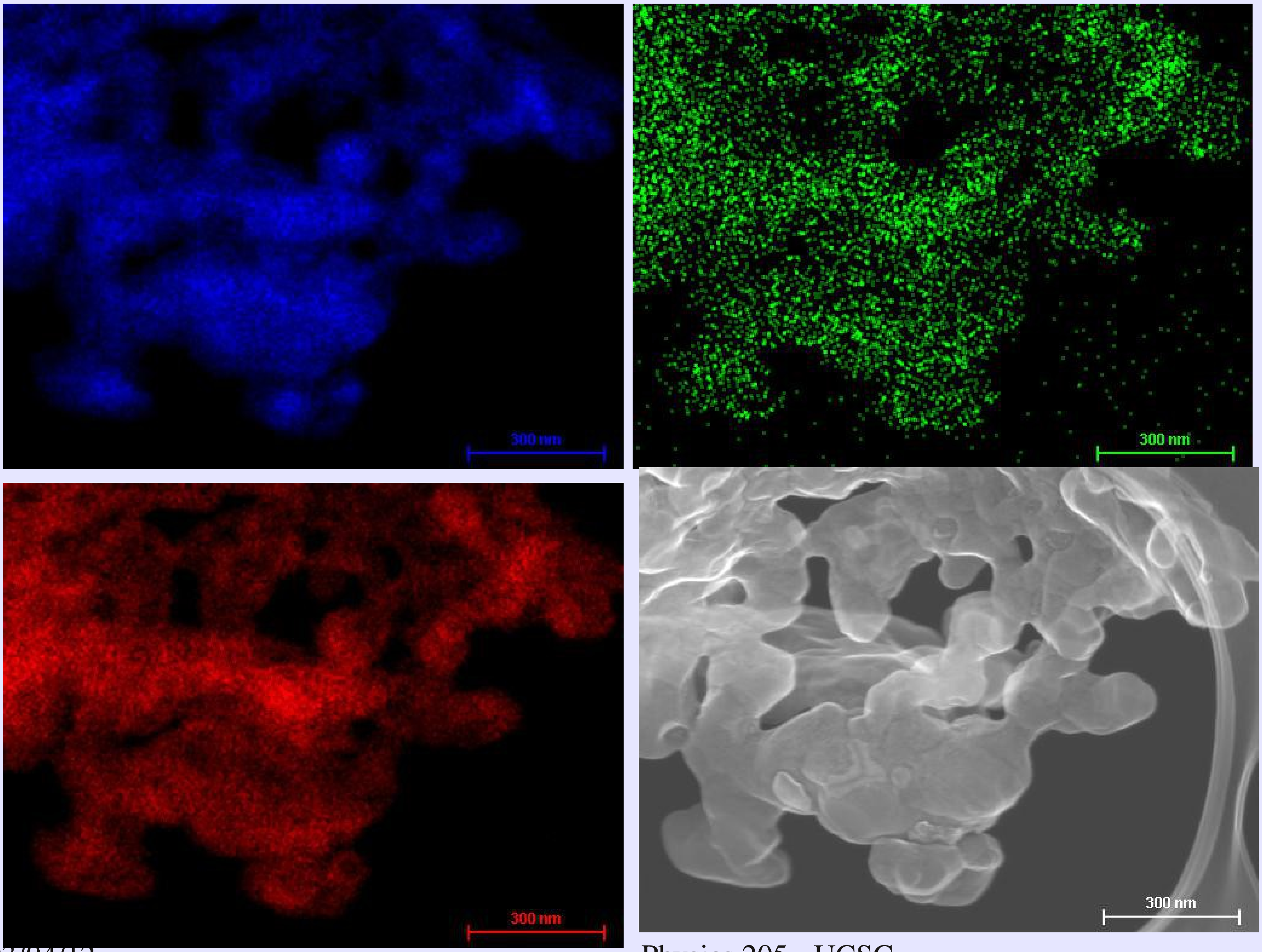


A large area of a single crystal grain.

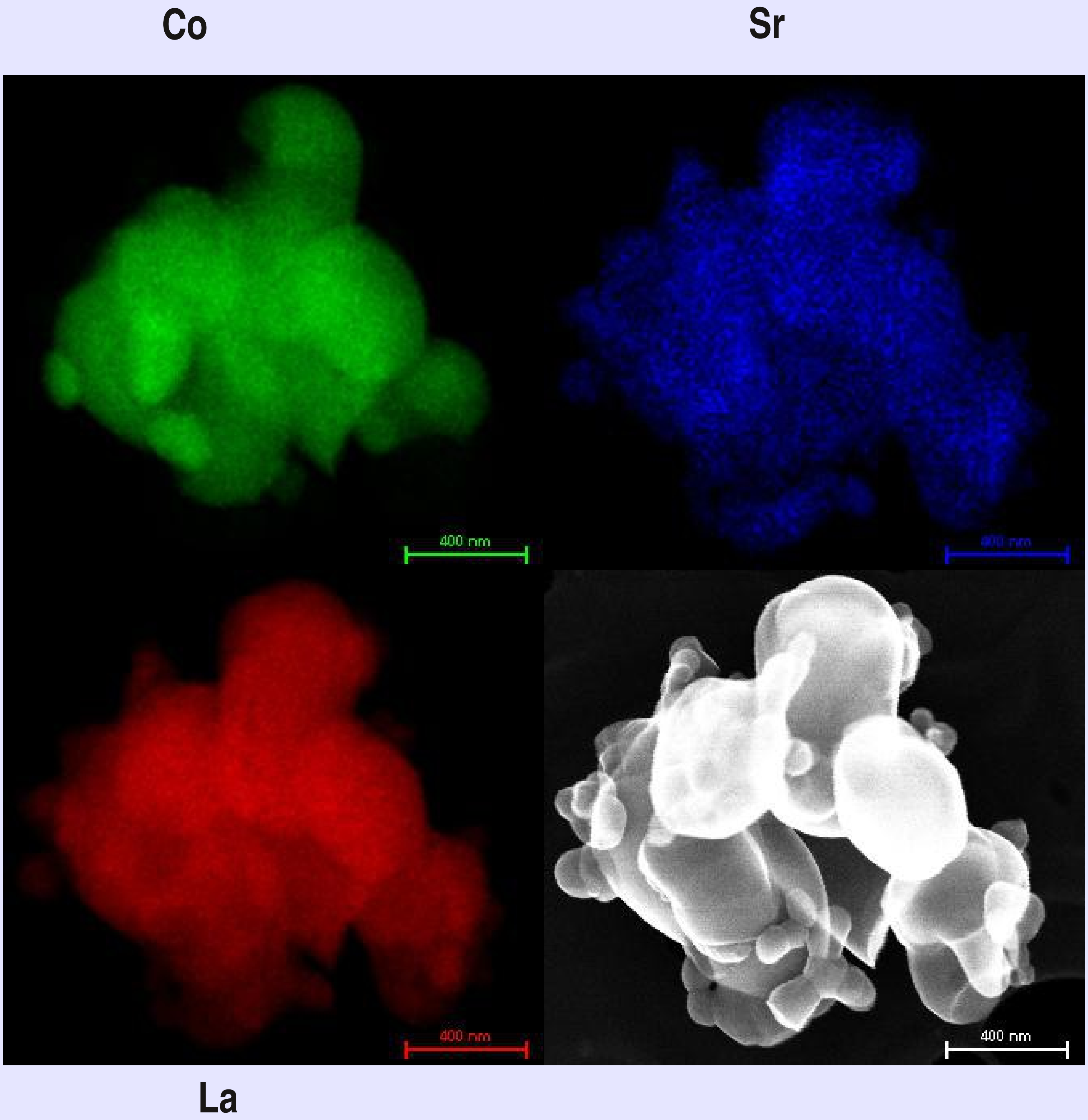


A closeup showing the particle edge.

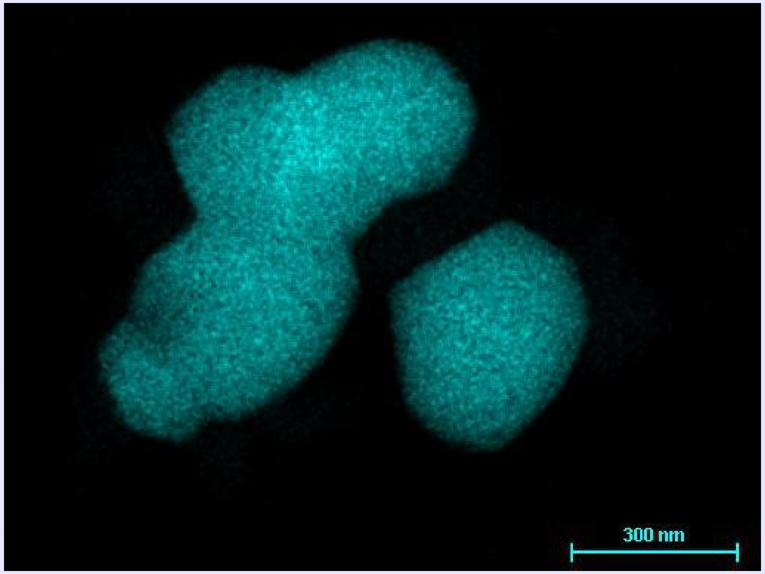
Co Sr



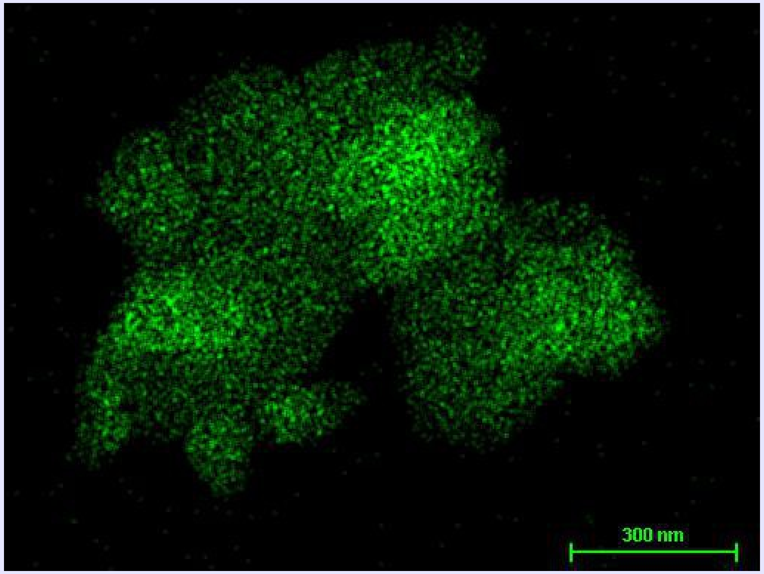
La

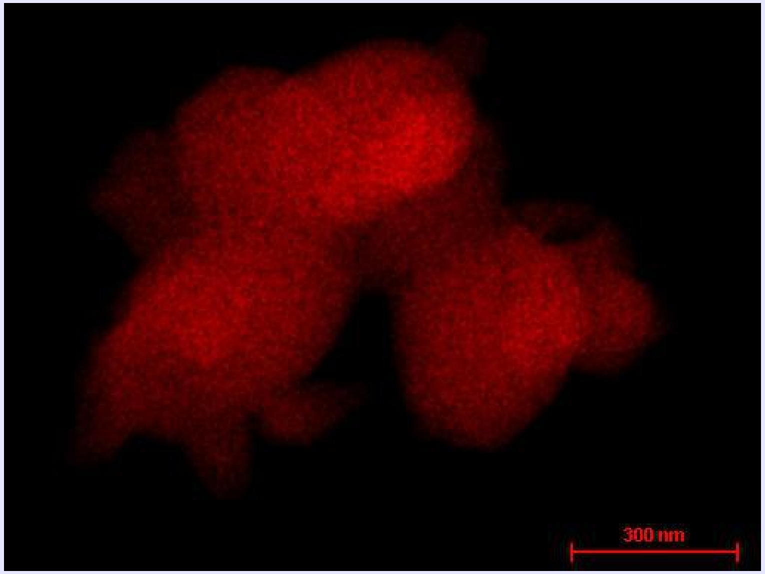

Co
Sr
400 nm
400 nm
400 nm
400 nm
La

Co

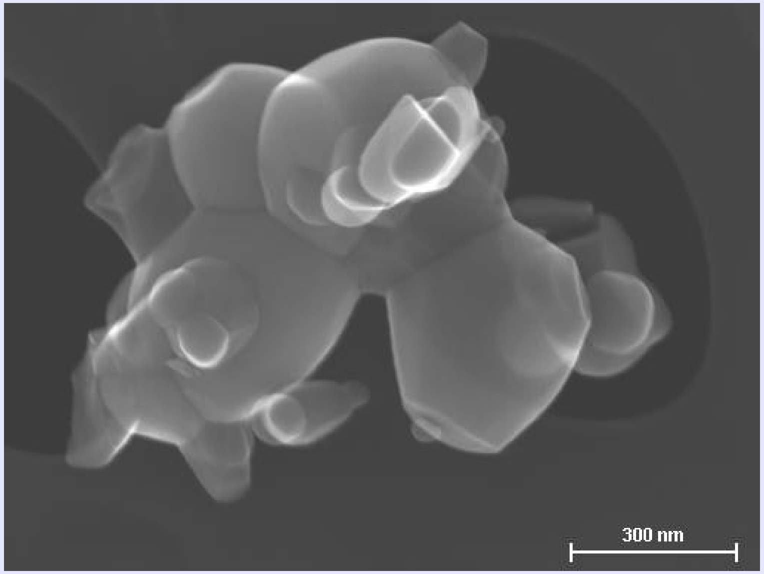


Sr

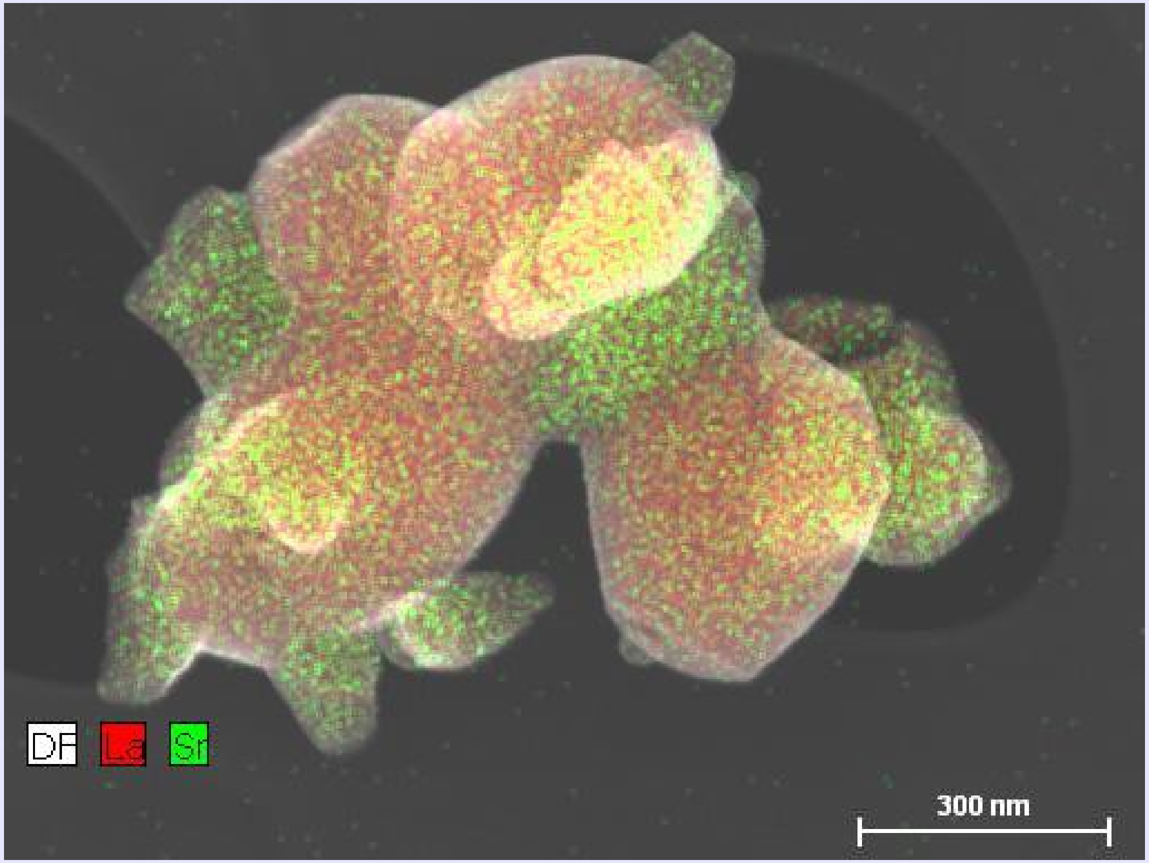




La



When there are impurities, they tend to form their own particles that may be attached to the LSCO particles. We are still working to find the best particle growth techniques to minimize impurities and yield the most uniform particles in size and Sr concentration.



pair distribution function

atomic pair distribution function (PDF)

$\rho(r) = \rho_0 g(r) = \frac{1}{4\pi N r} \sum_\nu \sum_\mu \delta(r - r_{\nu\mu})$

ν, μ indicate individual atoms

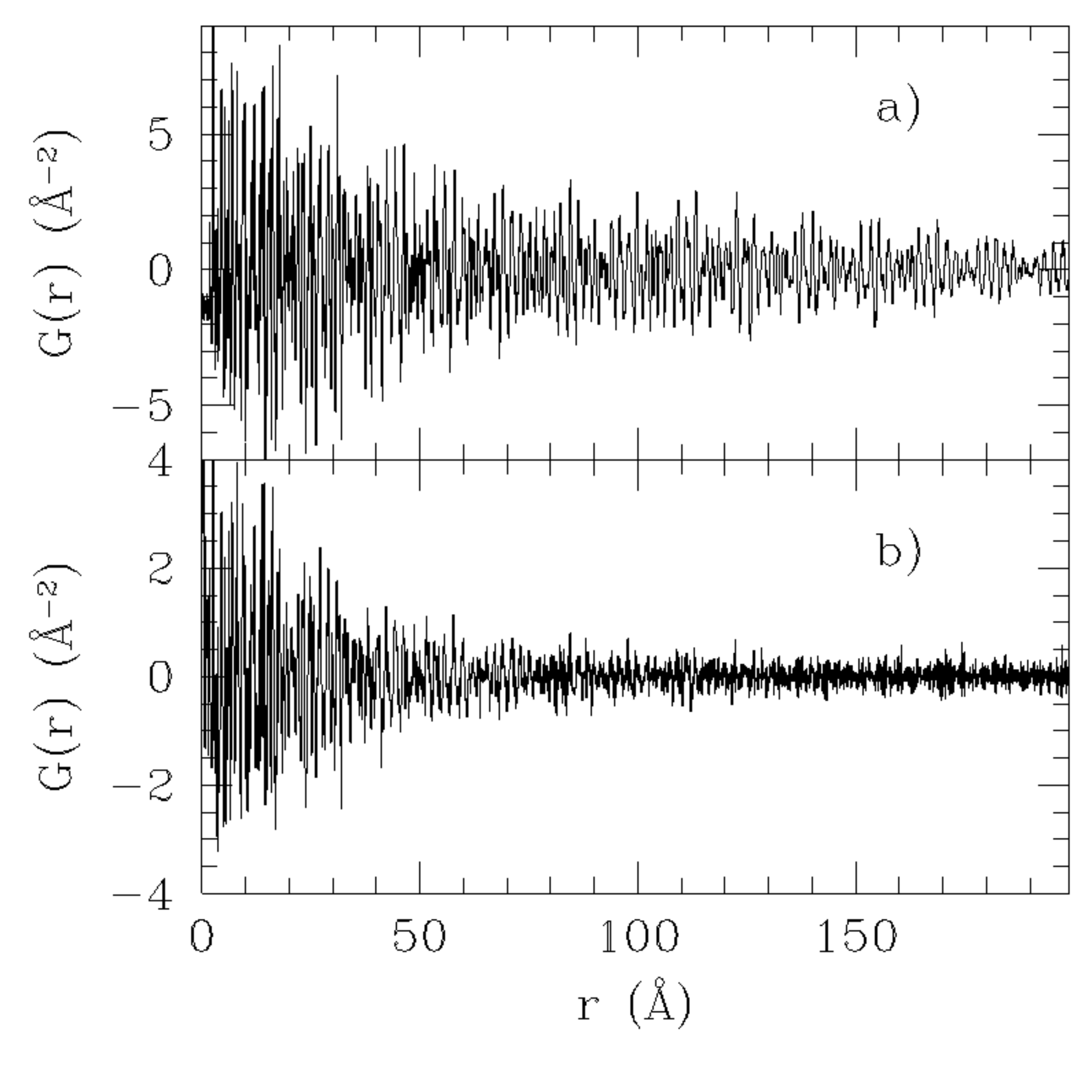
ρ_0 is number density of atoms

$G(r) = 4\pi\rho_0(g(r) - 1)$

$G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ$

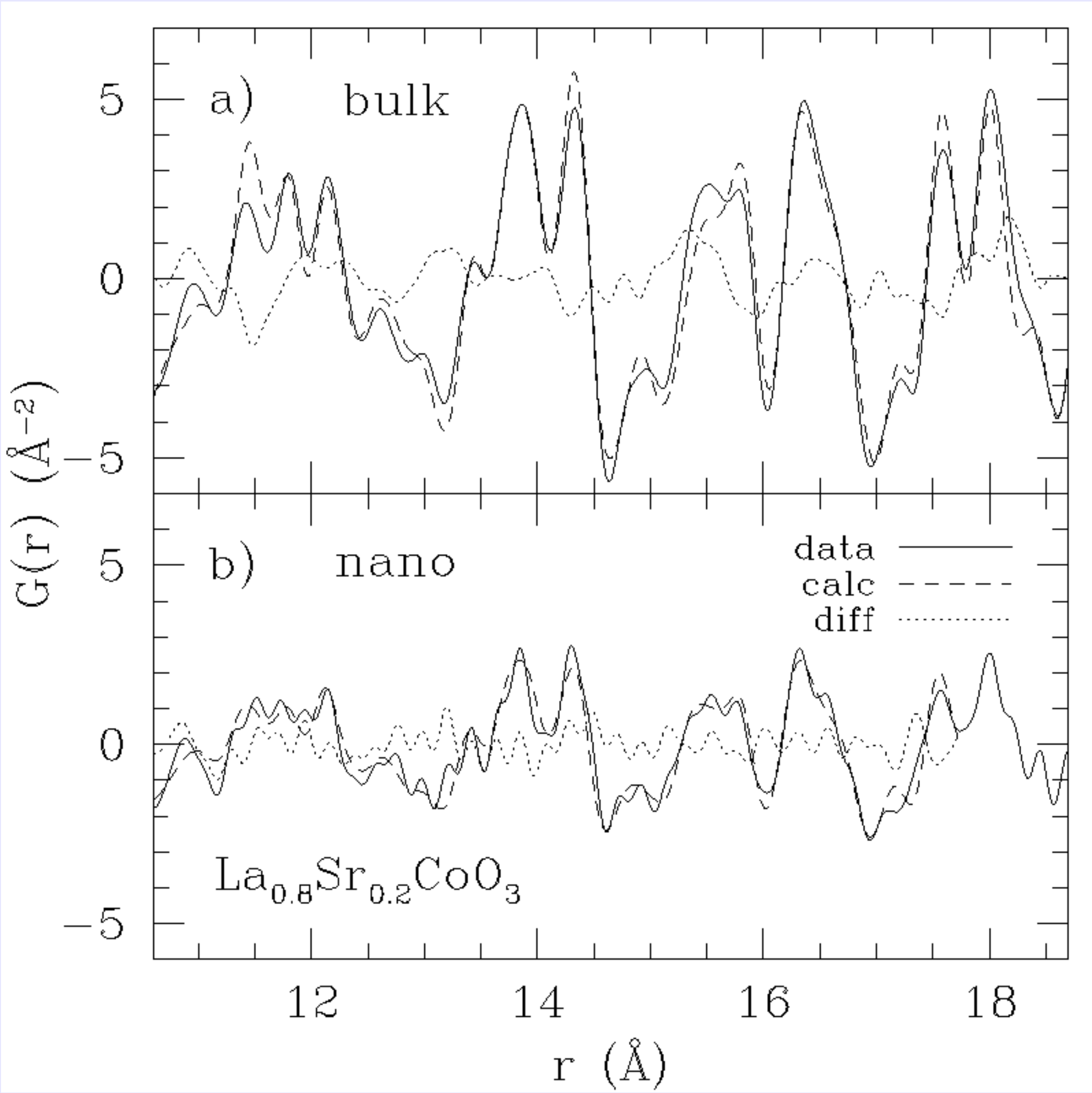
$S(Q)$ is the scattering intensity, structure factor

PDF of bulk and nanoparticle powders



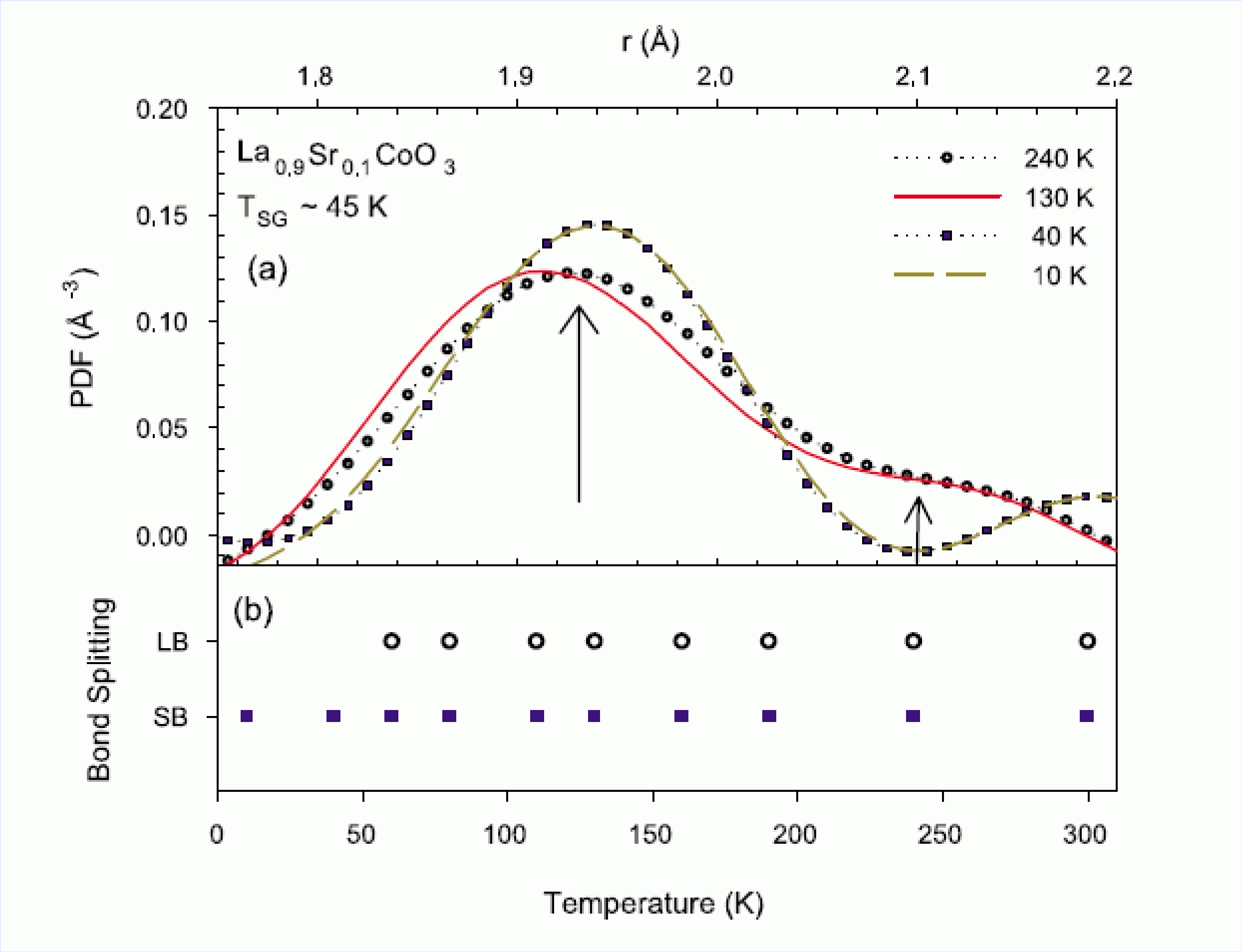
- *G(r)* in $La_{0.8}Sr_{0.2}CoO_3$ bulk powder sample.
- *G(r)* in $La_{0.8}Sr_{0.2}CoO_3$ nanoparticle powder sample. Correlations drop off as the particle size is approached, as expected.

PDF of bulk and nanoparticle powders



- *G(r)* in $La_{0.8}Sr_{0.2}CoO_3$ bulk powder sample at intermediate length scales.
- *G(r)* in $La_{0.8}Sr_{0.2}CoO_3$ nanoparticle powder sample. Correlations show the same structure as the bulk at least out to about 15nm.

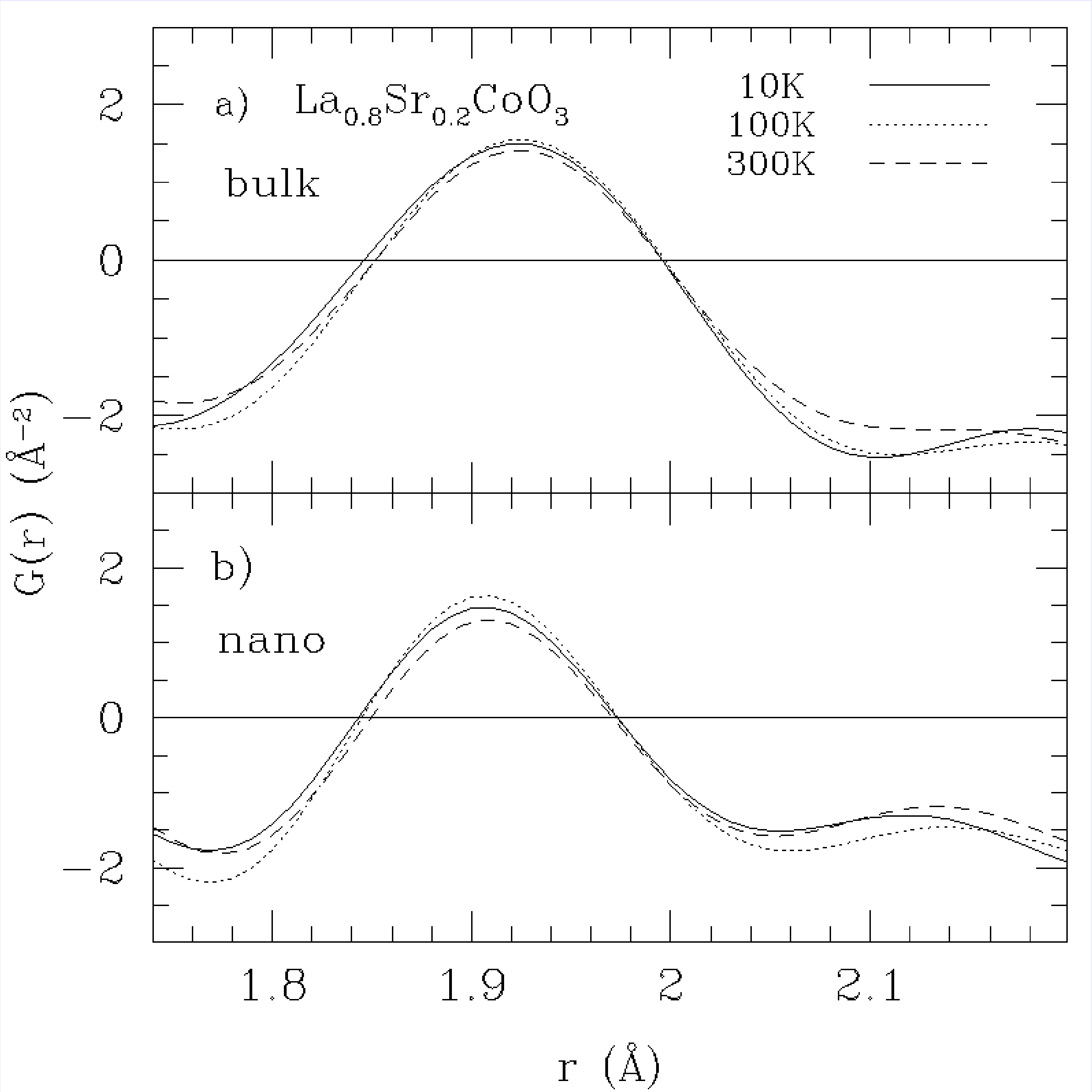
Previous Data of Jahn-Teller Distortion in Cobaltite



A previous neutron PDF study indicated a large J-T distortion, with the second peak at 2.1 Å only for temperatures of 50K or higher, but not at very low temperature. D. Louca and J.L. Sarrao, Phys. Rev. Lett. **91**, 155501 (2003). Many different experimental techniques indicated this as well.

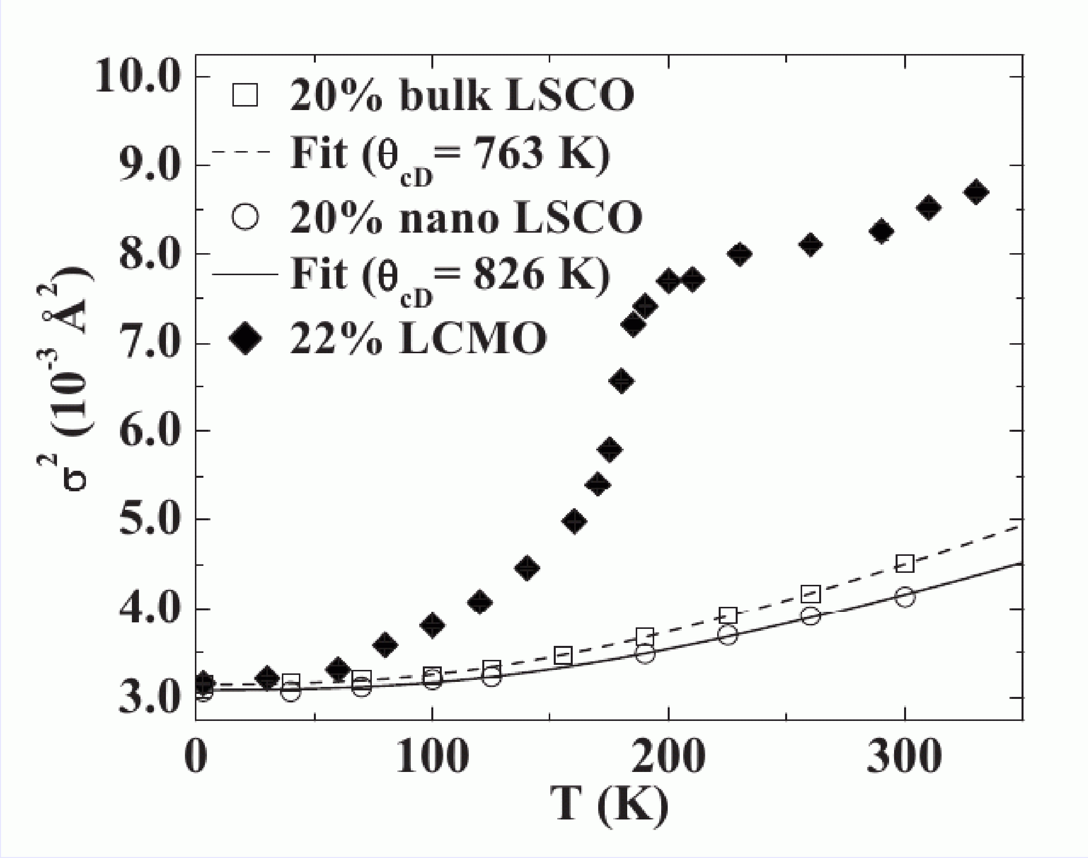
However, in our studies, we observed the distortion in neither bulk nor nanoparticle LSCO.

No J-T distortion in either bulk or nanoparticle powders



- The Co-O bond length shows no evidence for a distortion. The small peak is a result of the Fourier transform.
- There could be a very small distortion, or it could be only on a few sites.

EXAFS evidence against a large local Jahn-Teller distortion in the cobaltites

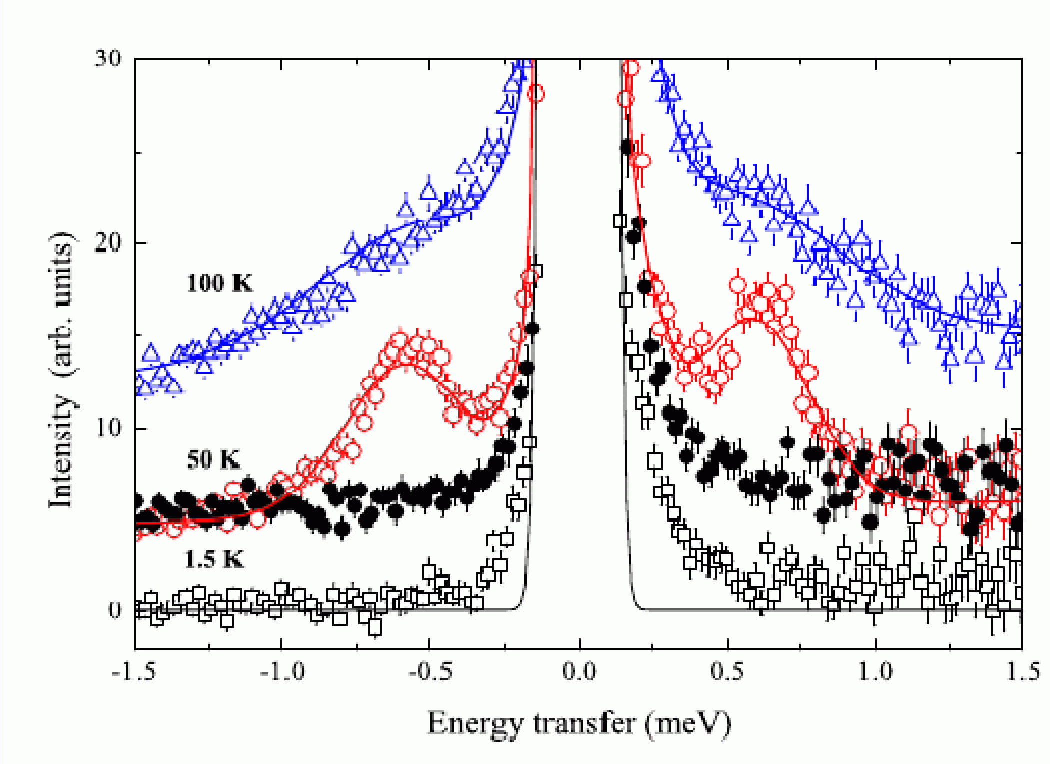


$\sigma^2 = \sigma_{static}^2 + \sigma_{phonon}^2 + \sigma_{J\text{-}T}^2$

The mangantites show a Clear J-T distortion below 200K.

The cobaltite bulk and nanoparticle systems show no J-T distortion, meaning it is either non-existent, or represents a very small distortion or few sites.

Excitations in bulk LCO

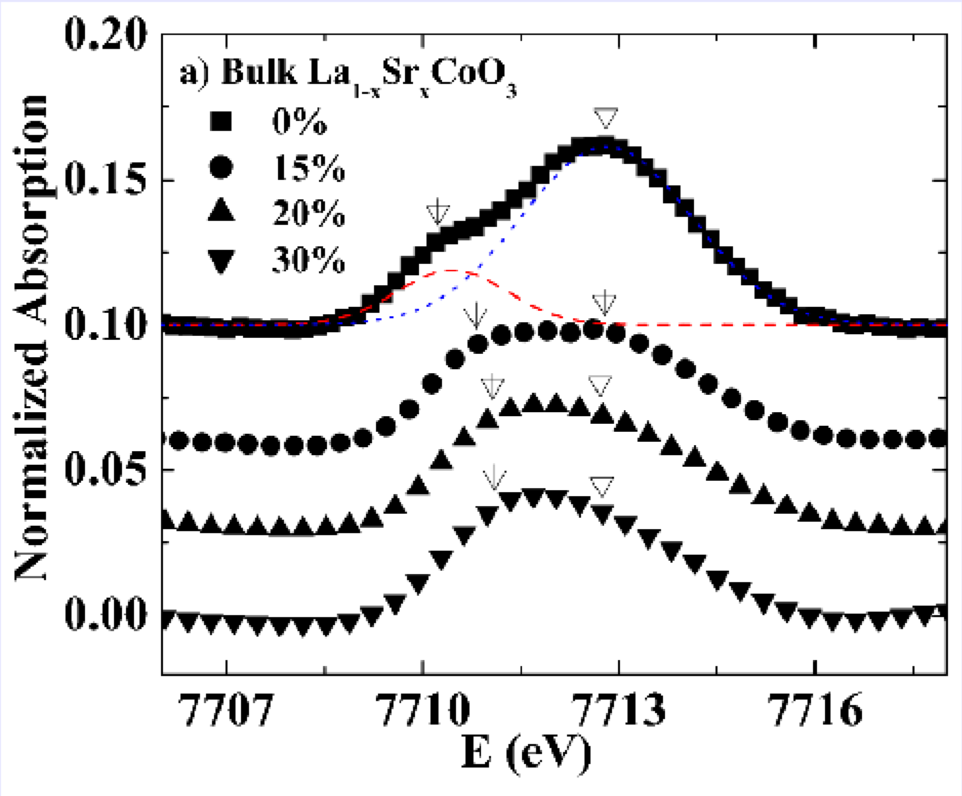


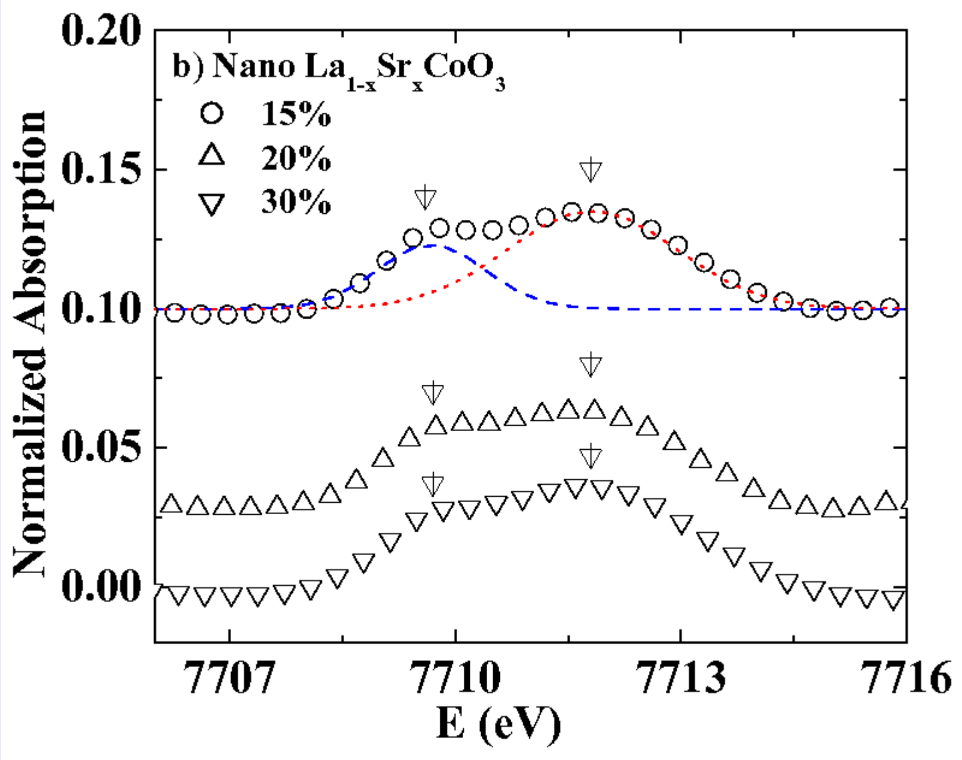
Podlesnyak, et al. were among the first to show experimentally that the transition at 90K was to the HS and not the IS, based on the observed excitations and the value of g ~3, compatible with 3.35 < g < 3.55 obtained by Noguchi, et al. The IS state would require g=2.

A. Podlesnyak, S. Streule, J. Mesot, M. Medarde, E. Pomjakushina, K. Condor, A. Tanaka, M. W. Haverkort, and D. I. Khomskii, Phys. Rev. Lett. 97, 247208 (2006)

S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, Phys. Rev. B 66, 094404 (2002).

X-ray absorption pre-edge peaks

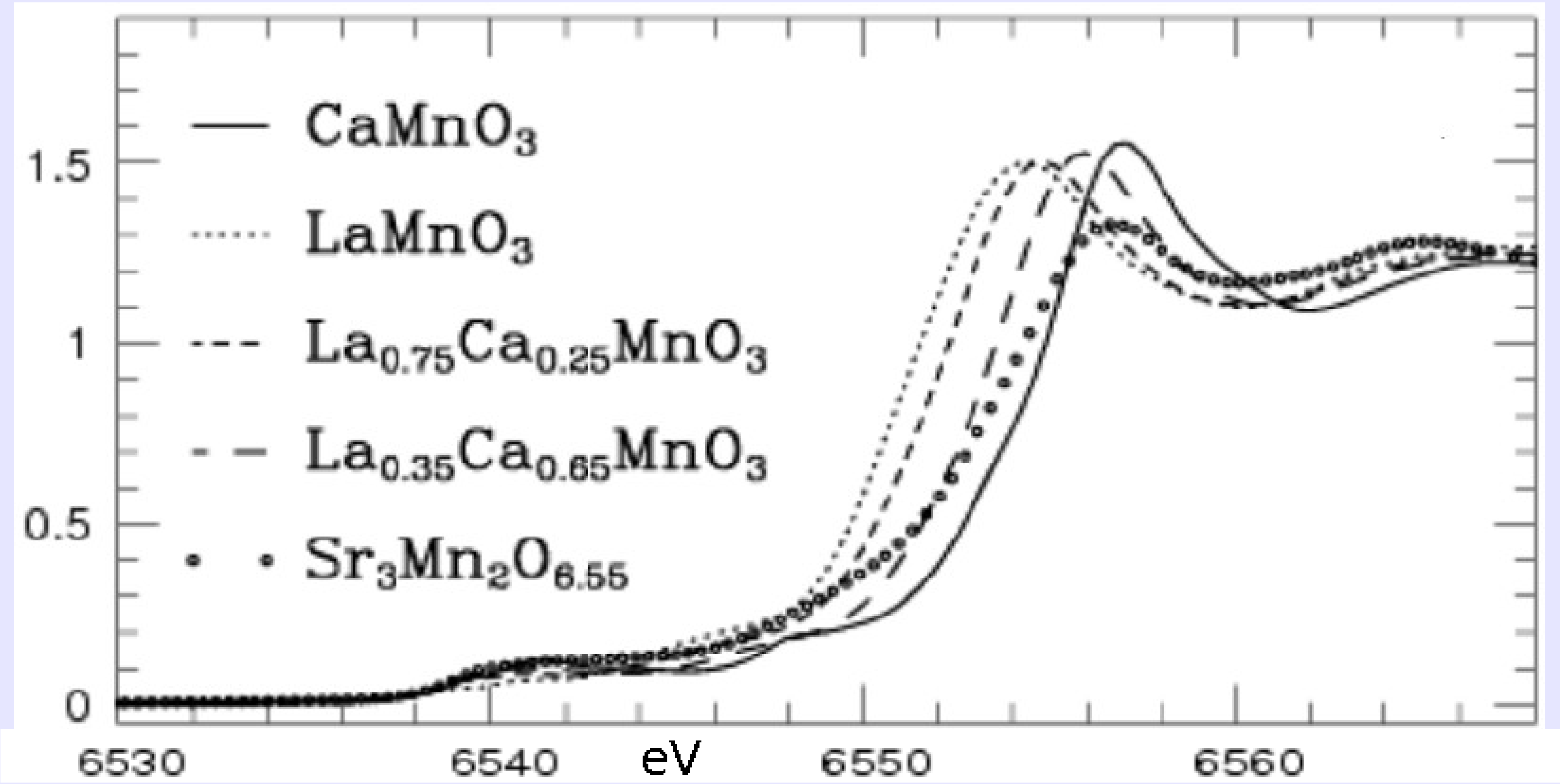




The main edge is 1s4p dipolar, the lower pre-edge is 1s3d quadrupolar and the upper pre-edge is a non-local 1s3d mediated by O and 4p/3d hybridization and has slightly less core screening (Vanko, et al. ArXiv:0802.2744v1)

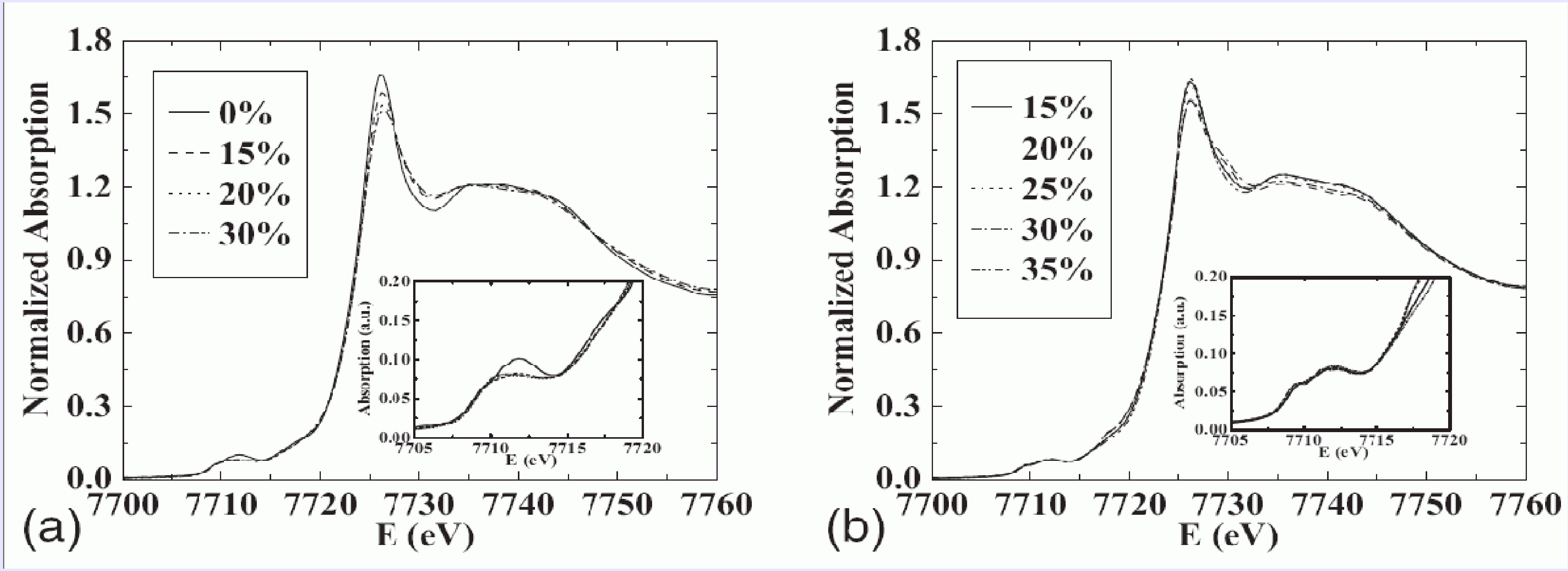
Bulk particles show a merging of the pre-edge peaks, but not the nanoparticles.

Typical shift in the x-ray absorption edge with doping



A typical shift in the edge with doping, in this case a manganite system. The shift is approximately 3eV/valence unity as Mn^{+3} changes to Mn^{+4}.
F. Bridges, et al., Phys. Rev. B 63, 214405 (2001).

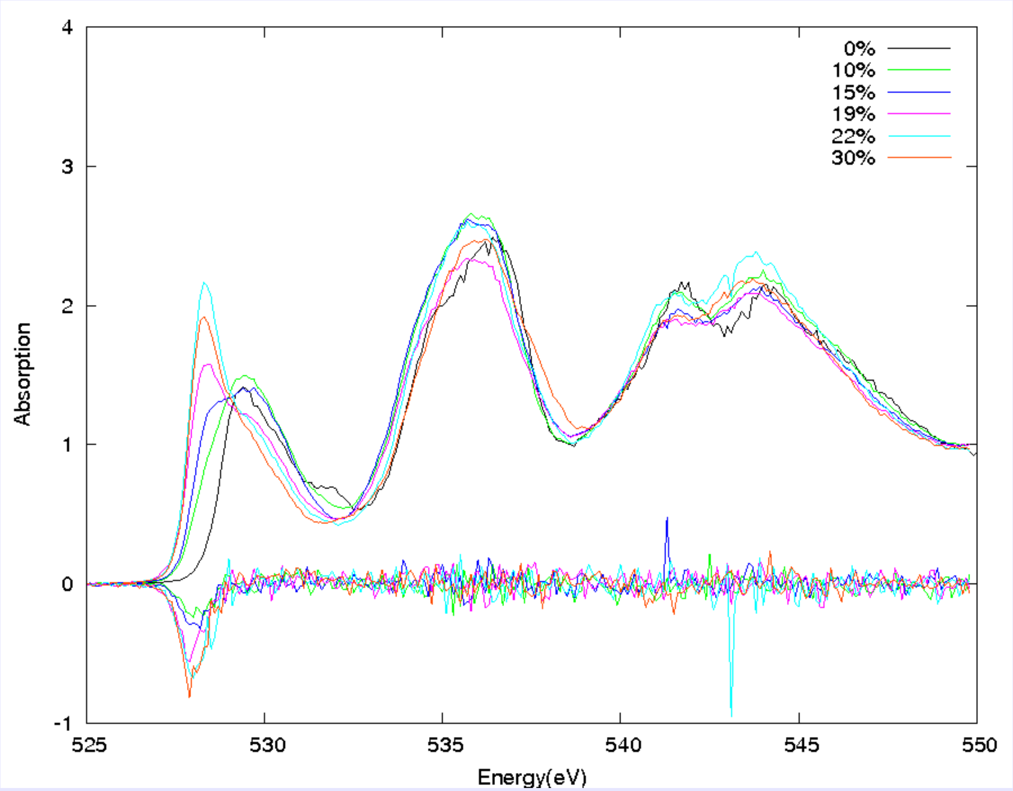
Lack of a shift in the x-ray absorption edge with Sr doping



The Co-K edge hardly shifts with Sr doping in either the bulk or nanoparticle Powders, which is not typical.

This indicates that the Co ions remain Co^{+3}, which suggests that holes are associated with the O ions, consistent with the observed small change in Co-O bond lengths.

X-ray magnetic dichroism: O K-edge for x ranging from 0 to 0.30

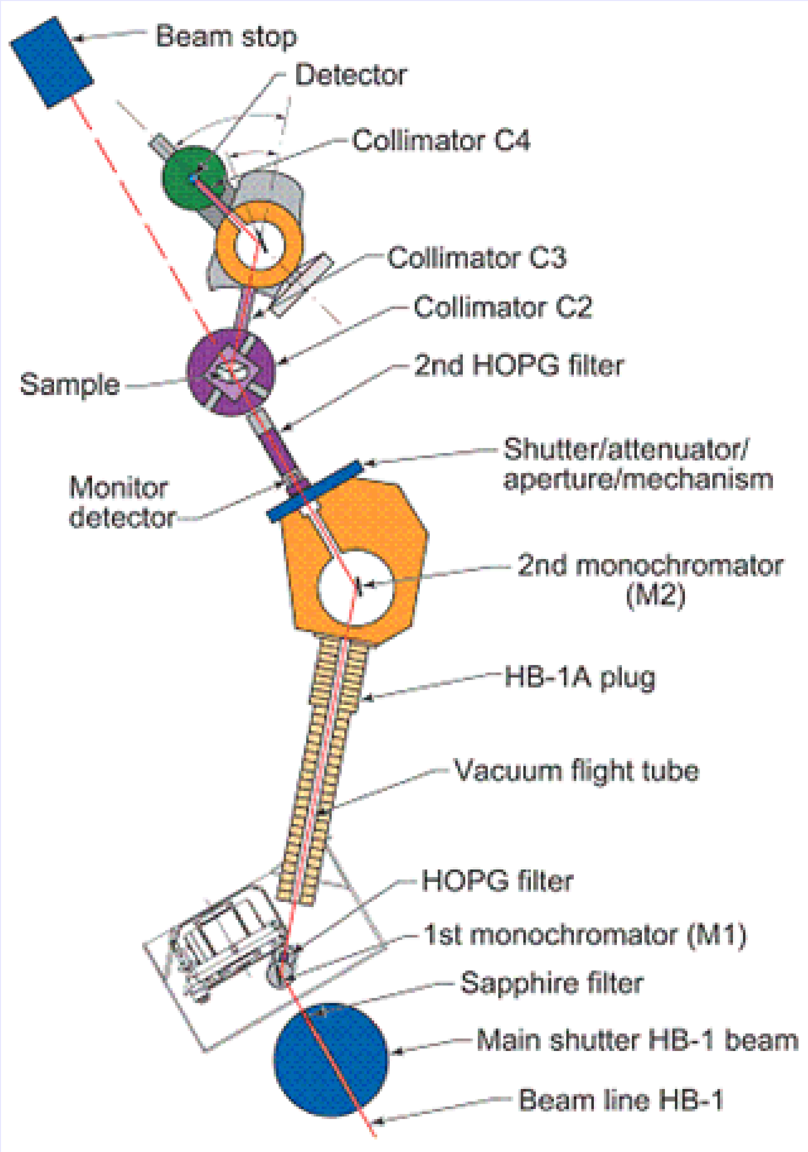


XAS in upper part, XMCD in lower part

Oxygen K-edge magnetic signal indicates magnetism and, therefore, holes are associated with the O sites

S. Medling, F. Bridges, J. W. Freeland, J. Mitchell, and H. Zheng (2010)

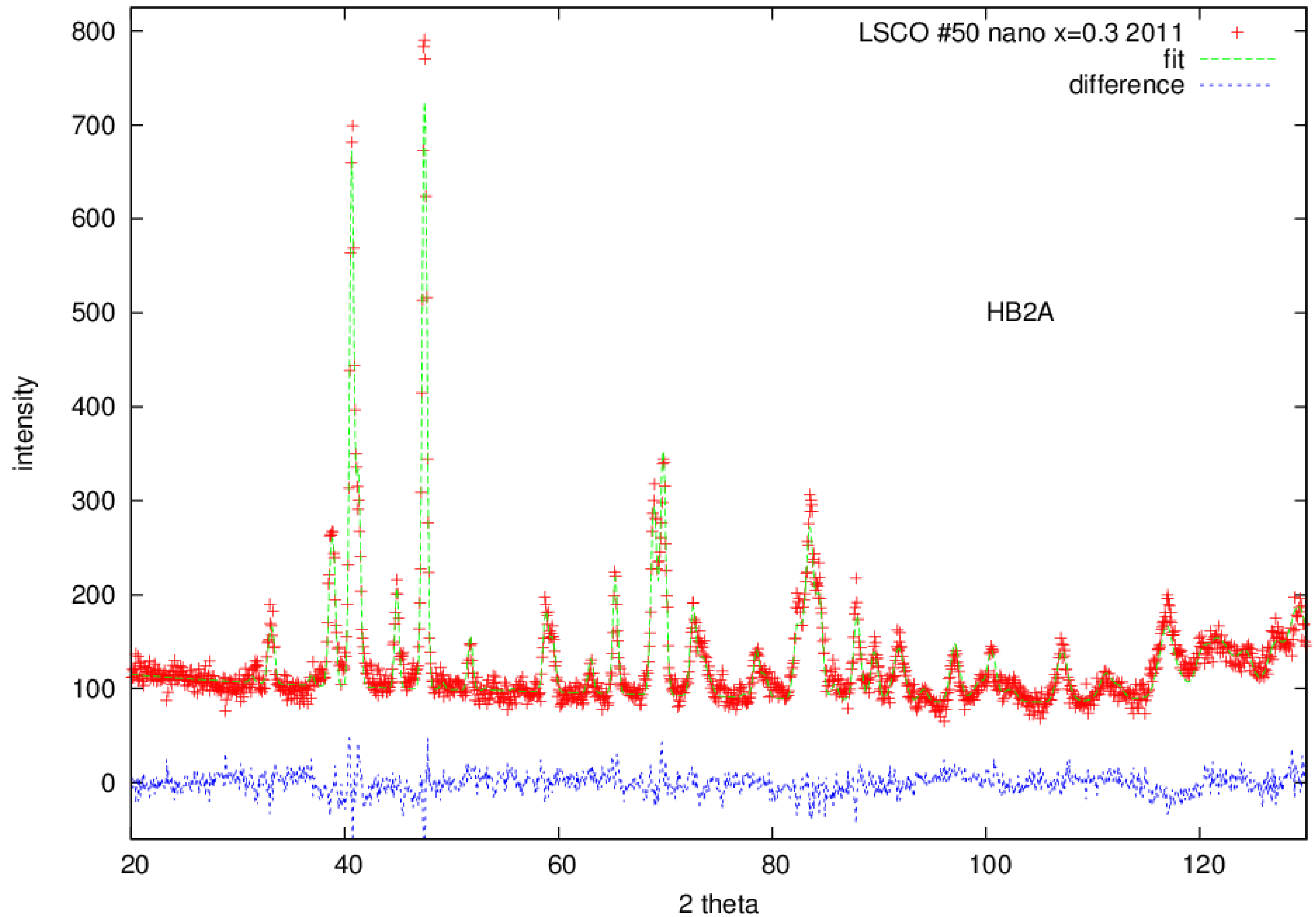
High Flux Isotope Reactor – Oak Ridge National Laboratory



HB-!A triple axis spectrometer at HFIR Oak Ridge National Laboratory

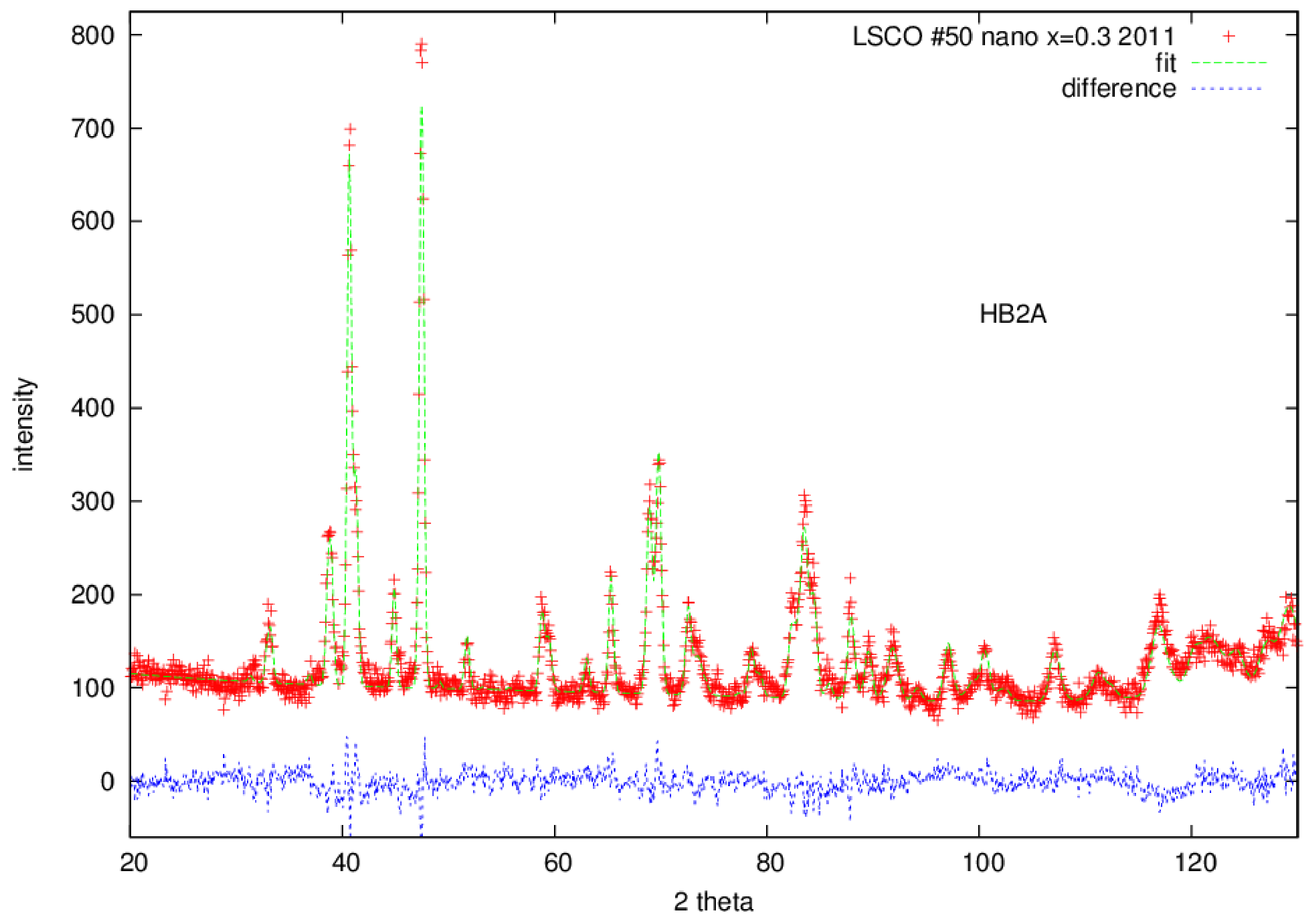
Spallation Neutron Source – Oak Ridge National Laboratory

Average structure of the nanoparticle powders



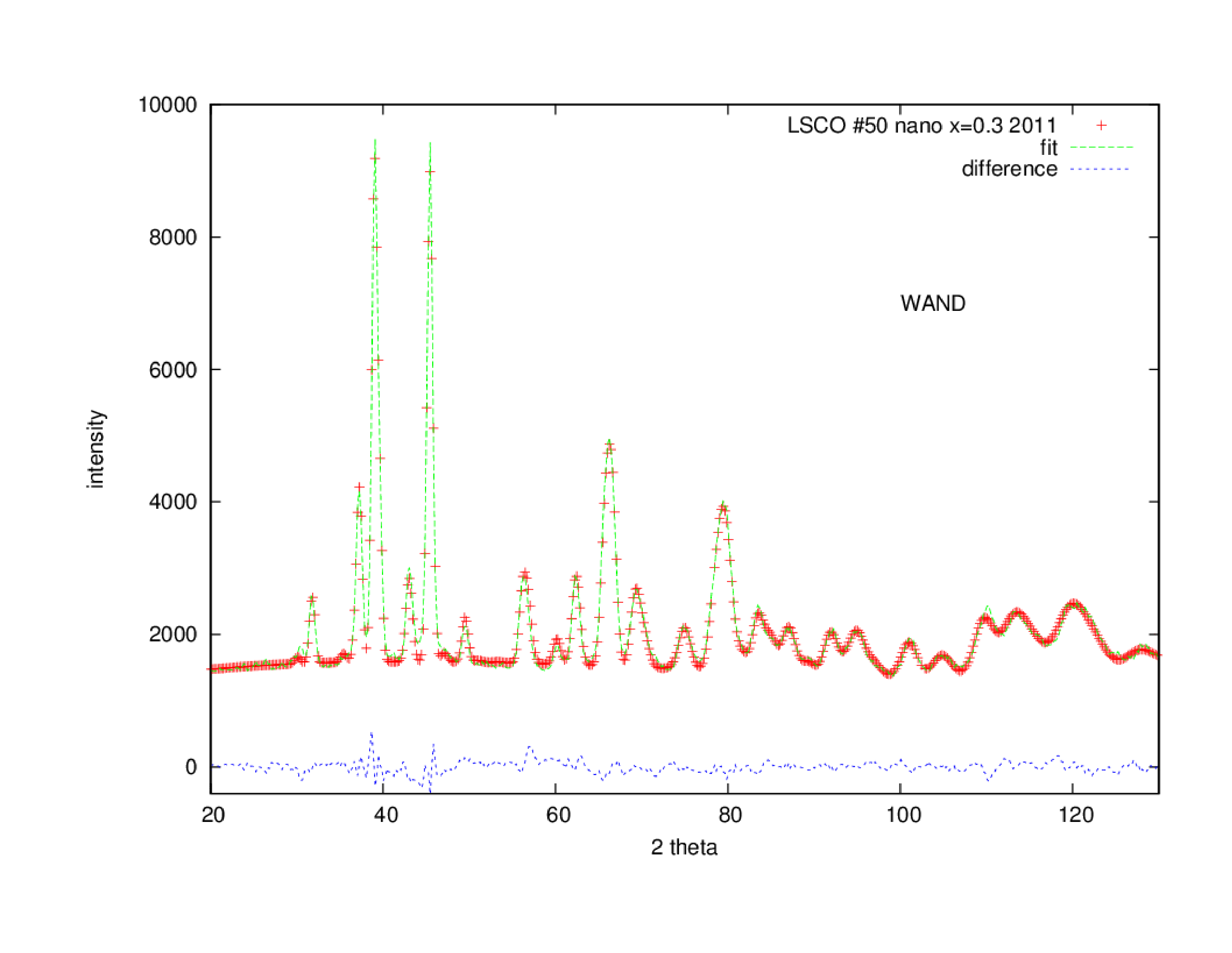
Average particle size ~19nm for this sample, but with a fairly wide range

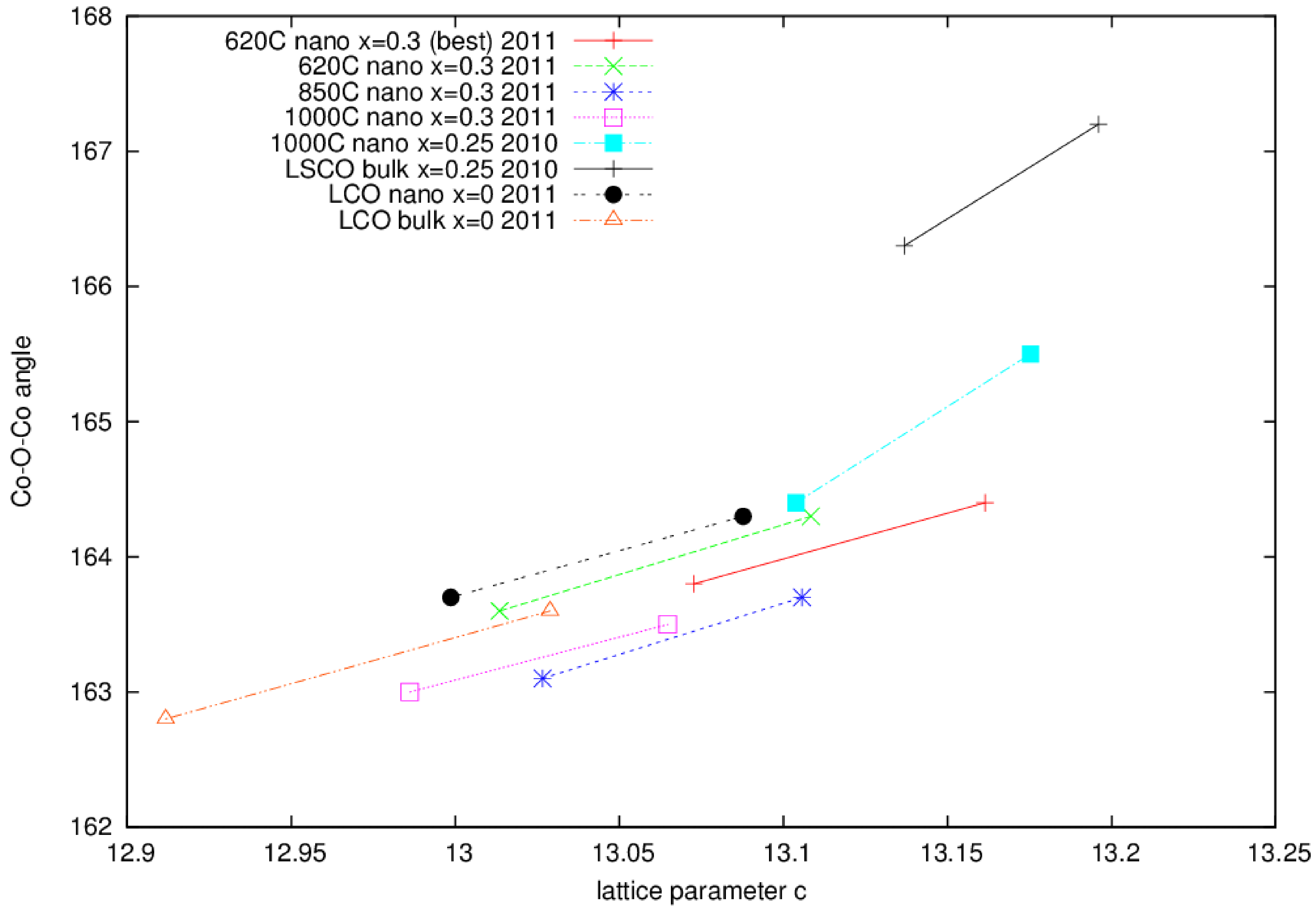
Average structure of the nanoparticle powders



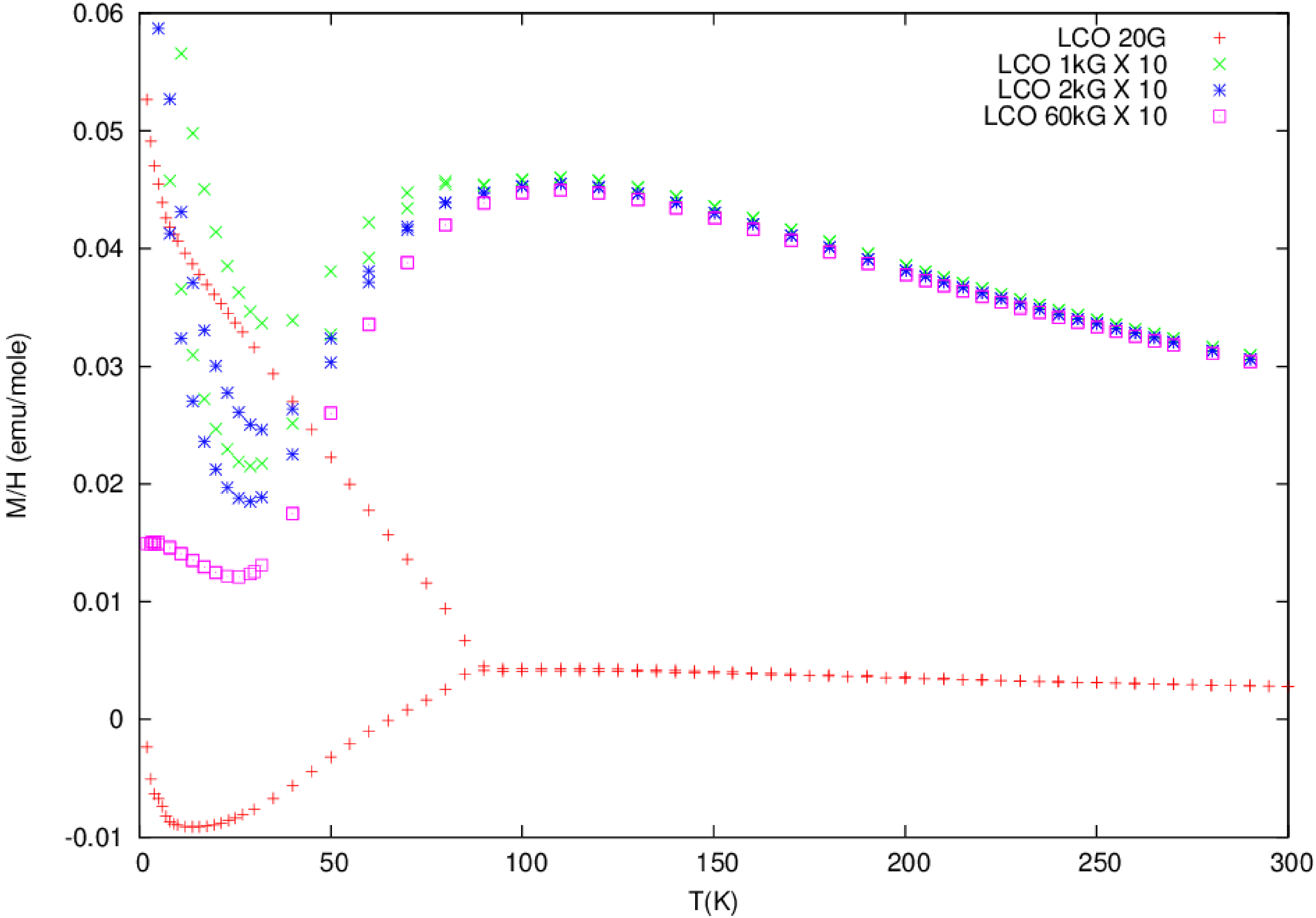
Average particle size ~19nm for this sample, but with a fairly wide range

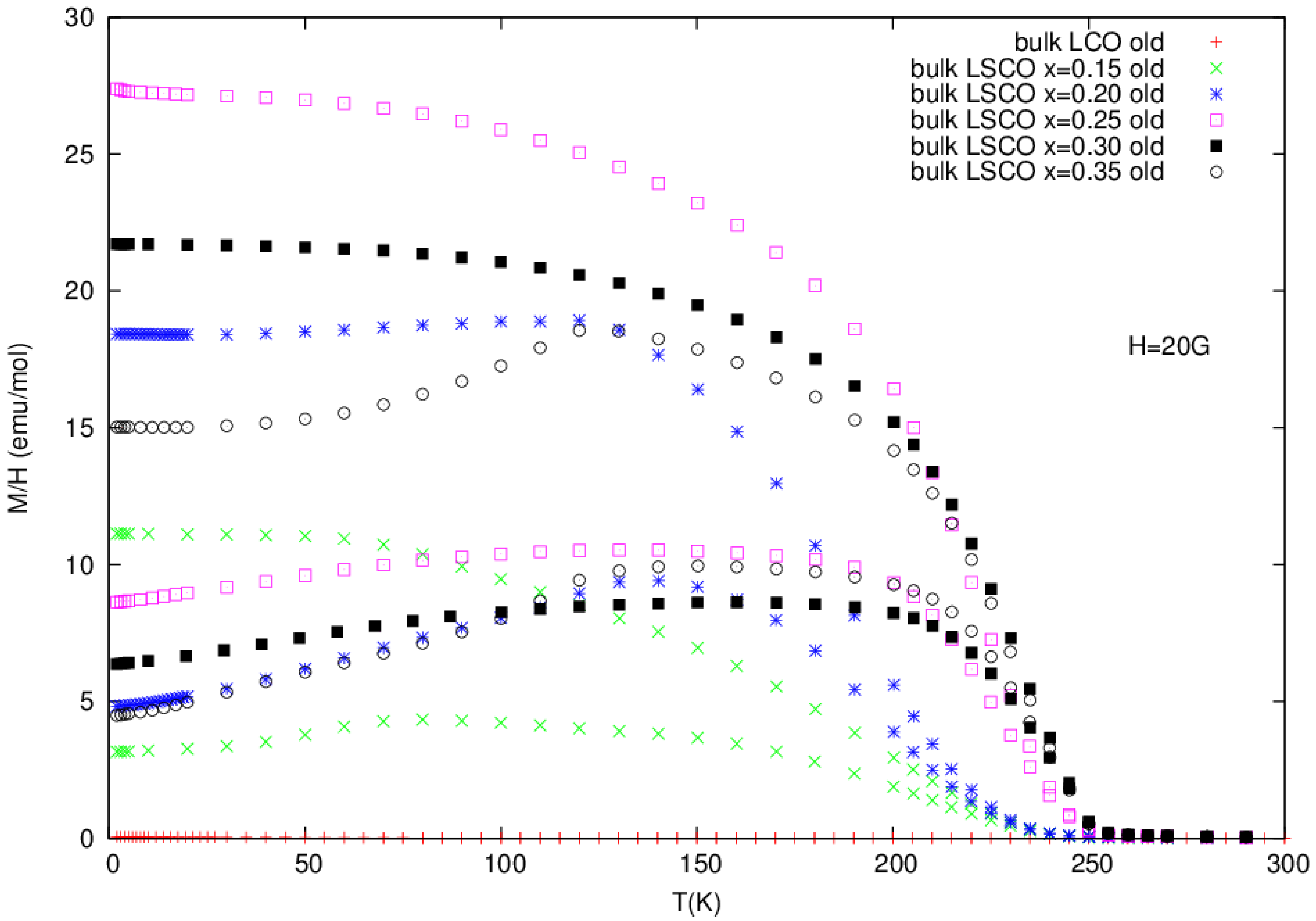
Average structure of the nanoparticle powders

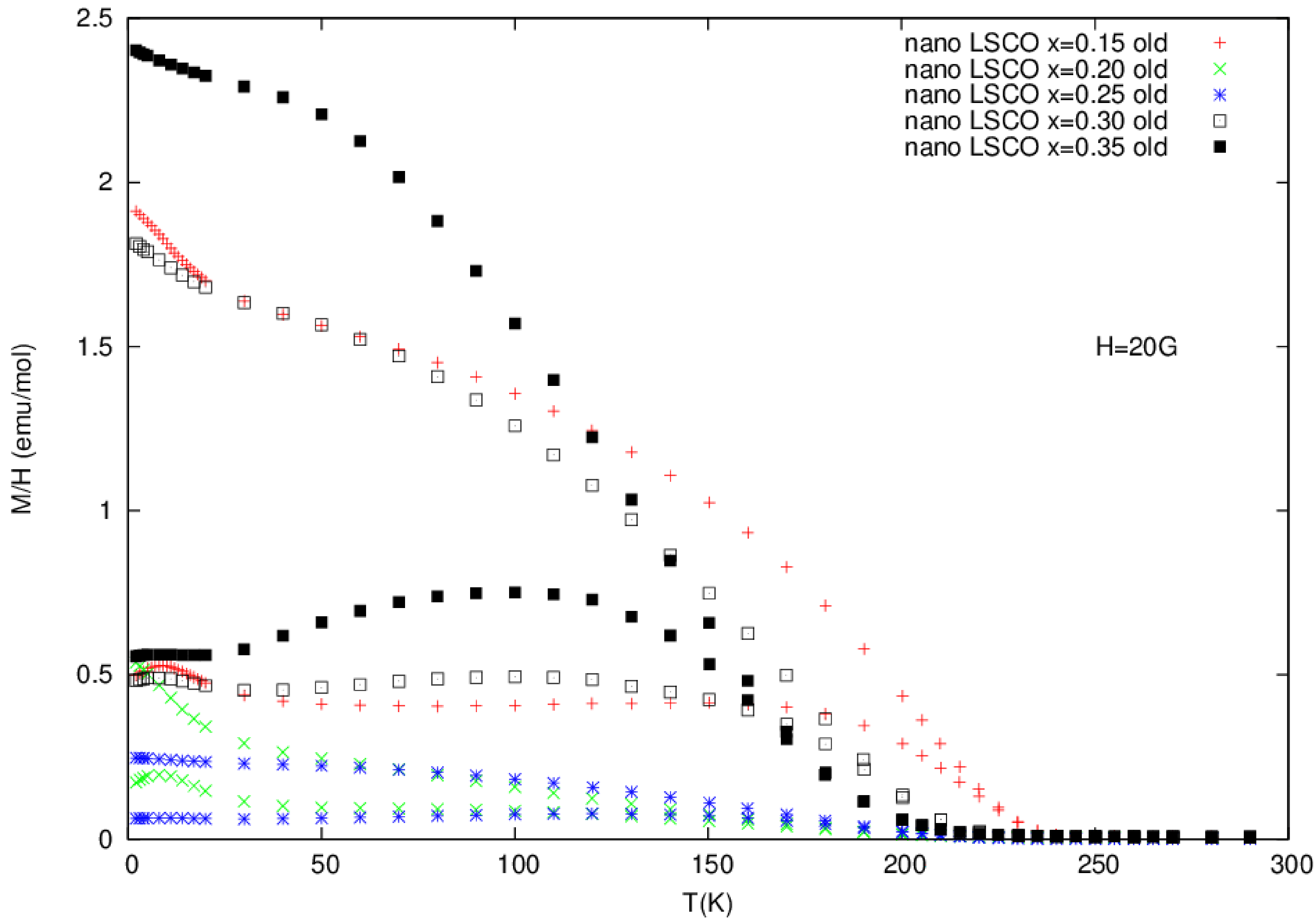




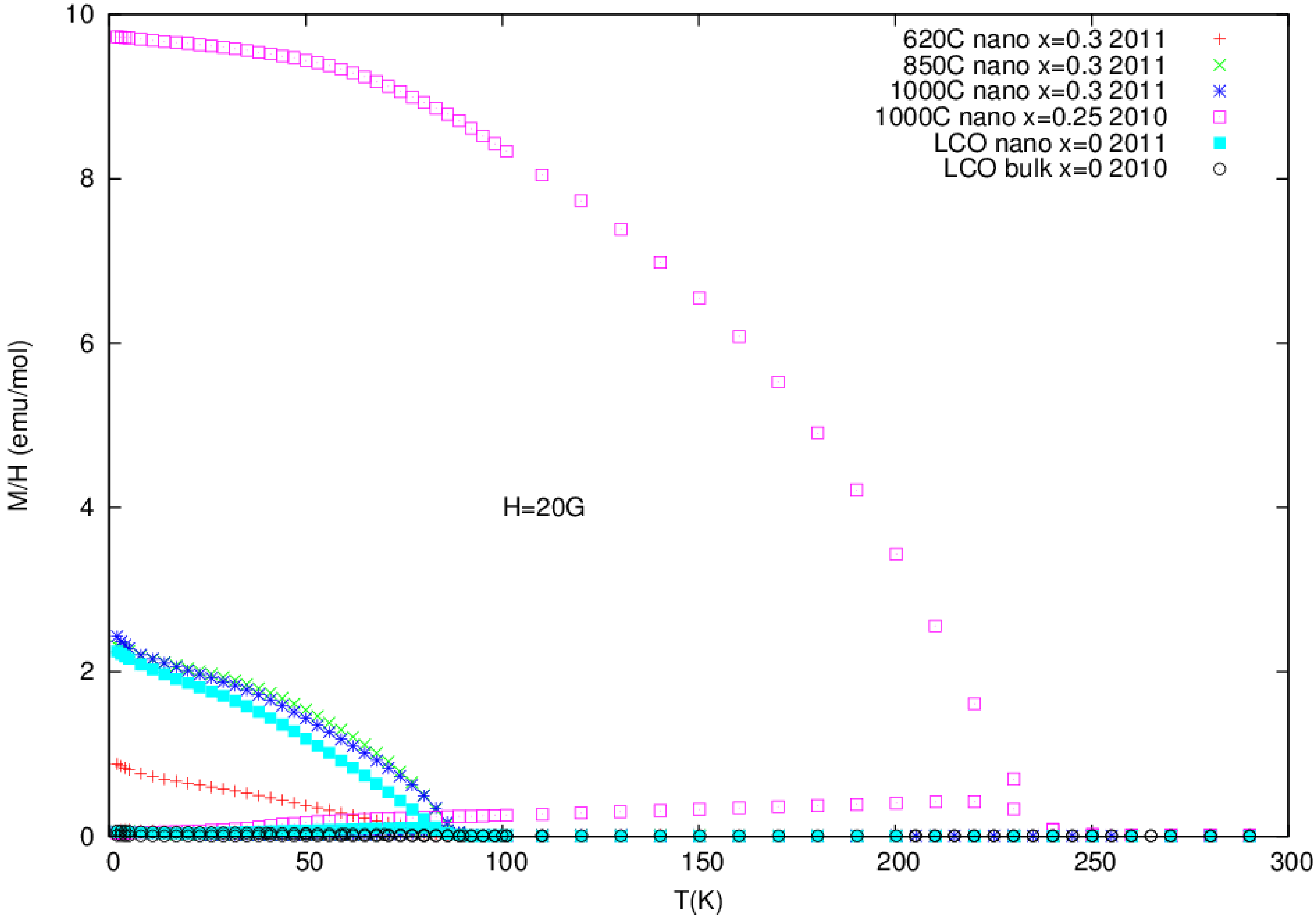
620C nano x=0.3 (best) 2011
620C nano x=0.3 2011
850C nano x=0.3 2011
1000C nano x=0.3 2011
1000C nano x=0.25 2010
LSCO bulk x=0.25 2010
LCO nano x=0 2011
LCO bulk x=0 2011
Co-O-Co angle
lattice parameter c
168
167
166
165
164
163
162
12.9
12.95
13
13.05
13.1
13.15
13.2
13.25

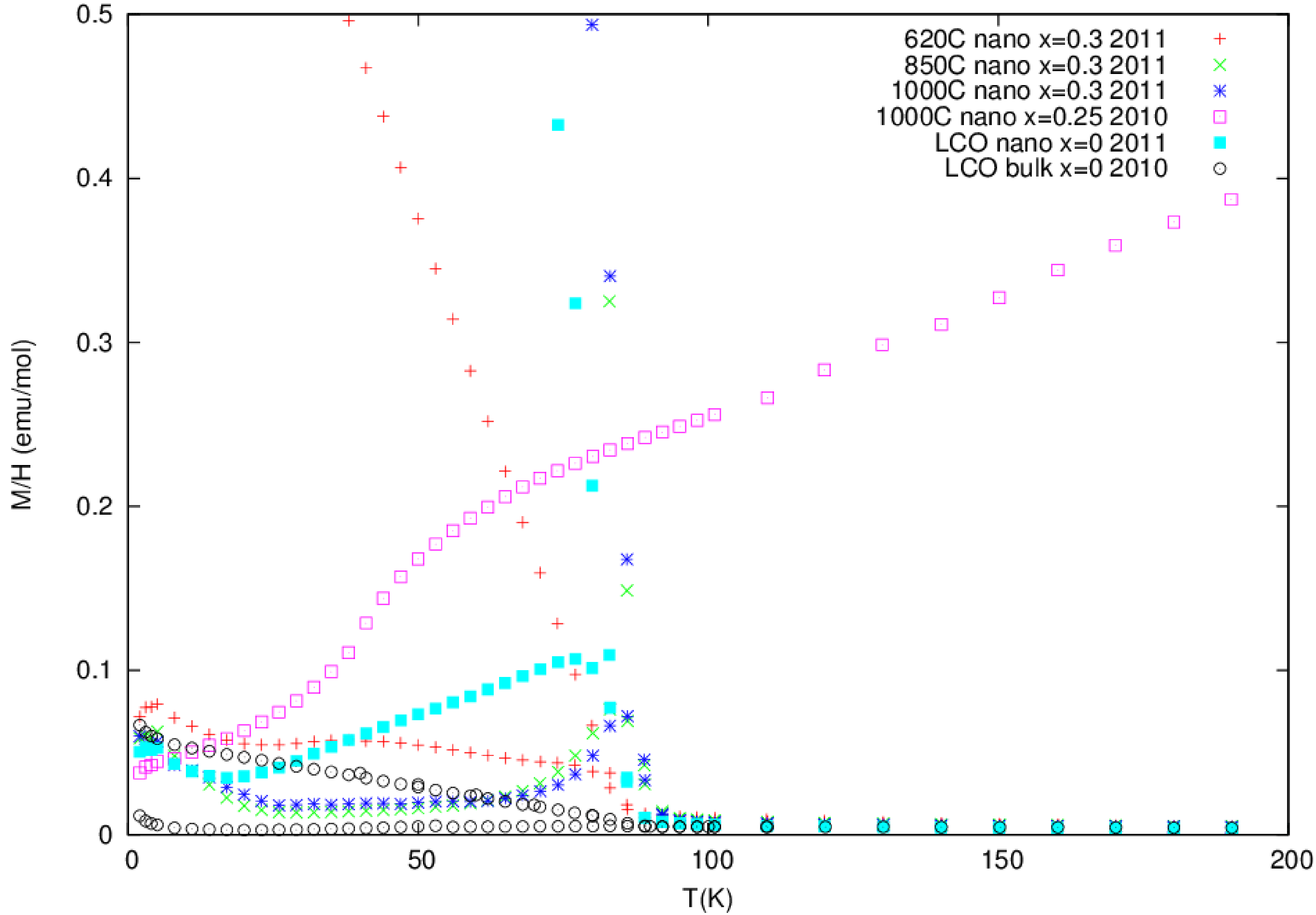

LCO 20G
LCO 1kG X 10
LCO 2kG X 10
LCO 60kG X 10
M/H (emu/mole)
T(K)
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
0
50
100
150
200
250
300


bulk LCO old
bulk LSCO x=0.15 old
bulk LSCO x=0.20 old
bulk LSCO x=0.25 old
bulk LSCO x=0.30 old
bulk LSCO x=0.35 old
H=20G
M/H (emu/mol)
T(K)
0
5
10
15
20
25
30
0
50
100
150
200
250
300



nano LSCO x=0.15 old
nano LSCO x=0.20 old
nano LSCO x=0.25 old
nano LSCO x=0.30 old
nano LSCO x=0.35 old
H=20G
M/H (emu/mol)
T(K)
2.5
2
1.5
1
0.5
0
0
50
100
150
200
250
300


620C nano x=0.3 2011
850C nano x=0.3 2011
1000C nano x=0.3 2011
1000C nano x=0.25 2010
LCO nano x=0 2011
LCO bulk x=0 2010
H=20G
M/H (emu/mol)
T(K)
0
2
4
6
8
10
0
50
100
150
200
250
300



620C nano x=0.3 2011
850C nano x=0.3 2011
1000C nano x=0.3 2011
1000C nano x=0.25 2010
LCO nano x=0 2011
LCO bulk x=0 2010
M/H (emu/mol)
T(K)
0
0.1
0.2
0.3
0.4
0.5
0
50
100
150
200

Conclusions

- Nanoparticles of $La_{1-x}Sr_xCoO_3$ are grown and characterized, with sizes 20 to 300nm.
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Thank you!

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