

AB INITIO MODELING: MECHANICAL AND THERMO-ELASTIC PROPERTIES OF CALCIUM CARBONATES POLYMORPHS

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INTRODUCTION

The present PhD Thesis provides a set of new computational, mechanical and thermodynamic data, aimed to provide a better characterization of calcium carbonate polymorphs, from the mineralogical, geophysical and petrographical (sedimentary and metamorphic petrography) point of view. Carbonates belong to the most abundant Earth materials, after silicates, and play an important role in the Earth's carbon cycle. Carbonates are a group of minerals in which the essential unit is the $(\text{CO}_3)^{2-}$ ion. This unit has a planar arrangement, with the carbon atom at the centre and oxygen atoms at the apices of an equilateral triangle (Zemann, 1981).

Calcium carbonate crystallizes naturally with either the calcite [$\text{CaCO}_3(\text{I})$] or aragonite (*Pm \bar{c} n*) structure. The other CaCO_3 polymorph is vaterite, which is metastable. The $(\text{CO}_3)^{2-}$ group is the fundamental chemical unit from which the carbonate minerals derive their identity. The other CaCO_3 carbonate studied in the present thesis is $\text{CaCO}_3(\text{II})$.

For the phases studied, the geometry of each calcium carbonate polymorphs was optimized by means of *ab initio* quantum mechanical calculation CRYSTAL code (Dovesi *et al.*, 2006, 2009). The choice of the exchange-correlation functionals used in the present *ab initio* quantum calculation were B3LYP (Becke, 1993) and WC1LYP (Wu & Cohen, 2006).

The vibrational modes were calculated in the quasi-harmonic approximation, and represented the eigenvalues of the mass-weighted Hessian matrix, which is nothing else than the second derivative of the potential energy as a function of coordinate displacement respect to the equilibrium position.

The bulk modulus, the thermal expansion, the specific heat, and the entropy were obtained in the limit of the quasi-harmonic approximation (Anderson, 1995), through the evaluation of the unit cell volume dependence from the frequencies of the vibrational normal modes (mode- γ of the Grüneisen's parameters) at the Γ point. The dispersion effects in the phonon spectra at various pressures were not taken into account for aragonite, but only for calcite, thanks to new version of the CRYSTAL code (Dovesi *et al.*, 2009). On the other hand, the Grüneisen's parameters corresponding to the zone-centre vibrational modes can reasonably be considered representative of the whole set of parameters, due to their large number, which depends upon the number of atoms in the unit cell.

The total pressure P, at each cell volume V, and the temperature T have been obtained using thermal physics approach of (Anderson, 1995).

APPLICATIONS OF QUANTUM-MECHANICAL *AB INITIO* CALCULATION USING THE CRYSTAL CODE, THE THERMO-ELASTIC EQUATION OF STATE, AND THE THERMODYNAMIC PROPERTIES OF CaCO_3 POLYMORPHS

*Calcite: Thermodynamic and thermo-elastic properties of (CaCO_3) calcite. An *ab initio* quantum-mechanical calculation*

The thermodynamic calculation of total pressures, bulk modulus, thermal expansion, heat capacity, and entropy of calcite were obtained through the *ab initio* calculation of the unit cell volume dependence of the total static energy, and of the frequencies of the vibrational normal modes, at the Γ point, within the framework of the quasi-harmonic approximation. The Acoustics modes frequencies were evaluated by means of a modified Kieffer's model (Kieffer, 1979 a, b) starting from the experimental elastic constants. Moreover, an attempt to

Table 2 - Thermodynamic properties at 298 K. Note that S was calculated in two modes: 2a) with the Kieffer model and taking into account the phonon dispersion contribution; 2b) as a function of T and P calculated at WC1LYP level. The experimental data are also reported for comparison with: 1 (Salje & Viswanathan, 1976); 2 (Staveley & Linford, 1969); 3 (Jacobs *et al.*, 1981); 4 (Gillet *et al.*, 1996); 5 (Bridgman, 1925); 6 (Redfern & Angel, 1999); 7 (Matas *et al.*, 2000); 8 (Robie *et al.*, 1979).

a

T=298 K	WC1LYP		Experimental		
	Kieffer	Dispersion			
K(T)	75.58		78.00[1]	73.15[5]	73.46[6]
K(P)	76.94		78.50[1]	2.99[1]	
(K ⁻¹)	1.70·10 ⁻⁵		1.77·10 ⁵ [1]		
S(Jmole ⁻¹ K ⁻¹)	91.45	* 91.66	91.70[8]		
Cp(Jmole ⁻¹ K ⁻¹)	81.79		83.50[8]		

b

	WC1LYP		Experimental	
	I	s	I	s
K(T) (Linear fit 100÷1000 K) at different P				
0	78.56	-0.0103		-0.011[4]
				-0.008[7]
1	88.06	-0.0143		
2	98.91	-0.0167		
(T) (Linear fit 500÷1000 K) at different P				
0	1.51·10 ⁻⁵	9.73·10 ⁻⁹	1.46·10 ⁻⁵ [1]	1.19·10 ⁻⁸ [1]
1	1.38·10 ⁻⁵	8.12·10 ⁻⁹		
2	1.26·10 ⁻⁵	6.99·10 ⁻⁹		

In Table 2b are presented: i) the linear fits of data calculated at WC1LYP level (column 3) concerning the bulk modulus as a function of temperature (100 ÷ 1000 K) at different pressures (0 - 2 GPa); ii) the thermal expansion as a function of temperature (500 ÷ 1000 K) at different pressures (0 - 2 GPa).

In summary, the thermodynamic properties values calculated at WC1LYP level were in a good agreement with experimental data. A better agreement between our calculated WC1LYP entropy values and the experimental ones, in all the explored 20 ÷ 1000 K temperature range, was evidenced. Our C_p data also gave a general low mean difference ($\cong 1$ J/moleK), although we had some mismatch at 298 and 1000 K: this might imply problems in some experimental data or in the estimation of α , K_T and V , in particular at 1000 K, where we observed the largest difference. A very good agreement between the calculated and the experimental data (column 5, Table 2b; Gillet *et al.*, 1996) was observed. All our thermal expansion values were in good agreement with the experimental ones: in particular, the slopes as a function of pressure seem good up to 1200 K. The slope of thermal expansion as a function of temperature seems reasonable at 0 GPa (Salje & Viswanathan, 1976) and decrease slowly raising the pressure up to 2 GPa. This last observation disagrees with some literature statements where calcite thermal expansion slope, with respect to temperature, remains substantially constant as the pressure is raised (Gillet *et al.*, 1996). In Table 2b are summarized all the calculated thermodynamic properties, at WC1LYP level (2a) at 298 K and at different pressures (2b).

Finally, this work confirms, in general, the previous experimentally-determined thermodynamic properties of calcite (Bridgman, 1925; Staveley & Linford, 1969; Salje & Viswanathan, 1976; Robie *et al.*, 1979; Jacobs *et al.*, 1981; Gillet *et al.*, 1996; Redfern & Angel, 1999; Matas *et al.*, 2000).

Aragonite: orthorhombic equilibrium structure and vibrational modes at point (quantum mechanical calculation)

The orthorhombic cell of aragonite contains four CaCO₃ formula units, for a total of N = 20 atoms; its sixty vibrational modes can be classified according to the Irreducible Representations of the *mmm* point group as follows:

$\Gamma_{\text{tot}} = 9A_g + 6A_u + 6B_{1g} + 9B_{1u} + 6B_{2g} + 6B_{2u} + 9B_{3g} + 6B_{3u}$. Where: $9A_{1g} + 6B_{1g} + 6B_{2g} + 9B_{3g}$ Raman active, $8B_{1u} + 5B_{2u} + 5B_{3u}$ IR active, $6A_{1u}$ inactive and $1B_{1u} + 1B_{2u} + 1B_{3u}$ acoustic.

In aragonite, where eight almost independent groups can be identified (four Ca²⁺ ions and four CO₃²⁻ units), vibrational modes can be grouped into two categories, namely: external (*E*; translational and rotational type) and internal (*I*) vibrations. External vibrations involve relative translations of the eight units and librations of the carbonate ions, as a result of the freezing, within the crystal, of free translations and rotations of each single free unit. Apart few cases, in aragonite, a clear-cut distinction between translational- and rotational-type modes cannot be made; in general, the vibrations with similar frequency and same symmetry can couple to each other to give more complex modes. The internal vibrations are those modes which involve deformation of the carbonate groups.

Due to the very different strength of the intra-CO₃²⁻ and inter-ionic forces, it might be expected that *E* modes have lower frequencies than those associated with *I* modes. Inspection of the eigenvectors of the Hessian matrix and their graphical representations with the aid of Jmol (open-source Java viewer for chemical structures in 3D, <http://www.jmol.org>) shows that such a separation between (*E*) and (*I*) modes can indeed be made. The equilibrium geometry, the static and high frequency dielectric tensors, the Born charge tensors, the central zone phonon frequencies, and IR intensities of aragonite were calculated with the CRYSTAL code, comparing two different basis sets of increasing size and B3LYP Hamiltonian. The vibrational frequencies were compared with the experimental data and, as can be seen in Table 3, it was found an excellent agreement.

Aragonite: ab-initio quantum-mechanical calculation of aragonite at high pressure: thermodynamic properties and comparison with the experimental data

Starting from the optimized equilibrium geometry of the orthorhombic aragonite primitive cell ($a = 5.0129 \text{ \AA}$, $b = 8.0587 \text{ \AA}$, $c = 5.8529 \text{ \AA}$, $V = 236.44 \text{ \AA}^3$, $E = -3766.0212796587 \text{ Ha}$, at the B3LYP level), obtained in a previous work (Pascale *et al.*, pers. comm.), new geometries were obtained for reduced volumes of the unit cell, which corresponded to pressures higher than zero. More precisely, these new optimized geometries corresponded to static pressures (1st term of formula by Anderson, 1995) ranging from $P_{\text{st}} = 0 \text{ GPa}$ at $V = 236.44 \text{ \AA}^3$ (equilibrium geometry) to $P_{\text{st}} = 28.62 \text{ GPa}$ at $V = 185.46 \text{ \AA}^3$. By expanding the cell, at volumes larger than those corresponding to the static limit, we observed a mode whose frequency was rapidly decreasing as the volume increased (soft mode); this is the A_u -mode at 35.2 cm^{-1} , for a cell volume varying from 242.15 \AA^3 to 185.47 \AA^3 .

Such mode reached a zero value of the frequency, possibly corresponding to a zone-centre soft-mode phase transition, for a volume greater than 245 \AA^3 (at the B3LYP level). For this reason it was not possible to use our calculation to predict the properties of aragonite at $P = 0 \text{ GPa}$ and $T > 600 \text{ K}$ (since, at those conditions, thermal expansion would produce calculated cell volumes larger than 245 \AA^3).

All the calculated thermodynamical properties are summarized in Tables 4 (a and b). Table 4a (referring to data evaluated at $T = 298 \text{ K}$) contains calculated values obtained by means of BM3 (column 2) and NumDeriv (column 3) methods for the following properties: bulk modulus K_T , thermal expansion α , entropy S , heat capacity (C_v and C_p). In columns 4 to 6 are reported, for comparison, some experimental values (from Martinez *et al.*, 1996; Salje & Viswanathan, 1976; Staveley & Linford, 1969).

The BM3 calculated values of the bulk modulus were in good agreement, in the whole pressure and temperature ranges considered (0 - 10 GPa and 298 ÷ 973 K), with the experimental ones, being the difference between the calculated and the experimental data less than 2 GPa. The agreement of the estimated thermal expansion coefficient [$\alpha(T)$], and its temperature dependence, with the experimental data was reasonably good. In particular, the calculated value at room temperature and pressure was under-estimated by $2.3 \cdot 10^{-6} \text{ K}^{-1}$ with

respect to the experimental data, whereas the slope of the $\alpha(T)$ curve appeared to be over-estimated; the magnitude of such a slope decreased as the pressure increased. Concerning heat capacity (C_v and C_{pBM3}), a very good agreement with the experimental values, in the 120 ÷ 300 K temperature range, was obtained.

Table 4 - Thermodynamic properties at 298 K as a function of T (4a) and P (4b) calculated according to BM3 and NumDeriv methods. The experimental data are also reported for comparison: 1) Martinez *et al.*, (1996); 2) Staveley & Linford (1969); 3) Gillet (1993); 4) Salje & Viswanathan (1976).

a

T=298 K	BM3	NumDeriv	Experimental		
Bulk Modulus	64.67	66.84	66.78 [2]	64.81 [1]	65.66 [4]
Thermal Expansion	$6.06 \cdot 10^{-5}$	$5.88 \cdot 10^{-5}$	$6.1 \cdot 10^{-5}$ [2]	$6.5 \cdot 10^{-5}$ [1]	$6.36 \cdot 10^{-5}$ [4]
S (Jmole⁻¹K⁻¹)	87.49	87.49	87.98 [2]	88[3]	78[4]
Cp(Jmole⁻¹K⁻¹)	83.06	82.44	82.55 [2]		
Cv (Jmole⁻¹K⁻¹)	74.96	74.96			

b

Method	BM3		NumDeriv		Experimental	
Function	I	s	I	s	I	s
P(Gpa)	Bulk Modulus as a function of Temperature (Linear fit 298÷773 K) at different pressures					
0	70.27	-0.022	75.24	-0.026	71.97	-0.02
2.5	80.49	-0.021				
5	90.91	-0.019				
7.5	101.1	-0.018				
10	111.2	-0.017				
P(Gpa)	Thermal expansion as a function of Temperature (Linear fit 298 ÷ 773 K) at different pressures					
0	$4.40 \cdot 10^{-5}$	$5.40 \cdot 10^{-8}$	$3.64 \cdot 10^{-5}$	$7.34 \cdot 10^{-8}$	$5.76 \cdot 10^{-5}$	$2.52 \cdot 10^{-8}$
2.5	$3.63 \cdot 10^{-5}$	$3.72 \cdot 10^{-8}$				
5	$3.15 \cdot 10^{-5}$	$2.61 \cdot 10^{-8}$				
7.5	$2.75 \cdot 10^{-5}$	$1.93 \cdot 10^{-8}$				
10	$2.40 \cdot 10^{-5}$	$1.54 \cdot 10^{-8}$				

On the whole, the present work confirms the values of some thermodynamic properties of aragonite, which have been experimentally determined in previous works (Staveley & Linford 1969; Salje & Viswanathan 1976; Holland & Powell, 1990; Gillet, 1993; Martinez *et al.*, 1996).

The A_u mode at 35.2 cm^{-1} (at a unit cell volume of 242.15 \AA^3) reached a zero value of the frequency for volumes above 245 \AA^3 ; this could possibly corresponds to a zone-centre soft-mode phase transition ($P = 0 \text{ GPa}$ and $T > 600 \text{ K}$ conditions), which require further investigation from both the theoretical and experimental sides.

Vaterite (μ - Calcite)

The cell parameters obtained for orthorhombic vaterite were: $a = 6.69422 \text{ \AA}$, $b = 8.50694 \text{ \AA}$, $c = 4.52341 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 257.597 \text{ \AA}^3$, and $E = -3.766173 \cdot 10^3 \text{ Ha}$, at the B3LYP level. For the *ab initio* calculations were utilized the same basis set as for aragonite BSD, and the results were then compared with the experimental results (Meyer, 1969).

The Born effective charge and dielectric tensors were obtained, with BSD and B3LYP calculations, using the CPHF method, which is available in the new test version CRYSTAL09 (Dovesi *et al.*, 2009). Diagonal elements were: $xx = 2.3336$, $yy = 2.7939$, $zz = 2.5996$.

The Raman vibrational modes were calculated using BSD, the same basis set as for aragonite, and B3LYP Hamiltonian. Only two exceptions were noted, namely the lowest ($< 300 \text{ cm}^{-1}$) and the highest ($> 1080 \text{ cm}^{-1}$) frequencies, for which the CRYSTAL calculation overestimated the experimental values as for both Raman and IR frequencies (LO-TO), by something between 7.3 and 22 cm^{-1} . The visualization of the eigenvectors of the Hessian matrix and their graphical representations with the aid of Jmol (open-source Java viewer for chemical structures in 3D, <http://www.jmol.org/>) showed that such a separation between *E*- and *I*-

can be noted, there is a good agreement between the frequencies calculated using B3LYP and those obtained by WC1LYP calculation.

CONCLUSIONS

The *ab initio* quantum mechanical calculation performed for the calcium carbonates polymorphs provided appropriate results both for the geometry of the crystallographic cell and for the vibrational normal modes. Therefore, it can be concluded that the CRYSTAL code is one of the best modellization method dedicated to the study of the solid phases (especially for the 3D crystalline structures), not only at the equilibrium, but, even more, under HP-HT conditions, which plays an important role in mineralogy, geophysics, petrology and materials industry.

The thermodynamical and thermo-elastic properties obtained through the vibrational normal modes, calculated with CRYSTAL code, in comparison with what stated by Debye (1912) “the frequencies in a crystal are distributed as though the solid were an isotropic elastic continuum rather than an aggregate of particles” and Einstein (1907) “all vibrational modes have the same frequency models” provide the appropriate underlying in the determination of mechanical and thermodynamical properties of the crystalline systems, such as the calcium carbonate types.

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