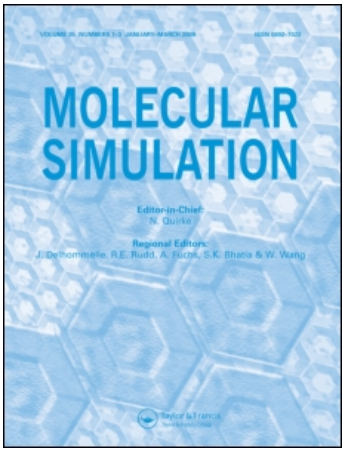

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A Transferable Interatomic Potential for Calcium Carbonate

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A TRANSFERABLE INTERATOMIC POTENTIAL FOR CALCIUM CARBONATE

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The development of an interatomic potential for calcium carbonate is described. The potential is fitted to calcite and then transferred to aragonite. The calculated structure and trend in lattice energies are both compared with experimental values.

KEY WORDS: Calcium carbonate, calcite, aragonite, potentials, energy minimisation

1 INTRODUCTION

Calcium carbonate, particularly in its calcite phase, is a mineral of great geochemical and geophysical importance. Computer modelling methods based on lattice energy minimisation are now well-established as a means of calculating the structures and lattice properties of solids [1]. These methods have not, to date, been extensively applied to solids involving molecular ions (e.g. carbonates, sulphates and phosphates), although some preliminary calculations have been carried out on sulphates [2, 3]. However, all these are important materials with roles in fields as diverse as process engineering, chemical engineering, geology and biomineralogy.

In this paper an interatomic potential is derived for calcite, and used to calculate the properties of aragonite. The strategy employed will be used in future studies of molecular ion materials.

2 POTENTIAL DEVELOPMENT FOR CALCITE

Most applications of lattice energy minimisation to solids, ranging from the most highly ionic (e.g. NaCl) to semi-ionic (e.g. SiO_2), have employed a fully ionic model supplemented by short range potentials, and in some cases, 3 body terms, to represent covalent effects. This approach has the advantage of consistency; there is no ambiguity in the choice of charges, and non-ionic effects are taken account of by the short range and 3 body potentials [1].

It is unfortunate but inevitable that this approach cannot be employed for calcium carbonate. Instead, it is necessary to allow the ionic charges to vary when fitting the potential, but since it is useful to retain a fully ionic description of calcium, Ca^{2+}, a strategy is adopted that the overall charge on the carbonate group is held at -2, and the carbon and oxygen charges allowed to vary within this constraint.

Table 1 Potential parameters for $CaCO_3$.

Charges (|e|)	q(Ca) = 2.0,	q(C) = 0.99805,	q(O) = −0.99935
Short range potentials			
Interaction		A (eV)	rho (Å)
Ca–O		8839.3	0.23813
C–O		3088.4	0.12635
O–O		36010.8	0.19756
Force constants			
Bond bending constant k_3 = 9.3179 eV rad^{-2}			
Torsional constant k_4 = 1.1392 eV			

An empirical fitting procedure is used to obtain the potential [1, 4]. This involves fitting to the structure, elastic and dielectric constants and phonon frequencies of calcite. Starting values for all potential parameters were obtained from previous studies on oxide systems.

The form of the potential employed is given below. It is divided into two-body, three-body and four-body terms. The two-body terms include the Coulombic interactions between ions, and short range interactions due to electron charge overlap; three-body terms describe bond-bending about each O–C–O bond, and four-body torsional terms retain the planarity of the CO_3^{2-} group.

$$\text{2-body terms: } V(r_{ij}) = q_i q_j / r_{ij} + A\exp(-r_{ij}/\rho) - Cr_{ij}^{\,6}$$

$$\text{3-body terms: } V(r_{ijk}) = 0.5k_3(\theta - \theta_0)^2$$

$$\text{4-body terms: } V(r_{ijkl}) = k_4[1 - S\cos[n\phi)]$$

In the above expression, $ijkl$ label ions with charges q_i, q_j, . . . , etc., A, and C are 2 body potential parameters, k_3 and k_4 are force constants, and θ, ϕ are bond-bending and dihedral angles.

The parameters obtained from the fit are given in Table 1.

3 APPLICATION OF THE POTENTIAL TO ARAGONITE

Having derived the potential described in the previous section, its transferability is tested by using it to calculate the structure of aragonite. Observed and calculated lattice parameters are compared in Table 2, and the agreement is seen to be good, indicating that the potential is transferable at least as far as structure is concerned.

A further point concerns the calculated lattice energies for the two polymorphs. It is known that calcite is the more stable phase under standard temperature and pressure conditions, yet the calculated lattice energies are −42.48 eV for calcite, and

Table 2 Comparison of observed and calculated structures for aragonite.

	Observed	*Calculated*
a (Å)	4.96	4.96
b (Å)	7.96	7.80
c (Å)	5.74	5.70

-42.52 eV for aragonite. Thus the enhanced stability of calcite must be due to entropic effects, a point borne out by experimental results [5] and by free energy calculations [6].

4 CONCLUSIONS

This paper describes a potential for calcium carbonate fitted to the calcite phase and transfered to aragonite. The potential calculates structural properties accurately, and predicts the correct trend in lattice energies. Moreover it can be used in defect calculations, provided the molecular anion CO_3^{2-} is treated as a single entity.

The potential is for a rigid ion system, i.e. ionic polarisability is neglected, which is important in the correct calculation of phonon frequencies and high temperature properties. Polarisability can be included by development of a shell model potential. Such a potential will be the subject of a future publication [6].

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