An equation of state for $CaCO_3$ at high pressures and temperatures

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From the standpoint of polymorphic transformations, calcium carbonate is a rather complicated compound: the number of its phases which were observed experimentally or predicted theoretically approaches ten. What adds more complexity is the fact that calcite-I – a thermodynamically stable state of $CaCO_3$ under ambient conditions – tends to form metastable modifications. That is why it is a problem to determine phase stability boundaries for $CaCO_3$, and discussion in the scientific literature continues up to now.

In this work we examine stability boundaries for three stable phases (calcite-I, aragonite and post-aragonite) and two metastable phases (calcite-III and calcite-VI) of $CaCO_3$ using the pseudo-potentials approach within density functional theory. It is shown that the state-of-the-art functionals PBESol and AM05 predict the equilibrium cell parameters of the phases, cold compression curves, and some mechanical properties better than the traditionally used PBE and LDA.

Quantum molecular dynamics is used to derive an equation of state (EOS) for $CaCO_3$ at temperatures $300 - 63000$ K and densities $1.585 - 7.943$ g/cm^3. For model systems, super-cells of calcite-I and aragonite are used, as well as a cubic super-cell containing 25 molecules of $CaCO_3$ that helped obtain thermodynamic parameters for liquid and amorphized calcium carbonate. The Hugoniot curve obtained from the EOS (the highest pressure 1.17 TPa at density 7.54 g/cm^3) agrees well with data from shock experiments reported in [1] and [2].

[1] N.G. Kalashnikov, M.N. Pavlovskiy, G.V. Simakov, R.F. Trunin, Izv. Acad. Sci. USSR Phys. Solid Earth 2, 23 (1973)

[2] S.G. Love, T.J. Ahrens, LPSC XXIX, 1206 (1998)