

Flexibility of Network Structures

N. Khosrovani and A. W. Sleight¹

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

Received September 29, 1995; accepted October 9, 1995

DEDICATED TO THE MEMORY OF ALEXANDER F. WELLS

Understanding the flexibility of network structures is important for comprehending how such structures react to changing pressure and temperature as well as intercalation reactions. Some network structures are highly flexible, whereas others are rather rigid. Simple modeling approaches can offer some understanding of this behavior. Rigid tetrahedra can fit together extremely well in the ideal cubic networks represented by cristobalite and sodalite. Significant strain exists in ten other cubic networks examined. High flexibility is found in networks represented by the sodalite, analcite, and rho zeolite structures. The network based on ZrO_6 octahedra and PO_4 tetrahedra in the ZrP_2O_7 structure is rigid in the cubic system, and it becomes less rigid when the symmetry is reduced to orthorhombic, monoclinic, and triclinic. © 1996 Academic Press, Inc.

INTRODUCTION

A. F. Wells is best known for the several editions of his large book (1). However, his original contributions to structural inorganic chemistry are debatably better illustrated by his smaller books on networks (2–4). One aspect of networks that he did not consider is their flexibility. There has been some tendency to view networks as rigid structures. In fact, some are rather rigid, whereas others are highly flexible due to the ease of varying certain bond angles. Cubic MO_3 networks based on MO_6 octahedra may be taken as an example. The linking of these octahedra gives the highly flexible perovskite structure if the cubic symmetry is relaxed. However, different connectivities of MO_6 octahedra give rigid networks in the case of the pyrochlore and cubic $KSbO_3$ structures.

In this paper, we consider the flexibility of cubic networks based on corner-sharing tetrahedra or mixed tetrahedra–octahedra. Flexibility is first considered in the parent structure, that is, the structure which possesses the highest symmetry consistent with a particular connectivity. Then we consider the degree to which flexibility is enhanced by removing symmetry elements. This is essentially the same approach that has been used by Parise *et al.* (5)

and Baur (6) on a more restricted basis set than presented here. A crystal mechanics force field approach to zeolite flexibility has been taken by Deem *et al.* (7).

MODELING APPROACH

We find that the flexibility of many framework structures can be well-simulated using DLS, a well-known approach to refining structures based on prescribed distances (8). This approach is most suitable for linked semirigid MO_x polyhedra connected by corner sharing only. In this approach, prescribed $M-O$ distances are given high weights. The prescribed $M-M$ distances, effectively the $M-O-M$ bond angles, are given low weights; and the $O-O$ distances, effectively $O-M-O$ angles, are given intermediate weights. The DLS approach is not suitable if there is considerable variation in the $M-O$ bond lengths or $M-O-M$ bond angles of a given MO_x polyhedron. This occurs for example for VO_6 and MoO_6 polyhedra. In those cases a DLS variation, DVLS which allows polyhedra distortions consistent with bond valence rules, may be used instead (9).

Our method of exploring flexibility of networks involves determining their reactions to compression or expansion. This is straightforward for cubic structures. One sets the cubic cell edge, a , to a range of different values and then conducts a DLS refinement with a fixed a . In this way, one determines how a particular network can react to positive or negative pressure. First, the refinements are conducted in the highest space group consistent with a particular connectivity of the network. Then, the refinements are repeated with certain symmetry elements removed, that is, in lower space groups or with larger unit cells.

A challenging aspect of our calculation is to locate all the minima of interest. We have focused on finding the global minimum for each network, but we have frequently found other minima that give nearly comparable fits. The way to find the global minimum as well as other minima is to start the DLS refinement with many different values of atomic positional coordinates.

For all the results reported in this paper, a consistent set of weights are used: 1.0 for the $M-O$ distance, 0.07 for the $O-O$ distance, and 0.04 for the $M-M$ distance. The

¹ To whom correspondence should be addressed.

M - O distances are given the highest weight since they show a very small range of observed values, but the O - O and M - M distances are given much lower weights since they show a wide range of observed values (5). The agreement factor R is defined by

$$R = \sqrt{\frac{\sum (w \cdot \delta d)^2}{\sum (w \cdot d)^2}},$$

where w is the weight, d is the interatomic distance, and δd is the difference between a particular distance and its prescribed distance. The prescribed M - O distance was not the same for all refinements (Table 1). Instead it was given a value consistent with the Al to Si ratio most often found for a particular zeolite. Such prescribed values then facilitate direct comparison of our results with experimental data. However, such comparison is still impeded by the effect on a of interstitial cations and molecules such as water. The prescribed O - O distance is always set according

to an ideal MO_4 tetrahedron, and the prescribed M - M distance is always based on an M - O - M angle of 145° .

A potential problem with DLS modeling is that non-bonded interatomic distances might become unacceptably short. We might, in fact, anticipate this problem as we compress a network structure. The DLS software only calculates the interatomic distances for atom pairs with prescribed distances. To deal with this problem, we checked for short nonbonded distances in our solutions. In fact, this was never found to be an issue for the compression range we consider in this paper.

RESULTS

The zeolite networks considered in this paper are rho, analcite (also known as analcime), ZK-5, faujasite, sodalite, ZSM-39, zeolite A (both ordered and disordered), melanophlogite, paulingite, and linde N. The R vs a plots are given in all cases, and corresponding angle vs a plots are given in some cases (Figs. 1–11). The minimum in the plot

TABLE 1
Residuals for Various Refinements

Network	Space group	$a(\text{\AA})^a$	# of variables	M - O distances	$R^b \times 10^4$
Zeolite A	$Pm\bar{3}m$	12.3560	6	1×1.670	11.4/25.4/60.4
Zeolite A	$P4m$	12.3561	10	1×1.670	9.8/24.2/58.7
Zeolite A	$Fm\bar{3}c$	24.7268	11	2×1.670	8.5/18.6/60.5
Zeolite A	$Fm\bar{3}c$	24.7270	11	$1 \times 1.730; 1 \times 1.610$	8.5/18.4/60.5
Rho	$Im\bar{3}m$	15.0092	5	1×1.620	4.0/27.7/58.6
Rho	$I\bar{4}3m$	14.8239	10	1×1.620	2.8/7.4/25.9
Analcite	$Ia\bar{3}d$	13.8763	4	1×1.647	4.4/51.8/73.2
Analcite	$I\bar{4}3d$	13.8743	9	1×1.647	4.5/14.4/64.7
Analcite	$I4_132$	13.8763	8	2×1.647	4.4/44.4/73.2
Faujasite	$Fd\bar{3}m$	24.8073	10	1×1.640	4.2/28.6/41.2
Faujasite	$F\bar{4}3m$	24.8081	21	2×1.640	3.8/24.1/41.5
Faujasite	$F4_132$	24.7944	17	2×1.640	3.4/22.5/39.7
Faujasite	$Fd\bar{3}$	24.7987	18	2×1.640	3.1/22.7/39.9
Sodalite	$P\bar{4}3n$	8.9882	3	$1 \times 1.720; 1 \times 1.610$	5.0/12.9/13.1
Sodalite	$P23$	8.9882	8	$1 \times 1.720; 1 \times 1.610$	5.0/12.9/13.1
Sodalite	$P\bar{4}3n$	8.9827	3	2×1.665	0.0 ^c /12.1/11.8
Sodalite	$P\bar{4}3m$	8.9827	5	1×1.665	0.0 ^d /16.7/16.4
Sodalite	$I\bar{4}3m$	8.9827	2	1×1.665	0.0 ^e /16.7/16.4
Sodalite	$I23$	8.9827	4	1×1.665	0.0 ^f /12.1/11.8
ZK-5	$Im\bar{3}m$	18.6823	10	1×1.620	6.9/23.3/60.5
ZK-5	$I\bar{4}3m$	18.6850	20	2×1.620	5.6/18.2/59.7
Paulingite	$Im\bar{3}m$	35.0267	68	8×1.620	5.6/17.6/60.7
Linde N	$Fd\bar{3}$	37.1348	72	$4 \times 1.740; 4 \times 1.610$	9.4/17.5/41.3
Melanophlogite	$Pm\bar{3}n$	13.7881	9	3×1.620	21.6/41.7/140.6
ZSM-39	$Fd\bar{3}m$	19.8159	8	3×1.600	27.7/71.5/185.5
ZSM-39	$F\bar{4}3m$	19.8181	17	6×1.600	26.5/51.8/185.6

^a The value of a when a is allowed to vary.

^b R value when a is allowed to vary/ R value after 2.7% compression/ R after 2.7% expansion.

^c The exact value of $R \times 10^4$ at minimum a is 0.0004.

^d The exact value of $R \times 10^4$ at minimum a is 0.0001.

^e The exact value of $R \times 10^4$ at minimum a is 0.0118.

^f The exact value of $R \times 10^4$ at minimum a is 0.0121.

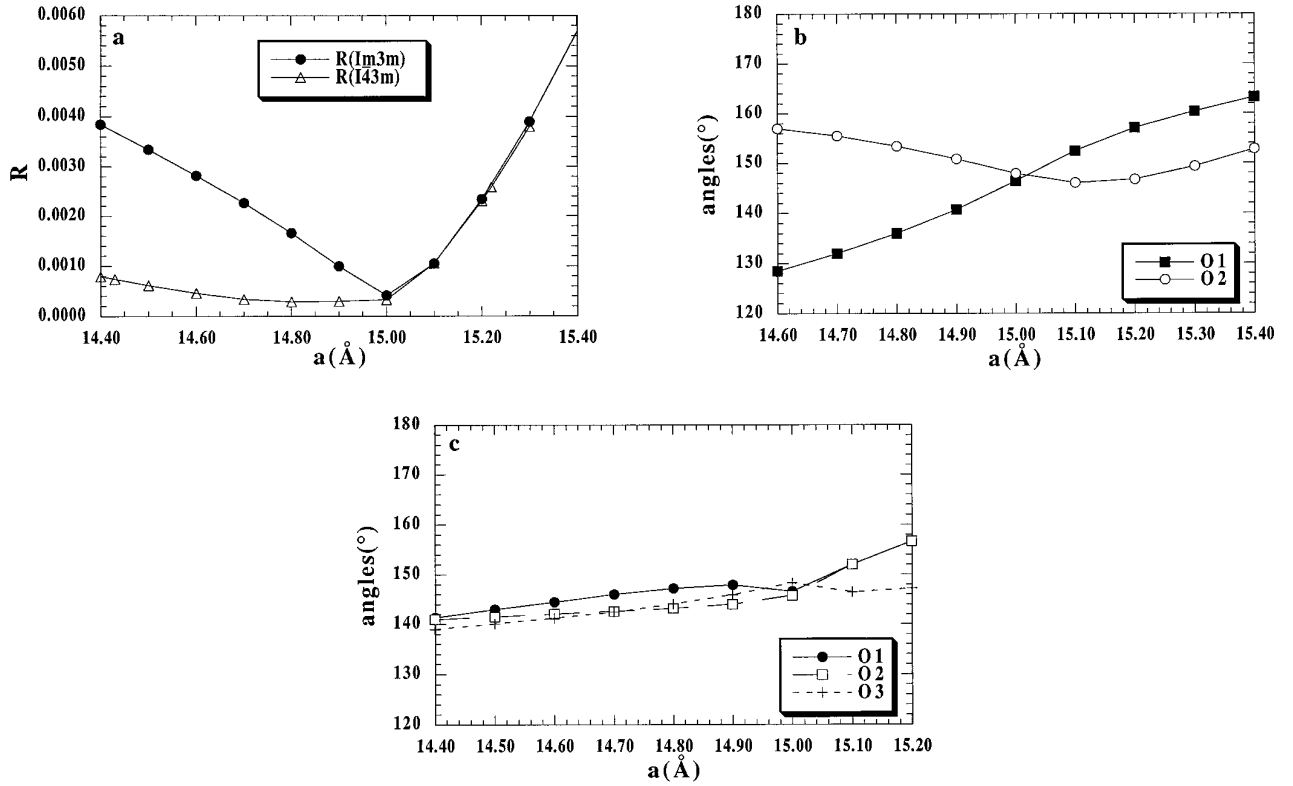


FIG. 1. Rho (a) R values in space groups $Im\bar{3}m$ and $I\bar{4}3m$. $M-O-M$ angles in space groups (b) $Im\bar{3}m$ and (c) $I\bar{4}3m$.

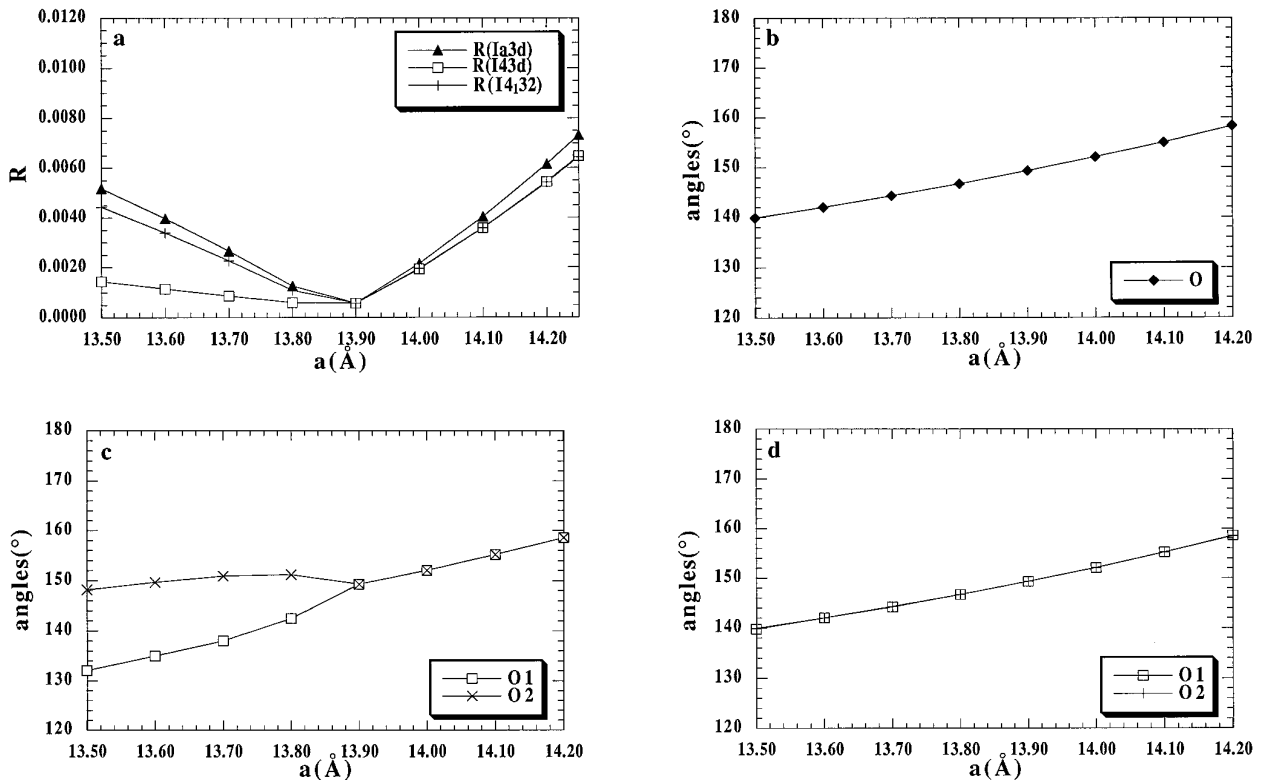


FIG. 2. Analcite (a) R values in space groups $Ia\bar{3}d$, $I\bar{4}3d$, and $I4_132$. $M-O-M$ angles in space groups (b) $Ia\bar{3}d$, (c) $I\bar{4}3d$, and (d) $I4_132$.

is found by actually allowing a to vary during the DLS refinement. The region to the right of the minimum is termed the expansion region, and the region to the left of the minimum is the compression region. The minimum value of R is an indication of how well regular tetrahedra can fit together with a given connectivity and $M-O-M$ angles not far from 145° . The high values of R for both ZSM-39 and melanophlogite indicate that these frameworks are under considerable strain relative to the other networks we have examined (Table 1). Exceptionally low values of R are found in several variations on the sodalite structure. The very low R value of sodalite can be obtained for any prescribed $M-O-M$ angle less than 160° , although

we prescribed 145° for the $M-O-M$ angle for the results shown in Table 1 and Fig. 4.

There are several aspects to network flexibility. Low values of R will promote some flexibility regardless of the slopes on either side of the minimum in the R vs a plots. However, we will focus on the slopes in these plots. A sharply defined minimum is a characteristic of a rigid network, and a broad minimum indicates a flexible network. Reducing lattice symmetry constraints sometimes, but not always, results in increased lattice flexibility. This increased flexibility can be very small (e.g., in faujasite) or it can be very large as in rho.

Some general trends are well illustrated with zeolite rho.

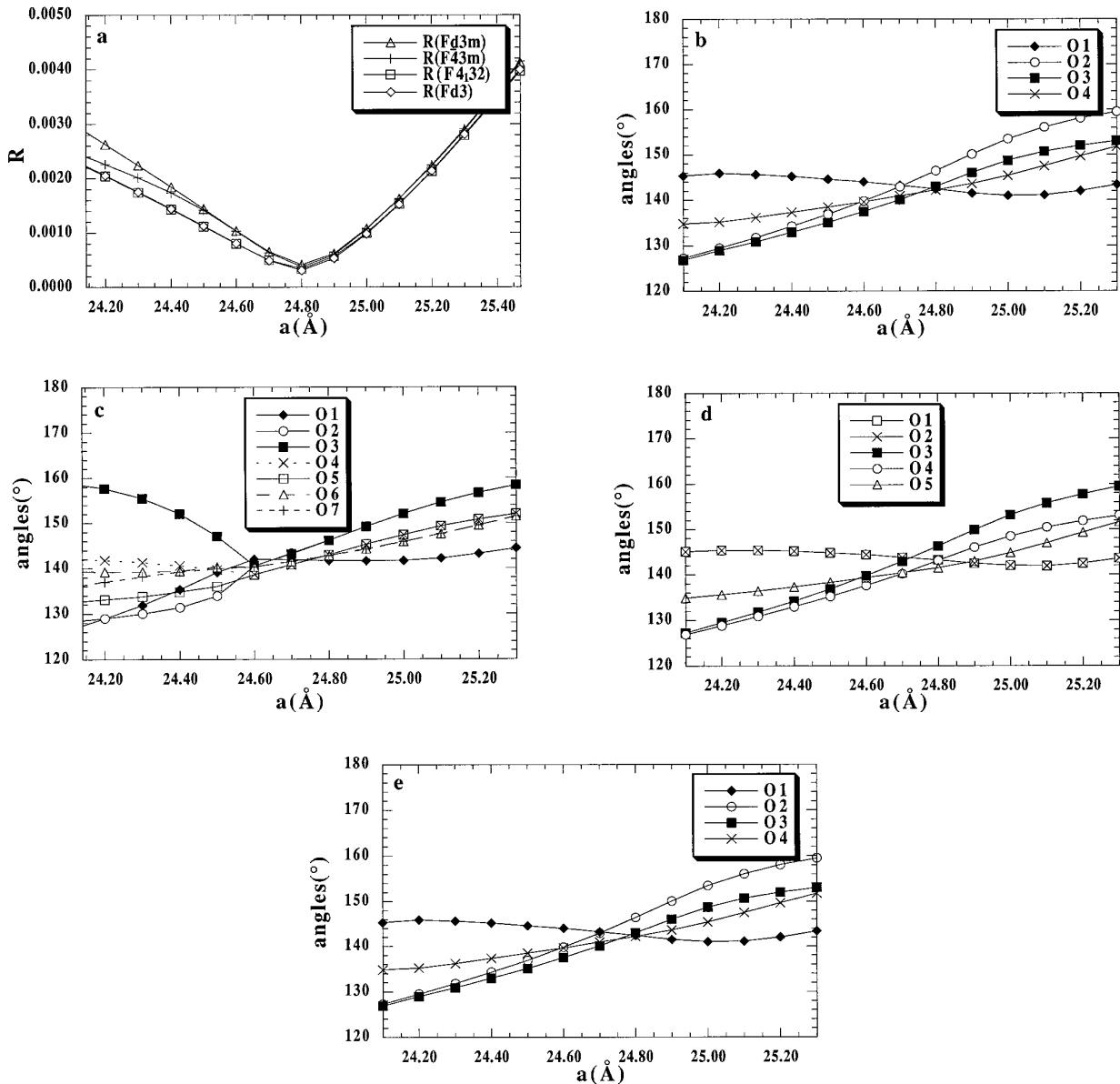


FIG. 3. Faujasite (a) R values in space groups $Fd3m$, $F\bar{4}3m$, $F4_132$, and $Fd3$. $M-O-M$ angles in space groups (b) $Fd3m$, (c) $F\bar{4}3m$, (d) $F4_132$, and (e) $Fd3$.

The value of R increases more steeply in the expansion region than in the compression region (Fig. 1a). Thus, it is basically easier to compress these networks than to expand them. However in real materials, compression may be impeded by interstitial cations and molecules which are ignored in our calculations. The effect of symmetry is generally more pronounced on compression than on expansion. Lowering of symmetry frequently gives a broader minimum; most of this effect is in the compression region.

The primary mechanism of compression in a zeolite is

decreasing $M-O-M$ angles, thereby decreasing $M-M$ distances. Thus, the trend shown in Fig. 1c is considered the normal behavior. All three $M-O-M$ angles are in general decreasing with decreasing a . Deviation from this behavior occurs as shown in Fig. 1b, where one of the two $M-O-M$ angles does not decrease with decreasing a in the compression region. This ‘‘abnormal behavior’’ can be an indirect result of either the network connectivity or the imposed lattice symmetry. In the case of rho, the $M-O-M$ angles behave more normally over the range considered when

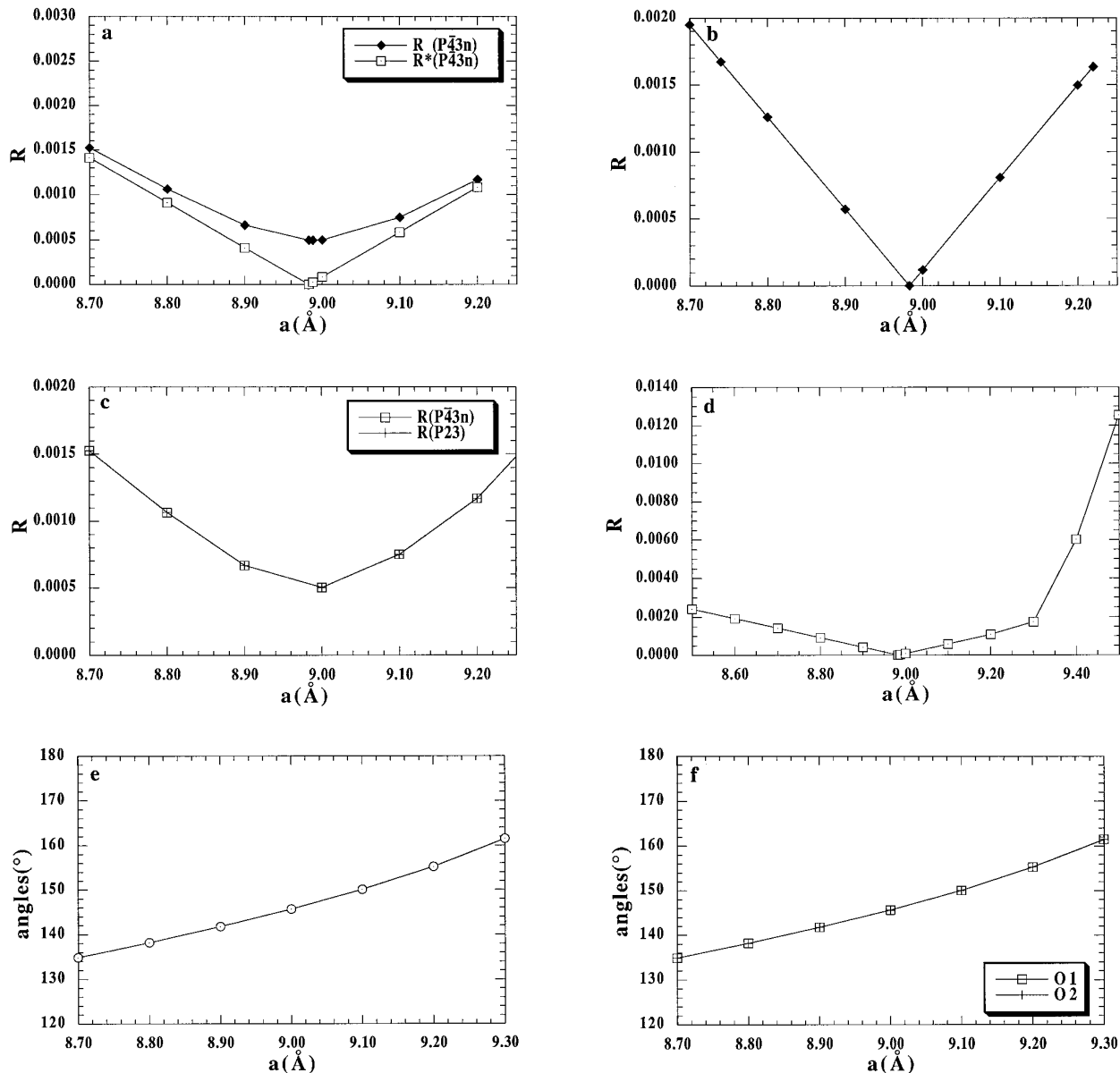


FIG. 4. Sodalite (a) R values in space group $P\bar{4}3n$. For R^* , the prescribed $M-O$ distance of 1.665 Å is used for both tetrahedral sites. For R , prescribed distances of 1.61 and 1.72 Å are used. (b) R value in space group $P\bar{4}3m$. One prescribed $M-O$ distance of 1.665 Å is used. (c) R values in space groups $P\bar{4}3n$ and $P23$. In both cases prescribed distances of 1.61 and 1.72 Å are used. (d) R values in space group $P\bar{4}3n$. This figure is the same as the graph for R^* in Fig. 4a, but it shows the behavior of R in the larger domain of a . (e) $M-O-M$ angles in space group $P\bar{4}3n$. Prescribed $M-O$ distances of 1.61 and 1.72 Å are used. (f) $M-O-M$ angles in space group $P\bar{4}3m$.

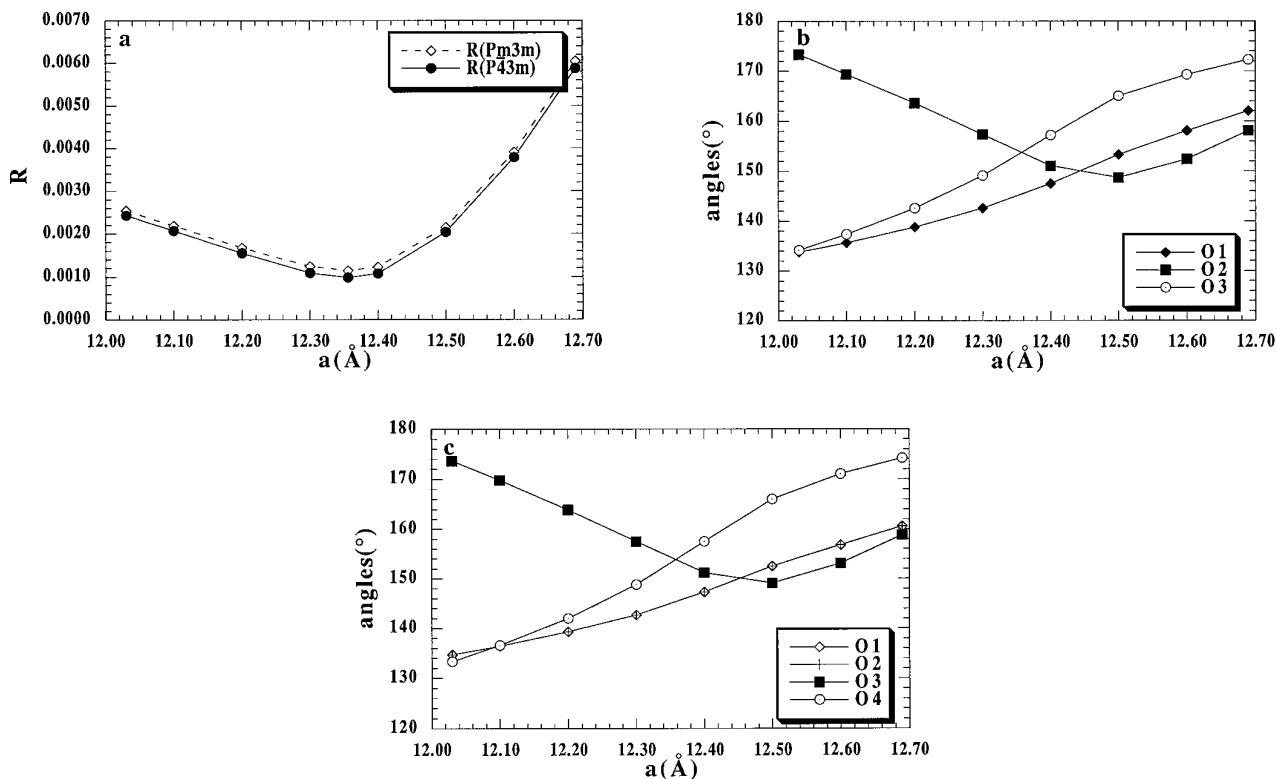


FIG. 5. Zeolite A (a) R values in space groups $Pm3m$ and $P43m$. $M-O-M$ angles in space groups (b) $Pm3m$ and (c) $P43m$.

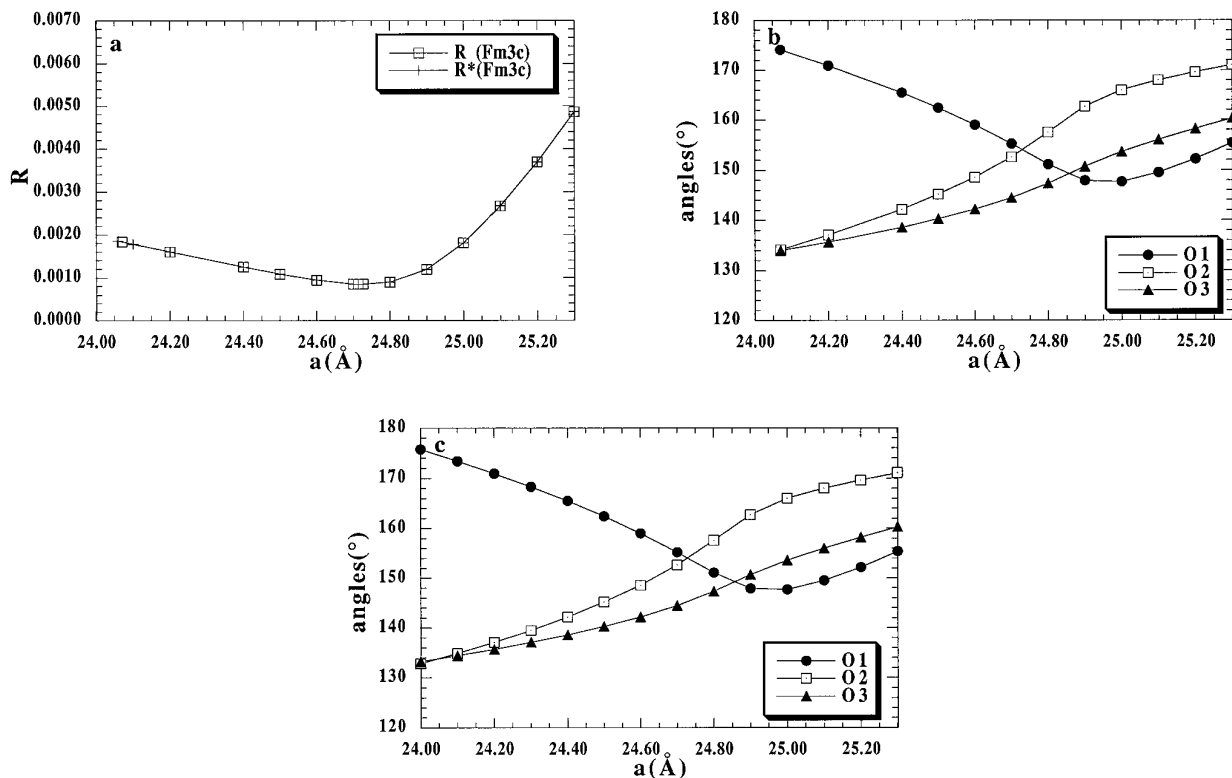


FIG. 6. Zeolite A (doubled cell) (a) R values in space group $Fm3c$. For R^* the prescribed $M-O$ distance of 1.67 Å is used for both tetrahedral sites. For R , prescribed distances of 1.61 and 1.73 Å are used. (b) $M-O-M$ angles in space group $Fm3c$. Prescribed $M-O$ distances of 1.61 and 1.73 Å are used. (c) $M-O-M$ angles in space group $Fm3c$. Prescribed $M-O$ distance of 1.67 Å is used for both tetrahedral sites.

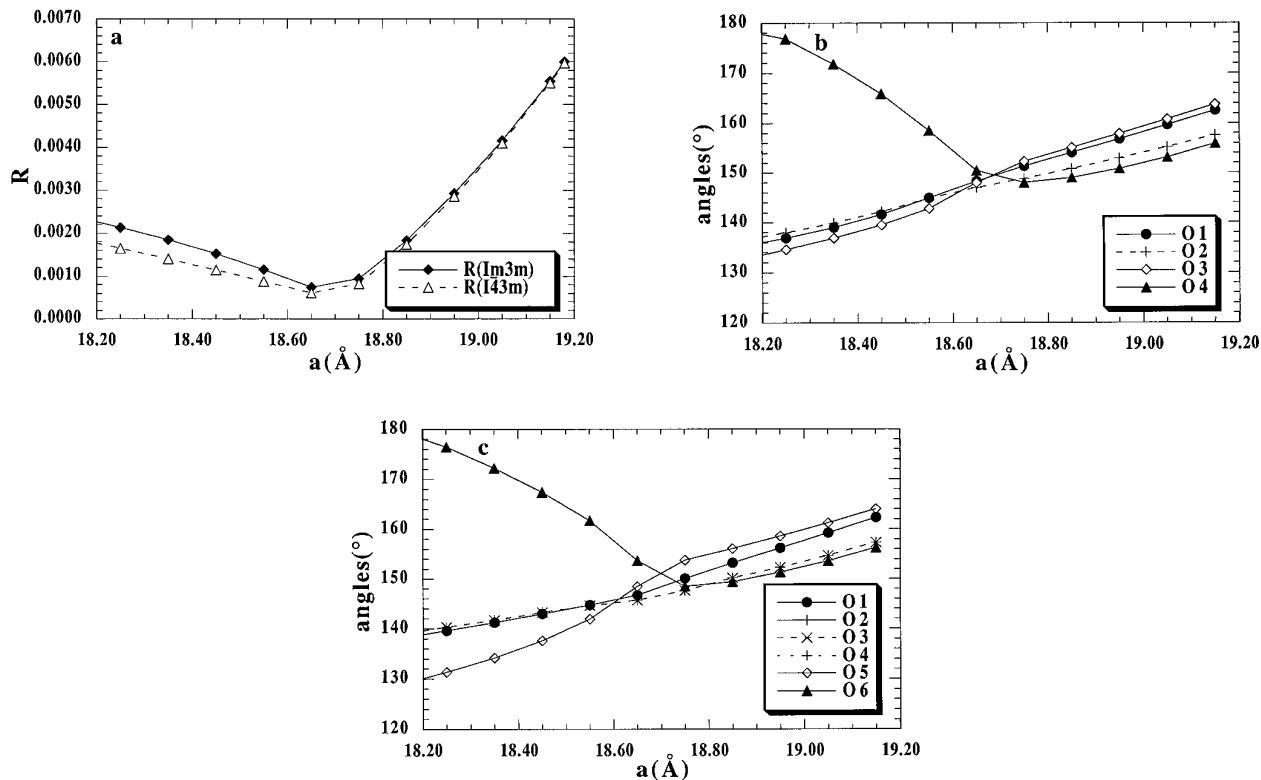


FIG. 7. ZK-5 (a) R values in space groups $I\bar{4}3m$ and $I\bar{4}3m$. $M-O-M$ angles in space groups (b) $I\bar{4}3m$ and (c) $I\bar{4}3m$.

the lattice symmetry constraint is relaxed in space group $I\bar{4}3m$ (Fig. 1c). For other networks such as those represented by ZK-5 and zeolite A, some reduction of lattice symmetry does not lead to “normal” behavior.

In the case of analcite, some of the trends mentioned for rho occur (Fig. 2). Here two lower space groups were considered. Both result in greater flexibility in the sense of a broader minimum. In the case of rho, the value of a for which R reaches a minimum changes significantly when the symmetry is reduced (Fig. 1a). However, there is essen-

tially no change in the position of this minimum as the symmetry is reduced for analcite (Fig. 2a).

The results for faujasite, sodalite, and zeolite A represent counter examples (Figs. 3–5). Flexibility is not much increased on considering lower symmetry cubic space groups for faujasite and zeolite A. The R vs a curves for faujasite are rather similar in space groups $Fd\bar{3}m$, $F\bar{4}3m$, $F4_132$, and $Fd\bar{3}$. The $M-O-M$ angles vs a plots are also similar for space groups $Fd\bar{3}m$, $F4_132$, and $Fd\bar{3}$. However, reducing the symmetry of the faujasite network from $Fd\bar{3}m$ to $F\bar{4}3m$

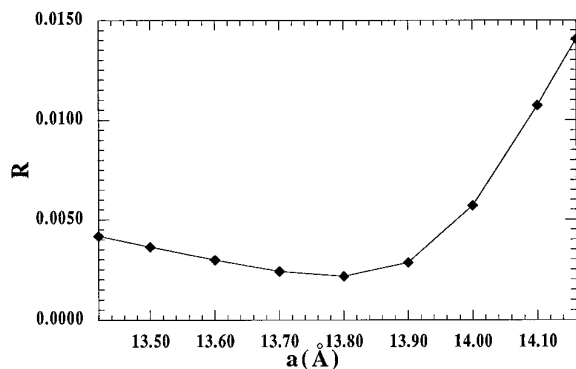


FIG. 8. R values for melanophlogite in space group $Pm\bar{3}n$.

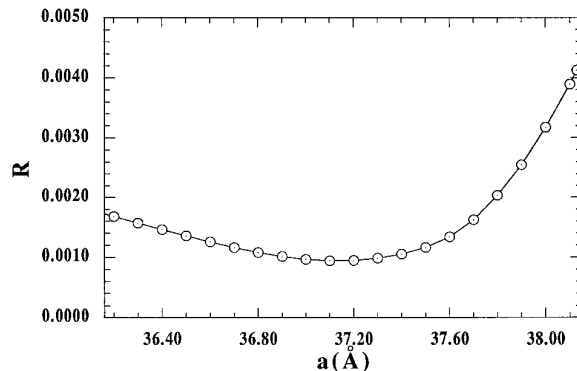


FIG. 9. R values for linde N in space group $Fd\bar{3}$.

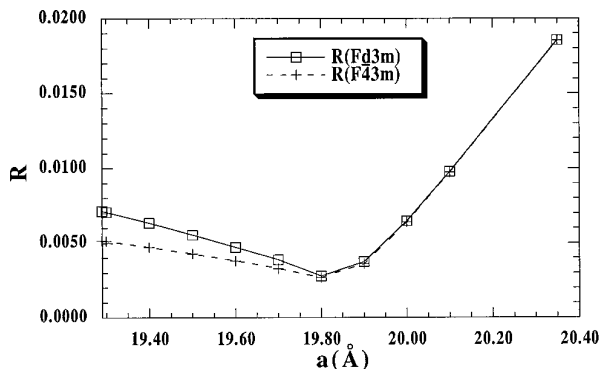


FIG. 10. R values for ZSM-39 in space groups $Fd\bar{3}m$ and $F\bar{4}3m$.

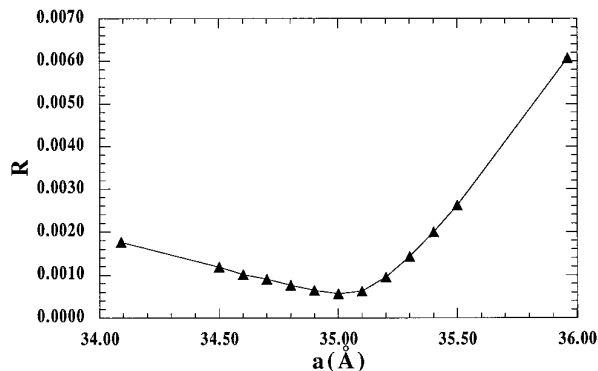


FIG. 11. R values for paulingite in space group $Im\bar{3}m$.

actually causes abnormal behavior (Fig. 3c). There are now seven different $M-O-M$ angles which are all significantly different in the compression region but these reduce to just the usual four different $M-O-M$ angles in the expansion region.

Both zeolite A and sodalite exist in ordered and disordered variations. That is, the tetrahedra can be all symmetry related or there can be two symmetry unrelated tetrahedra; one of these might be the Al site and the other the Si site. Thus in the ordered variation, we would have tetra-

hedra of two different sizes. The ordering causes a doubling of the unit cell size in zeolite A, but there is no increase in the size of the sodalite unit cell with ordering.

In the case of sodalite, an extremely low R value occurs at the minimum in the R vs a plot (Table 1 and Fig. 4). This occurs in space groups $P43m$, $P43n$, $I43m$, and $I23$. Over the region shown in Fig. 4a, the increase in R is nearly symmetric with respect to the minimum. However, at larger values of a (Fig. 4d), the usual steeper slope is found in the expansion region. When the tetrahedra are made dif-

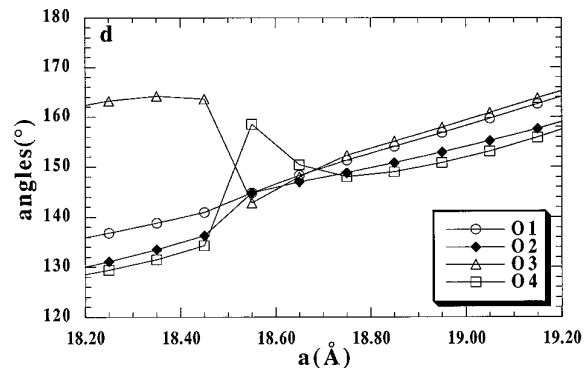
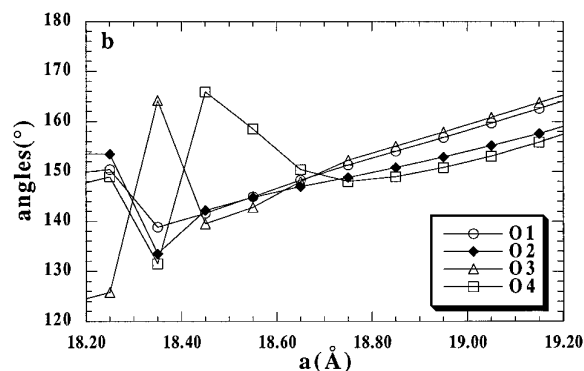
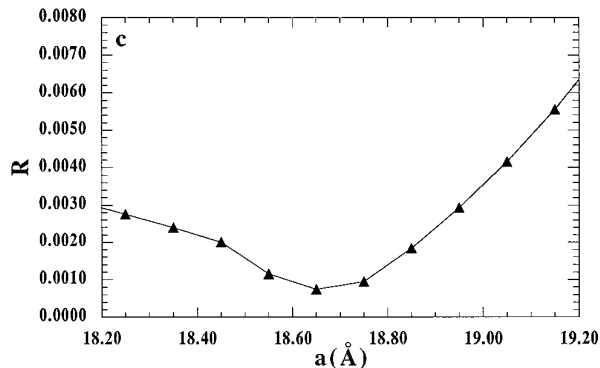
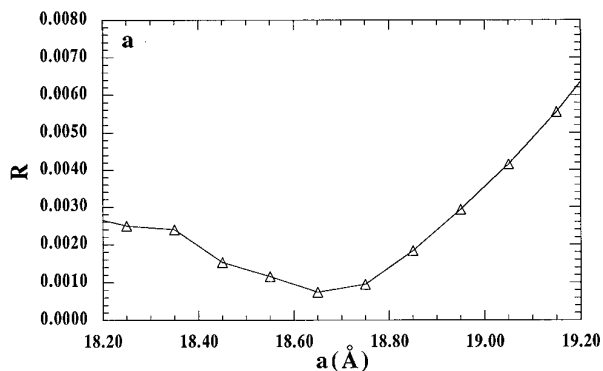


FIG. 12. ZK-5 (a) R values in space groups $Im\bar{3}m$ when the global minimum is not achieved at every a . (b) $M-O-M$ angles in space group $Im\bar{3}m$ related to Fig. 12a. (c) R values in space group $Im\bar{3}m$ when the global minimum is not achieved at every a (this solution is different from the solution given in Fig. 12a). (d) $M-O-M$ angles in space group $Im\bar{3}m$ related to Fig. 12c.

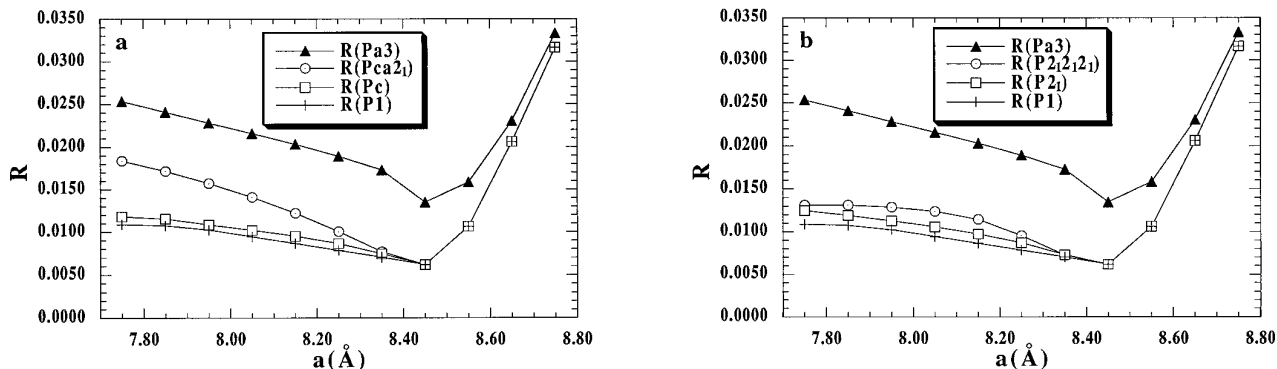


FIG. 13. ZrP_2O_7 (a) R values in space groups $Pa3$, $Pca2_1$, Pc , and $P1$. (b) R values in space groups $Pa3$, $P2_12_12_1$, $P2_1$, and $P1$.

ferent in size, the framework is strained and higher R values are obtained. Lowering the space group to $P23$ does not result in lower R values or more flexibility. The behavior of $M-O-M$ angles with changing a is normal (Figs. 4e and 4f).

Zeolite A was refined in four different ways (Table 1 and Figs. 5 and 6). The R value at the minimum is rather high in the ideal structure with the 12.36 Å cell where there can be no ordering of Al and Si on tetrahedral sites. Lowering the symmetry from $Pm3m$ to $P43m$ decreases the R at the minimum slightly from 11.4×10^{-4} to 9.8×10^{-4} , but there is essentially no increase in flexibility. Doubling of the cell edge of zeolite A is associated with ordering of Al and Si as there are now two crystallographically distinct tetrahedral sites. Refinements in this structure give a lower R (8.5×10^{-4}) regardless of whether the $M-O$ distances at the two sites are the same or different. This behavior is then very different than that found for sodalite. The value of a (or $2a$) for which R is a minimum for zeolite A shows essentially no change in response to lattice symmetry constraints or ordering of Al and Si. Plots of $M-O-M$ angles vs a show abnormal behavior regardless of ordering or space group (Figs. 5b, 5c, 6b, and 6c).

The flexibility for ZK-5 (Fig. 7) is rather similar to that of analcite in space group $I43d$. However, whereas the $M-O-M$ angles in analcite behave normally, this behavior is abnormal in ZK-5. Reducing the symmetry of ZK-5 from space group $Im3m$ to $I43m$ increases the flexibility somewhat, but the abnormal behavior of the $M-O-M$ angles remains. Figures 8–11 shows the behavior of melanophlogite, linde N, ZSM-39, and paulingite.

Figure 12 illustrates the type of results that can be obtained if a global minimum is not obtained at every value of a . The R vs a plot is not as smooth as usual, but the irregularities in the $M-O-M$ plots are far more dramatic. We conclude that in ZK-5 at least four good solutions exist in space group $Im3m$. These are evident in compression but not in expansion. In the compression region, normal behavior for $M-O-M$ angles occurs for several solutions

but not for the solution giving the lowest R values. The fact that there are several good solutions is another aspect of flexibility. The real structure could in principle fluctuate among these solutions. Finding several good solutions is not unique to ZK-5. This is our general finding for the compression region of the networks we examined.

In addition to networks based on tetrahedra only, we have examined one structure with a mixture of tetrahedra and octahedra. The structure is that of many pyrophosphates such as ZrP_2O_7 . The polyhedra share corners only, and all corners are shared. The structure of the high-temperature form of this material is cubic with P-O-P angles constrained by the space group ($Pa3$) to be 180° (10). We have previously presented some DLS calculations on this structure, but they dealt with a frustration issue rather than with flexibility (11). In the results we present here, the superstructure which can exist at lower temperatures is not considered.

The minimum R value for the ZrP_2O_7 network in its ideal symmetry (space group $Pa3$) is significantly higher than those for any of the zeolites we considered. Symmetry elements were removed in two different ways: $Pa3$ to $Pca2_1$ to Pc to $P1$ (Fig. 13a) and $Pa3$ to $P2_12_12_1$ to $P2_1$ to $P1$ (Fig. 13b). Cell edges were constrained to be equal and cell angles were fixed at 90° . Nonetheless, dramatic decreases in R occurred (Fig. 13). Thus, this network becomes much more flexible as symmetry constraints are removed. However, R values of ZrP_2O_7 remain high relative to those of zeolites, indicating a more rigid network. As generally occurs in the zeolite networks, the R vs a curves for ZrP_2O_7 also overlap in the expansion region.

DISCUSSION

All the networks we explore here are known to exist in real materials. However, our goal at this time is not to model the behavior of real materials. Rather, we are attempting to understand aspects of three-dimensional networks from the point of view of their geometry. In particu-

lar, we wish to understand flexibility of networks based on tetrahedra and octahedra which share corners only. Once we are convinced that we understand the geometric relationships of such networks, we can apply this understanding to real materials. Our investigation is only a beginning with this approach. There are many other networks that could be examined. We have focused on the global minima for each network, but we know that there are generally several other good solutions. Furthermore, the flexibility of all of these networks should be explored in noncubic space groups and with larger unit cells.

The simplest cubic network based on tetrahedra sharing corners could be regarded as cristobalite in its ideal structure. The connectivity of this structure forces 180° Si–O–Si bond angles if the tetrahedra are perfectly regular and the lattice symmetry is constrained to be cubic. In cubic β -cristobalite, the 180° Si–O–Si bond angles are assumed to be bent in a disordered fashion. In noncubic α -cristobalite, bending of the Si–O–Si angle is possible while maintaining regular tetrahedra. In all of the networks we have modeled (Table 1), the M –O– M angles approach 180° as they are stretched. However, only the network represented by cristobalite can fully achieve 180° M –O– M bond angles with regular tetrahedra.

As has been noted previously (5), the network represented by rho is very flexible if the ideal symmetry is relaxed. The sodalite network is also very flexible even in

the highest symmetry consistent with its connectivity. However, a factor not previously noted is that this flexibility is significantly decreased if tetrahedra of two different sizes are used. For analcite, high flexibility requires relaxing the ideal symmetry in a way which apparently has not been observed. Our results suggest that high pressure should induce lower symmetry structures for compounds with the analcite network.

REFERENCES

1. A. F. Wells, "Structural Inorganic Chemistry," 3rd ed. Oxford Univ. Press, Oxford, 1984.
2. A. F. Wells, "The Third Dimension in Chemistry." Clarendon Press, Oxford, 1962.
3. A. F. Wells, "Three-Dimensional Nets and Polyhedra." Wiley, New York, 1977.
4. A. F. Wells, "Further Studies of Three-dimensional Nets and Polyhedra." A.C.A. Monograph No. 8, 1979.
5. J. B. Parise, T. E. Gier, D. R. Corbin, and D. E. Cox, *J. Phys. Chem.* **88**, 1635 (1984).
6. W. H. Baur, *J. Solid State Chem.* **97**, 243 (1992).
7. M. W. Deem, J. M. Newsam, and J. A. Creighton, *J. Am. Chem. Soc.* **114**, 7198 (1992).
8. W. M. Meier and H. Villiger, *Z. Kristallogr.* **129**, 161 (1966).
9. H. Kroll, H. Maurer, D. Stöckelmann, W. Beckers, J. Fulst, R. Krüsemann, Th. Stutenbäumer, and A. Zingel, *Z. Kristallogr.* **199**, 49 (1992).
10. N. Khosrovani and A. W. Sleight, *Inorg. Chem.* in press.
11. V. Korthuis, N. Khosrovani, A. W. Sleight, N. Roberts, R. Dupree, and W. W. Warren, Jr., *Chem. Mater.* **7**, 412 (1995).