Modified electron gas modelings of calcite and aragonite: Comparison of polarizable anion and fully ionic methods

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Abstract

Modified electron gas (MEG) methods have yielded crystal structures, lattice energies, and bulk moduli in close agreement with experiment when used to model ionic solids, but, when these methods were applied to covalently bonded substances, the agreement between the model and experiment was not as close. The use of a shell model for anion polarization has improved agreement with experiment in the covalently bonded substances but has degraded such agreement in the ionic solids. These observations raise the question as to how well substances with both ionic and covalent bonds would be modeled using MEG methods, with and without allowances for anion polarization. Purely ionic modelings of calcite and aragonite, which disregard anion polarization, result in several significant errors. In the current work, we model these substances using polarizable anion MEG methods and obtain improved agreement with experiment for most, but not all, structure and energy parameters. Further improvements were obtained by using the polarizable ion approach in conjunction with the use of fixed CO_3 group geometries. We obtained a picture of the calcite-aragonite phase transition using the polarizable ion treatment that is an improvement over the purely ionic method. Our prediction for the transition pressure is still too high (100 kbar compared with the experimental value of 3 kbar), but the difference can be mainly attributed to the fact that the model calcite equilibrium cell volume is too small.

Introduction

Modified electron gas (MEG) methods for modeling crystal structures are appealing because of their conceptual simplicity and computational economy. Previous MEG modelings have reproduced experimental crystal structures and lattice energies quite closely when applied to binary oxides and halides (Gordon and Kim, 1972; Cohen and Gordon, 1975, 1976; Waldman and Gordon, 1979; Jackson and Gordon, 1988a) and to orthosilicates (Post and Burnham, 1986; Jackson and Gordon, 1988b) but less closely when applied to inosilicates and tectosilicates (Post and Burnham, 1986; Jackson and Gibbs, 1988; Jackson and Gordon, 1988c). Errors in the latter structure types are more pronounced because MEG theory assumes that the constituent atoms have closed-shell electronic configurations and rigid, spherical electron density distributions, so that interactions between pairs of atoms are treated as fully ionic. In the binary oxides and halides, the bonding is believed to be predominantly ionic, whereas in inosilicates and tectosilicates, the bridging Si-O-Si bonds are believed to have significant covalent character.

The effects of spherically symmetric electrostatic polarization of ions can be treated with the potential induced breathing (PIB) model (Boyer et al., 1985). Allowance for directional (bond) polarization of anions in MEG modelings improves agreement with experiment when applied to quartz, cristobalite, and coesite (Jackson and Gibbs, 1988; Jackson and Gordon, 1988c) but degrades agreement with experiment when applied to forsterite and Mg_2SiO_4 spinel.

It is of interest to examine the performance of MEG methods in modeling materials having both ionic and covalent bonds, as the $CaCO_3$ polymorphs are believed to have (cf. Reeder, 1983; Speer, 1983; Klein and Hurlbut, 1985). Fully ionic MEG modelings of calcite and aragonite (Lindsay, 1988) yield C-O bond lengths much shorter, and lattice energies much lower in magnitude, than those determined experimentally. The atomic positions in the model aragonite structure were markedly different from those deduced from X-ray diffraction data. Other recent theoretical studies have focused on deriving empirical parameters fitted to experimental dynamic and structural data (Dove et al., 1992; Pavese et al., 1992).

In the current work we evaluate the implications of introducing covalent character into the carbonate group by a polarizable anion MEG approach. The main issue

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TABLE 1. Calcite equilibrium structure with a fully ionic, variable $R(CO)$

	Calc.	Expt.
Unit-cell dimensions		
a (Å)	5.937	6.375
α (°)	49.71	46.08
V (Å³)	111.98	122.63
Variable atomic positional parameter		
O (x)	0.4923	0.5071
Interatomic distances (Å)		
CaO (6 bonds)	2.327	2.359
CO (3 bonds)	1.209	1.283
Other data		
W (kJ/mol)	−15312	−18430*
K_0 (kbar)	1225	826**

Note: W is for one formula unit. Calculated data are from Lindsay (1988). Experimental data are from Effenberger et al. (1981), except where noted.
  * Wagman et al. (1982).
  ** Dandekar and Ruoff (1968).

TABLE 2. Calcite—fully ionic model

Parameter	Variable $R(CO)$	Fixed $R(CO)$
a (Å)	5.93	5.90
α (°)	49.80	51.18
V (Å³)	111.98	115.04
W (kJ/mol)	−15312	−15231

is whether allowance for polarization of the O^{2-} electron density provides a better structural model for these phases, as evidenced by agreement with experiment. In addition, we review the results of the fully ionic modelings and analyze possible sources of error, other than those arising from the neglect of anion polarization (covalent) effects.

COMPUTATIONAL METHODS

The modified electron gas methods (Gordon and Kim, 1972; Waldman and Gordon, 1979; Muhlhausen and Gordon, 1981; Jackson and Gordon, 1988c) derive the electron density distribution of ions in crystals from the closed-shell Hartree-Fock electronic wave functions for that atom. The total electron density at any point in a crystal is modeled by a superposition of the electron density distributions of constituent ions. The present modelings exclude thermal and zero-point vibrational energies and employ the pair-potential approximation: the short-range repulsion energy is taken to be the sum of contributions from ion pairs only; many-body effects are not considered. The short-range repulsion energy, or pair potential, for a given ion pair is the sum of the nonpoint-coulombic (arising from overlapping electron densities), kinetic, exchange, and correlation energies. The lattice energy (W), in turn, is the sum of the point-coulombic and the short-range repulsion energies. In this study, the latter term treats only nearest neighbor and second nearest neighbor ion pairs.

The wave functions used for Ca^{2+} and C^{4+} are tabulated by Clementi and Roetti (1974). O^{2-} is unstable as an isolated ion; therefore, we calculate Watson-sphere-stabilized (Watson, 1958) wave functions for the ions of interest (Laws et al., 1971). The Watson sphere, a hypothetical spherical shell of charge q_{ws} (here +2) and radius r_0, provides a potential $V_{ws} = q_{ws}/r_0$ that stabilizes the isolated ion. In an ideal fully ionic crystal, O^{2-} ions are stabilized by the potential V_{site} at the O^{2-} sites because of the crystal field. The correct stabilized O^{2-} wave function for a model crystal structure is that for which $V_{ws} = V_{site}$; such a wave function is said to be electrostatically con-

sistent. Our method for achieving electrostatic consistency is described below.

The computer program Leminpi (Muhlhausen and Gordon, 1981) was used to calculate pair potentials and to determine minimum energy crystal structures. Pair potentials were calculated at intervals of 0.1 bohr (≈ 0.053 Å). We determined short-range repulsion energies from these pair potentials during energy minimization using cubic spline interpolation. If desired, these pair potentials can be fitted to an empirical or theoretical function of interatomic distance.

Determining a minimum-energy crystal structure is a two-stage process. In the first stage, a structure electrostatically consistent with each stabilized O^{2-} wave function is found. For each such wave function, W is calculated as a function of external pressure (P) over a series of P values. Each P value corresponds to a PV energy term, which Leminpi adds to the zero-pressure W value. We consider a structure to be electrostatically consistent when $2/V_{site} = r_0$ within 10^{-4} bohr ($\approx 5.3 \times 10^{-5}$ Å). Repeating this procedure for several stabilized O^{2-} wave functions gives a preliminary functional relationship between W and P. In the second stage of W minimization, these preliminary W-P data are fitted to an equation of state to obtain a smooth W-P curve and to determine the zero-pressure unit-cell volume and bulk modulus (K_0). We fitted our W-P data to a second-order Birch-Murnaghan equation (Birch, 1978) for a static crystal at absolute zero temperature, using the program Birnt (written by R. S. Hemley and modified by M. D. Jackson).

The methods described so far apply to both fully ionic and polarizable-anion MEG modelings and were also used in the study by Lindsay (1988). In the polarizable ion modelings, the Watson-stabilized O^{2-} ion is partitioned into a fixed core consisting of the nucleus and the core electrons and one or more movable (polarizable) shells containing the valence electrons. The actual number of electrons to be assigned to the core and to each shell depends to some extent on the properties to be modeled; considerations leading to our choices are explained in a later section.

Each shell is bound to the core by a restoring force $F_{rest} = -\mathbf{kx}$, where $\mathbf{x}$ is the displacement vector from the core center to the shell center, and $\mathbf{k}$ is the spring constant. We used a single shell on each O^{2-} ion and restricted $\mathbf{x}$ to lying along the C-O bond axis; this is a simplification of the two-shell model used in MEG modelings of silica (Jackson and Gordon, 1988c; Jackson and Gibbs, 1988). The choice of $\mathbf{k}$ is derived from the polarizability (α_{ion}) of O^{2-} and the short-range repulsion, which limits $\|\mathbf{x}\|$.

TABLE 3. Calcite—reduced-charge ionic model

Parameter	Scaled O^{2-}	Clementi O^-	Experiment
a (Å)	6.41	6.59	6.375
α (°)	59.10	58.70	46.08
V (Å³)	181.8	196.1	122.6
W (kJ/mol)	−3397	−3246	−5223

The average of the O^{2-} α_{ion} values parallel and perpendicular to the C-O bond in $CaCO_3$ is determined experimentally to be about 1.2 Å³ (Pastorek and Decius, 1979). The shifting of the polarizable shell is restricted by the short-range repulsion between the oxide shell and the C ion. Therefore, the polarizability of the anion shell is decreased to account for this effect. Following the method of Pearson et al. (1984), we chose α_{ion} = 0.3 Å³ for the oxide ion in the carbonate group.

In determining minimum W structures, we maintained observed space group symmetries. The calcite structure (space group $R\bar{3}c$) thus has three free variables—the two cell constants and one positional parameter for O. The aragonite structure (space group $Pmcn$) has 12 free variables—the three cell edge lengths, two positional parameters for each of Ca, C, and O1 (all situated on a mirror plane), and all three positional parameters for O2 (situated in a general position). In a refinement of the polarizable anion method and in one set of fully ionic calculations, we also held the C-O bond lengths, $R(CO)$, constant.

EXAMINATION OF THE FULLY IONIC MODELINGS

Calcite

Table 1 lists model and experimental crystal structure parameters and other data. The most significant discrepancies in the model structure are that it underestimates $R(CO)$ by about 6% and the magnitude of W by about 17% and that it overestimates K_0 by about 48%. Additionally, a is shorter, α is wider, and the cell volume is smaller than what was measured experimentally.

Initial examination of these results suggests that the disagreement between the model and observed crystal structures could perhaps be reduced by artificially lengthening the extremely short C-O bond. Accordingly, we repeated the fully ionic modeling with $R(CO)$ fixed at 1.283 Å, the experimental value. As seen in Table 2, a and α are in slightly poorer agreement, and W is in considerably poorer agreement, with experiment. Apparently, factors besides the short $R(CO)$ contribute to the errors in the fully ionic model calcite structure.

Another possibility we considered was that the discrepancies in the model structure might be due to the unrealistically high ionic charges, especially on C^{4+}. With this in mind, we modeled calcite using C^+ for C and O^- for O. The B isoelectronic Hartree-Fock wave function of Clementi and Roetti (1974) was used for C^+, and each of two types of wave function was used for O^- in separate calculations: (1) the Clementi-Roetti (1974) O^- wave

TABLE 4. Aragonite equilibrium structure—fully ionic, variable $R(CO)$

	Calc.	Expt.
Unit-cell dimensions		
a (Å)	5.786	4.962
b (Å)	6.327	7.971
c (Å)	6.037	5.739
V (Å³)	221.00	226.99
Variable atomic positional parameters		
Ca y	0.3279	0.4151
z	0.1722	0.2403
C y	0.8102	0.7627
z	0.0781	0.0850
O1 y	0.9931	0.9231
z	0.0370	0.0952
O2 x	0.4262	0.4729
y	0.7097	0.6801
z	0.1068	0.0870
Interatomic distances (Å)		
CO1	1.184	1.280
CO2	1.214	1.287
CaO1	3.542*	2.655
	2.476	2.655
	2.270	2.411
CaO2 (2 bonds)	2.419	2.526
(2 bonds)	2.652	2.541
(2 bonds)	2.531	2.448
Other data		
W (kJ/mol)	−15177	−18430**
K_0 (kbar)	1407	505†

Note: W is for one formula unit. Calculated data are from Lindsay (1988). Experimental data are from Dal Negro and Ungaretti (1971), except where noted.
* Included for comparison purposes; the distance is so long that these atoms should not be considered to be bonded to each other.
** Wagman et al. (1982).
† Hearmon (1946).

function, and (2) one derived from the Watson-sphere-stabilized O^{2-} wave functions described above by scaling the atomic orbital coefficients to reduce the number of electrons from ten to nine. With both types of O^- wave function, a is too long and α is even wider than when C and O had their original charges. The underestimation of W is nearly twice that made with the fully ionic model, and the cell volume is again much too large (Table 3). The errors in the fully ionic modelings therefore cannot be attributed solely to overly high ionic charges.

Aragonite

The discrepancies between model and observed aragonite structural and energetic properties (Table 4) are similar to those found for calcite: $R(CO)$ is underestimated by 6–7%, the magnitude of W is underestimated by 17–18%, and K_0 is overestimated, here by 180%. The unconstrained calculated and experimental atomic positional parameters differ markedly. Some of the calculated $R(CaO)$ values are in fair agreement with experiment, but one in particular is so long that the ions should not be considered to be bonded to each other. Two of the cell edges are longer and one is shorter than those measured experimentally, but the cell volume is in close agreement with experiment. It is smaller than that calculated for calcite, as it should be, but not by as much as what was found experimentally.

TABLE 5. Calcite—polarizable ion model

Shell electrons	2	4	6
a (Å)	6.46	6.43	6.41
α (°)	43.9	44.3	44.4
V (Å³)	117.8	117.9	117.0
$\|\mathbf{x}\|$ (Å)	0.27	0.12	0.06

Note: $\alpha_{ion} = 0.3$ Å³.

Modelings of aragonite with fixed R(CO) or reduced ionic charges were not attempted. As these approaches failed to improve the calcite modelings, we believe it unlikely that they would improve the aragonite modelings.

POLARIZABLE ION MODELINGS

Calcite

We initially examined shell-charge effects in modeling $CaCO_3$ by modeling calcite with three oxide shell charges, -2, -4, and -8. The resulting equilibrium structures are compared in Table 5. The main difference among these is in the resulting displacement of the shell center from the O^{2-} nuclear center toward the C^{4+} cation. Variations in local dipole moments along the C-O bond with varying shell charge are quite small, suggesting that the choice of shell charge is relatively unimportant when bond dipole moments are of primary interest. Our choice of a shell charge of -4 for subsequent modelings follows that used in previous polarization and refractive index calculations (Kim and Gordon, 1974; Pearson et al., 1984).

Equilibrium structural parameters, and W and K_0, determined with the polarizable anion model and by experiment are compared in Table 6. The value of R(CO) found with the polarizable anion model is even shorter than that found with the fully ionic model. The polarizable anion model undercorrects the unit-cell volume, W, and K_0, and overcorrects a and α, relative to the fully ionic model, but it does give results closer to experiment for all of these parameters.

Noting that the most significant error in the polarizable anion model structure is again the short R(CO), we perform calculations with R(CO) fixed at 1.283 Å. The resulting crystal structure is the closest to experiment of any we have obtained. On the other hand, the estimate

TABLE 6. Calcite equilibrium structure—variable R(CO)

	Fully ionic	Polarizable ion	Experiment
Unit-cell dimensions			
a (Å)	5.93	6.43	6.375
α (°)	49.82	44.34	46.08
V (Å³)	112.0	117.9	122.62
Variable atomic positional parameter			
O x	0.4923	0.4955	0.5071
Interatomic distances (Å)			
Ca-O (6 bonds)	2.327	2.340	2.359
C-O (3 bonds)	1.211	1.191	1.283
Other data			
W (kJ/mol)	−15312	−16581	−18430
K_0 (kbar)	1219	1040	826

TABLE 7. Calcite equilibrium structures—fixed R(CO)

	Polarizable ion model		Experiment
Shell model parameters			
α_{ion} (Å³)	0.3	0.33	—
$\|\mathbf{x}\|$ (Å)	0.11	0.12	—
Unit-cell dimensions			
a (Å)	6.38	6.38	6.375
α (°)	45.84	45.86	46.08
V (Å³)	121.6	121.8	122.6
Variable atomic positional parameter			
O x	0.5083	0.5081	0.5071
Interatomic distances (Å)			
Ca-O (6 bonds)	2.331	2.332	2.359
C-O (3 bonds)	1.283*	1.283*	1.283
Other data			
W (kJ/mol)	−16364	−16494	−18430
K_0 (kbar)	1036	1030	826

* Constrained.

of W is somewhat poorer and that of K_0 is only slightly better than those obtained using only the polarizable anion model (see Table 7). The main disadvantage of the polarizable anion, fixed R(CO) method is that it requires input of experimental data; in particular, to model different $CaCO_3$ phases or to study effects of elevated pressures, experimentally determined R(CO) values would be needed for each phase or at each pressure (or both). This difficulty could perhaps be circumvented by treating the CO_3^{2-} group as a rigid polyatomic ion, i.e., an anionic group with a geometry invariant to chemical environment or pressure changes. This is justifiable as a first approximation: the C-O bond is sufficiently stiffer than the Ca-O bond (at least in calcite) that variations in R(CO)

TABLE 8. Aragonite equilibrium structure—variable R(CO)

		Fully ionic	Polarizable ion	Experiment
Unit-cell dimensions				
a (Å)		5.79	4.86	4.962
b (Å)		6.33	7.86	7.971
c (Å)		6.04	5.95	5.739
V (Å³)		221.0	227.3	227.0
Variable atomic positional parameters				
Ca	y	0.3279	0.4156	0.4151
	z	0.1722	0.2441	0.2403
C	y	0.8102	0.7610	0.7627
	z	0.0781	0.0846	0.0850
O1	y	0.9931	0.9112	0.9231
	z	0.0370	0.0883	0.0952
O2	x	0.4262	0.4603	0.4729
	y	0.7097	0.6849	0.6801
	z	0.1068	0.0872	0.0870
Interatomic distances (Å)				
		1.184	1.181	1.280
CO1		1.214	1.186	1.287
CO2		3.542	2.633	2.655
CaO1		2.476	2.633	2.655
		2.270	2.453	2.411
CaO2 (2 bonds)		2.419	2.529	2.526
(2 bonds)		2.652	2.549	2.541
(2 bonds)		2.531	2.504	2.448
Other data				
W (kJ/mol)		−15179	−16568	−18430
K_0 (kbar)		1096	1014	505

TABLE 9. Aragonite equilibrium structure—fixed R(CO)

	Polarizable ion model		Experiment
Shell model parameters			
α_{ion} (Å³)	0.3	0.33	—
$\|x\|$ (shell shift, Å)	0.115	0.127	—
Unit-cell dimensions			
a (Å)	5.08	5.04	4.962
b (Å)	8.02	7.99	7.971
c (Å)	5.88	5.90	5.739
V (Å³)	239.3	237.6	227.0
Variable atomic positional parameter			
O x	0.4677	0.4693	0.4729
Interatomic distances (Å)			
CO1	1.280*	1.280*	1.280
CO2	1.287*	1.287*	1.287
Other data			
W (kJ/mol)	−16286	−16435	−18430
K_0 (kbar)	—	1014	—

* Constrained.

TABLE 10. Free energy (kJ) and ΔV (Å³) for variable C-O shell-model treatment of aragonite and calcite

P (kbar)	Calcite	Aragonite	ΔV (Å³)
0.0	−16581	−16568	−4.3
30.0	−16476	−16467	−4.0
50.0	−16407	−16400	−3.7
70.0	−16339	−16335	−3.6
100.0	−16239	−16239	−3.6
120.0	−16174	−16176	−2.9

Note: $\Delta V = V_{aragonite} - V_{calcite}$.

with pressure could be considered negligible relative to variations in R(CaO).

To test this rigid polyatomic ion approximation, we modeled the high-pressure behavior of calcite with R(CO) = 1.283 Å for all pressures. We used $\alpha_{ion} = 0.3$ Å³ for O²⁻, as in the earlier modelings, and then repeated the calculations using $\alpha_{ion} = 0.33$ Å³ to account for the effects of the longer R(CO) compared with the variable R(CO) modelings. Within the shell model, longer bonds lead to reducing the damping of α_{ion}. The predicted equilibrium structure is given in Table 7. The larger α_{ion} results in a slightly more stable lattice and a unit-cell volume in good agreement with experiment.

Aragonite

Results of a variable R(CO) modeling with $\alpha_{ion} = 0.3$ Å³ are given in Table 8. Two fixed R(CO) modelings were made, one with $\alpha_{ion} = 0.3$ Å³ and one with $\alpha_{ion} = 0.33$ Å³; these results are shown in Table 9. The polarizable ion model equilibrium structure is drastically improved over that found with the fully ionic model. The fixed R(CO) results are in slightly better agreement with experiment than the variable R(CO) results. The main discrepancy in each structure is an overestimate of c by 3–4%. The dipolar shell model omits quadrupolar and higher multipolar effects and therefore underestimates the interaction between adjacent carbonate groups. The addition of these attractive energy terms would tend to shorten this lattice constant. However, implementation of multipolar terms is beyond the scope of the present modeling.

Again, K_0 is overestimated with both the variable and the fixed R(CO) model, but the value is closer to the experiment in both models and is less than the K_0 calculated for calcite, which is in qualitative agreement with experiment.

Calcite-aragonite transition pressure

Using the free energy (G) values for calcite and aragonite calculated with variable R(CO) (Table 10), we esti-

mate a value of 100 kbar for the calcite-aragonite transition pressure; the experimental value is about 3 kbar at 298 K (Carlson, 1980). The model predicts a ΔV of −3.6 Å³ (about −3%) for the transition. This overestimation of the transition pressure is probably related to an unrealistically small difference between the calculated volumes of calcite and aragonite. The calculated calcite volume is smaller than the observed, but the calculated aragonite volume is in good agreement with experimental data.

With the phase transition, calculations with a fixed R(CO) model are not meaningful because fixing R(CO) has different effects on W (and so on G) in the two phases. With a fully ionic model (Lindsay, 1988), the G-P curves for calcite and aragonite did not cross each other at any physically meaningful pressure, and so a calcite-aragonite transition pressure could not be estimated. Although the transition pressure estimated with the polarizable ion model is much too high, this model does give qualitatively correct calcite-aragonite phase relations with respect to pressure.

CONCLUDING COMMENTS

Fully ionic modelings of calcite and aragonite have yielded values for crystal structure and energy parameters that depart significantly from their experimentally determined counterparts. Many of these discrepancies can be at least partially alleviated by allowing for anion bond polarization using a single-shell model. The results presented here, together with those obtained for inosilicates and tectosilicates, suggest that anion polarization needs to be taken into account when using MEG methods to model structures containing bonds believed to be largely covalent.

Some additional improvements in modeling calcite and aragonite seem to be obtainable by fixing the geometric parameters of the CO₃ groups at their experimental values, while allowing other geometric parameters to vary, in effect treating the CO₃ groups as rigid polyatomic anions. This possibility needs to be explored through modelings of other crystal structures, such as sulfates, that contain anionic functional groups believed to have predominantly covalent bonds.

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