

The Zeolite A Debate: How Wrong is a Nearly Correct Space Group?

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Abstract

The apparent contradiction between NMR and X-ray results concerning the Si,Al distribution in zeolite A is quantitatively analysed. It is concluded that the $Fm\bar{3}c$ structure model, based on X-ray refinements, is compatible with the NMR data if a cautious chemical-shift assignment is applied. The appropriate use of crystallographic approximations and their symmetry is discussed.

Introduction

A vehement debate about the Si,Al distribution in zeolite A ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$) has recently been published. According to solid-state NMR chemical-shift assignments, high-resolution electron microscopy and neutron diffraction analysis, it is claimed (Lippmaa, Mägi, Samoson, Tarmak & Engelhardt, 1981; Klinowski, Thomas, Fyfe & Hartman, 1981, and references cited therein) that any silicate tetrahedron in zeolite A is surrounded by one silicate tetrahedron and three aluminate tetrahedra, $\text{Si}(3\text{Al})$, and *vice versa*. This contrasts with the currently accepted picture (Smith & Pluth, 1981, and references cited therein) with regular Si,Al alternation, $\text{Si}(4\text{Al})$, space group $Fm\bar{3}c$ (Fig. 1).

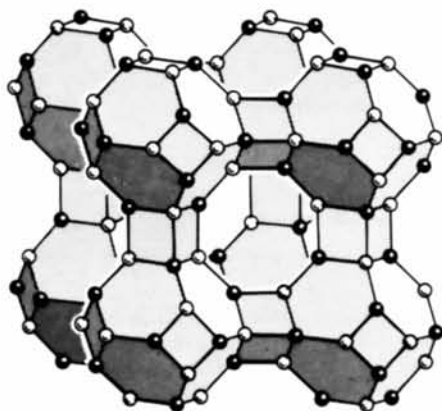


Fig. 1. Regular $\text{Si}(4\text{Al})$ alternation of Si and Al in the framework of zeolite A, space group $Fm\bar{3}c$.

Space group of zeolite A

The crystal structure of zeolite A was first refined in space group $Pm\bar{3}m$, $a = 12.3 \text{ \AA}$, by Broussard & Shoemaker (1960). There is only one $(\text{Si,Al})\text{O}_4$ tetrahedron in the asymmetric unit. The observed $T\text{--O}$ distances of this tetrahedron vary between $1.66(2)$ and $1.68(2) \text{ \AA}$ in good agreement with the average between expected Si--O and Al--O distances. We know today, especially from the marvellous NMR measurements of Lippmaa *et al.* (1981), that there is nearly perfect Si,Al order in zeolite A. Therefore, the $Pm\bar{3}m$ model should not be interpreted as 'requiring a random distribution of Si,Al' (Bursill, Lodge, Thomas & Cheetham, 1981) but as a superpositional model (a first approximation) of an ordered structure of lower symmetry. Fortunately, the first step on the way to find the lower symmetry of a second approximation is clearly indicated by the diffraction evidence. Weak (b) reflections could be observed long ago (*cf.* references in Bursill *et al.*, 1981) requiring a doubled cell constant. The observed Laue symmetry is $m\bar{3}m$ (Gramlich & Meier, 1971; McCusker & Seff, 1981). It is generally accepted that the $Pm\bar{3}m$ model is an interpretable first approximation of the zeolite A structure, although all b reflections are 'ignored'. A model in one of the maximal subgroups $Fm\bar{3}m$, $Fm\bar{3}c$, $Im\bar{3}m$ (*klassengleich*, *cf.* Neubüser & Wondratschek, 1966) must exist which is interpretable as a second approximation. $Fm\bar{3}c$ was selected for the refinement of hydrated Na-A zeolite because 'an extensive examination using diffractometer data showed the indices of the observable reflections to be either all even (a reflections) or all odd (b reflections). In addition, no b reflections hhh or hhl could be observed' (Gramlich & Meier, 1971).

This choice of $Fm\bar{3}c$ has been attacked because some reflections violating the c -glide condition could be observed in several dehydrated and cation-exchanged species: 'electron diffraction studies of dehydrated Na-A yielded results which implied that the currently accepted picture, 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+} , space group $Fm\bar{3}c$, is wrong' (Thomas, Bursill, Lodge, Cheetham & Fyfe, 1981).

The space-group assignment for V_3O_5 by Åsbrink (1980) has been invoked (Bursill *et al.*, 1981) to be exemplary in order to show how important a few very weak reflections could be for determining ordering of similar cations. Åsbrink selected $P2/c$ from the two possible space groups $P2_1/c$ and $P2/c$ (subgroups of $C2/c$) because three very weak $0k0$ reflections, k odd, conflicting with the 2_1 condition were observable. A completely ordered distribution of tri- and tetravalent vanadium resulted showing that the alternative space-group choice $P2_1/c$ was wrong. Åsbrink pointed out that refinement in a lower symmetry, Pc , was unsuccessful because of high correlations.

The situation seems to be similar for dehydrated zeolite A: Pluth & Smith (1980) observed five weak reflections conflicting with the c -glide condition of $Fm\bar{3}c$. But there is a remarkable difference: Åsbrink observed 50% of the accessible $0k0$ reflections, k odd (in fact three out of six) conflicting with the 2_1 condition. Only five out of about 75 accessible b reflections hhl and hhh , all odd, conflicting with the c -glide condition, were observed for the dehydrated zeolite A. Since $Im\bar{3}m$ can easily be ruled out (Gramlich & Meier, 1971), there remain two space-group candidates $Fm\bar{3}m$ and $Fm\bar{3}c$. Trials in $Fm\bar{3}m$ have been unsuccessful (*cf.* Appendix). It is therefore interesting to look for the reasons why electron diffraction shows that $Fm\bar{3}c$ is wrong. The essential conclusion of Bursill, Lodge, Thomas & Cheetham (1981) from their electron diffraction studies is 'thus any departure from $Fm\bar{3}c$ symmetry, say to $Fm\bar{3}$, must be very slight'. The situation is really very clear: the best space-group choice to a second approximation of the zeolite A structure is $Fm\bar{3}c$. The slight violations of the c -glide condition can be discussed with respect to a third approximation in a subgroup of $Fm\bar{3}c$. Like the $Pm\bar{3}m$ approximation the $Fm\bar{3}c$ model must be interpreted as a superpositional structure, which is again an approximation of the true structure. Åsbrink's experience with Pc confirms the danger of random information inherent in a too-low-symmetry refinement.

We show in the next section that a comparison between the two rival models Si(3Al) and Si(4Al) is in fact quite easy to perform in the second approximation, space group $Fm\bar{3}c$.

Si(3Al) against Si(4Al)

There are two independent positions T_1, T_2 for the tetrahedral atoms (Si,Al) in the $Fm\bar{3}c$ model. Whereas the situation is obvious for Si(4Al), $T_1 = \text{Si}$ and $T_2 = \text{Al}$, we have to look for the superpositional structure of possible Si(3Al) models. Four equivalent tetrahedra T_2 are linked to T_1 and *vice versa*. Let T_1 contain x Si and $(1 - x)$ Al on average. T_2 must then contain $\frac{1}{4}(3x +$

$1 - x)$ Al = $(x/2 + \frac{1}{4})$ Al and $\frac{1}{4}[x + 3(1 - x)]$ Si = $(-x/2 + \frac{3}{4})$ Si. Together with the condition Si:Al \approx 1:1 for zeolite A we find $x \approx \frac{1}{2}$. If Si(3Al) is true no significant change of the mean T -O distances, compared with the $Pm\bar{3}m$ approximation, should result. In order to be fair we have allowed for an extremely large range of Si-O distances from 1.57 to 1.65 Å (Fig. 2). Nevertheless, it is evident from Fig. 2 that the X-ray results are compatible with the Si(4Al) model but incompatible with Si(3Al).

However, the final assignment of Si,Al distributions by X-ray refinements has generally been depreciated. The results were characterized as 'rather arbitrary' (Lippmaa, Mägi, Samoson, Tarmak & Engelhardt, 1981). In our example of zeolite A the reproach was, more precisely, 'to adhere too rigidly to Loewenstein's rule' (Lodge, Bursill & Thomas, 1980). In order to convince our NMR colleagues we have looked for an independent redetermination of the zeolite A superstructure in the second approximation, $Fm\bar{3}c$. Fortunately, recent progress allows the direct determination of the phases of weak reflection classes like the b reflections (*cf.* Giacobozzo, 1980, pp. 215-216). Direct methods were applied as follows. The normalized structure factors (hydrated Na-A zeolite, data set of Gramlich & Meier, 1971) of the b reflections were multiplied by a rescale factor of nine. Reflections with $E \geq 1.6$ were used. The signs of nine a reflections (known from the $Pm\bar{3}m$ model) with the strongest E values were kept fixed, the sign of the b reflection 531 with the maximum number of relationships was kept + for complete origin definition. The programs for phase determination in the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) were used. The 25 strongest b reflections were introduced in the procedure. Finally, 22 of their signs agreed with those calculated from the Si(4Al) model. This independent confirmation of the Si(4Al) model in the $Fm\bar{3}c$ approximation is illustrated in Fig. 3.

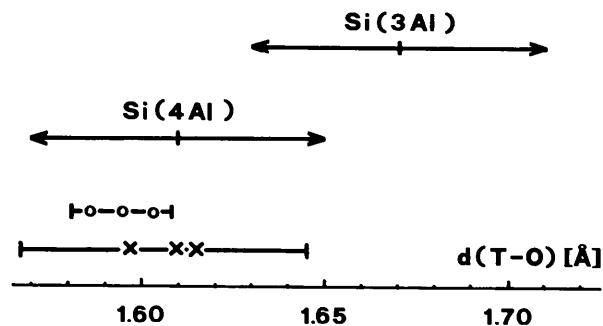


Fig. 2. Observed and expected T_1 -O distances in zeolite A, space group $Fm\bar{3}c$. Circles: Pluth & Smith (1980); crosses: Gramlich & Meier (1971). The expected $d(\text{Si}-\text{O})$ range, corresponding to Si(4Al), is taken from Hill & Gibbs (1979), with a 20% safety margin. The same deviations are allowed for Si(3Al), about the mean 1.67 Å, corresponding to $T_1 = \frac{1}{4}(\text{Si} + \text{Al})$ (Broussard & Shoemaker, 1960).

The two rival models can be compared with the NMR data in a similar manner. Fig. 4 shows chemical-shift measurements together with the original assignment ranges of Lippmaa, Mägi, Samoson, Tarmak & Engelhardt (1981). A general warning that smaller shift ranges shown for solids may be caused by the smaller number of solid samples studied (Lippmaa, Mägi, Samoson, Engelhardt & Grimmer, 1980) was

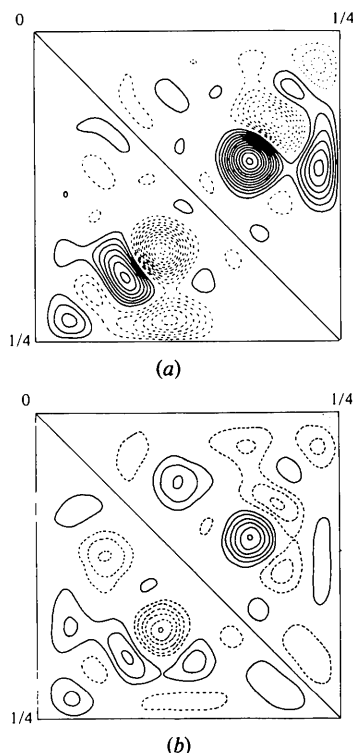


Fig. 3. Hydrated Na-A zeolite: section $z = 0$ of Fourier synthesis based on b reflections (odd indices). (a) Using all 90 measured b reflections, phases from refined Si(4Al) model. (b) E map, phases from statistics using the 25 strongest E 's.

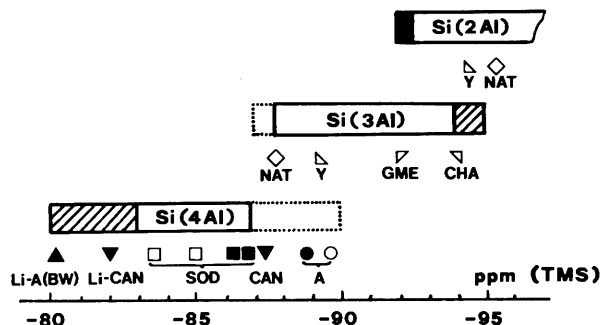


Fig. 4. ^{29}Si chemical shifts of some zeolites. Black symbols: Klinowski *et al.* (1981). White symbols: Lippmaa *et al.* (1981). The original assignment ranges of Lippmaa *et al.* are indicated together with expansions of Klinowski *et al.*, dashed, and Engelhardt, Lohse, Lippmaa, Tarmak & Mägi (1981), black. The dotted expansions are suggested in this paper in order to remove all inconsistencies.

recently confirmed by Klinowski, Thomas, Fyfe & Hartman (1981). The larger number of samples studied enlarged the assignment ranges considerably (Fig. 4) immediately showing that the assignment of Lippmaa *et al.* (1981), -83 to -87 in 10^6 for Si(4Al), was a preliminary one. Klinowski *et al.* (1981) expanded the range to -80 to -87 in 10^6 . The -87 in 10^6 limit was tacitly considered unviolable without any further comment. The consequences of this limitation are remarkable:

I. All assignment ranges Si(3Al), Si(2Al), Si(1Al) and Si(0Al) overlap sequentially by about 3 in 10^6 (Lippmaa, Mägi, Samoson, Tarmak & Engelhardt, 1981). Si(4Al) remains separated from Si(3Al) by a gap (*cf.* Fig. 4).

II. The chemical shift of cancrinite is (-87.2 ± 0.3) in 10^6 according to Thomas, Klinowski, Fyfe, Hartman & Bursill (1981). These authors (Klinowski, Thomas, Fyfe & Hartman, 1981) decide that the ordering of this cancrinite is Si(3Al), although it is not significantly outside the Si(4Al) range and although a lithium form of cancrinite shows definitely Si(4Al).

III. The chemical-shift values found for several different sodalite specimens lie within the Si(4Al) limits first published by Lippmaa *et al.* (1981), *cf.* Fig. 4. Nevertheless, in order to support their criticism of the Loewenstein rule, Klinowski, Thomas, Fyfe & Hartman (1981) postulate Si(3Al) ordering for the two samples at -86.4 (3) and -86.7 (3) in 10^6 in flagrant violation of their own precept that the range -80 to -87 in 10^6 is uniquely assigned to Si(4Al).

X-ray structure determinations including Si,Al distributions assigned by X-ray crystallographic work are the essential basis of the solid-state NMR assignment ranges. Therefore, it is not surprising that X-ray and NMR assignments are generally compatible. What happens if the disputed X-ray structure determination of zeolite A with its Si(4Al) distribution is included in this basis? The peculiar gap between Si(3Al) and Si(4Al) vanishes, all Si(n Al) chemical-shift assignment ranges overlap by about 3 in 10^6 . The internal inconsistencies concerning sodalite and cancrinite vanish. There remains no contradiction whatsoever.

Conclusion

Cautious interpretation of the recent solid-state NMR results does not allow the rejection of the currently accepted Si(4Al) model of the zeolite A structure. The recent criticism of the space-group assignment, $Fm\bar{3}c$, is based on inappropriate interpretations of the concept of crystallographic approximations.

Symmetry reduction of an idealized high-symmetry crystal-structure model can be performed stepwise using maximal subgroups (Neubüser & Wondratschek, 1966). If the symmetry of the 'true structure' is

sufficiently low several pathways through the maximal subgroups can be drawn. A network of symmetry reductions involving several approximations results, starting with the idealized high-symmetry space group and ending at the space group of the 'true structure'. Space groups outside this network are wrong, even if the corresponding structure models are nearly correct. Space groups involved in the network might be more or less convenient, especially if more than one pathway to the correct structure is feasible. Excessive removal of space groups from the network leaves no path to the correct structure.

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APPENDIX Zeolite A framework models

$Pm\bar{3}m$, $a = 12.3 \text{ \AA}$. This model is a generally accepted approximation of the zeolite A framework. As confirmed by the recent solid-state NMR results it must be interpreted as a superpositional structure of an ordered model. The remarkable pseudosymmetric properties have been discussed by Meier (1973).

$Fm\bar{3}c$, $a = 24.6 \text{ \AA}$. The Si(4Al) model is referred to as 'currently accepted' in the recent critical literature. We have shown that this model is compatible with all experimental results. However, partial occupancy factors of the extra framework atoms show that it should be interpreted as a superpositional structure too. The weak reflections not obeying the space-group extinction conditions can be easily explained by some correlated motion or by some short-range order of the extra framework atoms (Smith & Pluth, 1981). This interpretation is confirmed by the fact that not one of the observed X-ray reflections contradicting $Fm\bar{3}c$ is common to all cation-exchanged species.

$Fm\bar{3}m$, $a = 24.6 \text{ \AA}$. A model with Si(1Al) distribution has been published by Bursill *et al.* (1981), their Fig. 4. We regret that they do not give any comment on the local demixing of SiO₂ and NaAlO₂ and note that this model is in irrecoverable conflict with the NMR data.

$Fm\bar{3}$, $a = 24.6 \text{ \AA}$ ($Pm\bar{3}$, $a = 12.3 \text{ \AA}$). The first Si(3Al) model was proposed by Engelhardt, Zeigan, Lippmaa & Mägi (1980), space group $Pm\bar{3}$, $a = 12.3 \text{ \AA}$. Since the b reflections could not be explained Lodge, Bursill & Thomas (1980) proposed a model where excess of Si (or excess of Al, the small amounts deviating from Si:Al = 1:1) is clustered in alternating cuboctahedra. This clustering model has been disavowed by its own authors (Bursill, Lodge, Thomas & Cheetham, 1981; Thomas, Bursill, Lodge, Cheetham & Fyfe, 1981) in favour of $Pn\bar{3}n$ and $R\bar{3}$ models.

$Pn\bar{3}n$, $a = 24.6 \text{ \AA}$. This model with Si(3Al) distribution was proposed by Thomas *et al.* (1981) and Bursill *et al.* (1981). We remember that the latter accused Pluth & Smith (1980) of ignoring the five reflections (111; 17,3,3; 23,7,7; 13,13,11; 15,15,15) in conflict with $Fm\bar{3}c$. Unfortunately, the extinction condition of $Pn\bar{3}n$ (hkl : $l = 2n + 1$ are space-group extinct) is in conflict with all these five reflections as well. We note, in passing, that the reflections 111; 311; 333 of the electron diffraction pattern published by Bursill *et al.* (1981) are also forbidden in $Pn\bar{3}n$.

$R\bar{3}$, $a = 17.4 \text{ \AA}$, $\alpha = 59.5^\circ$. A model in $R\bar{3}$ with Si(3Al) distribution was derived by Bursill *et al.* (1981) from a slight rhombohedral distortion of the lattice, revealed by neutron powder analysis. This model conflicts with the 12,12,25 reflection (indices based on the cubic cell, $a = 24.6 \text{ \AA}$) observed for the K-exchanged zeolite by Pluth & Smith (1979) who, in their turn, have been criticized by Lodge *et al.* (1980) and Bursill *et al.* (1981) for having ignored this reflection. Furthermore, given that the small rhombohedral distortion reported by Bursill *et al.* (1981) is perfectly correct, there is no need for deriving Si(3Al) distribution from such an experimental result. Small deviations from cubic geometry could easily be explained by small distortions of the framework, caused by the dehydration and governed by some compound occlusion in the cavities, in agreement with the strong dependence of the distortion on the conditions of synthesis. The deviations from cubic symmetry, reported by Bursill *et al.* (1981) are 0.18° and, more than double, 0.38° for two differently prepared samples. Si:Al composition, however, is not significantly different (Si:Al = 1.02 ± 0.02 and 1.00 ± 0.02 respectively). The influence of preparation methods on compound occlusion in zeolite A has been studied by Basler & Maiwald (1979).

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Remarques sur la Symétrie Ponctuelle des Structures Modulées

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Abstract

The symmetry of solid modulated phases can be described by generalized four-dimensional groups, as proposed initially by de Wolff [*Acta Cryst.* (1974), **A30**, 777–785]. In this note alternative derivations of the point symmetries of these phases are given.

La description des phases solides modulées exige une généralisation de la notion de symétrie cristallographique: l'introduction d'une quatrième dimension t décrivant la phase de la modulation et ayant dans certains cas la signification d'un temps, et l'utilisation de super-groupes d'espace (de Wolff, 1974, 1977a,b; Janner & Janssen, 1977).

La supersymétrie ponctuelle des structures modulées a été discutée par de Wolff (1974). Les matrices d'un super-groupe ponctuel G_4 à quatre dimensions sont de la forme:

$$\left(\begin{array}{c|c} S_i & \\ \hline & \varepsilon_i \end{array} \right) = \left(\begin{array}{c|c} Q_i & \\ \hline & \varepsilon_i \end{array} \right)$$

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où S_i est une matrice 3×3 , Q_i une matrice 2×2 et $\varepsilon_i = \pm 1$. Un point \mathbf{r} de phase t est transformé suivant: $\mathbf{r}' = S_i \mathbf{r}$ et $t' = \varepsilon_i t$. Les matrices S_i forment le groupe ponctuel G_3 de la structure de base non modulée. G_4 est isomorphe de G_3 , et du groupe magnétique G'_3 obtenu à partir de G_3 en conservant les opérateurs S_i tels que $\varepsilon_i = +1$, et en remplaçant les S_i tels que $\varepsilon_i = -1$ par les antiopérateurs $S'_i = \varepsilon_i S_i$ correspondants.

Enfin, comme l'a montré De Wolff (1977a), une structure modulée est décrite par un vecteur \mathbf{k} de coordonnées irrationnelles tel que, pour tous les S_i de G_3 , $S_i \mathbf{k} = \varepsilon_i \mathbf{k}$, c'est-à-dire: $S'_i \mathbf{k} = \mathbf{k}$. Cette relation exprime l'invariance de \mathbf{k} dans le groupe G'_3 .

Nous rediscutons ci-après l'énumération des groupes G'_3 et l'orientation du vecteur \mathbf{k} .

1. Dans une opération S_i , \mathbf{k} se comporte comme un vecteur polaire ordinaire. En particulier:

- $\bar{1} \mathbf{k} = -\mathbf{k}$ (centrosymétrie)
- $n \mathbf{k} = \mathbf{k}$ (axe d'ordre n parallèle à \mathbf{k})
- $m \mathbf{k} = \mathbf{k}$ (miroir m parallèle à \mathbf{k})
- $m \mathbf{k} = -\mathbf{k}$ (miroir perpendiculaire à \mathbf{k}).

Dans le renversement du temps t' , \mathbf{k} change de signe
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