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The Limitations on Quasi-harmonic Thermal-Pressure Equations of State from Anisotropic Thermal Pressure

Ross Angel (1), Gabriele Zaffiro (1), Claudia Stangarone (1), Boriana Mihailova (2), Mara Murri (1), and Matteo Alvaro (1)

(1) Dept Earth & Environmental Sciences, University of Pavia, Pavia, Italy (rossjohnangel@gmail.com), (2) Mineralogisch-Petrographisches Institut, University of Hamburg, Hamburg, Germany

Thermal-pressure Equations of State (EoS) describe how the volume or density of a material changes with both pressure and temperature. Several EoS, including the Mie-Grüneisen-Debye (MGD), are based on the quasi-harmonic approximation (QHA). This says that the frequencies of the vibrational modes of the material are only directly dependent upon the volume, and only indirectly on the pressure and temperature through the changes they induce in the volume. Thus, under QHA, it is assumed that vibrational frequencies do not change along isochors (lines of constant volume). This is true for cubic crystals and elastically isotropic materials. However, MGD and other QHA-based EoS are frequently applied to non-cubic crystalline materials, to predict volumes and densities of mineral phases in applications as diverse as thermodynamic databases and geophysical models of the deep Earth and other planetary bodies.

The thermal pressure in a crystal is, in general, an anisotropic property. For any direction in a crystal it is defined as the ratio of the thermal expansion to the compressibility. The thermal pressure of a crystal defines how the unit-cell parameters change with P and T, and therefore it also controls how the cell parameters change along an isochor. The changes in the unit-cell parameters are strains, and the frequencies of phonon modes change under strain by an amount defined by their mode Grüneisen tensors [1]. When the thermal pressure is isotropic, as in cubic materials and approximately isotropic as in some non-cubic minerals such as quartz, unit-cell parameters remain constant along isochors and the QHA remains valid. When the thermal pressure is anisotropic, the unit-cell parameters change along isochors, even while the volume remains constant. Thus, the frequencies of vibrational modes change along the isochors and the QHA is invalid. This is confirmed by experimental measurements of the elastic properties of rutile, which cannot be fit with a MGD or other EoS based on the QHA. It also means that the components of the mode Grüneisen tensors have different values for temperature- and pressure-induced strains; this provides a simple way to detect from Raman spectra whether anisotropic thermal pressure is significant in a crystal.

[1] Angel et al. (2018) Zeit. Krist., in press, DOI: 10.1515/zkri-2018-2112

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