JOURNAL OF SOLID STATE CHEMISTRY 44, 41–49 (1982)

# Constituent Units and Framework Conformations in Zeolite Networks*

R. GRAMLICH-MEIER AND W. M. MEIER†

*Institut für Kristallographie und Petrographie, ETH Zürich, Switzerland*

Received October 28, 1981

The building units of known zeolite networks have been reinvestigated and related to the framework density. Only a relatively small number of four-connected nets, which can be generated readily from observed constituent units, are "permissible" zeolite networks. Criteria for gauging the "permissibility" of zeolite-type networks in terms of geometrical constraints caused by conformational requirements have been investigated.

## Introduction

Zeolites are porous tektosilicates and the various types of these remarkably stable host structures are best defined by the topology of their three-dimensional networks. These are most frequently depicted by means of skeletal diagrams showing the four-connected nets of *T*-sites ($T$ = Si, Al). Straight lines connecting the *T*-atom sites (which form the vertices of the nets) help one to visualize and to deal with the framework topology of complex zeolite structures. Each *T*-atom in a zeolite framework is tetrahedrally bonded to four oxygen atoms forming bridges to neighboring *T*-atoms. It must be noted that the straight connections in skeletal diagrams representing $T$–$O$–$T$ bridges are schematic in nature since $T$–$O$–$T$ angles are ideally around 140–150° and hardly ever 180°.

Around 40 topologically distinct zeolite networks have been found to occur to date. Illustrations of these nets have been collected in an atlas (*1*) which is updated periodically. Models of numerous zeolite-like networks can be built readily and hundreds of such hypothetical zeolite structures have been enumerated (but frequently not published) by many investigators. Various studies of this kind demonstrate that one can safely assume that the number of hypothetical model-based networks exceeds the number of known zeolite networks by many orders of magnitude. It seems worth investigating, therefore, how actually occurring four-connected zeolite nets differ from "purely" hypothetical ones.

In this work we deal briefly with some characteristics of four-connected nets observed in zeolite structures. This is followed by a short account on criteria which appear helpful for discerning "permissible" zeolite networks. This and similar investigations owe a great deal to A. F. Wells whose classic text (*2*) and original work on three-dimensional nets (collected in a mono-

---

* Dedicated to Professor A. F. Wells on his 70th birthday.

† To whom correspondence should be addressed.

0022-4596/82/100041-09$02.00/0

graph (*3*)) have been a constant source of stimulation.

## Characteristics of Four-Connected Nets Observed in Zeolites

All known zeolite framework types can be characterized in terms of finite component units. The secondary building units (SBUs) shown in Fig. 1 have been derived under the condition that a zeolite network is composed entirely of *one* kind of unit only (*4*). This is in line with the well-known principle that the number of essentially different kinds of constituents in a crystal structure tends to be minimal.

These SBUs for each zeolite network, which is designated using the conventional three-letter code for zeolite structure types, are listed in Table I. (For reasons which will become clear on closer examination of Table I the structure types or topologically distinct zeolite networks have been arranged in the order of increasing framework density expressed by the number of $T$-atoms per 1000 Å$^3$.) As can be seen in Table I, many of the zeolite networks can be generated from several different SBUs. For this reason, conventional classification systems of zeolite structure types based on SBUs are not completely unambiguous.

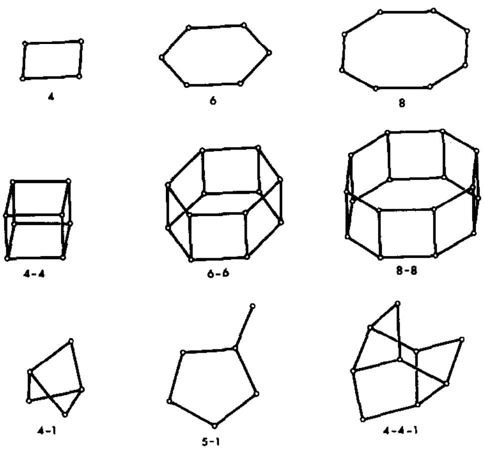

FIG. 1. Secondary building units.

There are only three distinct families of zeolite networks which can be defined unequivocally on this basis. These are marked by *a*, *b*, and *c* in Table I. The networks marked by *a* are made up of parallel single and/or double six-ring units, and the stacking of these "12-valent" SBUs can be readily described like polytypic sequencies of hexagonal layers or sphere packings (e.g., the hexagonal ERI net by AABAAC and the cubic SOD net by ABC). The families marked by *b* and *c* (the natrolite and mordenite families, respectively) can also be defined uniquely with SBUs. Another noteworthy conclusion which can be drawn from Table I is that only five out of the nine SBUs shown in Fig. 1 are strictly necessary to generate all the known zeolite framework types. These essential SBUs are the 4, 6, 4-1, 4-4-1, and 5-1 units.

Five-rings are observed in many zeolite networks but none of these can be built of five-ring units only. Networks of corner-sharing tetrahedra can be constructed from five-ring units but, in general, the resulting nets turn out to be quite dense. An example of a naturally observed net of this kind is that of the mineral petalite, $LiAlSiO_{10}$, containing 23.5 $T$-atoms per 1000 Å$^3$.

Larger polyhedral building units have also been proposed (*5*). These comprise the cage-type convex polyhedra shown in Fig. 2. These should be supplemented with the 6-6 and 8-8 units since the latter are also large enough to contain at least one atom site. In practice these cage units are often used to describe zeolite structures since these building blocks are easily recognizable. However, less than half of the known zeolite networks are based on cage-type units. It also follows from Table I that cage units generally lead to frameworks of low density. In addition to this, a general correlation of the type of building units and the framework density can be noted.

Building blocks which have not been considered so far are one-dimensional infinite

TABLE I

CONSTITUENT UNITS OF ZEOLITE STRUCTURE TYPES

| Structure type designation | | Secondary building units[a] | | | | | Cage units[b] | Tubular units[c] | Distinct families | Framework density[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Code | Full name | | | | | | | | | |
| FAU | Faujasite | 4 | 6 | | 6-6 | | B | | | 12.7 |
| LTA | Linde type A | 4 | 6 | 8 | 4-4 | | A,B | | | 12.9 |
| RHO | Rho | 4 | 6 | 8 | 8-8 | | A | | | 14.3 |
| GME | Gmelinite | 4 | 6 | 8 | 6-6 | | C | • | *a* | 14.6 |
| CHA | Chabazite | 4 | 6 | | 6-6 | | | | *a* | 14.6 |
| KFI | ZK-5 | 4 | 6 | 8 | 6-6 | | A | | | 14.7 |
| LEV | Levyne | | 6 | | | | | | *a* | 15.2 |
| GIS | Gismondine | 4 | | 8 | | | | | | 15.4 |
| EAB | TMA-E (AB) | 4 | 6 | | | | | | *a* | 15.4 |
| OFF | Offretite | | 6 | | | | D | • | *a* | 15.5 |
| PAU | Paulingite | 4 | | | | | | | | 15.5 |
| ERI | Erionite | 4 | 6 | | | | D | | *a* | 15.6 |
| LIO | Liottite | | 6 | | | | | | *a* | 15.7 |
| LOS | Losod | | 6 | | | | | | *a* | 15.8 |
| PHI | Phillipsite | 4 | | 8 | | | | | | 15.8 |
| AFG | Afghanite | 4 | 6 | | | | | | *a* | 15.9 |
| MER | Merlinoite | 4 | | 8 | 8-8 | | | • | | 16.0 |
| MAZ | Mazzite | 4 | | | | 5-1 | | • | | 16.1 |
| LTL | Linde type L | | 6 | | | | D | • | | 16.4 |
| CAN | Cancrinite | | 6 | | | | D | • | *a* | 16.7 |
| EDI | Edingtonite | | | | | 4-1 | | | *b* | 16.7[e] |
| THO | Thomsonite | | | | | 4-1 | | | *b* | 17.7[e] |
| NAT | Natrolite | | | | | 4-1 | | | *b* | 17.8[e] |
| STI | Stilbite | | | | | 4-4-1 | | | | 16.9 |
| HEU | Heulandite | | | | | 4-4-1 | | | | 17.0 |
| SOD | Sodalite | 4 | 6 | | | | B | | *a* | 17.2 |
| MOR | Mordenite | | | | | 5-1 | | • | *c* | 17.2 |
| DAC | Dachiardite | | | | | 5-1 | | | *c* | 17.3 |
| BRE | Brewsterite | 4 | | | | | | | | 17.5 |
| LAU | Laumontite | | 6 | | | | | | | 17.7 |
| FER | Ferrierite | | | | | 5-1 | | • | *c* | 17.7 |
| MEL | ZSM-11 | | | | | 5-1 | | • | *c* | 17.7 |
| MFI | ZSM-5 | | | | | 5-1 | | • | *c* | 17.9 |
| EPI | Epistilbite | | | | | 5-1 | | | *c* | 18.0 |
| YUG | Yugawaralite | 4 | | 8 | | | | | | 18.3 |
| ANA | Analcime | 4 | 6 | | | | | | | 18.6 |
| ABW | Li-A (BW) | 4 | 6 | 8 | | | | • | | 19.0 |
| BIK | Bikitaite | | | | | 5-1 | | | *c* | 20.2 |

[a] Shown in Fig. 1.

[b] Shown in Fig. 2.

[c] Shown in Fig. 3.

[d] Number of $T$-atoms/nm$^3$.

[e] Grouped together because of the characteristic 6.6 Å repeat in the fiber direction.

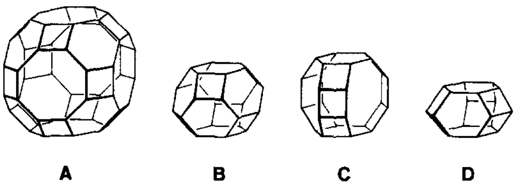

FIG. 2. Larger polyhedral building units and frequently occurring cages ($\alpha$-cage, A; sodalite cage, B; gmelinite cage, C; cancrinite cage, D).

cage or tubular building units (Fig. 3). They are included in this account primarily because of their chemical interest. Other one-dimensional infinite building units (chain units) have also been elucidated and are depicted elsewhere (*6*). In concluding the discussion of building units it should be emphasized that in all cases only topologically nonchiral units are acceptable if unnecessary complications are to be avoided.

From a more practical point of view, the data collected in Table I serve to show that the framework density, a figure which can be determined even for a zeolite with an unknown structure, can in fact provide information on the likely modular units of its silicate framework (particularly in conjunction with unit cell dimensions).

On comparing observed zeolite nets with a sizable number of hypothetical ones it becomes apparent that nets of high topological symmetry are favored. This is quite evident, for example, in the six-ring family of frameworks (*7*), marked by *a* in Table I. Listings of the maximum topological space group symmetry of observable zeolite frameworks (*1*, *8*) lend further support to this statement.

Unfortunately, the notation akin to the Schlaefli symbols for polyhedra, developed and used extensively by Wells (cf. *3*) for denoting three-dimensional nets, are not unequivocal. This can be illustrated, e.g., by $4^2 6^4$ which stands for both the SOD and the CAN net. For this reason and because this notation was obviously not devised for characterizing complicated zeolite networks, it has not been incorporated into Table I.

Coordination sequences $\{N_k\}$ which depend on topology only and which have been found to provide a numerical scale for expressing the degree of similarity of four-connected nets in zeolite structures (*8*) are mentioned only briefly here. The derivation of the necessary terms up to $N_5$ is somewhat cumbersome and quite prone to errors for $k \geq 4$. The higher terms of $\{N_k\}$ can be used to express the "topological density" of vertices in nets and correlate fairly well with framework density values (*8*, *9*). The latter have been given preference in this study for purely practical reasons.

## Possible Limiting Criteria for Likely Zeolite Framework Types

Many four-connected nets are evidently not "permissible" or at least less likely to be encountered as a zeolite network. In addition to the observed trend toward high symmetry configurations, stereochemical requirements (implying energetically favorable conformations) no doubt play a significant role in determining the chemical feasibility of a network. Chemical parameters which should be considered in assessing hypothetical zeolite frameworks are primarily $T$–$O$ bond distances and $O$–$T$–$O$ angles, and to a somewhat lesser extent $T$–$O$–$T$ angles. $T$–$O$ distances and tetrahedral angles, in particular, vary only within fairly narrow limits and impose geometrical constraints which can rule out certain configurations directly.

Models of likely zeolite networks can be tested with respect to geometrical requirements using the DLS method (*10*). This method of geometrical refinement of crystal structures makes use of the fact that the number of bond distances and angles in a network type structure is invariably greater than the number of atom coordinates. These can therefore be adjusted to fit prescribed distances and angles within the constraints imposed by the space group symmetry and other possible specifications (like cell dimensions, etc.) using the well-known least-squares method. The available computer program, DLS-76 (*11*), is very versa-

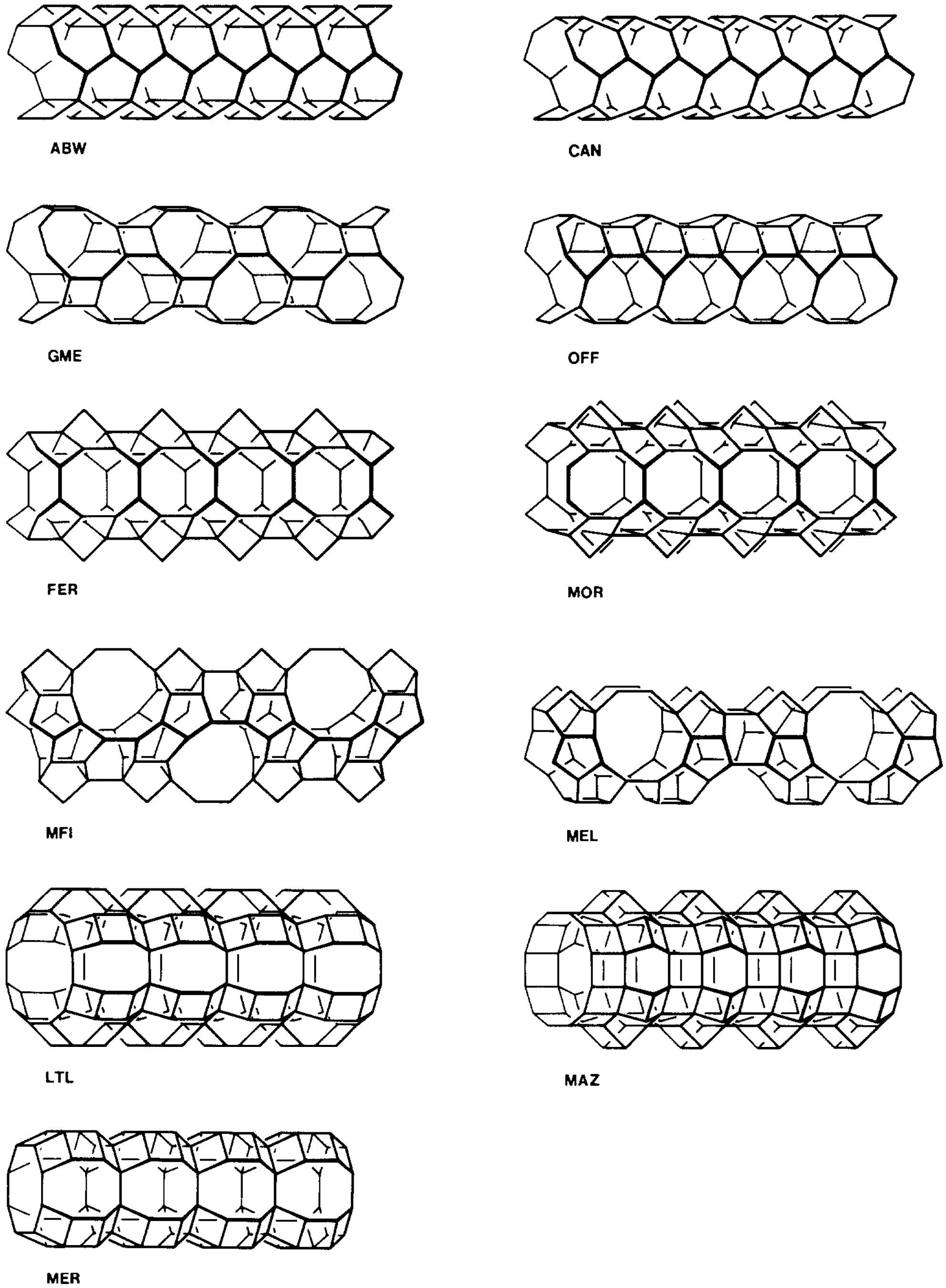

FIG. 3. Tubular building units (having at least eight-ring apertures).

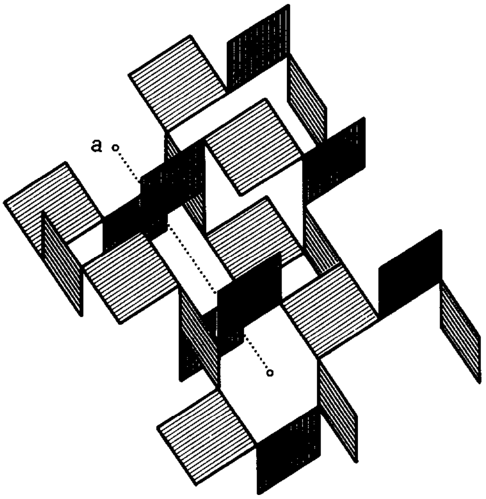

FIG. 4. Cubic $4^26^28^2$ net.

tile and can also accommodate subsidiary conditions, such as the interdependence of $T$–$O$ distances and $T$–$O$–$T$ angles in silicates (*12*). Hypothetical zeolite networks which cannot be satisfactorily optimized by DLS can be safely discarded. This potential aid has been applied in many structure determinations of zeolites, including that of ZSM-5 (*13*).

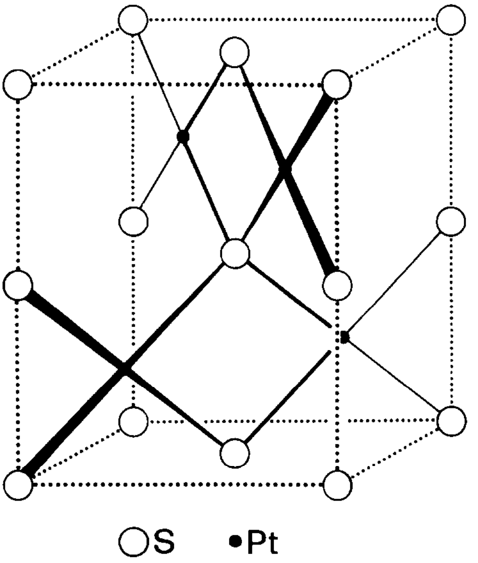

FIG. 5. Tetragonal $4^28^4$ net (adapted from *2*).

In order to illustrate the use of DLS in deriving possible zeolite networks, two interesting four-connected nets shown in Figs. 4 and 5 are considered briefly. The immediate question is simply: is it geometrically possible to build these nets from reasonably regular, corner-sharing tetrahedra and, if so, are critical distances and angular distortions within acceptable limits? The necessary model building to answer the questions is, in such cases, best done by computer simulation using DLS.

DLS refinement of the tetrahedral framework corresponding to the cubic $4^26^28^2$ net shown in Fig. 4 does in fact lead to a highly satisfactory solution with a mean residual $\bar{\rho}_w$ of less than 0.001 Å, provided the space group symmetry $Ia\bar{3}d$ (the maximum topological symmetry of the net) is lowered at least to the tetragonal subgroup $I4_1/acd$ (*14*). It is remarkable that customary models of this framework made of tetrahedra joined by flexible connecting tubes (representing $T$–$O$–$T$ bridges) look so strained that the structure appears hardly plausible, and yet it is the structure of one of the most common zeolites, that of analcime. It is even more remarkable that this zeolite structure, which is one of the most difficult to depict, was the very first one to be solved—a feat accomplished by W. H. Taylor (*15*) in 1930!

In evaluating the tetragonal $4^28^4$ net of PtS (Fig. 5) as a tetrahedral network type, in which both Pt and S are replaced by $T$-atoms, it is quite apparent that the symmetry has to be lowered substantially. The DLS test was therefore carried out in the space group $P1$ with 4 $T$-atoms per unit cell and unconstrained cell dimensions. Refinement proceeded to a $\bar{\rho}_w$ value of 0.028 Å (as compared with values of <0.005 Å for observed zeolite networks). The tetrahedra of the resultant structure are rather less distorted than one would expect, with $O$–$T$–$O$ angles ranging from 104 to 118° for former Pt sites and 106 to 112° for former S sites, while the *T–O–T* angles are all below 121°. It is mostly because of these unacceptably small *T–O–T* angles that this tetrahedral network can be ruled out as a possible silicate type framework.

Conformational parameters which have not been considered so far in the study of silicate frameworks include torsion angles describing the relative orientation of linked tetrahedra. Visual examination of wire models of all the known zeolite framework types seemed to indicate that neighboring tetrahedra in these nets more often form a "staggered" rather than an "eclipsed" arrangement. A number of representative and carefully analyzed zeolite structures was, therefore, examined quantitatively with respect to relevant conformational parameters, which could conceivably provide additional criteria for evaluating hypothetical structures.

Since neighboring tetrahedra in zeolite frameworks are not normally connected by a *straight* *T–O–T* bridge, their relative orientation cannot be described by a single torsion angle $\omega$ (defined by four atoms A, B, C, D in projection along B–C). Rather than using two torsion angles $\omega_0$ and $\omega_1$ to express the degree of twisting of two corner-sharing tetrahedra (Fig. 6), we have chosen the angular parameters $\Lambda$ and $\delta$. The twist angle $\Lambda$ is defined as

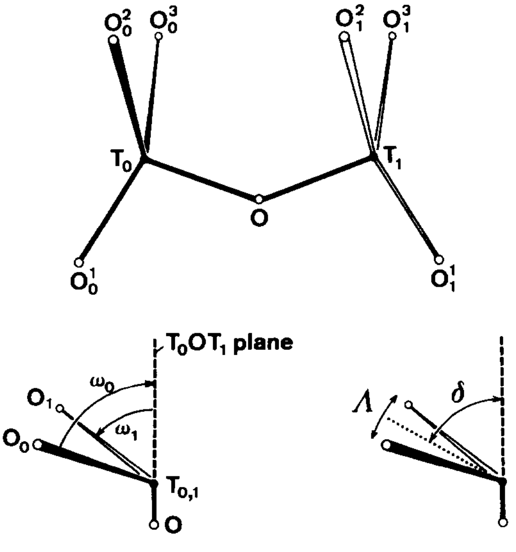

FIG. 6. Definition of twist ($\Lambda$) and directional angle ($\delta$).

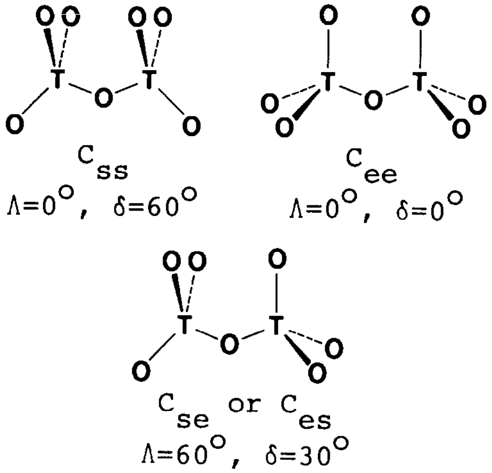

FIG. 7. Specific conformations of corner-sharing tetrahedra (e stands for eclipsed and s for staggered).

$$\Lambda = |\omega_0 + \omega_1|$$

in which $\omega_0$ refers to $|\omega|_{\min}$ and $\omega_1$ is chosen such that $|\omega_0 + \omega_1|$ is minimal. As shown in Fig. 6 the directional angle $\delta$ is then defined as

$$\delta = \left| \frac{\omega_0 - \omega_1}{2} \right| .$$

Since we are not concerned with stereoisomers in the present context, only the magnitudes of $\Lambda$ and $\delta$ have to be considered for

$$0 \le \Lambda \le 60^\circ \quad \text{and} \quad 0 \le \delta \le 60^\circ.$$[1]

For *T–O–T* angles of 180° the twist angle $\Lambda$ turns into a torsion angle and $\delta$ is no longer defined.

Specific conformations of paired tetrahedra are shown in Fig. 7. In a theoretical study of the electronic structure of disiloxane, $(SiH_3)_2O$, the relative stability of these

---

[1] If the tetrahedra are somewhat distorted, the values of $\Lambda$ and $\delta$ can fall slightly outside these ranges.

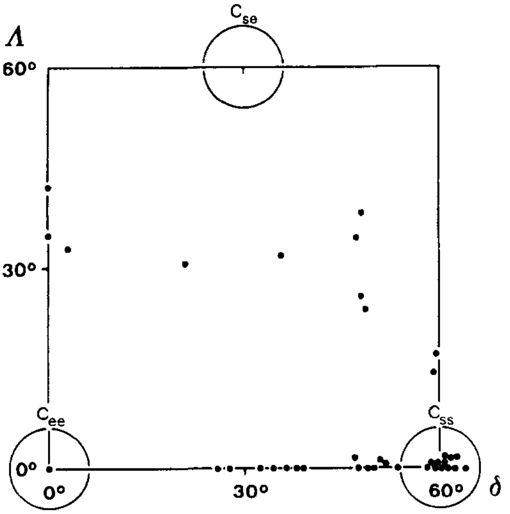

FIG. 8. Λ,δ plots for typical cage-type zeolites including CAN (*17*), CHA (*18*), ERI (*19*), FAU (*20*), GME (*21*), LTA (*22*), LTL (*23*), OFF (*24*), and SOD (*25*) type zeolites.

conformers was shown to follow the order $C_{ss} > C_{se} > C_{ee}$ (*16*). This result was also noted to agree with the finding that in sorosilicates the conformation $C_{ss}$ ($\Lambda = 0$; $\delta = 60°$) is observed much more often than $C_{ee}$ ($\Lambda = 0$; $\delta = 0$).

Conformational parameters, such as Λ and δ, can be expected to be more constrained in zeolite frameworks composed of cage units. The Λ,δ data, which were derived for a representative number of reasonably well-refined zeolite structures, are accordingly displayed separately (Fig. 8 for cage-type and Fig. 9 for other zeolite structures). Λ,δ parameters are spread more evenly for zeolites which do not have the configurational constraints imposed by cages (combined with high symmetry in general). Representative Λ,δ plots of zeolites with Si/Al ~ 1 have also been compared with such diagrams prepared for silica polymorphs but no significant differences in the distribution of these angular parameters could be found (*6*).[2] All these diagrams provide further evidence that $C_{ss}$ tends to be a somewhat favored conformation. The available data seem to indicate, however, that these conformational parameters play at best a secondary role in determining the "permissibility" of a zeolite network.

## Conclusions

Known zeolite networks provide a natural basis for deriving a very large number of interesting four-connected three-dimensional nets on purely topological grounds. The number of "permissible" types of zeolite frameworks is evidently limited, however, by conformational constraints. These must be investigated more extensively in order to gain a better understanding before the "permissibility" of hypothetical zeolite networks can be predicted reliably. There is little or no evidence that simple rules apply. Frequently observed deviations from ideal symmetry must at least in part be attributed to conformational requirements of the silicate framework. The role of conformational parameters in determining likely

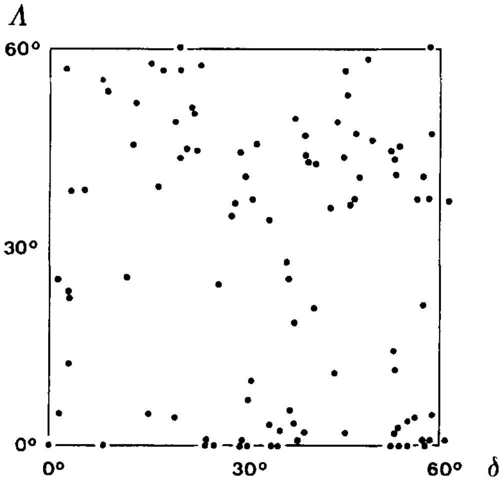

FIG. 9. Λ,δ plots for zeolites made of units other than cages. Included are FER (*6*), GIS (*26*), LAU (*27*), MFI (*13*), MOR (*28*), NAT (*29*), STI (*30*), and YUG (*31*) type zeolites.

---

[2] Nor could a dependance of the Λ,δ distribution on the *T–O–T* angles be observed.

configurations is not sufficiently appreciated yet in zeolite structural chemistry.

## Acknowledgments

We wish to thank G. O. Brunner, Dr. Volker Gramlich, and Dr. Lynne B. McCusker for helpful comments. This work was financially supported by the Swiss National Science Foundation.

## References

1. W. M. Meier and D. H. Olson, "Atlas of Zeolite Structure Types," International Zeolite Association Special Publication (1978).
2. A. F. Wells, "Structural Inorganic Chemistry," 4th ed., Oxford University Press, London (1975).
3. A. F. Wells, "Three-dimensional Nets and Polyhedra," Wiley-Interscience, New York (1977).
4. W. M. Meier, S.C. I. Monograph on "Molecular Sieves," p. 10, Society of Chem. Industry, London (1968).
5. D. W. Breck, *Adv. Chem. Ser.* **101,** 1 (1971).
6. R. Gramlich-Meier, Doctoral Thesis No. 6760, ETH Zurich (1981).
7. H. Rechsteiner, Thesis ETH Zurich (1979).
8. W. M. Meier and H. J. Moeck, *J. Solid State Chem.* **27,** 349 (1979).
9. G. O. Brunner, *J. Solid State Chem.* **29,** 41 (1979).
10. W. M. Meier and H. Villiger, *Z. Kristallogr.* **129,** 411 (1969).
11. Ch. Baerlocher, A. Hepp, and W. M. Meier, "DLS-76: A Program for the Simulation of Crystal Structures by Geometric Refinement," Institute of Crystallography, ETH Zurich (1978).
12. cf. R. J. Hill and G. V. Gibbs, *Acta Crystallogr.* **B35,** 25 (1979).
13. D. H. Olson, G. T. Kokotailo, S. L. Lawton, and W. M. Meier, *J. Phys. Chem.* **85,** 2238 (1981).
14. W. M. Meier, *Adv. Chem. Ser.* **121,** 39 (1973).
15. W. H. Taylor, *Z. Kristallogr.* **74,** 1 (1930).
16. R. Meier and T. K. Ha, *Phys. Chem. Minerals* **6,** 37 (1980).
17. O. Jarchow, *Z. Kristallogr.* **122,** 407 (1965).
18. J. V. Smith, R. Rinaldi, and L. S. Dent Glasser, *Acta Crystallogr.* **16,** 45 (1963).
19. L. W. Staples and J. A. Gard, *Mineral. Mag.* **32,** 261 (1959).
20. D. H. Olson, *J. Phys. Chem.* **74,** 2758 (1970).
21. K. F. Fischer, *N. Jb. Miner. Mh.* 1 (1966).
22. V. Gramlich and W. M. Meier, *Z. Kristallogr.* **133,** 134 (1971).
23. R. M. Barrer and H. Villiger, *Z. Kristallogr.* **128,** 352 (1969).
24. J. A. Gard and J. M. Tait, *Acta Crystallogr.* **B28,** 825 (1972).
25. J. Loens and H. Schulz, *Acta Crystallogr.* **23,** 434 (1967).
26. K. F. Fischer and V. Schramm, *Adv. Chem. Ser.* **101,** 250 (1971).
27. V. Schramm and K. F. Fischer, *Adv. Chem. Ser.* **101,** 259 (1971).
28. V. Gramlich, Doctoral Thesis No. 4633, ETH Zurich (1971).
29. W. M. Meier, *Z. Kristallogr.* **113,** 430 (1960).
30. E. Galli and G. Gottardi, *Acta Crystallogr.* **B27,** 833 (1971).
31. I. S. Kerr and D. J. Williams, *Acta Crystallogr.* **B25,** 1183 (1969).