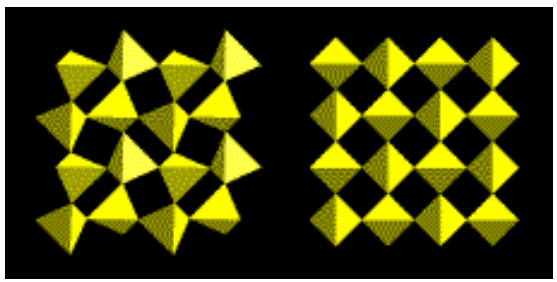
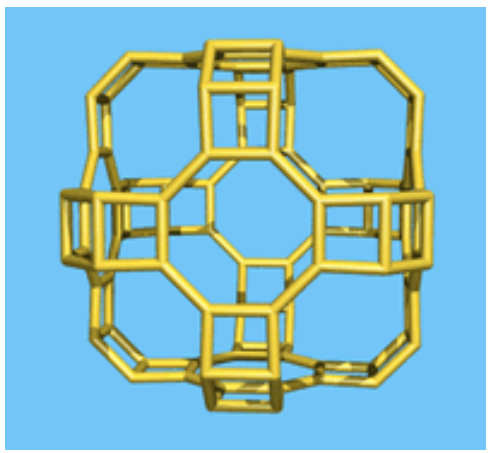
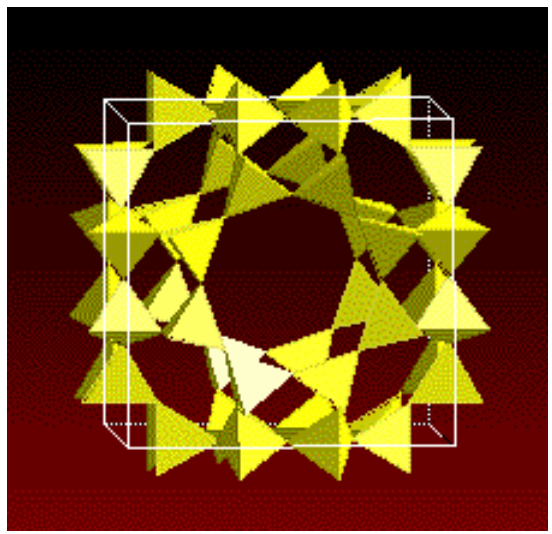
Modeling framework structures

Stephen A. Wells







Overview

- Frameworks, rigid units , flexibility and Rigid Unit Modes.
- Quantifying Rigid Unit motion in real space.

  - dynamic disorder in quartz.
- Geometric modeling and GASP.

  - a whole-body force model.

  - results on silicates.
- Extending geometric modelling to new fields.

  - work in progress.

Framework structures and Rigid Unit motion.

Many mineral structures, particularly the aluminosilicates, can be thought of as frameworks of connected polyhedra – for example the SiO_4 units in silica polymorphs.

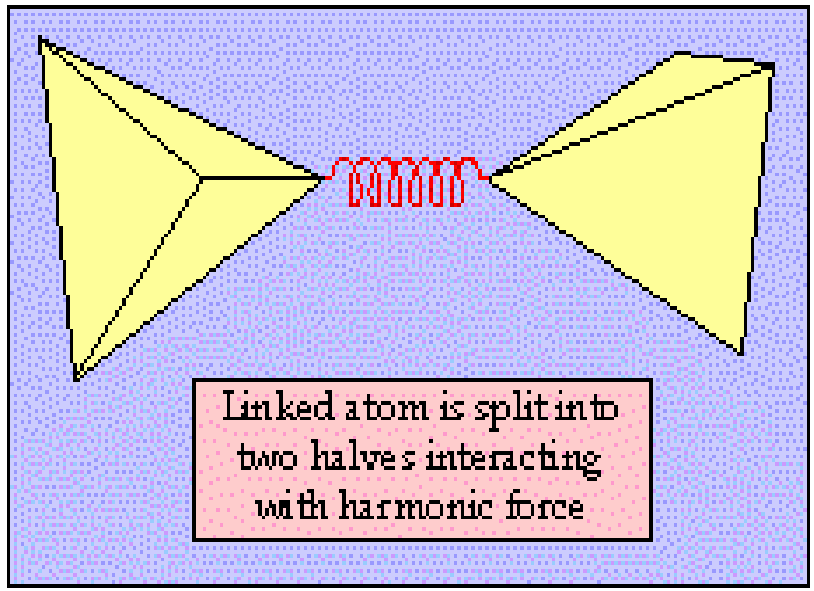
The energy cost for distorting polyhedra can be very high compared to the cost of moving the polyhedra relative to each other – e.g. rotating about a bridging oxygen – so to a first approximation we may consider the structure as a flexible network of rigid polyhedra.

Those modes of motion in which the polyhedra move and rotate without distortion are Rigid Unit Modes (RUMs), having low frequencies and high amplitudes. They are significant as soft modes in phase transitions, in NCTE, dynamic disorder and possibly in the response of a structure to defects.

RUMs in reciprocal space

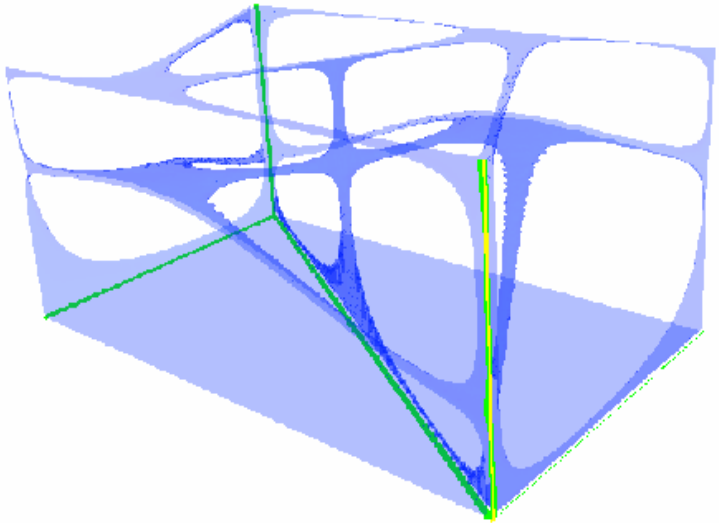
The split-atom model: constrain polyhedra using a single spring.

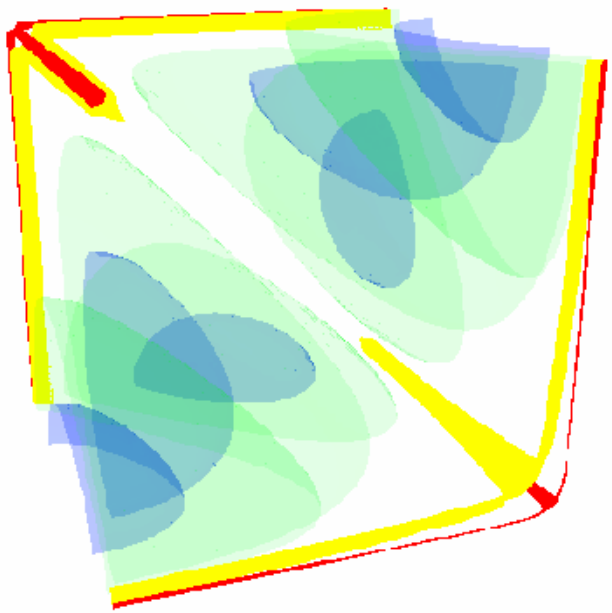
Rigid Unit Modes require no distortion of the spring and appear with zero frequency.



The CRUSH program (Dove *et al*.) identifies RUMs by lattice dynamics as zero-frequency modes. [In practice, these modes have frequencies of 0-2 THz, compared with 12-15 THz for distortions of the polyhedra].

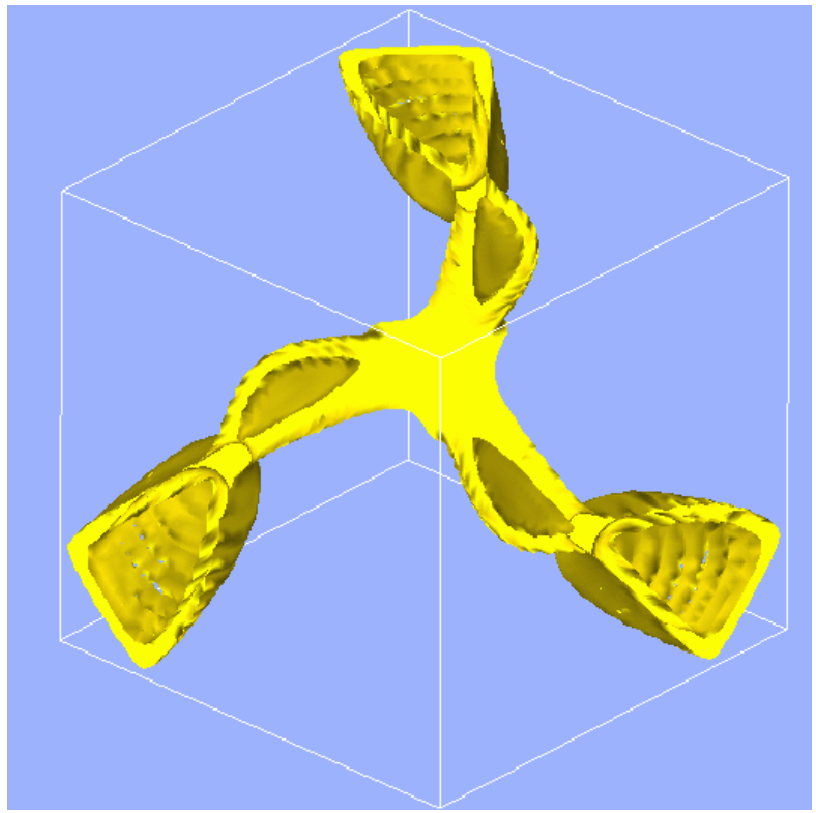
Flexible structures have a RUM landscape in reciprocal space.





RUM landscapes for minerals.

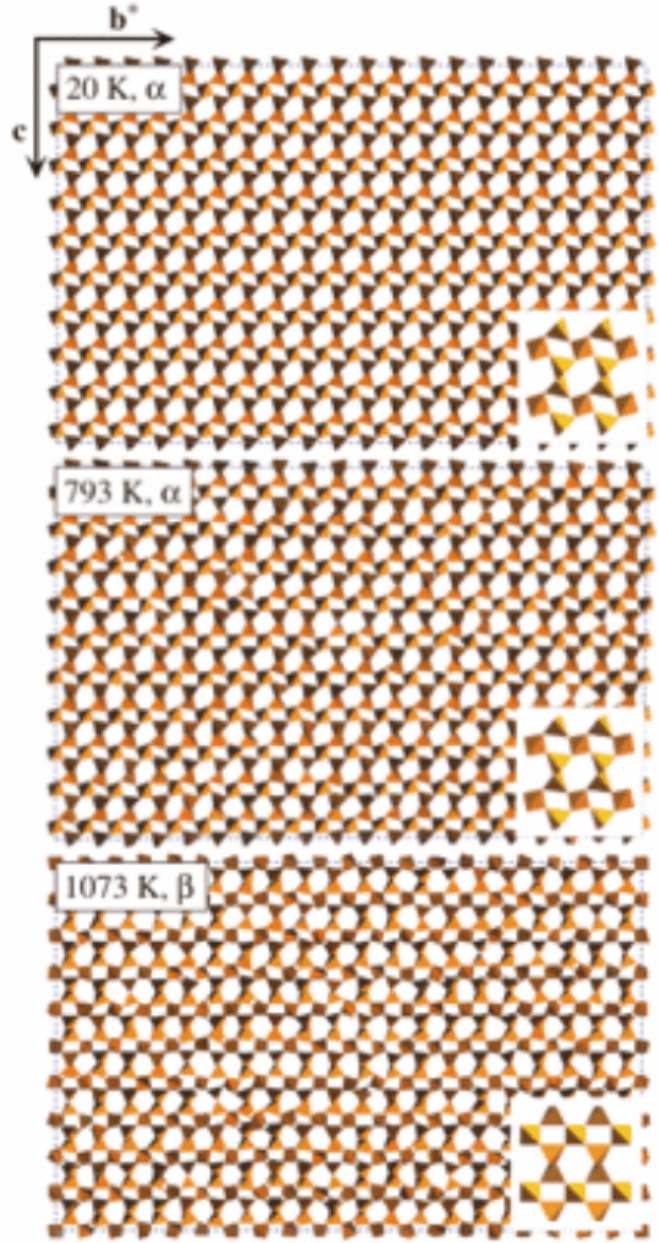
Anticlockwise from left: quartz, sodalite and zirconium tungstate.



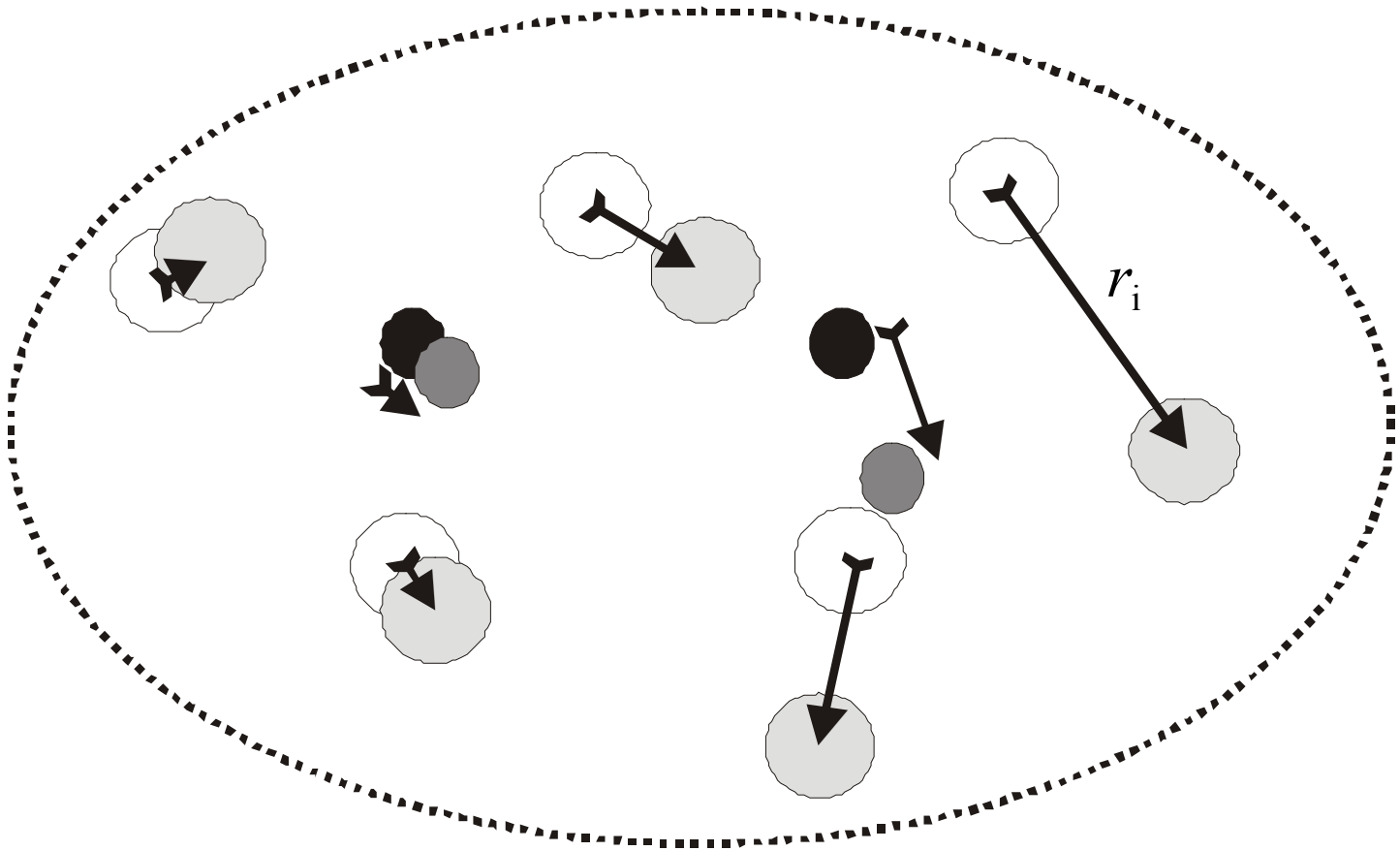
Rigid Unit motion in real space: dynamic disorder in quartz

Total neutron scattering data has information on both the average structure and the dynamic disorder. Reverse Monte Carlo modelling gives us snapshots of the behaviour of quartz.

How much of the disorder can be accounted for by Rigid Unit motion, and how much are the polyhedra distorted? We compare snapshots to find out.



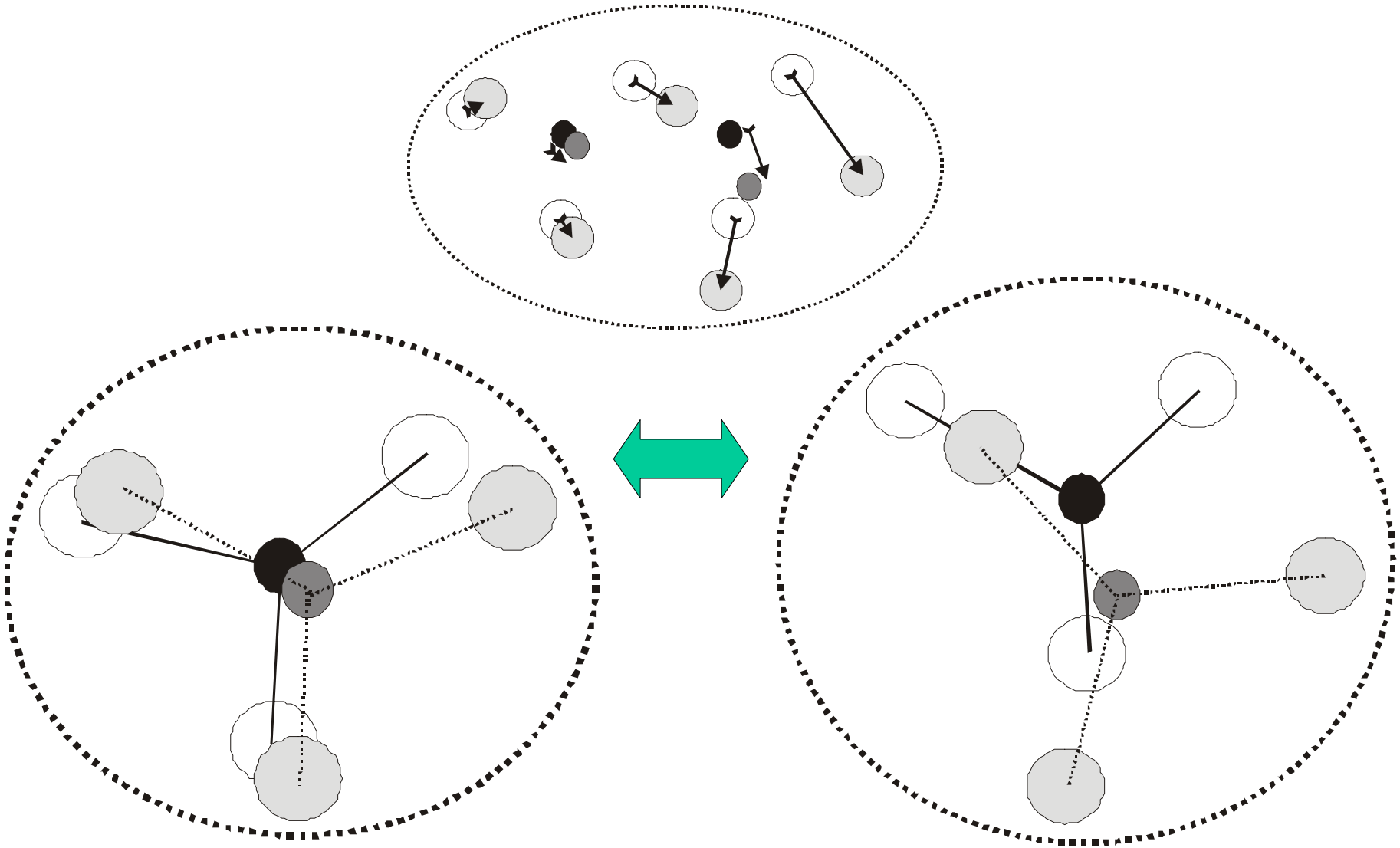
Real-space analysis



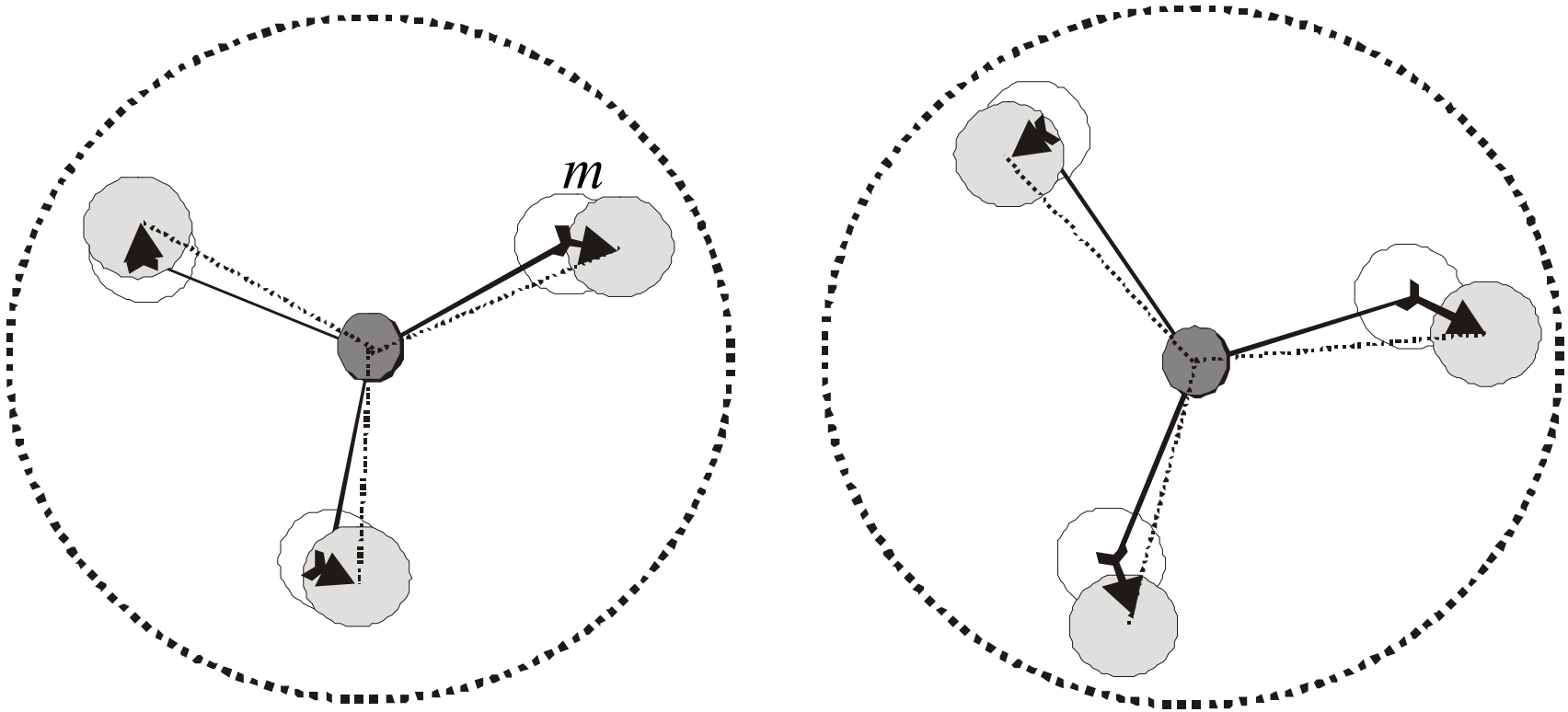
Each atom *i* is displaced by a vector r_i.

For each species we obtain an RMS motion, $r_{O,Si,\ldots}$

Decomposition into polyhedra…

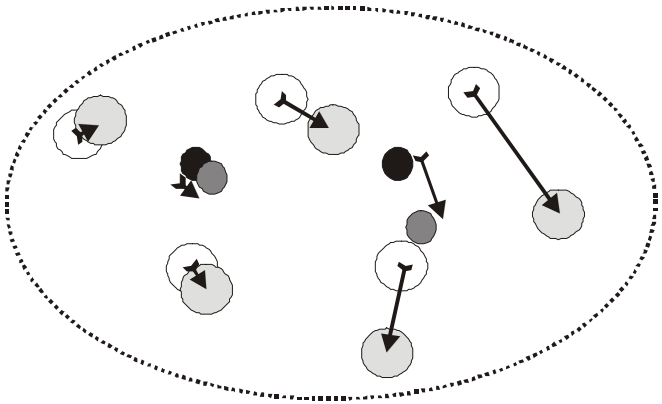


Matching polyhedra

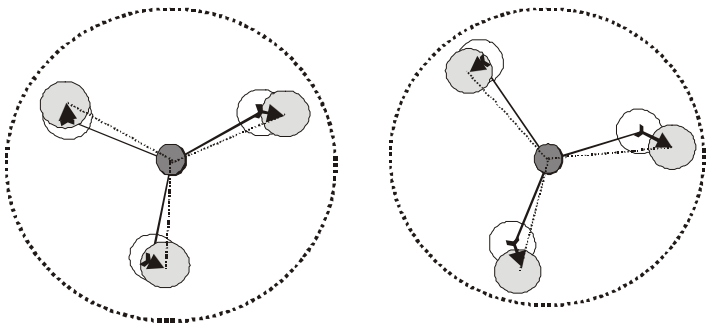


The polyhedra from one snapshot are matched to those in another by rotation so that the mismatches *m* are minimised. The residual mismatch resolves into Si-O stretching and O-Si-O bending components.

Significance of RUM motion



In the total motion of the structure there is a RMS displacement of vertex atoms, r_O.

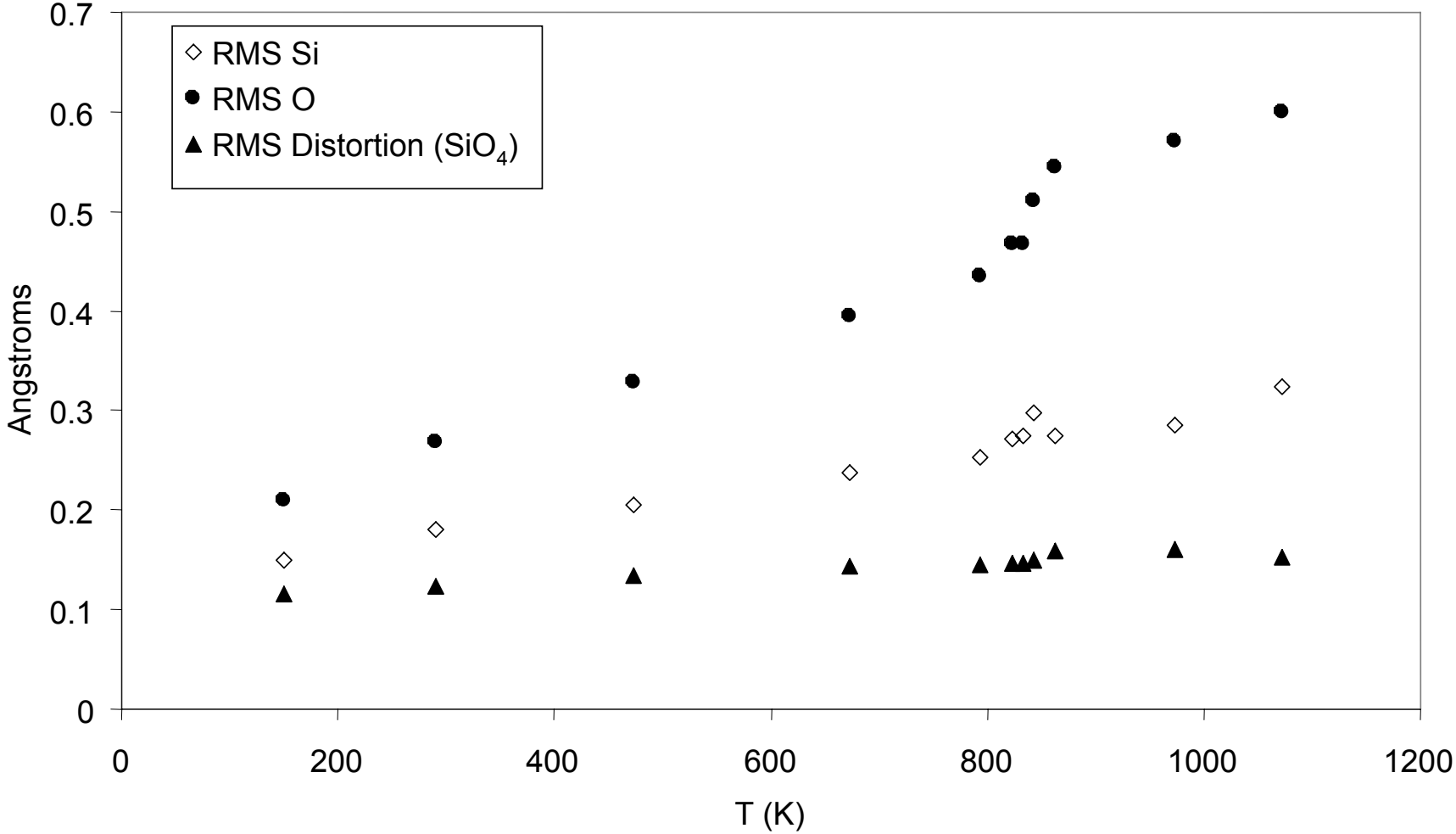


In the residual distortion of the structure there is a RMS displacement of vertices, *d*.

The ratio of r_O to *d* indicates the significance of RUM motion; a high ratio indicates large atomic motion with little polyhedral distortion.

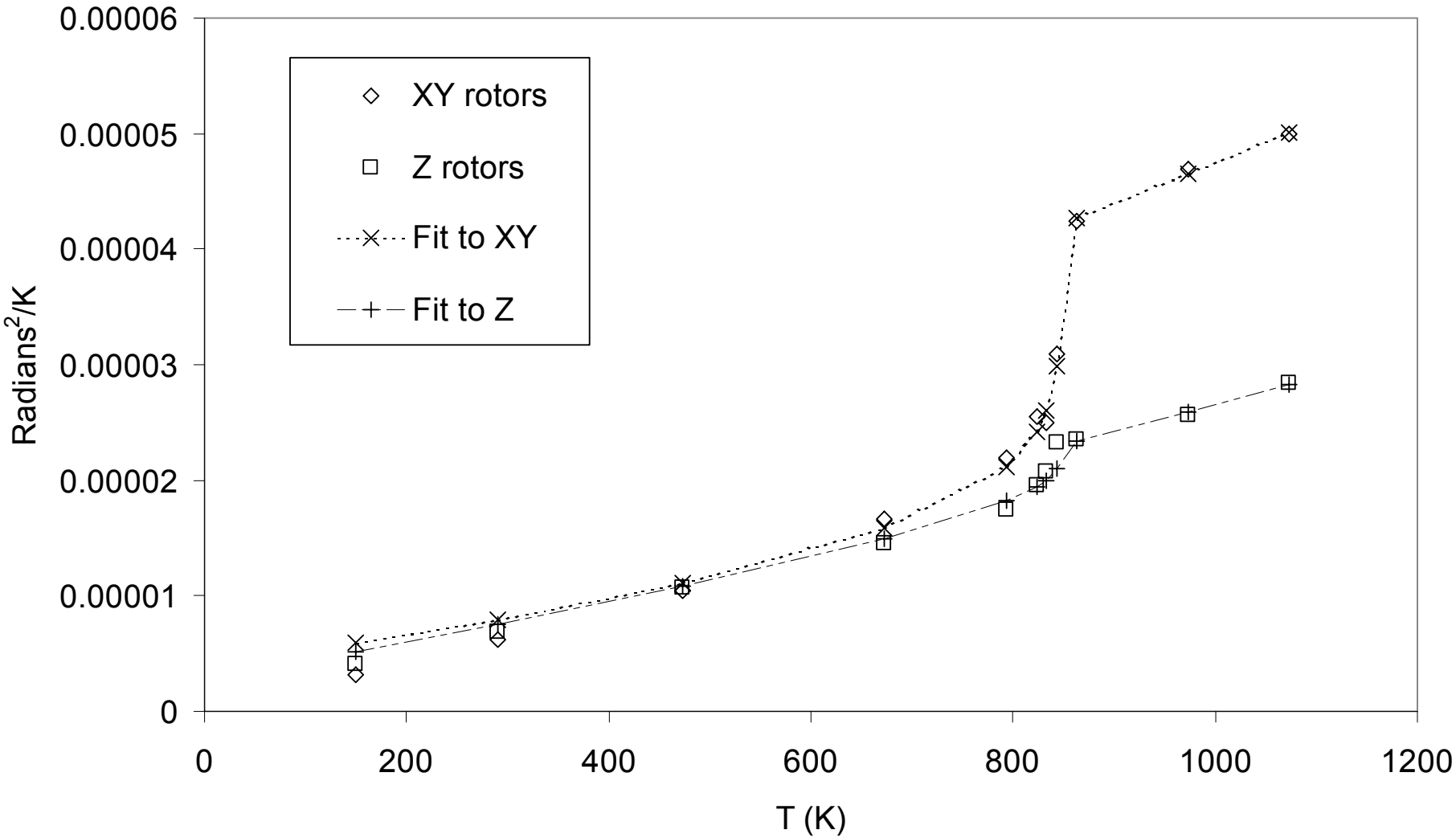
The magnitude of the rotation of the polyhedra is also interesting.

Dynamic disorder in quartz



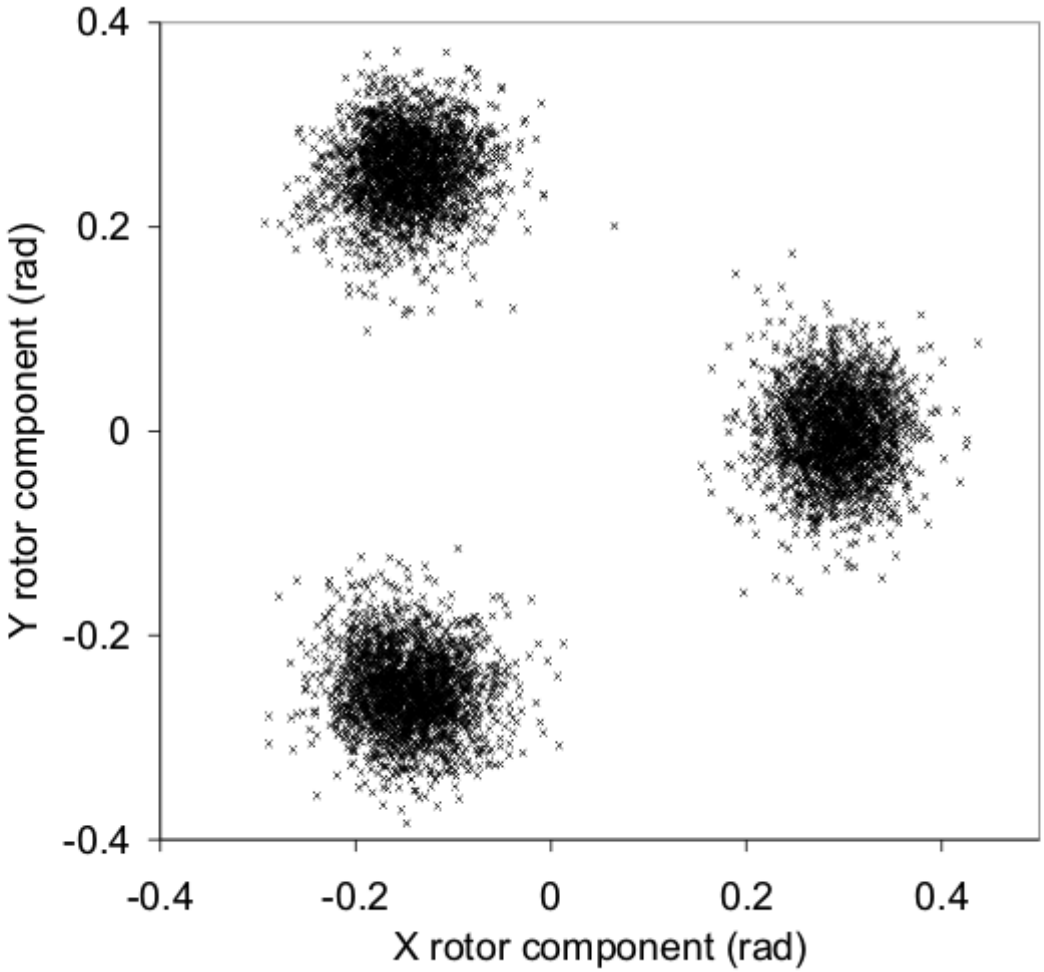
Each data point is the comparison of two RMC fits to the neutron data at a given temperature, for a configuration of 6000 polyhedra.

Phase transition and order parameter



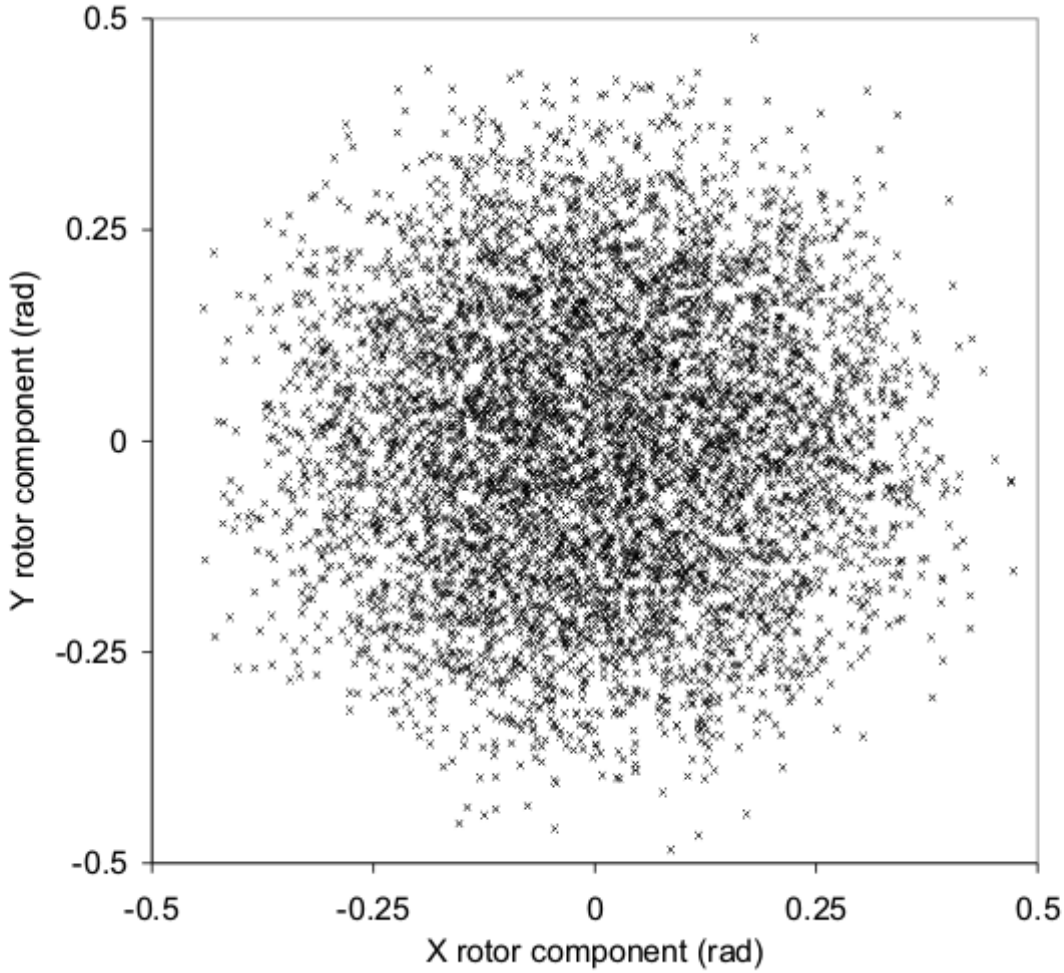
The fit is based on the split-atom model and has only one adjustable parameter.

Order parameter in alpha quartz



At low temperatures we see the rotation of polyhedra about <100> axes relative to the beta phase.

Order parameter in beta quartz



In the ideal beta phase, all polyhedra would lie at (0,0) in this rotor plot. High-T quartz does not resemble the beta-quartz X-ray structure.

Geometric modeling

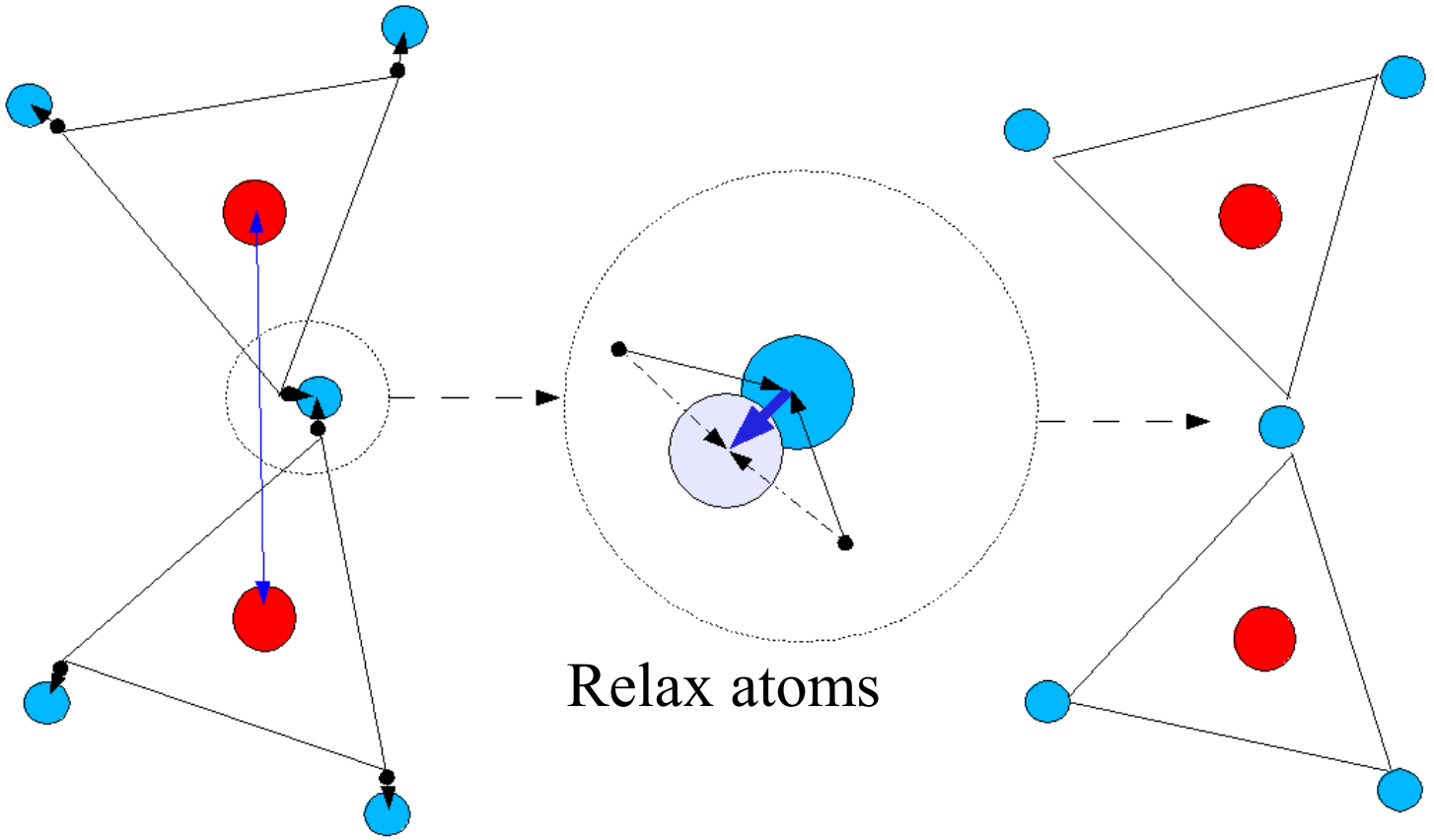
We have seen that we can quantify the mismatch between two polyhedra when they have been rotated to fit as closely as possible.

If we superimpose a geometrically ideal polyhedron over an SiO_4 group, we can quantify the deviation of the atomic positions from their ideal tetrahedral arrangement.

If we now hold the ideal polyhedron fixed we can allow the atoms to move to minimise their mismatch. Each atom moves towards its vertex, and the result is to idealise the polyhedron.

This suggests a ‘geometric potential’ or force model. Instead of using a series of two- and three-body potentials (Si-O, O-Si-O), we fit a ‘ghost’ SiO_4 body, then relax each atom towards its ‘ghost’ vertices.

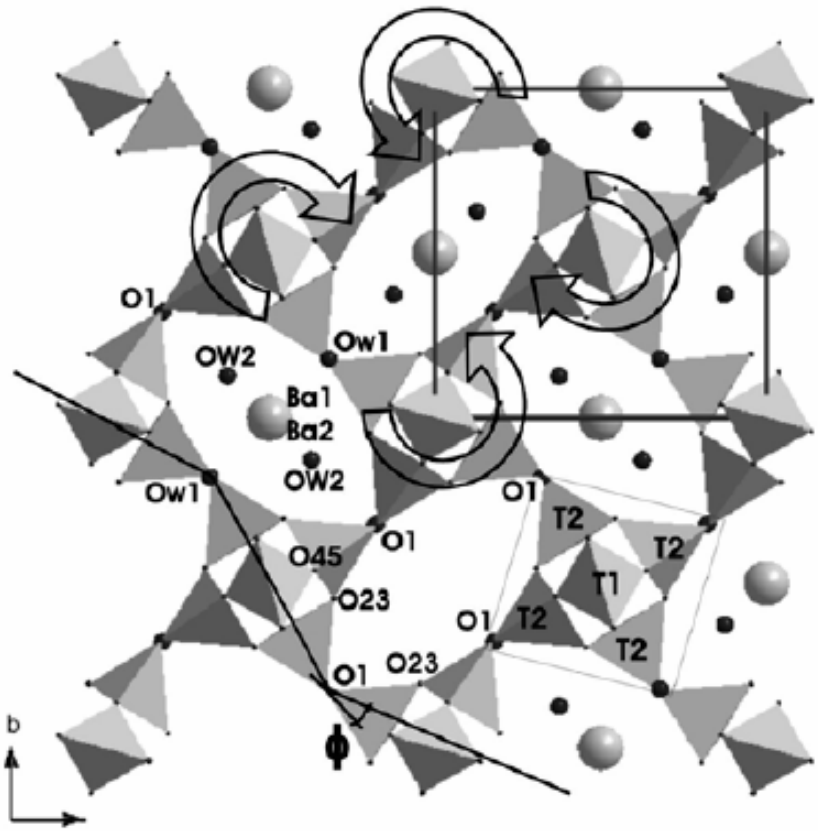
Geometric modeling

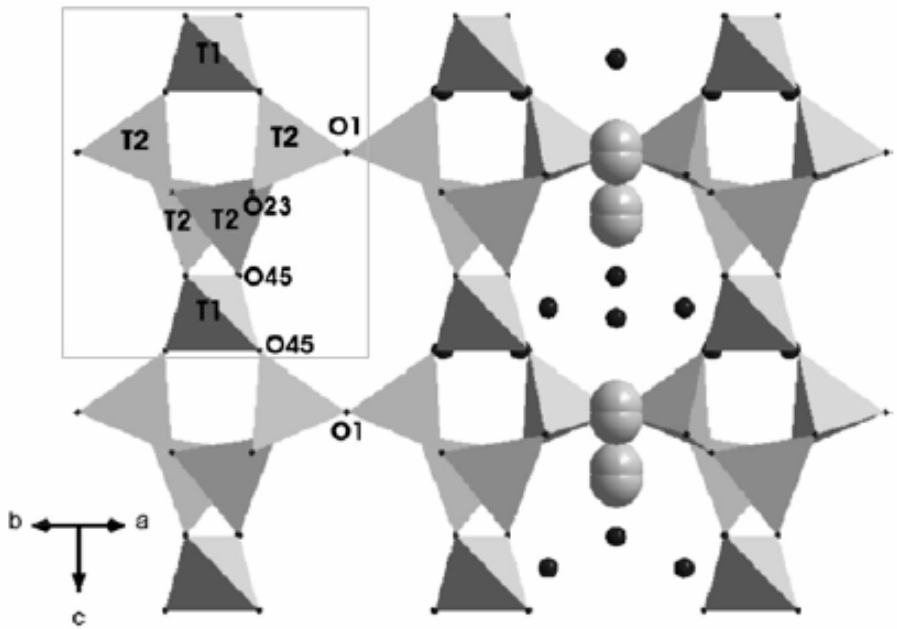


The fit is iterative, with the ‘ghost’ body capturing the collective motion of the polyhedra.

Edingtonite

This fibrous zeolite has an interesting compression mechanism based on the rotation of its secondary building units (SBUs). Experimental data from X-ray diamond-anvil; simulated using geometric modeling.





Simulation approach

Initial structure (fractional coordinates) from room-temperature X-ray data.

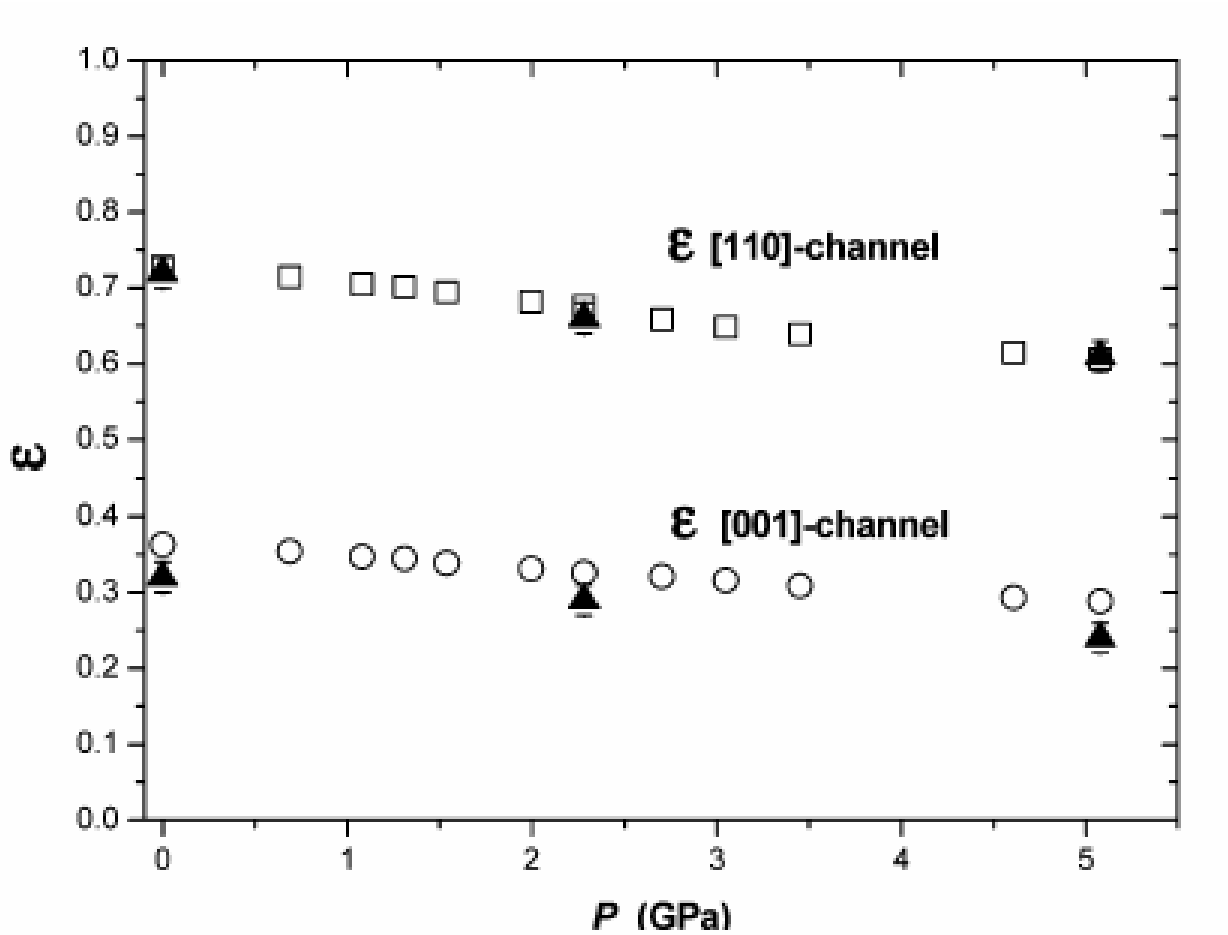
Cell parameters reduced in compression according to experimental observations (hydrostatic compression) or uniaxially.

Atomic coordinates relaxed using geometric modeling, in response to compression of cell parameters.

We obtain predictions for the variation of the channel ellipticities and the rotation of the SBUs, which can be compared with high-pressure X-ray structural determinations.

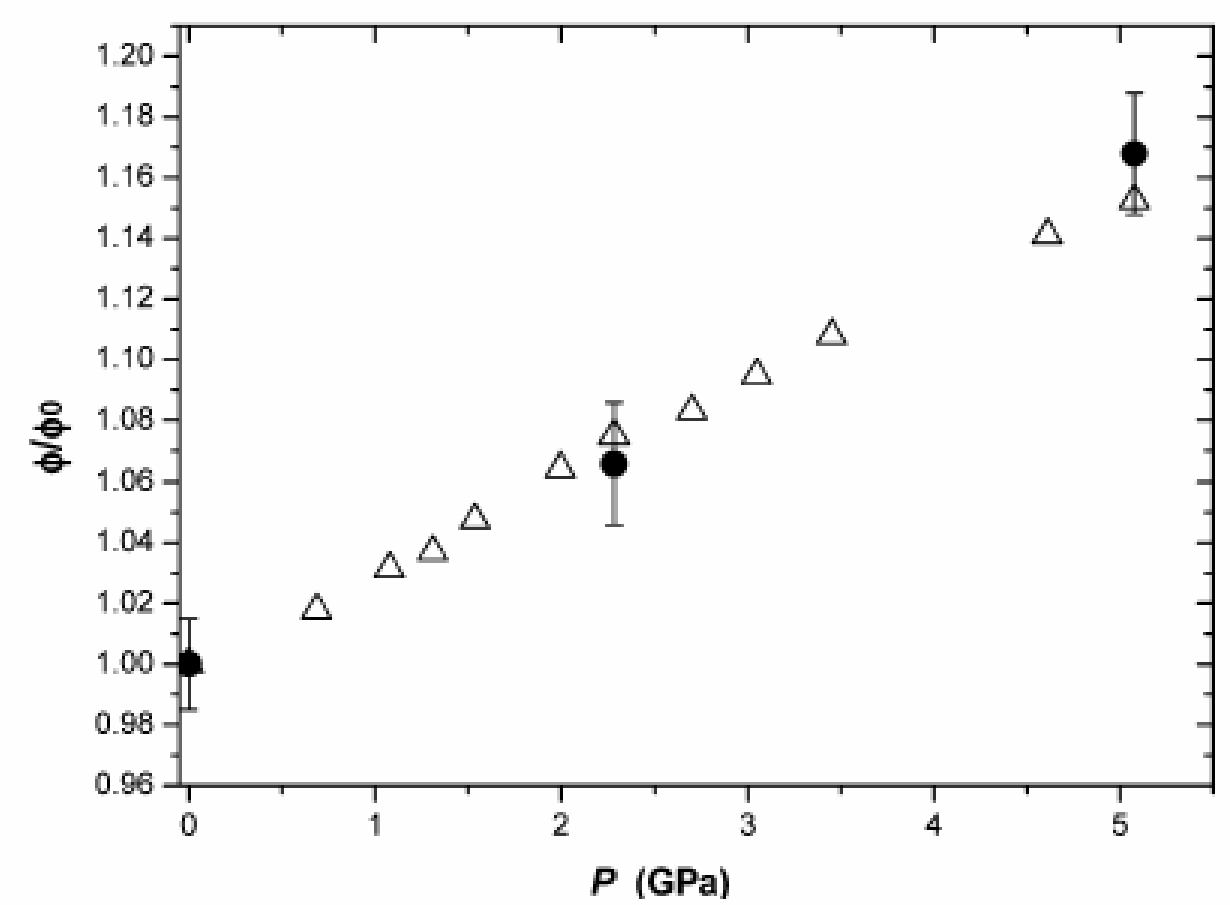
Simulation of uniaxial compression shows aspects of the compression mechanism not accessible to experiment.

Channel ellipticities



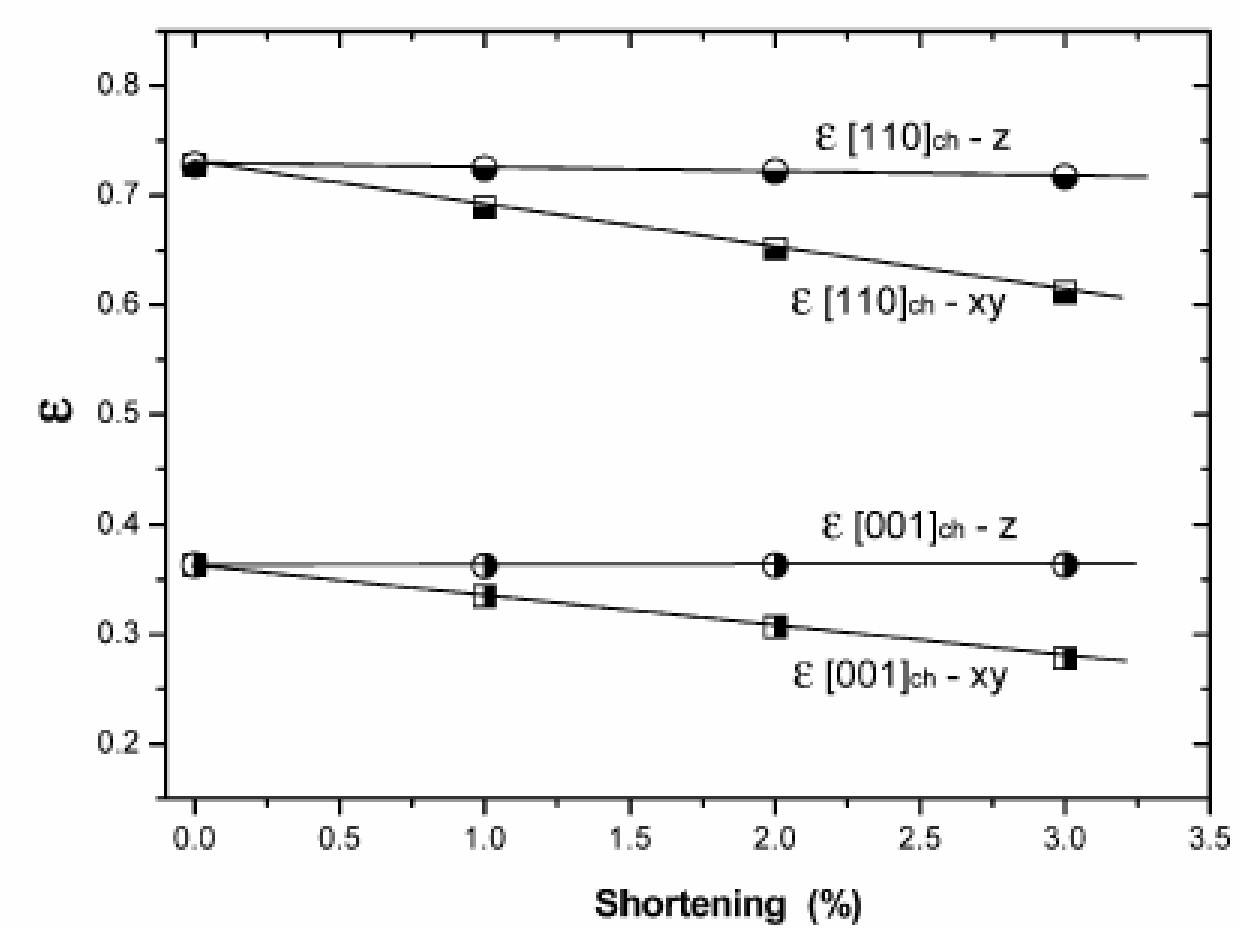
Both sets of channels become more elliptical on compression. Open marks, simulation; full marks, experimental data.

SBU rotation



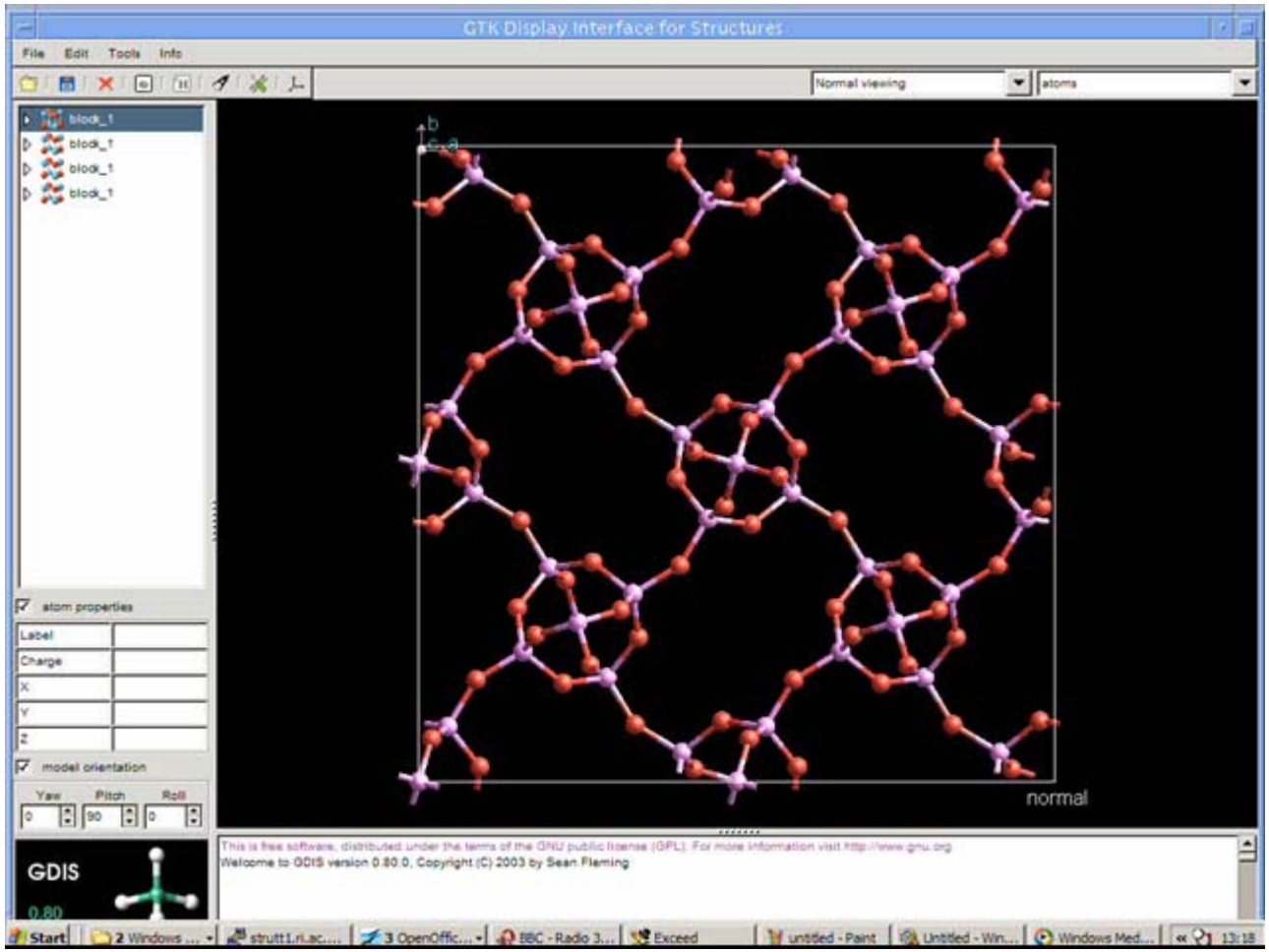
The rotation of the secondary building units is well described by the geometric model.

Uniaxial compressions



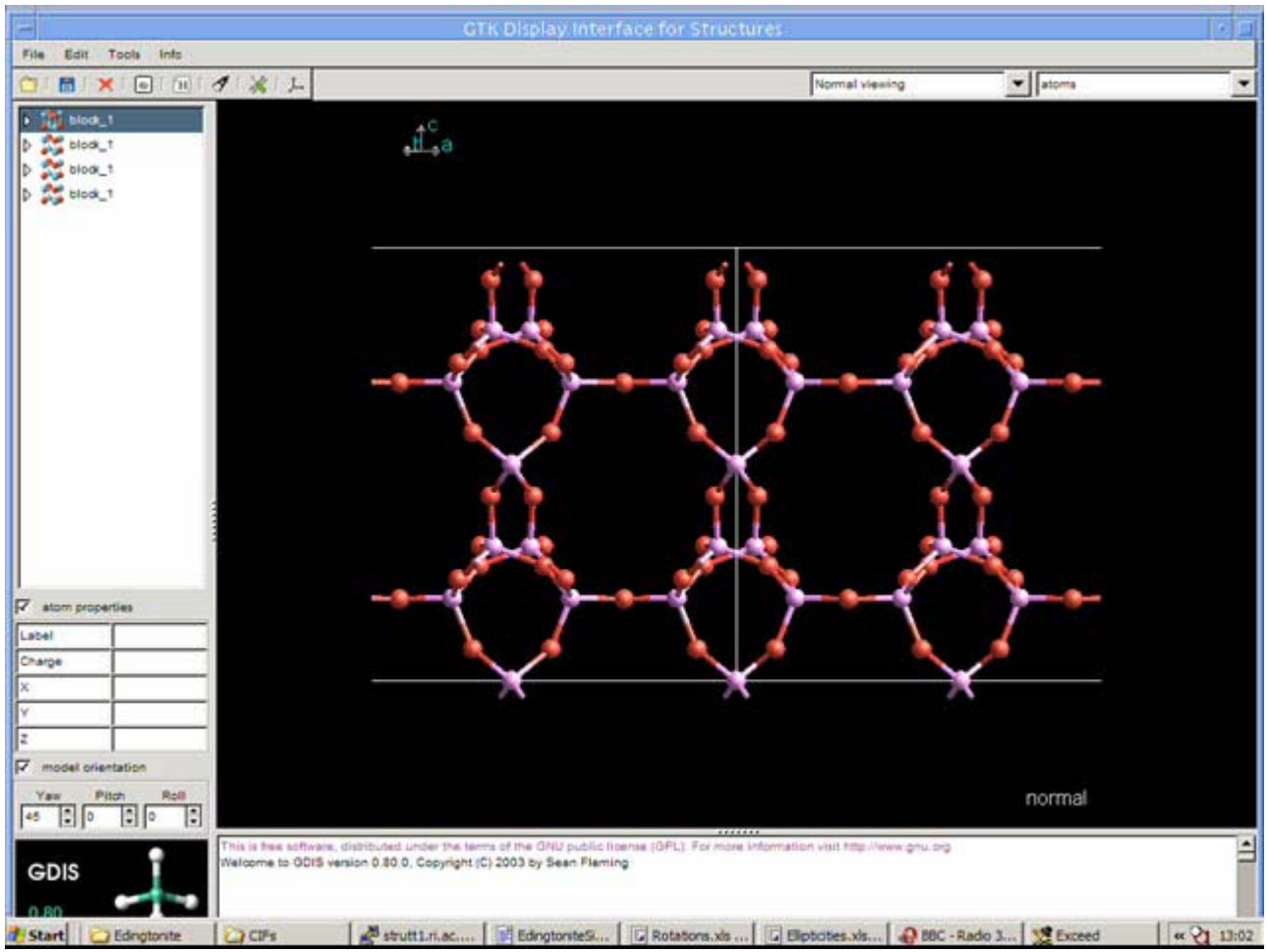
Simulations suggest that only compression in the x-y plane alters the channel ellipticities. Compression along the z axis causes isotropic compression of the channels.

Edingtonite compression 1



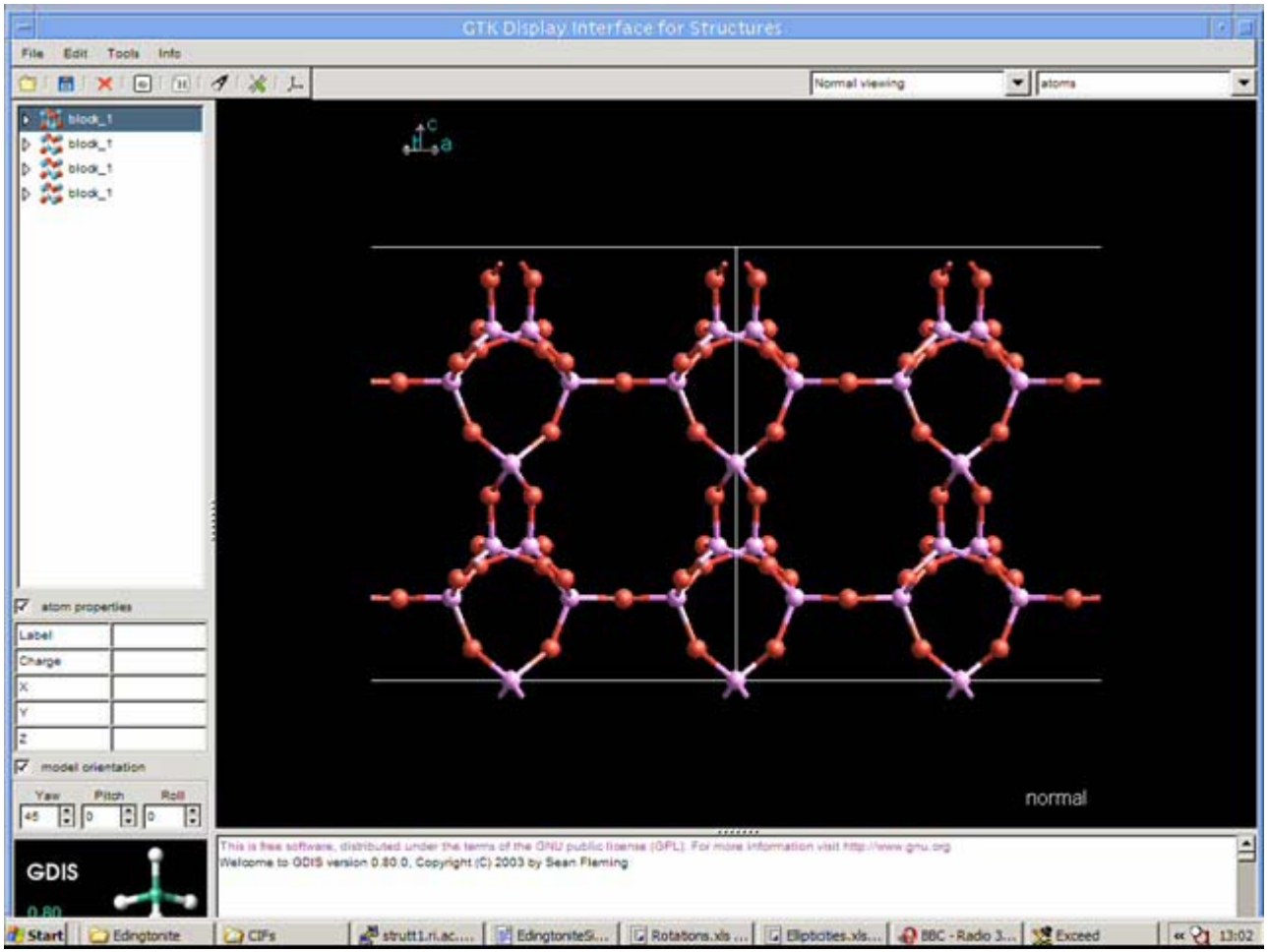
View along z axis, compression in x-y plane.

Edingtonite compression 2



View along [110] axis, compression in x-y plane.

Edingtonite compression 3



View along [110] axis, compression in z direction.

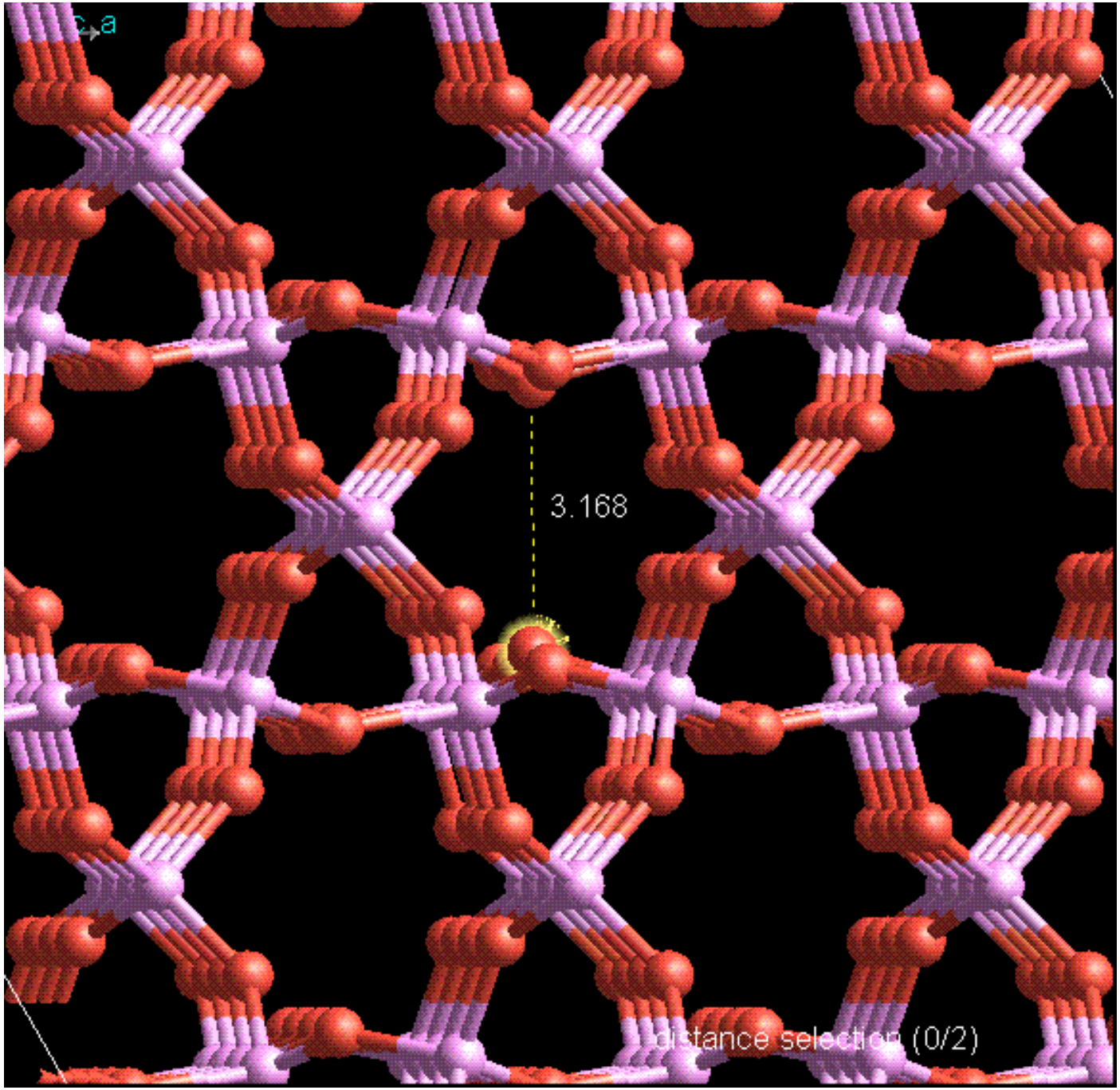
Variations in the quartz structure

The data from geometric analysis of quartz configurations from neutron scattering/RMC modeling suggests large-amplitude motions of the oxygen atoms, with consequent variations in the channel cross-section.

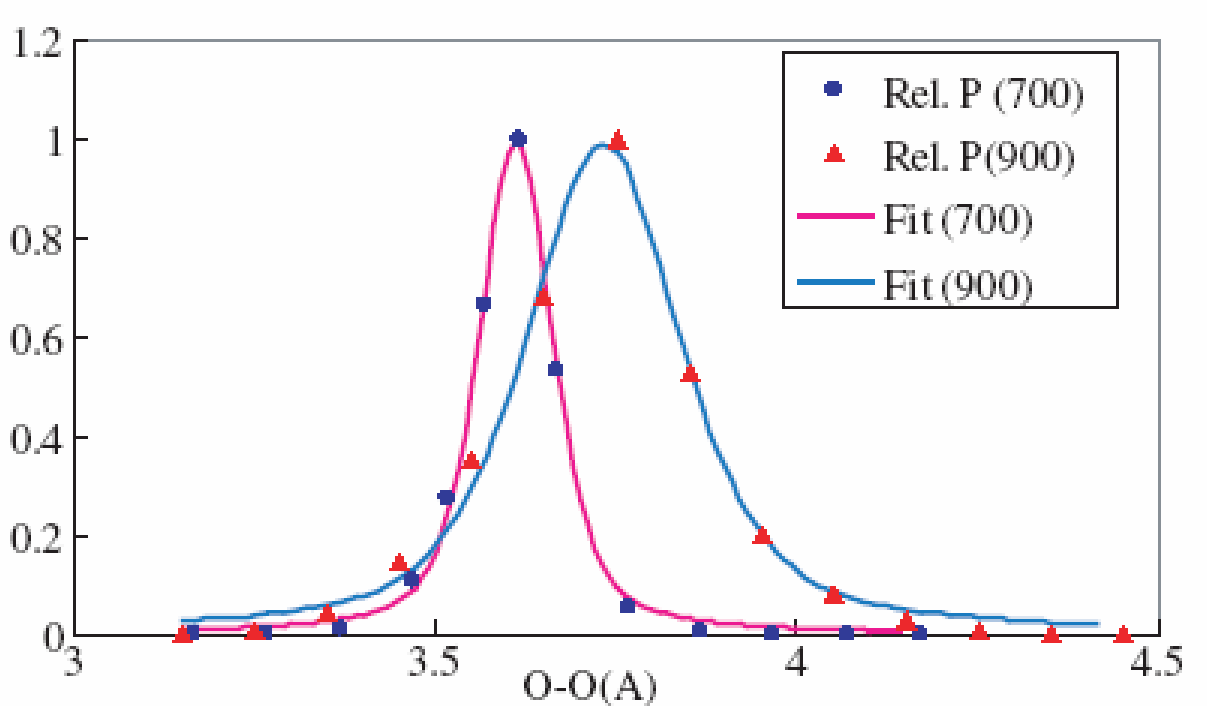
We investigate by constraining two opposing oxygen atoms in a large quartz supercell, and relaxing the structure geometrically. The process is rapid even for large, asymmetric cells.

The energy of each configuration is calculated by a single-point calculation with interatomic potentials (van Beest *et al*.).

We thus obtain the energy cost of variations in the channel width in quartz, and can estimate the likely degree of variation due to dynamic disorder at different temperatures.


c
a
3.168
distance selection (0/2)

Quartz channel widths



The energy cost of variations in the channel width is low (approx 0.5 eV for a variation of +/- 0.5 Angstroms). Calculating an Arrhenius factor exp(-E/kT) at each width gives an estimated probability distribution.

The FWHM in beta-quartz is about 0.25 Angstroms. Activation processes depending on channel width can be strongly affected by variations on this scale.

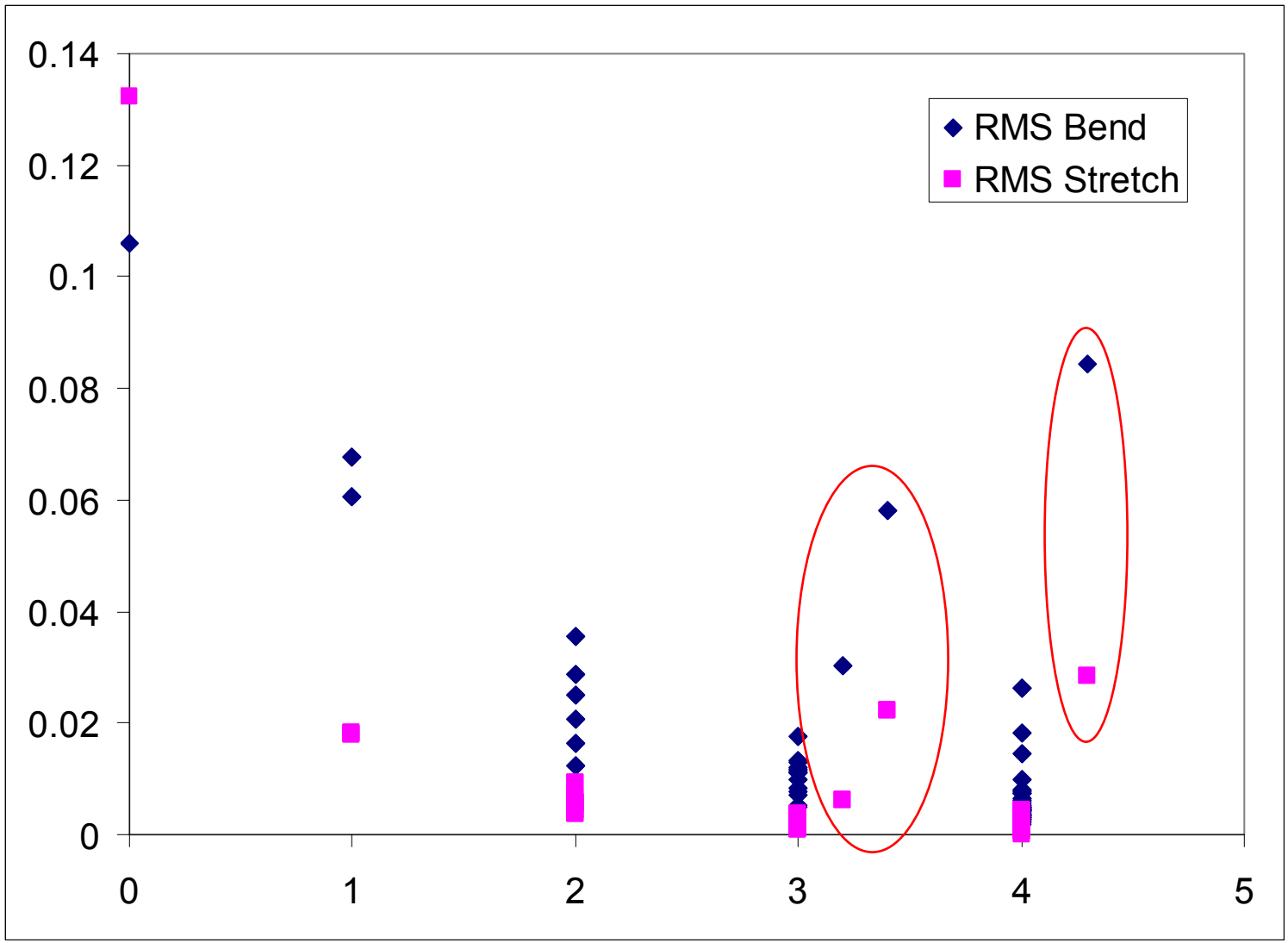
Defect accomodation

The flexibility of a silicate framework may influence the propagation of strain. The response of the framework to the introduction of a defect (e.g. Al substituting for Si, with a consequent increase in size of the Al-containing tetrahedron) will depend on this strain propagation.

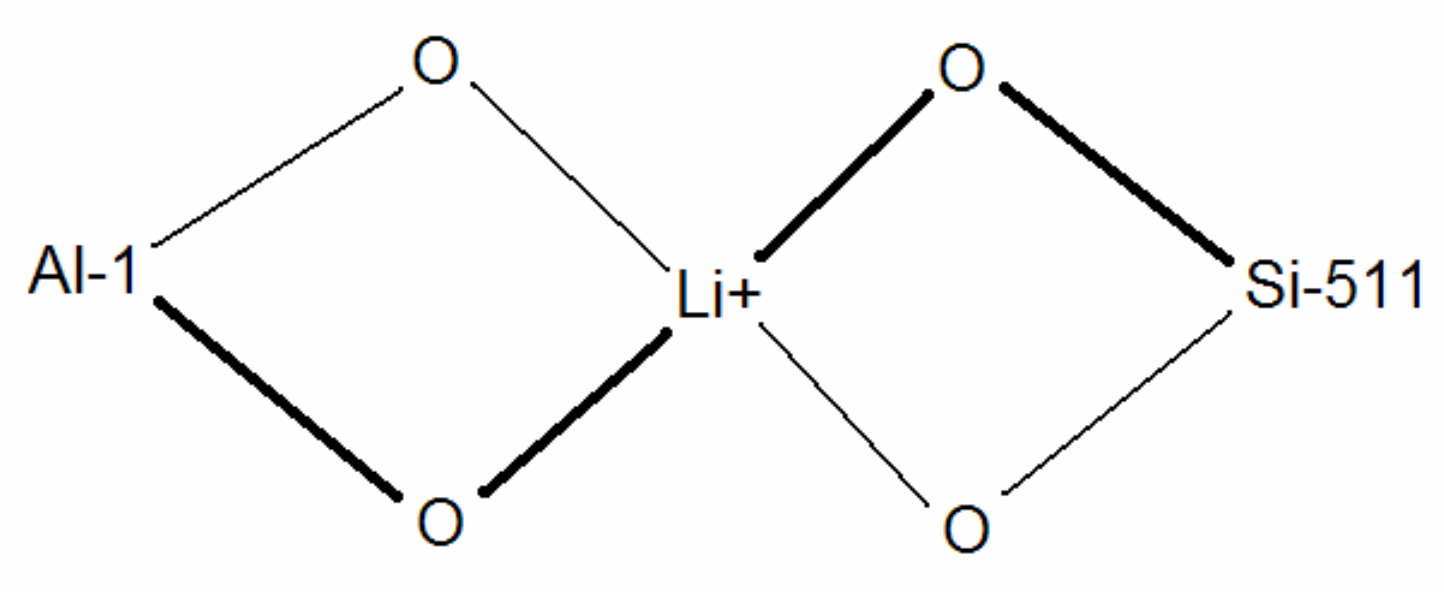
We introduce an Al substitutional defect into a large quartz supercell (a,c of order 30 Angstroms), with charge balanced by a lithium ion in the channel adjacent to the Al site. Li-Al-Si-O potentials of Calleja *et al*.

Geometric comparison of the perfect and defective structures shows the degree of distortion of the polyhedra adjacent to the defect site.

Tetrahedra neighbouring the Al site.

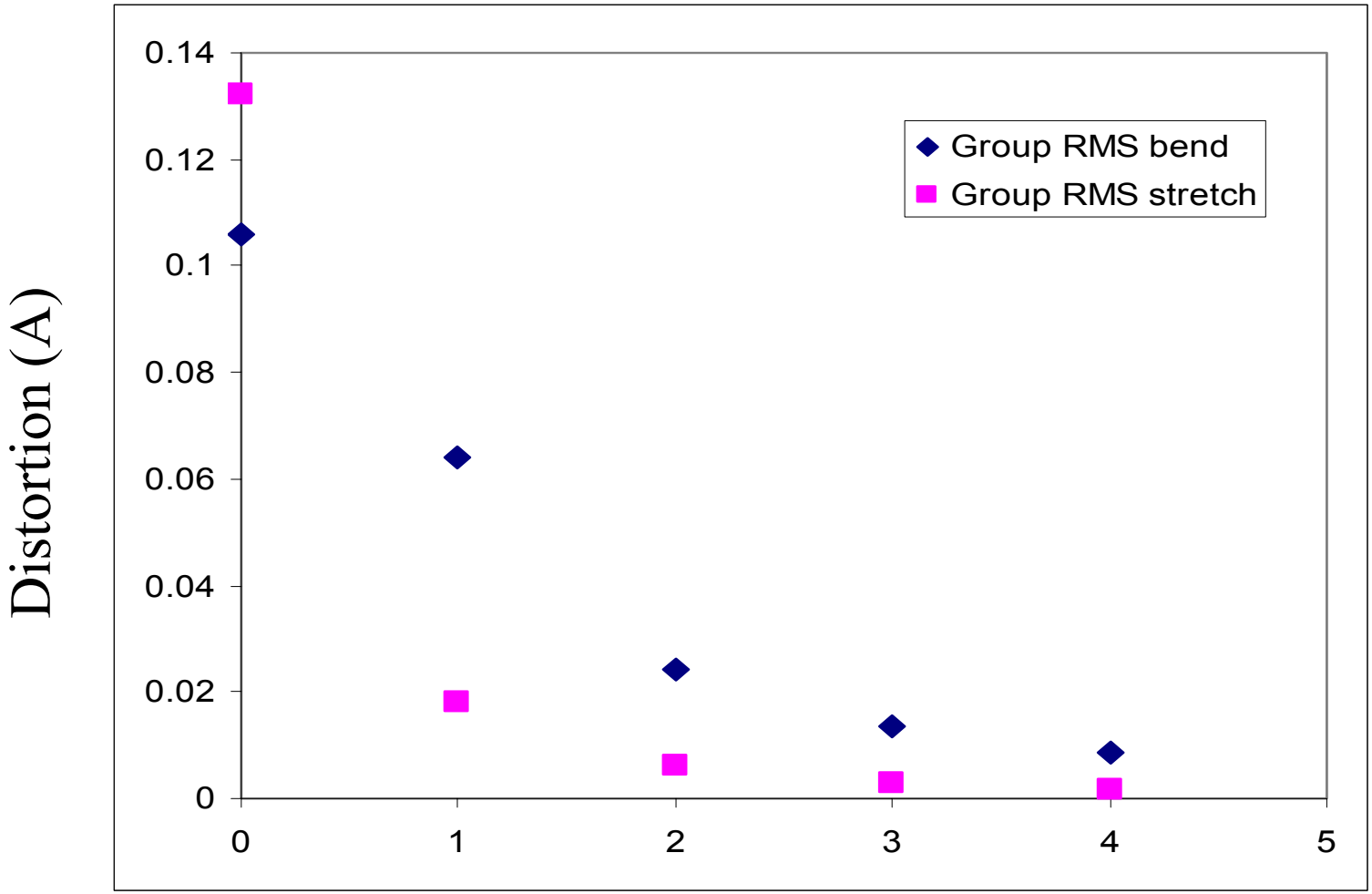


Lithium coordination



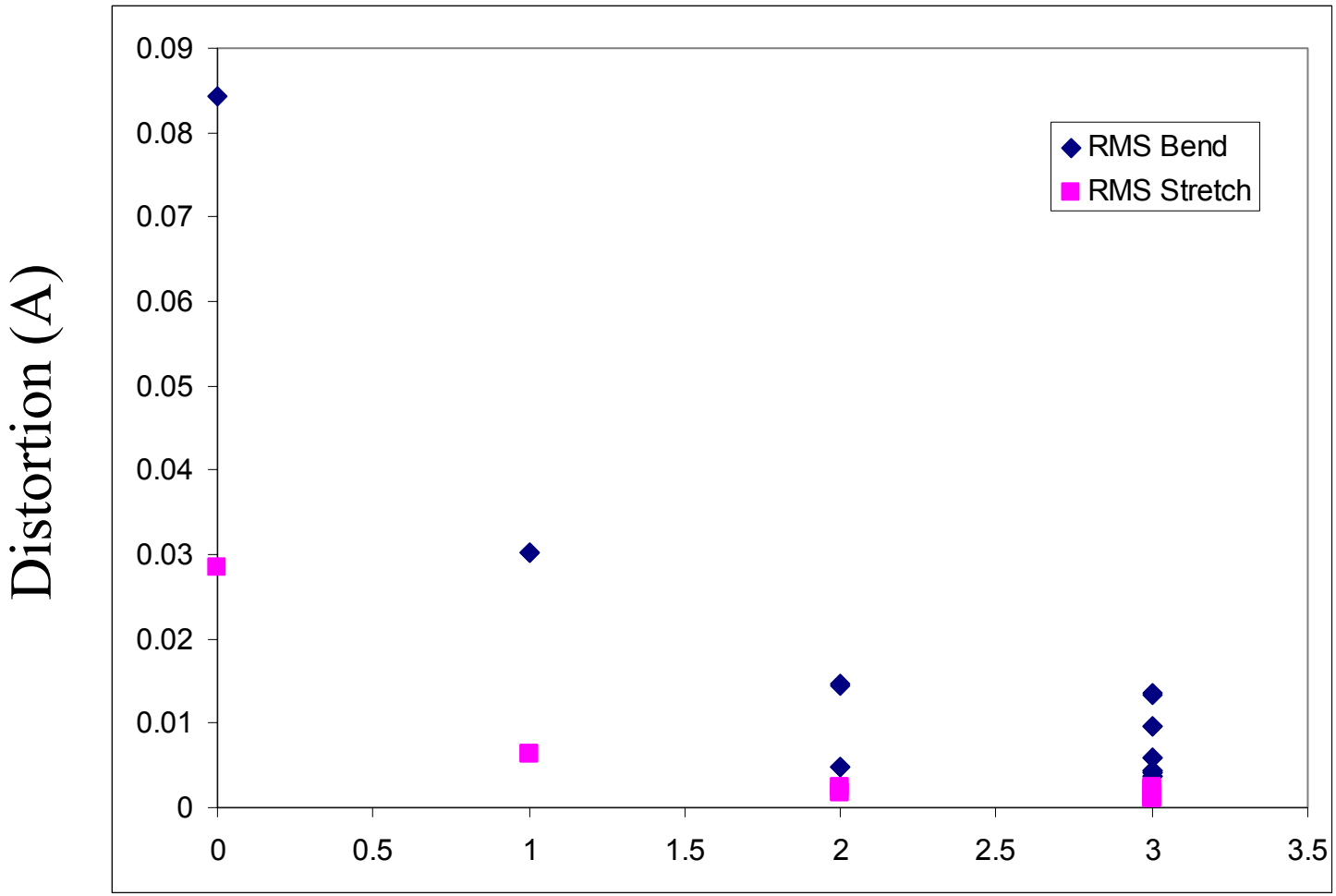
The unusually distorted polyhedron (Si-511) is coordinated to the lithium, causing a variation in the O-Si-O angle. This accounts for the large bending variation in this polyhedron.

Relaxation around the Al site



Neighbours of Al site, excluding Si-511 and its neighbours.

Relaxation around Si-511



The neighbours of Si-511 display a similar pattern of relaxation.

Extensions and work in progress

Further investigation of the strain response to defects is under way.

We are adapting the geometric simulation for use in generating hypothetical tetrahedral framework structures.

FRODA (Framework Rigidity Optimised Dynamic Algorithm) is an extension of geometric simulation to peptides and proteins. The ‘ghost’ bodies in this case will no longer be ideal tetrahedra, but rather the rigid clusters identified by flexibility analysis (FIRST). These range from single sp2/sp3 centers to protein rigid cores containing thousands of atoms. Geometric simulation will allow us to rapidly explore the low-energy dynamics of proteins by the collective motion of rigid clusters.

Conclusions

Geometric analysis gives a whole-body measure of the amplitude of rigid-unit motion and of polyhedral distortion.

Quartz and other framework silicates display a very high amplitude of atomic motion that is achieved via cooperative, rigid-unit motion. This affects dynamic disorder, transport properties and the propagation of strain.

Geometric simulation is a rapid method for optimising framework structures. It has been successfully applied to various aspects of silicate framework behaviour. It has potential for application to protein mobility.

Acknowledgements

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