## LETTER TO THE EDITOR

# Experimental verification of a predicted negative thermal expansivity of crystalline zeolites

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**Abstract.** Computational techniques predict that several microporous zeolitic structures have unusual negative coefficients of thermal expansion. High-resolution powder diffraction techniques confirm the qualitative aspects of these simulations.

Zeolites are an important class of framework-structured microporous solids which have attracted widespread interest because of their intriguing and varied crystal architectures and their widespread applications as heterogeneous catalysts in cracking, isomerization and other reactions. Typical framework structures are shown in figure 1. The materials are normally aluminosilicates with the negative charge of the framework being compensated by extra framework cations and/or protons present as bridging OH groups. Purely siliceous samples (i.e. $SiO_2$ polymorphs) can, however, be prepared for several zeolitic structures.
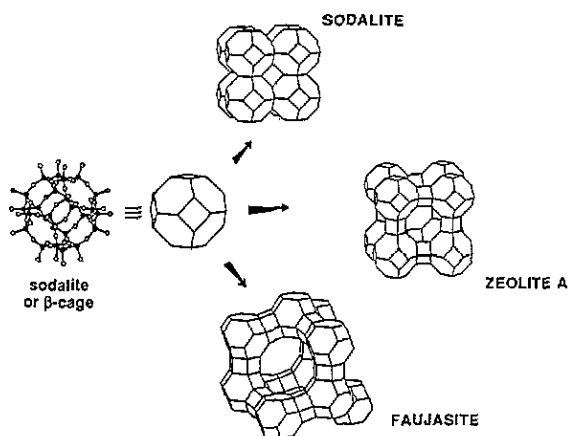


**Figure 1.** The sodalite or $\beta$-cage, linked to create the structures of sodalite, zeolite A and faujasite (zeolite X/Y).

The unusual structural properties of these materials might be expected to result in corresponding unusual physical properties. In this letter we highlight one such example by showing that several structures show negative coefficients of thermal expansion, a property which we have predicted using theoretical techniques and subsequently verified experimentally using high-resolution powder diffraction methods.
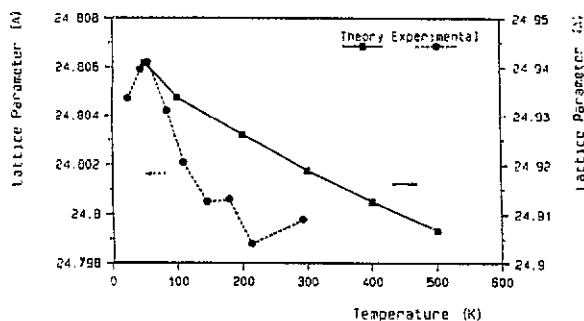
**Figure 2.** Calculated and experimental lattice parameters for Na–zeolite X.
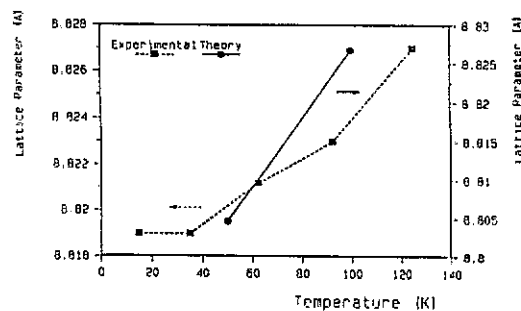


**Figure 3.** Calculated and experimental lattice parameters for sodalite.

Recent work [1–3] has shown that computationally based lattice energy calculations can model detailed aspects of the structural properties of zeolites. The techniques have recently been extended [4] to allow calculations of free energies, enabling lattice expansivities and phase transitions to be studied. Free-energy calculations require, of course, the estimation of the entropy $(S)$ in addition to the energy $(U)$. For periodic systems, $S$ may be written, within the harmonic, lattice dynamical approximation as:

$$S = k \sum_{i}^{M} \left[ -\ln\left(1 - e^{-x}\right) + x/\left(e^{x} - 1\right) \right]$$

where $x = h\nu_i/kT$, in which $\nu_i$ are the phonon frequencies, and where the summation includes all phonon branches over the entire Brillouin zone. In practice the integration is carried out numerically by sampling appropriate points within the zone according to procedures developed by Filippini *et al* [5]. $U$ is calculated by standard lattice energy procedures that we have used elsewhere [1, 2, 6]. The evaluation of both $U$ and $S$ requires the specification of interatomic potentials, for which we use the Born shell model potentials that we have successfully employed in earlier simulation studies of zeolites [1–3]. In essence, our procedure is therefore to calculate $F = U - TS$ which is then minimized with respect to both the cell dimensions and atomic coordinates of the crystal under study. The calculations can be conveniently carried out by the program PARAPOCS developed by Parker and coworkers [4]. The present calculations were performed using the CRAY XMP48 supercomputer at the SERC ATLAS Laboratory.

Application of these methods to the cases of both purely siliceous faujasite and to $Na^+$ zeolite X gives the results, summarized in figure 2 and table 1($a$). A significant contraction in the lattice parameter with temperature is predicted. Similar results were obtained for several other zeolites including silicalite and zeolite A. In contrast, calculations for purely siliceous sodalite give a more normal expansion of the lattice parameter with temperature as shown in figure 3 and table 2($a$).

**Table 1.** (*a*) Calculated lattice parameters for zeolite X. (*b*) Experimental lattice parameters frozeolite X.

| (*a*) | Temperature (K) | Zeolite-X[a] (Å) | Na-zeolite-X[b] (Å) |
|---|---|---|---|
| | 50 | 24.2946 | 24.9409 |
| | 100 | 24.2908 | 24.9337 |
| | 200 | 24.2804 | 24.9261 |
| | 300 | 24.2695 | 24.9189 |
| | 400 | 24.2593 | 24.9125 |
| | 500 | 24.2494 | 24.9067 |

[a] Purely siliceous faujasite.
[b] Na–zeolite-X (Si/Al = 1.526).

| (*b*) | Temperature (K) | Na–zeolite-X[a] (Å) |
|---|---|---|
| | 24.9(5) | 24.8047(5) |
| | 43.3(5) | 24.8059(5) |
| | 54.6(5) | 24.8062(7) |
| | 84.7(5) | 24.8042(6) |
| | 109.9(5) | 24.8021(11) |
| | 145.5(5) | 24.8005(7) |
| | 179.0(5) | 24.8006(10) |
| | 217.2(5) | 24.7988(8) |
| | 293.0(5) | 24.7998(8) |

[a] Na–zeolite-X (Si/Al = 1.54).

**Table 2.** (*a*) Calculated lattice parameters for sodalite. (*b*) Experimental lattice parameters fro gallosodalite.

| (*a*) | Temperature (K) | Lattice parameter (Å) |
|---|---|---|
| | 50 | 8.8046 |
| | 100 | 8.8267 |

| (*b*) | Temperature (K) | Lattice parameter (Å) |
|---|---|---|
| | 15.4 | 8.8190(3) |
| | 35.2 | 8.8190(2) |
| | 62.5 | 8.8212(5) |
| | 92.5 | 8.8230(4) |
| | 125.9 | 8.8270(3) |

To test these predictions we have undertaken high-resolution powder diffraction studies of dehydrated Na–zeolite X and gallosodalite (the latter being chosen because of the availability of a high-quality powder sample). We employed the high-resolution powder diffractometer, based on the Hart–Parrish design [7, 8] available at station (8.3) of the Synchrotron Radiation Source (SRS) of the SERC Daresbury Laboratory. The instrument is capable of yielding lattice parameters with a precision of greater than one part in $10^5$. Data were collected using an Oxford Instrument Cryostat for temperatures between 4 K and 300 K. The results are presented in tables 1(*b*) and 2(*b*); they are also shown diagrammatically in figures 2 and 3.

The experimental results indicate that the qualitative predictions of the simulations are correct. Negative thermal coefficients of expansion are measured as calculated for zeolite

X, while the converse behaviour is found for sodalite. There is, of course nothing unique in this behaviour of zeolites, as similar effects are seen for example in $\alpha$-$SiO_2$. It is, however, gratifying that modelling techniques are able to predict such a subtle feature of the thermal properties of these materials. We should note, however, that in the case of zeolite X the calculations underestimate the magnitude of the negative coefficient of expansion. Moreover, the experimental data indicate that the lattice parameter begins to rise at $T >$ 200 K whereas the calculations predict continued contraction. The discrepancies may be due to uncertainties concerning the samples (e.g. the presence of significant quantities of water or other sorbents) but it is also clear that the calculated expansivity is highly sensitive to the parametrization of the interatomic potential. Higher-quality parametrizations may be needed to achieve quantitative reliability from the simulations; although we note that in the case of the sodalite system the discrepancies between theory and experiment are much smaller.

The question of the origin of the effect is an intriguing one. The failure to observe the negative expansivity in sodalite suggests that low-frequency modes attributable to the interconnections between, for example, sodalite cages (which are fused, rather than bridged in sodalite) may be responsible. Further analysis of the calculations is in progress.

## References

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