

Lattice Energy Minimization as a Complementary Technique to Refine Structures Obtained by High-Resolution Electron Microscopy

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Received July 11, 1983; in revised form September 27, 1983

The lattice energy minimization (L.E.M.) technique is a useful tool to refine structure when the sample is not available in large quantities as may be the case when observed by electron microscopy. L.E.M. has been applied to $\text{Na}_2\text{Ti}_3\text{O}_{19}$, a structural model of which had been given by Y. Bando, M. Watanabe, and Y. Sekikama, *Acta Crystallogr. B* **35**, 1541-1545 (1979); *J. Solid State Chem.* **33**, 412-419 (1980). Correct positions for the sodium ions have been found and the coordinates of the titanium Ti^{4+} and oxygen O^{2-} ions refined by minimizing the forces acting on these ions. Coordinates calculated by that method represent a considerable improvement compared to the starting set. Furthermore it is shown that the description of $\text{Na}_2\text{Ti}_3\text{O}_{19}$ in the $C2/m$ space group can only be an average since the Na ions respect only partially that symmetry.

1. Introduction

Lattice simulation techniques have been applied recently to structural studies of several oxides and bronzes such as $\text{TiO}_2(\text{B})$, $\text{VO}_2(\text{B})$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$, and $\text{Na}_2\text{Ti}_3\text{O}_7$ (Catlow *et al.* (1)) as well as minerals such as silicates and perovskites (Parker *et al.* (2)).

The method assumes that a "trial" model (frequently an ideal model) is known or may be proposed; such models are usually based on regular octahedra or tetrahedra, e.g., TiO_6 or SiO_4 polyhedra. Computational effort is saved if cell parameters are available, although this is not essential. If cell parameters are provided as in the work discussed in his paper, the lattice energy of the crystal is then minimized with respect to all atomic coordinates. In the references

quoted above, these techniques based on energy minimization were able to predict correctly the observed distortions from the ideal structure for all the atoms within the unit cell of the crystal.

In some of these studies the crystal structures were known rather accurately from X-ray single crystal studies ($\text{Na}_2\text{Ti}_6\text{O}_{13}$ and $\text{Na}_2\text{Ti}_3\text{O}_7$, Andersson and Wadsley (3, 4)) or approximately from X-ray powder data ($\text{VO}_2(\text{B})$, Theobald, Cabala, and Bernard, 1976). In some cases the structure had only been guessed by isotypical comparison ($\text{TiO}_2(\text{B})$, Marchand, Brohan, and Tournois, 1980). But in all cases where previous data were available, whether for the titanate bronzes or for the silicates, the deviations from ideal models based on regular polyhedra were correctly reproduced by

the L.E.M. techniques; these studies established the technique as a reliable predictive tool for structural studies of ionic and semi-ionic compounds. However, it might be argued that the information was already available either from X-ray diffraction or from isotypical observation or that it could have been obtained from neutron powder diffraction studies as the material was available in bulk quantities. Thus if the time and cost of these preparations and measurements were ignored, the usefulness of L.E.M. for structural refinement could be disputed.

In contrast the present paper considers materials where samples are not available in large quantities so that measurements using X-ray or neutrons are not possible, as is, for example, the case when the sample is observed only in the high-resolution electron microscope. The compound considered is $\text{Na}_2\text{Ti}_9\text{O}_{19}$, evidence of the existence of which has been given by Bando *et al.* (5), Watanabe *et al.* (6), and by Bando himself (7) in four papers. Electron diffraction patterns and high-resolution electron microscopy have shown that the crystal structure was monoclinic $a = 12.2 \text{ \AA}$, $b = 3.78 \text{ \AA}$, $c = 15.6 \text{ \AA}$, $\beta = 105^\circ$. From systematically absent reflections the following possible space groups were found $C2$, Cm , and $C2/m$. From convergent beam electron diffraction the space group was selected as $C2/m$. The framework was described and positions for the different atoms were given taking into account reasonable metal-oxygen distances. The aims of the paper are therefore to locate the positions of the sodium ions in $\text{Na}_2\text{Ti}_9\text{O}_{19}$, to determine the influence of these cations on the surrounding framework, and to comment on the interpretation of partial occupancy factors in crystallographic refinements.

2. Calculations

All calculations used the METAPOCS program (Catlow *et al.* (8); Parker *et al.* (2)).

TABLE I
POTENTIAL PARAMETERS
SHORT-RANGE POTENTIALS REPRESENTED BY
FUNCTIONS OF THE FORM $A \exp(-r/\rho) - Cr^{-6}$

Interaction	Potential set 1		
	A	ρ	C
Ti-O	656.740	0.40431	0.0
Na-O	1226.800	0.30650	0.0
O-O	22764.300	0.14900	27.063
Potential set 2			
Ti-O	754.2	0.38739	0.0
Na-O	1226.800	0.30650	0.0
O-O	22764.3	0.14900	27.063

The program combines lattice energy calculation, using the Ewald method (9) for the Coulomb term, with efficient minimization procedures. Greater details of the techniques can be found in the monograph of Catlow and Mackrodt (10). The calculation requires the specification of interatomic potentials and of a starting configuration for the minimization procedure. The potentials used in the present study are based on the ionic model, with central force short-range potentials for which an analytical form is employed, generally the Buckingham potential:

$$V = A \exp(-r/\rho) - Cr^{-6}$$

In the present as in our previous studies of $\text{TiO}_2(\text{B})$ (Catlow *et al.* (1)) ionic polarization is neglected although this may be included by the shell model of Dick and Overhauser (11) (see also Catlow and Mackrodt (10)). Two sets of potential parameters were used. The first were as in our earlier studies of $\text{TiO}_2(\text{B})$ taken from the work of Catlow and James (12). The second were taken from recent work of Lewis (13). Both sets are reported in Table I.

For the starting configuration we used the atomic coordinates and the space group $C2/m$ given by Bando (7), for which a few points should be stressed.

(i) in Bando's paper some ambiguity rises from the fact that the Ti(1) symbol is used twice. We changed 2Ti(1)(2c) into 2Ti(5)(2c).

(ii) All oxygen and titanium atoms given in the list have $y = 0$ except O(1) which has $y = \frac{1}{2}$ (as in International Tables).

(iii) Na(1) is given as (2a): $x = 0$ $y = 0$ $z = 0$. We consider that a (2b) position ($y = \frac{1}{2}$) at the center of a "perovskite-like" hole is more likely. In our calculations we will try both possibilities.

(iv) The Na(2) position is given as (4i). Assuming that the Na(1) position is fully occupied, it follows that indeed these (4i) positions can only be occupied by 2 atoms (one in each tunnel). If there were two in each tunnel the distance between them would be only $b/2 = 1.89 \text{ \AA}$. We will return to this point later in relation to statistical distribution and partial occupancies.

It seems that a (4f) position is also acceptable. Again there should be only one Na in each tunnel.

An illustration of the octahedral framework of this starting set (Fig. 1) shows that the octahedra are rather distorted and even different in size and that some titanium atoms are considerably off center. Nevertheless it can be taken as a reasonably good starting set. On the other hand the Na positions are less certain and so it was decided to concentrate on this problem and try different combinations of Na⁺ positions.

Several Na⁺ distributions have been tried as shown in Table II which give a variety of positions available for Na atoms (referred to as P1 to P11) and combinations of them (sets 1 to 10). Application of METAPOCS to the starting configurations discussed above led to satisfactory convergence in all cases.

As discussed elsewhere in greater detail (Catlow *et al.* (8)) convergence is taken to have been achieved when the maximum change in the fractional coordinate is $\leq 10^{-7}$ per iteration. This generally leads to a con-

TABLE II
STARTING SETS OF Na COORDINATES

(a) Examples of positions for Na atoms
(in crystallographic coordinates)

P1	0	$\frac{1}{2}$	0
P2	$\frac{1}{2}$	0	0
P3	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{1}{2}$
P4	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{2}$
P5	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
P6	$\frac{3}{4}$	0	$\frac{1}{2}$
P7	$\frac{1}{4}$	0	$\frac{1}{2}$
P8	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$
P9	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{2}$
P10	0	0	0
P11	$\frac{1}{2}$	$\frac{1}{2}$	0

(b) Examples of sets (4 Na in each set)

S1	= P1 + P2 + P3 + P4
S2	= P1 + P2 + P3 + P5
S3	= P1 + P2 + P6 + P7
S4	= P1 + P2 + P6 + P8
S5	= P1 + P2 + P7 + P9
S6	= P1 + P2 + P6 + P9
S7	= P7 + P9 + P10 + P11
S8	= P6 + P8 + P10 + P11
S9	= P6 + P9 + P10 + P11
S10	= P6 + P7 + P10 + P11

vergence in the lattice energy of $< 10^{-5} - 10^{-6}$ as discussed below.

3. Results

(3.1) Presentation of Results

The program determines the positions for the atoms in an orthonormal reference system. These are not the type of coordinates normally used in crystallographic work, so it is necessary to return to a crystallographic cell by a matrix transformation and apply appropriate shifts to all coordinates. This is done routinely after every METAPOCS calculation. In the present example a further treatment of the results is advisable, due to loss of symmetry. Indeed in the case of Na₂Ti₉O₁₉ there is no reason whatsoever why the symmetries of space group $C2/m$ should be kept rigorously by the atoms, since the sodium atoms introduced in that calculations occupy only

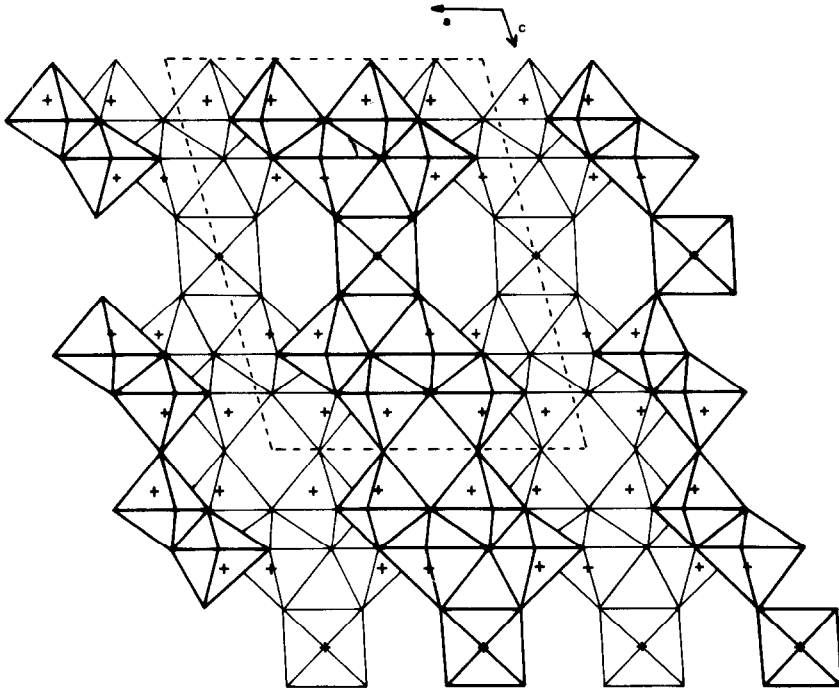


FIG. 1. Representation of the starting structure. Framework of TiO₆ octahedra (Ti atoms are indicated by crosses).

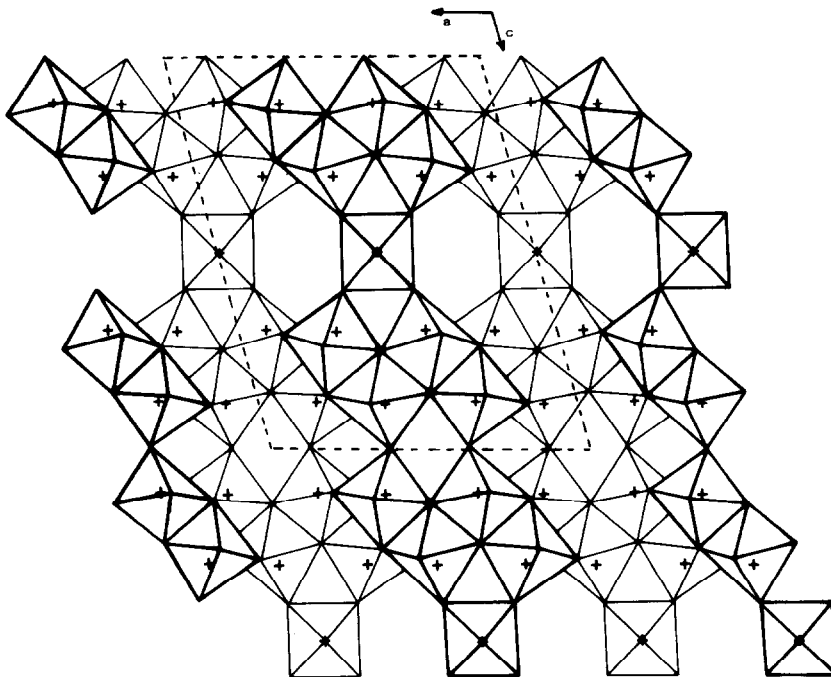


FIG. 2. Representation of the refined structure.

some equivalent positions and so *do not* respect that symmetry. In crystallographic terms the site is said to be partially occupied. The site symmetry of each atomic position is dependent on the distribution of all the other atomic positions. Thus because not all of the 4(*i*) Na(2) sites are filled this will affect the symmetry of the TiO₆ framework. Nevertheless the deviation from symmetry *C2/m* is small for all sets of equivalent atoms that were complete at the start of the calculation. An estimate of the discrepancy will be given later on and it seemed appropriate to try to fit that symmetry as far as possible. So the results were averaged and final coordinates were given in the following way:

average value (taking into account
the symmetry) + corrective term

Shifts of the whole structure and averaging of coordinates have been made in such a way that corrective terms are the smallest possible ones. Averaging has not been done for Na atoms because some equivalent atoms are absent. Whenever a coordinate is fixed by symmetry (fixed values in *C2/m* can be 0, $\frac{1}{4}$, $\frac{1}{2}$, . . .) that value has been chosen as the average to display discrepancies from what the coordinate should be, according to a crystallographer's point of view; again this has not been done for the Na atoms because the symmetry concept does not hold for them. It must be pointed out that

(a) Symmetry is not used in the calculations except in building the starting set, i.e., symmetry constraints are *not* imposed during the minimization.

(b) Every atom in the cell is considered as an individual and relaxes independently.

(c) If there had been 4 Na(2) cations, then the atomic coordinates would clearly reflect their symmetry. The departure from symmetry reflects the fact that some 4(*i*) sites are empty.

(d) To do the averaging use has been

TABLE III
COMPARISON OF ENERGIES OBTAINED BY USING
TWO DIFFERENT POTENTIALS

	Potential 1	Potential 2	Energy difference
S7	112.555	114.611	2.056
S6	113.227	115.275	2.048
S2	113.260	115.308	2.048
S1	113.262	115.311	2.049
S3	113.292	115.337	2.045
S5	113.295	115.344	2.048

Note. Lattice energies given in electron-volts per Ti atom.

made of those simple relationships existing between equivalent positions in a given space group. In more complicated space groups, least-square fittings may be used as well.

(3.2) Effect of Choice of Potentials

As noted above calculations of energies have been performed using two different sets of short-range Born–Mayer–Buckingham potentials. Lattice energies calculated from these two potentials are different; the second potential gives energies per titanium atom that are some 2 eV lower for all coordinate sets as is apparent from Table III. Inspection of the table emphasizes an important point, namely, that if the energies were classified in order of decreasing values the order of coordinates sets would have been the same whether the calculations were done using the first or the second set of potential parameters. Moreover differences in results were almost the same for all sets as shown in Table III.

This shows that an accurate knowledge of the potential is not critical in finding which is the more stable configuration. Let us recall that potentials were obtained independently from studies on TiO₂ and Na compounds.

Furthermore coordinates obtained from both calculations were close in all cases. Many trials were performed using both po-

TABLE IV
COMPARISON OF SHIFTS IN COORDINATES AFTER
USING THE TWO DIFFERENT POTENTIALS

		Δx (Å)	Δy (Å)	Δz (Å)
S5	MXS	.595	.246	.739
	MXD	.046	.246	.068
	AVD	.017	.079	.024
S3	MXS	.626	.295	.781
	MXD	.040	.059	.073
	AVD	.014	.016	.020
S1	MXS	.601	.247	.670
	MXD	.033	.024	.047
	AVD	.014	.010	.019
S2	MXS	.603	.300	.713
	MXD	.093	.300	.123
	AVD	.032	.202	.027
S6	MXS	.607	.226	.787
	MXD	.088	.226	.084
	AVD	.022	.072	.026
S7	MXS	.614	.370	.793
	MXD	.065	.106	.051
	AVD	.027	.048	.025

Note. All atoms considered here except Na. Same sets as in Table III. MXS, maximum shifts; MXD, maximum absolute difference in shifts; AVD, average absolute difference in shifts.

tentials, some of which are given in Table IIb. Only in one case did the use of two different potentials lead to two different configurations (with major differences in Na positions). In all other cases the shifts were similar for almost all atoms (not considering the sodium atoms). To demonstrate this, differences in shifts along x , y , and z have been calculated in Ångströms for all atoms. Shifts along y coordinates may be rather different in that they are sometimes zero (when potential number 2 is used) and other times up to 0.3 Å. This suggests that potential 2 is better, as the results on y seem more stable. Nevertheless the overall configuration is not affected.

On the other hand some x and z coordinates are subjected to very large shifts. Table IV shows what the maximum absolute shifts are, for the same sets as in Table III.

That table contains also the maximum difference observed between the whole final shifts for all atoms. Obviously some atoms are subjected to rather large displacements but in the same directions and the displacements are almost the same regardless of the potential. In fact the average of the absolute value of the shifts differences is much less than this, as indicated in the same Table IV. This shows that results are not strongly dependent on the potential, except for y values. In the remainder of our discussion we concentrate on results obtained with potential 2.

(3.3) Effect of the Starting Set of Coordinates

Symmetry-related sets and lattice energies. Symmetry-related sets are, for example, S4 and S5 or sets S7 and S8. These calculations lead to symmetry-related shifts and final coordinates, so the differences between calculated final lattice energies (in all symmetry-related cases) were less than $10^{-5}/10^{-6}$ eV per titanium atom.

Stability of minimization procedure. Starting sets that correspond to similar environments of Na ions but with slightly different coordinates give identical results. The difference in lattice energies is as low as 10^{-5} eV per titanium and the difference in atomic positions is less than 10^{-4} Å. This shows that L.E.M. indeed converges to well-defined minima.

Na ions positions: general features. In all cases where two Na ions were situated at starting positions P10 and P11 (S7 to S10) suggested by BANDO and co-workers, the y coordinate was considerably changed and the Na ions ended in positions that were not far from P1 and P2. This result confirms our suggestion made in paragraph 2(iii).

On the contrary, during calculations using S7 to S10 most atoms were disturbed considerably and the final positions corresponded to major shifts compared to the starting set. Final energies were also much

TABLE V
AVERAGE SHIFTS FOR 12 SETS FROM TABLE III

Ti(5)	0.042(0.045) 0.018(0.059)	-0.091(0.305) -0.033(0.228)	-0.001(0.004) 0.000(0.004)
Ti(1)	-0.188(0.046) 0.182(0.055) -0.185(0.045) 0.180(0.055)	0.063(0.118) -0.039(0.133) -0.049(0.124) 0.069(0.123)	0.303(0.015) -0.300(0.020) 0.301(0.018) -0.305(0.016)
Ti(2)	-0.231(0.017) 0.226(0.021) -0.235(0.013) 0.216(0.020)	0.084(0.151) 0.013(0.158) -0.069(0.141) 0.079(0.138)	0.112(0.044) -0.103(0.049) 0.091(0.039) -0.104(0.043)
Ti(3)	-0.081(0.023) 0.077(0.028) -0.084(0.022) 0.076(0.028)	-0.049(0.133) 0.073(0.130) 0.065(0.125) -0.042(0.141)	0.245(0.046) -0.239(0.047) 0.238(0.048) -0.241(0.047)
Ti(4)	0.597(0.019) -0.608(0.016) 0.591(0.016) -0.603(0.015)	-0.042(0.128) 0.081(0.138) 0.068(0.114) -0.026(0.146)	0.039(0.026) -0.039(0.024) 0.033(0.021) -0.028(0.019)
O(1)	-0.013(0.038) 0.008(0.039)	-0.077(0.254) -0.024(0.187)	0.005(0.015) -0.001(0.016)
O(2)	-0.258(0.123) 0.252(0.134) -0.260(0.124) 0.252(0.134)	0.087(0.165) -0.064(0.171) -0.063(0.174) 0.085(0.162)	0.046(0.012) -0.043(0.011) 0.043(0.013) -0.047(0.010)
O(3)	-0.003(0.046) -0.010(0.056) 0.004(0.043) -0.007(0.058)	0.053(0.104) -0.031(0.119) -0.038(0.111) 0.065(0.107)	-0.553(0.075) 0.549(0.077) -0.548(0.074) 0.549(0.078)
O(4)	-0.065(0.022) 0.062(0.021) -0.068(0.026) 0.080(0.020)	0.030(0.078) -0.022(0.078) -0.048(0.068) 0.036(0.073)	0.218(0.036) -0.196(0.022) 0.205(0.039) -0.196(0.026)
O(5)	-0.193(0.118) 0.130(0.094) -0.109(0.096) 0.212(0.100)	-0.033(0.163) -0.064(0.181) -0.032(0.109) 0.002(0.147)	0.100(0.040) -0.116(0.030) 0.119(0.030) -0.105(0.042)
O(6)	0.315(0.039) -0.323(0.041) 0.319(0.037) -0.320(0.043)	-0.004(0.100) 0.066(0.096) 0.029(0.081) -0.001(0.103)	-0.006(0.033) 0.009(0.040) -0.017(0.031) 0.009(0.033)
O(7)	0.116(0.081) -0.159(0.086) 0.181(0.085) -0.095(0.063)	-0.085(0.216) -0.057(0.211) -0.015(0.167) -0.017(0.148)	0.032(0.027) -0.006(0.025) 0.020(0.030) -0.036(0.026)
O(8)	0.431(0.027) -0.459(0.019) 0.451(0.023) -0.440(0.030)	-0.032(0.045) 0.032(0.084) 0.011(0.057) -0.025(0.090)	0.696(0.041) -0.733(0.041) 0.705(0.034) -0.703(0.047)
O(9)	-0.262(0.036) 0.258(0.044) -0.265(0.037) 0.257(0.043)	-0.044(0.109) 0.061(0.107) 0.055(0.104) -0.033(0.117)	-0.224(0.064) 0.219(0.057) -0.217(0.061) 0.222(0.058)
O(10)	-0.037(0.016) 0.035(0.022) -0.039(0.016) 0.032(0.022)	0.018(0.046) 0.012(0.048) -0.011(0.049) 0.026(0.050)	-0.111(0.043) 0.116(0.034) -0.115(0.041) 0.105(0.038)

Note. ESD given in parentheses.

higher in this case. This shows that hypotheses S7 to S10 were wrong.

The influence of the positions for the two

other sodium positions will be discussed later.

Evolution of the framework. When comparisons are made between results obtained with sets S1 to S6, it appears that the titanium and oxygen are subjected to similar shifts regardless of the Na positions. In order to compare the effect of L.E.M. on the framework shifts from the starting positions given by Bando to the final positions were calculated (for example, for sets S1 to S6 and some other sets as well). It appeared that the titanium and oxygen atoms were subjected to similar shifts regardless of the Na positions.

To demonstrate this, standard deviations have been calculated in a number of different combinations of results, for example, by considering all the sets mentioned in Table III and even by including a set like S7, which is not particularly good: the general trend is not changed. Table V gives the resulting average shifts and ESD's for the 12 calculations in Table III including potentials 1 and 2. Of course sodium atoms are not considered in this averaging since the starting positions were different. Among 112 x - and z -coordinates to be defined 84 have shifts larger than twice the standard deviations. This simply shows that most of the atomic positions significantly improved after L.E.M.

Thus the octahedral framework appears to be largely independent of the Na positions. This result has consequences both for the efficiency of the L.E.M. technique and the mobility of Na in the structure. Thus L.E.M. will yield similar results even if some initial atomic coordinates are wrong. So it is not necessary to try too many sets to find the right minimum. The second point follows from the fact that L.E.M. shows that the structure of the framework is not strongly disturbed when Na atoms are moved along tunnels parallel to y ($x = \mp\frac{1}{4}$; $z = \frac{1}{2}$). So if one is interested in the insertion and the mobility of Na ions in

the structure, these tunnels are a permanent feature of the framework and a possible path for the Na^+ ions.

Lower energy structures. In this paragraph we compare results obtained with the same potential, i.e., potential 2; as noted above these are assumed to be the best results. Two sodium atoms are placed in P1 and P2 (2b Wyckoff positions). The problem is to locate the 2 other sodium atoms. Sets S1 to S5 correspond to 2 sodium atoms placed in two different holes, while in S6 the two atoms are in the same hole. Energy calculations show that S6 is less stable (although no Na–Na short-range potential was introduced). This accords with simple chemical intuition.

In the four best sets from Table I the two sodium atoms under consideration have following y coordinates (in order of increasing energy): S5 ($y = 0, y = \frac{1}{2}$); S3 ($y = 0, y = \frac{1}{2}$); S1 ($y = \frac{3}{4}, y = \frac{3}{4}$); S2 ($y = \frac{3}{4}, y = \frac{1}{4}$). The most stable positions correspond to sodium atoms in positions $y = 0$ or $\frac{1}{2}$.

Discussion

(1) Final Positions for the Lowest Energy Sets (S5 or S4)

The coordinates for equivalent atoms are given in Table VI. It appears that the final structure is not any more exactly symmetrical in that it does not respect exactly the $C2/m$ symmetry. Average x , y , and z coordinates are calculated for the first atom in each set of equivalent atoms (2 or 4 atoms according to Wyckoff positions).

If the structure was perfectly symmetrical all corrective terms in Table VI should be zero. It is because these terms have all the same sign, that the structure is no longer symmetrical. The discrepancy is maximum for Ti(5) ($\Delta x = 0.07 \text{ \AA}$) and for O(1) ($\Delta x = 0.04 \text{ \AA}$). For most atoms it is 0.01 \AA or less. The average absolute discrepancy $\Delta\rho = (\Delta x^2 + \Delta y^2 + \Delta z^2)^{1/2}$ is 0.012

\AA , which compares well with ESD in atomic positions found by X-ray refinements.

On the other hand positions for the third and fourth atoms are quite far from the half-occupied (4i) position ($\frac{3}{4}, \frac{1}{2}, \frac{1}{2}$). The discrepancy is 0.5 \AA which is high. This is mainly due to the fact that, what appears as the center of the hole on a (010) projection, is not really the center of the section of the tunnel at $y = \frac{1}{2}$. Furthermore because the position is not fully occupied, the Na atom does not respect the symmetry and cannot stay exactly in a symmetrical environment.

Other atoms react to that lack of symmetry by leaving their own ideal positions. Atoms that are most affected are those that are close to these sodium atoms. For example, O(1) is attracted by the close Na ($|\Delta x| = 0.04 \text{ \AA}$) while Ti(5) is repelled by it ($|\Delta x| = 0.06 \text{ \AA}$); O(5) atoms follow this displacement ($|\Delta x| = 0.014 \text{ \AA}$).

Interatomic distances in the starting and the final results are listed in Table VII. Oxygen-oxygen distances in octahedra after L.E.M. range from 2.42 to 2.89 \AA , which represents a considerable improvement compared to the O–O distances in the starting set (2.07 to 3.01 \AA).

(2) The Notion of Partial Occupancy Factor

From interatomic distances calculations it appears that the size of the cavity which contains the sodium ion is slightly smaller than for the empty equivalent site; the distance from the center to the surrounding oxygen atoms is decreased by an average of 0.011 \AA . Furthermore the shape of this neighborhood is slightly changed, some O–O distances being changed by some 0.07 \AA .

It is of common use among crystallographers to solve some crystal structures by introducing partial occupancy factors, when the stoichiometry requires a statistical distribution of some kind of atoms on a given crystal site. Of course refinements

TABLE VI
CRYSTALLOGRAPHIC COORDINATES FOR THE BEST
FINAL RESULTS OBTAINED BY USING SET 5 AND
POTENTIAL 2

	x	y	z
NA	-0.00013 0.49987 0.79105 0.29105	0.50000 0.00000 0.50000 0.00000	0.00054 0.00054 0.50320 0.50320
Ti(5)	0.00000 + 0.00560 0.50000 + 0.00560	0.00000 + 0.00000 0.50000 + 0.00000	0.50000 - 0.00027 0.50000 - 0.00027
Ti(1)	0.18307 - 0.00027 0.81693 - 0.00027 0.68307 - 0.00027 0.31693 - 0.00027	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.11932 + 0.00012 0.88069 + 0.00012 0.11932 + 0.00012 0.88069 + 0.00012
Ti(2)	0.08055 - 0.00043 0.91945 - 0.00043 0.58055 - 0.00043 0.41945 - 0.00043	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.30396 - 0.00044 0.69604 - 0.00044 0.30396 - 0.00044 0.69604 - 0.00044
Ti(3)	0.89182 - 0.00047 0.10819 - 0.00047 0.39182 - 0.00047 0.60819 - 0.00047	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.11402 + 0.00012 0.88599 + 0.00012 0.11402 + 0.00012 0.88599 + 0.00012
Ti(4)	0.79770 - 0.00030 0.20231 - 0.00030 0.29770 - 0.00030 0.70231 - 0.00030	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.30048 + 0.00057 0.69953 + 0.00057 0.30048 + 0.00057 0.69953 + 0.00057
O(1)	0.00000 - 0.00354 0.50000 - 0.00354	0.00000 + 0.00000 0.00000 + 0.00000	0.50000 + 0.00003 0.50000 + 0.00003
O(2)	0.12421 - 0.00035 0.87580 - 0.00035 0.62421 - 0.00035 0.37580 - 0.00035	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.00315 + 0.00005 -0.00315 + 0.00005 0.00315 + 0.00005 -0.00315 + 0.00005
O(3)	0.34681 - 0.00045 0.65319 - 0.00045 0.84681 - 0.00045 0.15319 - 0.00045	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.11208 + 0.00004 0.88793 + 0.00004 0.11208 + 0.00004 0.88793 + 0.00004
O(4)	0.24293 + 0.00024 0.75708 + 0.00024 0.74293 + 0.00024 0.25708 + 0.00024	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.26154 + 0.00095 0.73847 + 0.00095 0.26154 + 0.00095 0.73847 + 0.00095
O(5)	0.08563 + 0.00112 0.91437 + 0.00112 0.58563 + 0.00112 0.41437 + 0.00112	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.40615 - 0.00008 0.59386 - 0.00008 0.40615 - 0.00008 0.59386 - 0.00008
O(6)	0.92330 - 0.00038 0.07670 - 0.00038 0.42330 - 0.00038 0.57670 - 0.00038	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.24698 - 0.00003 0.75302 - 0.00003 0.24698 - 0.00003 0.75302 - 0.00003
O(7)	0.86091 + 0.00131 0.13910 + 0.00131 0.36091 + 0.00131 0.63910 + 0.00131	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.40177 + 0.00021 0.59824 + 0.00021 0.40177 + 0.00021 0.59824 + 0.00021
O(8)	0.63509 - 0.00043 0.36492 - 0.00043 0.13509 - 0.00043 0.86492 - 0.00043	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.29282 - 0.00130 0.70718 - 0.00130 0.29282 - 0.00130 0.70718 - 0.00130
O(9)	0.72728 - 0.00036 0.27273 - 0.00036 0.22728 - 0.00036 0.77273 - 0.00036	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.13463 - 0.00022 0.86537 - 0.00022 0.13463 - 0.00022 0.86537 - 0.00022
O(10)	0.04616 - 0.00029 0.95385 - 0.00029 0.54616 - 0.00029 0.45385 - 0.00029	0.00000 + 0.00000 0.00000 + 0.00000 0.50000 + 0.00000 0.50000 + 0.00000	0.14453 + 0.00004 0.85547 + 0.00004 0.14453 + 0.00004 0.85547 + 0.00004

could be done by ignoring symmetry so atoms could be considered as individuals. But this is usually not done and calculations are usually performed by assuming that the structure has the whole symmetry group of all the atomic sites which have full occupancy. This is obviously not the case if the exact neighborhood of a given ion has to be considered with accuracy.

In principle X-ray diffraction lead to precise determinations of the atomic positions; but in the case of partial occupancy the interatomic distances around that site are only averaged values and the calculations of ESD overestimate the accuracy of the results.

On the contrary present methods in L.E.M. ignore that averaging, as L.E.M. assumes that charges on individual atoms are integers and a given ion can only be present or not. If an interstitial ion is present the atoms in the neighborhood are shifted and these shifts are much larger than what is usually considered as a "good" estimated standard deviation on atomic positions found from X-ray studies. So it appears that L.E.M. is able to display

TABLE VII
RANGE OF DISTANCES IN THE STARTING
STRUCTURE AND IN STRUCTURE REFINED
BY L.E.M.

	Bando	L.E.M.
Ti(5)-O	1.89-2.21	1.89-2.05
Ti(1)-O	1.52-2.26	1.76-2.16
Ti(2)-O	1.56-2.36	1.58-2.42
Ti(3)-O	1.52-2.34	1.78-2.02
Ti(4)-O	1.71-2.34	1.57-2.52
O(1)-O	2.81-2.91	2.70-2.79
O(2)-O	3.01	2.62-2.84
O(3)-O	2.21-2.91	2.47-2.81
O(4)-O	2.45-2.63	2.43-2.72
O(5)-O		2.60-2.89
O(6)-O	2.42-2.69	2.46-2.80
O(7)-O	2.56-2.81	2.70-2.81
O(8)-O	2.43-2.63	2.42-2.86
O(9)-O	2.07-2.69	2.46-2.86

the difference between occupied and unoccupied sites and L.E.M. seems able to give a better insight in the close neighborhood of a partially filled site than the conventional X-ray diffraction methods.

We should note that a field closely related to the preceding one concerns the study of structures with substitutional replacement (as, for example, substitution of chlorine by bromine) as in ionic *solid solutions* when individual interatomic bond lengths are rather different and the X-ray diffraction technique leads to "poor reliability factors." The fact that bond lengths are changed when isomorphic substitution takes place, leads to a smearing of the structure that may be referred to as "static Debye-Waller effect" (Huang (14) but it is usually ignored by crystallographers, whereas this effect can be treated straightforwardly by L.E.M.

(3) Migration of Na Atoms along the Tunnels and Holes Parallel to y

Sodium atoms placed in P1 and P2 are confined there since the energy barrier to displace them off is ≈ 3 eV per sodium. So if any migration of sodium atoms is to occur it may only be for the two other atoms. In fact there is little energy difference between S5 and S3; and the same for S1 and S2. Sets like S1 or S2 are less stable; they represent a rather high barrier to move Na atoms along y .

In S5 atoms stay on different levels, while in S1 they are on the same level. So if a displacement of the sodium atoms along the tunnels is examined, no cooperative transport is to be expected in that these atoms will not move by equal quantities in the same direction at the same time. If they would, they would not go through the lowest possible energy barrier at any time. It is more likely that these sodium atoms would move independently in each hole. Defect calculations as in the HADES (Catlow *et*

al. (15) or CASCADE (Lesley, (16) codes would be of value.

(4) Efficient Procedure for L.E.M. Calculations

The results discussed in this paper has led to the suggestion of several rules for an efficient strategy for L.E.M. studies. These are

—Potential parameters are obtained by studying *known* structures containing the same ions as the one under study.

—Trial models are constructed from structures based on regular polyhedra.

—If general trends appear in most calculations, it is worthwhile to include these shifts in starting sets for further trials; one is likely to get a lower energy in fewer iterations. It is also advisable to ensure that trial configurations are not exactly symmetrical in order to check if the symmetry is reproduced by L.E.M.

—The lowest energy configuration should be taken as the "best" structure.

Acknowledgments

One of us (F.R.T.) acknowledges support from the NATO for a Scientific and Technical Grant. We also acknowledge financial support from AERE Harwell and SERC.

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