# A Reassessment of Zeolite A: Evidence that the Structure is Rhombohedral with Unexpected Ordering in the Aluminosilicate Framework

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*Summary* A new structural model for zeolite A (rhombohedral $R\bar{3}$) differs from the one currently accepted (cubic $Fm3c$) in that each tetrahedrally co-ordinated $Si^{4+}$ ion is surrounded, *via* oxygen bridges, by three (not four) $Al^{3+}$ ions and one $Si^{4+}$ ion, and each $Al^{3+}$ ion by three (not four) $Si^{4+}$ and one $Al^{3+}$.

RECENTLY[1] we raised the question as to whether the structure of zeolite A (idealized formula $M^+_{12}Al_{12}Si_{12}O_{48}.27H_2O$) had been correctly identified. This discussion arose initially because our electron microscopic and, in particular, our electron diffraction studies of dehydrated Na-A yielded results which implied that the currently accepted picture [see Figure (a)], in which each $Si^{4+}$ ion is surrounded, *via* oxygen bridges, by four $Al^{3+}$ ions and each $Al^{3+}$ likewise by four $Si^{4+}$ ions, space group $Fm3c$, is wrong. Further, independent evidence that the accepted structure[2,3] merits re-investigation came from the high-resolution n.m.r. studies of Lippmaa *et al.*,[4] who reported that each $Si^{4+}$ is surrounded, *via* oxygens, by three $Al^{3+}$ and one $Si^{4+}$, and that, conversely, each central $Al^{3+}$ also displays 3:1 co-ordination (*i.e.* there are three $Si^{3+}$ and one $Al^{3+}$ ions in the first tetrahedral shell).

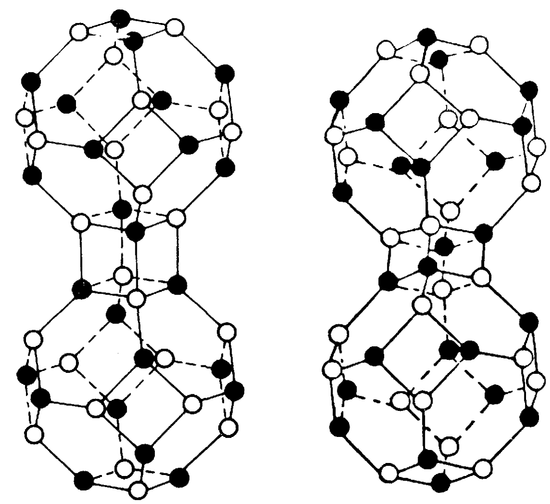
On the tacit assumption that the zeolite A structure has a cubic unit cell, we tentatively[1] suggested that, when the Si/Al ratio is unity, the space-group is $Pm3$ and that, in general (Si/Al $\neq$ 1), the space group is $Fm3$.

We have now completed neutron diffraction studies (Rietveld powder analysis[5,6]) at 5 and 298 K, as well as high-resolution (magic-angle spinning), solid-state $^{29}Si$ n.m.r. measurements[7,8] and further electron microscopic analysis on a specially prepared sample of dehydrated Na-A possessing a Si/Al ratio of $1{\cdot}00 \pm 0{\cdot}02$. Our results indicate the following.

(a) There is a doubled unit cell, *i.e.* two joined cuboctahedra ($\beta$-cages) constitute the repeat unit (from electron diffraction). Due allowance has been made for the complications that arise from double or multiple diffractions, and we conclude that the structure has *ca.* 24·6 rather than 12·3 Å repeats.

(b) The co-ordination is unmistakably 3:1 (from solid-state n.m.r. studies).

(c) The space group is $R\bar{3}$ (from neutron diffraction). The diffraction peaks cannot be indexed with, and the structure does not refine in, $Fm3c$. Moreover, the $^{29}Si$ n.m.r. resonance at *ca.* −84 p.p.m. characteristic of 4:0 co-ordination, in sodalite for example, is absent, the peak instead appearing at *ca.* −89 p.p.m., which signifies 3:1 co-ordination.



(a) (b)

FIGURE. (a) In the currently accepted model for the structure of zeolite-A, two cuboctahedra (*i.e.* $\beta$-cages) are joined at the so-called 'double-four' rings. At the vertices of the cuboctahedra $Si^{4+}$ (●) and $Al^{3+}$ ions (○) alternate such that 4:0 co-ordination results, *i.e.* each $Si^{4+}$ is surrounded tetrahedrally by four $Al^{3+}$ ions, *via* oxygen bridges, which, for simplicity are not shown. This double unit of cuboctahedra repeats itself three-dimensionally resulting in a cubic ($Fm3c$) space group. (Exchangeable cations not shown). (b) In the new model the cuboctahedra ($\beta$-cages) are slightly distorted (not shown) and again repeat themselves three-dimensionally, yielding a rhombohedral space-group $R\bar{3}$. The ordering scheme within the aluminosilicate framework is such that each $Si^{4+}$ ion is surrounded by three $Al^{3+}$ and one $Si^{4+}$, and each $Al^{3+}$ by three $Si^{4+}$ and one $Al^{3+}$ (3:1 co-ordination). $Al^{3+}$–O–$Al^{3+}$ bridges, hitherto discounted (see text), are an integral feature of the structure. In the new model there are centres of inversion at the mid-points of the double-four rings. Note that two kinds of six-rings, differing in Si,Al sequence, occur in the new model, and there are also two types of four-ring. (Exchangeable cations not shown).

The hitherto unsuspected rhombohedral distortion (or pseudo-cubic nature) of the structure was uncovered using neutrons of wavelength 2·96 Å. The splitting of the peaks, *e.g.* 8,8,0, at first suggested that the sample was biphasic, but the 12,0,0 peak is not split, signifying that the sample is monophasic. We have analysed crystallographically all the possible combinations of the two cuboctahedra linked by a cube that satisfy the known facts pertaining to the structure, taking cognizance of the n.m.r. results and the conclusion from our neutron scattering measurements that the cuboctahedra are slightly distorted such that they no longer possess four, but only one 3-fold axis. The unique result is shown schematized, in part, in Figure (b), from which we note that the 'doubled' entity (pseudo-cubic unit cell repeat 24·6 Å) consists of an enantiomeric pair of (slightly distorted) cuboctahedra, *i.e.* $C_3^1.\underset{\sim}{C}_3^2$ in the Schoenflies notation.

We have also discovered a possible new cubic model for dehydrated Na-A when the Si/Al ratio is not unity. It is made up of a combination of distorted ($C_{3i}$) cuboctahedra, arranged such that their unique 3-fold axes are aligned along the four <111> directions. This cubic structure (space group *Pn3n*) possesses pseudo-cubic (*i.e.* face-centred cubic *Fm3c*) and pseudo *Pm3* symmetry.

When Si/Al = 1·00 the unit cell dimensions in $R\overline{3}$ are $a$ = 17·401 ± 0·001 Å, $\alpha$ = 59·53° (± 0·01°). When Si/Al = 1·10, $a$ = 17·352 ± 0·001 Å, $\alpha$ = 59·84 ± 0·01°. Both sets of dimensions refer to 5 K. A full description of the new structural analysis, and the implications of the new model are given elsewhere.[9] It is of interest that the structure contains hitherto discounted Al–O–Al linkages and that, in the new model, two types of hexagonal rings occur, one symmetrical the other unsymmetrical. Both these features, as well as others, are likely to influence the chemical properties of zeolite-A.

We note also that this relatively unconventional combination of techniques: high-resolution, magic-angle-spinning n.m.r. spectroscopy, neutron powder diffraction (profile analysis), and electron microscopy, constitutes a powerful and potentially widely applicable method of structural analysis.

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