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Ab initio assessment of the Mie-Grüneisen equation of state: application to the high thermobaric regimes of the Earth's deep interior

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The most popular isothermal equations of state in the Earth Sciences (viz. the Murnaghan and the Birch-Murnaghan EoS) are based on the application of finite strain theory. Extension of strain theory to high thermobaric regimes may lead in some circumstances to physical unsoundness in material properties (negative thermal expansivity, hence entropy increase with pressure) due to a poor account of thermal effects [1,2]. First principles theory overcomes this problem by treating through a Mie-Grüneisen approach [3,4] the static and vibrational contributions to pressure (i.e. the static and thermal pressure) in a different way: the former by the assessment of sufficiently accurate potential wells at the athermal limit, the latter by a quasi-harmonic treatment of phonon contributions to the bulk energy of the substance.

In this paper, we present the results of ab initio modelling of the thermodynamic and thermoelastic properties of deep mantle phases in the MgO-SiO_2 system through the application of the hybrid B3LYP density functional method in the framework of LCAO approximation and Bloch's theorem [5]. The minerals investigated in this study are periclase (MgO), stishovite (SiO_2), the Mg_2SiO_4 polymorphs (forsterite, Mg-wadsleyite and Mg-ringwoodite), phase anhydrous B ($Mg_{14}Si_5O_{24}$) and the high-pressure polymorphs of $MgSiO_3$ (C2/c clinoenstatite, tetragonal majorite and Mg-akimotoite). The vibrational density of state (vDOS) of these minerals has been reproduced through a full phonon dispersion calculation or, alternatively, a modified Kieffer's model [6]. Both methods reproduce satisfactorily the vDOS, allowing an accurate determination of the equation of state parameters and thermodynamic properties as well [7,8,9]. The calculated values show a good agreement with experimental results and concur to define an internally-consistent thermodynamic dataset suited for the computation of phase equilibria between pure phases at very high pressures and temperatures. The results obtained for phase equilibria of geophysical interest are discussed, along with some possible petrological implications concerning phase relations and seismic discontinuities in the Earth's mantle.

[1] Helffrich, G., and Connolly, J.A.D. (2009) American Mineralogist, 94, 1616-1619.
[2] Jacobs, M.H.G, and Oonk, H.A.J. (2000) Phys. Chem. Chem. Phys., 2, 2641-2646.
[3] Grüneisen, E. (1912) Annalen der Physik, 39, 257-306.
[4] Born, M., and Huang, K. (1954) Dynamical Theory of Crystal Lattices, Clarendon Press, Oxford.
[5] Becke, A.D. (1993) J. Chem. Phys., 98, 5648-5652.
[6] Kieffer, S.W. (1979) Rev. Geophys. Space Phys., 17, 35-59.
[7] Ottonello, G., Civalleri, B., Ganguly, J., Vetuschi Zuccolini, M., and Noel, Y. (2009) Phys. Chem. Minerals, 36, 87-106.
[8] Ottonello, G., Vetuschi Zuccolini, M., and Civalleri, B. (2010) CALPHAD, 33, 457-468.
[9] Ottonello, G., Civalleri, B., Ganguly, J., Perger, W.F., Belmonte, D., and Vetuschi Zuccolini, M. (2010) American Mineralogist, 95, 563-573.