Simulation of Structural Transformation in Aragonite CaCO₃

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Abstract. The structural transformation in aragonite CaCO₃ is simulated by molecular dynamics. The simulations are based on the potentials calculated from the Gordon-Kim modified electron gas formalism. We found two phase transitions in aragonite at high temperature.

INTRODUCTION

At room temperature and ambient pressure, aragonite is a metastable polymorph of calcium carbonate CaCO₃ whose crystallization occurs frequently in nature (shells, corals, mineral sediments, etc.). It transforms into calcite that is the stable polymorph of calcium carbonate when heated (1). In this paper we describe first-principle simulations of structural transformations in aragonite using ab initio inter-ionic potentials developed for ion molecular solids.

A full description of the procedure for obtaining both inter- and intramolecular potentials from quantum-chemistry calculations has been given elsewhere (2). Only a brief discussion related to aragonite will be presented here. We first performed a quantum chemistry structural optimization for the CO₃ ion to search for the atomic configuration that gives the lowest self-consistent Hartree-Fock energy by using GAUSSIAN94 commercial package (3). The intramolecular potentials were described by the harmonic expansion whose ab initio force constants were calculated from the optimized structure of CO₃ by GAUSSIAN94. In order to determine the intermolecular/ionic interactions, the CO₃ molecular charge density was first decomposed onto the carbon and oxygen atoms in the spirit of a Mulliken population analysis (4). Then, using these charge densities and the free ion charge density for the Ca²⁺ ion, we computed the short-range pair potentials between these ions according to the Gordon-Kim electron gas model (5). The long-range Coulomb interactions were calculated using the fractional Mulliken charges of C and O atoms as: +0.8721e and -0.9574e, respectively, together with the ionic charge of Ca²⁺.

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STATIC RELAXATION OF ARAGONITE

Using the intra-molecular and inter-molecular ionic interaction potentials obtained above, we performed a static relaxation calculation for aragonite with the \( Pmcn \) symmetry constraints. This determines the positions of the atoms and the lattice vectors that correspond to the minimum of the theoretical potential-energy surface. Our relaxation was performed for an infinite lattice by applying periodic boundary conditions, and followed a Newton-Raphson algorithm. The standard technique of the Ewald sum was used to calculate the lattice energy and forces, etc.

The parameters for the relaxed structure along with the experimental values (6) for aragonite at room temperature are given in Table 1. Our relaxed structures are in good agreement with experiment as far as the reduced (fractional) basis vectors are concerned. The discrepancy is comparable with the thermal fluctuation of the atomic positions at room temperature. The average lattice constants for the relaxed structure are a few percent shorter than the experimental values, as is typical for Gordon-Kim potentials. Also, the experimental values of these parameters are room temperature values and thus include the effects of the thermal expansion, while the relaxed lattice is static and without temperature effects.

We also performed static relaxation without the \( Pmcn \) symmetry constraints and the results are the same as those obtained with constraints.

MOLECULAR-DYNAMIC SIMULATIONS OF THE PHASE TRANSITIONS

In our simulation we used a periodic super-cell with 540 ions formed by tripling the \( Pmcn \) orthorhombic unit cell in all three directions. Starting from the theoretical relaxed structure obtained previously, we first quenched the sample to remove any residual kinetic energy in the relaxed structure, and then, heated the sample in 100K stages. At each stage the averages of the ion positions, the energy, etc., were taken over 10ps using a 1fs molecular-dynamics time step.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Theory</th>
<th>Experiment</th>
<th>Diff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>9.0880</td>
<td>9.3761</td>
<td>-3.07</td>
</tr>
<tr>
<td>( b )</td>
<td>14.0420</td>
<td>15.0621</td>
<td>-6.77</td>
</tr>
<tr>
<td>( c )</td>
<td>10.5190</td>
<td>10.8459</td>
<td>-3.01</td>
</tr>
<tr>
<td>( y/b ) of C (1)</td>
<td>0.7665</td>
<td>0.7627</td>
<td>0.45</td>
</tr>
<tr>
<td>( z/c ) of C (1)</td>
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<td>-0.0850</td>
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</tr>
<tr>
<td>( y/b ) of Ca (1)</td>
<td>0.4139</td>
<td>0.4151</td>
<td>-0.29</td>
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<tr>
<td>( z/c ) of Ca (1)</td>
<td>0.7617</td>
<td>0.7597</td>
<td>0.26</td>
</tr>
<tr>
<td>( y/b ) of O (1)</td>
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<td>0.9231</td>
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<tr>
<td>( z/c ) of O (1)</td>
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<tr>
<td>( x/a ) of O (2)</td>
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<td>0.6801</td>
<td>0.12</td>
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<tr>
<td>( z/c ) of O (2)</td>
<td>-0.0765</td>
<td>-0.0870</td>
<td>-12.07</td>
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</table>
We found two phase transitions occurring in aragonite in our simulation. Fig.1(a,b) and Fig.1(c,d) show the projections of the ion positions in the average structure just below and above the first transition, respectively. In the plot the lines connect the carbon atoms with the nearest oxygen atoms and the ellipses indicate the thermal motion of the atoms. The system still has the aragonite structure at 1613K, but the carbonate ions have become partially disordered, with some carbonate ions hopping 120° about their triad axes as shown in Fig.1(a). In aragonite, between each pair of planes of Ca atoms there are two planes of carbonate groups, staggered, and with carbonate groups pointing in opposite direction as in Fig.1(b). At 1706K the system suddenly transforms into a new structure. All the carbonate ions rotate +30° or -30° about their triad axes as shown in Fig.1(c). The two staggered planes of carbonates planes become a single plane midway between the planes of Ca atoms, and all the carbonate groups point to the same direction as shown in Fig.1(d). The collective rotations of the CO$_3$ groups cause an abrupt increase of the lattice constant in the aragonite $b$ direction and contraction in the $a$ direction. This is illustrated in Fig.2, which shows the lattice constants as a function of temperature for the MD run.

FIGURE 1. Projections of the atomic positions: (a, c) along $c$ axis, (b, d) along $a$ axis of aragonite in the average structure obtained from the MD simulation at 1613K and 1706K, respectively.
The carbonate ions in the new structure also are partially disordered, and as the temperature continues to increase, more and more carbonate ions begin hopping (Fig.3(a)). When all the carbonate ions are disordered at 1938K as shown in Fig.3(b), the structure has assumed to form a higher symmetry phase. This phase transition is signaled by an anomaly of the specific heat. The continuous changes of the lattice constants (Fig.2) indicate that this phase transition is second-order. The carbonate ions are performing hindered rotation and the average orientations of carbonate ions are random above this phase transition temperature.

**FIGURE 2.** Lattice constants as a function of temperature for the MD run on aragonite.

**FIGURE 3.** Projections of the atomic positions along the c axis of aragonite in the average structure obtained from the MD simulation at: (a) 1845K, (b) 1938K.
FIGURE 4. Projections of the atomic positions: (a) along the c axis, (b) along the a axis of calcite.

DISCUSSION

The aragonite is a metastable phase of carbonate in nature. It transforms to calcite on heating. The transformation occurs at any temperature between 350-750K according to the composition, purity and origin of the product. The synthetic, pure aragonite has the highest transformation temperature (1). The transformation from aragonite to calcite involves large translations of Ca ions and the carbonate ions in the ab plane as can be seen by comparing Fig.1 and Fig.4. Fig.4 shows the projections of calcite along the c and a axis. This component of the transformation involves a radical re-packing of the ions and lies far outside the time scales accessible to molecular dynamics. Thus, our simulation results can not be directly compared with the experiment. However, the new structure obtained by our simulation has some similarities with the calcite. From Fig.1(d) and Fig.4(b), one can see that our new structure and calcite both have a single plane of carbonate groups midway between each pair of planes of Ca atoms, and all the CO3 groups point to the same direction.

The potential energies in the theoretical calcite, aragonite, and our new structure are -1.16911, -1.16685, and -1.16745 Hartree per formula in ground state, respectively. The ground states of the calcite and aragonite were obtained by static relaxation, and that of our new structure was obtained by quenching the new structure at 1706K to 0K. Our new structure has lower energy than aragonite, so it is more stable than aragonite, but it is still less stable than calcite because it has more energy than calcite.

ACKNOWLEDGMENTS

This work was supported by the U.S. Army Research Office under Grants Nos. DAAG 55-97-1-0106 and DAAG 55-98-1-0273. The computer facility was supported by Nebraska-EPSCoR-NSF Grant EPS-9720643.

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