research papers

Aplanarity of CO_3 groups: a theoretical investigation

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Density functional theory-based calculations have been used to demonstrate that the aplanarity of CO_3 groups in some carbonates such as dolomite, $CaMg(CO_3)_2$, aragonite, $CaCO_3$, and norsethite, $BaMg(CO_3)_2$, is a ground-state property. This distortion stabilizes dolomite by $\sim$500 J mol^{-1}. Up to at least 6 GPa, the aplanarity of CO_3 groups in dolomite is independent of pressure. In aragonite the aplanarity increases slightly on increasing pressure, while a significant tilting of the CO_3 groups occurs. The calculations do not support previous findings of anomalously low values for the pressure derivative of the bulk moduli, B', of aragonite and dolomite. Instead, the computed pressure dependences of the unit-cell volumes correspond to $B' = 5.0\ (5)$ for aragonite and $B' = 4\ (1)$ for dolomite, when fitted with a third-order Birch–Murnaghan equation-of-state.

1. Introduction

With increasing precision of experimental structure determinations it has become obvious that the CO_3 group is aplanar in many carbonates if its point symmetry in the structure allows this (Zemann, 1981). The aplanarity, d, *i.e.* the distance between the C atom and the plane defined by the O atoms, is generally rather small, $d \leq 0.03$ Å. Only in a few cases have larger values been reported, such as in norsethite, $BaMg(CO_3)_2$, where $d = 0.044\ (7)$ Å (Effenberger & Zemann, 1985), and in thaumasite, $Ca_3Si(OH)_6CO_3SO_4{\cdot}12H_2O$, with $d = 0.060\ (9)$ Å (Effenberger, Kirfel, Will & Zobetz, 1983). However, to the best of our knowledge no low-temperature studies exist attempting to clarify if this aplanarity is a ground-state property or if it is due to thermal excitation. While systematic studies of the dependence of the aplanarity of CO_3 groups on composition have been presented (Beran & Zemann, 1977; Zemann, 1981; Chevrier *et al.*, 1992), very little is known on the variation of d with pressure. We know of only one such study on dolomite and ankerite (Ross & Reeder, 1992), where the aplanarity of the CO_3 groups was found to be independent of pressure. Whether or not the aplanarity of CO_3 groups is a ground-state property and how it changes with increasing pressure has been studied here by quantum mechanical calculations, using dolomite, $CaMg(CO_3)_2$, aragonite, $CaCO_3$, and norsethite, $BaMg(CO_3)_2$, as examples. Dolomite was chosen since a direct comparison with experimental data (Effenberger *et al.*, 1981; Reeder & Markgraf, 1986; Ross & Reeder, 1992; Effenberger, Kirfel & Will, 1983) is possible. This allows us to establish the reliability and accuracy of the calculations and hence the predictive value for the data obtained for the more complex aragonite and norsethite structure. The calculations for norsethite were used

to establish if large aplanarities are also well described with the approach employed here and to determine if the space group of norsethite in the ground state is $R\bar{3}m$ or $R32$.

Quantum mechanical models are well established to study details of structural distortions and structure–properties relations (Winkler, 1999). They are generally precise enough to accurately reproduce subtle structural details, which is not always the case with empirical potentials. We will show here that the energy difference between a planar and an aplanar group is too small to be reliably represented by empirical models. In fact, rather sophisticated electrostatic models aimed at elucidating the origin of the aplanarity have been unsuccessful (Heiss & Zemann, 1984). For solids the most often used technique for quantum mechanical calculations is based on the density functional theory, DFT (Hohenberg & Kohn, 1964; Kohn & Sham, 1965; Parr & Yang, 1989; Kryachko & Ludena, 1990), which has also been used here.

For an understanding of the high-pressure behavior of minerals, equation-of-states are used to extrapolate known $V(P,T)$ relationships to higher pressures and temperatures. For such an extrapolation to be reliable, it is important that the pressure derivative of the bulk modulus B' is determined with sufficient accuracy. In a recent study of the equation-of-state of aragonite and dolomite, rather low values of $B' = 2.7$ (7) and 2.3 (5) have been suggested for aragonite and dolomite, respectively (Martinez *et al.*, 1996). In an earlier study a much higher value of $B' = 10$ (2) has been obtained for dolomite (Fiquet *et al.*, 1994). Quantum mechanical calculations such as those performed here are known to generally give reliable values for B' and hence these values have been computed here as well.

2. Computational details

The quantum mechanical calculations performed here are based on density functional theory, DFT. While DFT itself is exact (Hohenberg & Kohn, 1964), practical calculations require an approximation for the treatment of the exchange and correlation energies. Here, exchange–correlation effects were taken into account using the 'generalized gradient approximation', GGA (Perdew & Wang, 1992), as implemented by White & Bird (1994). Results based on GGA calculations are generally in better agreement with experiment than those obtained with the local density approximation, LDA.

The DFT calculations were performed with a plane-wave basis set for the charge density and wavefunctions (Payne *et al.*, 1992). This has advantages with respect to the calculation of forces and stresses compared with other, more complex, basis sets (Singh, 1994). However, as it is impractical to explicitly consider tightly bound core electrons when using a plane-wave basis set, pseudopotentials have to be used which mimic the screening of the Coulomb potential of the nucleus by the core electrons. A number of approaches for the construction of pseudopotentials have been presented in the literature (Bachelet *et al.*, 1982; Kleinman & Bylander, 1982). State-of-the-art are very efficient 'ultrasoft' pseudopotentials, which require a comparatively small number of plane waves (Vanderbilt, 1990; Kresse & Hafner, 1994). Such ultrasoft pseudopotentials were used here, with a maximum cutoff energy of the plane waves of 380 eV. In addition to the cutoff energy, only one further parameter determines the quality of the calculations, namely the density of points with which the Brillouin zone is sampled. In the present study, 12, 38 and 110 k points have been used for the sampling of the irreducible part of the Brillouin zone in the aragonite, dolomite and norsethite calculations, respectively. They were chosen according to a prescription by (Monkhorst & Pack, 1976) and correspond to distances between sampling points of 0.05 (aragonite), 0.04 (dolomite) and 0.02 (norsethite) reciprocal lattice units. The calculations were fully converged with respect to k-space sampling. The calculations were performed with academic and commercial (Molecular Simulations Inc., 1998) versions of the total energy code CASTEP (CAmbridge Serial Total Energy Package), which is described elsewhere (Payne *et al.*, 1992; Teter *et al.*, 1989). All structural parameters which are not constrained by the space-group symmetry, $R\bar{3}$ and *Pbnm* for dolomite and aragonite, respectively, were relaxed during the full geometry optimizations. For norsethite, full geometry optimizations were performed with space groups $R\bar{3}m$ and $R32$. After achieving self-consistency, the remaining forces on the atoms were always less than $0.05\ \mathrm{eV\,\mathring{A}^{-1}}$. Residual stresses were always within 0.1 GPa of the applied external stress.
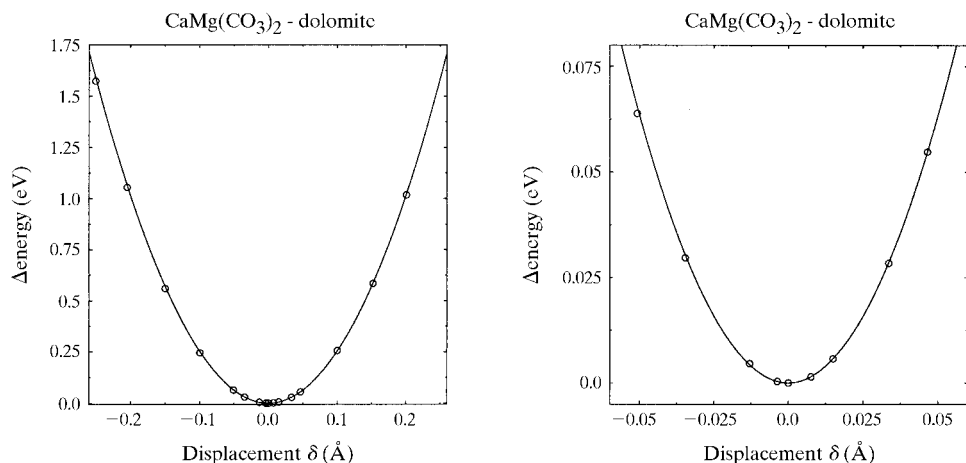
Figure 1
Computed dependence of the total energy on the displacement of the C atom from its equilibrium position at 0, 0, 0.24313. No asymmetry on large displacements (left) or a deviation from a harmonic potential indicated by the full line is observable close to a planar group (right). A planar group corresponds to a displacement of the C atom of +0.015 Å.

Table 1
Calculated and experimentally determined (Effenberger, Kirfel & Will, 1983; Ross & Reeder, 1992) structural parameters of dolomite.

The 'conventional X-ray model' of Effenberger, Kirfel & Will (1983) was used for all values given in the table for dolomite. The Wyckoff positions are 3(a) 0,0,0 for Ca, 3(b) 0,0,1/2 for Mg, 6(c) 0,0,z for C and 18(f) x, y, z for O. α is the angle of the in-plane rotation of the CO_3 group (Beran & Zemann, 1977) and d is the distance between the plane formed by the O atoms and the C atom. The experimentally determined B and B' values are from Martinez et al. (1996). The error given for the theoretical bulk modulus and its pressure derivative is obtained from the least-squares fit of the equation-of-state.

	Calc. (this study)	Exp.	Diff. (%)	Calc. 5 GPa (this study)	Exp. 4.7 GPa
a (Å)	4.8581	4.808 (1)	1.0	4.8030	4.7636 (5)
c (Å)	16.229	16.022 (3)	1.3	15.761	15.582 (3)
C(z)	0.24313	0.24287 (3)		0.2434	0.2439 (8)
O(x)	0.24913	0.24796 (6)		0.2509	0.2496 (6)
O(y)	−0.02970	−0.03470 (7)		−0.0304	−0.0359 (6)
O(z)	0.24406	0.24402 (2)		0.2443	0.2443 (2)
B (GPa)	86 (5)	90.7 (7)	−5		
B'	4 (1)	2.3 (5)			
C−O (Å)	1.289	1.2850 (4)	0.3	1.284	1.283 (2)
α (°)	5.6	6.35 (5)	−12	5.7	6.6
d (Å)	0.015	0.018 (1)	−17	0.015	0.015
Ca−O (Å)	2.397	2.3822 (4)	0.6	2.349	2.339 (3)
Mg−O (Å)	2.127	2.0880 (5)	1.8	2.085	2.048 (3)

3. Results

3.1. Dolomite

For dolomite, full geometry optimizations were performed in space group $R\bar{3}$. The results for the ambient-pressure structure are given in Table 1, where they are compared with experimental data from Effenberger, Kirfel & Will (1983). Predicted structural parameters at 5 GPa are also listed in Table 1, where they are compared with experimental data at 4.7 GPa (Ross & Reeder, 1992).

The good agreement between the calculated and the experimentally determined structure extends to subtle details, specifically the in-plane rotation of the CO_3 groups (Beran & Zemann, 1977) and their aplanarity. In agreement with the experimentally determined structure, in the relaxed structure the C atom is displaced towards the nearest 'Mg layer'. For the C atom at 0, 0, 0.2491, this layer is formed by the Mg atoms with $z = 1/6$. The nearest Mg atom is 3.067 Å away, while the closest Ca is slightly further apart, namely 3.164 Å, and is part of a 'Ca layer' at $z = 1/3$. The next-nearest neigbours are 4.169 (Mg) and 3.946 Å (Ca) away. A third-order Birch–Murnaghan equation-of-state has been fitted to the computed pressure dependence of the unit-cell volume for pressures up to 6 GPa, giving $B = 86$ (5) GPa and $B' = 4$ (1). The computed relative linear compressibilities a/a_0 and c/c_0 are 2.3×10^{-3} and 5.5×10^{-3} GPa^{-1}, respectively, in agreement with experimental values (Ross & Reeder, 1992; Martinez et al., 1996). A detailed analysis of the response of the structure to increasing pressure showed that the aplanarity of the CO_3 group does not change as a function of pressure. The in-plane rotation of the CO_3 group with respect to the crystallographic axes, as defined in

Beran & Zemann (1977), is also independent of pressure. As could be expected from general crystal chemical considerations, the CO_3 group is comparatively rigid. On compression to 6 GPa, both the Mg−O and Ca−O distances shrink by ∼2.3%, significantly more than the 0.5% decrease in the C−O distances. These findings also agree with experimental observations (Ross & Reeder, 1992).

We have studied the dependence of the total energy as a function of the displacement of the C atom in order to better understand the interaction within the CO_3 group. The results are shown in Fig. 1, from which it can be concluded that there is no detectable asymmetry of the potential along the hexagonal c axis and there is no indication of any deviation from a harmonic potential. From these calculations we can obtain the energy by which the aplanarity of the CO_3 group stabilizes the structure, which is ∼0.005 eV per formula unit, 482 J mol^{-1}.

3.2. Aragonite

For aragonite, full-geometry optimizations were performed in the space group Pbnm for pressures of 0–10 GPa. The results for the structure at ambient pressure are given in Table 2, where they are compared with experimental data from Jarosch & Heger (1986). Here again, structural details such as the relative elongation of the C−O(2) bond with respect to the C−O(1) bond are correctly reproduced by the quantum mechanical model. The pressure dependence of the unit-cell volume is shown in Fig. 2, where a fit with a third-order Birch–Murnaghan equation-of-state is shown as well. This fit gave a bulk modulus $B = 58$ (2) GPa, while the pressure derivative was computed to be $B' = \partial B/\partial P = 5.0$ (5).

The computed linear relative compressions of the axes agree with the experimental data (Martinez et al., 1996). Here we obtain $a/a_0 = 4.2 \times 10^{-3}$, $b/b_0 = 5.6 \times 10^{-3}$ and $c/c_0 = 2.6 \times 10^{-3}$ GPa^{-1}, while the experimental values are 4.2 (2) $\times 10^{-3}$, 5.8 (2) $\times 10^{-3}$ and 2.4 (2) $\times 10^{-3}$ GPa^{-1}, respectively (Martinez et al., 1996). On compression a significant structural change is the tilting of CO_3 groups with respect to each other. The CO_3 groups are essentially parallel in the ambient-pressure structure. On increasing pressure, the angle between the planes of two CO_3 groups stacked on top of each other along the crystallographic b axis increases linearly from 1° at 0 GPa to 6° at 10 GPa. Concomitant with this tilting is a small increase in the aplanarity of the CO_3 group, where the

Table 2
Calculated and experimentally determined (Jarosch & Heger, 1986) structural parameters of aragonite.

The given values refer to space group *Pbnm*. The bulk modulus was obtained by fitting a third-order Birch–Murnaghan equation-of-state to the computed volumes. The experimental data for the bulk modulus is from Martinez *et al.* (1996).

	Calc. (this study)	Exp.	Diff. (%)	Calc. 10 GPa (this study)
a (Å)	8.0183	7.9672 (6)	0.6	7.6831
b (Å)	5.8343	5.7407 (4)	1.6	5.5118
c (Å)	5.0129	4.9611 (4)	1.0	4.8863
V (Å^3)	234.5	226.9	3.3	206.9
Ca (x)	0.41292	0.41508 (5)		0.41552
Ca (y)	0.76195	0.24046 (8)		0.76230
C (x)	0.76197	0.76211 (4)		0.76763
C (y)	−0.07730	−0.08518 (6)		−0.08882
O(1)(x)	0.92163	0.92224 (4)		0.93315
O(1)(y)	−0.08357	−0.09557 (8)		−0.10832
O(2)(x)	0.68058	0.68065 (3)		0.68284
O(2)(y)	−0.08065	−0.08726 (5)		−0.08727
O(2)(z)	0.47246	0.47347 (5)		0.47646
B (GPa)	58 (2)	65.4 (5)	−11	
B'	5.0 (5)	2.7 (7)	85	
C−O(1) (Å)	1.281	1.2772 (5)	0.3	1.276
C−O(2) $2 \times$ (Å)	1.292	1.2847 (3)	0.6	1.284
O(1)−C−O(2) (Å)	120.3	120.28 (2)	0.02	120.4
O(2)−C−O(2)	119.3	119.30 (3)	± 0	119.0
d (Å)	0.025	0.0280 (5)	10	0.030

distance d from the C atom to the plane defined by the O atoms increases from $d = 0.025$ to 0.030 Å. Pressure-induced changes of the symmetrically inequivalent Ca−O bond lengths are not very different and approximately inversely proportional to their lengths at ambient pressure. The two shorter Ca−O(1) and Ca−O(2) bonds change by 2.7 and 3.4% on compression to 10 GPa, while the longer bonds change by ∼4.5%. The bond-length distortion, *bld*, for the Ca−O coordination polyhedron

$$bld = 100/n \sum_{i}^{n} (|d_i - \bar{d}|/\bar{d})$$

decreases slightly from 3.30 to 2.95%, *i.e.* this coordination polyhedron becomes slightly more regular.

3.3. Norsethite

The computation of the ground-state structure of norsethite had two aims. First, we wanted to ensure that the calculations reproduce even comparatively large aplanarities. Secondly, the space group of the ground-state structure has not been unambiguously determined yet, as from room-temperature X-ray diffraction data it is difficult to distinguish between three very similar atomic arrangements (Lippmann, 1968; Effenberger & Zemann, 1985). Two of the structure models have space group $R\bar{3}m$, but differ in that the oxygen position is split in one structural model, while in the other all positions are fully occupied. The structure model in space group $R32$ has fully occupied positions only (Lippmann, 1968; Effenberger & Zemann, 1985). We used the two fully ordered structures

suggested by Effenberger & Zemann (1985) in which the Wyckoff sites 18(h) ($R\bar{3}m$) or 18(f) ($R32$) are fully occupied as 'trial structures' for the full-geometry optimizations. An energy minimization was successful in space group $R32$, *i.e.* we found a force- and stress-free relaxed structure. We did not succeed in relaxing the model for which the space-group symmetry was constrained to $R\bar{3}m$. Hence, we conclude that if a fully ordered model is an appropriate description of the norsethite structure, then the ground-state symmetry will be $R32$. The results for the structure with space group $R32$ at ambient pressure are given in Table 3, where they are compared with experimental data from Effenberger & Zemann (1985).

From the comparison in Table 3, the computed c lattice parameter is 5.4% longer than the experimental value and the in-plane rotation of the CO_3 group is also significantly overestimated. The error in the unit-cell constant is noticeably larger than the errors observed in the calculations for dolomite and aragonite, which in turn are consistent with the usual error of ∼2% commonly encountered in geometry optimizations. It is possible that the origin of the discrepancy between theoretical and experimental results is due to the structural model that we employed in the calculation. As has been mentioned above, an alternative description of the structure suggested by Effenberger & Zemann (1985) is based on space group $R\bar{3}m$, but with O atoms occupying Wyckoff site 36(i) with an occupancy of 0.5.
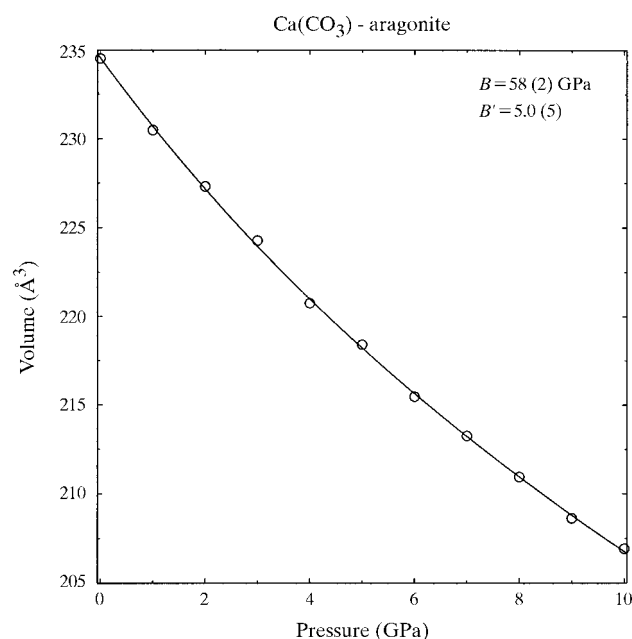
Figure 2
Unit-cell volume of aragonite as a function of pressure. The line is a fit with a third-order Birch–Murnaghan equation-of-state.

Table 3
Calculated and experimentally determined (Effenberger & Zemann, 1985) structural parameters of norsethite.

Ba is located on 0,0,0; Mg is on $0,0,\frac{1}{2}$, C on $0,0,z$ and O on x,y,z. α is the angle of the C—O bond direction with the x axis.

	Calc. (this study)	Exp.	Diff. (%)
a (Å)	5.0613	5.022 (1)	1.0
c (Å)	17.676	16.77 (1)	5.4
c/a	3.492	3.339	4.6
V (Å^3)	392.1	366.3	7.0
C(z)	0.2398	0.2392 (3)	
O(x)	0.1684	0.164 (5)	
O(y)	−0.1243	−0.129 (5)	
O(z)	0.2418	0.2416 (2)	
C—O (Å)	1.288	1.273 (1)	1.1
d (Å)	0.035	0.044 (7)	20
α (°)	25	26 (1)	4
Ba—O (Å)	2.916	2.88 (2)	1.3
Ba—O (Å)	3.104	3.03 (2)	2.5
Mg—O (Å)	2.112	2.06 (2)	2.5

However, this model cannot be tested with conventional quantum mechanical approaches such as that employed here. This will not significantly influence our findings with respect to the aplanarity, as the other structural parameters, notably the cation–oxygen distances and the large aplanarity of the CO_3 group, are modelled well.

4. Summary and discussion

The good agreement between the experimental data for the ambient-pressure structures and the calculated values allows us to conclude that on the level of theory employed here the aplanarity of the CO_3 groups in dolomite, aragonite and norsethite is a ground-state property. This finding is very likely valid for other carbonates with aplanar groups (Zemann, 1981). From our calculations and experiments (Ross & Reeder, 1992), it follows that the aplanarity is maintained even at high pressures. For dolomite, this distortion stabilizes the structure by 0.005 eV = 482 J mol^{-1}. It is rather surprising how strong the tendency to maintain the aplanarity is. In dolomite, for example, it is the strong C—O bonds which are compressed on increasing pressure, where one might have expected that the aplanarity would increase to change these bonds as little as possible. The frozen phonon calculations for CO_3 groups in dolomite show that there is no indication of a distortion of the potential from a parabolic shape close to the equilibrium structure. These observations raise the question under which circumstances a CO_3 group will stay planar and when an aplanar group is more favorable. While we did not attempt to answer this in the present study, it is now clear that calculations in the athermal limit can be used to investigate this problem. It is unlikely that calculations based on empirical potentials can be used for such a study. The energy differences between planar and aplanar groups are tiny in comparison to the total lattice energy. Hence, transferable potential parameters would have to be developed which have a precision of

better than 10^{-6}. This can generally not be achieved with force-field calculations. The predictive power of 'semi-empirical' methods such as those based on the modified electron gas approach (Gordon & Kim, 1972) is also insufficient. In a fully ionic approach the predicted lattice parameters differ by 15% from the experimental values (Lindsay & Jackson, 1994). Even after the introduction of a parameter describing the polarizability of the oxygen ions, bond lengths within the CO_3 group are underestimated by more than 8%, while the bulk modulus is significantly overestimated (Lindsay & Jackson, 1994).

For dolomite, the calculated high-pressure data agree with the experimentally determined structural parameters, thus demonstrating the reliability of the approach here. We are therefore confident that our predictions for the high-pressure behavior of aragonite are reliable. The present calculations also answer the question raised in the introduction, namely whether the pressure derivative of the bulk modulus B' is anomalously small in aragonite and dolomite. It is well known that GGA calculations often predict too small bulk moduli. This is also evident here, where the computed bulk moduli are 5 and 12% lower than the most recent experimental values for dolomite and aragonite, respectively (Martinez et al., 1996). However, the derivative of the bulk modulus is usually in much better agreement with experimental data. The calculated data are 4 (1) and 5.0 (5), which we trust are closer to the true value than the anomalously low values reported by Martinez et al. (1996) or the very high value derived by Fiquet et al. (1994).

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