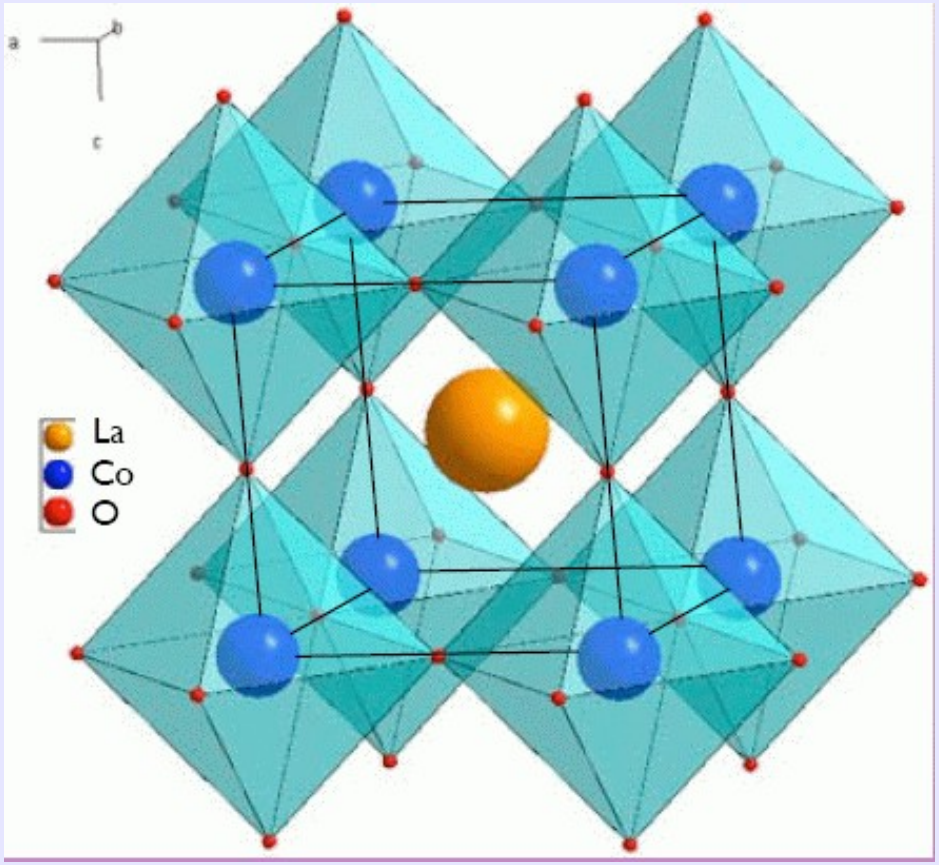
Neutron Scattering and $La_{1-x}Sr_xCoO_3$ Bulk and Nanoparticles

David P. Belanger and Alice M. Durand

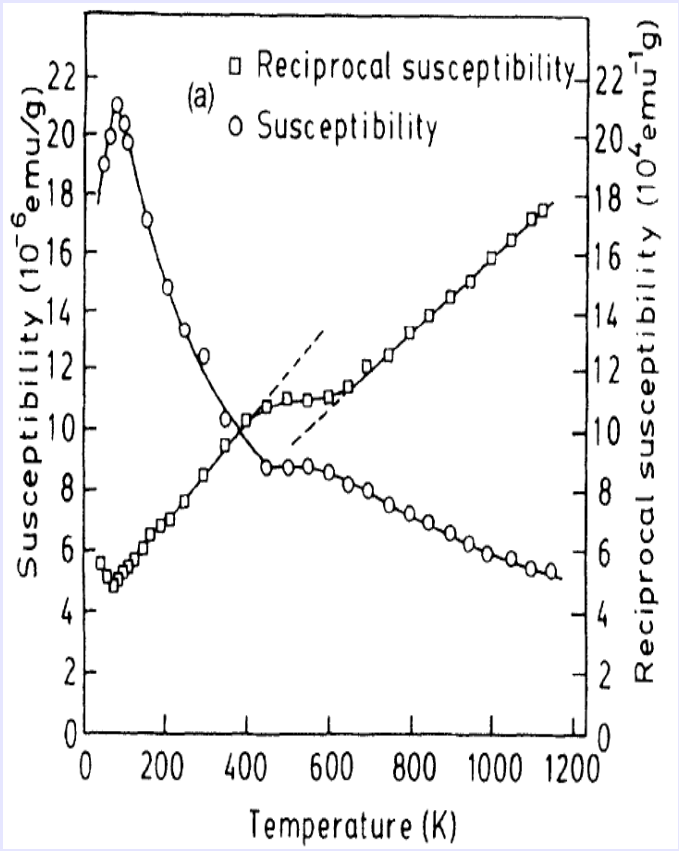


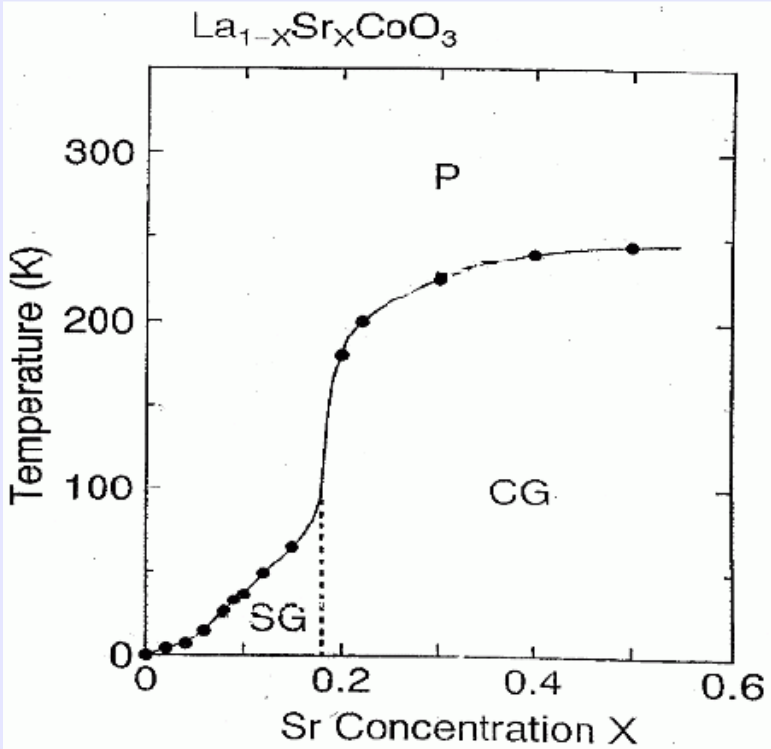
- Bulk system has been studied since the 1950's and yet it is not well understood (Goodenough).
- Neutron scattering techniques can be used to look at the long-range and short-range structure and magnetism and can probe excitations.
- Nanoparticles of this system have significant practical importance, but the effect of reducing to nanometer sizes is poorly understood.

Main Collaborators and Acknowledgments

- Alice Durand – UCSC
- Nalini Sundaram – UCSC
- Ingrid Anderson – UCSC
- Yu Jiang – UCSC
- Frank (Bud) Bridges – UCSC
- Thomas Proffen – Lujan Center, Los Alamos National Lab
- Corwin Booth – Lawrence Berkeley National Lab
- Feng Ye – Oak Ridge National Laboratory
- Jaime Fernandez-Baca – Oak Ridge National Laboratory

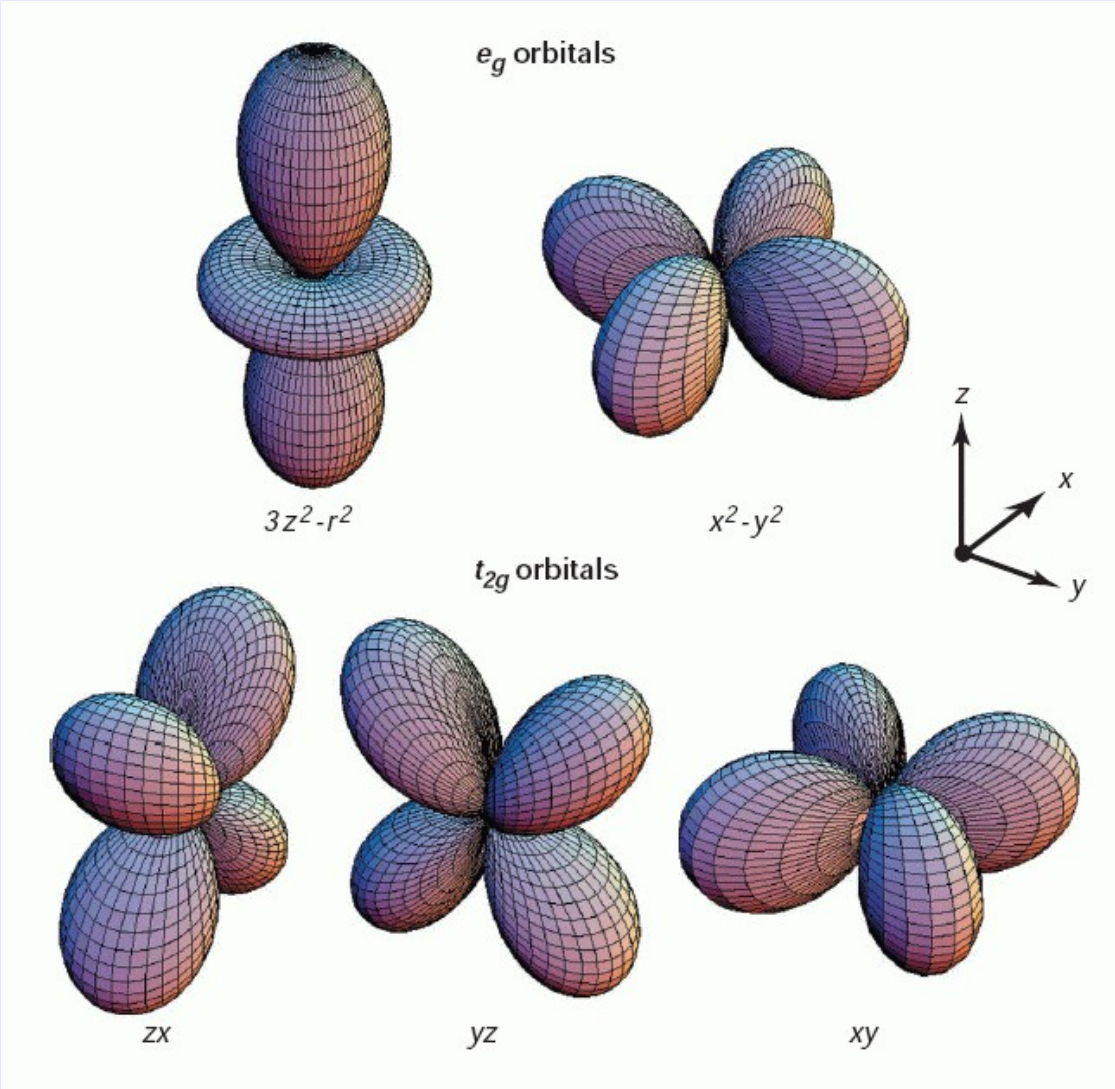
Magnetic Phase Diagram



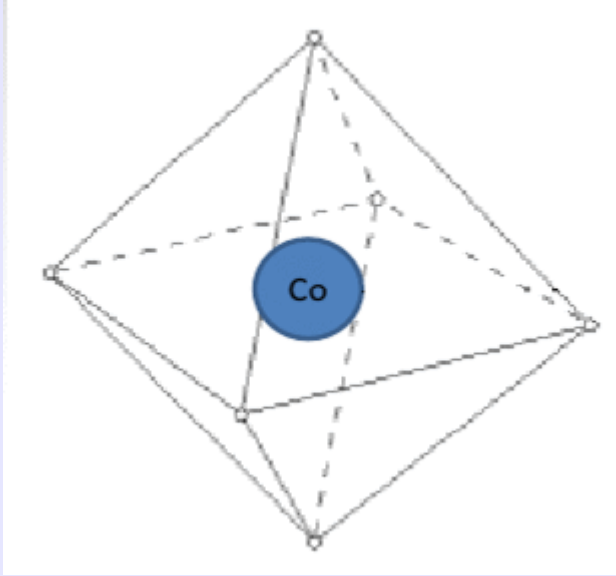


- K. Asai, P. Gehring, H. Chou, and G. Shirane, Phys. Rev. B **40**, 10982 (1989); V. G. Bhide, D. S. Rajoria, G. R. Rao, and C. N. R. Rao, Phys. Rev. B **6**, 1021 (1972).
- M. Itoh, I. Natori, S. Kubota, and K. Motoya, J. Phys. Soc. Japan **63**, 1486 (1993).

e_g and t_{2g} orbitals

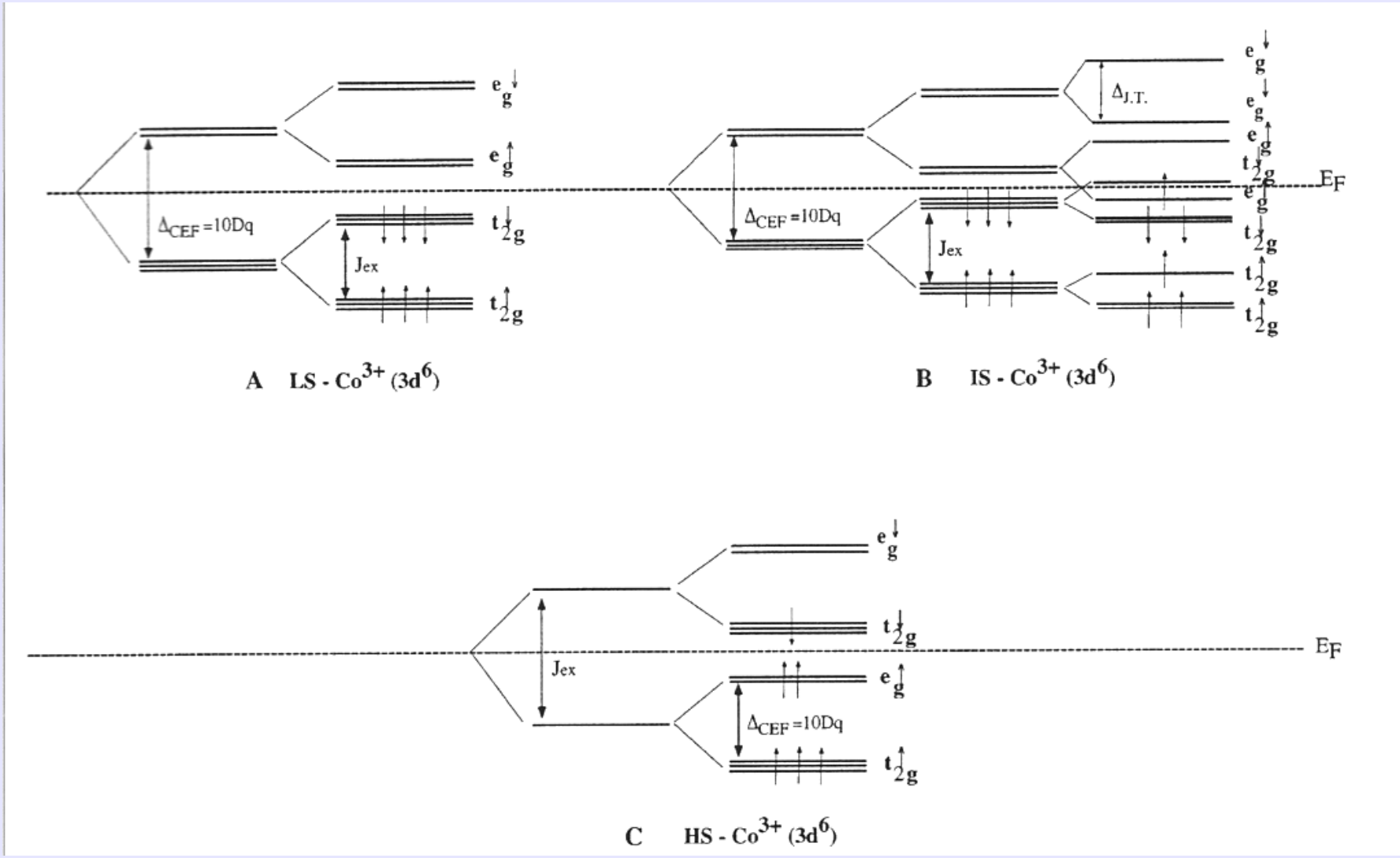


- Y. Tokura and N. Nagaosa, Science **288**, 462 (2008).

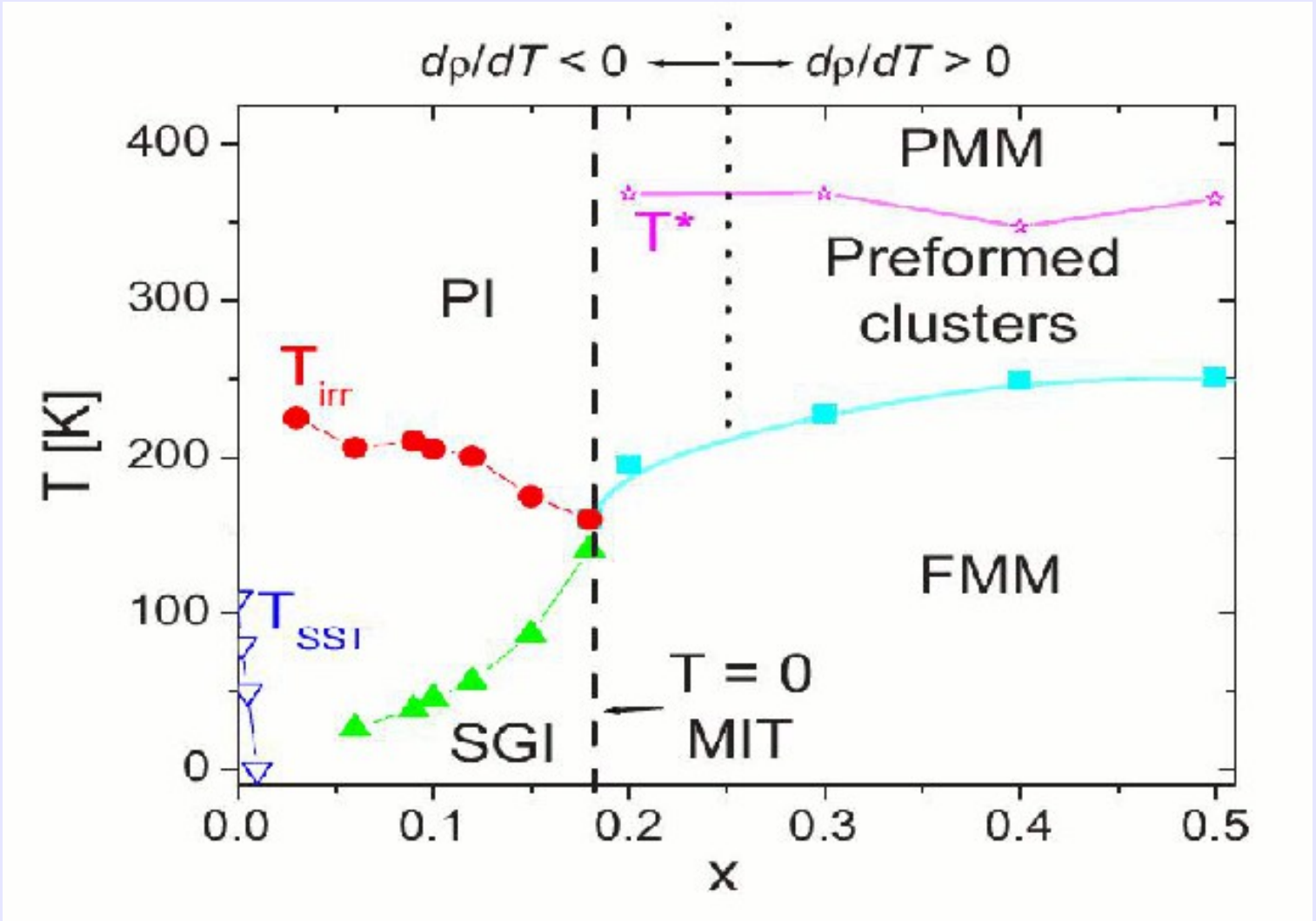


Possible Local Co Spin States in $LaCoO_3$

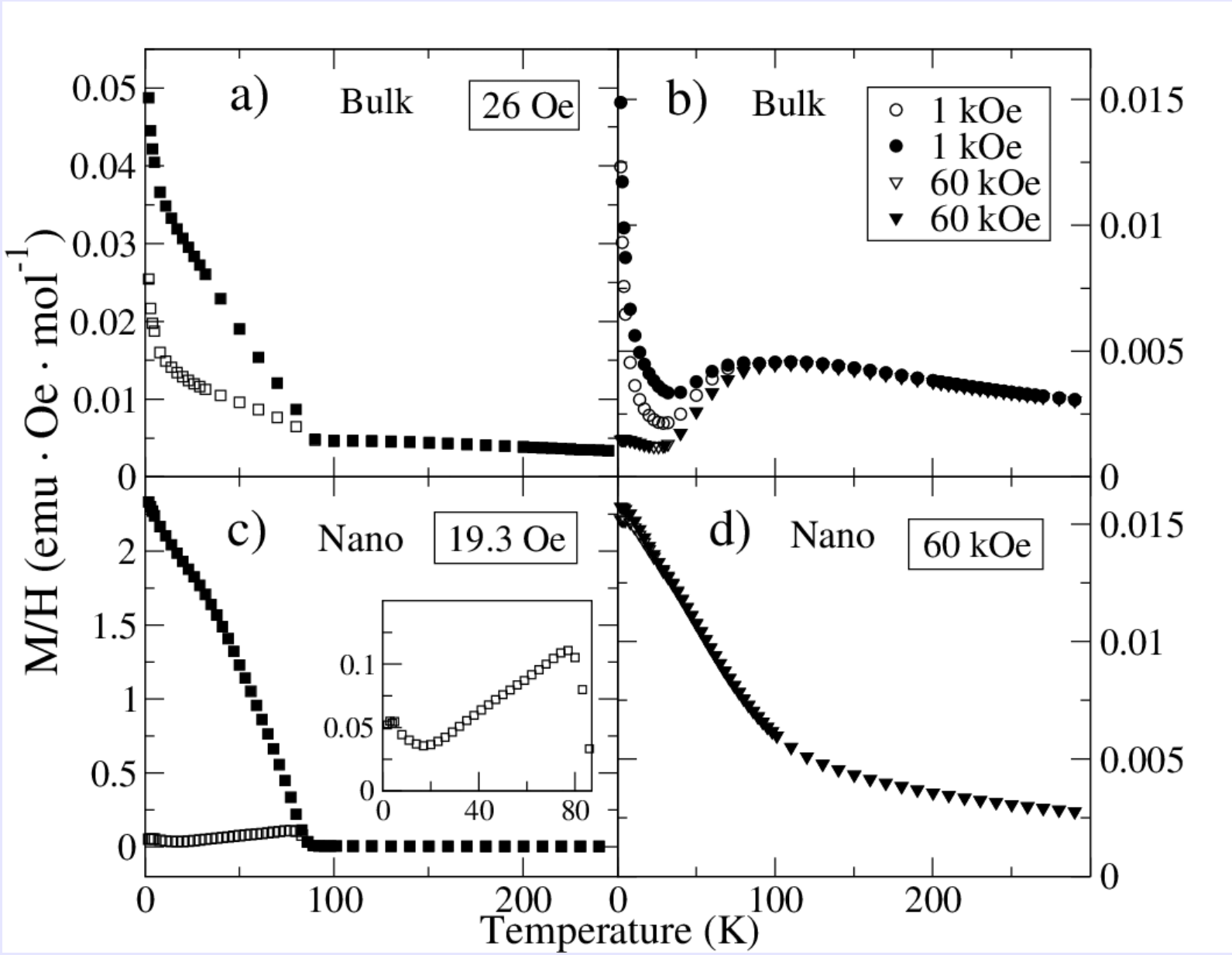
Toulemonde, et al., J. Solid St. Chem. **158**, 208 (2001)

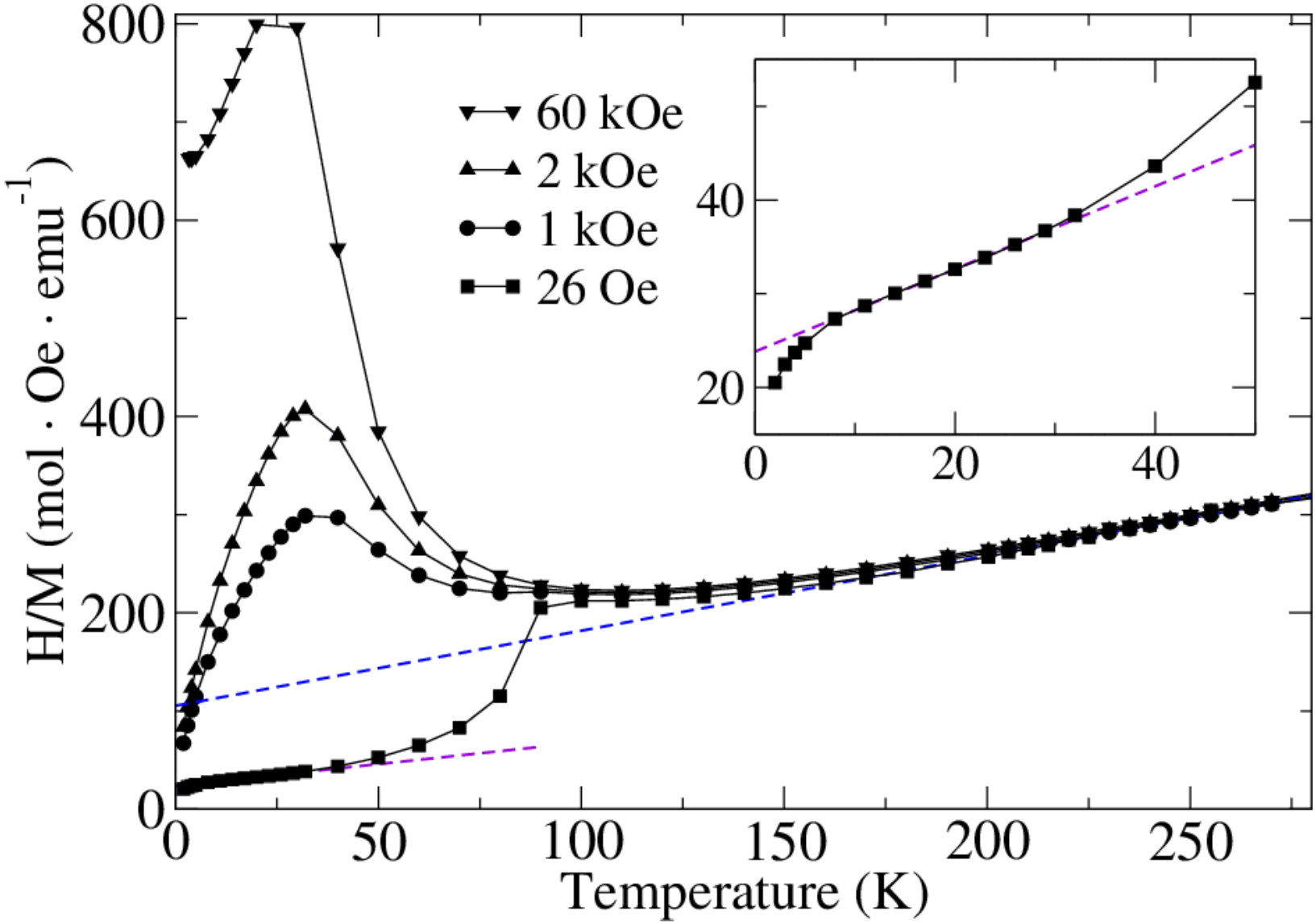


Phase Diagram



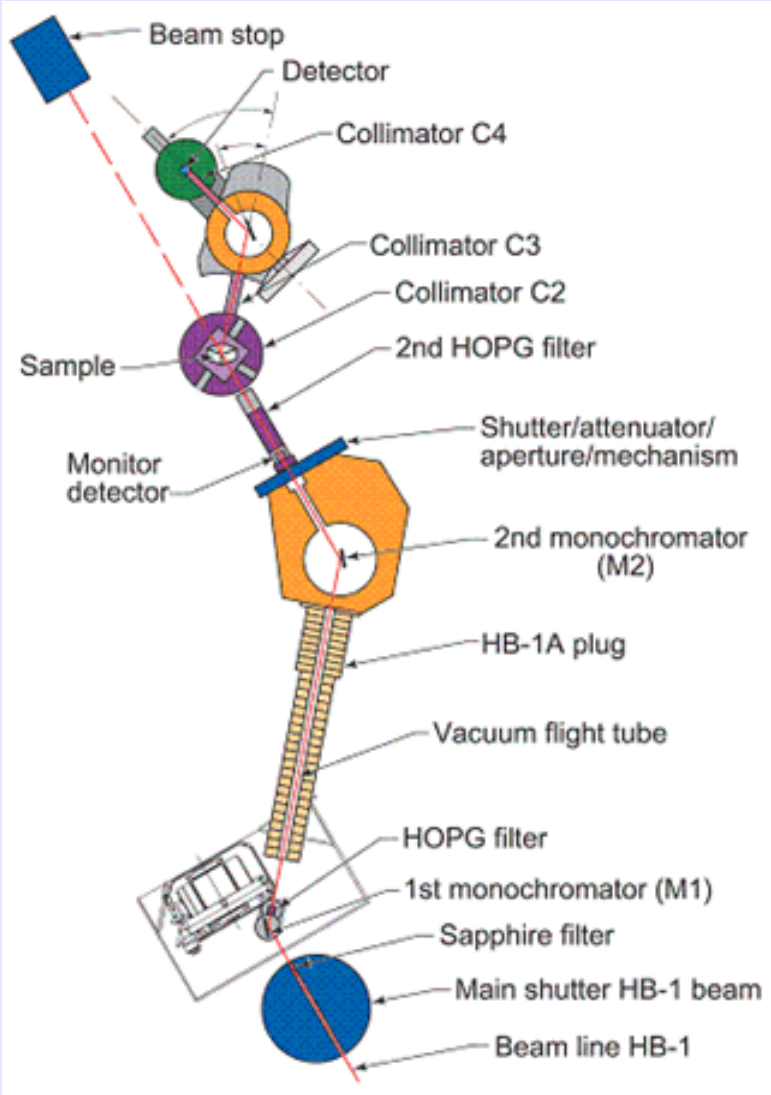
C. He, M. A. Torija, J. Wu, J. W. Lynn, H. Zheng, J. F. Mitchell, and C. Leighton, Phys. Rev. B **76**, 014401 (2007).


a)
Bulk
26 Oe
b)
Bulk
1 kOe
1 kOe
60 kOe
60 kOe
c)
Nano
19.3 Oe
d)
Nano
60 kOe
M/H (emu · Oe · mol^{-1})
Temperature (K)

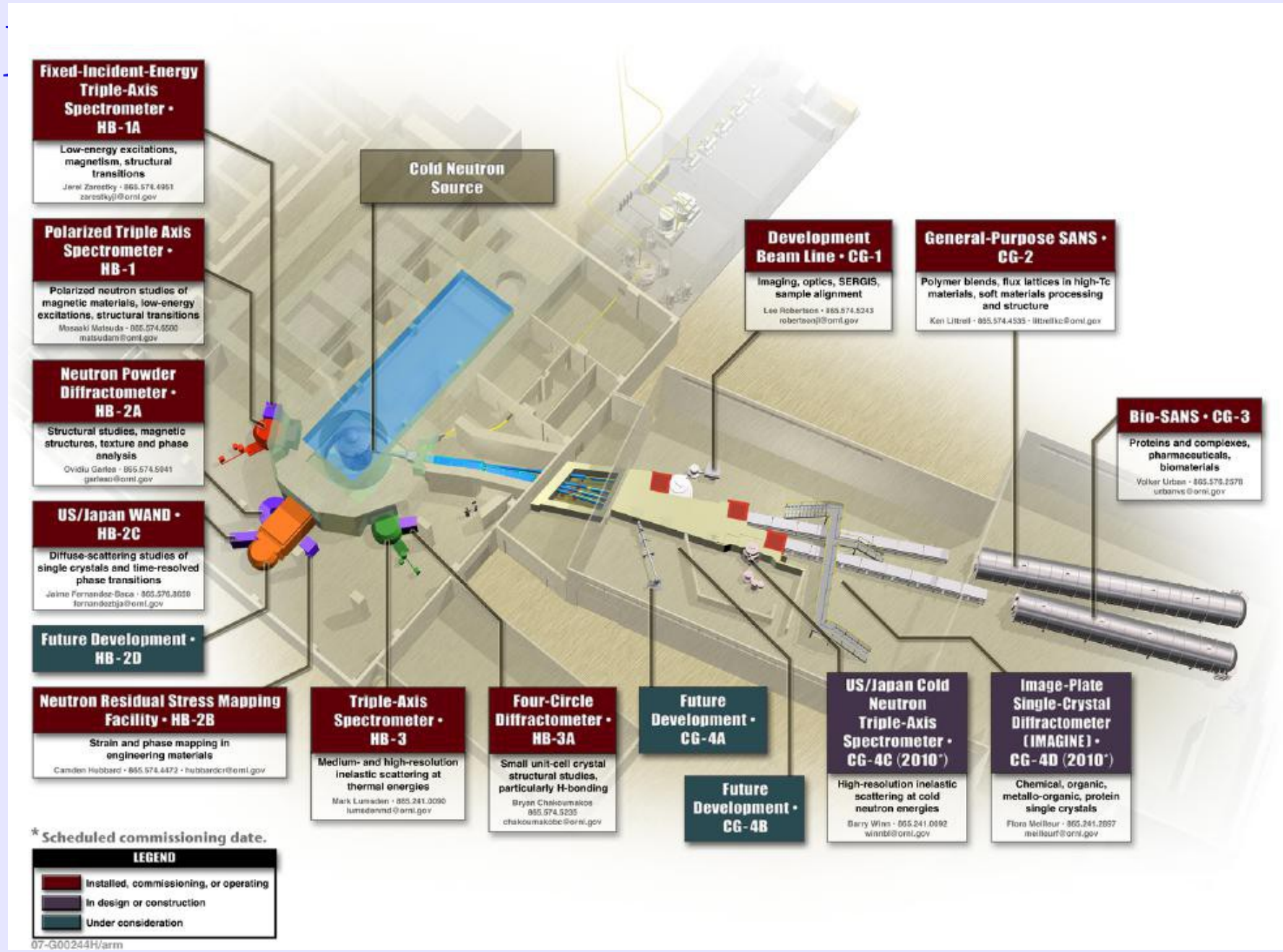

800
600
400
200
0
H/M (mol · Oe · emu^{-1})
60 kOe
2 kOe
1 kOe
26 Oe
40
20
0
20
40
0
50
100
150
200
250
Temperature (K)

Reactor-based neutron scattering

Typical triple-axis spectrometer

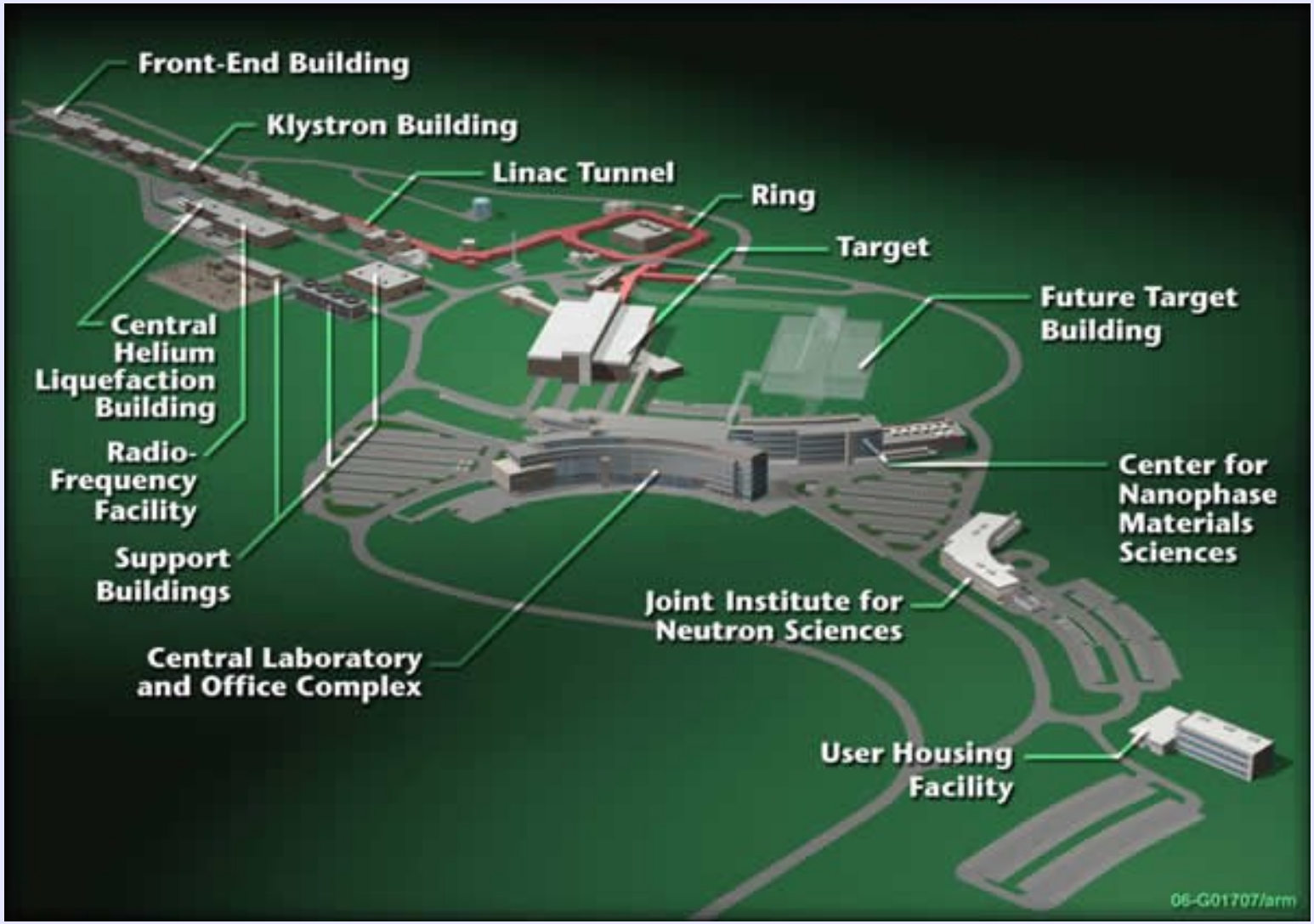


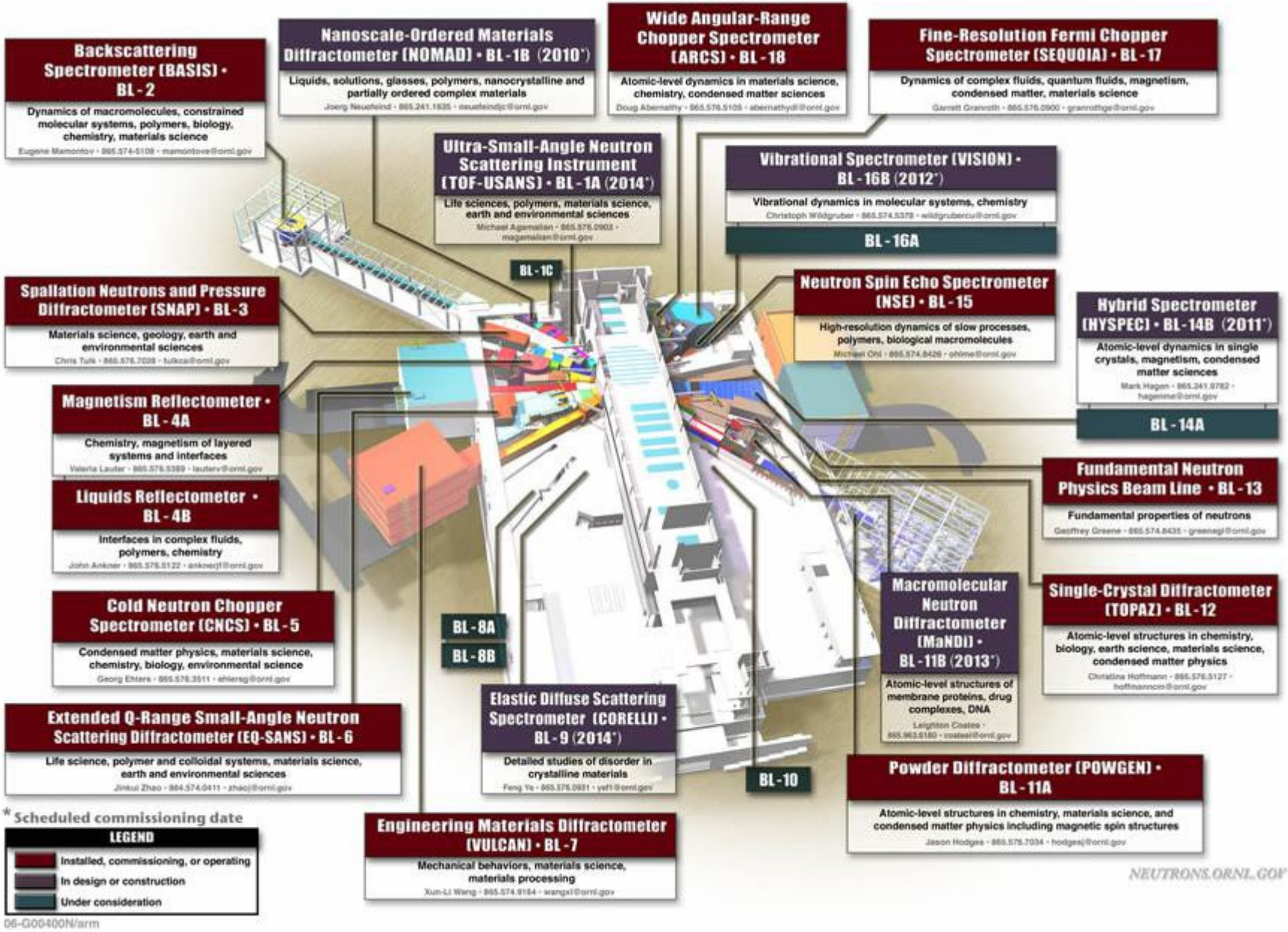
HB1A triple axis spectrometer


Fixed-Incident-Energy Triple-Axis Spectrometer • HB-1A
Low-energy excitations, magnetism, structural transitions
Jerel Zaretsky • 865.574.4951
zaretskyj@ornl.gov
Polarized Triple Axis Spectrometer • HB-1
Polarized neutron studies of magnetic materials, low-energy excitations, structural transitions
Masaaki Matsuda • 865.574.6500
matsudam@ornl.gov
Neutron Powder Diffractometer • HB-2A
Structural studies, magnetic structures, texture and phase analysis
Ovidiu Garlea • 865.574.5041
garleao@ornl.gov
US/Japan WAND • HB-2C
Diffuse-scattering studies of single crystals and time-resolved phase transitions
Jaime Fernandez-Baca • 865.576.8039
fernandezbja@ornl.gov
Future Development • HB-2D
Neutron Residual Stress Mapping Facility • HB-2B
Strain and phase mapping in engineering materials
Camden Hubbard • 865.574.4472 • hubbardcr@ornl.gov
Cold Neutron Source
Triple-Axis Spectrometer • HB-3
Medium- and high-resolution inelastic scattering at thermal energies
Mark Lumsden • 865.241.0090
lumsdenmd@ornl.gov
Four-Circle Diffractometer • HB-3A
Small unit-cell crystal structural studies, particularly H-bonding
Bryan Chakoumakos
865.574.5235
chakoumakosbc@ornl.gov
Future Development • CG-4A
Future Development • CG-4B
Development Beam Line • CG-1
Imaging, optics, SERGIS, sample alignment
Lee Robertson • 865.574.5243
robertsonj@ornl.gov
General-Purpose SANS • CG-2
Polymer blends, flux lattices in high-Tc materials, soft materials processing and structure
Ken Littrell • 865.574.4535 • littrellkc@ornl.gov
Bio-SANS • CG-3
Proteins and complexes, pharmaceuticals, biomaterials
Volker Urban • 865.576.2578
urbanvs@ornl.gov
US/Japan Cold Neutron Triple-Axis Spectrometer • CG-4C (2010*)
High-resolution inelastic scattering at cold neutron energies
Barry Winn • 865.241.0092
winnbl@ornl.gov
Image-Plate Single-Crystal Diffractometer (IMAGINE) • CG-4D (2010*)
Chemical, organic, metallo-organic, protein single crystals
Flora Meilleur • 865.241.2697
meilleurf@ornl.gov
* Scheduled commissioning date.
LEGEND
Installed, commissioning, or operating
In design or construction
Under consideration
07-G00244H/arm

Spallation Neutron Source

Spallation Neutron Source




Backscattering Spectrometer (BASIS) • BL-2
Dynamics of macromolecules, constrained molecular systems, polymers, biology, chemistry, materials science
Nanoscale-Ordered Materials Diffractometer (NOMAD) • BL-1B (2010*)
Liquids, solutions, glasses, polymers, nanocrystalline and partially ordered complex materials
Wide Angular-Range Chopper Spectrometer (ARCS) • BL-18
Atomic-level dynamics in materials science, chemistry, condensed matter sciences
Fine-Resolution Fermi Chopper Spectrometer (SEQUOIA) • BL-17
Dynamics of complex fluids, quantum fluids, magnetism, condensed matter, materials science
Ultra-Small-Angle Neutron Scattering Instrument (TOF-USANS) • BL-1A (2014*)
Life sciences, polymers, materials science, earth and environmental sciences
Vibrational Spectrometer (VISION) • BL-16B (2012*)
Vibrational dynamics in molecular systems, chemistry
BL-16A
BL-1C
Spallation Neutrons and Pressure Diffractometer (SNAP) • BL-3
Materials science, geology, earth and environmental sciences
Neutron Spin Echo Spectrometer (NSE) • BL-15
High-resolution dynamics of slow processes, polymers, biological macromolecules
Hybrid Spectrometer (HYSPEC) • BL-14B (2011*)
Atomic-level dynamics in single crystals, magnetism, condensed matter sciences
BL-14A
Magnetism Reflectometer • BL-4A
Chemistry, magnetism of layered systems and interfaces
Liquids Reflectometer • BL-4B
Interfaces in complex fluids, polymers, chemistry
Fundamental Neutron Physics Beam Line • BL-13
Fundamental properties of neutrons
Cold Neutron Chopper Spectrometer (CNCS) • BL-5
Condensed matter physics, materials science, chemistry, biology, environmental science
BL-8A
BL-8B
Macromolecular Neutron Diffractometer (MaNDi) • BL-11B (2013*)
Atomic-level structures of membrane proteins, drug complexes, DNA
Single-Crystal Diffractometer (TOPAZ) • BL-12
Atomic-level structures in chemistry, biology, earth science, materials science, condensed matter physics
Extended Q-Range Small-Angle Neutron Scattering Diffractometer (EQ-SANS) • BL-6
Life science, polymer and colloidal systems, materials science, earth and environmental sciences
Elastic Diffuse Scattering Spectrometer (CORELLI) • BL-9 (2014*)
Detailed studies of disorder in crystalline materials
BL-10
Powder Diffractometer (POWGEN) • BL-11A
Atomic-level structures in chemistry, materials science, and condensed matter physics including magnetic spin structures
Engineering Materials Diffractometer (VULCAN) • BL-7
Mechanical behaviors, materials science, materials processing
* Scheduled commissioning date
LEGEND
Installed, commissioning, or operating
In design or construction
Under consideration
06-G00400N/arm
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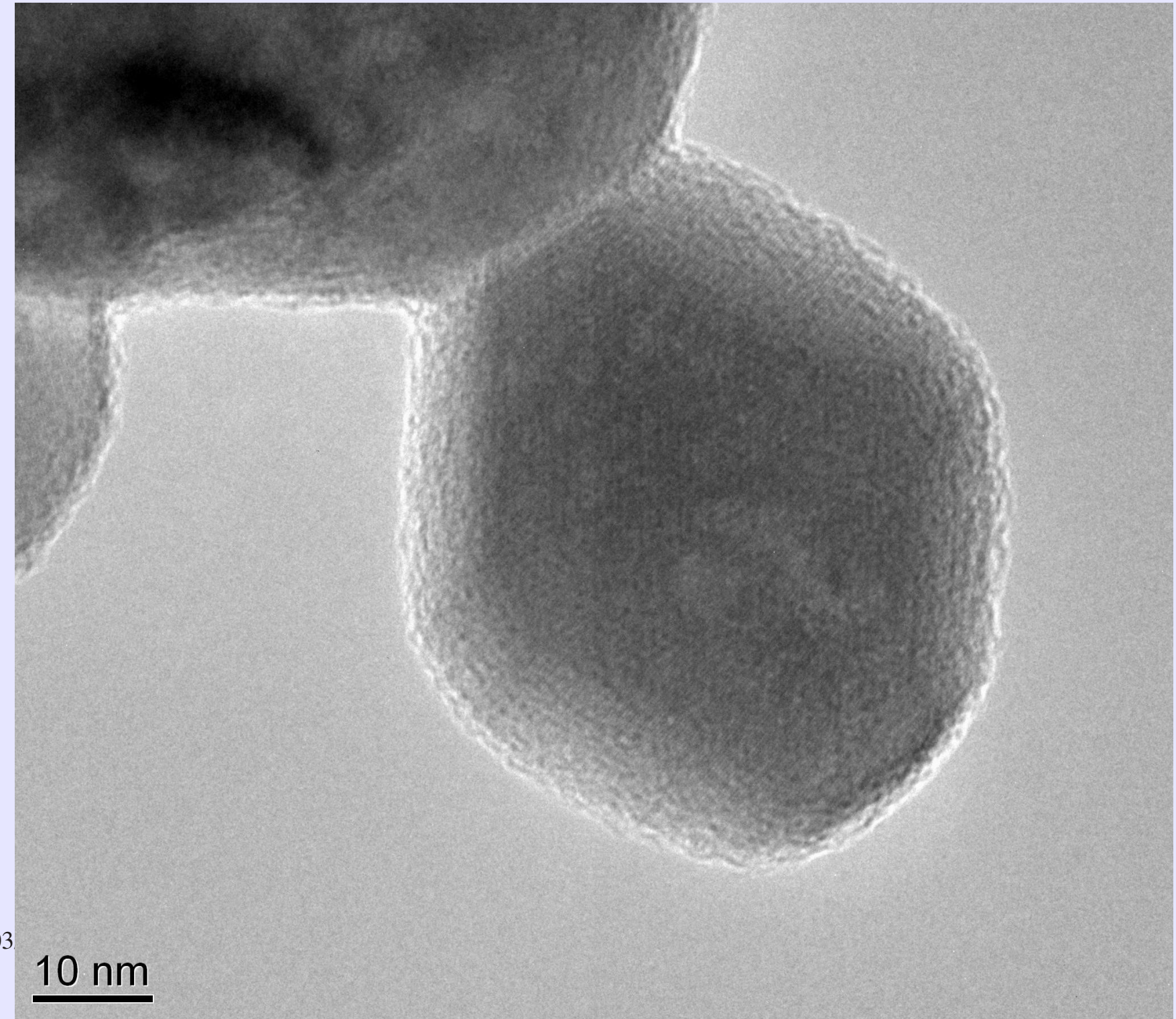
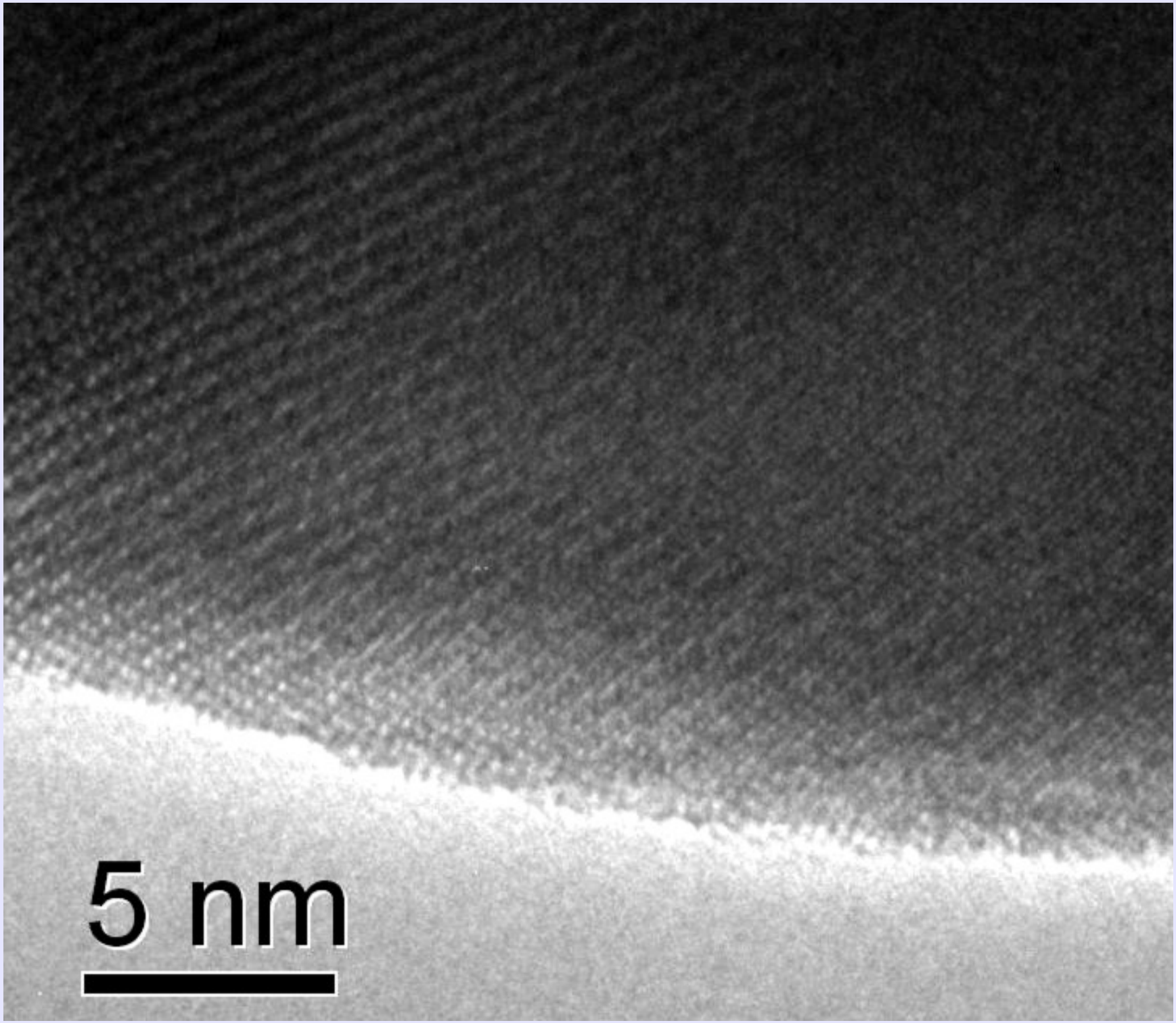
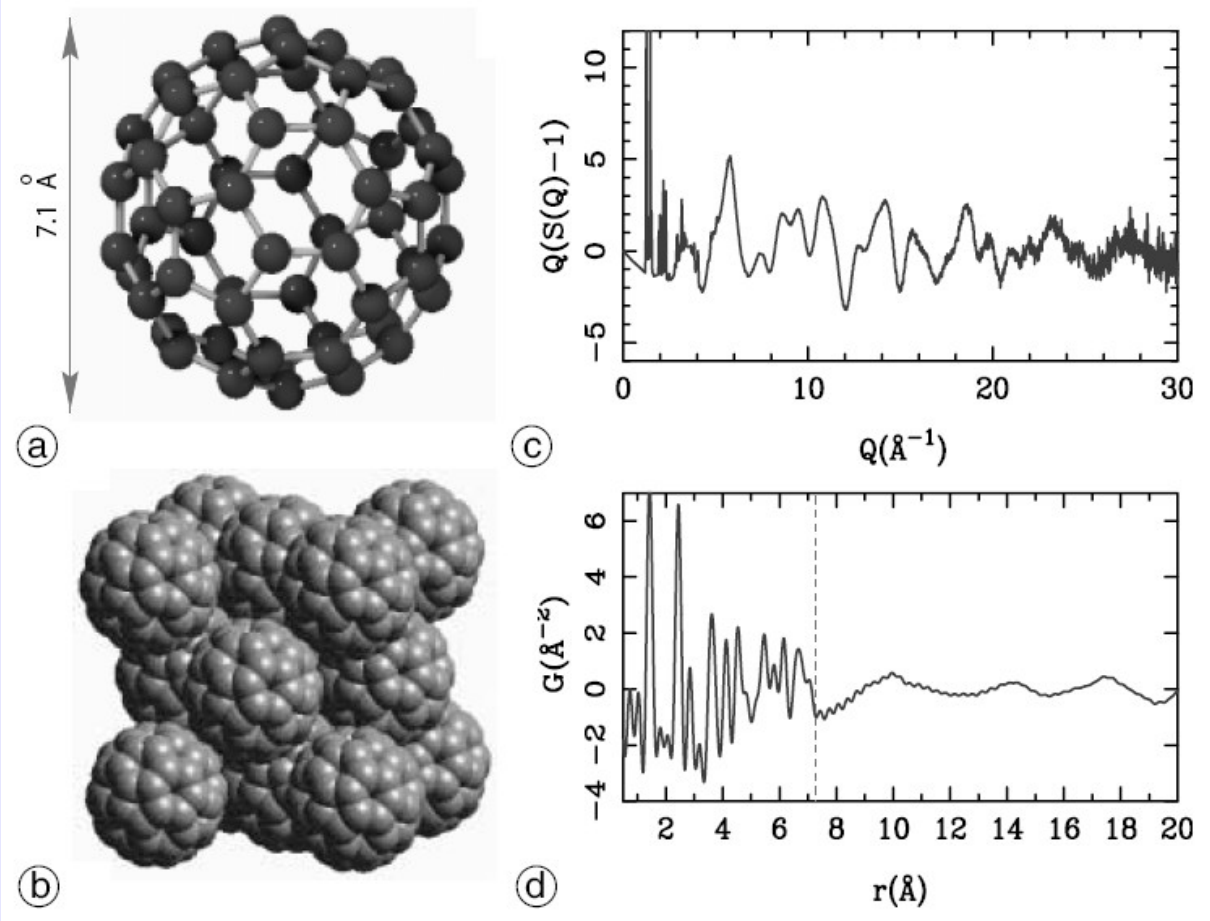


03


5 nm

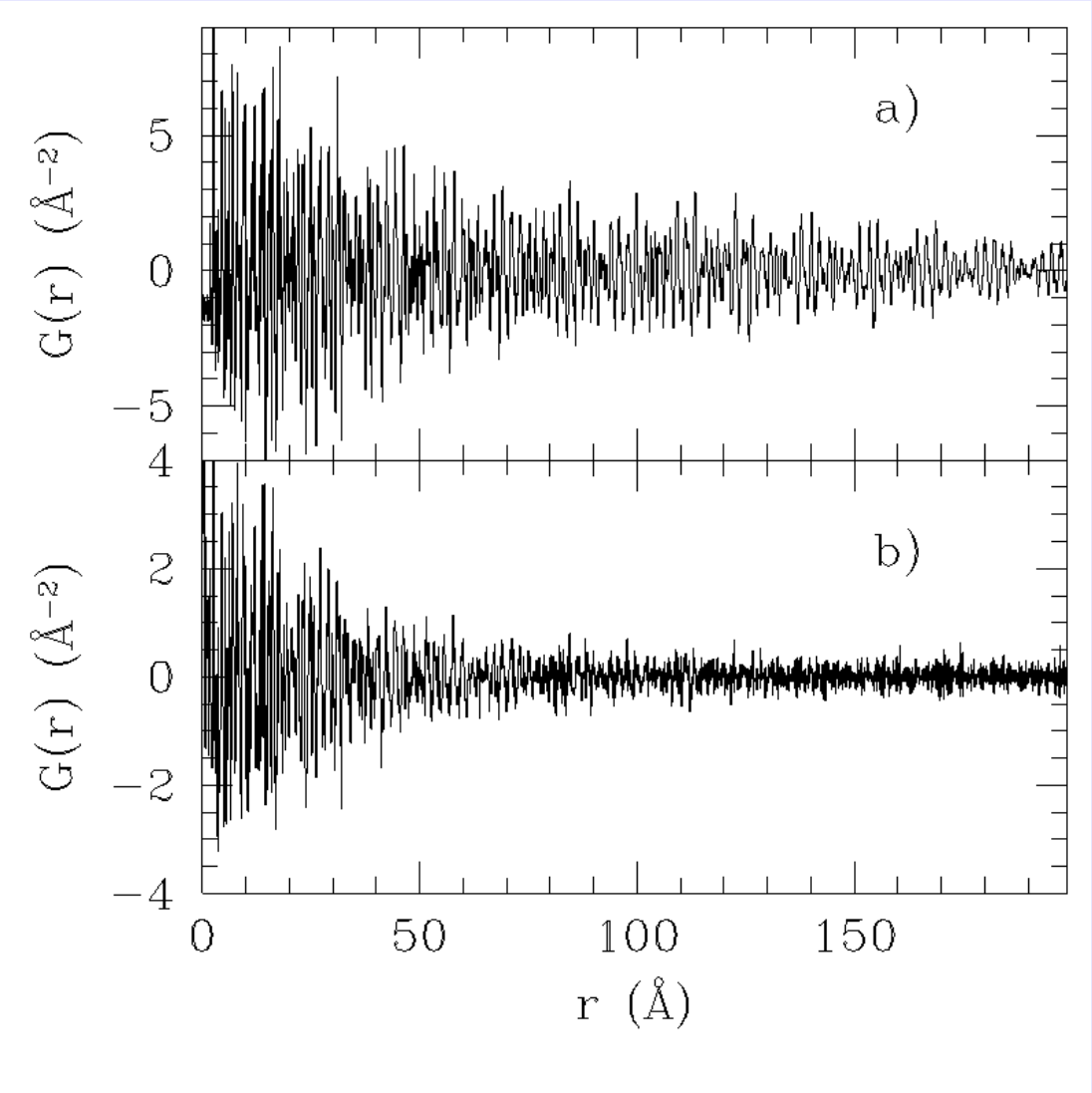
Neutron PDF of Buckeyballs



- The local structure is well characterized for r<7Å, the size of the buckeyballs.
- The structure at larger r gives correlations of spatial arrangements between the buckeyballs.

- T. Egami and S. J. L. Billinge, “Underneath the Bragg Peaks, Structural Analysis of Complex Materials”, Pergamon, 2003

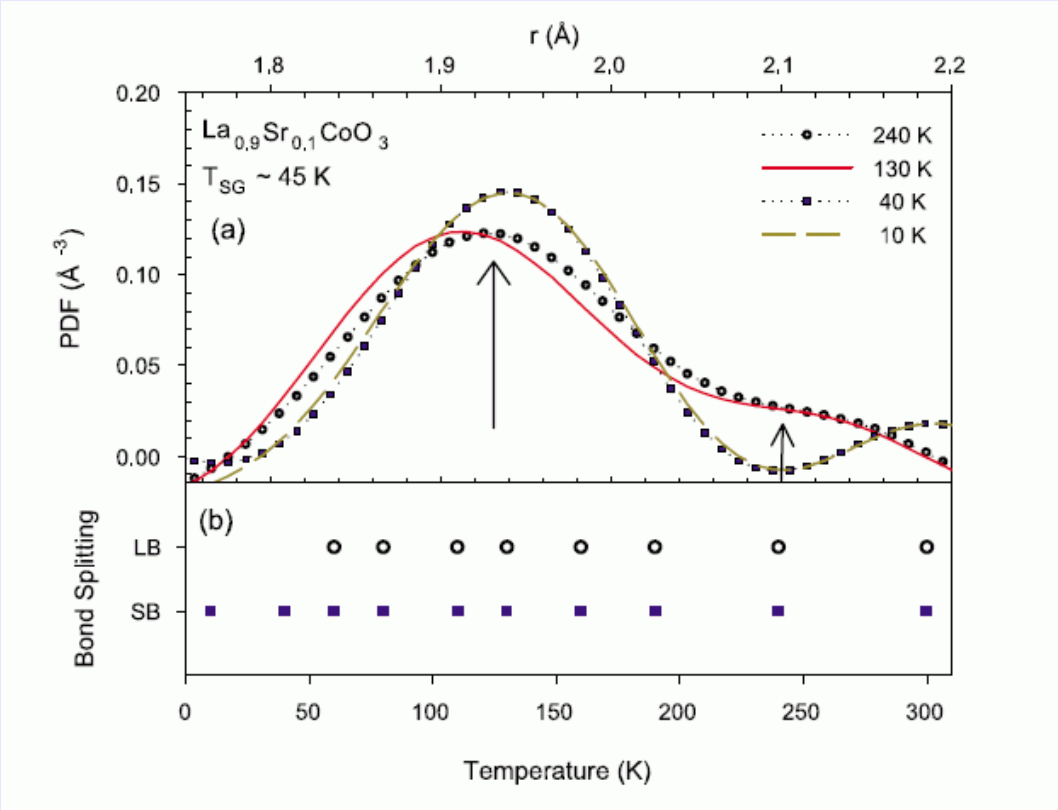
PDF of bulk and nanoparticle powders



- *G(r)* in $La_{0.8}Sr_{0.2}CoO_3$ bulk powder sample.

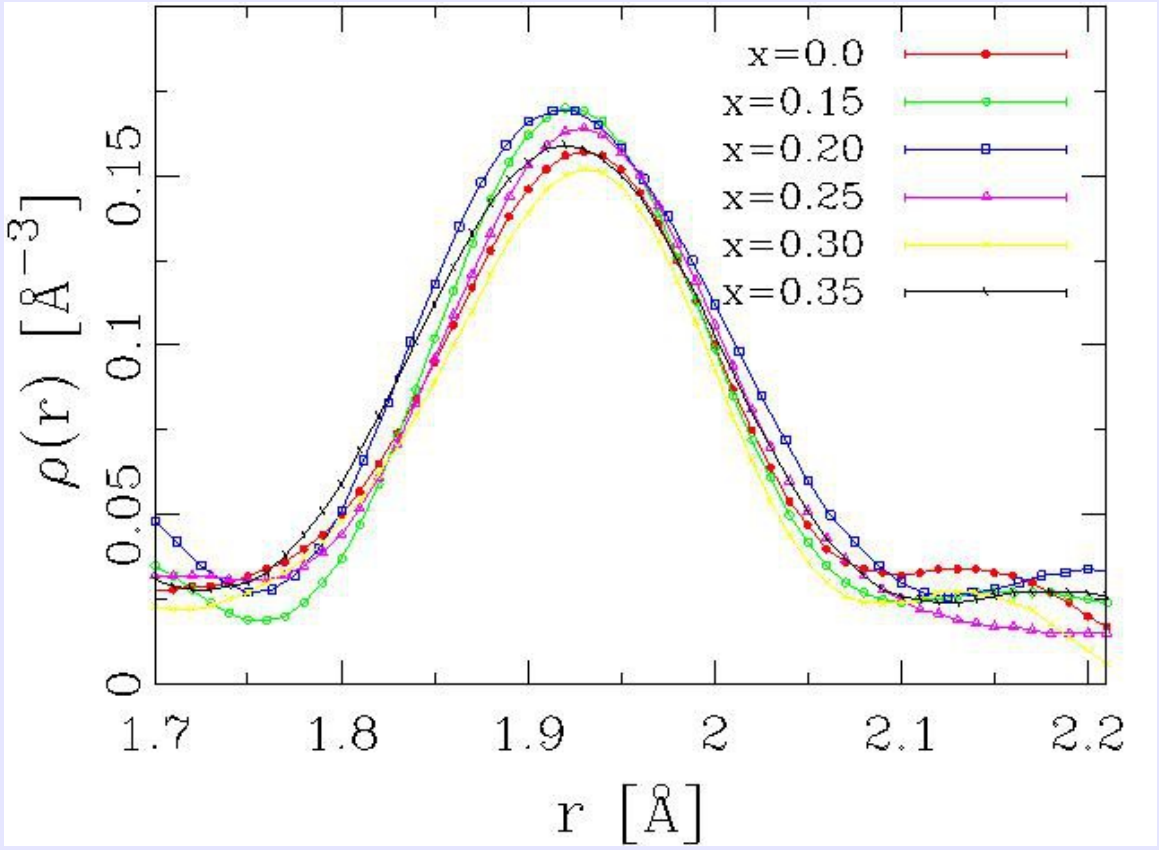
- *G(r)* in $La_{0.8}Sr_{0.2}CoO_3$ nanoparticle powder sample. Correlations drop off as the particle size is approached, as expected.

Previous "Observation" of Jahn-Teller Distortion in Cobaltites



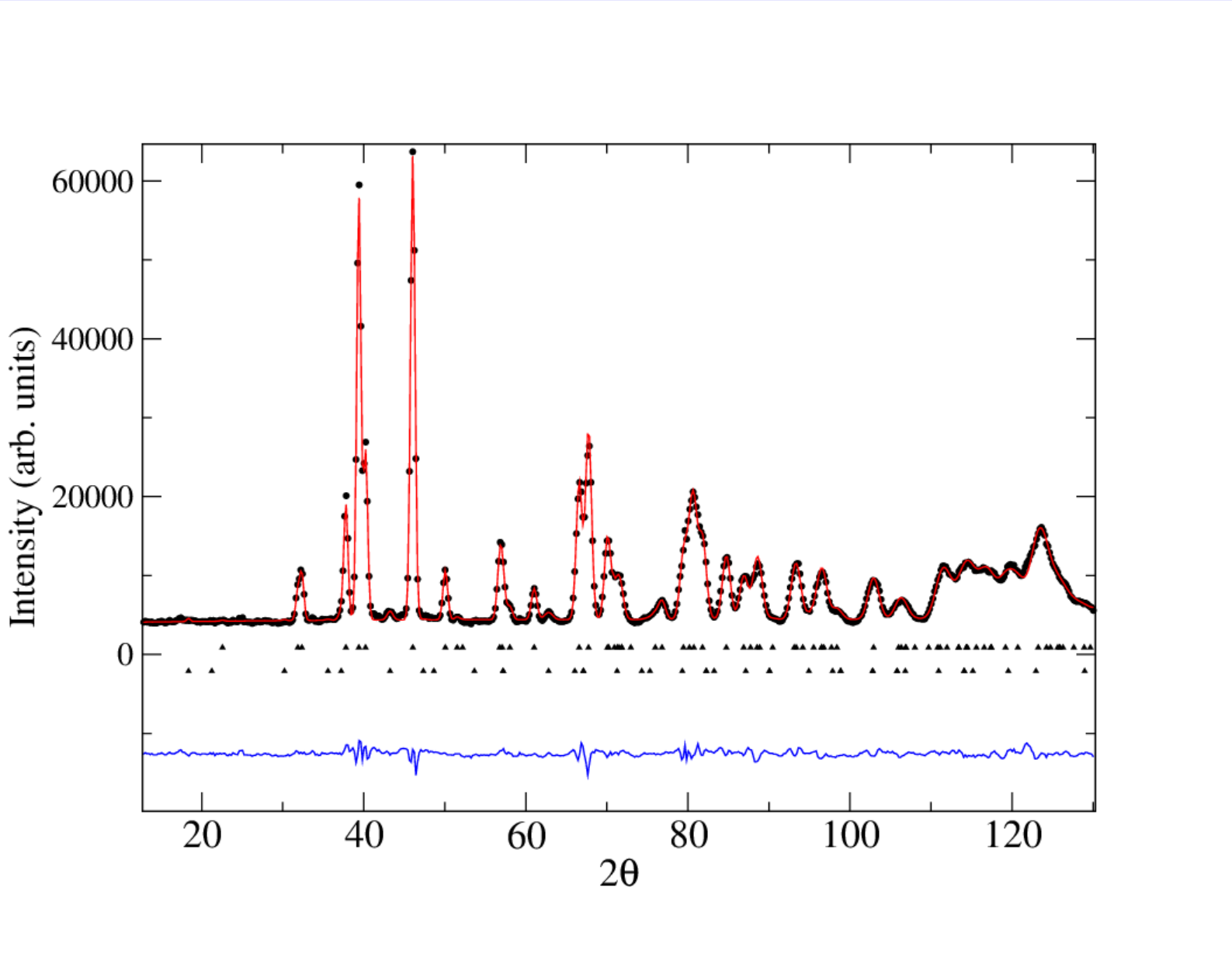
- A previous neutron PDF study showed an apparent large J-T distortion, with the second peak at 2.1 Å only for temperatures of 50K or higher, but not at very low temperature.
- This was taken to be direct evidence for the population of the IS state as the temperature increased.
- D. Louca and J.L. Sarrao, Phys. Rev. Lett. **91**, 155501 (2003).

No neutron PDF evidence for a Jahn Teller distortion at T=300K in $La_{1-x}Sr_xCoO_3$

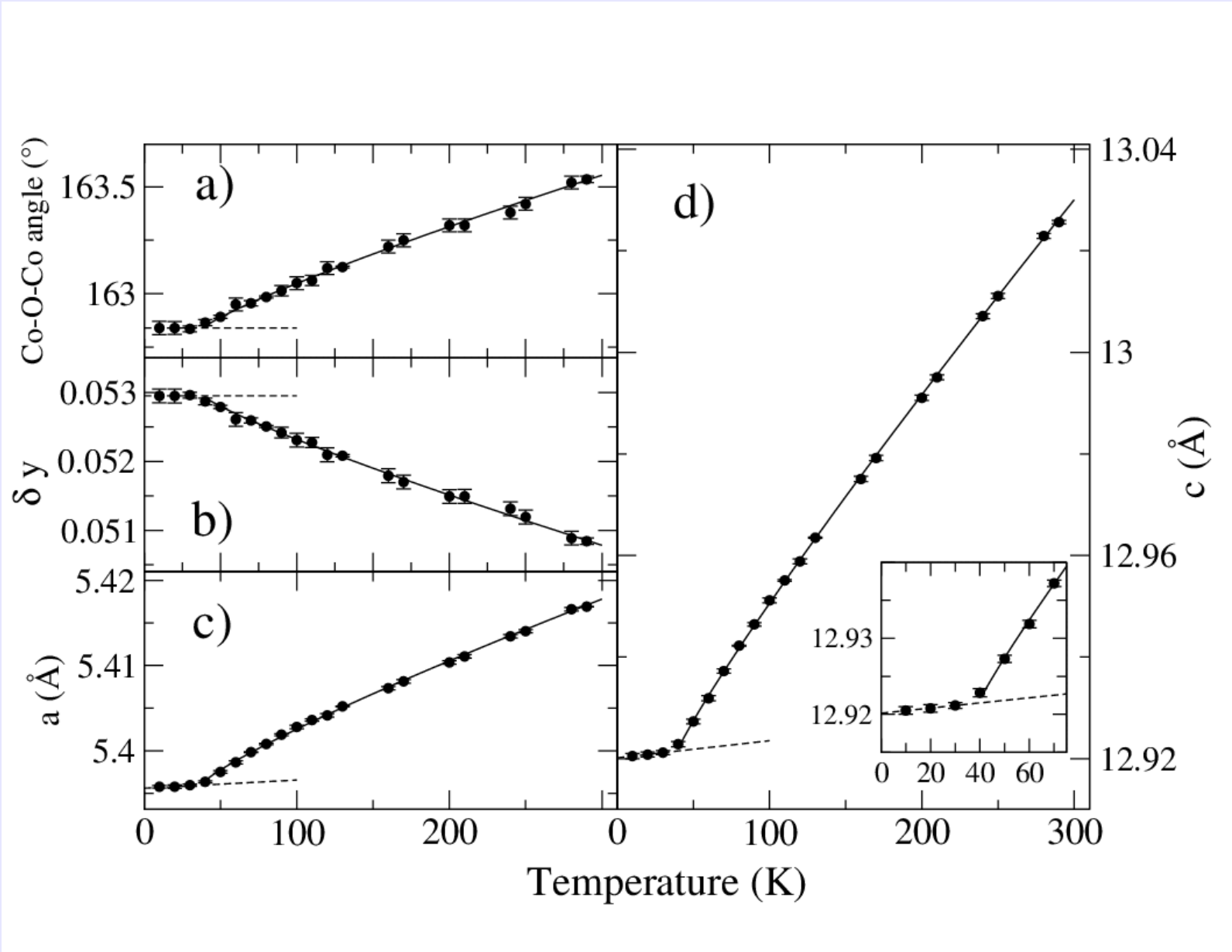


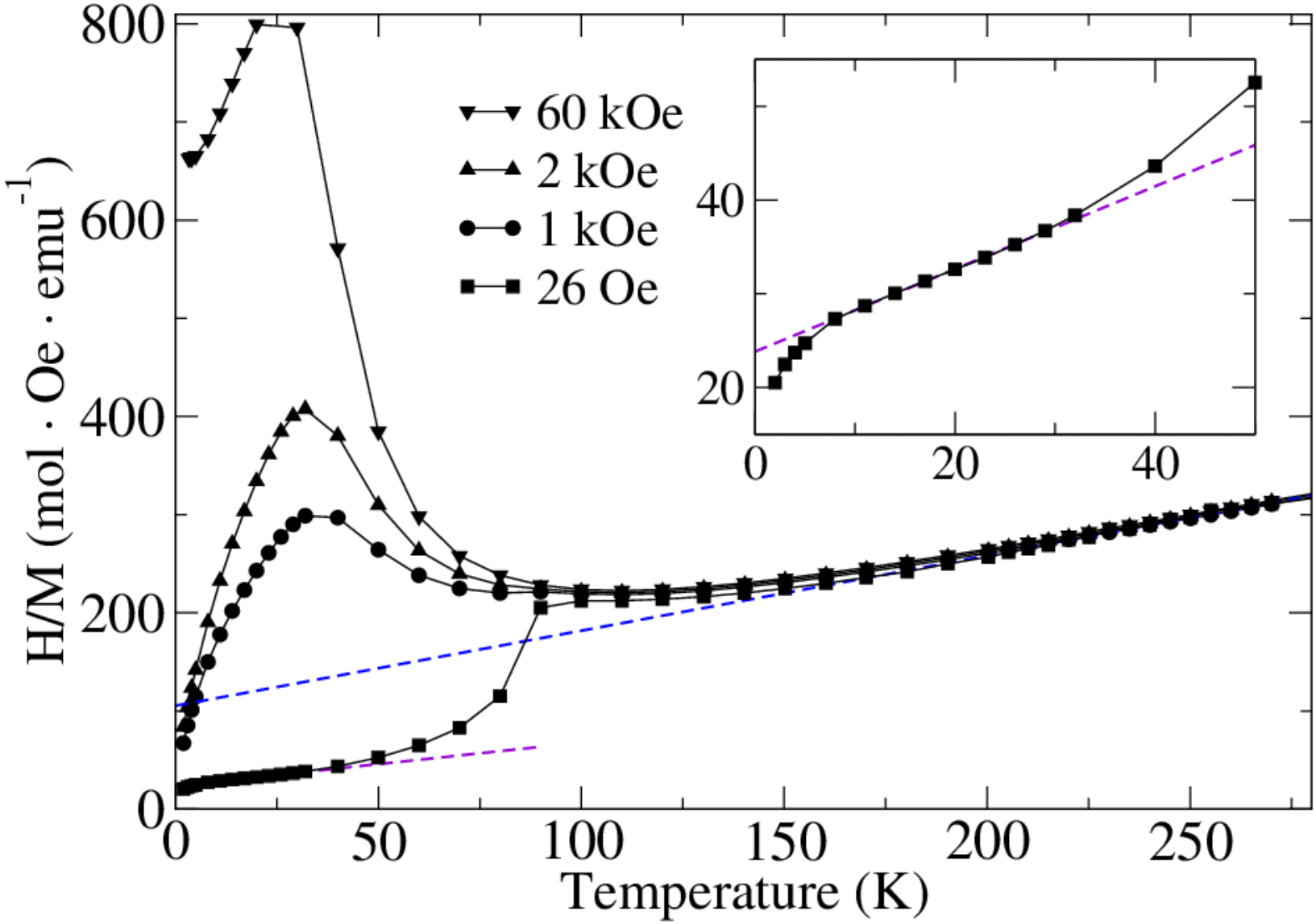
- The main peak is the Co-O bond at 1.92 Å, as previously observed
- The peak reported by Louca, et al. at 2.1 Å is not evident at any concentration or temperature.
- The small peaks are artifacts of the Fourier transform.
- Note that the Co-O bond length does not change much with Sr doping.
- Los Alamos NPDF

WAND (ORNL) diffraction pattern

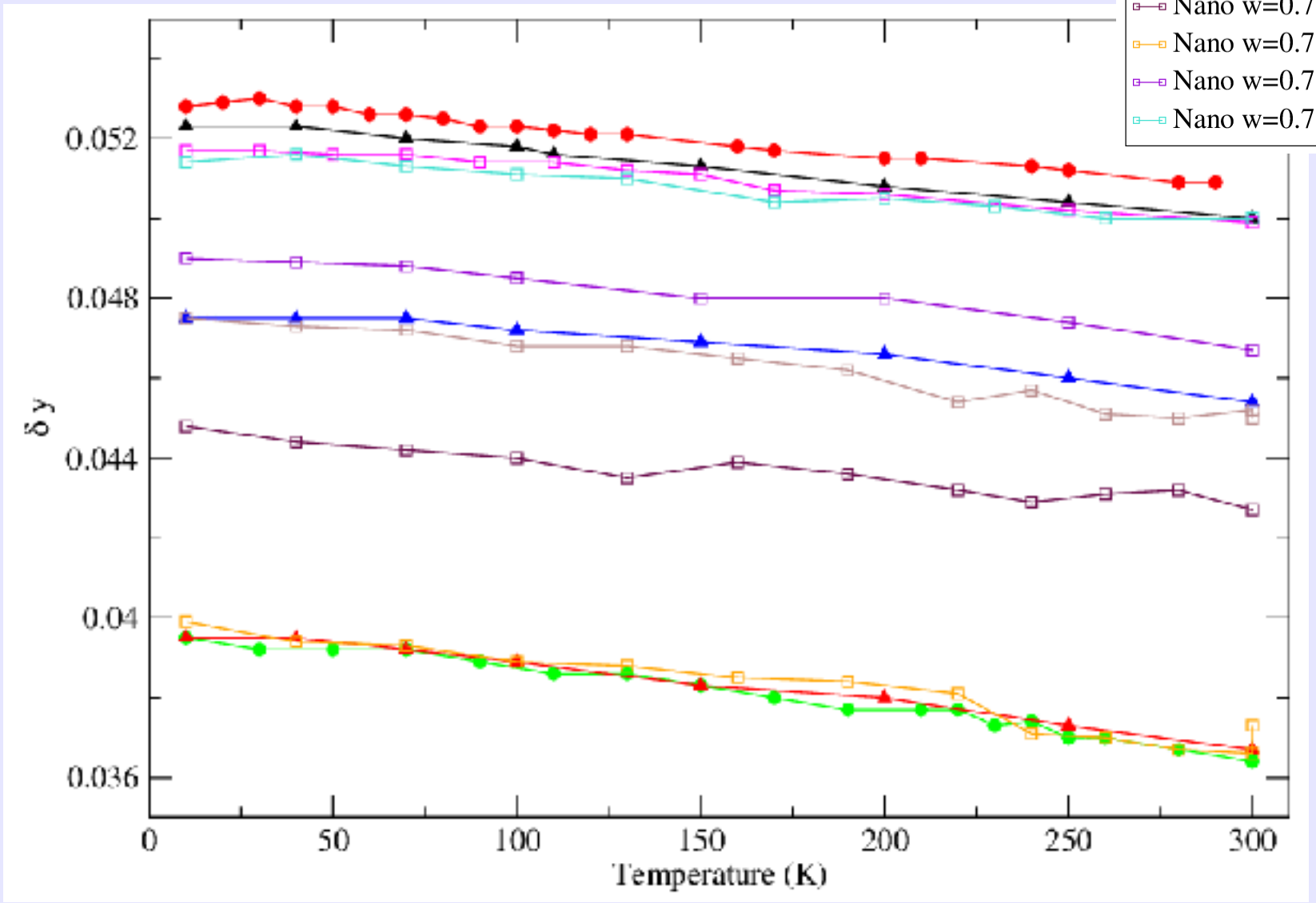


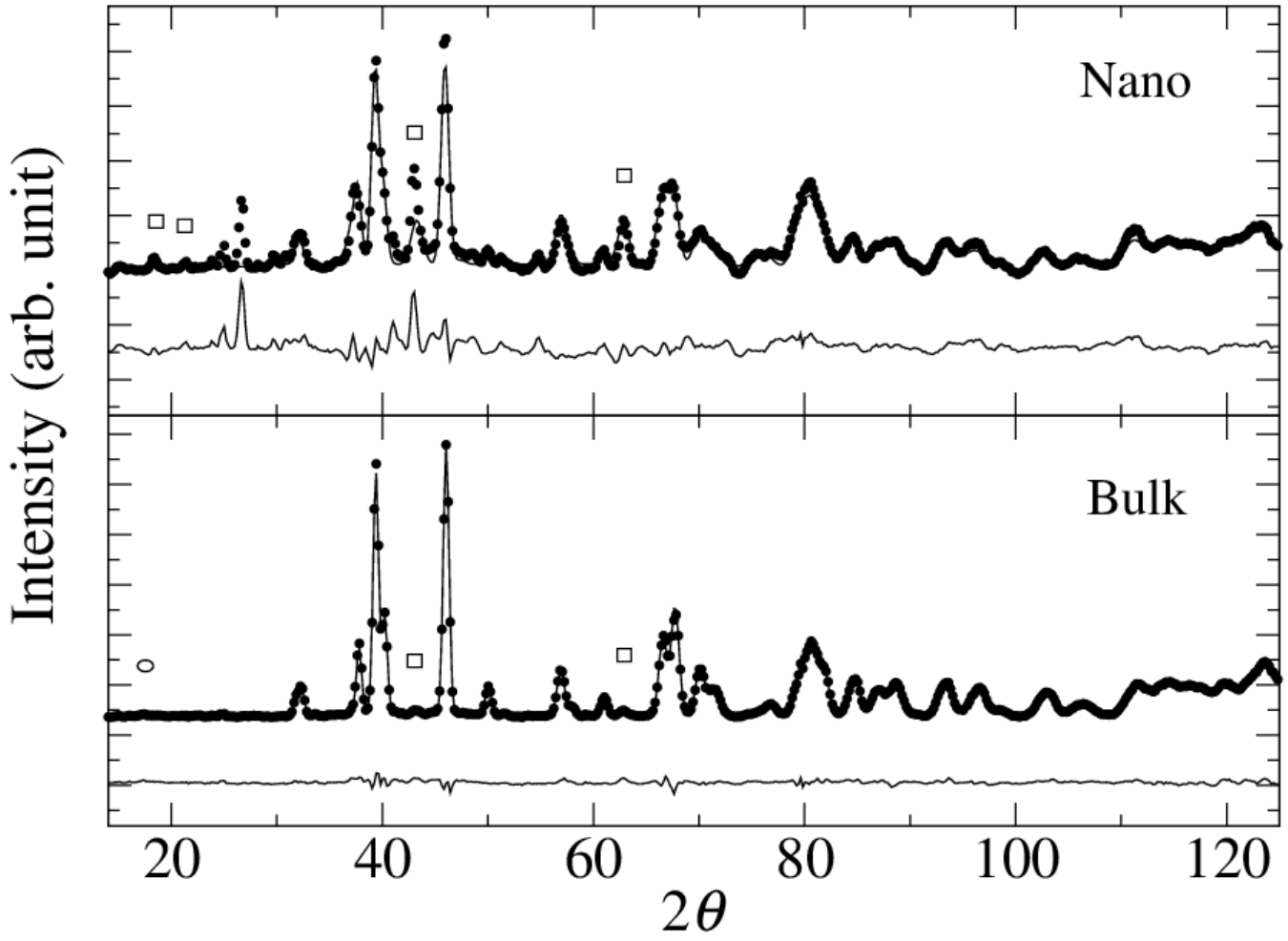
Structural Phase Transition

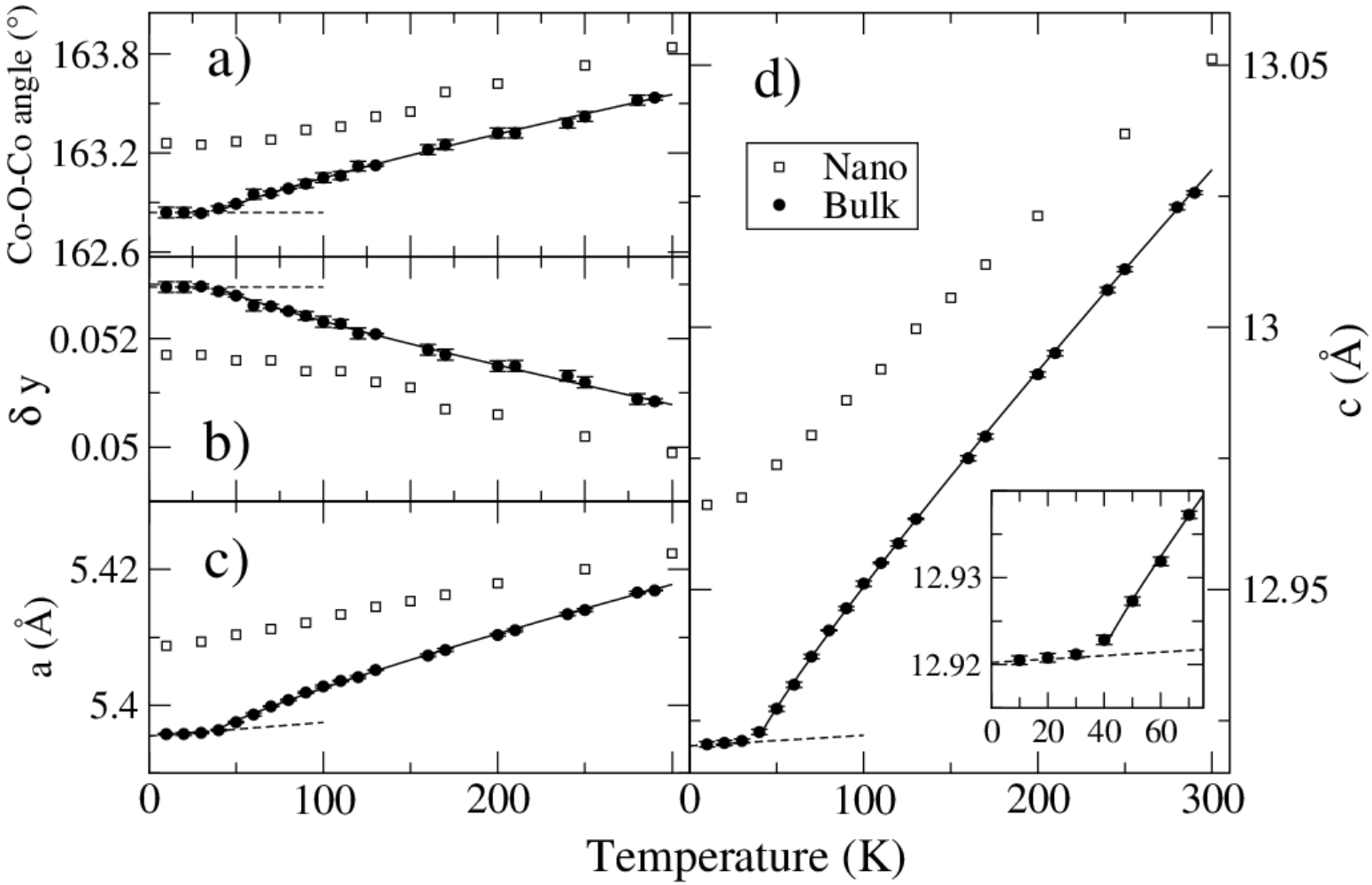


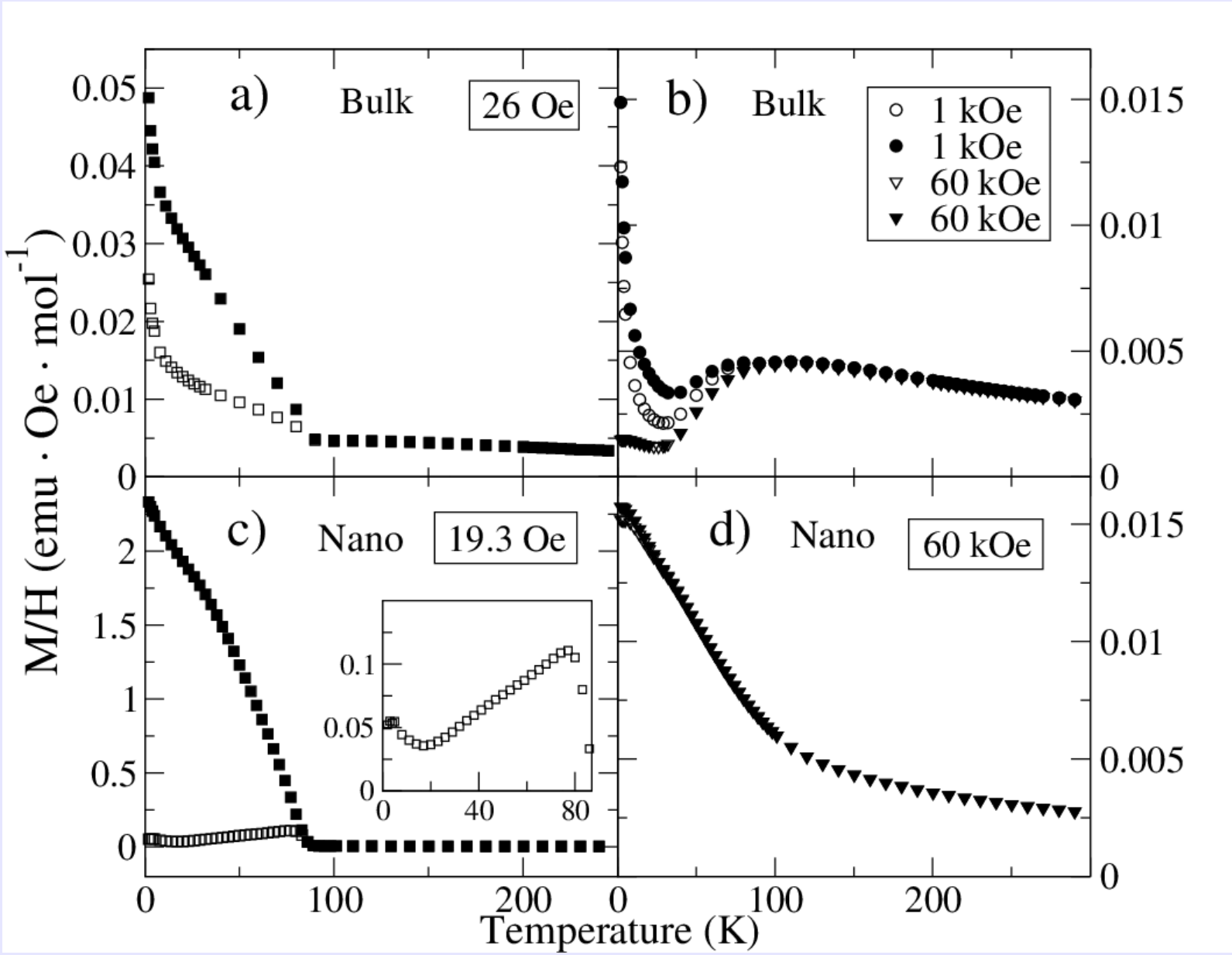

800
600
400
200
0
H/M (mol · Oe · emu^{-1})
60 kOe
2 kOe
1 kOe
26 Oe
40
20
0
20
40
0
50
100
150
200
250
Temperature (K)

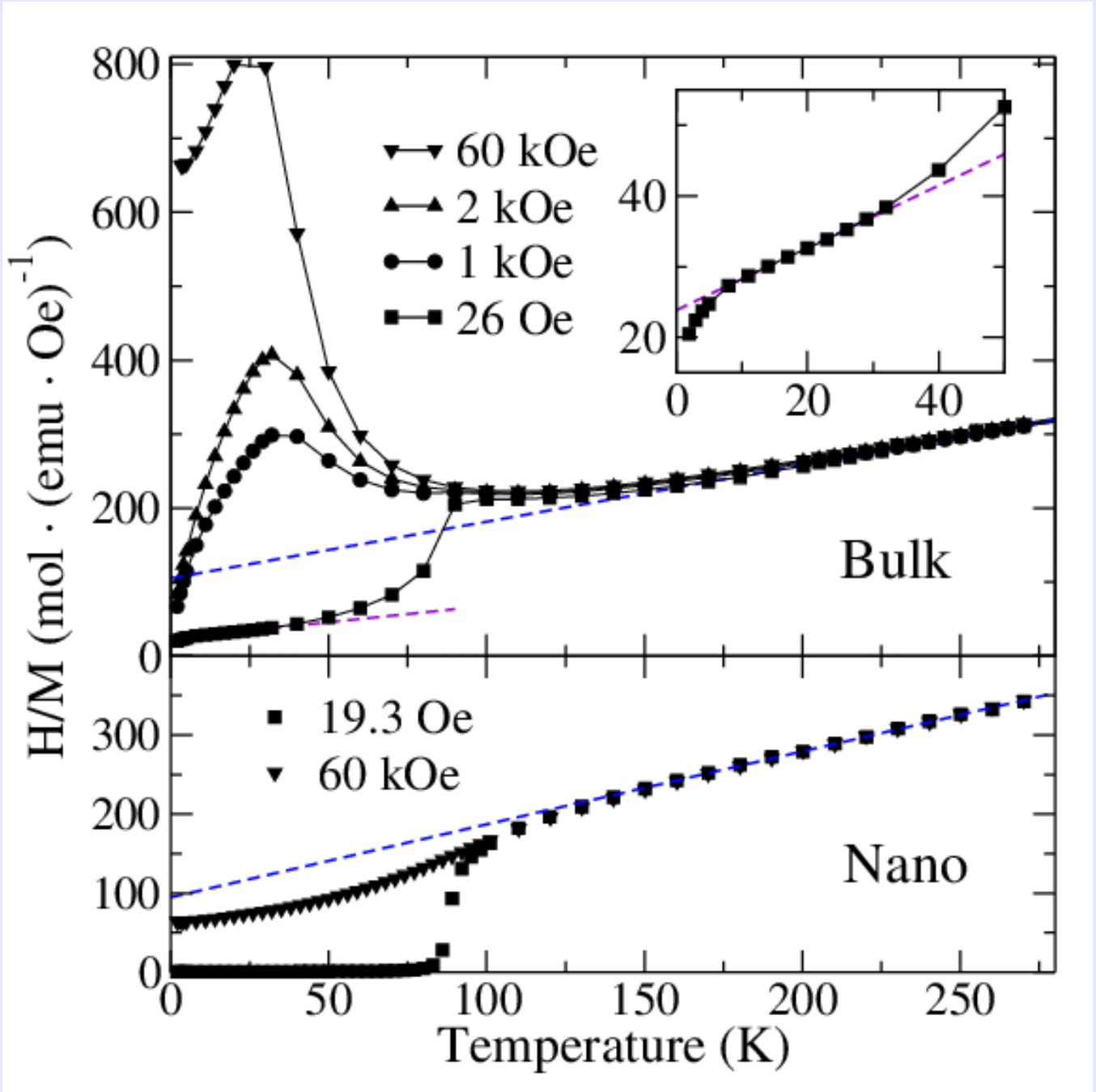
Magnetism depends on the rotation of the octahedra




Nano
Bulk
Intensity (arb. unit)
20
40
60
80
100
120
2θ


a)
b)
c)
d)
Co-O-Co angle (°)
163.8
163.2
162.6
δ y
0.052
0.05
a (Å)
5.42
5.4
Nano
Bulk
13.05
13
12.95
c (Å)
12.93
12.92
0
20
40
60
0
100
200
0
100
200
300
Temperature (K)


a)
Bulk
26 Oe
b)
Bulk
1 kOe
1 kOe
60 kOe
60 kOe
c)
Nano
19.3 Oe
d)
Nano
60 kOe
M/H (emu · Oe · mol^{-1})
Temperature (K)


800
600
400
200
0
H/M (mol · (emu · Oe)$^{-1}$)
60 kOe
2 kOe
1 kOe
26 Oe
40
20
0
20
40
Bulk
300
200
100
0
19.3 Oe
60 kOe
Nano
0
50
100
150
200
250
Temperature (K)

Conclusions

- Nanoparticles of $La_{1-x}Sr_xCoO_3$ are grown and characterized, with sizes 20 to 300nm.
- Neutron scattering can look at long-range and short-range order as well as magnetism and excitations.
- The neutron PDF techniques show no significant Jahn-Teller distortion in bulk or nanoparticle powders. This is consistent with the results Bud Bridges and his group obtained with EXAFS.
- We have shown that the strange magnetic behavior in $LaCoO_3$ is not a result of the Jahn-Teller distortion, but rather the structural and magnetic cooperative behaviors in the system.
- Local excitation models are not adequate to describe the behavior of $LaCoO_3$ or $La_{1-x}Sr_xCoO_3$.