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Structure Prediction of Transition-Metal Oxides using Energy-Minimization Techniques

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Abstract

Computational techniques, based on the minimization of the crystal energy with respect to atomic coordinates, are shown to predict correctly complex crystal structures; illustrations of the technique are given by application to a number of titanium and vanadium oxygen compounds. Two types of compound are considered in this initial study: the $TiO_2(B)$ and $VO_2(B)$ structures and the titanates $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$. In all cases the deviations of the observed structures from ideal models based on regular TiO_6 octahedra are correctly reproduced by the energy-minimization techniques. The work establishes the techniques as a reliable predictive tool for structural studies of ionic and semi-ionic compounds.

1. Introduction

Computer-simulation techniques – of which a general review is available (Catlow & Mackrodt, 1982) – have in recent years been applied to a wide range of structural problems in the field of complex and disordered ionic solids. The most successful studies have concerned the structures of defect aggregates (Catlow, 1981; Catlow & Fender, 1975) and of extended planar defects (Cormack, Jones, Tasker & Catlow, 1982; James, 1979; Catlow & James, 1978, 1982) in non-stoichiometric oxides. The techniques, which rest ultimately on the Born model of the ionic solid (Born & Mayer, 1932), are based on energy minimization, either of ion coordinates around a defect centre or of the coordinates of ions within the unit cell of a perfect crystal structure. Related techniques have, we note, been applied with success to the study of molecular crystals (see *e.g.* Timofeeva, Chernikova & Zorkii, 1980). In addition, early applications to inorganic materials are reported by Slaughter (1966) and by Busing (1970). However, owing to recent advances both in computer power and in our understanding of interatomic potentials, the method is now applicable to several classes of inorganic solid including structures with large complex unit cells.

An added incentive for such work is provided by the fact that it has become increasingly common for new inorganic solids to be available only in powder form (and often only in small quantities), thus prohibiting structural determination from single-crystal studies. In many cases, however, it is possible to deduce a number of structural details from its powder diffraction pattern (see, for example, Cheetham & Taylor, 1977) especially if done in conjunction with electron microscopy. Unit-cell parameters can usually be found, and, by analogy with the powder patterns of other, known, phases, some insight into its crystal chemistry may be obtained; for instance, in oxides, the nature and linkage of the coordination polyhedra may be apparent.

We aim in this and a subsequent paper (Parker, Catlow & Cormack, 1984) to show that, using such information and our computer-simulation methods, it is possible to calculate the minimum-energy configuration of the structure; that is to say, we can predict the equilibrium crystal structure given only the interatomic potential and an initial structure – which need not be very close to equilibrium. This approach is particularly useful when the initial structure can be constructed as an ideal structure based on, for example, regular polyhedral units.

The present paper will be concerned with complex transition-metal oxides: we shall examine the viability of the techniques by considering the recently discovered $TiO_2(B)$ (Marchand, Brohan & Tournoux, 1980) and $VO_2(B)$ (Theobald, Cabala & Bernard, 1976) phases, and a number of titanates, including the $Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$ (Andersson & Wadsley, 1961, 1962) structures. The structures of all these compounds may be described in terms of distortions from ideal models using regular TiO_6 octahedra.

The results of our study suggest that the technique can enjoy considerable success for those systems for which reliable interatomic potentials are available – a conclusion supported and amplified by the discussion, in a subsequent publication (Parker, Catlow & Cormack, 1984), of mineral structures. Indeed, we believe that with the availability of efficient lattice-summation and energy-minimization routines,

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together with increasingly reliable potentials for inorganic materials, the type of procedure we describe could become a generally useful adjunct to inorganic crystal-structure determination.

2. Techniques and potentials

2.1. *Computational methods*

The basis of our technique is simple: an initial trial model, usually based on regular coordination polyhedra (as discussed in the *Introduction*), is proposed for the crystal structure; interatomic potentials, generally based on an ionic model with short-range repulsive terms, are specified; and the lattice energy is minimized with respect to the coordinates of all atomic positions within the unit cell. Two special features deserve emphasis.

The first concerns the handling of the long-range Coulomb summations. These are treated using the widely applied Ewald method (Tosi, 1964; Catlow & Norgett, 1978), which takes advantage of the rapid convergence of lattice sums for a Gaussian charge distribution when these are summed in reciprocal space.

Secondly, efficient minimization methods are essential if the calculations are to be computationally viable. The methods employed in our codes are, where possible, based on an adaptation of the Newton–Raphson procedure, with the update of the Hessian matrix, following the approach of Fletcher & Powell (1963). For very large unit cells, with present computer memory, matrix methods may not be feasible and the more slowly convergent conjugate gradients techniques must be used. We have developed a generalized program for the prediction of crystal structures by energy minimization (*METAPOCS**); the program is based on efficient calculations of lattice energies (see Catlow & Mackrodt, 1982), combined with minimization routines. Greater details are given elsewhere (Catlow, Cormack & Parker, 1984).

In the present study, cell dimensions were constrained to their experimentally observed values, since these were known. However, we should note here that the technique can be extended without difficulty (although at the cost of greatly increased computer time) to include variation of the unit-cell vectors (Cormack, 1982). This may be necessary if the technique is applied to structures for which these parameters are not accurately known. In addition, calculations in which cell dimensions are allowed to vary will place greater demands on the reliability of the interatomic potentials. We have therefore undertaken such calculations for a number of systems, the results of which will be reported shortly.

Table 1. *Potential parameters*

Short-range potentials are represented by a function of the form

$$A \exp(-r/\rho) - C/r^6.$$

Interaction	A(eV)	ρ(Å)	C(eV Å^{-6})
V–O	640·690	0·40431	0·0
Ti–O	656·740	0·40431	0·0
Na–O	1226·800	0·30650	0·0
O–O	22764·300	0·14900	27·063

Another important feature of our method is that no explicit symmetry relations between the various atomic positions are assumed: all the coordinates are treated as independent variables in the minimization process and their relaxations are determined solely by the interatomic potentials and the (imposed) unit-cell parameters. This means that the calculations can distinguish between different space groups (see, for example, Gregson, Catlow, Chadwick, Lander, Cormack & Fender, 1983). In all the cases reported in this paper, the calculations reproduced the observed site symmetries – except, of course, for $TiO_2(B)$ whose structure has not yet been determined experimentally. We should note that it is now well established (Catlow & Mackrodt, 1982; Catlow, 1980) that the limitations on the reliability of the technique follow only from those of the interatomic potentials used in the simulations. These are discussed in the next section.

2.2. *Potentials*

Our potentials for TiO_2, VO_2 and the titanates are based on the ionic model, with integral ionic charges of 4+ and 2− for the cation and anion respectively (1+ for Na, of course). Pair potential models are assumed for the short-range interactions; in the present case we use a simple Buckingham form, so that the total pair-wise interaction is represented by the function

$$V_{ij}(r) = A_{ij} \exp(-r/\rho_{ij}) - C_{ij} r^{-6} + \frac{q_i q_j}{r}. \qquad (1)$$

Parameters for the Ti···O, V···O potentials are taken from separate studies on the rutile-structure phases of TiO_2 and VO_2 (James, 1979) and for Na–O from Na_2O (J. R. Walker, *personal communication*). These parameters are reported in Table 1. These potentials were derived for octahedrally coordinated cations; it may be necessary to make small modifications if the potentials are to be used for differently coordinated cations.

In the present study we have used a rigid-ion model, *i.e.* one that excludes any treatment of ionic polarization from our calculations. This approximation would impose some limitation on the accuracy of our results, although we believe, in general, that polarizability has a relatively minor effect on structural

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* Minimization of Energy Techniques Applied to Prediction of Crystal Structures.

properties, notwithstanding the fact that in certain special cases, principally ferroelectric materials, the displacements caused by polarizability may be of considerable importance. If necessary, polarization could be incorporated into our calculations *via* the shell model of Dick & Overhauser (1958) which treats the ion as a massless electron shell connected to a core by a harmonic spring. The advantages, in lattice simulation, of shell-model treatments of ionic polarization are discussed by Catlow (1980). We note, however, that inclusion of polarization increases the requirements of the calculation as to both CPU memory and execution time by a considerable amount; and that the principal advantages of its inclusion arise when a correct description of the dielectric properties is essential as, for example, when considering charged point defects. The structural features under consideration in this work are far less sensitive to the dielectric properties than the elastic properties and an acceptable model may be obtained using a rigid-ion model as we have done.

3. Calculation and results

The two types of crystal structure discussed in this paper are, as noted, both based on TiO_6 octahedra with both corner and edge sharing of the octahedral units. First we consider the TiO_2 (B) and VO_2 (B) structures. These phases, which are metastable with respect to the rutile-structure phase, are prepared by hydrolysis of $K_2Ti_4O_9$ (Marchand, Brohan & Tournoux, 1980) and by controlled reduction of V_2O_5 (Theobald, Cabala & Bernard, 1976). The powder X-ray study, reported by Theobald *et al.* (1976) for the case of VO_2 (B), yields a structure based on a unit of four corner-shared VO_6 octahedra arranged as in the ReO_3 structure. Different units are connected by edge sharing as illustrated in Fig. 1, which shows an ideal model based on regular octahedra; the observed structure is shown in Fig. 2. No structural refinement is available for the TiO_2 (B) phase, which, however, we assume to be isostructural with VO_2 (B). Next, we consider the titanates $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ which contain Na^+ ions in interstitial tunnels in an open structure again based on corner and edge sharing; the structures are illustrated in Figs. 3 and 4.

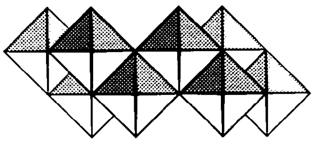

Fig. 1. The ideal structure of the B phases of TiO_2 and VO_2. Note the sharing of edges between the octahedra.

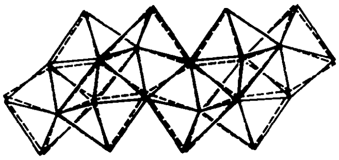

Fig. 2. Comparison of the experimentally determined structure (broken lines) and the predicted structure (solid line) for VO_2. The close similarity of these structures illustrates that the distortions from ideal are well reproduced by our model.

As remarked earlier, the structural feature of major concern in the present study is the extent to which the observed structures differ from the ideal models based on regular octahedra illustrated for example in Fig. 1. That such distortions are considerable is seen by comparing the latter models with the observed structures given in Figs. 2–4. It will be our aim in the following section to assess the extent to which the observed distortions are reproduced by our energy-minimization techniques.

3.1. VO_2 (B) *and* TiO_2 (B) *structures*

The calculations were performed using the unit-cell dimensions reported for VO_2 (B) by Theobald *et al.* (1976) and for TiO_2 (B) by Marchand *et al.* (1980). For both compounds the ideal structures (Fig. 1) were used as the starting points and the energy minimized with respect to the coordinates of all ions. The coordinates of the equilibrated structure are reported in

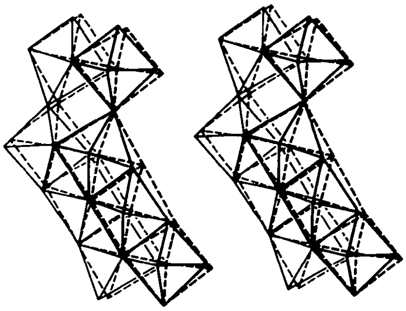

Fig. 3. Comparison of the experimental (broken line) and predicted (solid line) structures for $Na_2Ti_3O_7$. The Na sites (which are not shown) lie in between the sheets of edge-sharing TiO_6 octahedra.

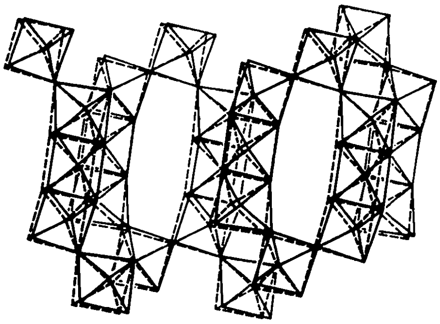

Fig. 4. Comparison of the experimental (broken lines) and predicted (solid lines) structure for $Na_2Ti_6O_{13}$. The Na sites (which are not shown) lie in the oblong channels which are visible in the figure.

Table 2. *Structural parameters for* $VO_2(B)$ *and the discrepancies in the thermal parameters*

(*a*) Structural parameters of $VO_2(B)$

		Idealized structure	X-ray structure	Predicted structure	Δ_1*	Δ_2†	Predicted coordinates for $TiO_2(B)$
V(1)	*x*	0·278	0·3050	0·3145	0·0270	0·0095	0·3159
	z	0·666	0·7245	0·7222	0·0579	−0·0023	0·7222
V(2)	*x*	0·388	0·4018	0·4047	0·0138	0·0029	0·4028
	z	0·333	0·3000	0·2630	−0·0333	−0·0370	0·2644
O(1)	*x*	0·333	0·3626	0·3722	0·0293	0·0096	0·3726
	z	0·000	0·9907	0·9902	−0·0093	−0·0005	0·9914
O(2)	*x*	0·222	0·2377	0·2371	0·0155	−0·0006	0·2363
	z	0·333	0·3725	0·3424	0·0392	−0·0301	0·3424
O(3)	*x*	0·445	0·4336	0·4427	−0·0119	0·0091	0·4429
	z	0·666	0·5954	0·6329	−0·0712	0·0375	0·6310
O(4)	*x*	0·112	0·1415	0·1439	−0·0295	0·0024	0·1456
	z	0·666	0·7289	0·7236	0·0623	−0·0053	0·7230

(*b*) Comparison of the discrepancies between the observed and calculated structure parameters and the observed thermal parameters

	Δ(Å)			Δ(Å)			Δ(Å)	
	Obs‡	Calc§		Obs‡	Calc§		Obs‡	Calc§
V(1)	0·214	0·115	O(1)	0·303	0·116	O(3)	0·303	0·264
V(2)	0·214	0·240	O(2)	0·303	0·193	O(4)	0·303	0·045

* Difference between the X-ray and the ideal structures.

† Difference between the predicted and the X-ray structures.

‡ Δ_{Obs} has been taken to be $3(\overline{U^2})^{1/2}$, where $B=8\pi^2\overline{U^2}$ is the quoted temperature factor (taken from Theobald *et al.*, 1976). This represents realistic limits to the expected agreement between calculated and observed coordinates.

§ This is the difference between the observed and calculated positions.

Table 2(*a*) together with, for the case of VO_2 (*B*), the observed structure. For VO_2 (*B*) we also report the experimentally observed displacements from ideal coordinates, and the discrepancies between calculated and experimental coordinates.

On examining Table 2(*a*) we note first that the experimental coordinates and those obtained for the equilibrated structure are in good agreement; the discrepancies (see Table 2*b*) are probably within the accuracy of the experimental structure; indeed, they are all within three times the thermal parameter, $(\overline{U^2})^{1/2}$, which is probably the best agreement that can be expected for a prediction procedure which omits the effects of thermal motions. More significantly, the displacements of the observed structure from the ideal models are well reproduced by the calculations. The magnitude and complexity of the displacements evident from comparison of Figs. 1 and 2 and from the displacements given in Table 2(*a*) should be emphasized, while the close agreement between theory and experiment is demonstrated by the near coincidence of the experimental with the calculated structure which is displayed in Fig. 2.

Table 3. $Na_2Ti_3O_7$ *structural parameters*

		X-ray	Predicted	Δ*
Na(1)	*x*	0·682	0·6588	−0·0232
	z	0·595	0·5908	−0·0042
Na(2)	*x*	0·508	0·4953	−0·0127
	z	0·154	0·1519	−0·0021
Ti(1)	*x*	0·0278	0·0442	0·0164
	z	0·2806	0·3075	0·0269
Ti(2)	*x*	0·2467	0·2642	0·0175
	z	0·6730	0·6734	0·0004
Ti(3)	*x*	0·1420	0·1574	0·0154
	z	0·9811	0·9957	0·0146
O(1)	*x*	0·221	0·1916	−0·029
	z	0·195	0·1871	−0·008
O(2)	*x*	0·140	0·1674	0·0270
	z	0·473	0·4761	0·003
O(3)	*x*	0·438	0·4478	0·010
	z	0·645	0·6732	0·028
O(4)	*x*	0·314	0·3058	−0·008
	z	0·885	0·9037	0·019
O(5)	*x*	0·997	1·0166	0·020
	z	0·745	0·7308	−0·0140
O(6)	*x*	0·791	0·8127	0·022
	z	0·313	0·3212	0·008
O(7)	*x*	0·905	0·9177	0·013
	z	0·031	0·0364	0·005

* Difference between the predicted and X-ray structures.

3.2. *The titanates* $Na_2Ti_6O_{13}$ *and* $Na_2Ti_3O_7$

Ideal models were again used as starting points for these calculations. Equilibrated structures are reported in Tables 3 and 4 where they are compared with experiment. Once more, good agreement between theory and experiment is obtained as illustrated in Figs. 3 and 4. Energy minimization, clearly, again leads to distortions from the ideal structures which are close to those observed experimentally.

Table 4. $Na_2Ti_6O_{13}$ *structural parameters*

		Ideal	X-ray	Predicted	Δ*
Ti(1)	x	0·1230	0·1137	0·1074	0·0063
	y	0·0000	0·0000	0·0000	—
	z	0·1270	0·0895	0·0839	0·0056
Ti(2)	x	0·1860	0·1705	0·1568	0·0137
	y	0·0000	0·0000	0·0000	—
	z	0·4440	0·4332	0·4400	0·0068
Ti(3)	x	0·2450	0·2287	0·2202	0·0085
	y	0·0000	0·0000	0·0000	—
	z	0·7540	0·7726	0·7887	0·0161
Na	x	0·4350	0·4540	0·4637	0·0097
	y	0·0000	0·0000	0·0000	—
	z	0·1900	0·2508	0·2636	0·0128
O(1)	x	0·0	0·0	0·0	—
	z	0·0	0·0	0·0	—
O(2)	x	0·2450	0·2280	0·2461	0·016
	z	0·2540	0·2470	0·2299	0·017
O(3)	x	0·0590	0·0710	0·0790	0·008
	z	0·3100	0·2910	0·28810	0·003
O(4)	x	0·3130	0·2820	0·3009	0·019
	z	0·5710	0·5740	0·5634	0·011
O(5)	x	0·1220	0·124	0·1357	0·012
	z	0·6270	0·617	0·6179	0·001
O(6)	x	0·372	0·358	0·3505	0·007
	z	0·881	0·884	0·8812	0·003
O(7)	x	0·184	0·167	0·1554	0·012
	z	0·944	0·927	0·9180	0·009

* Difference between predicted and X-ray structures.

4. Discussion

The agreement between predicted and experimental structures for the compounds discussed in this paper is remarkable. All structures show strong deviation from ideal models based on regular octahedra; these complex distortions are accurately reproduced by our energy-minimization techniques. The relaxation energies are considerable; the calculated values are given in Table 5. Relaxation arises from the need to adjust bond lengths, notably between those octahedra which share edges. This major effect is fully reproduced by our calculations.

We should note that, in view of the rather high values for the reliability (R) factors (presented in Table 6) for the refinements on which the published structures are based, it is a distinct possibility that our predicted coordinates are superior to the presently quoted experimental values. It would clearly be of interest to test this by a more detailed experimental study.

The success of our calculations has two major consequences. Firstly it provides further evidence for the viability of the potential models used in the study. Unlike calculated lattice energies, structures are very sensitive to the interatomic potentials – particularly the short-range components. The ability of our potential models to reproduce the complex low-symmetry distortions from ideality that are found in the observed structures suggests that the component pair potentials are valid over a wide range of interatomic separations.

Table 5. *Relaxation energies*

	E_{rel}(eV)		
Structure	per unit cell	per formula unit	per Ti (or V)
VO_2 (B)	78·49	9·81	9·81
TiO_2 (B)	76·73	9·59	9·59
$Na_2Ti_3O_7$	81·44	40·72	13·57
$Na_2Ti_6O_{13}$	137·69	68·85	11·47

Table 6. *R factors for published structures*

Structure	R factor (%)	Remarks	Reference
VO_2 (B)	10·1	Powder pattern	Theobald *et al.* (1976)
$Na_2Ti_3O_7$	13·2	$h0l$ terms } single crystal	Andersson & Wadsley (1962)
	14·9	hkl terms	
$Na_2Ti_6O_{13}$	11·9	$h0l$ terms } single crystal	Andersson & Wadsley (1961)
	15·9	hkl terms	

Secondly, the results clearly establish the energy-minimization methods as a predictive tool in structural inorganic chemistry. With the exception of the TiO_2 (B) phase, the structures discussed have all been studied experimentally and have yielded reasonably satisfactory refinements. The technique could now clearly be of great use in studying structures for which adequate refinements are difficult to obtain.

Finally, we should consider the extent to which the techniques we have discussed are generally applicable. The work described in this paper establishes their validity when applied to transition-metal oxides and, by implication, other ionic and semi-ionic compounds. Application to other classes of material depends on the success in developing appropriate interatomic potentials. A subsequent paper (Parker, Catlow & Cormack, 1984) will show how for one large and important class of compounds, namely mineral systems, the development of such models has proved to be possible.

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Structure Prediction of Silicate Minerals using Energy-Minimization Techniques

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Abstract

Energy-minimization techniques are applied to the prediction of the structures of a range of silicate minerals. Interatomic potential models for silicates are developed, based on an ionic description. Such potentials are shown to yield accurate structures for olivines and for ring- and chain-structure silicates. No evidence is found for a large Si···Si short-range repulsion or for strong differences in the bonding of bridging and non-bridging oxygen ions. The calculations are also successful in predicting the effects of temperature and pressure on the structural parameters of garnets and olivines.

1. Introduction

In a recent study (Catlow, Cormack & Theobald, 1984) we showed that energy-minimization procedures could accurately predict the structures of a number of transition-metal oxides. In the present paper we apply these techniques to the study of silicate minerals. The work is motivated by the enormous diversity of silicate structural chemistry, and the valuable rôle which could be played by reliable theoretical methods in rationalizing and predicting structural variations within this class. An additional incentive for theoretical work is provided by the importance, in geophysical contexts, of knowledge of the structure and properties of minerals, often relating to conditions where reliable experimental data cannot be collected.

Central to the area of structure prediction of minerals by minimization procedures is the question of bonding and interatomic potentials in these systems. A large amount of work has been devoted to this problem (see, for example, Gibbs, 1982; Pauling, 1980; O'Keeffe & Hyde, 1978; Baur, 1972). Our approach, which is amplified in § 2, is based on the ionic model description; and, while we are well aware of the limitations in such models when applied to silicates, one of the main conclusions of this paper is that these models provide at least a basis for an acceptable description of the interaction potentials in silicate minerals.

The compounds examined in this paper contain either isolated SiO_4 groups or silicate rings and chains. Details of the results of applying minimization techniques to these systems are presented in § 3 after the description of techniques and potentials that is given below.

2. Simulation methods and interatomic potentials

The basic principle of our method is simple. As discussed by Catlow *et al.* (1984), calculation of the crystal energy of the structure under investigation is

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