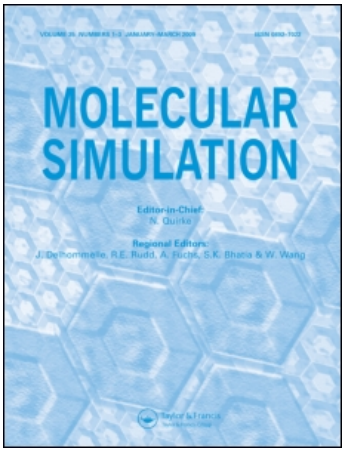

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Computer-aided Topological Analysis of the Faujasite Lattice II: Monte Carlo Solution for Zeolite-Y

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COMPUTER-AIDED TOPOLOGICAL ANALYSIS OF THE FAUJASITE LATTICE II: MONTE CARLO SOLUTION FOR ZEOLITE-Y

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In this paper we extend to the case of Zeolite-Y the topological analysis of the Aluminum distributions of the Faujasite lattice proposed in a previous paper. Here the exact counting of all the inequivalent configurations is complicated by the huge number of possible structures, but the physically relevant distributions can be found by using a Monte Carlo method which turns out to be very efficient. We compare, whenever possible, the Monte Carlo results with the exact countings, and in all these cases we find a perfect agreement. Thus the approach seems to be applicable to the study of every class of Zeolites. In the first two sections the method is introduced, and in the third one the relevant results for the Zeolite-Y are presented and discussed.

KEY WORDS: Zeolite-Y, Löwenstein rule, topological analysis, Monte Carlo algorithm.

1. INTRODUCTION

In a previous paper [1] we proposed a systematic study of the possible configurations of Al and Si atoms on a Faujasite lattice. In that work we solved exactly the case of Zeolite-X, in which the ratio r between the number N_{Si} of Silicon atoms and the number of N_{Al} of Aluminum atoms ranges from 1.0 to 1.5. In the present work we discuss the case of Zeolite-Y, that is the Aluminum-poor Faujasite structure.

In Figure 1 the super-cage characterizing the Faujasite structure is presented. Several chemical processes take place into this cavity : selective absorption (Zeolites are known in general as *molecular sieves*), catalysis of cracking reactions, exchange of cations, and so on [2]. All these processes are strongly influenced by the profile of the electrostatic potential inside the cavity produced by the fractional charges of the tetrahedral sites and by the extra-cations present in the lattice. Hence the knowledge of the ratio r does not describe the Zeolite in an accurate way, and more information about the topological structure of the different distributions of Aluminum and Silicon atoms is needed. X-ray crystallographic analysis is not able to distinguish between Aluminum and Silicon atoms on a Zeolite lattice, and theoretical results become thus very significant to help the analysis of other types of experimental data (for a NMR approach to the problem see for example reference [3]).

Two physical parameters were considered in reference [1], *i.e.* the topological energy per double Sodalite E and the dipolar moment D: the couple (E, D) is an effective topological index discriminating among different configurations with fixed r and is independent of both the lattice parameter and the fractional electronic charge.

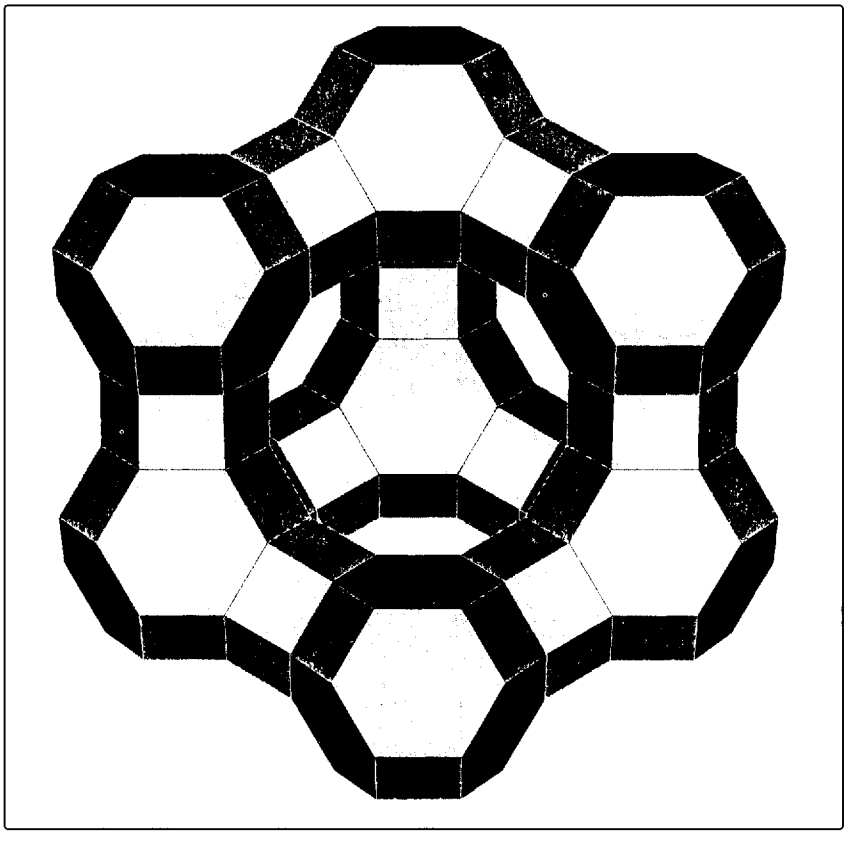

Figure 1 The Faujasite's super-cage.

The dimensionless definition of E is given (according to references [1, 3]) in equation (1) (to follow). The dimensionless dipolar moment D was computed (in terms of fractional coordinates [1]) with respect to four privileged observers corresponding to sites I placed at the centers of the four exagonal prisms attached to a single Sodalite cage. In general these sites are capable to host cations (see for example reference [4]), and a nonzero value of the dipolar moment increases locally the possibility, generally shown by Faujasite lattices, to host extra-framework cations [3]. Hence we are interested in characterizing different configurations on the Faujasite lattice according to the corresponding values of E and D because they measure, respectively, the abundancy of the configuration and its efficiency in hosting cations.

The possible distributions of Aluminum atoms on the infinite Faujasite lattice were obtained from a given configuration on the Double Sodalite (figure 2) via the translational symmetry operators of the f.c.c. space group. These distributions are constrained by the Global Löwenstein Rule (GLR), which states that two Aluminum atoms on the infinite lattice can not be next neighbours. We were able to count all the possible topologically inequivalent configurations on the infinite lattice for the Zeolite-X with a given ratio r (or, equivalently, with a given number of Aluminum atoms N_{Al}).

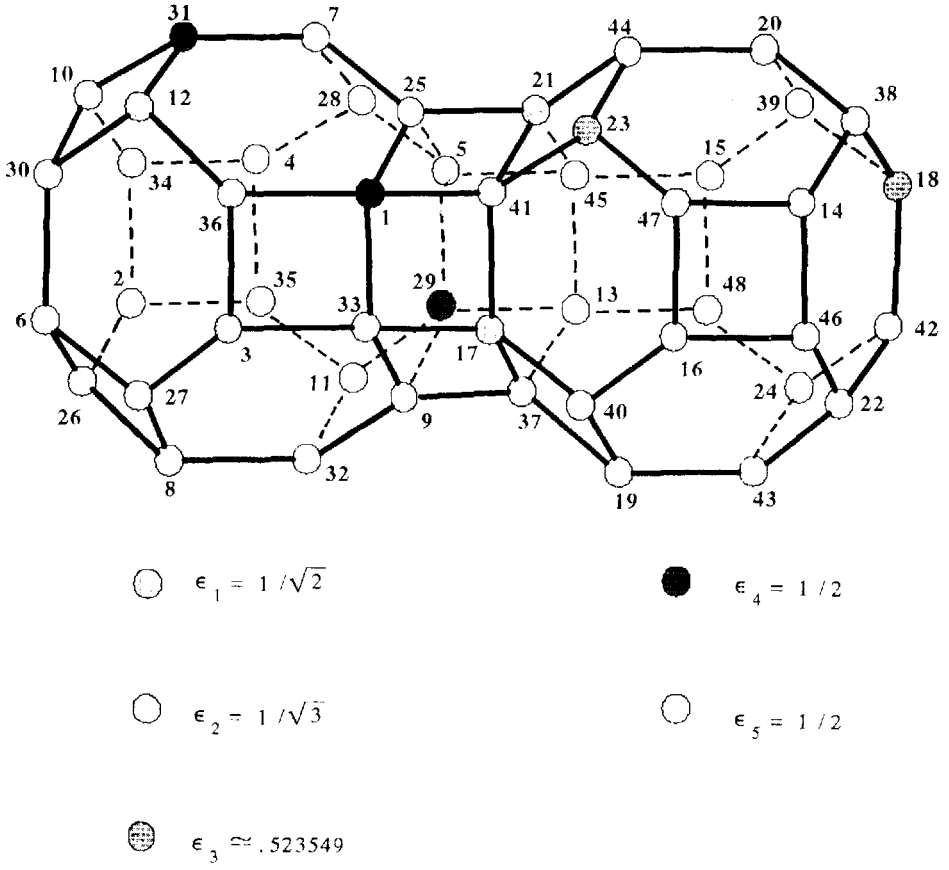

Figure 2 The Double Sodalite. Following ref. [1], the topological contacts $\{\varepsilon_i, i = 1, \ldots, 4\}$ represent the contributions to the energy E due to site 1 (see formula (1)). The dipolar moment D is obtained by summing the four contributions related to the sites I placed at the center of the hexagonal prisms surrounding the single Sodalites.

In the case of Zeolite-Y the low number of Al atoms does not guarantee that the distribution of these atoms on the infinite lattice could be obtained by symmetry from a given configuration on the Double Sodalite. In the present paper we maintain this last Ansatz to have a simple role that allows us to take into account GLR in the boundness of the Double Sodalite, but in this way only a subset of the possible configurations on the infinite lattice is studied. The low number of Al atoms makes GLR not so effective in reducing the number of the possible distributions on the lattice; thus the number of configurations to be generated and sorted to solve exactly the case of Zeolite-Y would be too large even for a big computer. For example, in the case $N_{Al} = 16$ the number of possible configurations with $N_w = 0$, which is a small subset of the total number of configurations, is $\binom{24}{8} \simeq 7.3 \cdot 10^5$. However, relevant information is related to the values of E and D, and it can be obtained in a more selective and efficient way.

The aim of the present work is to develop a Monte Carlo (MC) method to select

the configurations with minimum energy and with maximum dipolar moment with $N_{Al} = 16, 14, 12$ (Section 2). As will be shown, a partial check of the Monte Carlo results is still possible, and all the results that can be obtained in an exact way are in agreement with the ones obtained via Monte Carlo.

2. MONTE CARLO ALGORITHM

As explained in reference [1], it is useful to represent a given configuration on the Double Sodalite as a 48-dimensional vector $\vec{c}$ with components $c_i = 1$ if we have an Al atom on the i-th vertex, and $c_i = 0$ otherwise. This choice allows a very easy computation of the topological energy and the dipolar moment of the configuration corresponding to $\vec{c}$. In particular E is given by the formula

$$E = \frac{1}{2} \sum_{i,j=1}^{48} c_i M_{ij} c_j, \tag{1}$$

where the matrix M is given in reference [1]. By using this matrix it is not necessary to check if two given Aluminum atoms are interacting or not, and computations are much faster. In fact it is known [5] that the use of bit maps in a Monte Carlo code improves the updating and managing procedures of the relative positions (and hence of the energies) of the particles.

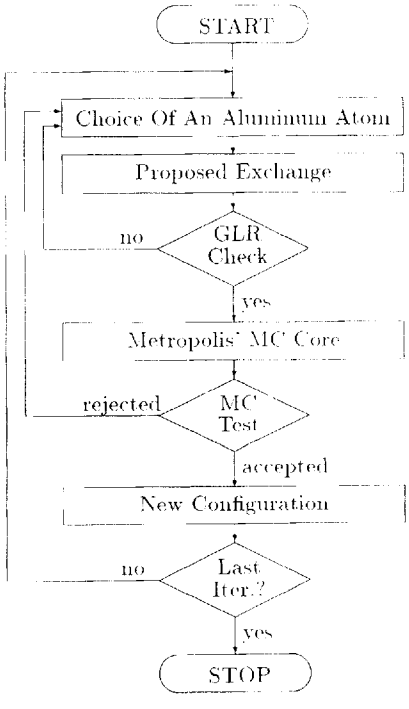

Figure 3 The conceptual flow chart showing the structure of the computer codes that perform the MC search for physically interesting configurations.

By keeping N_{Al} fixed, it is possible to look for the configuration with minimum E and for the one with maximum D using the well known Metropolis algorithm [6]. By denoting with E_M the Metropolis' energy (ΔE_M is minus the logarithm of the acceptance probability), the first search is done with $E_M = E$ while the second one is done with $E_M = -D$.

It is useful to distinguish between the subset of vertices 1 to 24 in Figure 2 (the "black bush") and the complementary subset (the "white bush") [1]. These two bushes are connected by symmetry operators (mirror planes); in order not to count equivalent configurations twice, we use the conventions to describe any configuration, with N_{Al} fixed, in such a way that the majority of the *Al* atoms lie on the black bush. Hence the number N_w of *Al* atoms on the white bush is a measure of the balance of the configuration and it strongly affects E and D (the value $N_w = N_{Al}/2$, which corresponds to the maximum balance, was forbidden by GLR in the Zeolite-X case, but it is allowed starting from $N_{Al} = 16$).

The general structure of the MC computer program is sketched in Figure 3: starting from a given configuration an *Al* atom is (sequentially) chosen and a possible exchange of position with a *Si* atom is proposed (thus the total number of *Si* and *Al* atoms is conserved). At this point there is a hierarchy of tests: first of all one checks whether the proposed configuration satisfies the GLR constraint or not; if the answer is yes the usual Metropolis' MC test is performed, otherwise a new *Al* atom is chosen and the procedure restarts.

We developed two different criteria to perform the exchange of positions between an *Al* atom and a *Si* atom on the Double Sodalite. The first one is devised in order to optimize the probability of increasing the number Nw of Al atoms on the white bush: the position of an Al atom is exchanged with the one of a next neighbour Si atom; this exchange involves the four next neighbours of a given vertex as embedded in the infinite lattice: periodicity effects are easily taken into account through the knowledge of the connectivity matrix. We showed in reference [1] that the minimum of the energy seems to be attained by configurations with N_w maximum, because in this case the Aluminum density decreases. This result holds also in Zeolite-Y case, and the first exchange criterion is very effective in driving the system towards the configuration with minimum energy if we start from a configuration with $N_w = 0$. The second criterion for moving Aluminum atoms on the Double Sodalite is not affected by the value of N_w: one simply chooses the Silicon atom at random, and then the hierarchy of tests is performed; this technique is not so effective if one is looking for the minimum energy, but it is very fast to find the maximum dipolar moment, which corresponds to configurations with $N_w = 0$.

This last remark allows writing a Monte Carlo code for searching the configurations with maximum dipolar moment which completely neglects the vertices of the white bush. Needless to say, the method is very fast, but it is tailored on this particular problem and is not expected to be easily generalizable. The three methods converge to the same solutions.

In order to study the presence of local minima we introduced a temperature factor in the definition of the acceptance probability p_a in the Metropolis' algorithm through the following term:

$$p_a = \exp - \frac{\Delta E_M}{T}, \tag{2}$$

with E_M given by E or $-D$. A value of T greater than 1 increases the probability of

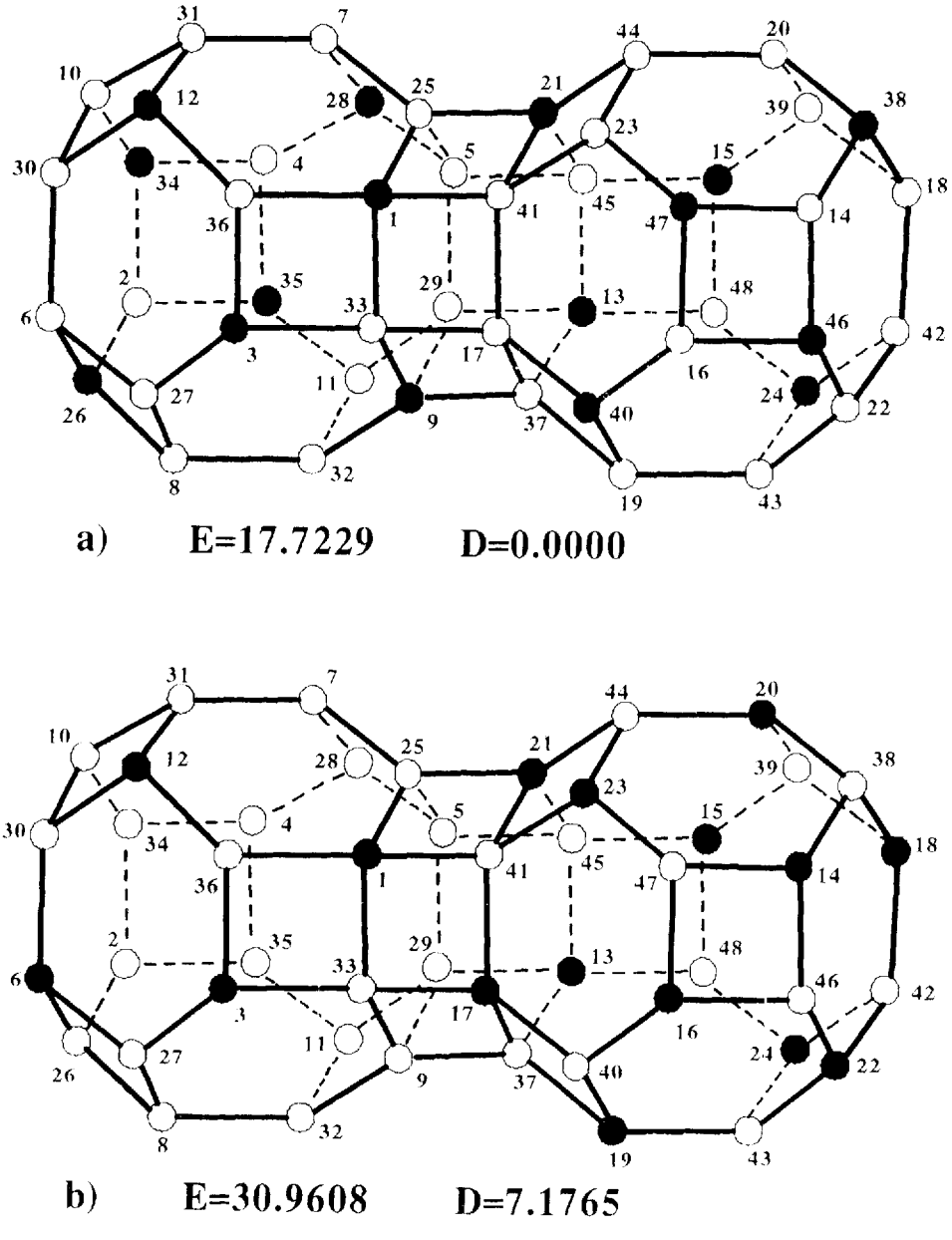

Figure 4 Minimum energy (a) and maximum moment (b) configurations for the case $N_H = 16$; the configuration (a) has $N_w = 8$, while (b) has $N_w = 0$.

generating energetically unfavoured configurations; this increases the probability of leaving some false minimum and allows a wider exploration of the shape of the E_M hypersurface. To look for different attraction zones we tried different starting values of T and different starting configurations. Then we lowered the temperature in order to converge to the local minimum. In all cases the extremal values of E and D were the same we found using simply $T \sim 1$. This supports our belief that the E_M hypersurface is globally convex.

3. RESULTS

In this paragraph the results of the Monte Carlo search for the minimum value of E and the maximum value of D in the cases $N_{\mathrm{Al}} = 16, 14, 12$ are presented and compared (when possible) with the exact topological solutions.

In the case $N_{Al} = 16$ the minimum value of E is $E = 17.7229$ and it is attained by a single family of centrosymmetric configurations with $N_w = 8$ (Figure 4a). The maximum value of the dipolar moment is $D = 7.1765$ which is attained by a family of equivalent configurations with $E = 30.9608$ and $N_w = 0$ (Figure 4b). We performed a systematic search in the case $N_w = 0$ using the (E, D) method explained in reference [1], and we solved exactly the case $N_{Al} = 8$ using the topological method. In both cases we found exactly the same results presented above. It is interesting to notice that these two checks required several hours of CPU time on a DIGITAL WS3200 MicroVAX, while the Monte Carlo search required just a few minutes.

The configuration presented in Figure 4a has intrinsic multiplicity $g = 6$. This means that there are six apparently different distributions with the same pair (E, D) which are connected by one of the 48 operators of the symmetry group Fd3m characterizing the Faujasite lattice. The multiplicity can be found by using an appropriate computer code that, starting from a configuration generated by MC, multiplies it by the set of matrices $\{\Lambda^\alpha, \alpha = 1, \ldots, 48\}$ which constitute the regular representation of the symmetry group, and selects non identical configurations. Using the same method the multiplicity of the configuration in Figure 4b is $g = 48$. With the set of operators described above it is always possible to transform a MC-generated structure in such a way as to obtain a distribution on the Double Sodalite with an Aluminum atom on the vertex number one, as shown in Figures 4–6.

In the case $N_{\mathrm{Al}} = 14$ the situation is quite different: indeed we have four inequivalent configurations with the same minimum value $E = 12.5851$ and dipolar moments ranging from $D = 0$ to $D = 1.7794$. In this case we found some configurations with minimum energy and N_w lower than the maximum allowed; as a matter of fact, two of the configurations have $N_w = 7$ but two more configurations with minimum energy have $N_w = 6$. In Figure 5a we present the configuration on the Double Sodalite with the maximum value of D among the ones with minimum energy (the multiplicity of this configuration is $g = 48$ and N_{w} is equal to 7), and in Figure 5b the centrosymmetric configuration with $N_w = 6$ and $g = 24$ is shown. Once more, the same result is found also with the exact topological solution of the cases $N_{\mathrm{w}} = 6$ and $N_w = 7$. In our opinion this extra degeneracy is due to the short range of the interactions $\{\varepsilon_i\}$ shown in Figure 2. When we have a low density of Aluminum atoms this short range produces a lack of information about the topology of the Al distribution. We tried to solve this degeneracy by introducing a new contact, shown as ε_5 in Figure 2 (the two *Al* atoms involved are at the same distance as the two atoms

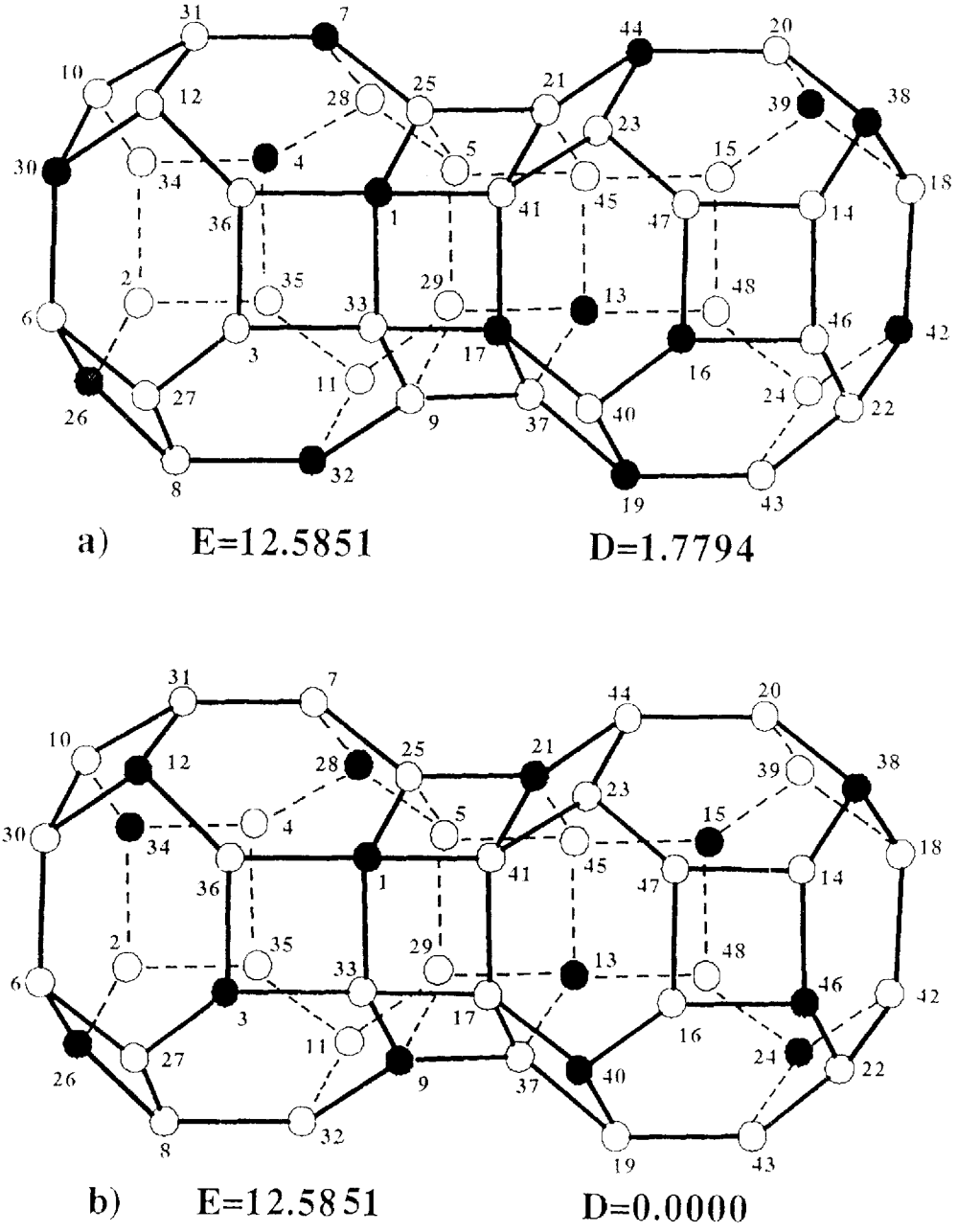

Figure 5 Two minimum energy configurations for the case $N_w = 7$ and corresponds to the maximum value of D among the configurations with minimum energy. In (b) the centrosymmetric configuration with $N_w = 6$ is shown.

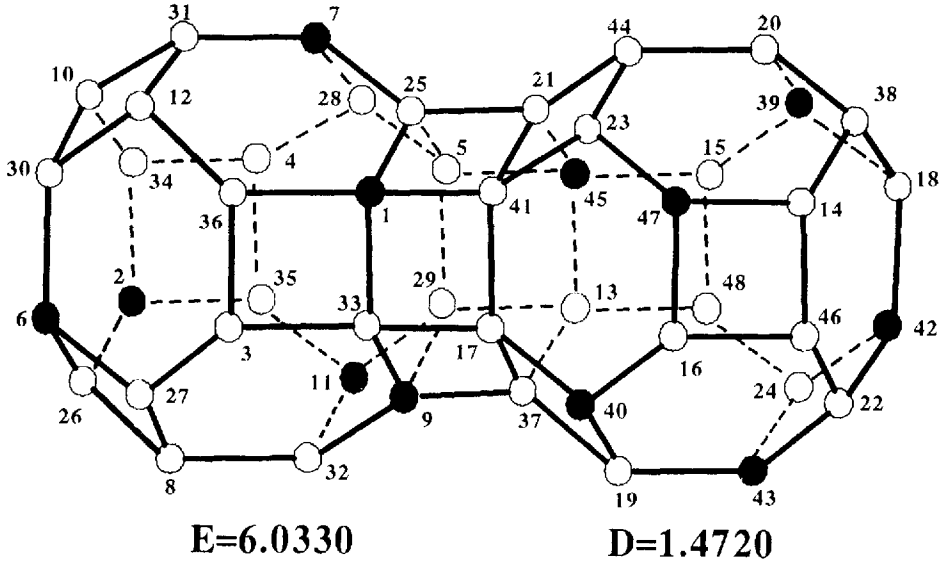

Figure 6 The unique configuration with minimum energy in the case $N_{Al} = 12$.

involved by contact ε_4), but at least for the configurations with minimum energy the contact ε_5 never contributes and hence the degeneracy is not removed. This problem is equivalent to finding a (hopefully) non-degenerate topological index for the Faujasite lattice. At present the search of topological indices for infinite three-dimensional lattices with minimum degeneracy is in progress [7] (for an introduction to the one-dimensional case see, for example, reference [8]).

In the case of the Zeolite-X we found that the configurations with maximum dipolar moment have an energy that is (in the case $N_{Al} = 18$) at most 30% greater than the minimum value. Even in the case $N_{Al} = 16$ we find now that the energy of the configurations with maximum dipolar moment is roughly twice the minimum value of E (see for comparison Figure 4). The same phenomenon is still more enhanced in the cases $N_{Al} = 14$ and $N_{Al} = 12$; as a matter of fact, with $N_{Al} = 14$ the family of configurations with maximum dipolar moment is characterized by the pair ($E = 23.7288$, $D = 8.7399$), and in the case $N_{Al} = 12$ we found a maximum dipolar moment configuration with ($E = 18.0991$, $D = 10.3923$). If the energy of a given configuration is supposed to measure the probability of finding it in the crystal, it is clear that the configurations with maximum D have a doubtful physical meaning; in other words, these very peculiar Aluminum distributions correspond to a situation in which all the Alumina are on the same Sodalite ($N_{Al} = 12$) or to a configuration with twelve Alumina on one Sodalite and the two remaining *Al* atoms in adjacent positions on the second Sodalite ($N_{Al} = 14$). In both cases we obtain a structure where the Alumina are concentrated in such a way as to maximize the density on a subset of the basic building block, and this situation is physically not stable because relaxation phenomena are expected to happen.

From the theoretical point of view the search of configurations with the maximum value of D is an interesting problem in itself. However, for practical applications it is perhaps more important to look for configurations that are termodynamically fa-

voured and at the same time very efficient in hosting cations. For this reason we prefer to present in Figure 5 the configuration with maximum dipolar moment related to the minimum value of the energy (in the case of $N_{Al} = 16$, corresponding to Figure 4, the minimum energy structure is unique, and hence this possibility does not exist). Accordingly, in Figure 6 only the structure of Zeolite-Y with minimum energy for the case $N_{Al} = 12$ is shown. The configurations with maximum D is very simple and it was already described above.

As in the case $N_{Al} = 16$, we generated all the configurations with $N_w = 0$ also in the cases $N_{Al} = 14$ and $N_{Al} = 12$, searching for the maximum dipolar moment. These scannings confirm the MC results presented above, and it is extremely reasonable that these two configurations should give the maximum value of D for their value of N_{Al}. We remark, however, that our MC procedure with $E_M = -D$ finds the configurations with maximum dipolar moment very quickly.

Coming back to the case $N_{Al} = 12$, we found a unique family ($g = 12$) of configurations with the minimum value of energy $E = 6.0330$; a dipolar moment $D = 1.4720$ (Figure 6) corresponds to this configurations. In spite of the low number of *Al* atoms the MC procedure does not produce configurations with the same energy and different values of D or N_w, as happened for example in the $N_{Al} = 14$ case. In order to investigate this surprising feature, we have performed a systematic search for other configurations with the same E by generating all the configurations with $N_{Al} = 12$ and $N_w = 5, 6$, and this search confirmed the MC result. It is interesting to notice that in this case configurations exist with *Al* atoms that are energetically isolated (*i. e.* the interaction matrix does not connect these atoms with any of the other Alumina in the infinite lattice), but the configuration in Figure 6 has no non-interacting Alumina: this means that, for $r \leqslant 3$, the only way to have an isolated atom is to group the remaining ones with high density in a complementary part of the lattice; thus the total energy in this case turns out to be greater than the minimum value.

4. CONCLUSIONS

In this work we proposed a Monte Carlo method to search for configurations with interesting physical properties among the possible distributions of *Al* and *Si* atoms on the Faujasite lattice in the case of Zeolite-Y. The presence of GLR and the periodicity of the lattice brings to a hierarchy of tests to be performed to check both the fulfilment of the constraints and the Metropolis' condition. In the search for the minimum energy, the GLR constraint allows avoiding the testing of a large number of energetically unfavoured configurations where two *Al* atoms are next-neighbours.

We obtained rather easily the configurations with minimum energy E and the ones with maximum dipolar moment D. We found a perfect agreement between the MC predictions and the exact results where a comparison was possible. In every case, the MC results were obtained using CPU times lower than those required by the topological exact method by two or three orders of magnitude, and computer codes much simpler. The MC approach relies on the knowledge of the connectivity matrix and of the interaction matrix M of the lattice; for this reason the use of this pair of topological indices (or of any improvement of them) and the MC search are generalizable to other binary inorganic lattices with minor modifications.

Crystal modelling results can help in understanding the physical content of the

topological indices, and *vice versa* our method can provide a set of privileged input configurations for crystal modelling calculations.

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