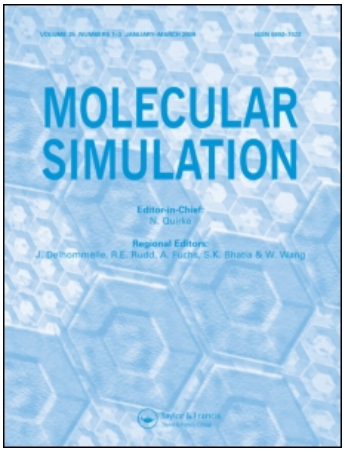

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Computer-Aided Topological Analysis of the Faujasite Lattice I: Exact Solution for Zeolite-X

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COMPUTER-AIDED TOPOLOGICAL ANALYSIS OF THE FAUJASITE LATTICE I: EXACT SOLUTION FOR ZEOLITE-X

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In order to study the possible configurations of Aluminum and Silicon atoms on a Faujasite lattice, two different methods of analysis are presented. The first method is based on the study of the physical properties of different lattice structures: the energy and the dipolar moment. The second one examines the topological properties of the configurations in order to count the inequivalent lattice structures. An original algorithm selects the configurations to be generated and compared in order to keep the computer time required at an acceptable level. The results from the two methods are compared and found to be in agreement.

In this paper we specialize our study to zeolite-X but the methods are general and can be applied to other types of lattices.

KEY WORDS: Zeolite-X, Löwenstein Rule, topological analysis.

1. INTRODUCTION

Faujasites are a class of the wide family of zeolites showing interesting properties for industrial applications: Faujasites are able to sorb in a selective way gases, vapours and liquids; to catalize cracking reactions; and to exchange cations.

One of the parameters affecting these properties is the aluminum content, expressed by the ratio r between the number N_{Si} of Si atoms and the number N_{Al} of Al atoms. It should be noticed that in general the knowledge of r does not define in unique way the lattice structure. Hence a theoretical study of the possible configurations is important in order to improve the understanding of the physical and chemical properties of this class of zeolites.

The aim of the present work is to analyze the topological features of the different configurations of Al atoms on the faujasite framework, and to compare these features with related information from the energy (E) and the dipolar moment (D). We plan to check if the couple (E,D) can discriminate among the different lattice structures those that are topologically inequivalent. We shall show that this is not the case, because "accidental" degenerations among different structures can occur. We shall specialize our study to the case of the more Al rich faujasite, zeolite-x, in which the ratio r ranges from 1 to 1.5. Effects coming from the presence of oxygen atoms are neglected.

Table 1 Fractional coordinates for a faujasite lattice (a = 25.076 Å) are reported [6]. The last column shows the next neighbour sites in the lattice after a translation of the FCC groups. In the present paper the Löwenstein Rule is applied also to this kind of contact (GLR).

vertex	*x/a*	*y/a*	*z/a*	*GLR*
1	0.12460	−0.05440	0.03720	–
2	0.12460	0.30440	0.21280	44
3	0.12540	−0.05440	0.21280	42
4	0.12540	0.30440	0.03720	43
5	0.03720	0.12460	−0.05440	–
6	0.21280	0.12460	0.30440	48
7	0.21280	0.12540	−0.05440	46
8	0.03720	0.12540	0.30440	47
9	−0.05440	0.03720	0.12460	–
10	0.30440	0.21280	0.12460	40
11	−0.05440	0.21280	0.12540	38
12	0.30440	0.03720	0.12540	39
13	−0.12460	0.05440	−0.03720	–
14	−0.12460	−0.30440	−0.21280	32
15	−0.12540	0.05440	−0.21280	30
16	−0.12540	−0.30440	−0.03720	31
17	−0.03720	−0.12460	0.05440	–
18	−9.21280	−0.12460	0.30440	36
19	−0.21280	−0.12540	0.05440	34
20	−0.03720	−0.12540	−0.30440	35
21	0.05440	−0.03720	−0.12460	–
22	−0.30440	−0.21280	−0.12460	28
23	0.05440	−0.21280	−0.12540	26
24	−0.30440	−0.03720	−0.12540	27
25	0.12460	0.03720	0.05440	–
26	0.12460	0.21280	0.30440	23
27	0.12540	0.03720	0.30440	24
28	0.12540	0.21280	−0.05440	22
29	−0.05440	0.12460	0.03720	–
30	0.30440	0.12460	0.21280	15
31	0.30440	0.12540	0.03720	16
32	−0.05440	0.12540	0.21280	14
33	0.03720	−0.05440	0.12460	–
34	0.21280	0.30440	0.12460	19
35	0.03720	0.30440	0.12540	20
36	0.21280	−0.05440	0.12540	18
37	−0.12460	−0.03720	0.05440	–
38	−0.12460	−0.21280	−0.30440	11
39	−0.12540	−0.03720	−0.30440	12
40	−0.12540	−0.21280	0.05440	10
41	0.05440	−0.12460	−0.03720	–
42	−0.30440	−0.12460	−0.21280	3
43	−0.30440	−0.12540	−0.03720	4
44	0.05440	−0.12540	−0.21280	2
45	−0.03720	0.05440	−0.12460	–
46	−0.21280	−0.30440	−0.12460	7
47	−0.03720	−0.30440	−0.12540	8
48	−0.21280	0.05440	−0.12540	6

2. THE MODEL

Following the ideas of Klinowski and coworkers [1], we choose as the basic building unit of the whole lattice two 24-vertices sodalite cages connected by an exagonal prism. This building unit, called a *double sodalite*, describes the whole crystal lattice through the translational symmetry operators related to a face-centered lattice. This choice is compatible with space groups Fd3 and Fd3m, describing the faujasite lattice [2]. In Table 1 we report the relative fractional coordinates of the 48 sites defining the double sodalite shown in Figure 1. Labelling an arbitrary site on the hexagonal prism as vertex number one, it is useful to label all other sites in such a way that any pair of vertices that correspond to the numbers from 1 to 24 are not next neighbours. We call the subset of vertices 1 to 24 the "black bush," and the complementary subset the "white bush." A possible choice of labels is also shown in Figure 1. This choice is in agreement with a description of the lattice utilizing the Fd3 space group in which the two bushes are not equivalent.

The configurations of Al atoms on the lattice are constrained by a requirement, known as Löwenstein Rule (LR), that forbids to two Al atoms to occupy two adjacent positions. The LR may be understood in terms of the tendency of the system to minimize the electrostatic repulsive interaction between Al^{3+} ions. In our approach the LR rule is globally imposed on the complete lattice. In order to give a precise prescription about the implementation of LR on the boundaries of the basic building unit we introduce the Ansatz that the Al distribution on the whole lattice is obtained from the double Sodalite using the symmetry operators (in our case the translational ones of the fcc lattice). Thus we imagine connecting every vertex of the double sodalite with connectivity three to a suitable vertex of the same structure that corresponds by translation to the fourth next-neighbour. The last column of Table 1 reports the contacts which are forbidden by LR. In this way periodicity effects are easily studied.

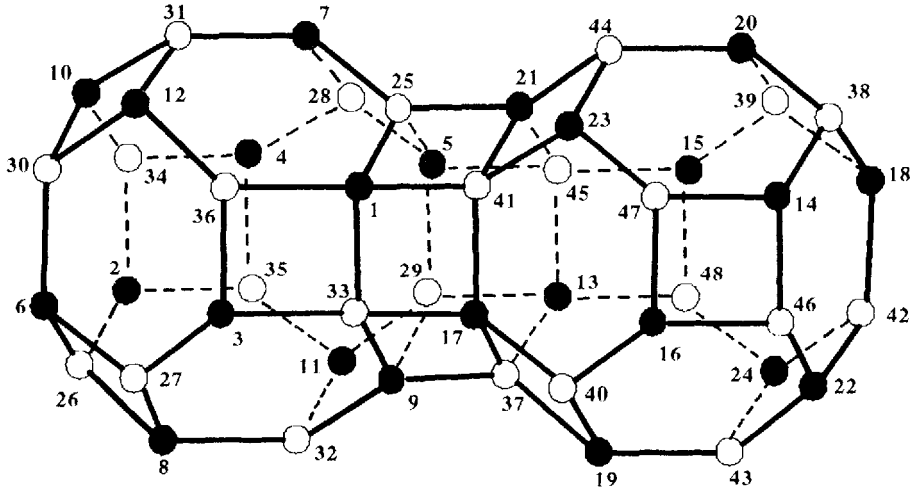


Figure 1 The double sodalite. The solution in the case $N_{Al} = 24$ and our choice for the labels of the sites are shown (Al atoms are represented as black balls).

We call the set of four next-neighbours of a given vertex just described the *dynamical next-neighbours* of that vertex.

This Global Löwenstein Rule (GLR) will result as a very strong and effective constraint in defining the physically admissible distributions of Al atoms on the lattice.

Our symmetry Ansatz and, consequently, the application of GLR are not universally accepted. An example of interpretation of the experimental data in which LR is imposed just on the 48 sites but not globally is reported in [3].

The physical signatures which were employed to classify the Al distributions are two: the topological energy E and the topological dipolar moment D. Following the elegant formalism adopted in [1], we compute the topological energy E by taking into account only four kinds of $Al^{3+} - Al^{3+}$ contacts, namely the ones shown in Figure 2. The corresponding contributions are, respectively

$$\varepsilon_1 = \frac{1}{\sqrt{2}} \qquad \varepsilon_3 \simeq 0.523549$$
$$\varepsilon_2 = \frac{1}{\sqrt{3}} \qquad \varepsilon_4 = \frac{1}{2} \tag{1}$$

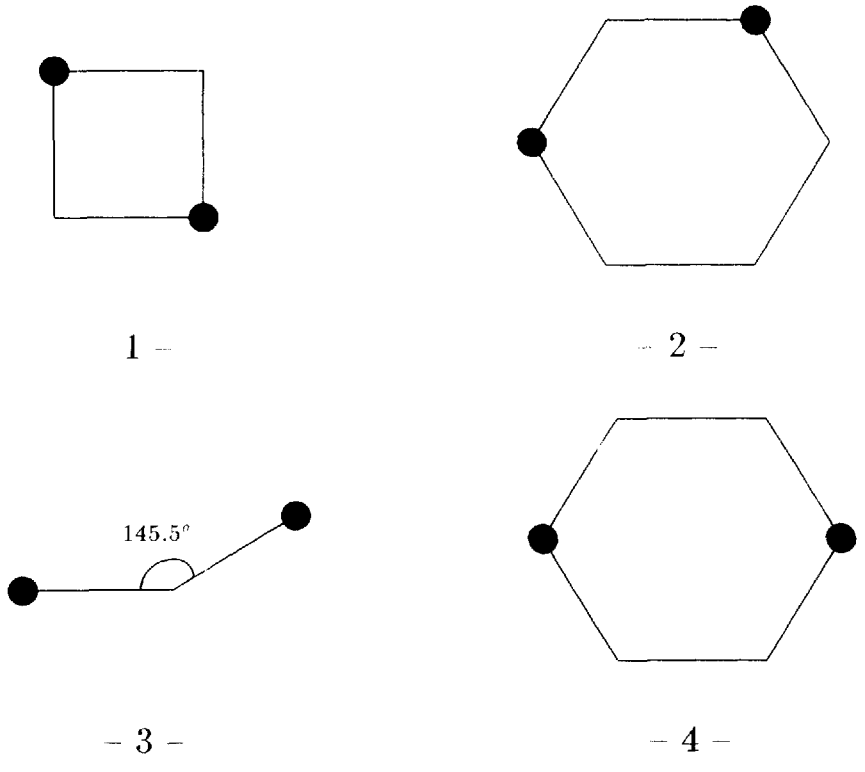


Figure 2 The four possible contacts considered in the present work.

The quantities $\{\varepsilon_i\}$ are dimensionless and universal, i. e. they are independent both of the fraction of electronic charge sitting on any aluminum vertex and from the cell parameters of the faujasite lattice.

The contribution given by ε_3 is an improvement of the Klinowsky Model and enters in the computation of E when we consider two next nearest neighbour Al atoms belonging to two different sodalite cages (an example is given by the pair 1-23 in Figure 1). It is interesting to notice that, in the infinite lattice, all the atoms are equivalent and every one of them possesses three type-1, four type-2, two type-3 and two type-4 contacts.

We represent a configuration on the double sodalite as a 48-digit binary number or, equivalently, as a 48-dimensional vector $\vec{c}$ whose components are 1 if we have an Aluminum on the corresponding vertex, or 0 if we have a Silicon atom. It is useful to build a 48 × 48 symmetric matrix M which contains the map of the contacts for each crystallographic site, in such a way that the energy E_i corresponding to the i-th Aluminum of the double sodalite is given by the formula

$$E_i = \sum_{j=1}^{48} M_{ij}\, c_j, \tag{2}$$

while the total energy of the given configuration is

$$E = \frac{1}{2} \sum_{i=1}^{N_{Al}} E_i\, c_i. \tag{3}$$

We stress that E contains not just the contribution of contacts of Al atoms inside the double sodalite, but also contacts with atoms of adiacent sodalite cages (divided by two because every contact of this type belongs to two different double sodalites), and thus it can be interpreted as the energy of the double sodalite imbedded in the infinite lattice. The vector $\vec{c}$ satisfies the obvious constraint $\|\vec{c}\|^2 \equiv \Sigma_i c_i^2 = N_{Al}$. Moreover, in our study the vector $\vec{c}$ is compatible with GLR.

In table 2 the structure of the matrix M is reported: the integers shown are the indices of the contribution ε_i contained in the corresponding entry of M; the use of this matrix greatly simplifies the system's energy evaluation. In general, there exist different configurations that are degenerate in energy. In order to distinguish among them, we introduce the dipolar moment D which gives informations about the degree of symmetry of the configuration. A nonzero value of the dipolar moment increases locally the possibility, generally shown by faujasite lattices, of hosting extra-framework cations [1].

The dipolar moment was computed with respect to sites I placed at the centers of the four exagonal prisms attached to a single sodalite cage. In general these sites exhibit the ability to host cations; see for example reference [4].

In evaluating the dipolar moments we computed the four contributions supposing the sites I as imbedded in a centrosymmetric environment that is obtained from the basic structure using the translations of fcc lattice. In this way we obtain four different vectors $\{\vec{\mu}_i,\ i = 1, \ldots, 4\}$, and the total dipolar moment D is defined as $D \equiv \Sigma_i \|\vec{\mu}_i\|$. Configurations with the same total moment D differ only in the fact that different sites I permute the local moments. In this analysis we define different distributions with the same value of E and D as *physically* equivalent. With fixed N_{Al}, this physical sorting of the configurations appears to be very powerful in reducing the number of inequivalent possible lattice structures.

Table 2 The M matrix. It shows the interactions of the vertices of Figure 1 with the other sites according to the convention: $1 = \varepsilon_1$, $2 = \varepsilon_2$, $3 = \varepsilon_3$, $4 = \varepsilon_4$.

vertex	*energy contributions*
1	0010202020020000130010300000404000000000000000000
2	0001020202200000000313010000004040000000000000000
3	1000020220020000310003010000040400000000000000000
4	0100202002200000000130103000040400000000000000000
5	2002001020201030000013000000000040400000000000000
6	0220000102023010000000310000000004040000000000000
7	2002100002020301000031000000000004040000000000000
8	0220010020200103000000130000000040400000000000000
9	2020200200101300103000004040000000000000000000000
10	0202022000001003130100000040400000000000000000000
11	0202200210003100030100000404000000000000000000000
12	2020022001000013010300004040000000000000000000000
13	0000130010300010202020020000000000000000040400000
14	0000003130100001020202200000000000000000004040000
15	0000310003011000020220020000000000000000004040000
16	0000001301030100202002200000000000000000040400000
17	1030000013002002001020200000000000000000000004040
18	3010000000310220000102020000000000000000000000404
19	0301000031002002100002020000000000000000000000404
20	0103000000130220010020200000000000000000000004040
21	1300103000002020200200100000000000004040000000000
22	0031301000000202022000010000000000004040000000000
23	3100030100000202200210000000000000004040000000000
24	0013010300002020022001000000000000004040000000000
25	0000000040040000000000000001202020020000100313000
26	0000000004400000000000000010020202200000300100013
27	0000000040040000000000000100020220020000013000031
28	0000000004400000000000000100020200220000003103100
29	4004000000000000000000002002000120201300000001003
30	0440000000000000000000002200010020200130000300l
31	4004000000000000000000020020100020200310000013O
32	0440000000000000000000022010002020310000000310
33	0000400400000000000000002020200200011003130000000
34	0000044000000000000000002020220001030910013O000
35	0000400400000000000000002022002010001.000310000
36	0000044000000000000000020200220100003103100000O
37	0000000000000000000040040000100313000001202020O2
38	0000000000000000000044000003001001300100202022O
39	0000000000000000000400400000130003101000202200Z
40	0000000000000000000044000000310310010002020022O
41	0000000000004004000000001300000010032002000120Z0
42	0000000000000440000000000013000030010220001002O2
43	0000000000004004000000000031000001302002010002O2
44	0000000000000044000000000310000000310022010002O2O
45	0000000000000004004000010031300000020202002000l
46	0000000000000000044000003001001300000202022000l0
47	0000000000000004004000001300031000002022002010O
48	0000000000000000044000000310310000002020022010O0

3. THE SYMMETRIES

In the present section we discuss the topological features of the double sodalite; this building block admits 48 symmetry operators, which are the products of the basic symmetry operations (2-, 3-, $\bar{3}$-, $\bar{4}$-fold axes; mirror plane m, and center of inversion) of Fd3m group. We numbered these operators in such a way that the first twenty-four leave the two bushes invariant, while the other twenty-four elements that complete the group exchange a "white" vertex with a "black" one and *vice versa*. Two different configurations of aluminum and silicon atoms on the double sodalite are said to be *topologically equivalent* if it exists an element of the symmetry group that transforms one of the configurations into the other.

It is natural to obtain a faithful representation of the symmetry group as a subgroup of the group of permutations of 48 objects, i.e. as square matrices Λ^{α}_{ij}, α, i, $j = 1, \ldots, 48$, such that

$$\Lambda^{\alpha}_{mn} = \begin{cases} 1 & \text{if the transformation } \alpha \text{ maps the } n\text{-th vertex on the } m\text{-th} \\ 0 & \text{otherwise} \end{cases}; \qquad (4)$$

this is called the *regular representation* of the group.

We obtained the matrices $\{\Lambda^{\alpha}\}$ and the multiplication table using a computer program, and we checked against possible errors that this table fulfills the requirements of group theory and (in a number of cases) that the product of two matrices reproduces the result of the composition of the corresponding transformations.

It is possible to check that, given any pair of vertices i and j on the lattice, it exists and it is unique the symmetry operator that maps the first site on the second one. This remark is extremely useful in building the topologically inequivalent configurations on the lattice because it is not necessary to generate and compare *all* the configurations on the double sodalite with given N_{Al}. For example, if we are studying the number of inequivalent configurations with 20 Al atoms on one of the bushes, we can reduce from $2 \cdot \binom{24}{20}$ to $\binom{23}{19}$ the number of configurations to be generated and compared by simply noticing that we can always choose the configurations in such a way that the first Al atom sits on the vertex (say) number one. The analysis of the topological features induced by GLR will help in order to perform an exhaustive search for all the possible inequivalent lattice structures.

4. TOPOLOGICAL PROPERTIES OF THE CONFIGURATIONS

As said before, our goal is to count the topologically inequivalent configurations made of N_{Al} Al atoms and $48 - N_{Al}$ Si atoms, $N_{Al} = 18, 20, 22, 24$, on the double sodalite in such a way that, in the infinite lattice, no pair of Al atoms are next neighbours (GLR rule). Thanks to GLR we can build an algorithm that is useful in order to avoid to generate an huge number of configurations that are obviously not allowed. From now on we introduce the convention to put the greater number of Al atoms on the black bush. Moreover, we shall indicate with N_w the number of Al atoms on the white bush; of course the number of Al atoms on the black bush will be $N_{Al} - N_w$. As will be clear in the following, the algorithm gives the values of N_w that are allowed by a certain value of N_{Al}, and we generate the configurations with fixed N_{Al} and N_w.

The $N_{Al} = 24$ ($r = 1$) case is very simple, because there exists just one inequivalent configuration on the lattice, say the one we obtain putting Al atoms on the vertices of the black bush and Si atoms on the others (this configuration is presented in Figure 1).

Consider now the $N_{Al} = 22$ ($r = 1.18$) case. We can prove that there are no possible configurations with one (or more) Al atoms on the white bush and twenty one (or less) Al atoms on the black one. This is easily shown because the GLR implies that one Al atom on the white bush requires four Si atoms on his dynamical next-neighbours (all belonging to the black bush); but in this way one can have a maximum of twenty Al atoms on the black bush, and we obtain a configuration with $N_{Al} = 21$. Hence we shall be interested in the case with one Al atom on the white bush and all the others on the black one ($N_w = 1$) starting with the $N_{Al} = 20$ case ($r = 1.4$).

If we put two Al atoms on the white bush ($N_w = 2$), we have to be careful because there are cases in which one or more Si atoms are next-neighbours of both the alumina. Anyway, a simple computer code shows that there exist configurations with two vertices on one of the bushes with 6, 7 or 8 different next-neighbours (obviously all belonging to the other bush), and hence we can have at most 18 Al atoms on the black bush if we have 2 of the same atoms on the white one. This means that we can find the first examples of these configurations in the $N_{Al} = 20$ case. This result is confirmed by experimental data: as long as the ratio r is near one, the distribution of Al atoms is bounded to sit on one of the bushes, being Fd3 the space group that describes this subset of the crystallographic positions (see for example [2]). On the contrary, when the ratio r is greater than 1.2 it is possible to describe the crystallographic structure of zeolite-X with the Fd3m space group, that does not distinguish between the two bushes [2].

Following this line of reasoning, it is possible to characterize the topological features of admissible configurations (restricted by GLR) on the double sodalite. In Table 3, the results for various values of N_w are shown. From this table it is apparent that in the case $N_{Al} = 18$ ($r = 1_{2\,3}$) we have configurations with zero to six Al atoms on the white bush, and hence with eighteen to twelve of them on the black one. The maximum value of N_{Al} that allows the same number of Al atoms on the two bushes is $N_{Al} = 16$ ($r = 2$). However, this case is beyond the scope of this paper [5].

Table 3 Topological properties of configurations with different numbers of Al atoms on the white bush: in the second column the minumum number of next neighbours is shown; in the third column the maximum number of Al atoms on the black bush is hence computed, and in the last column the highest value of N_{Al} that admits configurations with the given number of Al atoms on the white bush is presented.

Al atoms on the white bush	*min. number of next neigh.*	*Al atoms on the black bush*	*total number of Al atoms*	*interesting value of N_{Al}*
1	4	20	21	20
2	6	18	20	20
3	8	16	19	18
4	10	14	18	18
5	11	13	18	18
6	12	12	18	18
7	14	10	17	16
8	15	9	17	16

5. RESULTS

In this paper we introduced two different criteria in order to count the inequivalent configurations of Al and Si atoms constrained by the GLR on the double sodalite: the first one was based on physical considerations on the total energy and dipolar moment of the configurations, whilst the second one was based on the topological study of the different distributions of atoms on the lattice. In this section we present the results for both types of analyses, and we compare the results.

As stated in section 4, the case $N_{Al} = 24$ is trivially solved: it is sufficient to put all the Al atoms on the vertices of one of the bushes, and the Si atoms on the remaining sites (see Figure 1.). To this structure (and to its dual configuration, obtained via a reflection) there corresponds an energy $E = 65.7338$ and a vanishing value for the dipolar moment (the configuration is obviously centrosymmetric with respect to all the four positions introduced in section 2.).

The case $N_{Al} = 22$ presents $\binom{24}{22}$ configurations, that are grouped in 15 families characterized by the couple (E, D). The lowest energy in this case is $E = 54.7782$; it should be noticed that this system is highly degenerate in energy: there are indeed ten of these families (for a total of 168 configurations) with this value of E. In order to remove this degeneration we introduced the second parameter D, and in effect it will be shown in the following that these 15 families are the same that are obtained from the topological analysis.

The ten families with $E = 54.7782$ have dipolar moments ranging from $D = 0$ to $D = 1.8941$; among them we obtained also the two configurations reported in [1] for the case $r = 1.18$. Two of the remaining five families have $E = 55.4853$ and among them we find 12 configurations (a single family) with the maximum dipolar moment $D = 2.1479$ (see Figure 3.).

In the $N_{Al} = 20$ case with no Al atoms on the white bush there are 431 families labelled by different values of (E,D). We found 282 configurations with the minimum value of the energy $E = 43.8225$, and among them the moment ranges from $D = 0$ to $D = 2.1152$. The maximum value of the dipolar moment is, in this case, $D = 3.9737$, and it is possessed by a unique family of 24 elements with energy $E = 46.8391$ (Figure 4.).

Studying the cases with one or two Al atoms on the white bush we found respectively 20 and 2 configurations physically inequivalent, and increasing N_w we notice a systematic decrease of the energy due to the increasing of the mean distance among the alumina. As a matter of fact in the $N_w = 1$ case the minimum value of the energy is $E = 43.1443$; there are 8 families with this value of E, and among them the minimum and the maximum value of the dipolar moment are $D = 0.5067$ and $D = 1.9831$ respectively; the absolute maximum for D is $D = 2.4075$, to which corresponds a family of configurations with $E = 43.7990$. In the $N_w = 2$ case the two inequivalent configurations have the same energy $E = 42.4661$, but the values of the dipolar moment are different: $D = 0.6992$ (see Figure 5a) and $D = 1.3304$. The multiplicity g of the first structure is 24 and the one of the second configuration is 48. It should be noticed that both the minimum value of E and the maximum value of D decrease when N_w increases.

In this case the multiplicities of the two inequivalent configurations are easily understood: the only way to have $N_w = 2$ in the $N_{Al} = 20$ case is to put the two Al atoms on opposite sites of a square plaquette in the double sodalite; the two families

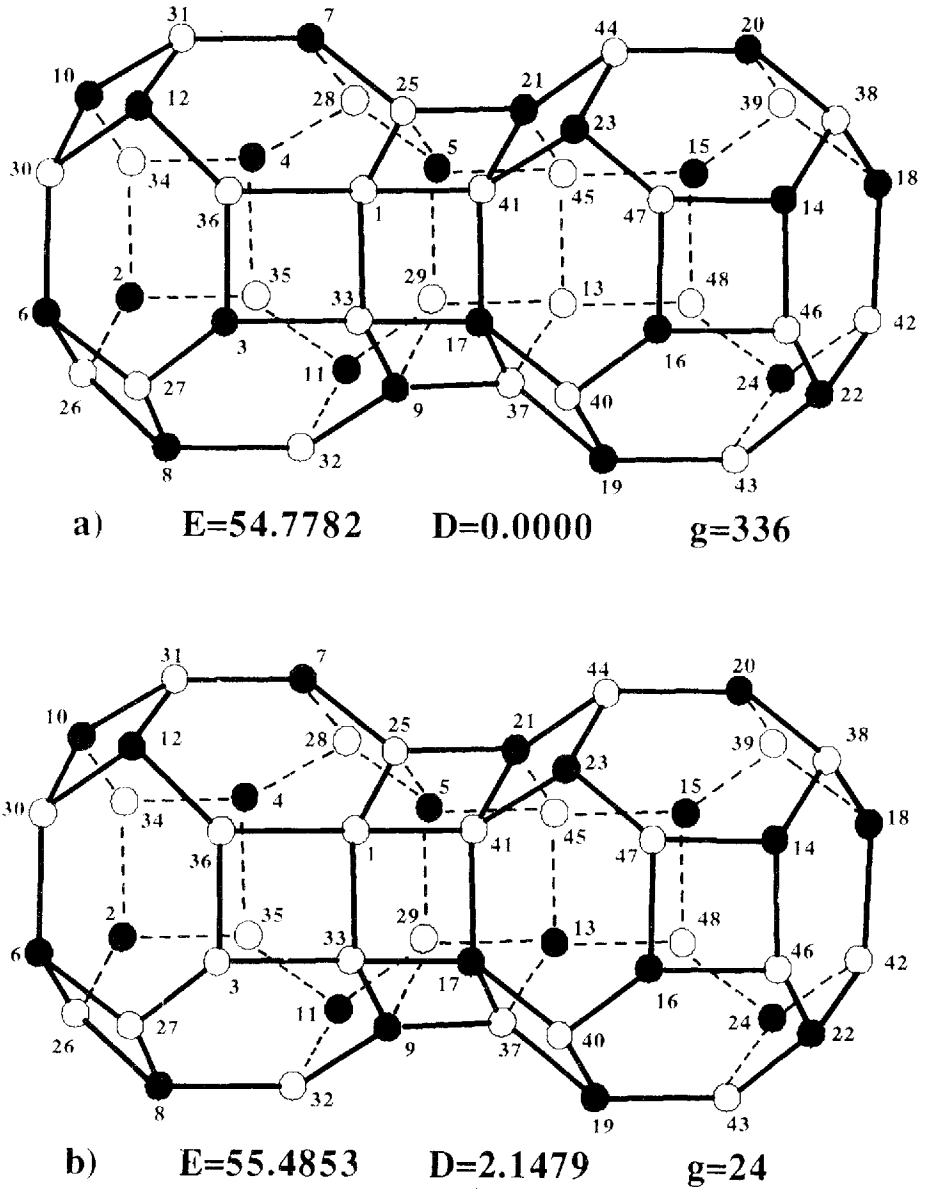
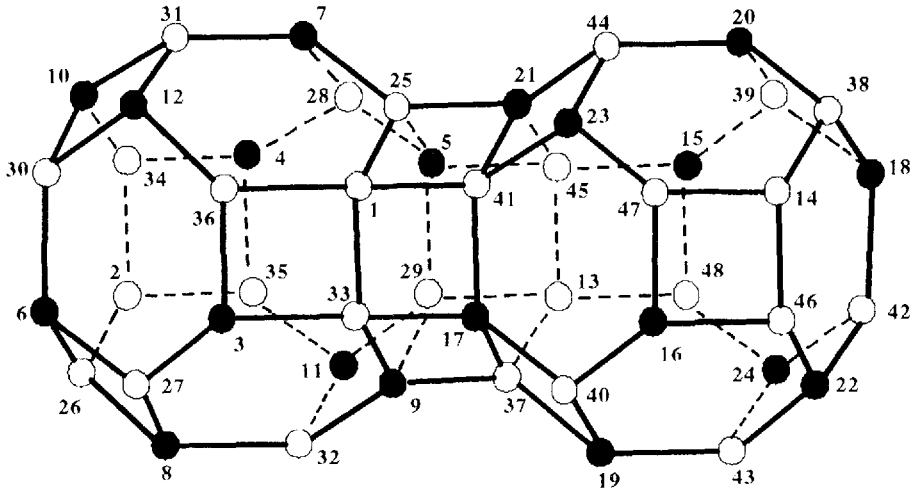


Figure 3 Minimum energy (a) and maximum moment (b) configurations for the case $N_{Al} = 22$. g represents the multiplicity of the configuration.

correspond to square plaquettes that belong to the hexagonal prisms and to the ones that are adjacent to the prisms; as a matter of fact, there are 24 square plaquettes of the first type (and hence 48 different configurations), and 12 square plaquettes of the second type (and hence 24 different configurations).



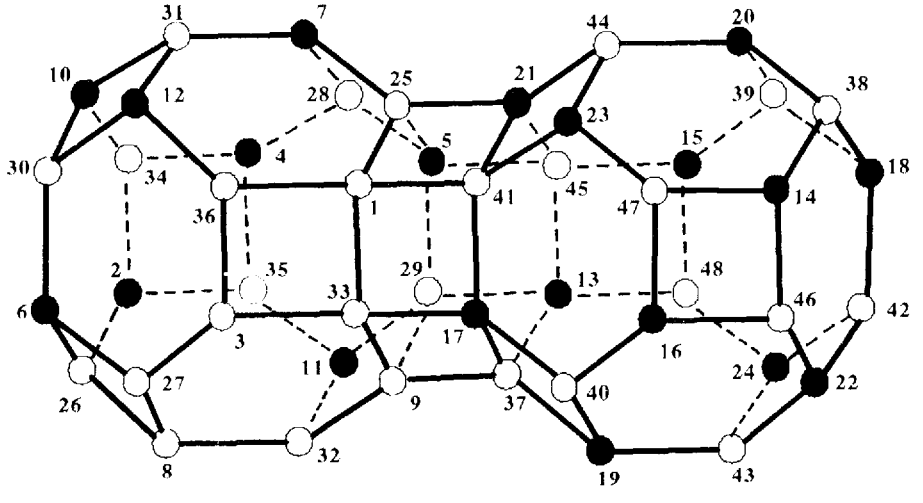
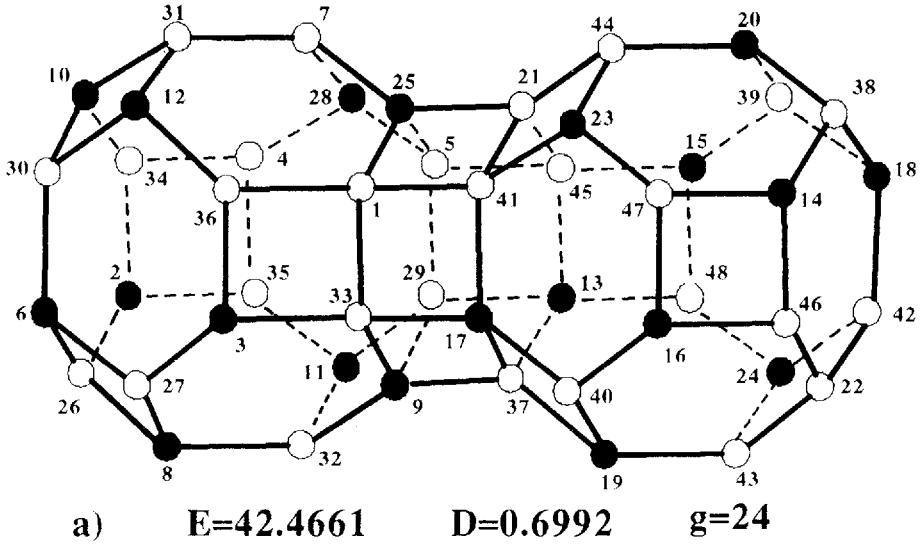


Figure 4 Minimum energy (a) and maximum moment (b) configurations for the case $N_{Al} = 20$, $N_w = 0$. g represents the multiplicity of the configuration.

We conclude with the $N_{Al} = 18$ case. This case is quite complicated because all the values of N_w from zero to six are allowed. With $N_w = 0$ there are 4809 different families; the minimum value of the energy is $E = 32.8669$, to which corresponds the dipolar moment $D = 0$. The maximum value of the moment is $D = 5.6380$. There



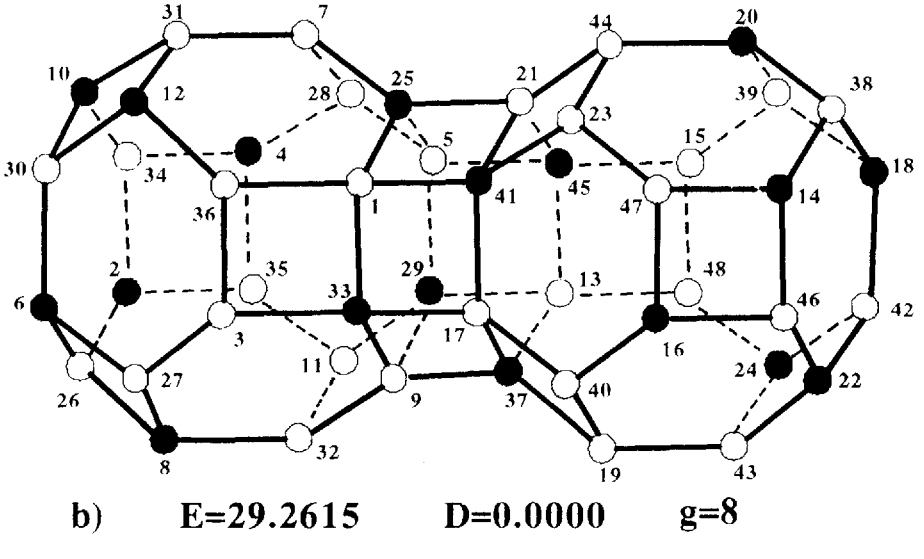


Figure 5 (a) Minimum moment configuration for the case $N_{Al} = 20$, $N_{u} = 2$. (b) Unique configuration for the case $N_{Al} = 18$, $N_{u} = 6$. g represents the multiplicity of the configuration.

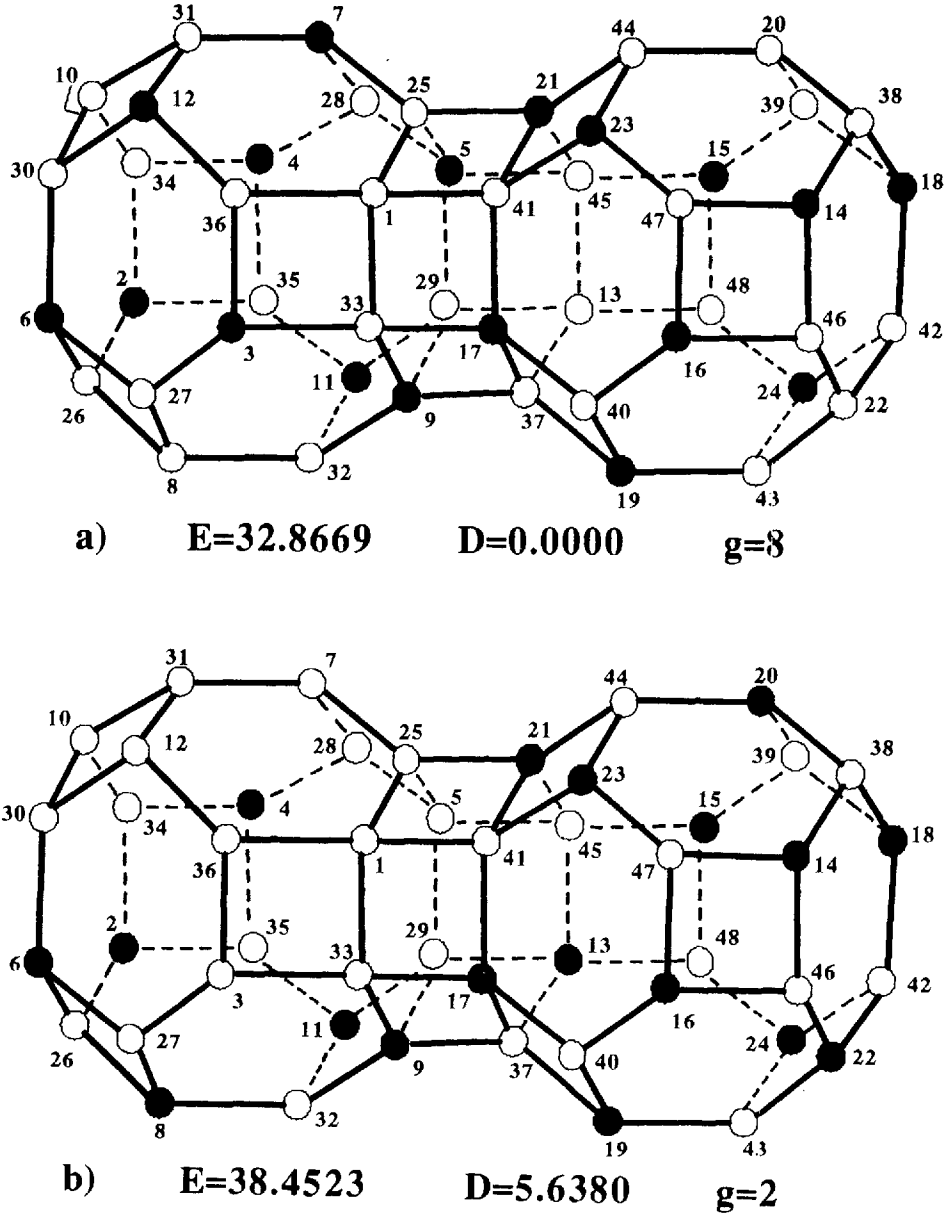


Figure 6 Minimum energy (a) and maximum moment (b) configurations for the case $N_{Al} = 18$, $N_w = 0$. g represents the multiplicity of the configuration.

is just one family of configurations with this value of D; the corresponding value of the energy is $E = 38.4523$ (see Figure 6). The results for the cases $N_w = 1, \ldots, 6$ are shown in Table 4: in the first column there is the value of N_w, in the second one the number of families for that given value of N_w, in the third one the minimum value of

Table 4 Main results for the energy and dipolar moments of the physically inequivalent configurations with $N_{Al} = 18$, $N_w = 1, \ldots, 6$. In the first column there is the value of N_w, in the second one the number N_f of families for that given value of N_w, in the third one the minimum value of the energy, in the fourth the corresponding value(s) for D, in the fifth one the maximum value of D found and in the last one the corresponding value of E.

N_w	N_f	E_{min}	D	D_{max}	E
1	1109	32.7122	1.7795 1.0292 0.5064 0.4851	4.1066	35.2825
2	290	31.6651	0.8909	3.0284	33.9731
3	64	31.0642	1.2692	2.3981	32.2189
4	12	30.4633	0.0	2.0342	31.9095
5	2	29.8624	0.40989	0.5187	30.1539
6	1	29.2615	0.0		

the energy, in the fourth the corresponding value(s) for D, in the fifth the maximum value of D found and in the last one the corresponding value of E. It is easy to recognize the same trends explained above: the minimum energy and the maximum dipolar moment at fixed number of Al atoms on the white bush are monotonically decreasing functions of N_w. Hence in the case $N_{Al} = 18$ the minimum value of E is attained by the configurations with $N_w = 6$ (see Figure 5b and Table 4), and the maximum value of D is attained by the family of configurations with $D = 5.6380$ that were mentioned before in the case $N_w = 0$.

To topologically solve the $N_{Al} = 22$ case we resort to the properties discussed in section 4; due to the fact that the only configurations allowed by the GLR in this case have all the alumina on the same bush, it is sufficient to start with 24 Al atoms on the black bush and then generate all the configurations obtained by substituting two Al atoms with Si atoms. Remembering that we are always free to put one of the new silicon atoms on vertex (say) number 1, we have to generate just 23 configurations. These configurations are then rotated using the symmetry operators and compared among themselves. The result is that there are only 15 different possible structures in the infinite lattice with 22 aluminum atoms and 26 silicon atoms. Hence it appears that the GLR is very effective in reducing the number of admissible configurations, and that by exploiting the symmetries it is possible to reduce by a huge amount the computer time required in building and comparing the configurations. in this non-trivial but simple case it is possible to compare in detail the results coming from this method with the ones presented above. If we generate all the $\binom{24}{22}$ possible configurations and we group in families all the distributions that are topologically equivalent, we get exactly the same grouping that we obtained from the energy and the dipolar moment. This complete agreement will be lost in the more complex cases $N_{Al} = 20$ and $N_{Al} = 18$, in which some "accidental" degenerations among configurations that are topologically inequivalent will occur. This fact will imply that in general the families of configurations obtained with the first criterion can be the union of different families coming from the topological sorting. Of course we checked that, as expected, all the configurations contained in the same topological family have the same value of E and D.

The same line of reasoning explained above can be followed in order to solve the

$N_{Al} = 20$ case. As said before, the larger amount of configurations comes when we put all the alumina on the same bush. In this case there are indeed 462 topologically inequivalent configurations. As special cases there are 20 inequivalent configurations with $N_w = 1$ and 2 more configurations with $N_w = 2$. Hence, we found 484 inequivalent configurations constrained by GLR in this case. As before, in the $N_w = 0$ case there are accidental degenerations in (E, D) among different families. In the cases with $N_w = 1$ and $N_w = 2$ the configurations are much more constrained by the GLR and no accidental degeneration can occur.

The $N_{Al} = 18$ case is conceptually identical but much more complicated. The number of configurations to be generated and compared in order to exhaust this case would be surely prohibitive without the remarks above about the symmetry properties and the ones induced by the GLR. As a result, we found 5683 inequivalent configurations with no Al atoms on the white bush, and moreover 1140, 295, 65, 12, 2 and 1 inequivalent configurations with, respectively, one to six Al atoms on the white bush. The total number of topologically distinguished configurations in this case is hence 7198. Once more, the number of the families of configurations with different values of (E, D) is lower. It is apparent from Table 4 that in the more constrained cases ($N_w = 4, \ldots, 6$) the agreement between the two methods is perfect. Needless to say, this remark is not only important in order to emphasize the compatibility between the two approaches, but also in order to display the absence of errors in coding the methods.

6. CONCLUSIONS

In this paper we presented two different methods to count the number of distinguished configurations of N_{Al} Al atoms and $(48 - N_{Al})$ Si atoms on a faujasite lattice taking the Global Löwenstein Rule into account.

The first one analyzes the configurations looking for different values of the couple (E, D); in this way we group the configurations in families that are called *physically inequivalent*. The second one exploits the symmetry properties of the lattice in order to obtain the set of the *topologically inequivalent* configurations.

The first method is much faster than the second. The second approach is designed to count the number of "intrinsically"different lattice structures. A major drawback of this method is the large computer time required to generate all the "interesting" configurations and to transform them using a representation of the symmetry operators in order to discard all the configurations that are not independent. Our study indicates, however, that accidental degenerations in (E, D) are possible.

The two methods are interesting because they are applicable to any other lattice structure without major changes (provided that the number of configurations to be checked is not too large). An approximate version of the first method, relying on Monte Carlo algorithms, is under study in order to obtain some results also in cases (such as zeolite-Y) in which the exhaustive study is too lengthy [5].

The results from the first method required a total of ten hours on a RT-IBM computer. For the second method we needed roughly fifty hours on a Digital VAX-750 computer. All the computations were performed after the developement of a set of original computer codes, written independently by the two authors as a further check against possible errors.

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References

[1] J. Klinowski, S. Ramdas, J.M. Thomas, C.A. Fyfe and J.S. Hartman, A Re-Examination of Si, Al Ordering in Zeolites NaX and NaY, *J. Chem. Soc; Faraday Trans; 2*,**78,** 1025–1050 (1982).
[2] E. Dempsey, in Molecular Sieves, *Soc. Chem. Ind.*, London, 1968, page 293.
[3] M.T. Melchior, D.E.W. Vaughan and A.J. Jacobson, Characterization of the Silicon-Aluminum Distribution in Synthetic Faujasite by High-Resolution Solid State ^{29} Si NMR, *J. Am. Chem. Soc.*, **104,** 4859–4864 (1982).
[4] W.J. Mortier, Compilation of Extra-Framework Sites in Zeolites, Butter & Co. Pub. Ltd., UK 1982.
[5] G. Melegari, O. Ori, work on Zeolite-Y in progress.
[6] R.A. Jackson, private communication.