Pair Distribution Function analysis applied to negative thermal expansion materials

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Cuprite structure: introduction

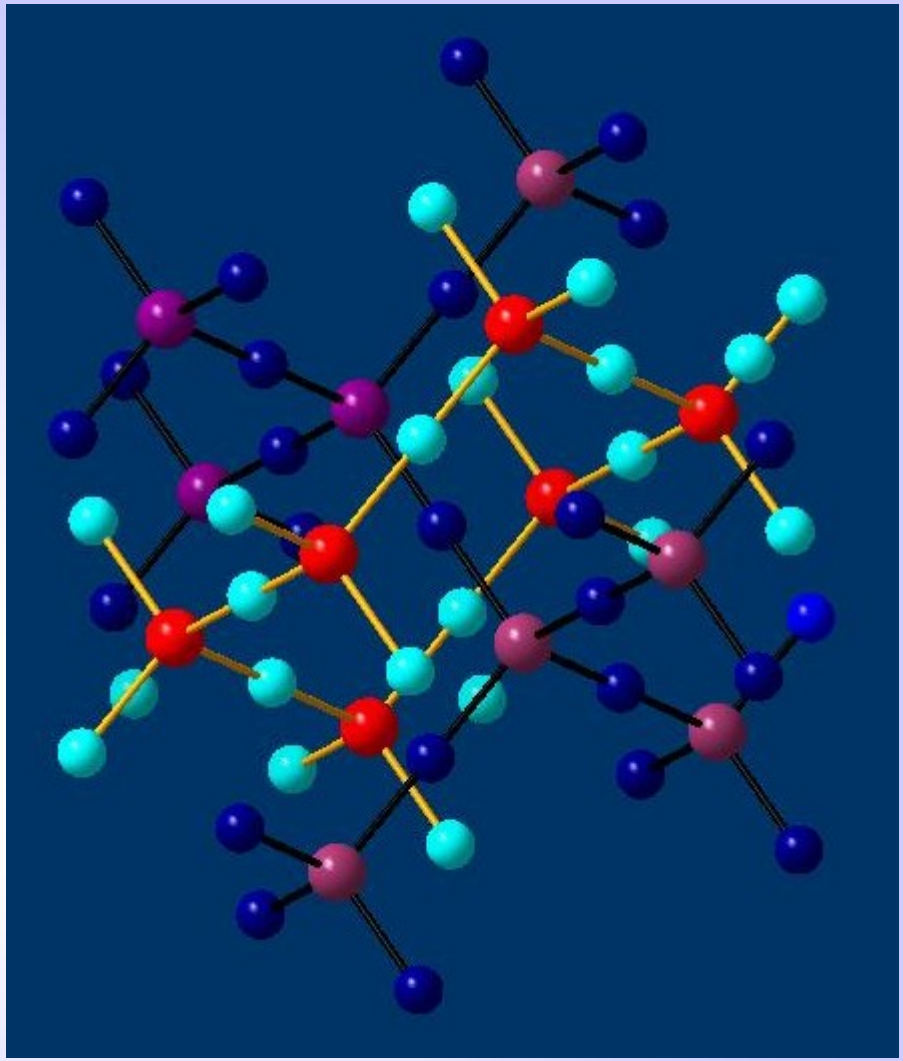
Cuprite structure is shared only by cuprite (Cu_2O) and silver (I) oxide (Ag_2O): it can be described by two interpenetrating chains of corner-sharing M_4O tetrahedra, where M represents the metal atom. Oxygen atoms are the centres of the tetrahedra, while the metal atoms are the vertexes.

Space group Pn-3m

Metal in 4b)	0.25	0.25	0.25
Oxygen in 2a)	0.00	0.00	0.00

Cell parameters at room temperature:

Cu_2O	a=4.27014 (7) Å
Ag_2O	a=4.7361 (1) Å



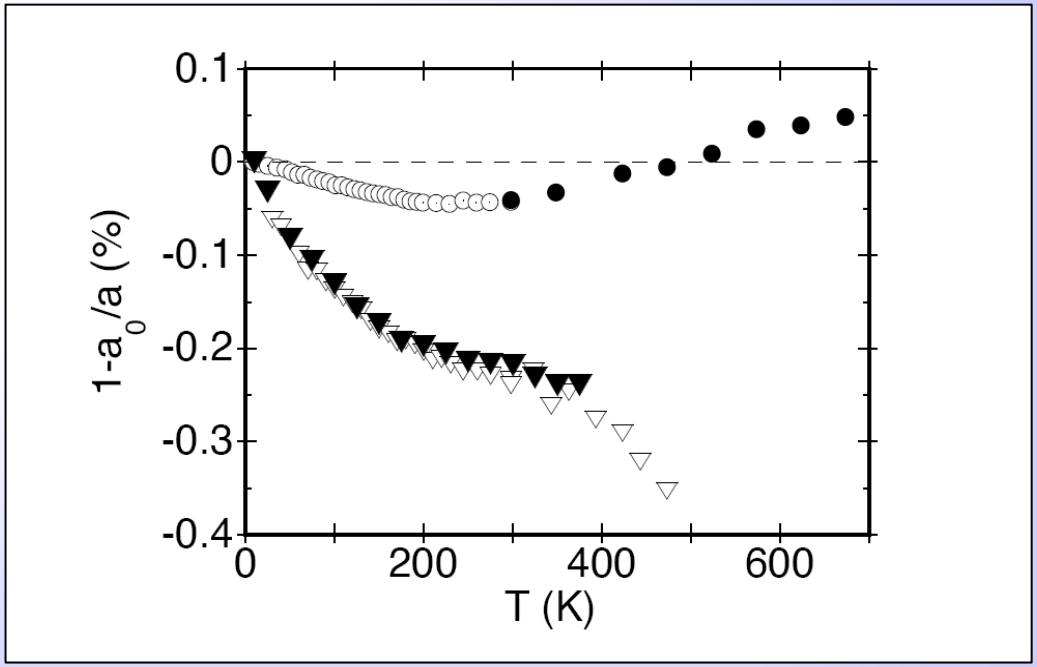
Cuprite structure: thermal behavior

Cuprite and silver oxide both exhibit a wide temperature range with a negative thermal expansion:
Cu_2O between 5 and about 200 K
Ag_2O between 5 and its decompostion temperature (about 500 K)

Some samples of Ag_2O also show a phase transition at low temperature (below 30 K), while other samples retain the high temperature structure down to 5 K. Both categories of samples have the same thermal expansion (i.e. the same slope in the cell parameter vs temperature curve)

The reasons for this peculiar thermal behavior are still not completely clear.

A lot of work has already been done on this structure, by comparing the MSD (Mean Square Displacements) from anisotropic refinement of thermal parameters, obtained by powder diffraction and the MSRD (Mean Square Relative Displacements) from the second cumulant analysis of EXAFS data in the same temperature range.



Cuprite structure: EXAFS versus DIFFRACTION

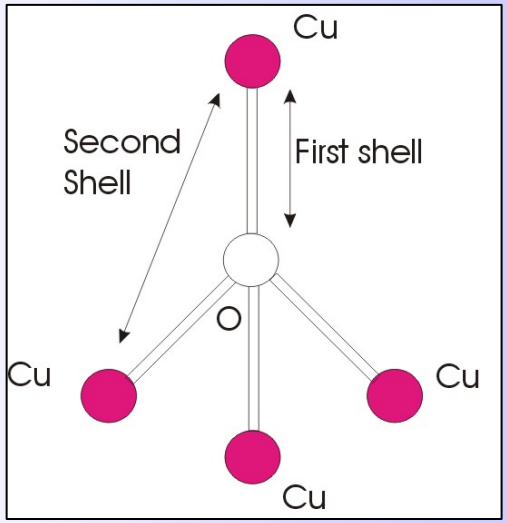
The second EXAFS cumulant corresponds to the parallel Mean Square Relative Dispacement (MSRD) of observer (*o*) and back-scattered (*j*) atoms:

$$C_2^* = \left\langle \left(\hat{R} \cdot \vec{u}_j \right)^2 \right\rangle + \left\langle \left(\hat{R} \cdot \vec{u}_o \right)^2 \right\rangle - 2 \left\langle \left(\hat{R} \cdot \vec{u}_j \right) \left(\hat{R} \cdot \vec{u}_o \right) \right\rangle$$

Displacement Correlation Function (DCF)

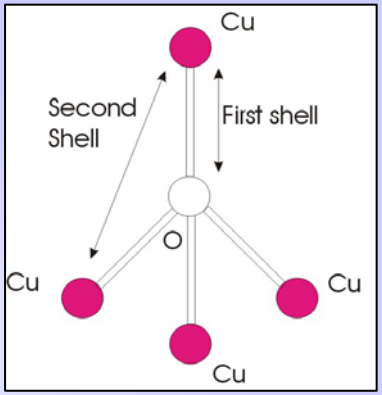
"Diffraction MSD" = $U_{//}$ (j) + $U_{//}$ (o)

$$MSD = \left\langle \left(\hat{R} \cdot \vec{u}_j \right)^2 \right\rangle + \left\langle \left(\hat{R} \cdot \vec{u}_o \right)^2 \right\rangle$$



From the comparison between MSRD from EXAFS and MSD from diffraction you can obtain the displacement correlation function, i.e. a measure of how correlated is the vibrational motion of the atoms involved

Cuprite structure: EXAFS versus DIFFRACTION

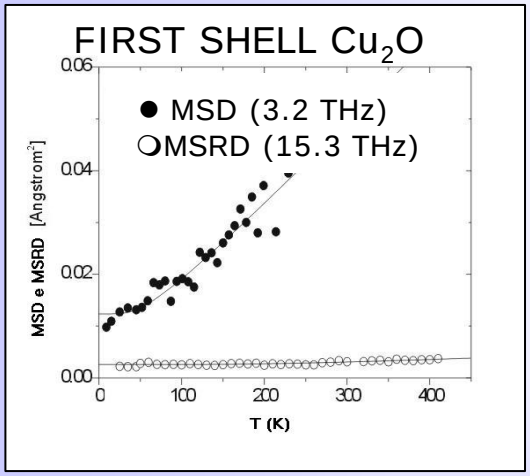


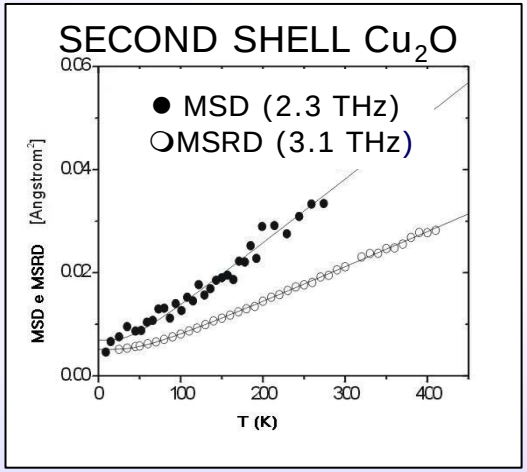
Black dots: diffraction MSD
White dots: EXAFS MSRD

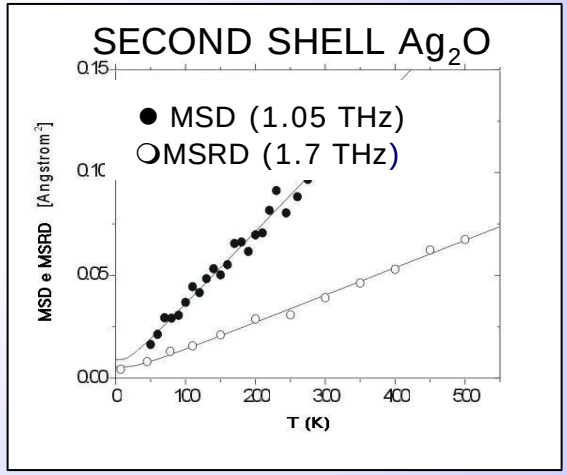
Einstein fit (vibrational properties only) → In parenthesis the force constance of the bond stretching between the two atoms involved

$$k = \mu(2\pi\nu_E)^2 = \mu\omega_E^2$$

The tetrahedron is much stiffer against stretching than against bending



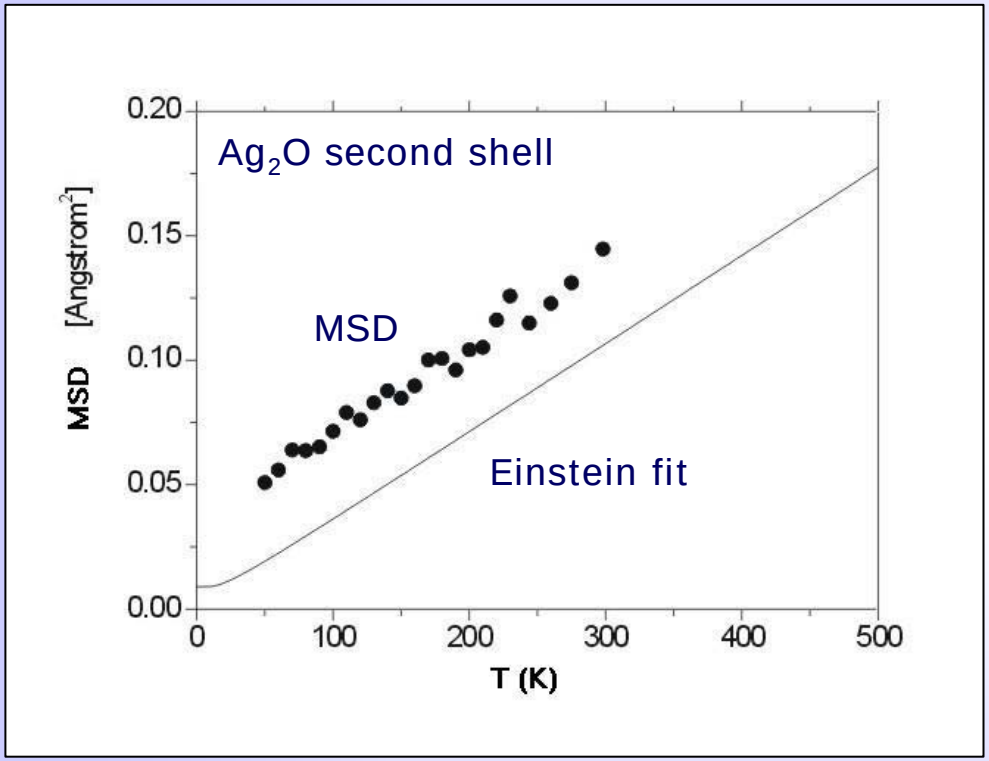




Cuprite structure: EXAFS versus DIFFRACTION

Einstein fit → vibrational properties ONLY

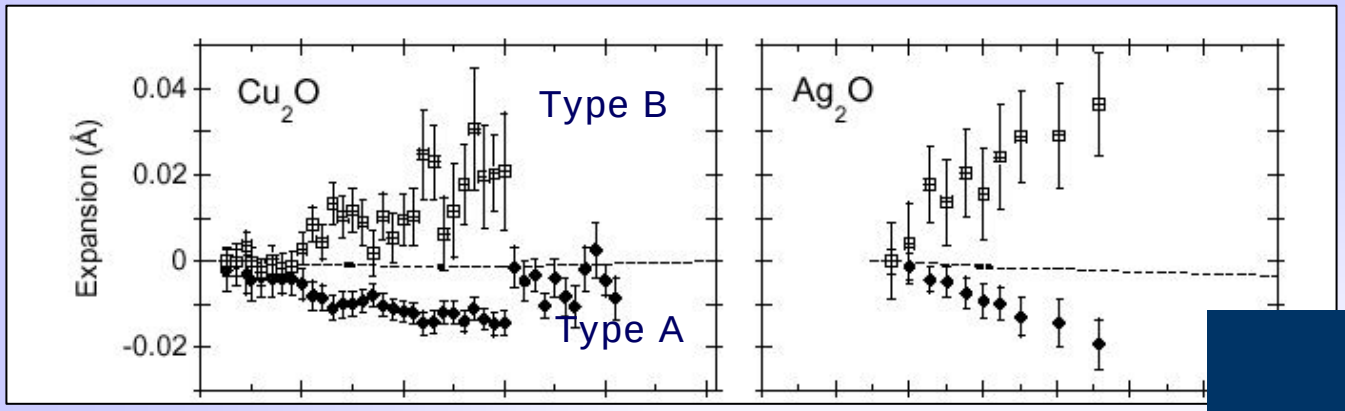
$$\sigma_j^2(\omega_E) = \frac{\hbar}{\mu\omega_E}\left[\frac{1}{2} + \frac{1}{e^{\hbar\omega_E/kT} - 1}\right] = \frac{\hbar}{2\mu\omega_E}\coth\left(\frac{\hbar\omega_E}{2kT}\right)$$

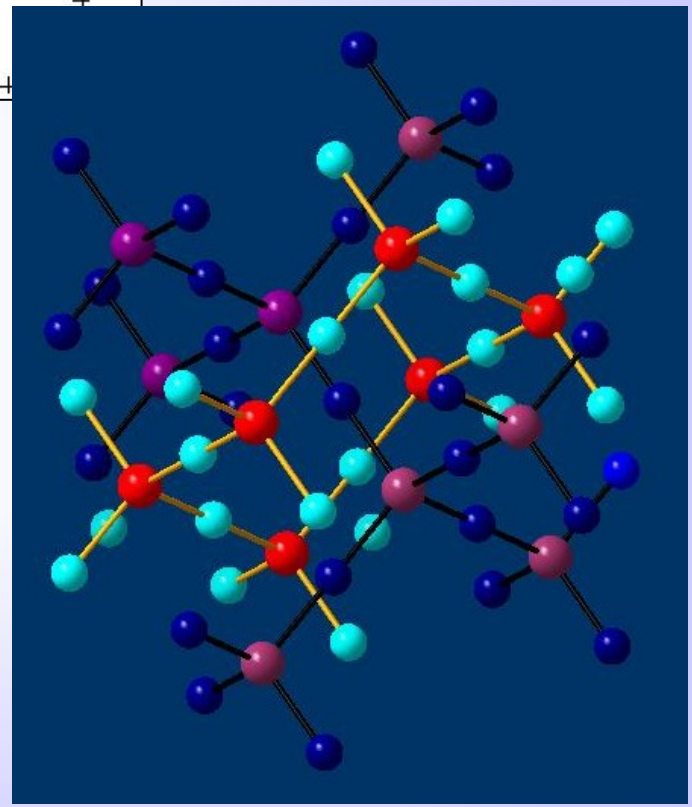


For Cu_2O the MSD can be fitted with an Einstein model and their intercept at 0 K corresponds to a zero point motion

In Ag_2O to fit the MSD with an Einstein model you need to shift the MSD → their large intercept at 0 K is a clear indication of static disorder

Cuprite structure: more EXAFS results on M-M bond





SECOND SHELL

There are 12 next-nearest neighbours for each metal atom

Of them, 6 belong to the same network as the centre atom (type A), 6 belong to the other network (type B)

Type A → negative thermal expansion
Type B → positive thermal expansion

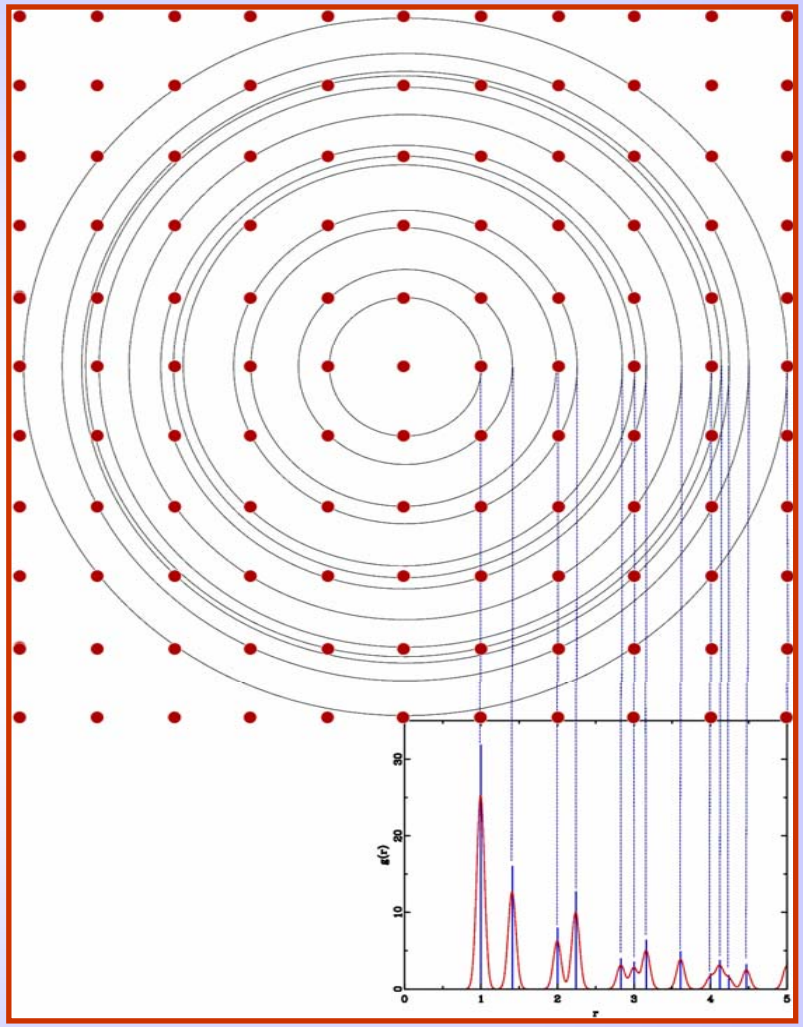
Cuprite structure: what else can we do?

The comparison between EXAFS and diffraction vibrational properties produced very important information on local and average behaviour, but **the reasons for negative thermal expansion are not yet completely understood.**

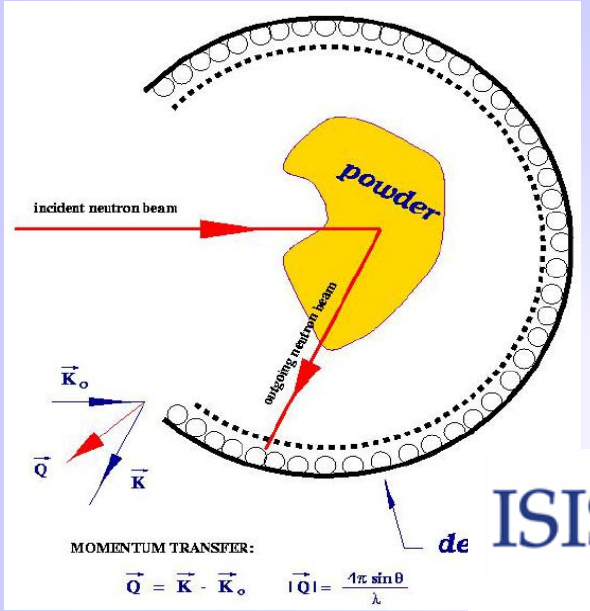
Try to extract the information hidden in the diffuse scattering.

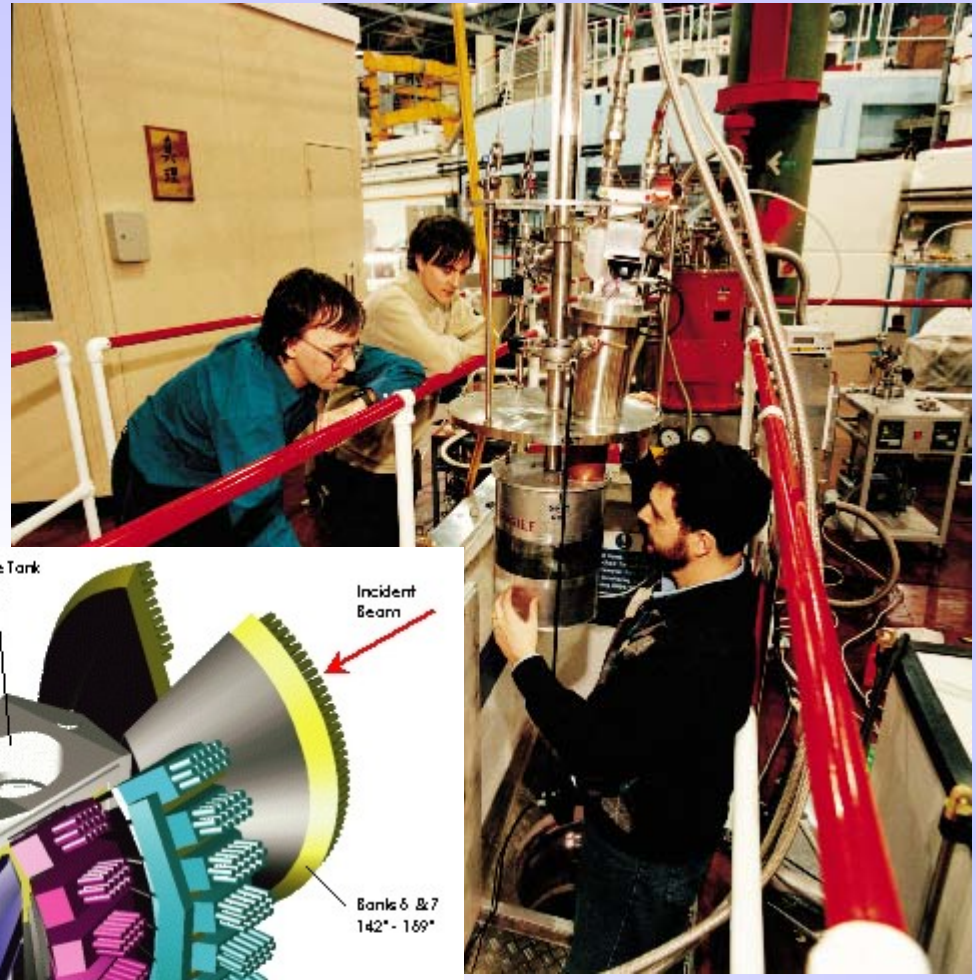
Use the Pair Distribution Function!

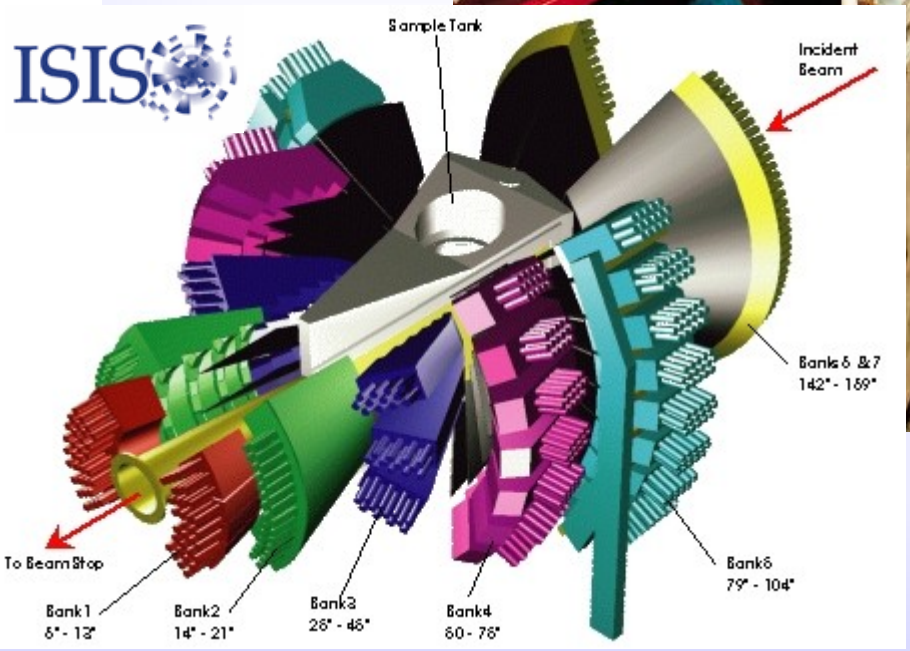
The study of temperature dependent PDF can provide a lot of information on structural variations (and also local distortions) with temperature and hopefully will help in understanding the thermal behaviour of cuprite structure.



Experimental: the GEM beamline



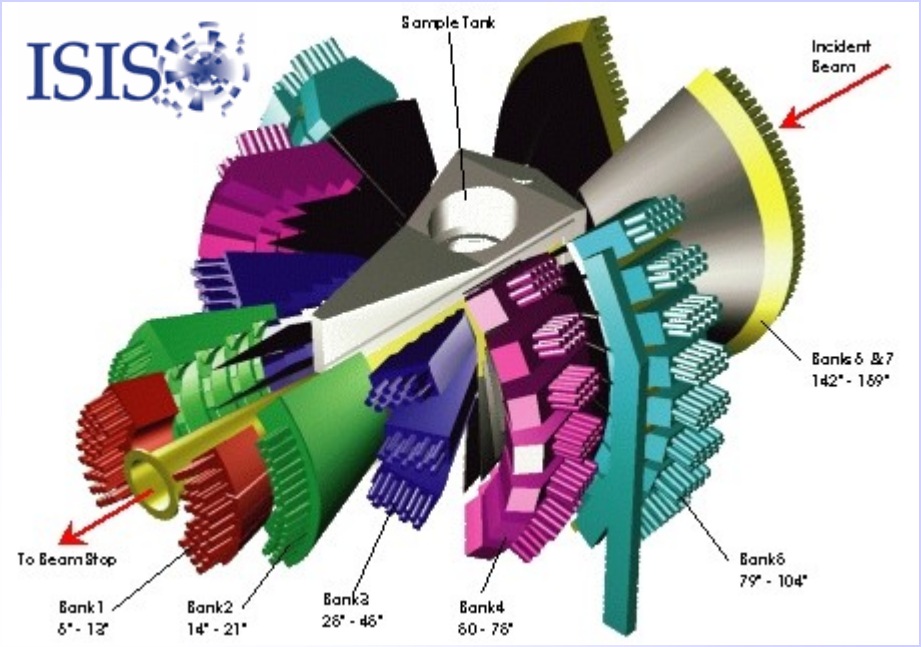




Experimental details

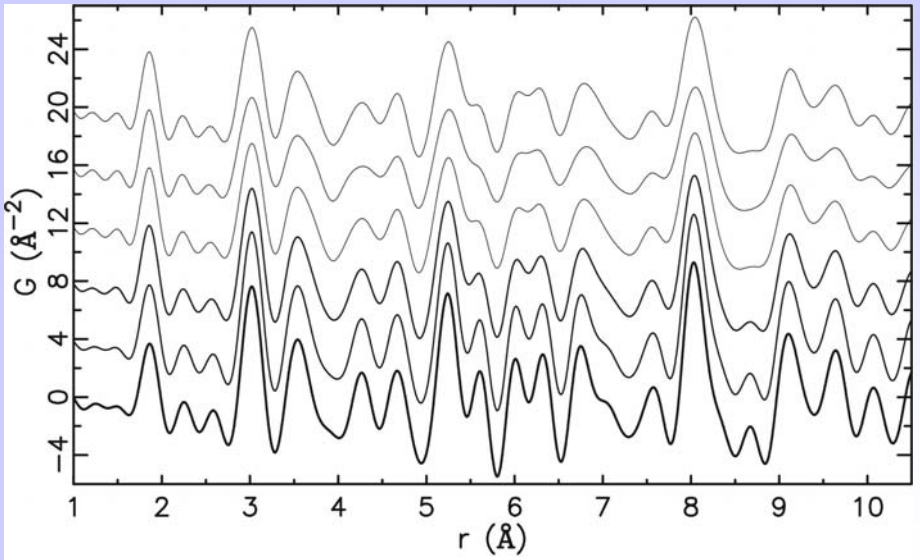
- 5 hours collection time at each T
- TOF
- Nominal Qmax > 80 $Å^{-1}$
- Cryofurnace, from 10 K up to 400 K
- many temperatures collected

Data normalization and reduction to get the PDF is performed with PDFGetN

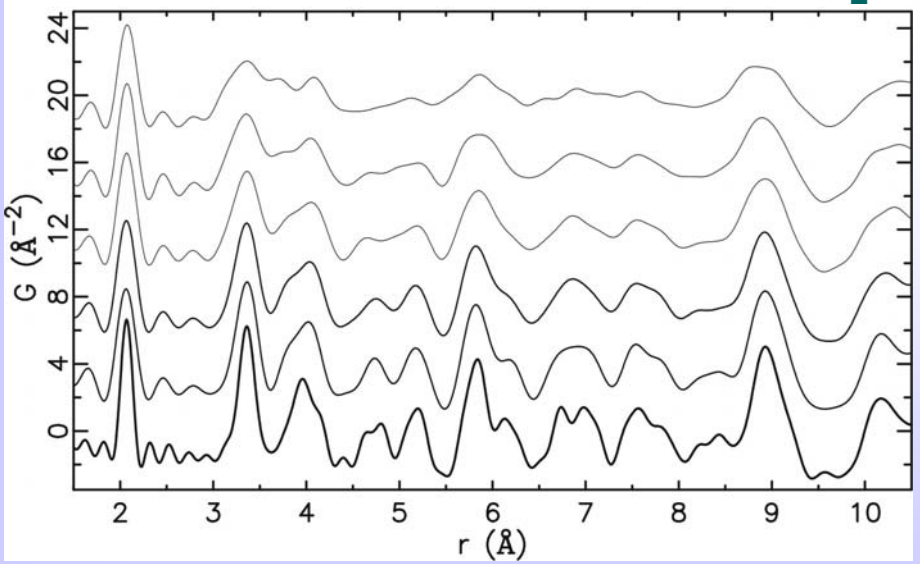


PDF data at first glance…

Cu_2O

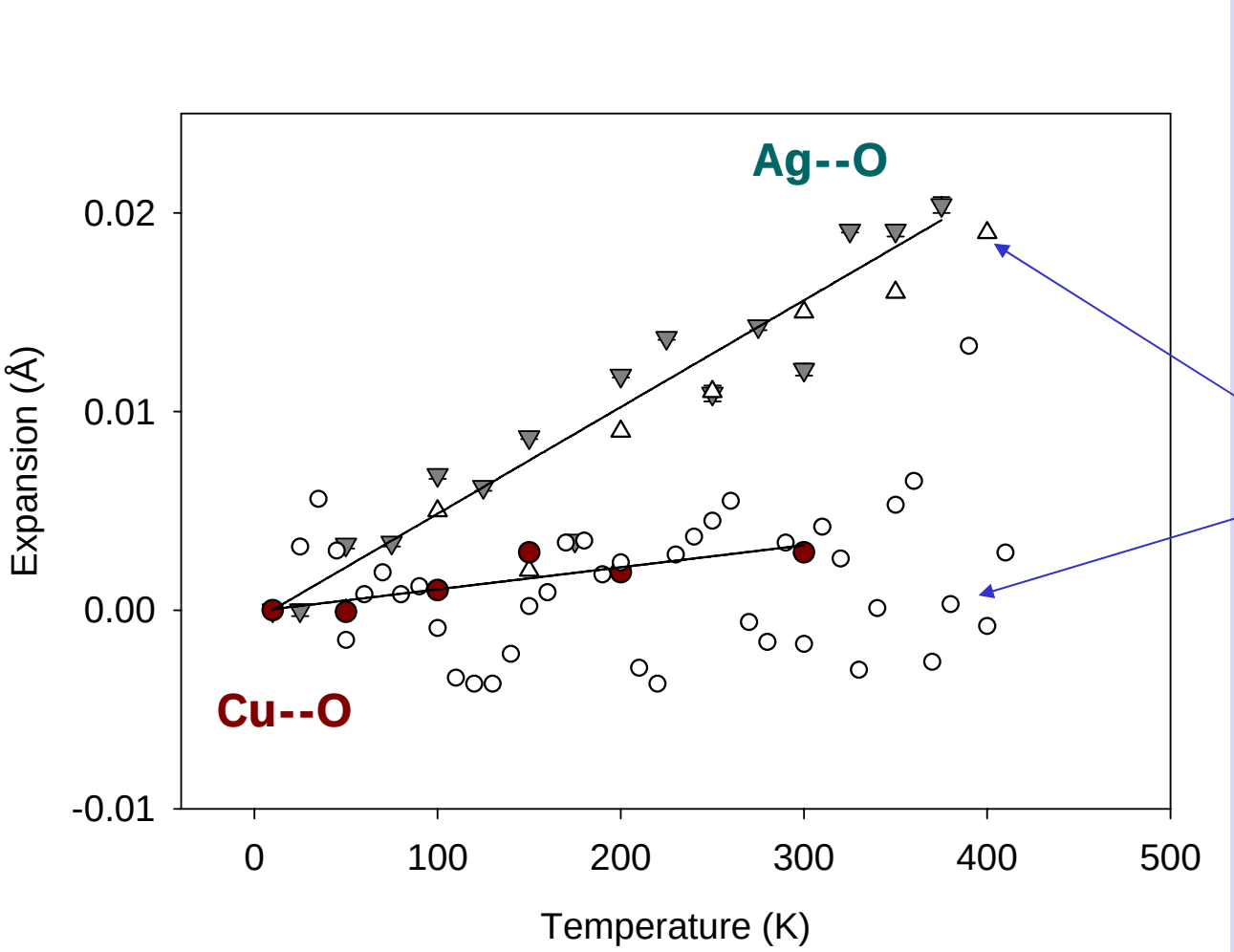


Ag_2O

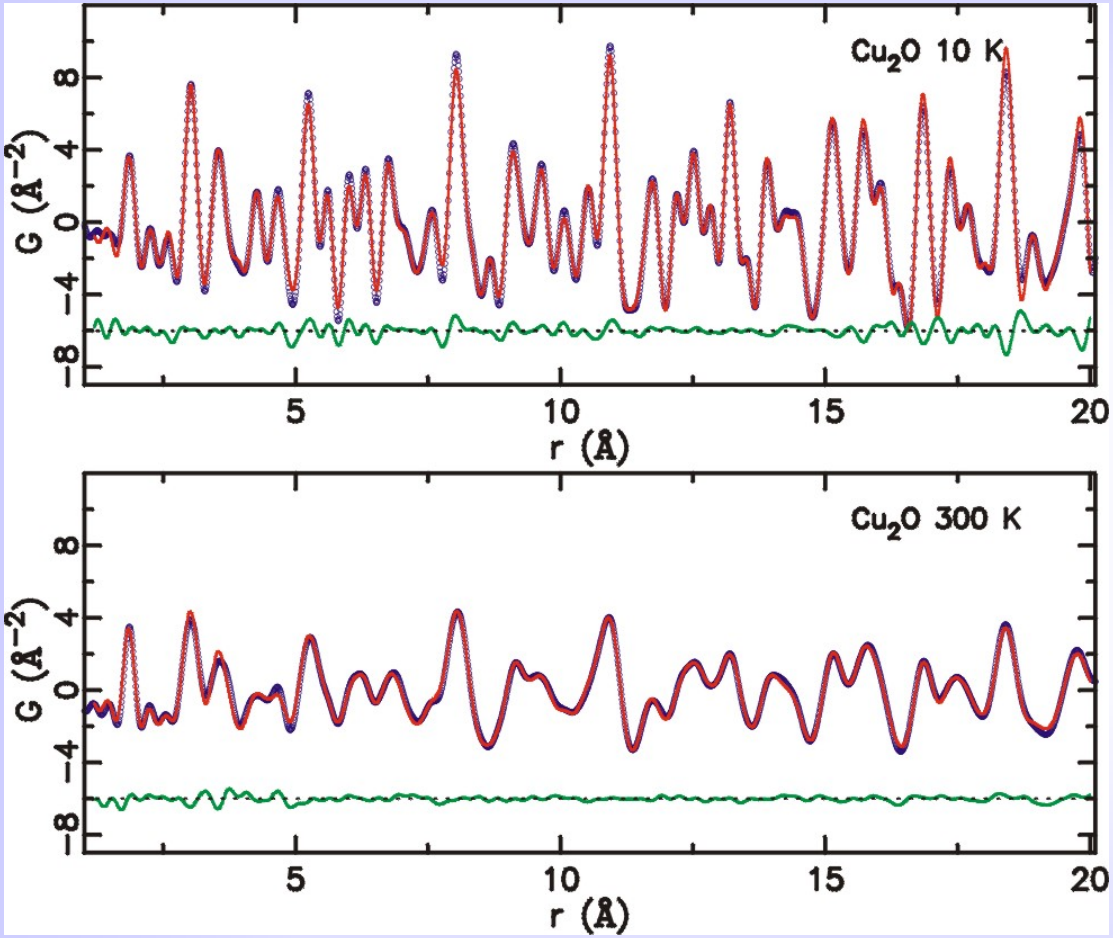


PDF vs EXAFS: first shell analysis

First shell peak position → Gaussian fit of PDF data



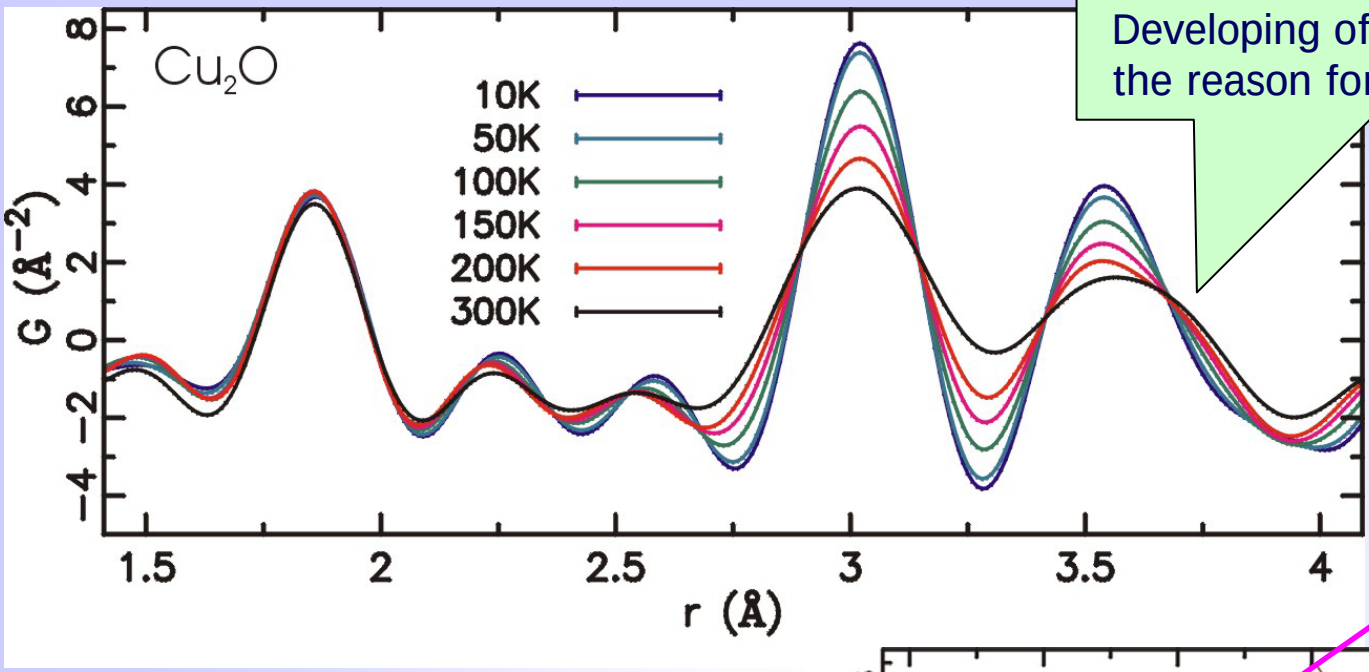
PDF analysis: Cu_2O



Main features:

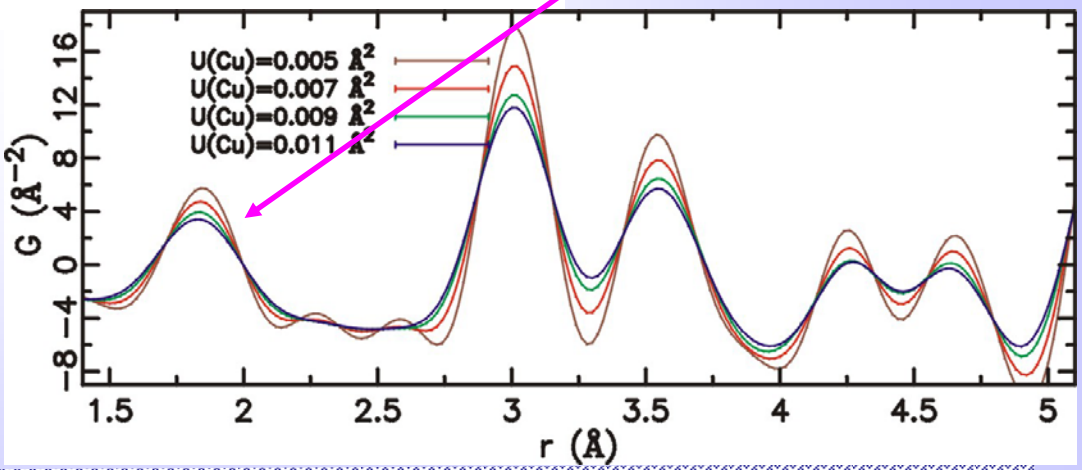
1) Dramatic decrease in intensity, too much for thermal effects only?
2) All the peaks are much broader → different distances contributing to one peak
3) The first peak remains the same at all temperatures (4 equal distances in the tetrahedron)
4) The second peak at 300 K is half of its intensity at 10 K and much broader

PDF analysis: Cu_2O, a closer look



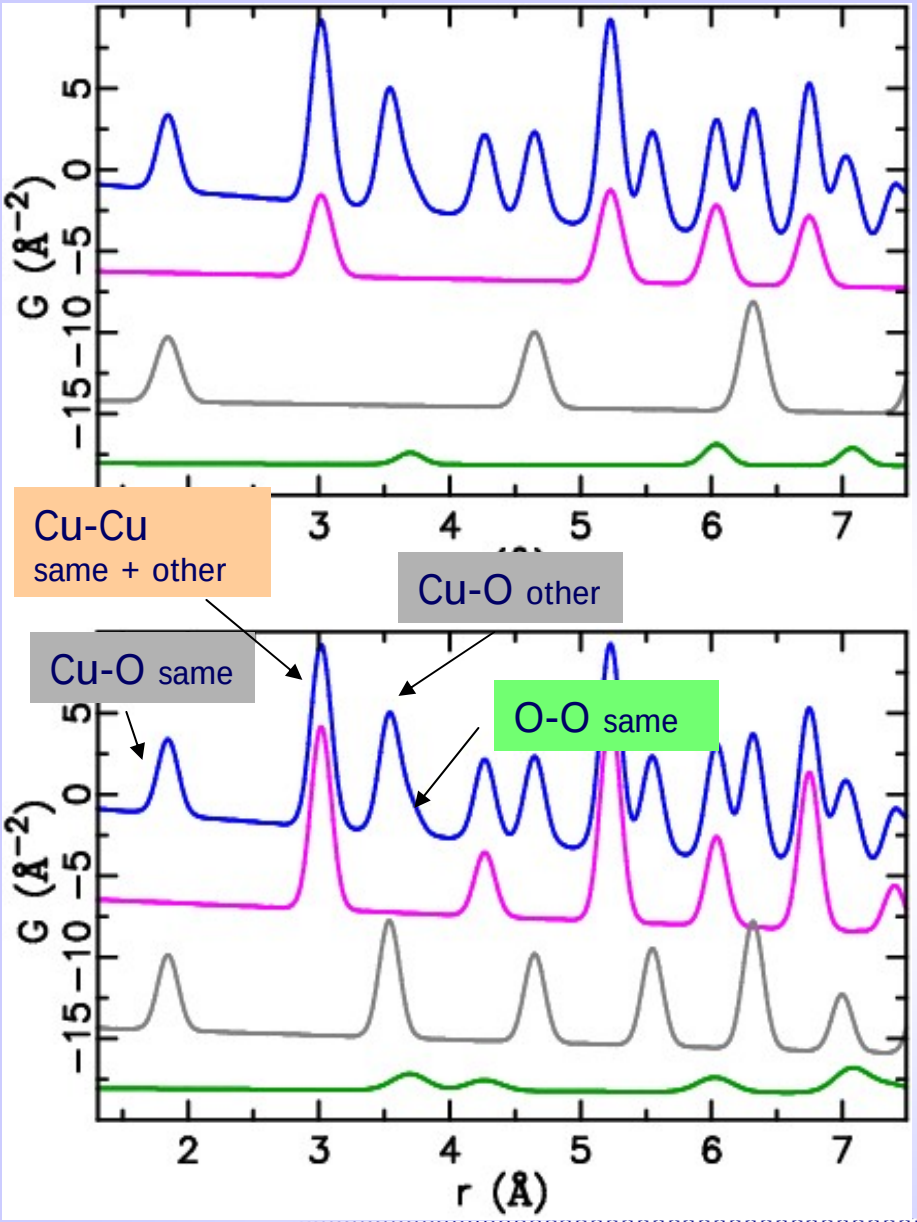
Developing of a shoulder: what's the reason for that?

Motion correlation was neglected



Broadening of peaks → spreading of distances (distortion) or thermal effect?

PDF analysis: which is which?



TOTAL

1 network Cu-Cu

1 network Cu-O

1 network O-O

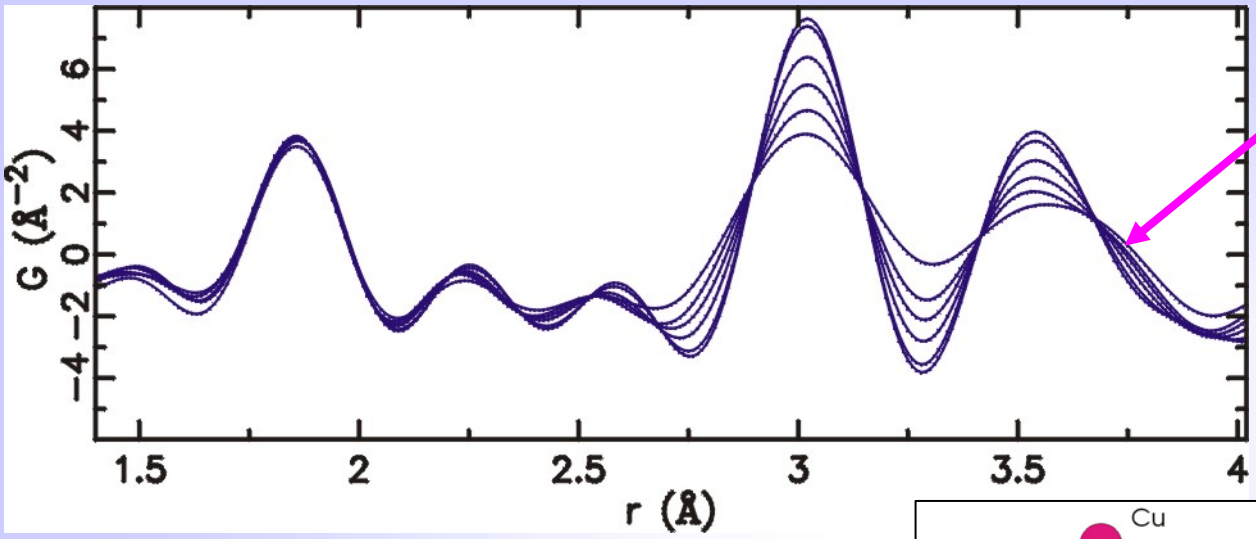
TOTAL

Cu-Cu

Cu-O

O-O

PDF analysis: Cu_2O



The peak is the combination of a Cu-O distance (Cu and O on different networks) and an O-O distance (the oxygens are on the same network)

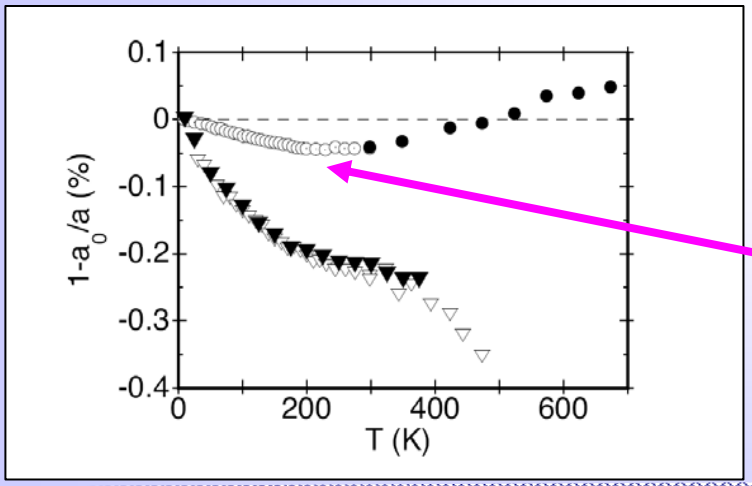
- Developing of TWO Cu-Cu distances, i.e. the tetrahedron changes only its solid angle

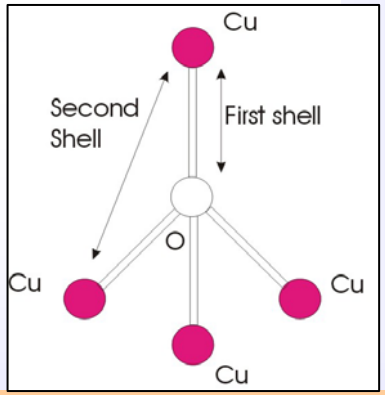
Or

- Different distances for Cu-Cu on the same network or on different networks

Or

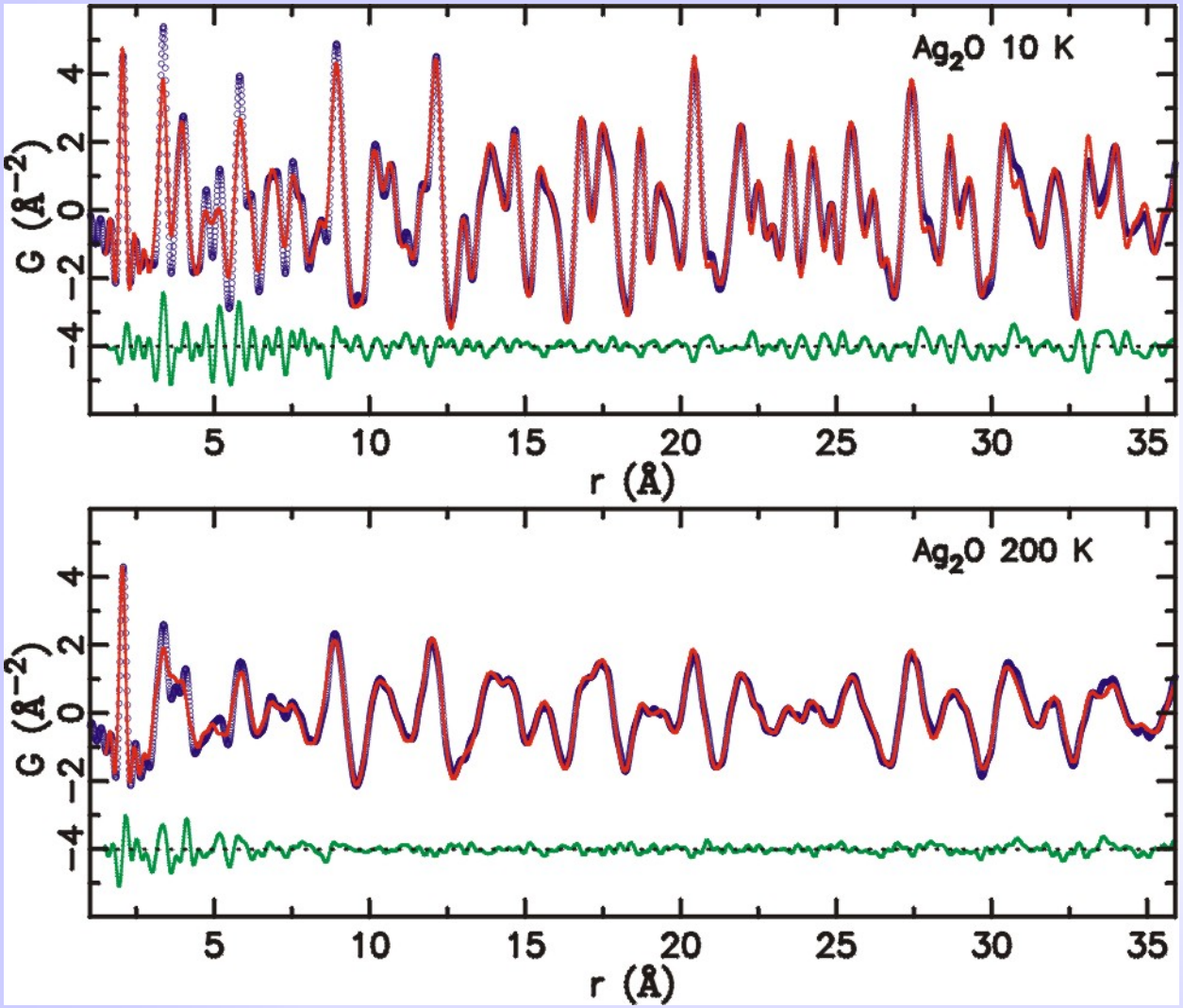
- Both



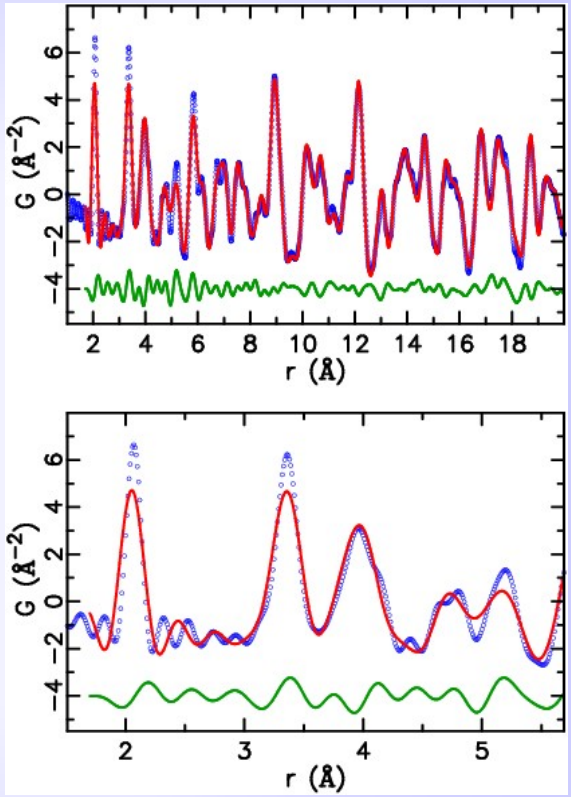


The shoulder at about 3.7 Å appears at about 200 K: inversion of the thermal behavior → the thermal expansion becomes positive

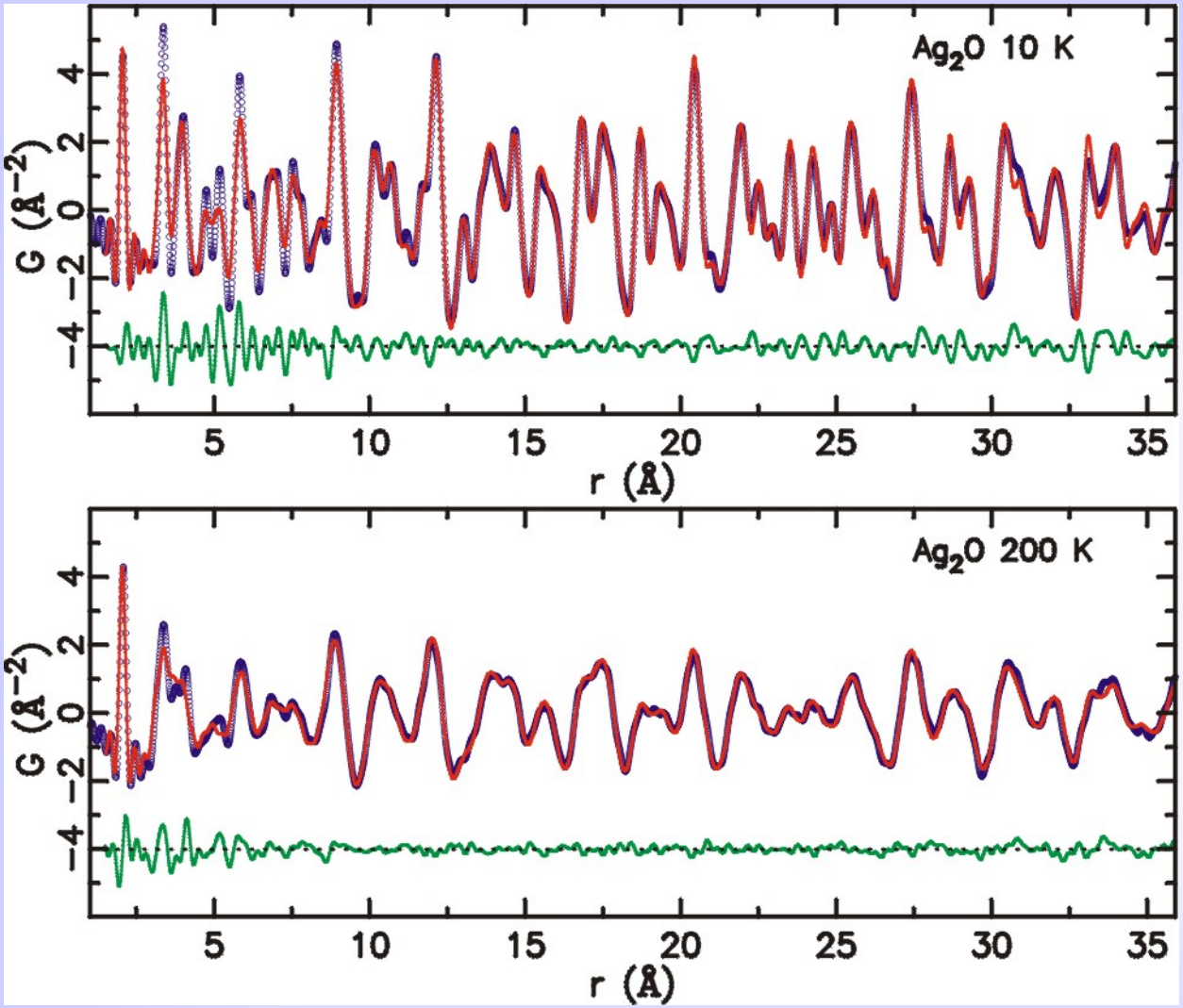
PDF analysis: Ag_2O



Ag_2O 10 K



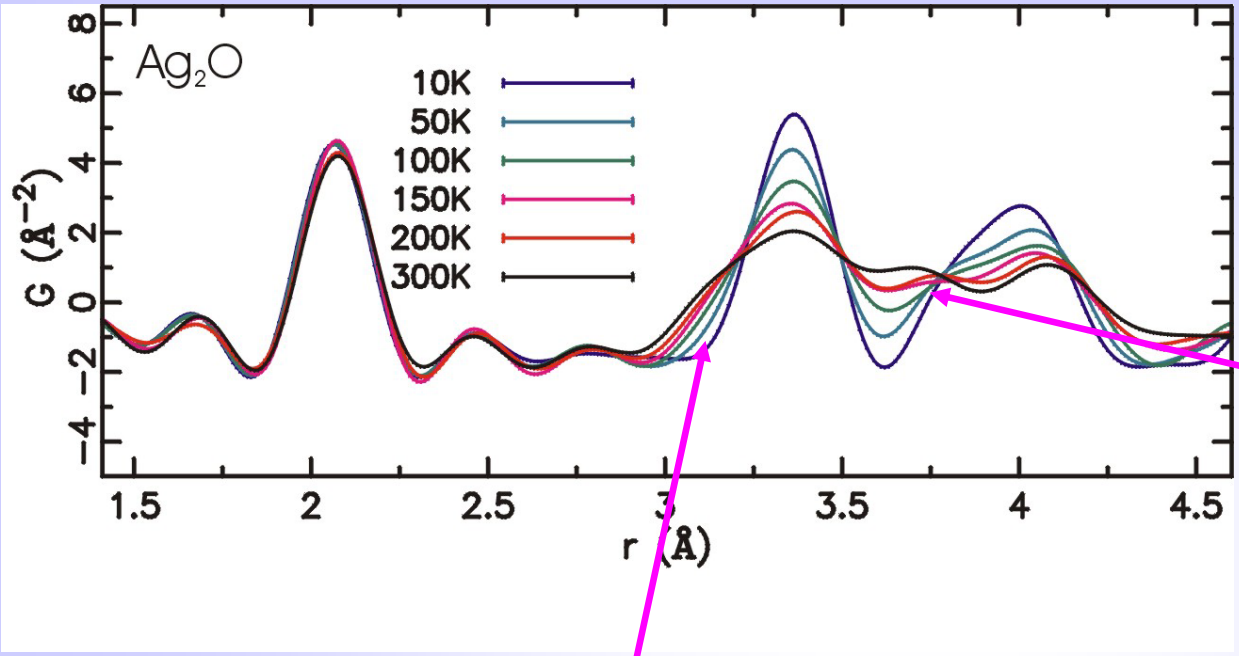
PDF analysis: Ag_2O



Main features:

1) The first peak remains the same at all temperatures (4 equal distances in the tetrahedron)
2) The second peak should be more intense at low T if no distortion were present
3) A lot is going on with temperature
4) There a large difference between the PDF calculated from the "crystallographic" structure and the experimental one, even at 10 K **especially at low r (below about 8-10 Å)**

PDF analysis: Ag_2O



Two features almost flattening with temperature

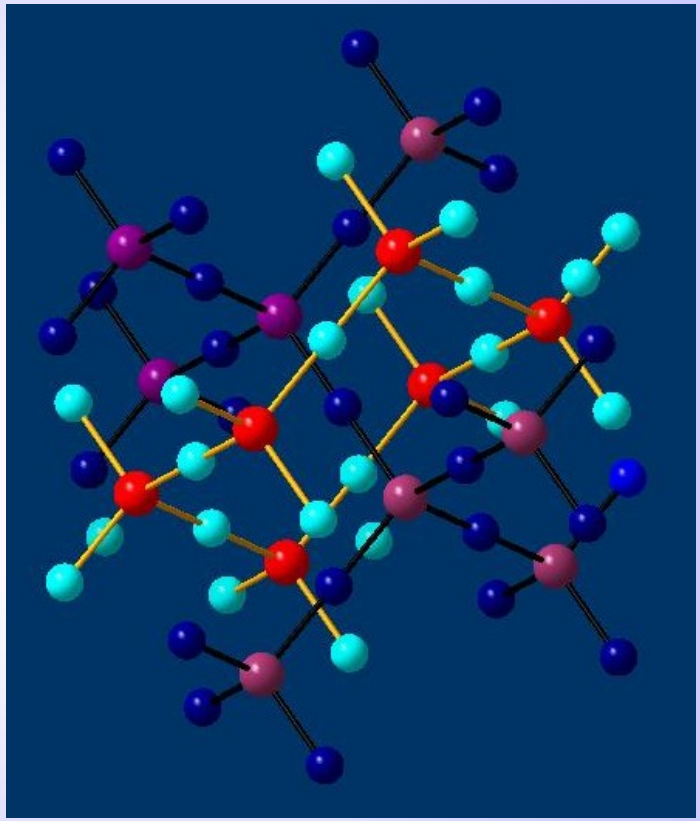
Developing of a shoulder in the second peak → more distortion than in Cu_2O

A lot of distortions appear with temperature: how can we model those?

PDF analysis: a different approach

Even with a simple structure like the cuprite one it is not straighforward to find a model that can justify the variations with temperature of the PDF data

GEOMETRIC REFINEMENT METHOD
with
SIMULATED ANNEALING



The model structure is refined through simulated annealing against the experimental PDF data, taking into account the local bonding geometry as a constraint

PDF analysis: geometrical modelling

ADVANTAGES

- ✓ Simple to use
- ✓ Comparison of a large model with the experimental data (good "statistics" on defects)
- ✓ The local bonding geometry is kept
- ✓ Control of the degrees of freedom in a chemically reasonable way

DISADVANTAGES

- ✓ Time consuming (large models)
- ✓ Unicity of the model

PDF analysis: geometrical modelling

What is simulated annealing (SA)?

From Wikipedia:

By analogy with the physical process (metal annealing), each step of the SA algorithm replaces the current solution by a random "nearby" solution, chosen with a probability that depends on the difference between the corresponding function values and on a global parameter *T* (called the *temperature*), that is gradually decreased during the process. The dependency is such that the current solution changes almost randomly when *T* is large, but increasingly "downhill" as *T* goes to zero. The allowance for "uphill" moves saves the method from becoming stuck at local minima.

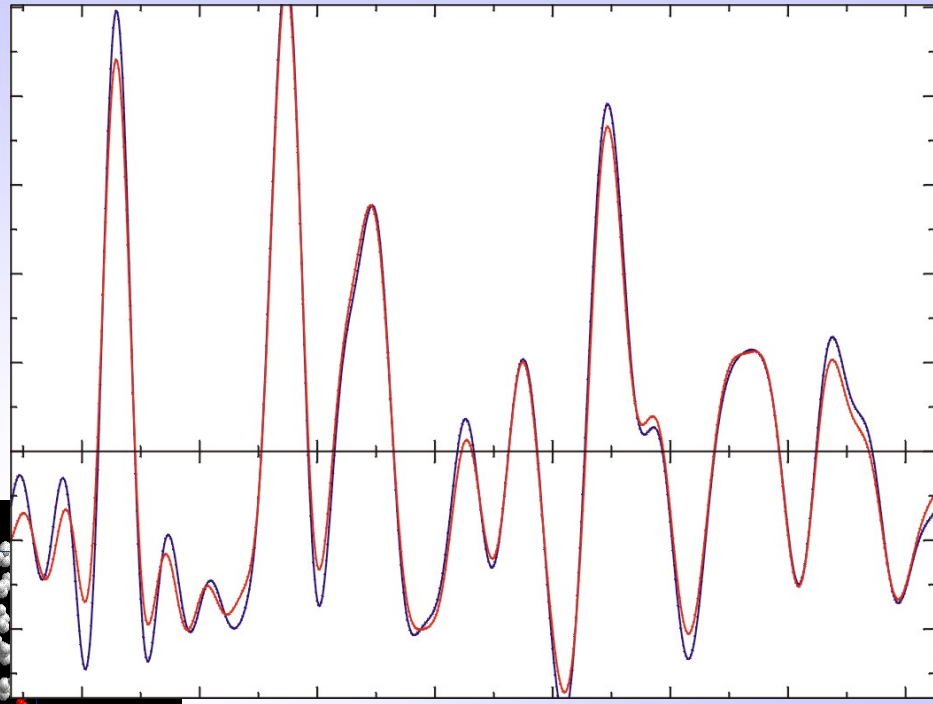
How did we apply it?

- **Large model structures (10x10x10 unit cells, about 50 Å wide)**
- **The structural units (tetrahedra) can be rotated with respect to each other and distorted to a pre-defined level (that can change during the "refinement")**
- **Each "temperature" is explored for 1 000 000 tries**

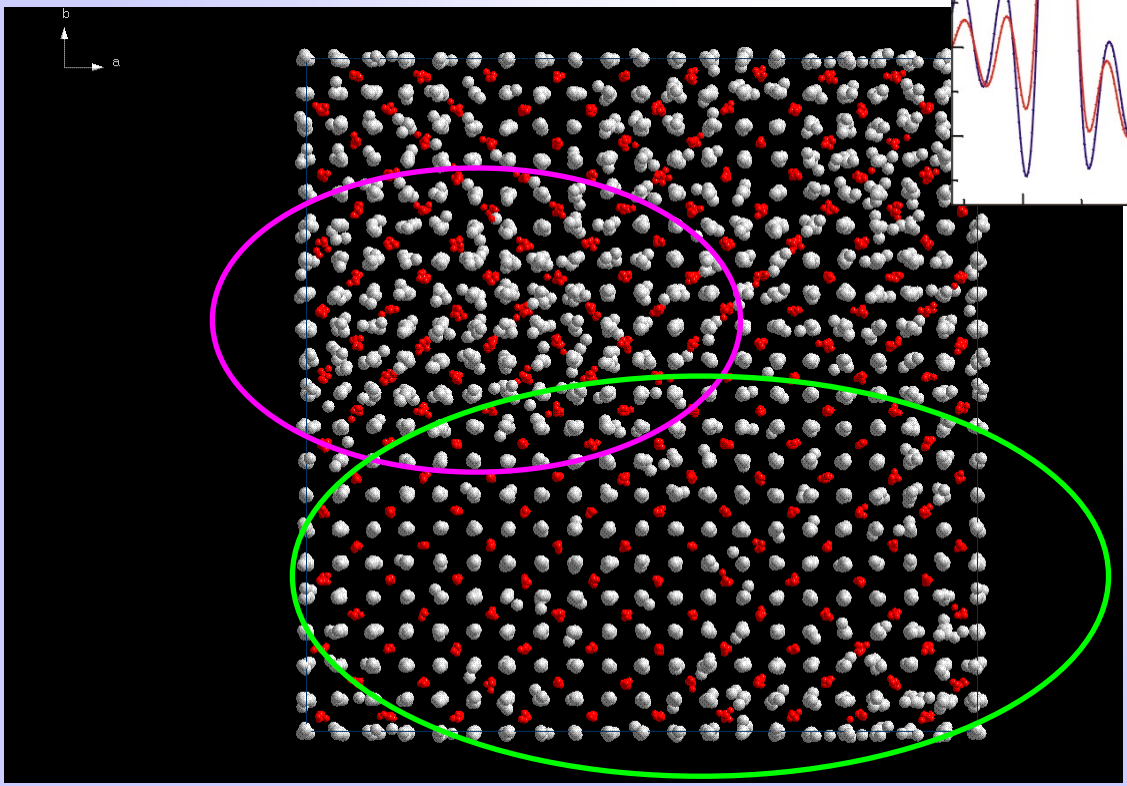
Geometrical modelling: Ag_2O results

Silver oxide at T=25K

Projection along **c**

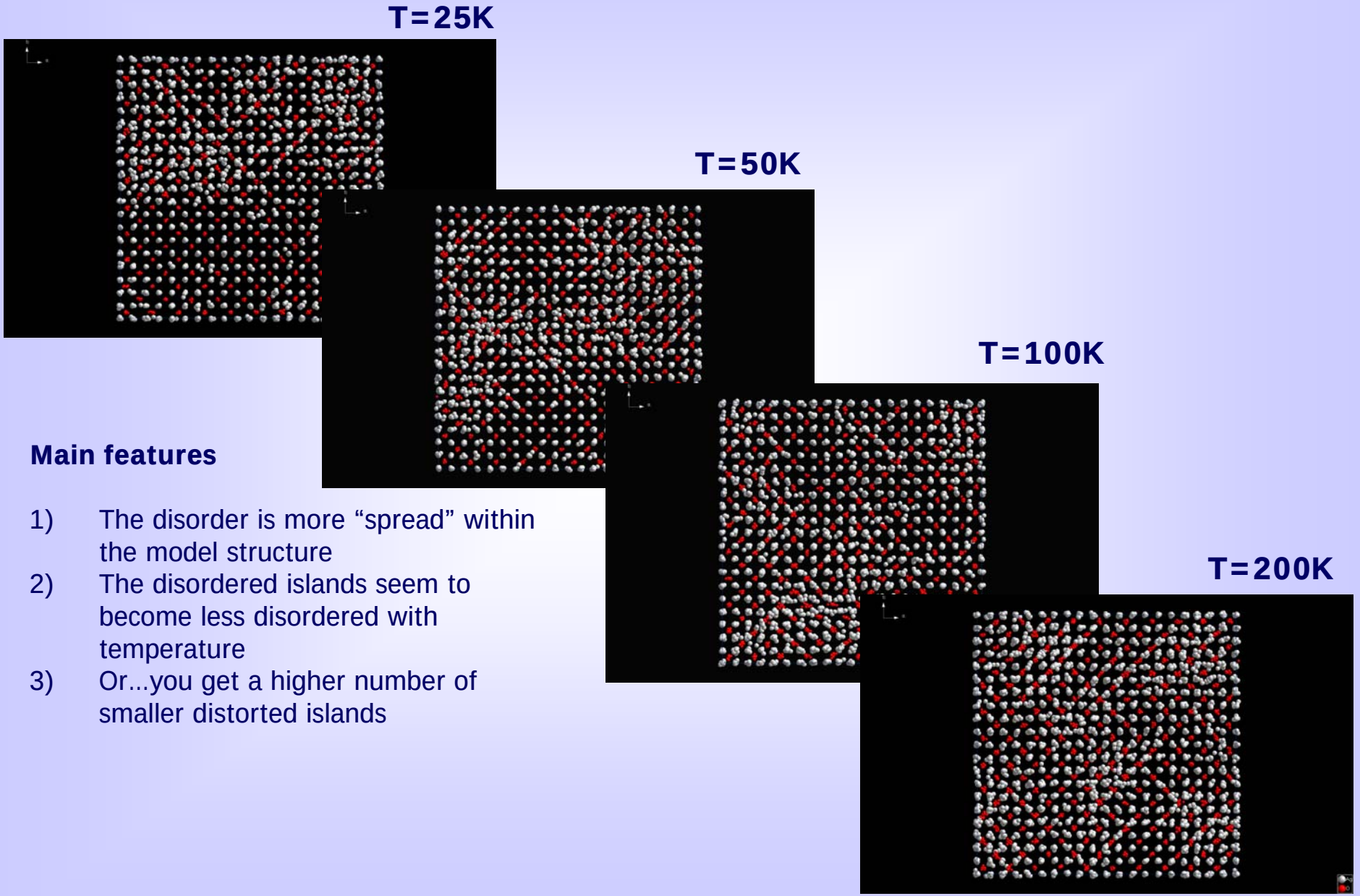


Disordered island of about 10 Å



Very ordered matrix (it's a projection!)

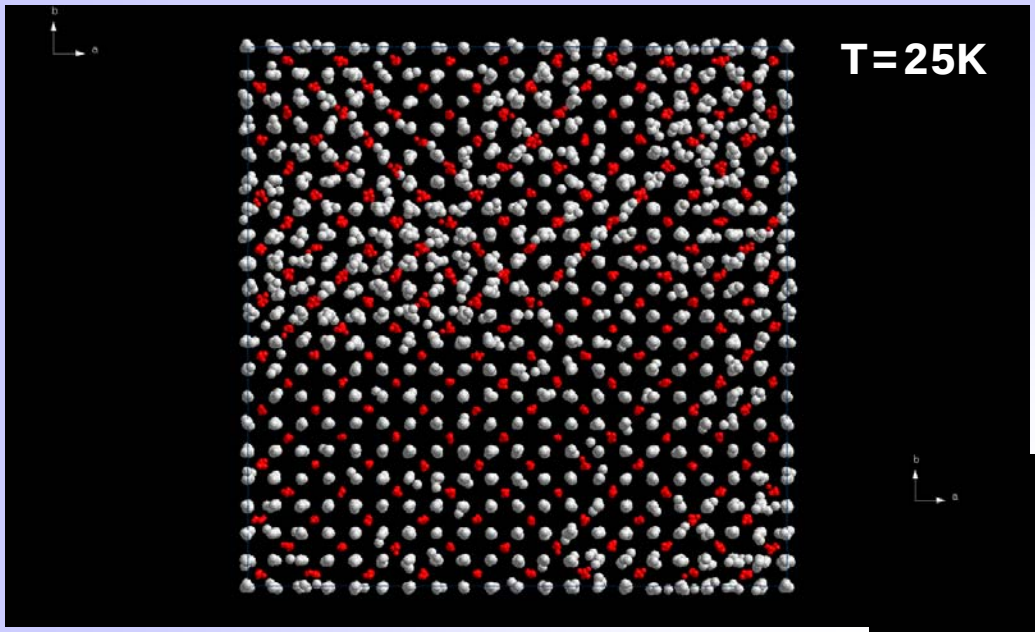
Geometrical modelling: Ag_2O results versus temperature



Main features

1) The disorder is more “spread” within the model structure
2) The disordered islands seem to become less disordered with temperature
3) Or...you get a higher number of smaller distorted islands

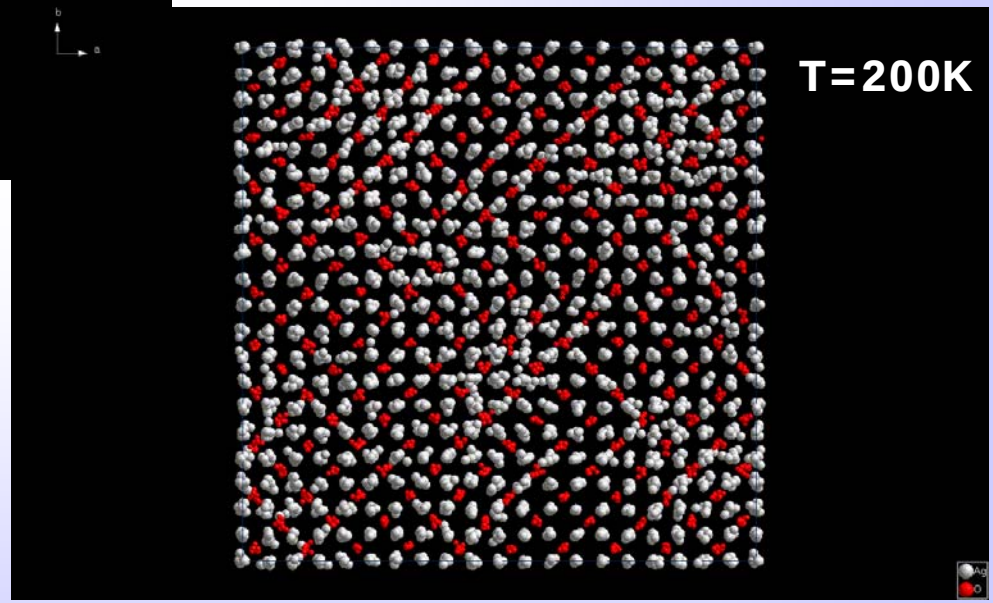
Geometrical modelling: Ag_2O results versus temperature



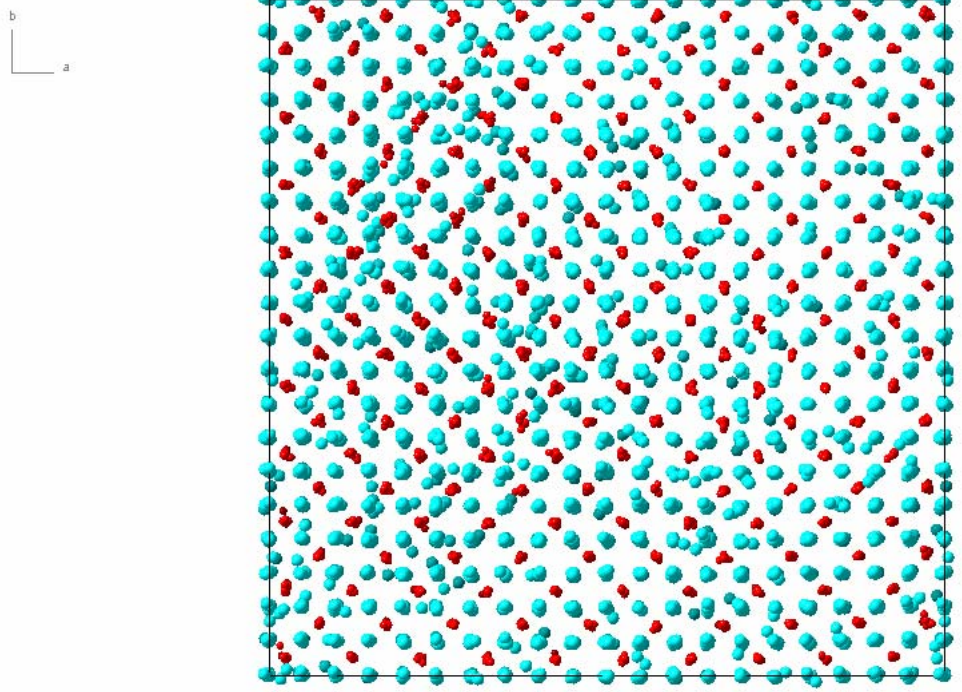
The really important question now is...

Is this really THE model?

1. **The same result comes out with different SA strategies**
2. **The same result comes out at EVERY temperature**

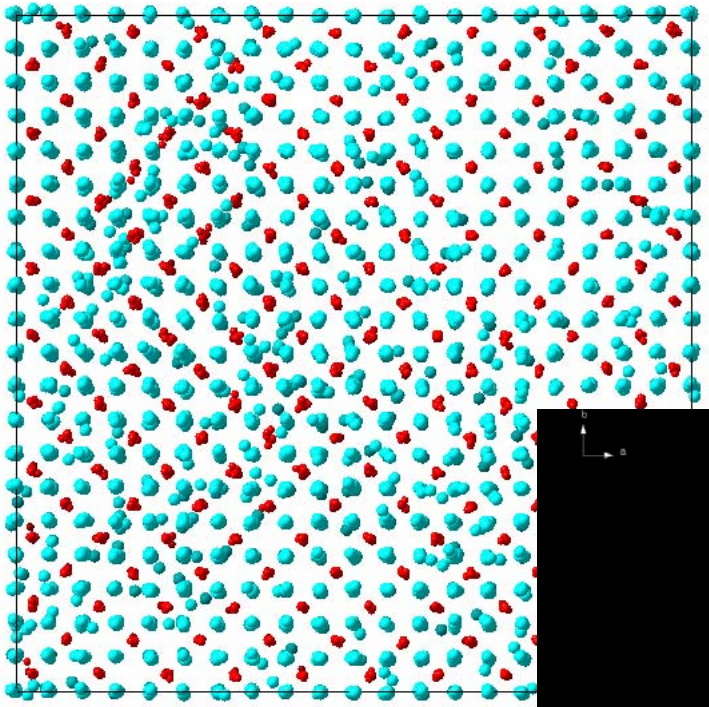


Geometrical modelling: Cu_2O results



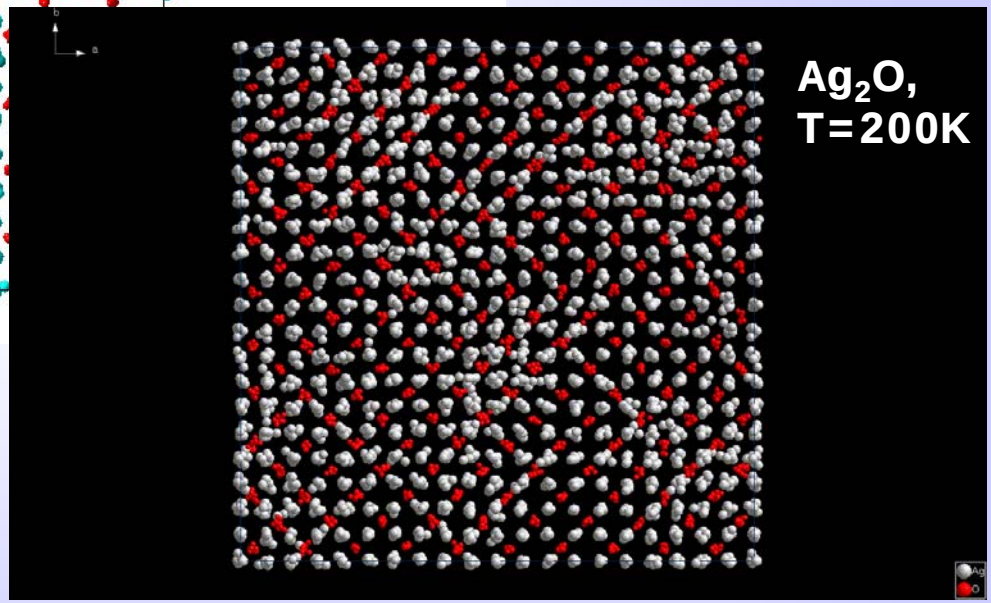
Cu_2O,
T=200K

Geometrical modelling: Cu_2O results



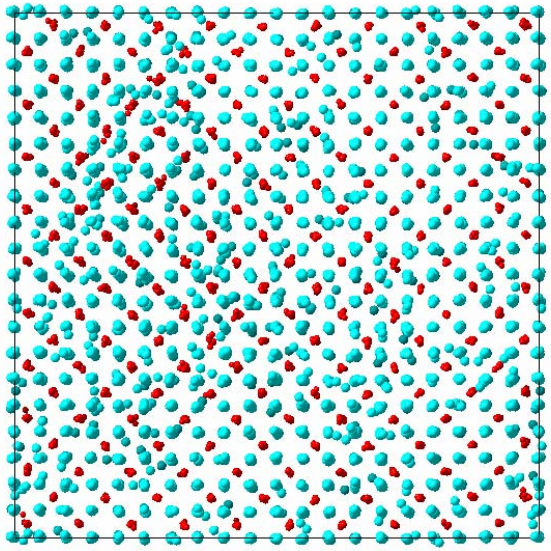
Cu_2O, T=200K

A small degree of distortion appears, but still there are distorted islands in an ordered matrix



The first sign of distortion appears at 200 K

Geometrical modelling: Cu_2O results



Cu_2O, T=200K

More evidence that this could be a meaningful model…

1. The same result as for Ag_2O comes out for high temperature Cu_2O
2. No significant distortion is present for temperatures below 200 K, i.e. the crystallographic model fits the PDF data properly

Conclusions

1) There are local distortions in the structure, both in copper oxide and in silver oxide
2) The distortions appear at relatively high temperature in Cu_2O, at about 200 K, in correspondence with the inversion in thermal expansion
3) The distortions are present in Ag_2O structure even at the lowest temperature measured, in agreement with the signs of static disorder from X-ray diffraction MSD
4) The geometric modelling of the PDF data showed the presence of local distortions about 10 Å wide, that become smaller and more spread with temperature
5) The results from geometric modelling are in agreement with the PDF refinement using the crystallographic model, that shows a worse agreement at r below 10 Å

May these distorsions have an influence on the peculiar thermal behaviour of the cuprite structure?

We still don't know, but ...

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Do these distorsions have a relationship with the peculiar thermal behaviour of the cuprite structure?

We still don't know, but ...

Thanks to...

- All the people in Michigan who taught me how to use PDF...
- to you all for your attention...