First Shell EXAFS Analysis

Anatoly Frenkel

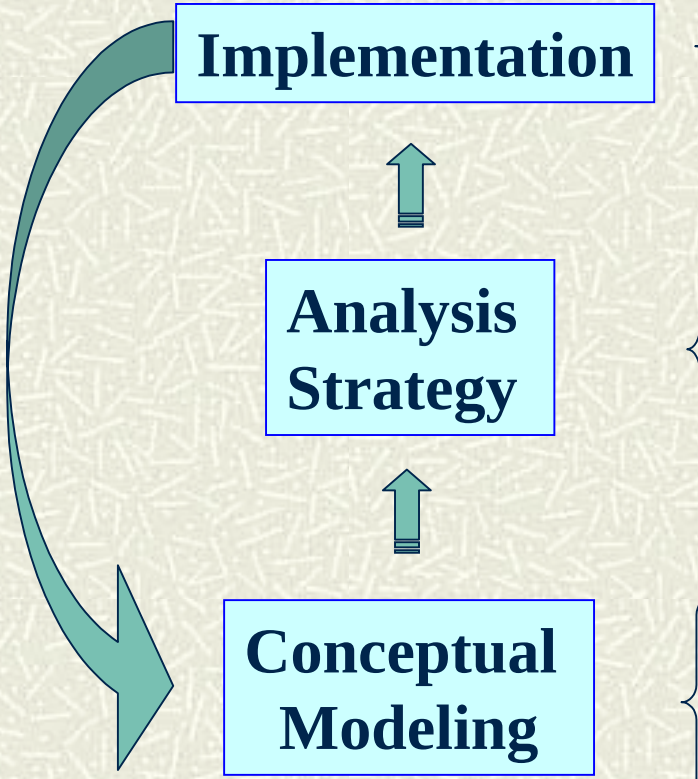
Physics Department, Yeshiva University, New York, NY 10016
frenkel@bnl.gov

General strategy:

-Collect good data
-Come up with a physically reasonable, constrained model
-Test your model on a reference compound
-Fit it to the unknown sample data
-Be conservative with the number of fitting parameters

"Bottom-up" approach – the preferred strategy of the First Shell Analysis:

(You will avoid going in the wrong direction too early…)



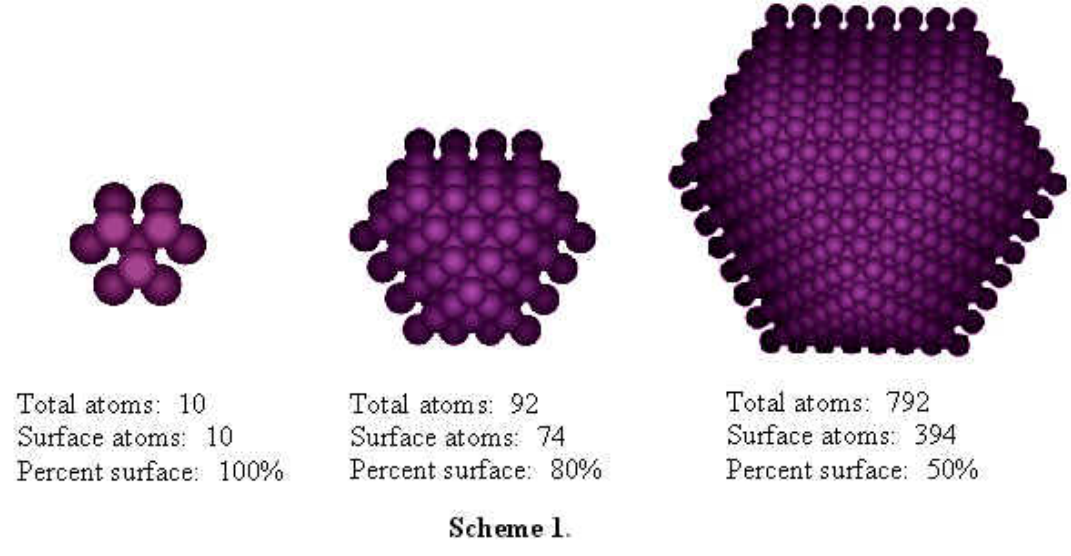
Find the best analysis software that can implement your strategy.
Not all packages are universally good.

-Plan on doing reality checks;
-Reference compounds should be measured and analyzed first;
-Try to maximize the number of degrees of freedom in the fits
(use constraints, experimental/theoretical info etc.)

Linear fit is better than nonlinear fit!

-Start with the crude picture first, then refine it;
-Homogeneous or heterogeneous environment?
(bulk or nano, eq. or ineq. unit cell positions, solution or separate phases etc.)

Test case: supported Pt nanoparticles

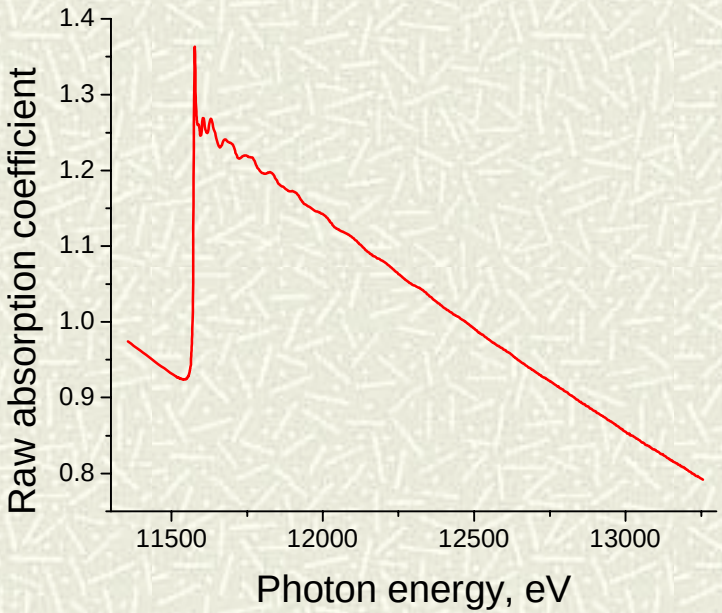


Scheme 1.

What are we after?

-Size,
-Structure,
-Thermal properties.

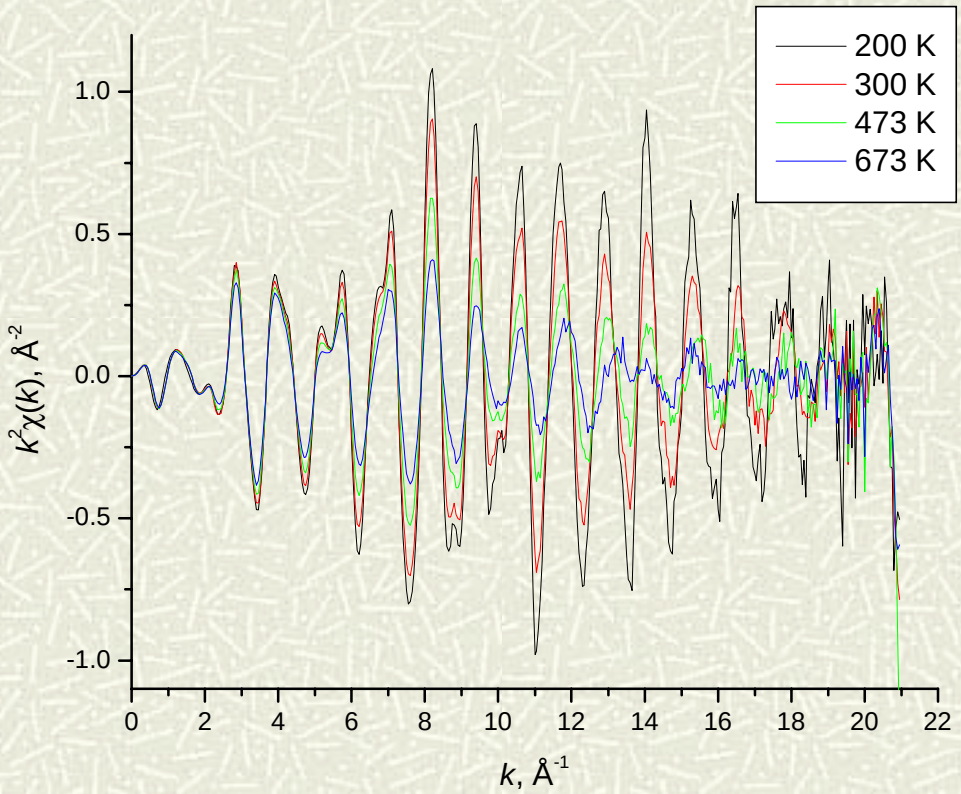
(Beamline: X16C, NSLS)



What relevant info can be found from EXAFS?

-Model of atomic packing,
-Average CN,
-Average distances,
-Average disorder

EXAFS data measured of particles of ~20 Å in size:



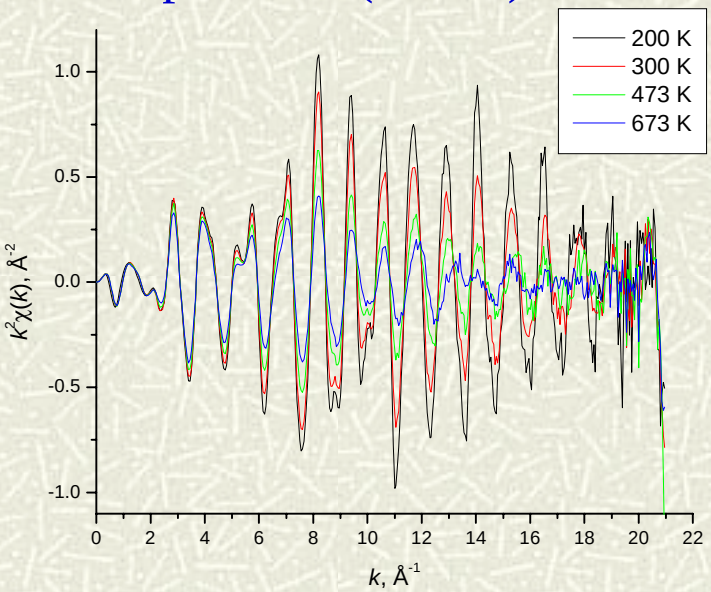
Can we tell what is the particle's structure?

Whether particles agglomerate at high T?

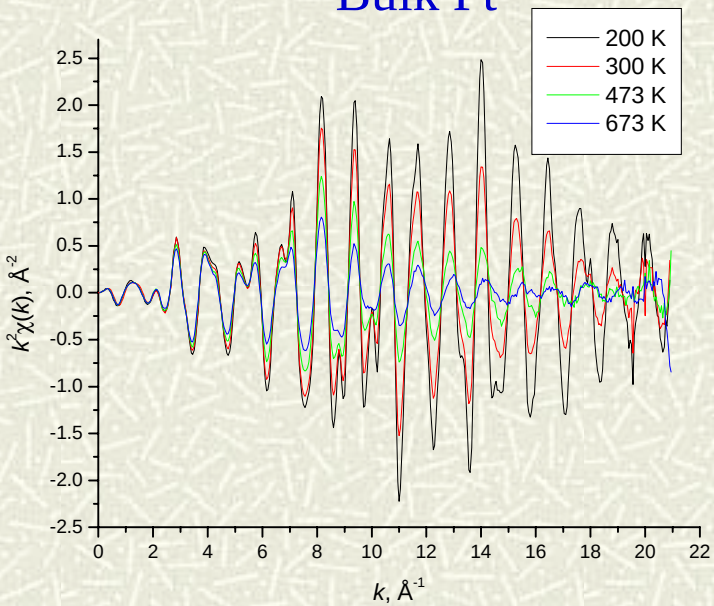
Whether the changes are dominated by atomic rearrangements or by thermal disorder?

Can we answer the same questions if a reference compound is measured as well?

Pt particles (~20 Å)



Bulk Pt



$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\text{eff}}(k)\right| e^{-2\sigma^2 k^2} \sin\left[2kr - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$

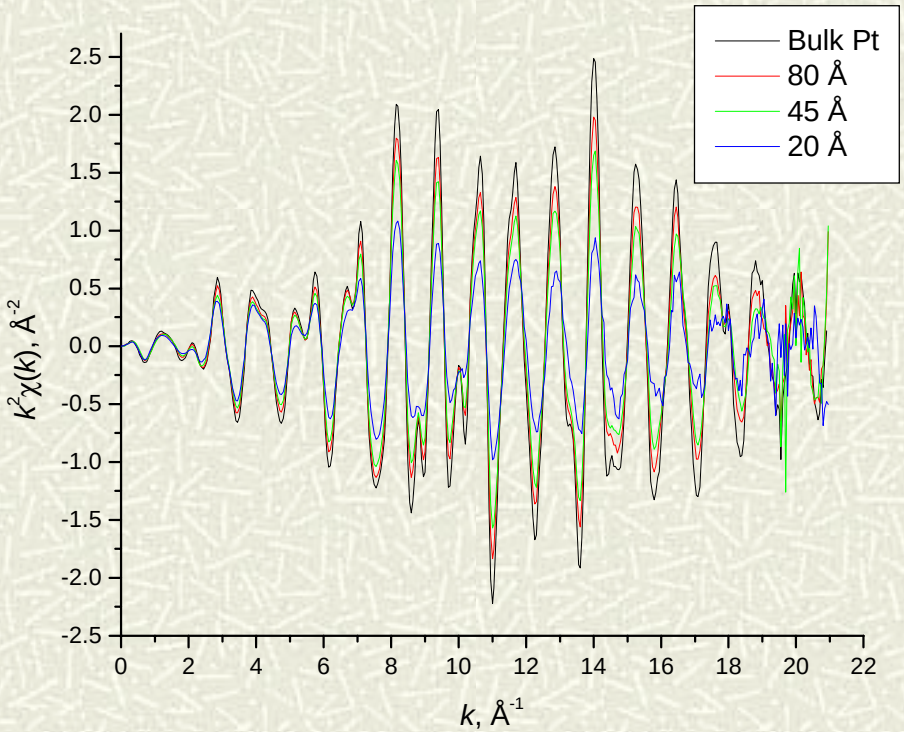
Can we tell what is the particle's structure? -Yes, consistent with *fcc*

Whether particles agglomerate at high T? - Most likely no, the size effect is not evident

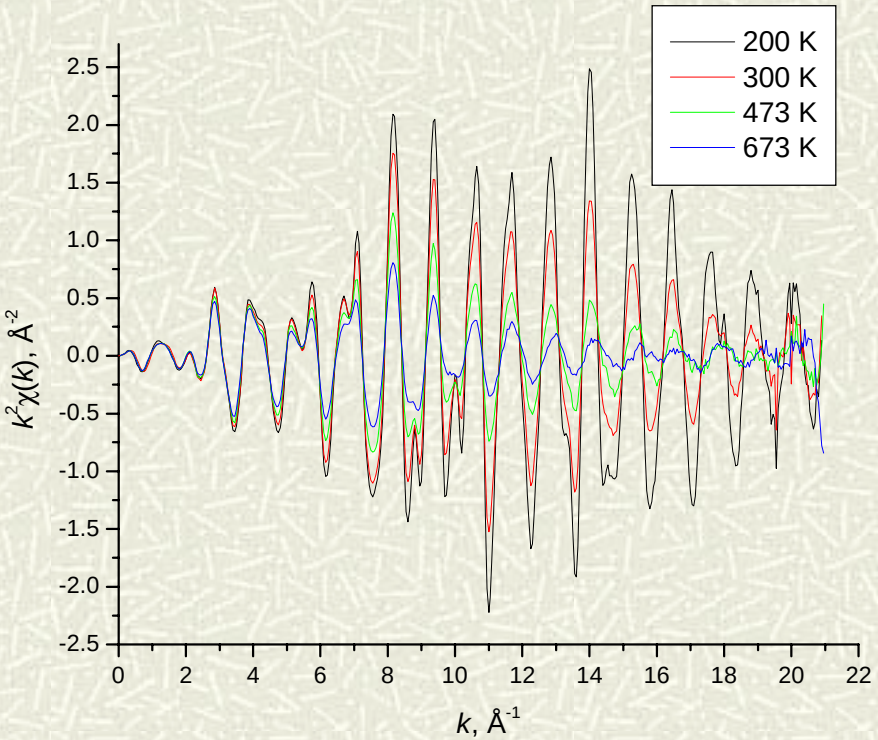
Whether the changes are dominated by atomic rearrangements or by thermal disorder?

How to tell size dependence from temperature dependence?

T=200 K; Size is varied



Bulk Pt; Temperature is varied



$$\chi(k) \sim N\, e^{-2\sigma^2 k^2}$$

As a function of size, EXAFS amplitude is scaled ***uniformly*** throughout the *k*-range

As a function of temperature, EXAFS amplitude is scaled ***nonuniformly***

How to model metal (Pt) foil data:

Pt foil, T=200 K

guess S02 = 0.9
guess ss1 = 0
guess dr1 = 0
guess th1 = 0
guess e0 = 0

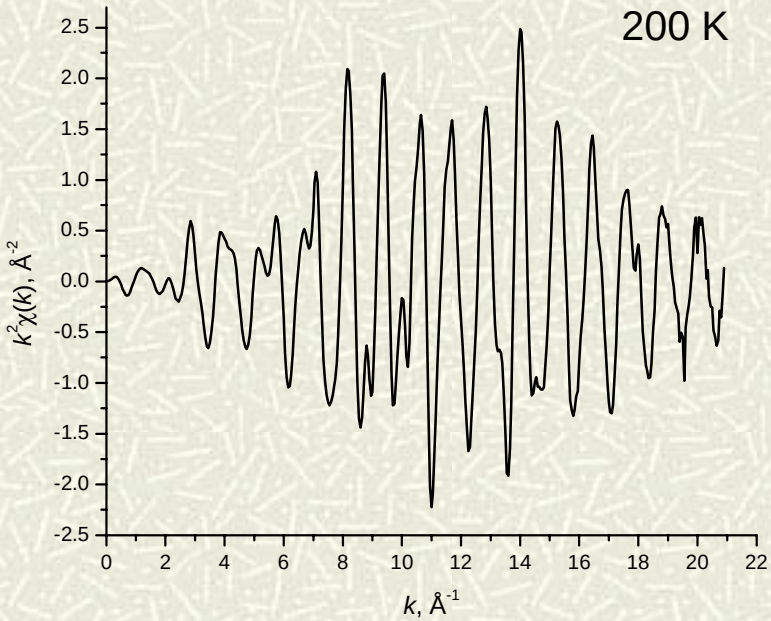
$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\,\mathrm{eff}}(k)\right| e^{-2\sigma^2 k^2} \times \sin\left[2kr - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$

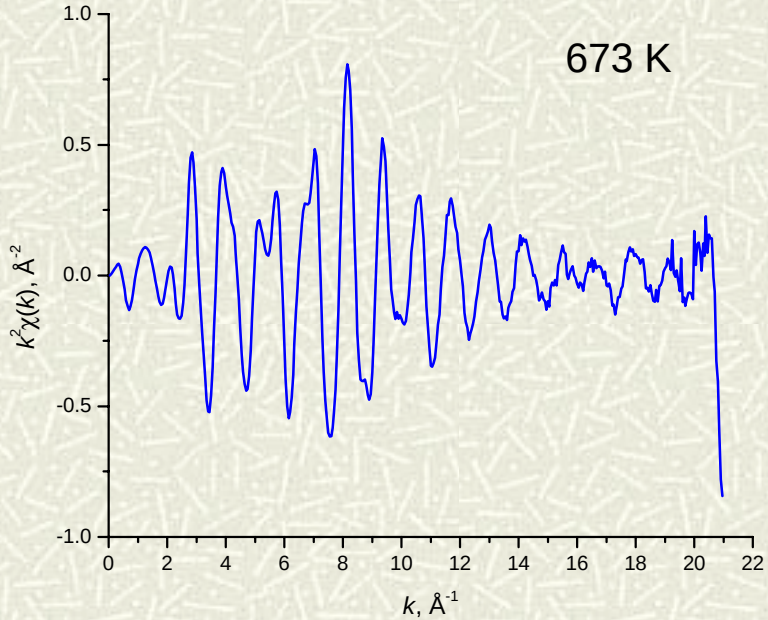
data = ptfoil-200avk.chi
out = ptfoil-200avk

rmin = 2.1 rmax = 3.3
kmin = 2 kmax= 20 w = 2 dk=2

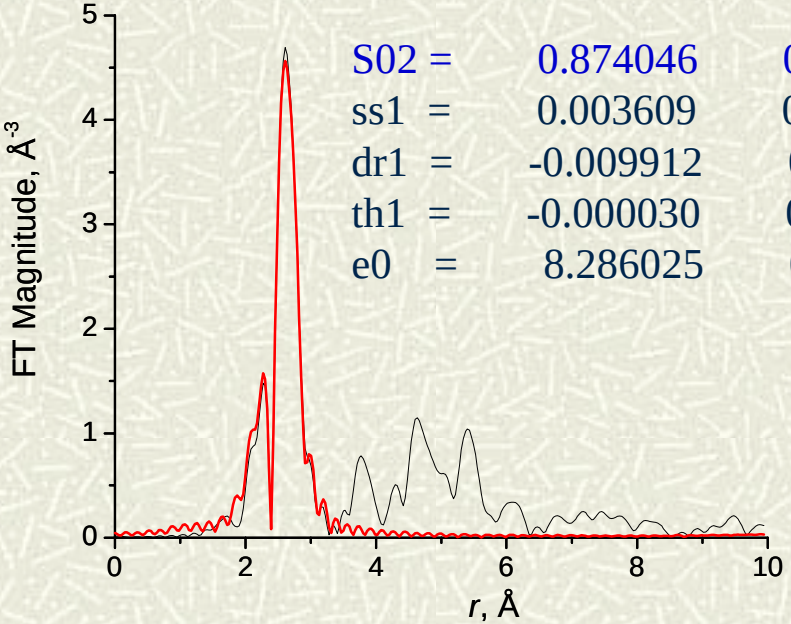
!% 1st path:

e0shift	1	e0
amp	1	S02
path	1	p1.dat
id	1	SS Pt-Pt(1), r=2.7719
delr	1	dr1
sigma2	1	abs(ss1)
third	1	th1





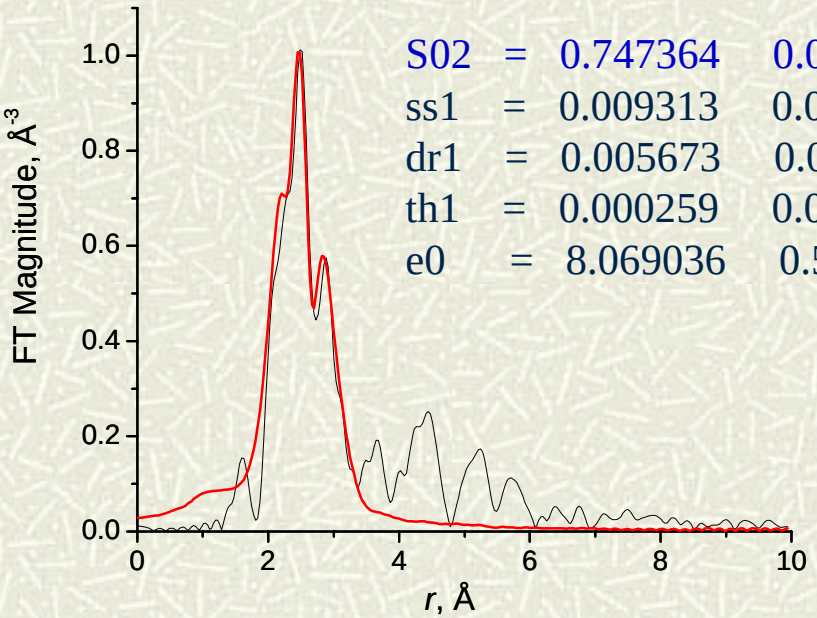
Fit Results



S02 =	0.874046	0.033009
ss1 =	0.003609	0.000106
dr1 =	-0.009912	0.003630
th1 =	-0.000030	0.000019
e0 =	8.286025	0.590203

This is not physically reasonable….

What caused S02 to be different at 200 K and 673 K?



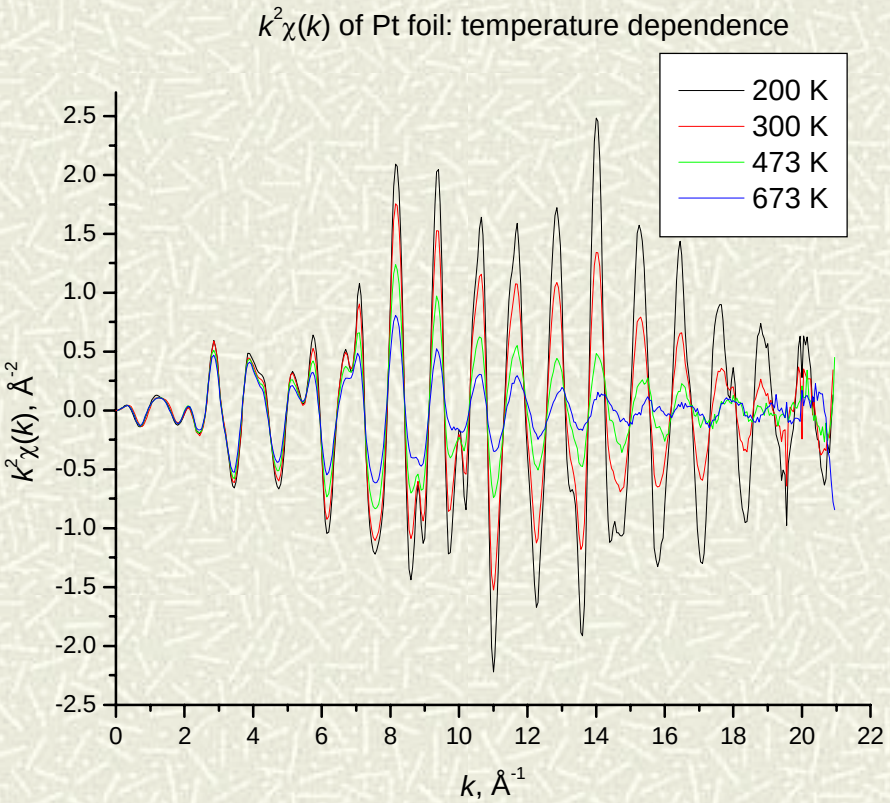
S02	=	0.747364	0.044827
ss1	=	0.009313	0.000385
dr1	=	0.005673	0.007571
th1	=	0.000259	0.000076
e0	=	8.069036	0.594447

- correlation with other fit variables:

$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\text{eff}}(k)\right| e^{-2\sigma^2 k^2} \times \sin\left[2kr - \frac{4}{3}C_3 k^3 + \delta(k)\right]$$

How to break the correlation?

$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\text{eff}}(k)\right| e^{-2\sigma^2 k^2} \sin\left[2kr - \frac{4}{3}C_3 k^3 + \delta(k)\right]$$



One possible solution:
a multiple-data-set (*mds*) fit.

What variables are not expected to change at different temperatures?

ΔE_0, N $\qquad$ σ_s^2 , Θ_E

$$\sigma^2 = \sigma_s^2 + \sigma_d^2$$

$$\sigma_d^2 = \frac{\hbar}{2\omega\mu}\frac{1+\exp(-\Theta_E/T)}{1-\exp(-\Theta_E/T)}$$

Multiple-Data-Set Fit

```
title = Pt L3-edge, foil
data  = ptfoil-200avk.chi    out = ptfoil-200avk
rmin  = 2.1   rmax = 3.3
kmin  = 2   kmax= 20    w = 2  dk =2

path        1  p1.dat
id          1  SS Pt-Pt1
e0shift     1  e0
amp         1  S02
delr        1  dr11
sigma2      1  abs(ss11)
third       1  th11

next data set

data  = ptfoil-300avk.chi   out = ptfoil-300avk
rmin  = 2.1   rmax = 3.3
kmin  = 2   kmax= 20    w = 2  dk =2

path        1  p1.dat
 id         1  SS Pt-Pt1
 e0shift    1  e0
 amp        1  S02
 delr       1  dr12
 sigma2     1  abs(ss12)
 third      1  th12

next data set
…….. ptfoil-473avk.chi …….
next data set
…….. ptfoil-673avk.chi …….

set ss11      = abs(ss011) + eins(200, theins1)
set ss12      = abs(ss011) + eins(300, theins1)
set ss13      = abs(ss011) + eins(473, theins1)
set ss14      = abs(ss011) + eins(673, theins1)

guess e0      =   0.
guess s02     = 0.9
guess ss011 = 0
guess theins1 = 200
```

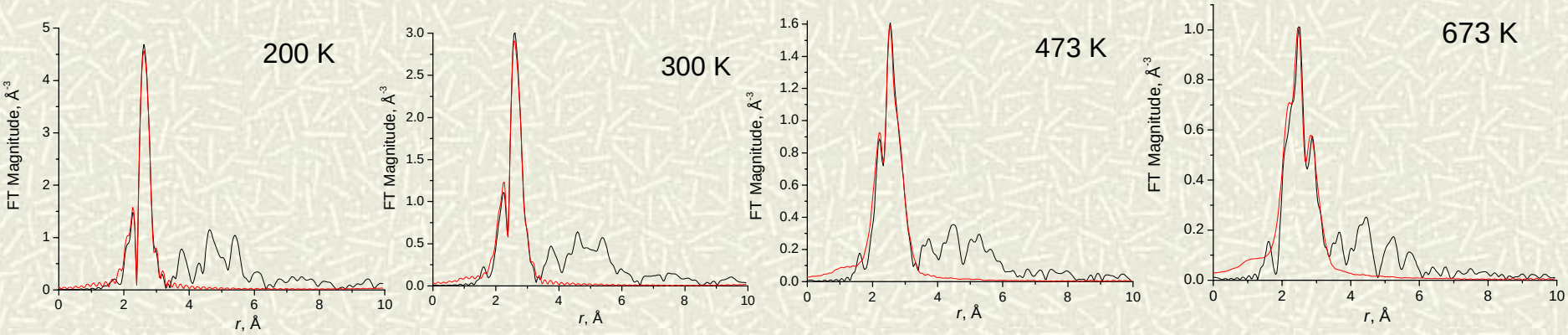
$$\sigma^2 = \sigma_s^2 + \sigma_d^2$$

$$\sigma_d^2 = \frac{\hbar}{2\omega\mu}\frac{1+\exp(-\Theta_E/T)}{1-\exp(-\Theta_E/T)}$$

```
guess dr11    =   0
guess dr12    =   0
guess dr13    =   0
guess dr14    =   0

guess th11    =   0
guess th12    =   0
guess th13    =   0
guess th14    =   0
```

MDS fit results



ss011	=	0.000533	0.000093
theins1	=	189.743073	2.311668
s02	=	0.836704	0.017830
dr11	=	-0.011222	0.002248
dr12	=	-0.009361	0.003034
dr13	=	-0.000354	0.003642
dr14	=	0.006588	0.004801
th11	=	-0.000035	0.000013
th12	=	-0.000017	0.000022
th13	=	0.000113	0.000033
th14	=	0.000267	0.000060
e0	=	8.064717	0.271896

Physical (chemical, engineering, mat.science, life science etc.)

reality checks:

1) Debye temperature: 240 K for Pt
As obtained (through Θ_E): 253(3) K

2) Static disorder σ_s^2: ~0
3) Corrections to model distances: ~0

4) Thermal expansion: evident

5) S02: reasonable (between 0.7 and 1.0)

How to tell right from wrong?

$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\text{eff}}(k)\right| e^{-2\sigma^2 k^2} \sin\left[2kr - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$

Pretend, we do not believe in “third cumulants”.

With C_3

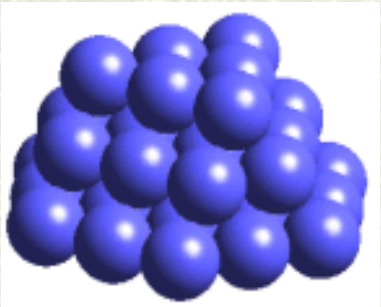
ss011	=	0.000533	0.000093
theins1	=	189.743073	2.311668
s02	=	0.836704	0.017830
dr11	=	-0.011222	0.002248
dr12	=	-0.009361	0.003034
dr13	=	-0.000354	0.003642
dr14	=	0.006588	0.004801
th11	=	-0.000035	0.000013
th12	=	-0.000017	0.000022
th13	=	0.000113	0.000033
th14	=	0.000267	0.000060
e0	=	8.064717	0.271896

Without C_3

ss011	=	0.000472	0.000127
theins1	=	187.676941	3.088949
s02	=	0.840180	0.024436
dr11	=	-0.007120	0.001032
dr12	=	-0.008353	0.001577
dr13	=	-0.010902	0.002108
dr14	=	-0.011235	0.002930
e0	=	7.728140	0.271577

How to model XAFS data in nanoparticles?

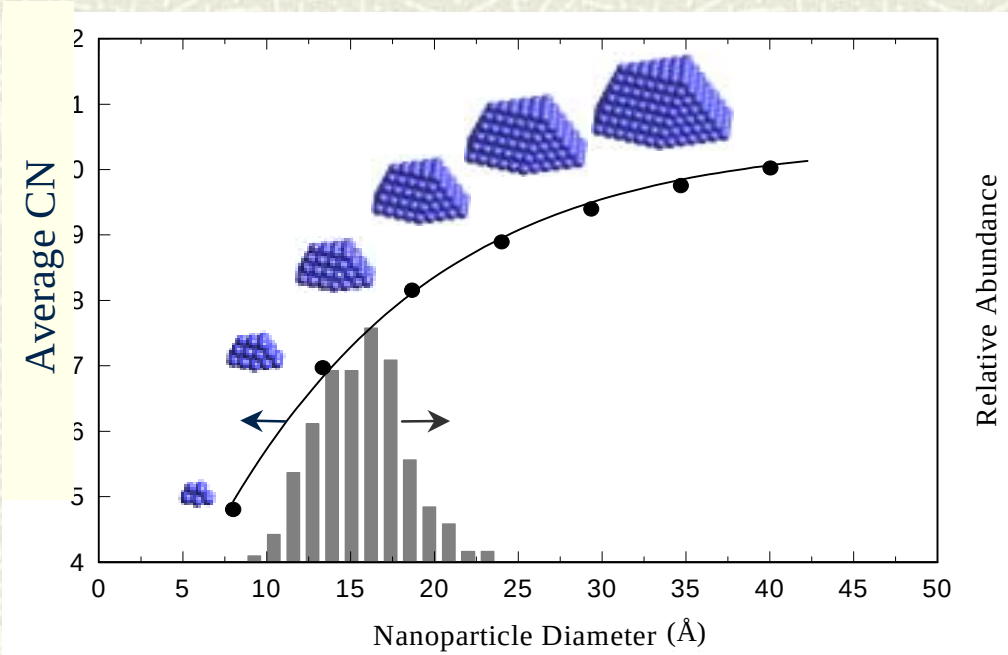
A priori knowledge or a working hypothesis must exist
(the "zero" approximation)
otherwise: the transferability of amplitude/phase will not work!)



1) Hemispherical
2) Crystal order
3) Size: about 20 Å

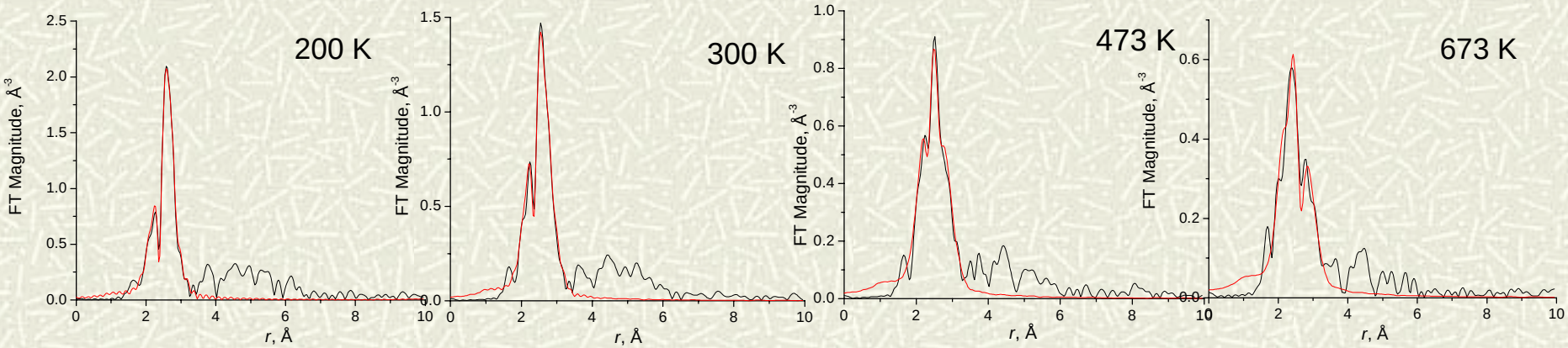
What information can be obtained from 1st shell EXAFS analysis?

1) Size of the particle (via N)
2) Distances, thermal vibration, expansion
3) Static disorder (icosahedral? surface tension?)



MDS fit (1shell) to the nanoparticles EXAFS

- Coordination number is now guessed (a variable)
- S_0^2 is fixed to be equal to that in Pt foil EXAFS
- E0 is fixed to be equal to that in Pt foil EXAFS



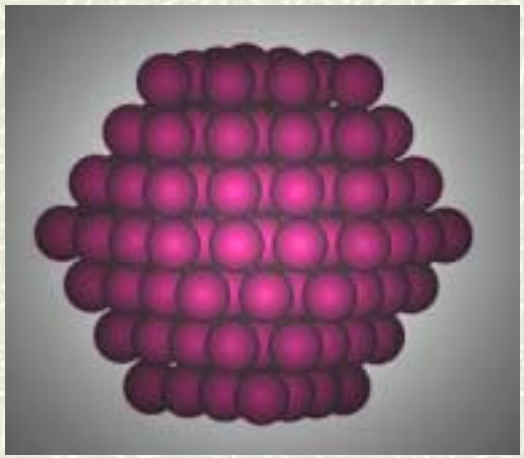
ss011	=	0.001676	0.000177
theins1	=	191.842209	3.893480
n1	=	7.879327	0.197850

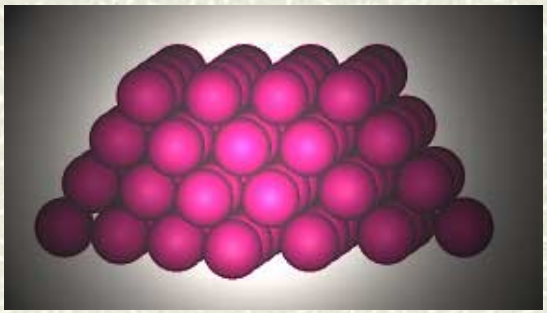
dr11	=	-0.015809	0.003938
dr12	=	-0.011870	0.002064
dr13	=	-0.008558	0.003883
dr14	=	-0.000845	0.004875
th11	=	-0.000017	0.000030
th12	=	0.000055	0.000019
th13	=	0.000159	0.000047
th14	=	0.000421	0.000079

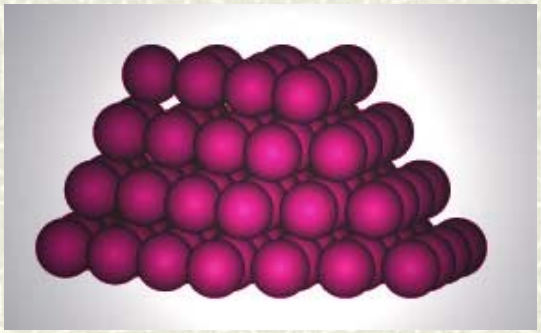
To get the most out of the data, the Multiple-Scattering Analysis is often needed.

What are the limitations of the 1st Shell Analysis in the case of nanoparticles?

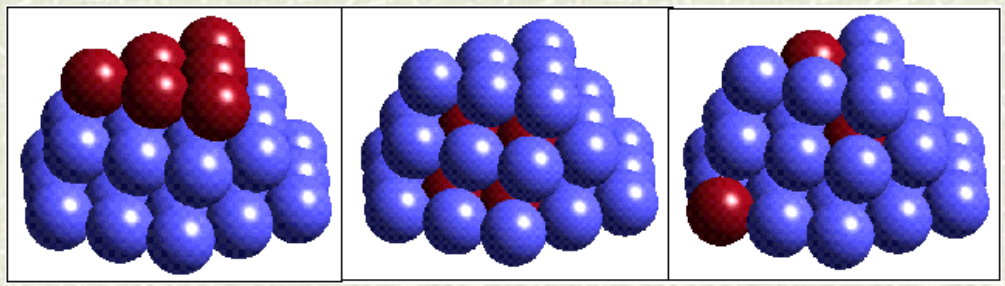
-Shape, Size, Surface orientation – are not revealed through the 1NN CN







-Short Range Order in nanoparticle alloys:

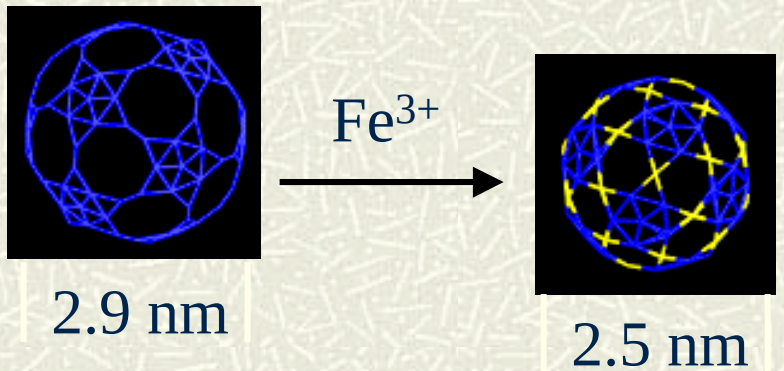


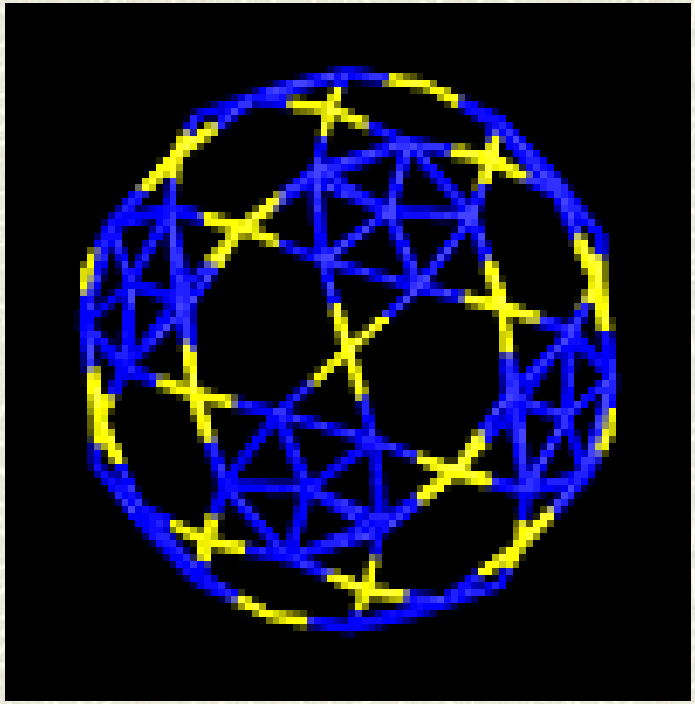
Another example:

Giant inorganic molecules, Polyoxomolybdates (POMs):

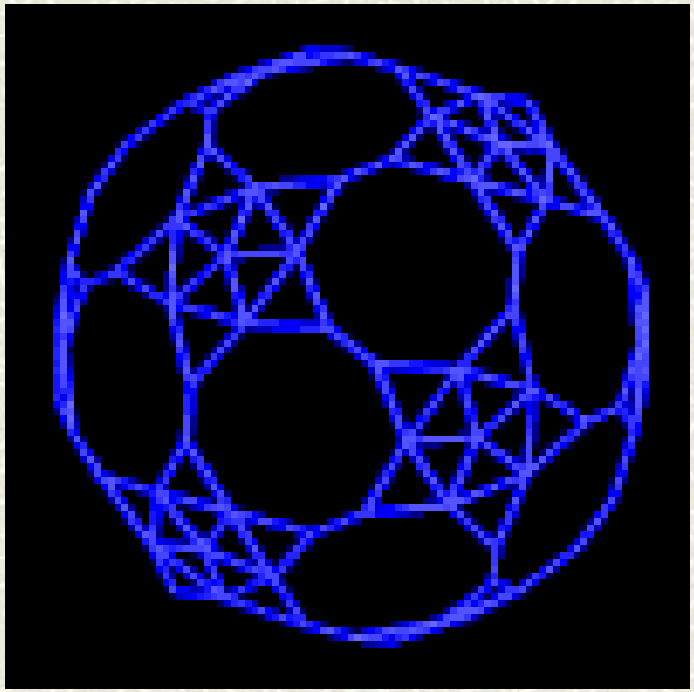
$[Mo_{132}O_{372}(HCOO)_{30}]$ $[Mo_{72}Fe_{30}O_{252}]$

$\{Mo_{132}\}$ $\{Mo_{72}Fe_{30}\}$





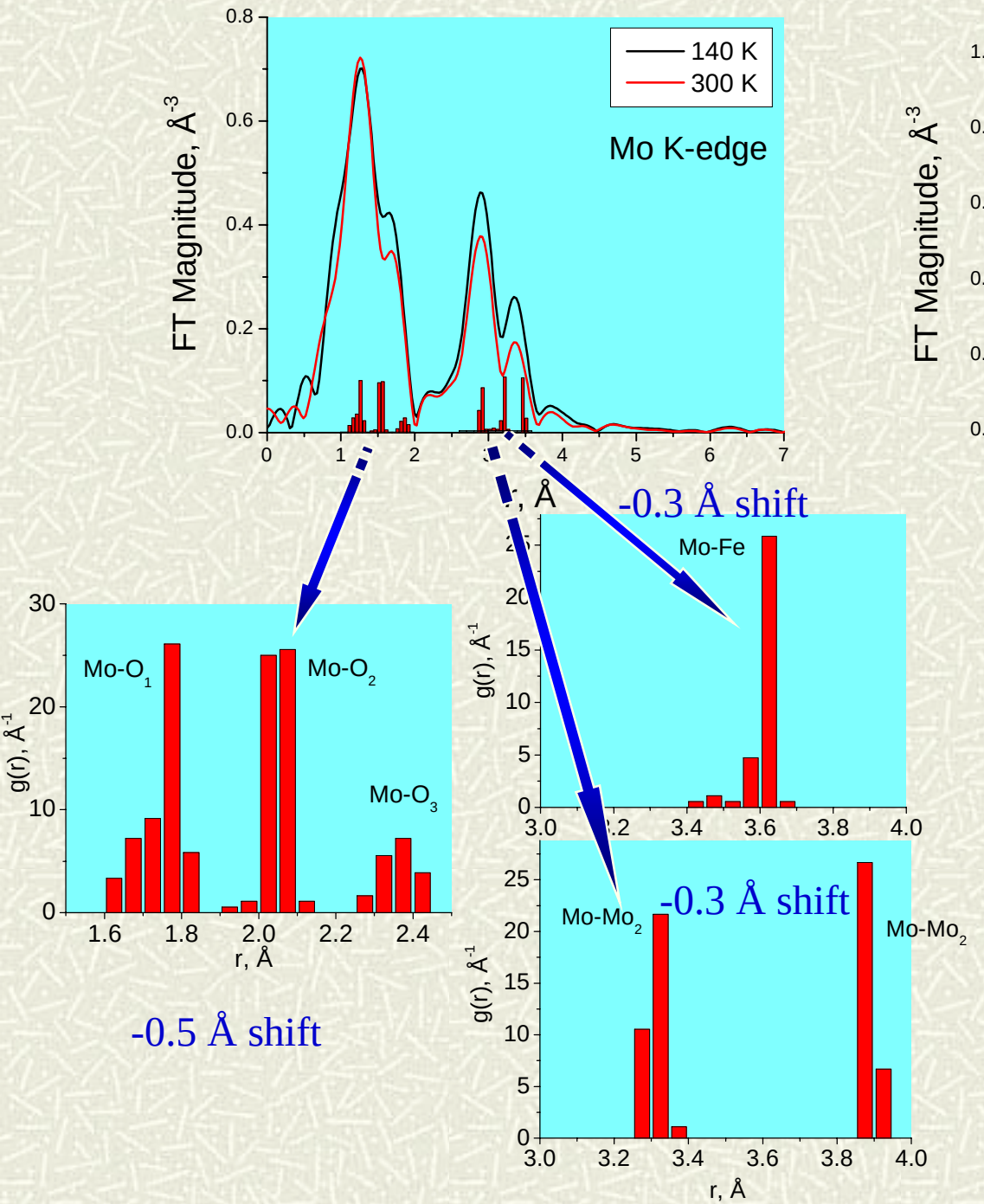
$\{Mo_{72}Fe_{30}\}$

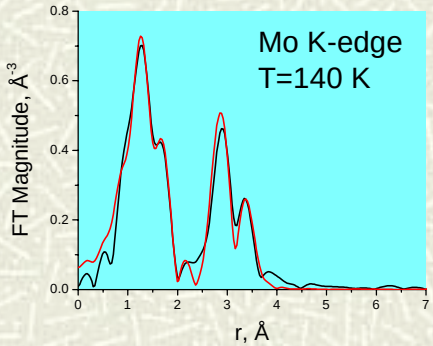


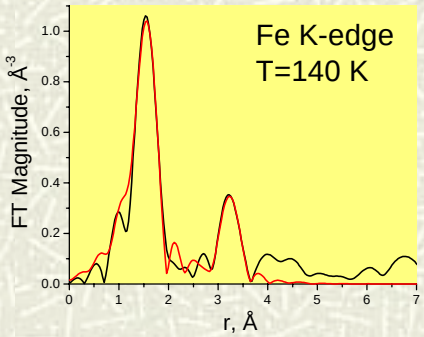
$\{Mo_{132}\}$

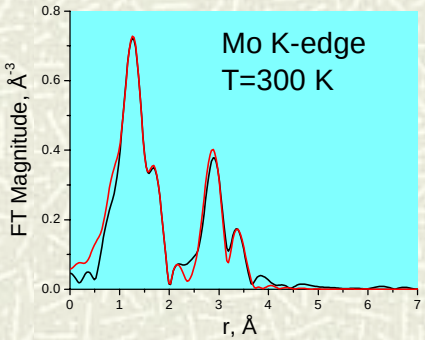
Modeling pair distribution functions using XRD results

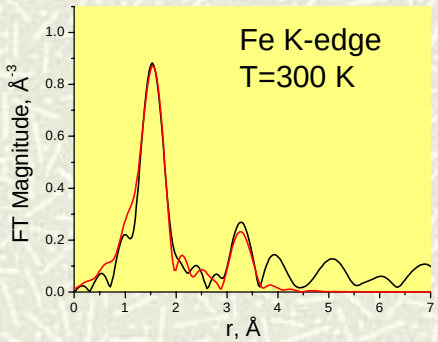
$$g_{AB}(r) = \frac{dN_{AB}}{dr}$$

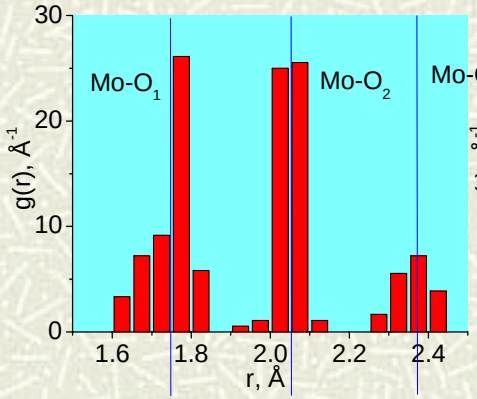

140 K
300 K
Mo K-edge
FT Magnitude, Å-3
r, Å
-0.3 Å shift
Mo-Fe
Mo-O1
Mo-O2
Mo-O3
-0.5 Å shift
Mo-Mo2
Mo-Mo2
-0.3 Å shift
g(r), Å-1
r, Å
140 K
300 K
Fe K-edge
FT Magnitude, Å-3
r, Å
-0.3 Å shift
Fe-Mo
Fe-O1
-0.5 Å shift
Fe-O2
g(r), Å-1
r, Å

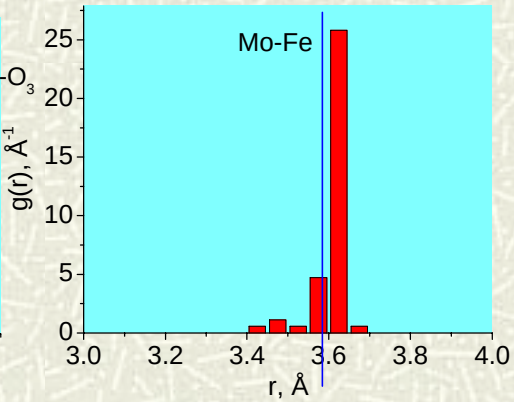


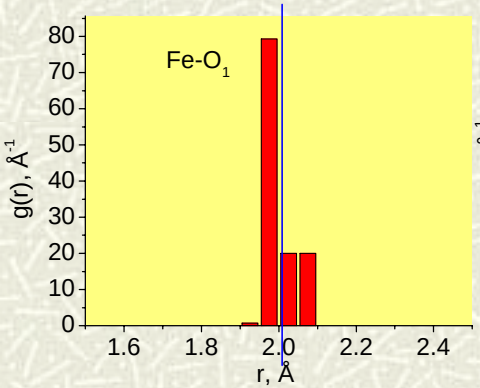


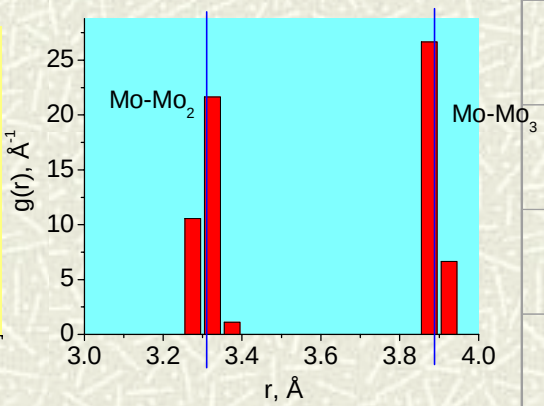




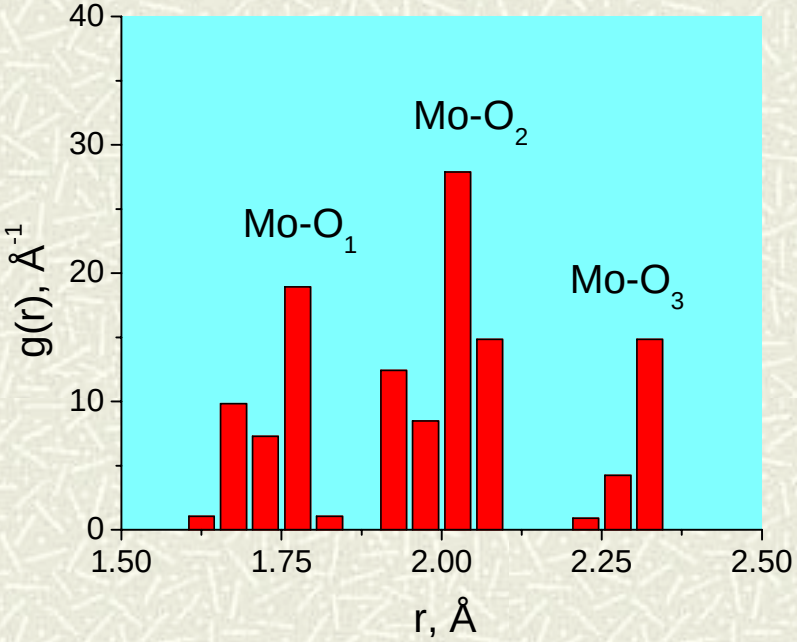


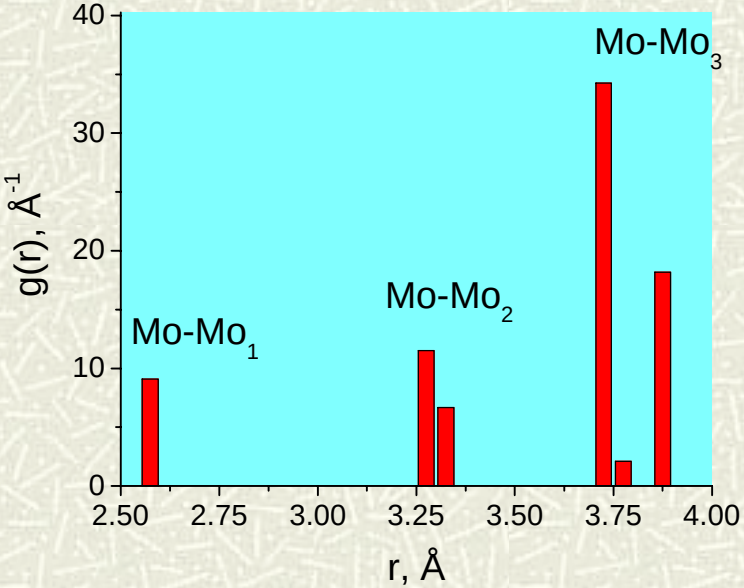




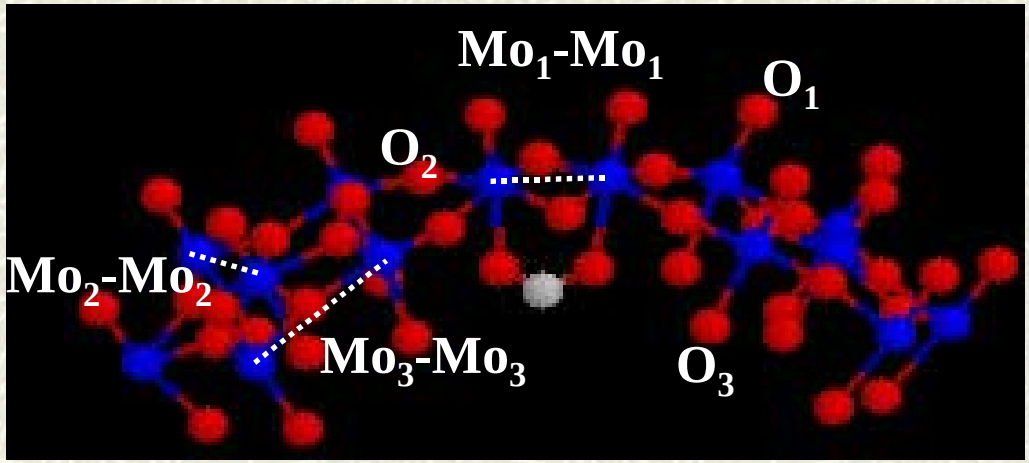


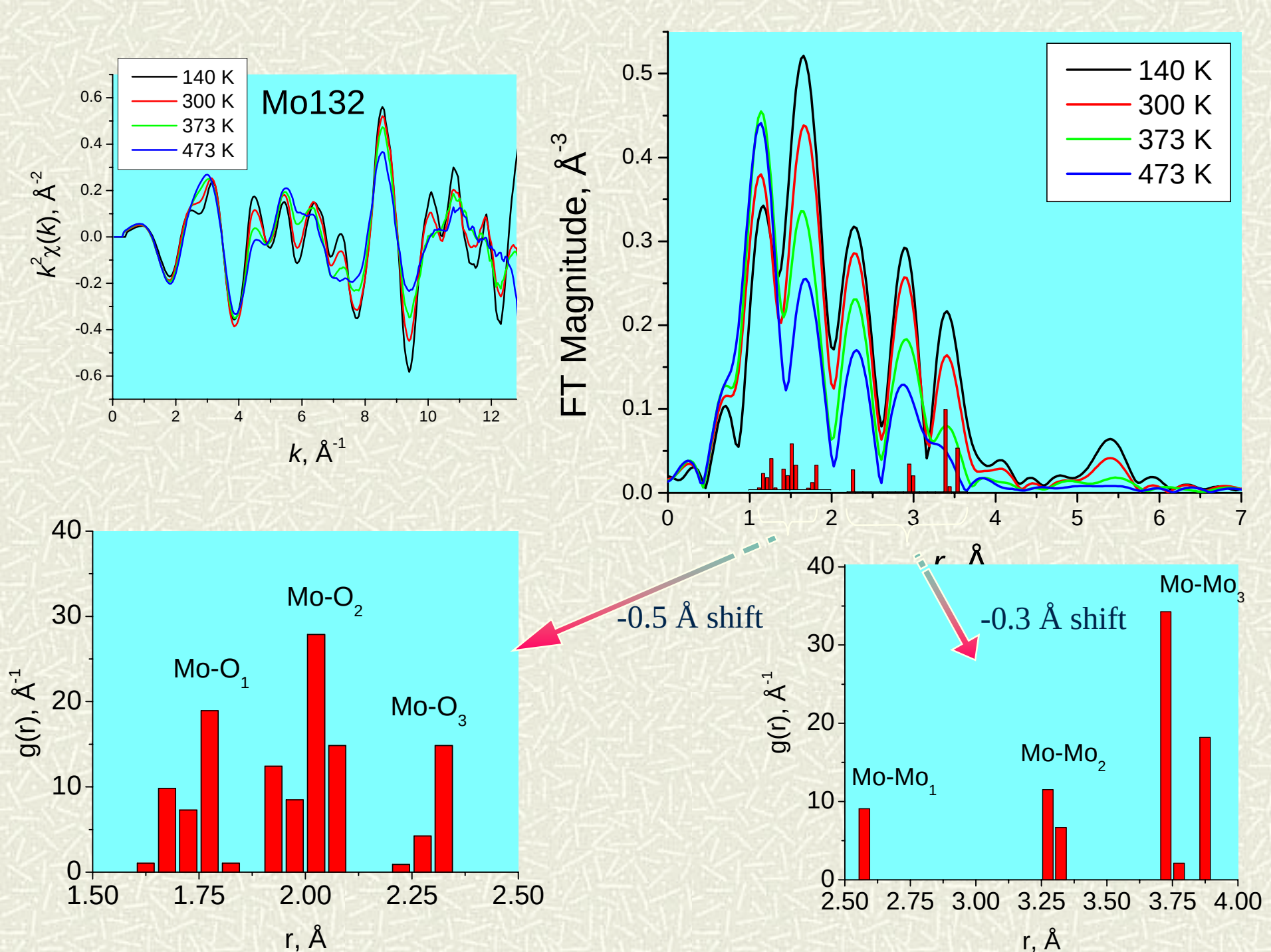
Bond	N		140 K	300 K
$Mo\text{-}O_1$	2.67	***r* (Å)**	**1.75(1)**	**1.75(1)**
		σ (Å^2)	0.0036(5)	0.0038(3)
$Mo\text{-}O_2$	2.50	***r* (Å)**	**2.05(1)**	**2.05(1)**
		σ (Å^2)	0.0040(9)	0.0051(7)
$Mo\text{-}O_3$	1.00	***r* (Å)**	**2.37(3)**	**2.37(2)**
		σ (Å^2)	0.0052(37)	0.0067(30)
Fe-O	6.00	***r* (Å)**	**2.00(1)**	**2.00(1)**
		σ (Å^2)	0.0018(14)	0.0040(17)
$Mo\text{-}Mo_2$	1.67	***r* (Å)**	**3.31(1)**	**3.31(1)**
		σ (Å^2)	0.0027(5)	0.0037(4)
Fe-Mo	4.00	***r* (Å)**	**3.58(2)**	**3.61(3)**
		σ (Å^2)	0.0103(13)	0.0140(21)
Mo-Fe	1.67	***r* (Å)**	**3.58_f**	**3.61_f**
		σ (Å^2)	0.0103_f	0.0140_f
$Mo\text{-}Mo_3$	1.67	***r* (Å)**	**3.89(2)**	**3.90(2)**
		σ (Å^2)	0.0053(14)	0.0090(19)

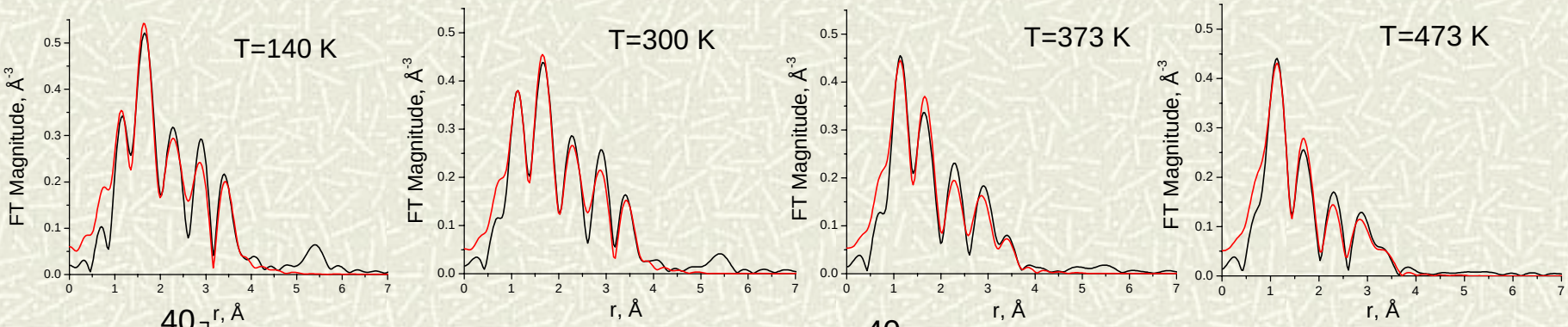

Mo-O2
Mo-O1
Mo-O3
g(r), Å-1
r, Å

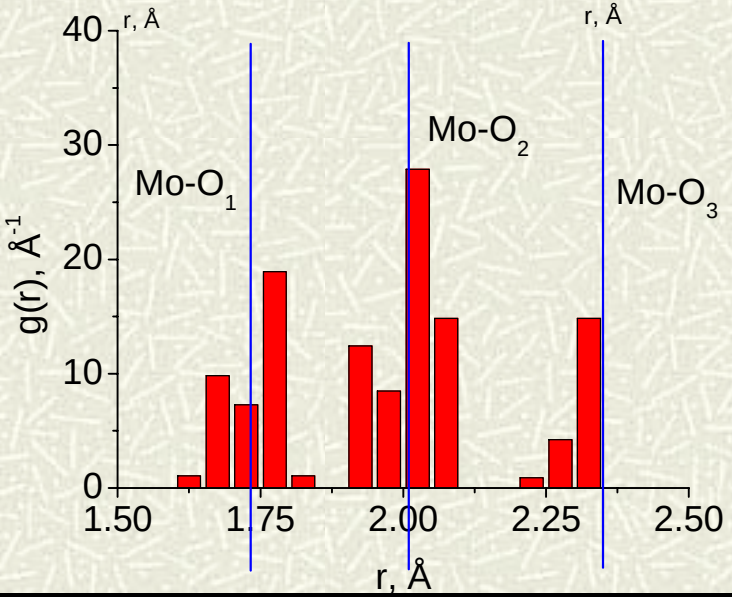

Mo-Mo3
Mo-Mo2
Mo-Mo1
g(r), Å-1
r, Å

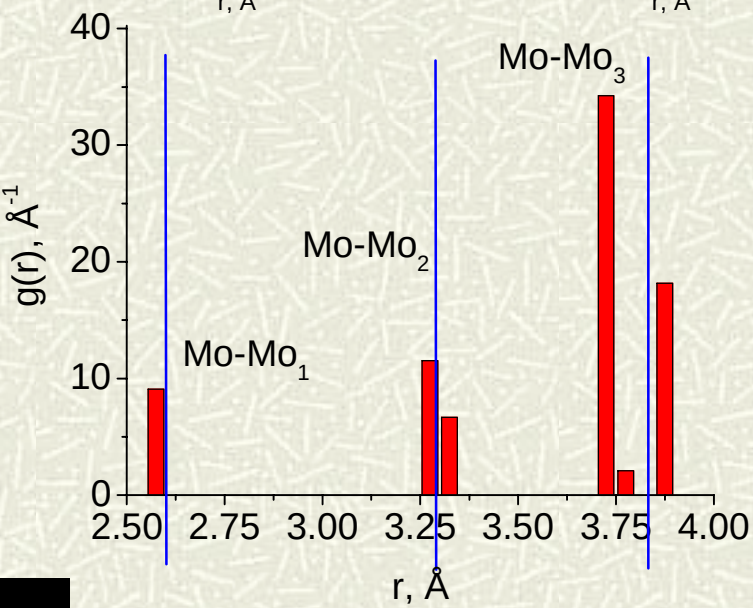
Mo_{132}

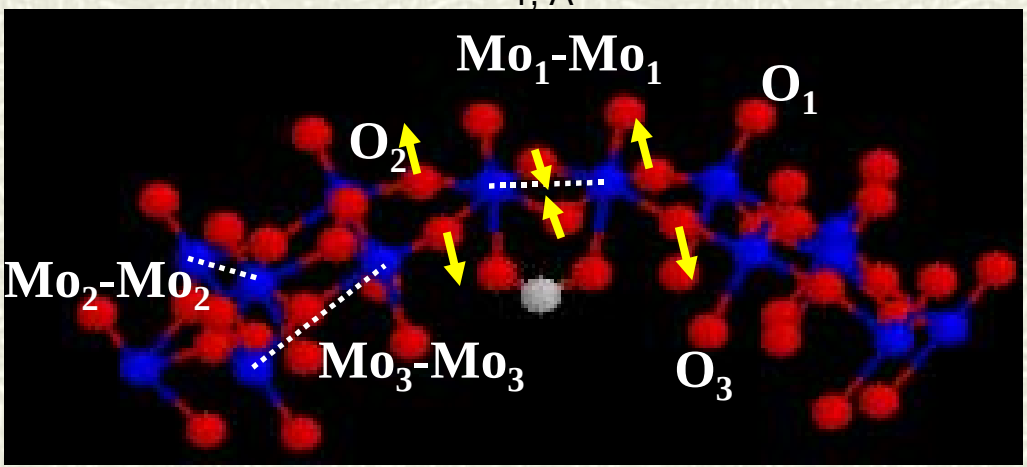

Mo1-Mo1
O1
O2
Mo2-Mo2
Mo3-Mo3
O3


140 K
300 K
373 K
473 K
Mo132
$k^2\chi(k)$, Å^{-2}
k, Å^{-1}
FT Magnitude, Å^{-3}
r, Å
-0.5 Å shift
-0.3 Å shift
Mo-O$_1$
Mo-O$_2$
Mo-O$_3$
Mo-Mo$_1$
Mo-Mo$_2$
Mo-Mo$_3$
g(r), Å^{-1}
r, Å









Asymmetric distortion of MoO_6 octahedron

References

(send reprint requests to: frenkel@bnl.gov)

1) A. I. Frenkel, C. W. Hills, and R. G. Nuzzo,
***Feature Article, J. Phys. Chem.* B, 105, 12689-12703 (2001).**

2) A. I. Frenkel, M. S. Nashner, C. W. Hills, R. G. Nuzzo, and J. R. Shapley,
***Science Highlights, NSLS Activity Report* 1999, NSLS, Brookhaven National Laboratory, 2000.**

3) A. I. Frenkel,
***J.Synchrotron Rad.*, 6, 293 (1999).**

4) C. W. Hills, M. S. Nashner, A. I. Frenkel, J. R. Shapley, and R. G. Nuzzo,
***Langmuir*, 15, 690-700 (1999).**

5) M. S. Nashner, A. I. Frenkel, D. Somerville, C. W. Hills, J. R. Shapley, and R. G. Nuzzo,
***J. Am. Chem. Soc.*, 120, 8093-8101 (1998).**

6) M. S. Nashner, A. I. Frenkel, D. L. Adler, J. R. Shapley, and R. G. Nuzzo,
***J. Am. Chem. Soc.*, 119, 7760 (1997)**