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Grüneisen parameters and isothermal equations of state

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ABSTRACT

The Grüneisen parameter (γ) is of considerable importance to Earth scientists because it sets limitations on the thermoelastic properties of the lower mantle and core. However, there are several formulations of the Grüneisen parameter in frequent use which not only give different values for γ at ambient pressure but also predict a varying dependence of γ as a function of compression. The Grüneisen parameter is directly related to the equation of state (EOS), yet it is often the case that both the form of γ and the EOS are chosen independently of each other and somewhat arbitrarily. In this paper we have assessed some of the more common definitions of the Grüneisen parameter and the EOS, and have applied them to a test material. Of the EOS considered, when compared against ab initio compressional data for hcp-Fe as our exemplar, we find that the fourth order logarithmic and Vinet relations describe the material with the highest accuracy. Of the expressions for γ considered, it has been suggested, on theoretical grounds, that the modified free-volume formulation should be expected to give the most realistic description of the thermoelastic behavior of a material. However, when we use the fourth order logarithmic EOS to obtain the compressional behavior of the various Grüneisen parameters, we find that there is, in fact, poor agreement between the modified-free-volume formulation and the Mie-Grüneisen parameter obtained directly from ab initio free energy calculations on hcp-Fe. We conclude that none of the analytical forms of gamma are sufficiently sophisticated to describe the thermoelastic behavior of real materials with great accuracy, and care must therefore be taken when attempting to model the thermoelastic behavior of solids to ensure that the appropriate γ (ideally obtained from experiments or ab initio calculations) and equations of state are used.