Have the Structure and Space-group of A-Type Zeolite been Correctly Assigned?

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Summary The results of recent electron diffraction and solid-state n.m.r. studies are incompatible with the accepted space-group of zeolite A (idealized formula $M^{+}_{12}Al_{12}Si_{12}O_{48}.27H_2O$); it is argued that the space-group is *Pm*3 when Si/Al is unity, and *Fm*3 when this ratio deviates from unity.

IT is notoriously difficult to determine the crystal structure of synthetic zeolites, partly because of the close similarity in *X*-ray scattering power of Si and Al, but also because the minute crystallites of such material that are available are normally too small for *X*-ray analysis. For zeolite A, used[1] extensively in a wide range of commercial and laboratory processes, accumulated evidence, based on early[2] *X*-ray powder and later[3] single-crystal studies, points to the *Fm*3*c* space-group with structure schematised in the Figure (a) ($a = 24{\cdot}6$ Å).

This structure and space-group constitute the basis of numerous discussions of the physico-chemical properties of A-type zeolites. Moreover, recent[4] structural refinements

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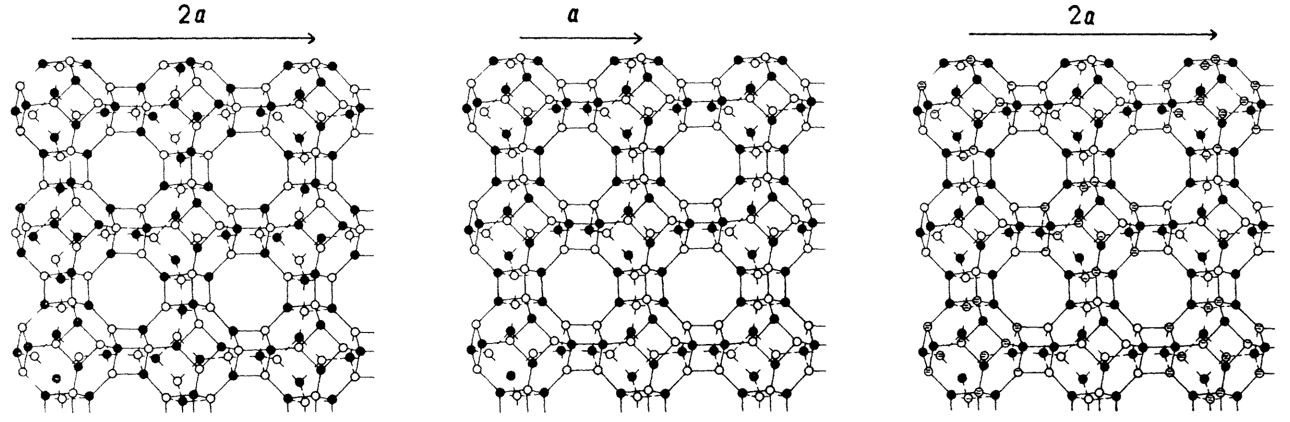

(a) *Fm* 3c (b) *Pm* 3 (c) *Fm* 3

FIGURE. Schematic illustration of the crystal structure of the framework in A-type zeolite. (For simplicity, the oxygen atoms that link the Si and Al ions at each vertex in the cubo-octahedra and cubes are not shown.) (a) Currently accepted structure (space group *Fm*3*c*), (b) proposed new structure when Si/Al = 1 (space group *Pm*3), and (c) proposed new structure when Si/Al ≠ 1 (space group *Fm*3). Filled circles represent Si (or Al), open circles Al (or Si), and partially shaded circles excess of Si (or excess of Al) when Si/Al > 1 or < 1, respectively.

which, *inter alia*, seek to locate the positions of exchangeable cations in the hydrated and dehydrated zeolites, tacitly assume the correctness of these assignments. There are now reasons for disputing these assignments and our work, which will be fully reported elsewhere, leads us to propose alternatives.

The evidence comes chiefly from electron diffraction studies (obtained in the course of high-resolution imaging by electron microscopy) of dehydrated Na-A and other zeolites.[5] Briefly, superlattice ordering of the Si^{4+} and Al^{3+} ions in the zeolitic framework is readily apparent; such long-range order is not at all readily detectable by *X*-rays owing to the extreme weakness of superlattice spots. In particular, the electron diffraction patterns we have observed are irreconcilable with the *Fm*3*c* space-group.

Strong corroborative evidence for the inadequacy of the currently accepted structure comes from the high-resolution, solid-state (magic-angle spinning) ^{29}Si n.m.r. studies of Engelhardt and Lippmaa[6] who (from their chemical shift data) concluded that, in the A-zeolites, the majority of the Si ions were attached (*via* oxygens) to three Al and one Si ions. We believe that the structure shown in the Figure (b) (space-group *Pm*3, *a* = 12·3 Å) implied by the n.m.r. results is correct when the Si/Al ratio is unity, but that, for values of Si/Al greater or less than unity, the correct structure is as shown in the Figure (c), space-group *Fm*3 (*a* = 24·6 Å). We note, in passing, that four *X*-ray observed[4] reflexions 9 9 9, 21 21 9, 31 1 1, and 25 12 12, that do not comply with the *Fm*3*c* space-group, and were ignored by Pluth and Smith[4] in their refinement, are consistent with *Fm*3. Indeed these authors themselves state that 'the possibility of lower symmetry (than *Fm*3*c*) must be considered.'

Two general points emerge from our work. First, that electron diffraction is, in general, a much more convenient method than *X*-ray diffraction for detecting superlattice ordering (though not, *in general*, for unambiguously identifying space groups). Second, there is a tendency in silicate chemistry to adhere too rigidly to Loewenstein's rule[7] which, in essence, states that, in the linked tetrahedral framework of aluminosilicates, no two adjacent tetrahedra are likely to be occupied by Al^{3+}. This rule is obeyed in the structure shown in the Figure (a), but contravened in (b) and (c).

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