

Structure Predictions in Inorganic Solids

C. M. Freeman^a and C. R. A. Catlow^b

^a BIOSYM Technologies Inc., 10065 Barnes Canyon Road, Suite A, San Diego, CA 92121, USA

^b Davy Faraday Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK

Energy minimization methods are able to model accurately the crystal structure of the rutile polymorph of titanium dioxide starting from random atomic distributions within the experimentally determined unit cell dimensions; the results suggest how such methods could be used in predicting certain classes of inorganic crystal structure.

Several studies have been reported recently in which computational methods have been employed to develop detailed structural models for inorganic crystals starting from few initial assumptions. Deem and Newsam¹ successfully applied simulated annealing techniques to modelling zeolite struc-

tures; while Pannetier *et al.*² have used related methods to predict crystal structures of the complexity of NbI₃. In both cases the 'penalty function' used in the Monte Carlo method depended on the deviation of computed structural variables (*e.g.* bond lengths) from standard values as in the distance

least-squares method of Meier and Villiger.³ At the same time we have shown that energy minimization procedures based on accurate calculations of the total lattice energy can model precisely the subtle structural features of complex inorganic materials, for example, the monoclinic distortion of the purely siliceous zeolite silicalite⁴ and the polymorphism of zeolite Beta.⁵

In view of the precision of lattice energy minimization techniques we have investigated the extent to which they may be used in the modelling, rather than refinement, of inorganic crystal structures. The example we have chosen is TiO₂, a crystalline material which displays polymorphism with all polymorphs having non-cubic unit cells and several formula units per cell. Our method consists of first generating random distributions of Ti and O ions with the correct density and stoichiometry, within the experimentally determined unit cell volume.⁶ A Monte Carlo driven simulated annealing algorithm is then used to refine the random starting point. Here, we use a highly simplified two-body potential model based on a repulsive r^{-12} interaction with the repulsion between anions and cations being half that of anion-anion and cation-cation pairings. The purpose of this initial simulated annealing treatment is to set up a sensible, random arrangement for the components of the simulated system. Long range coulombic interactions are neglected at this stage.

Next, we undertake lattice energy minimization with respect to atomic coordinates (but with no variation of the cell dimensions) until a stable minimum is identified. Following this constant pressure lattice energy minimization is applied, allowing cell dimensions to equilibrate. Both sets of calculations employed the METAPOCS⁷ code, which carries out a full lattice energy calculation with an Ewald summation of the coulombic term and a real space evaluation of the short range terms. Pair potentials are used for the latter with an improved

parameterization for the Ti-O interaction⁸ reported in Tables 1 and 2. The final stage of the calculation allows atomic polarization of the component ions of the structure through the shell model of Dick and Overhauser.⁹

Table 1 Potential model for rutile: parameters (taken from ref. 8)

Short range potentials of the form: $V(r) = A e^{-r/\rho} - Cr^{-6}$	
Cation charge/e	4.0
$A(\text{Ti-O})/\text{eV}$	760.47
$\rho(\text{Ti-O})/\text{\AA}$	0.3879
$A(\text{O-O})/\text{\AA}$	22764.3
$\rho(\text{O-O})/\text{eV}$	0.1490
$C(\text{O-O})/\text{eV \AA}^{-6}$	27.88
Cation shell charge/e	1.11
Anion shell charge/e	-2.53
Cation spring constant/ eV \AA^{-2}	37.3
Anion spring constant/ eV \AA^{-2}	86.4

Table 2 Calculated and experimental crystal properties

Crystal property	Calculated value	Experimental value
Static dielectric constants		
ϵ_{\perp}	66.4	86
ϵ_{\parallel}	169.0	170
High frequency dielectric constants		
ϵ_{\perp}	2.21	6.83
ϵ_{\parallel}	2.37	8.43
Elastic constants/ 10^{-11} dyn cm^{-2}		
C_{11}	26.77	27.01
C_{33}	55.17	48.19
C_{12}	19.85	17.66
C_{13}	19.54	14.80
C_{44}	10.19	12.39
C_{66}	21.17	19.30
Equilibrium structure		
Lattice parameters/ \AA a, b	4.521	4.593
c	3.212	2.958
Rutile 'u' parameter/lattice units	0.305	0.305

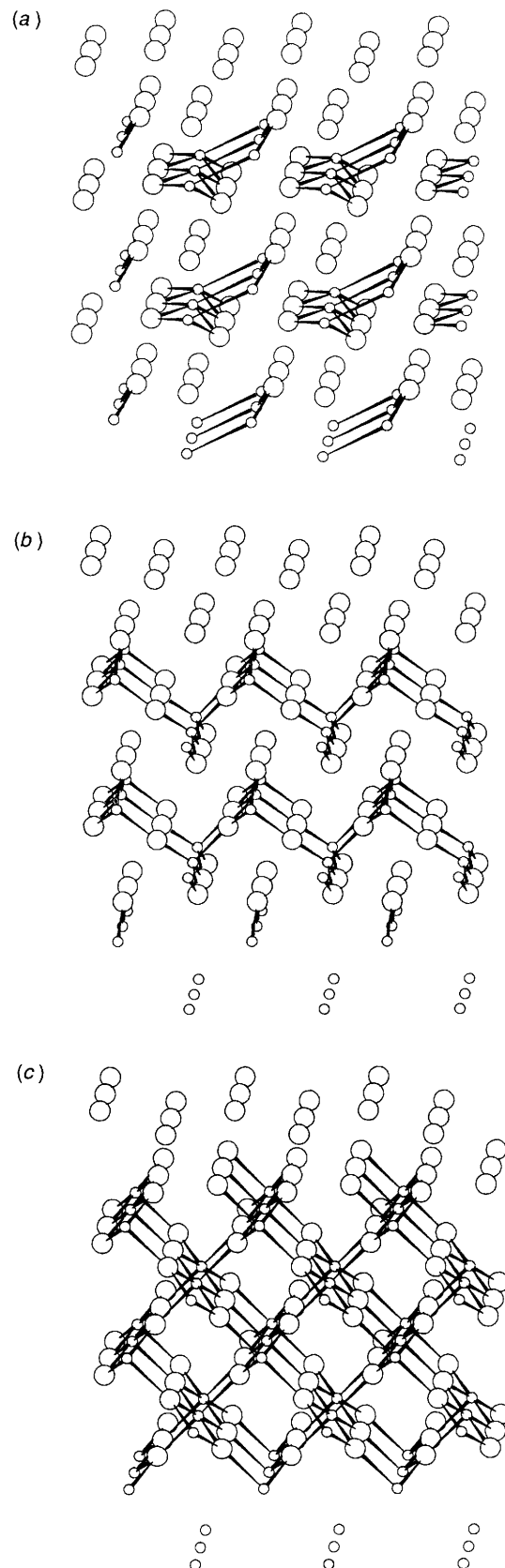


Fig. 1 (a) Candidate TiO₂ structure form simulated annealing procedure. (b) After 90 steps of minimization. (c) Final simulated TiO₂ structure.

The modelling sequence described above was applied to 50 random initial configurations with six ions in the simulation box (*i.e.* two formula units of TiO_2). When the shell model is employed this is equivalent to a minimization with 36 variables. We note that symmetry is not employed in the simulation. The results of the procedure can be summarized as follows. The rutile structure was obtained in 41 of the trials, with a density close to the experimental value. Of the nine structures which failed to converge to rutile, six had less favourable lattice energies and low calculated densities and could, therefore, be readily discounted using energetic and cell volume criteria. Three starting points produced structures with low densities but slightly higher lattice energies than that calculated for the rutile itself. Again these structures had anomalously high unit cell volumes. However, their unrealistic lattice energies indicate that the lattice potential model used here may yield unrealistic energies with large departures from equilibrium Ti-O geometries. Hence, we find that in each case for which energy minimization was possible, and led to a structure near to the experimental density, an accurate representation of the crystallographic structure for rutile was obtained. The process of the energy minimization is illustrated in Fig. 1. Here, we show 'bonding' between ions based on proximity with the same distance criteria being used in each figure; Ti ions are drawn with the smaller radius. The sequence shows the initial arrangement of Ti and O ions, Fig. 1(a); Fig. 1(b) shows the structure after 90 steps of minimization (employing the Newton Raphson procedure of the METAPOCS code); Fig. 1(c) is the energy minimized structure, which is an accurate model of the rutile structure.

The implication of the success of the study is that minimization methods are a powerful tool in crystal structure prediction. In the present work, they have been combined with a simple starting point definition procedure to yield successful results for the rutile structure. This is remarkable in view of the fact that large numbers of local minima commonly present a severe limitation in the application of energy minimization to complex chemical systems. For example, although accurate potential functions are available for biochemical systems,¹⁰ structural prediction for protein systems

based solely on energy considerations are rendered impossibly time consuming by the profusion of local minima exhibited by such systems.¹¹ However, the fact that we initially constrain the crystal system to occupy the experimental cell dimensions appears to provide a sufficiently strong constraint to force convergence to the observed structure. For more complex structures it will be necessary to use more sophisticated methods to construct the initial configuration.¹² The choice of lattice parameters for the cell and the determination of the number of formula units per cell will also need refinement. Here, the incorporation of experimentally derived knowledge may prove useful. For example, in the present study, we have made use of the known density of TiO_2 to discriminate between some of the structures obtained. Deem and Newsam¹ have made use of the known symmetry in their investigation of zeolite structures. Given progress in the algorithms for the construction of trial structures, minimization methods could become a general technique in inorganic structure prediction.

Received, 19th August 1991; Com. 1/04335H

References

- 1 M. W. Deem and J. M. Newsam, *Nature*, 1989, **342**, 260.
- 2 J. Pannetier, J. Bassas-Alsina, J. Rodriguez-Carvajal and V. Caignaert, *Nature*, 1990, **346**, 242.
- 3 W. M. Meier and H. Villiger, *Z. Kristallogr.*, 1969, **129**, 411.
- 4 R. G. Bell, R. A. Jackson and C. R. A. Catlow, *J. Chem. Soc., Chem. Commun.*, 1990, 782.
- 5 S. M. Tomlinson, R. A. Jackson and C. R. A. Catlow, *J. Chem. Soc., Chem. Commun.*, 1990, 813.
- 6 W. H. Baur and A. A. Khan, *Acta Crystallogr., Sect. B*, 1971, **27**, 2133.
- 7 S. C. Parker, A. N. Cormack and C. R. A. Catlow *Acta Crystallogr., Sect. B*, 1984, **40**, 200.
- 8 C. R. A. Catlow, C. M. Freeman and R. L. Royle, *Physica*, 1984, **B40**, 200.
- 9 B. G. Dick and A. W. Overhauser, *Phys. Rev.*, 1958, **B112**, 90.
- 10 A. T. Hagler, S. Lifson and P. Dauber, *J. Am. Chem. Soc.*, 1979, **101**, 5122.
- 11 H. A. Scheraga, *Biopolymers*, 1981, **20**, 1877.
- 12 T. J. McLarnan, *J. Sol. State Chem.*, 1978, **26**, 235.