Grüneisen parameters and isothermal equations of state

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{auth: in all other Anderson papers, editor change K_0 to K_{T_0} and K' to K_T' following the same pattern. So we made those changes here as well; please review all instances carefully and let us know if corrections are needed.}

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.

INTRODUCTION

The Grüneisen parameter is an important quantity in geophysics as it often occurs in equations which describe the thermoelastic behavior of materials at high pressures and temperatures. The value for γ is used to place constraints on geophysically important parameters such as the pressure and temperature dependence of the thermal properties of the mantle and core, the adiabatic temperature gradient and the geophysical interpretation of Hugoniot data.

The Grüneisen parameter has considerable appeal to geophysicists because it is an approximately constant, dimensionless parameter that varies slowly as a function of pressure and temperature. It has both a microscopic and macroscopic definition, the former relating it to the vibrational frequencies of atoms in a material, and the latter relating it to familiar thermodynamic properties such as heat capacity and thermal expansion. Unfortunately, the experimental determination of γ,

defined in either way, is extremely difficult; the microscopic definition requires a detailed knowledge of the phonon dispersion spectrum of a material, whereas the macroscopic definition requires experimental measurements of thermodynamic properties at high pressures and temperatures. As a result of the difficulty associated with obtaining experimentally an accurate value for γ, a number of more approximate expressions have been suggested (see Poirier 1991 for a review). Many of these expressions relate γ at atmospheric pressure ($P = 0$) to the first derivative of the bulk modulus with respect to pressure (K_T'), via $\gamma = \frac{1}{2}K_T' - x$, where x is a constant. These relations may be expanded to take into account the variation of γ with pressure. In these more general cases, γ(P) is a function of the equation of state. Despite the intrinsic relationship between γ and the EOS (see, for example, Irvine and Stacey 1975), it is frequently the case that the choice of the functional form of both the Grüneisen parameter and the equation of state to which it should be related are made independently of each other and somewhat arbitrarily; this has resulted in a literature in which there is a wide range of values of γ for many geologically relevant materials.

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It is, therefore, important to investigate more carefully how the value of γ and its compressional behavior are affected by (1) the choice of the formulation of γ and (2) the use of different equations of state. This paper serves to address this problem and is set out as follows: we shall firstly review the various formulations of γ, stating how they may be obtained directly from the equations of state; we then review a variety of some of the more commonly used EOS including, for comparison, a simple Born-Mie function. This paper differs from previous analytical approaches (e.g., see Irvine and Stacey 1975; Stacey 1995), in that we then test the ability of the various EOS to describe how the density of a material varies as a function of pressure, using pressure-volume data obtained from ab initio calculations on hcp-Fe as an example; using the most appropriate EOS, we then evaluate the various analytical γ; finally, we compare these values of γ with the more fundamental Mie-Grüneisen parameter derived independently from ab initio free energy calculations.

THE GRÜNEISEN PARAMETERS

The microscopic definition of the Grüneisen parameter (Grüneisen 1912) is written in terms of the volume dependence of the ith mode of vibration of the lattice (ω_i) and is given by:

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V} \tag{1}$$

However, evaluation of all γ_i throughout the Brillouin zone is impossible without some lattice dynamical model or high pressure inelastic neutron scattering data.

It can be shown (e.g., Barron 1957) that the sum of all γ_i throughout the first Brillouin zone leads to a macroscopic or thermodynamic definition of γ which may be written as:

$$\gamma_{th} = \frac{\alpha V K_T}{C_V} \tag{2}$$

where α is the thermal expansion, V is the volume, K_T is the isothermal bulk modulus and C_V is the heat capacity at constant volume. Evaluation of γ_{th} is also very difficult, however, because it requires experimental measurements of α, K_T, etc. at extreme conditions of pressure and temperature which are not readily attainable.

Integrating Equation 2 with respect to temperature at constant volume leads to the Mie-Grüneisen expression for γ (see, e.g., Poirier 1991):

$$\gamma = \frac{P_{th} V}{E_{th}} \tag{3}$$

where P_{th} is the thermal pressure and E_{th} is the thermal energy. This too is difficult to determine because the thermal energy is not readily obtained experimentally. However, it is possible, in principle, to obtain P_{th} and E_{th} from ab initio free energy calculations (e.g., Vočadlo et al. 1999) which therefore gives us the opportunity of using this approach to obtain the true thermodynamic γ of a material.

In the past, however, when ab initio approaches were less routinely available, more approximate forms of γ were developed, all of which are based upon a number of assumptions (see e.g., Poirier 1991). Traditionally, among the various gam-

mas, three have often been used: the Slater gamma, γ_S (Slater 1939), the Dugdale-MacDonald gamma, γ_{DM} (Dugdale and MacDonald 1953), and the Vaschenko-Zubarev or free-volume gamma, γ_{VZ} (Vaschenko-Zubarev 1963). More recently, a correction has been applied to the latter, resulting in a modified free-volume gamma, γ_{mfv}, (Barton and Stacey 1985; Stacey 1995). At atmospheric pressure (taken as $P = 0$) they all depend solely on K_0' (dK/dP at $P = 0$) and are given by:

$$\gamma_S = \frac{1}{2}K_{T_0}' - \frac{1}{6} \tag{4}$$

$$\gamma_{DM} = \frac{1}{2}K_{T_0}' - \frac{1}{2} \tag{5}$$

$$\gamma_{VZ} = \frac{1}{2}K_{T_0}' - \frac{5}{6} \tag{6}$$

$$\gamma_{mfv} = \frac{1}{2}K_{T_0}' - 0.95 \tag{7}$$

It appears that in the past, the use of one or other of these expressions has been a matter of personal choice, yet all are based upon a number of assumptions, so in deciding upon an appropriate form of gamma, it seems sensible to assess the approximations made in their derivation. One of the most favoured Grüneisen parameters used in the past has been the Slater formulation, γ_S; however, this definition is only valid if there is no volume dependence of Poisson's ratio. It also relies on the validity of the Debye approximation upon which it is based, in which all the lattice vibrations are described in terms of a single Debye mode. At the time, the adoption of the Debye approximation by Slater (1939) was acceptable; however, more recently, much more detailed analysis of lattice dynamics and its affect on γ has shown that the Debye approximation gives a poor description of complex real materials. Similarly, the Dugdale-MacDonald formulation, γ_{DM}, is derived from a simplification of lattice dynamics in which the material is modeled by a one-dimensional lattice undergoing one-dimensional harmonic oscillations (see Irvine and Stacey 1975); it is also apparent that this too is a gross approximation as it can only include longitudinal acoustic vibrations and cannot, therefore, describe accurately the three-dimensional compressional behavior of even the simplest material. The Vaschenko-Zubarev formulation, γ_{VZ}, is based upon free-volume theory which describes interatomic interactions in a three-dimensional lattice by anharmonic central pairwise potentials between nearest neighbor atoms. This model, therefore, automatically incorporates the volume dependence of Poisson's ratio lacking in the Slater formulation, and overcomes some of the shortcomings of the γ_{DM} associated with its one-dimensional treatment. More recently, however, the modified free-volume gamma has been proposed (Barton and Stacey 1985; Stacey 1995) which takes into account the correlated motion of atoms, which were not considered in the original development of the free-volume gamma.

The above formulations of γ may all be derived from a more general expression for γ which takes into account how γ varies as a function of pressure (see e.g., Poirier 1991):

$$\gamma = -\frac{V}{2}\left(\frac{\frac{\partial^2(PV^{2x/3})}{\partial V^2}}{\frac{\partial(PV^{2x/3})}{\partial V}}\right) + \frac{(x-2)}{3} \tag{8}$$

where x = 0,1,2, ~2.35 for γ_s, γ_{DM}, γ_{VZ}, and γ_{mfv} respe:klively. It can be? ;en from this equation that not only will the various γ behave differently under compression through the parameter x, but also that the Grüneisen parameter is a direct function of the chosen equation of state, which defines P as a function of V. We also note that Equation 8 implicitly defines the functionality of the parameter q $(=\partial\ln\gamma/\partial\ln V)$, which is also widely, but arbitrarily, used in the geophysical literature.

From the arguments mentioned earlier it would appear reasonable that of the approximate definition of gamma described above, the most appropriate would be the modified free-volume formulation. Such a choice is made all the more credible when it is compared with the γ of Barron (1955) and Vovadlo et al. (1994), who have shown that a full lattice dynamics treatment gives a $P = 0$ relation for gamma of:

$$\gamma_{LD} = \frac{1}{2}(\pm 0.02)\,K_{T_0}^{'} - 0.9(\pm 0.02) \qquad (9)$$

Although the high pressure formulism for γ_{LD} has not been calculated, it is reasonable to expect that it will be closer to γ_{mfv} than to any of the other definitions mentioned earlier.

In order to confirm, or otherwise, that the modified-free-volume formulation is more likely to describe the behavior of a real material than the other forms considered here, we wish to compare the various gamma and EOS, via Equation 8, against recent highly accurate ab initio data for our example material of hcp-Fe.

EQUATIONS OF STATE

There are many proposed equations of state available in the literature (see, e.g., Poirier 1991), but we shall confine our study to some of those more commonly adopted: the second-order Birch-Murnaghan EOS (Birch 1938, 1947), the third order Birch-Murnaghan EOS, the third order logarithmic EOS (Poirier and Tarantola 1998), the fourth order logarithmic EOS and the Vinet EOS (Vinet et al. 1987, 1989, derived from Rydberg 1932). As an interesting comparison, we shall also consider the EOS derived directly from a Born-Mie interatomic potential of the form:

$$U = -\frac{a}{V^{m/3}} + \frac{b}{V^{n/3}} \qquad (10)$$

The Born-Mie function gives an analytical value for pressure $P(V)$, the bulk modulus at atmospheric pressure, K_{T_0}, and its pressure derivative, K_{T0}', for a given $a, b, m,$ and n via:

$$P = -\frac{1}{3}amV^{-(m/3+1)} + \frac{1}{3}bnV^{-(n/3)} \qquad (11)$$

$$K_{T_0} = -\frac{ma}{3}\left(\frac{m}{3} + 1\right)V_0^{-(m/3+1)} + \frac{nb}{3}\left(\frac{n}{3} + 1\right)V_0^{-(n/3+1)} \qquad (12)$$

and

$$K_{T_0}^{'} = \frac{m + n + 6}{3} \qquad (13)$$

where V is the volume, V_0, the equilibrium volume at zero pressure, and m and n, respectively, embody the range of the attractive and repulsive part of the effective potential.

The other equations of state considered may be expressed as a function of density, via $c = \rho/\rho_0$, as follows:
the second order Birch-Murnaghan EOS;

$$P = \frac{3K_{T_0}}{2}(c^{7/3} - c^{5/3}) \qquad (14)$$

the third order Birch-Murnaghan EOS;

$$P = \frac{3K_{T_0}}{2}(c^{7/3} - c^{5/3})[1 - \frac{3}{4}(K_{T_0}^{'} - 4)(c^{2/3} - 1)] \qquad (15)$$

the third order logarithmic EOS;

$$P = K_{T_0}\,c\ln c\left(1 + \frac{1}{2}(K_{T_0}^{'} - 2)\ln c\right) \qquad (16)$$

the fourth order logarithmic EOS;

$$P = c\left(\begin{array}{l} K_{T_0}\ln c + \frac{1}{2}K_{T_0}(K_{T_0}^{'} - 2)(\ln c)^2 \\[2mm] + \frac{1}{6}[K_0^2 K_0^{''} + K_{T_0} + K_{T_0}(K_{T_0}^{'} - 2) \\[2mm] + K_{T_0}(K_{T_0}^{'} - 2)^2](\ln c)^3 \end{array} \right) \qquad (17)$$

the Vinet EOS;

$$P = 3K_{T_0}c^{2/3}\left(1 - c^{-1/3}\right)\exp\left(\frac{3}{2}(K_{T_0}^{'} - 1)\left(1 - c^{-1/3}\right)\right) \qquad (18)$$

The functional form and sensitivity of the free-volume γ_{VZ} to this selection of EOS and reasonable values of K' are exemplified in Figures 1 and 2. The diverse behavior of γ as a function of EOS and also of K' illustrates the necessity to examine these equations of state in more detail in order to ascertain which one best describes the behavior of a material under compression. In the following section, we compare the ability of the EOS in Equation 11 and Equations 14–18 to accurately describe compressional behavior of a real material, using as our exemplar $P(V)$ data for hcp-Fe as determined by ab initio calculations. The advantage of ab initio data is that they are precise (as well as giving a relatively accurate description of a real material) and can also be calculated to virtually arbitrary limits in pressure.

FITTING THE EQUATIONS OF STATE TO AB INITIO PV DATA

In order to provide a pressure-volume data set against which to test these different EOS, ab initio electronic structure pseudopotential calculations were performed on the hexagonal close-packed phase of iron at a number of fixed volumes. For details of the methodology, see Vočadlo et al. (1997, 1999).
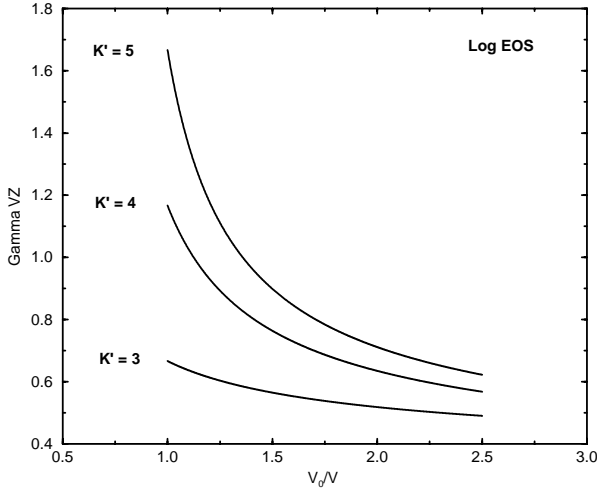
FIGURE 1. The functional form of the free-volume Grüneisen parameter as a function of compression using a truncated third order logarithmic EOS (Poirier and Tarantola 1998); the curves are for a K'_{T_0} of 3, 4, and 5 respectively.
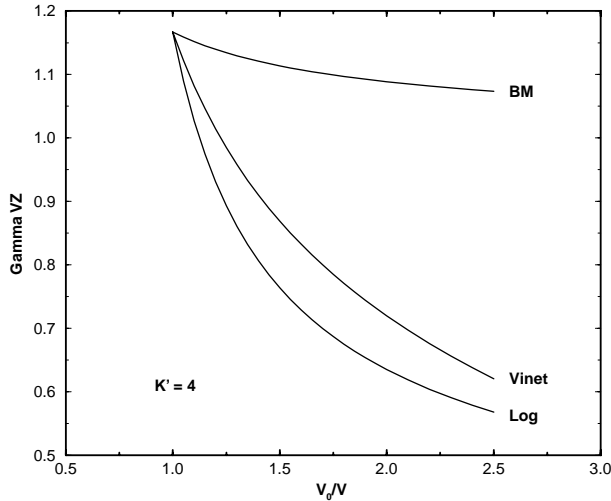

FIGURE 2. The variation of the free-volume Grüneisen parameter as a function of compression, for $K'_{T_0} = 4$, using a Birch-Murnaghan, third order logarithmic and Vinet EOS.

TABLE 1. Fitted parameters to the various equations of state

	V_0 (Å³)	K (GPa)	K'	K'' (1/GPa²)	χ^{2*}
Born-Mie†	10.25	194 (1057)	4.4 (700)		21
BM2	10.39 (6)	308 (8)			443
BM3	10.32 (2)	287 (3)	4.37 (4)		37
Log3	10.15 (5)	326 (7)	4.89 (12)		250
Log4	10.26 (1)	293 (7)	4.69 (1)	−0.02(1)	1
Vinet	10.24 (1)	297 (1)	4.73 (2)		5

* $\chi^2 = \Sigma_i w_i [Y_i(\text{obs.}) - Y_i(\text{calc.})]^2/(N - P + C)$.
† V_0 parameter was chosen as the minimum energy volume as obtained from the ab initio calculations; K and K' derived from values for m and n - equations 12 and 13; χ^2 value refers to the fitting of *a, b, m*, and *n* in Equation 10.

TABLE 2. Correlation coefficients (%)

	V_0–K	V_0–K'	K–K'	V_0–K''	K–K''	K'–K''
BM2	93					
BM3	55	28	61			
Log3	70	31	40			
Log4	73	59	21	59	58	84
Vinet	57	25	61			
	a-b	*a-m*	*a-n*	*b-m*	*b-n*	*m-n*
Born-Mie	100	99.997	99.995	99.997	99.995	99.985

Note: *a, b, m, n* from Equation 10.

however, that despite the excessively large standard errors, the K and K' derived were essentially identical over the entire range of fitted values (varying by <1 GPa in K and < 0.02 in K').

Figure 3 shows that, superficially, all EOS seem to fit the data reasonably well; however, on closer inspection (Fig. 4) it can be seen that the second order Birch-Murnaghan and the third order logarithmic EOS give relatively poor fits. Indeed, only the Vinet and fourth order logarithmic EOS fit the data very well. This is reflected in the statistics associated with the fitting of Equations 10–14 (Table 1), where the excellent fit of the fourth order logarithmic and Vinet EOS is demonstrated by their low standard errors and low χ^2 values, whereas the converse is the case for second order Birch-Murnaghan and third order logarithmic EOS.

It would appear, therefore, that (at least for the example chosen) the fourth order logarithmic and Vinet EOS give a far better representation of compressional behavior than other EOS which are frequently found in the literature.

DETERMINATION OF γ USING THE FOURTH ORDER LOGARITHMIC EQUATION OF STATE

Using Equation 8 and the fourth order logarithmic EOS defined by the parameters in Table 1, it is possible to obtain γ(c) for each of the approximate formulations of gamma discussed earlier. The results are shown in Figure 5. For comparison we have also plotted the thermodynamic γ(T = 2000) obtained directly from first principles free energy calculations using the Mie-Grüneisen relation in Equation 3 (Alfe et al. in preparation). These are highly accurate calculations which give a γ_0 of ~1.6 ([compared with that derived from experimental data of ~1.7 (see Anderson 1988)] decreasing to ~1.4 at core volumes [compared with a core value of ~1.3 ± 0.1 (see Anderson 1988; Stacey 1995)]. Using the fourth order logarithmic EOS to calculate the various analytical gamma, it would seem, from inspection of Figure 5, that the ab initio data are best represented by a Dugdale-MacDonald Grüneisen parameter in the
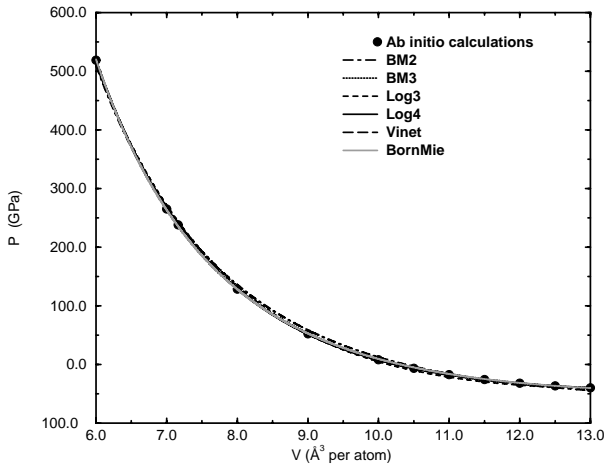
These ab initio calculations are not only invaluable in providing a test data set, but also enable us to calculate the internal energy of our system, and therefore provide an independent means of calculating γ through the Mie-Grüneisen relation (Eq. 3). Each of the EOS (Eqs. 11 and 14–18) were fitted to our calculated *PV* data set in order to determine the parameters V_0, K, and in some cases, K', K''; the statistics relating to the goodness of fit are shown in Table 1.

In deriving these results it was found that it was extremely difficult to effectively fit the parameters of the Born-Mie equation because there is a very shallow minimum in fitting-parameter space; this results in a very high correlation between the parameters *a, b, m*, and *n* in Equation 10 (Table 2) which are, as a result, very poorly determined. It should be noted,

FIGURE 3. The second and third-order Birch-Murnaghan, third and fourth order logarithmic, Vinet and Born-Mie equations of state fitted to ab initio pseudopotential calculations for hcp-Fe; superficially, all the EOS fit the data reasonably well.
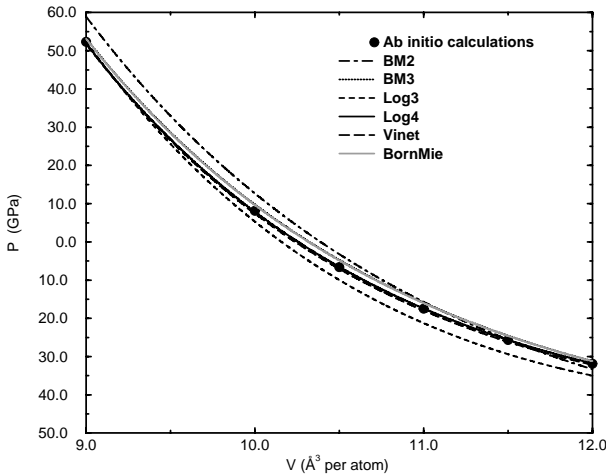

FIGURE 4. An enlargement of Figure 3; on this scale it becomes clear that the fourth order logarithmic and Vinet EOS give excellent fits to the calculated data.

FIGURE 5. The variation of the various Grüneisen parameter as a function of compression using the fourth order logarithmic EOS and Equation 8 and also that obtained directly from ab initio calculations using the Mie-Grüneisen relation (T = 2000 K).

density range $1.1 < c > 1.4$. As we discuss below, we do not believe, however, that this should be interpreted as a validation of the Dugdale-MacDonald approximation, but is, rather, a fortuitous result. Figure 5 also shows that the formulation of the analytical Grüneisen parameter which has previously been suggested to be the most rigorous, γ_{mfv}, in fact agrees poorly with that derived from first principles.

DISCUSSION AND CONCLUSION

There are a number of points that require some discussion before a conclusion can be reached: (1) There is no explicit temperature dependence in the various analytical forms of gamma as they are intended to describe behavior at the classical limit ($C_V \rightarrow 3R$), whereas the ab initio calculations upon
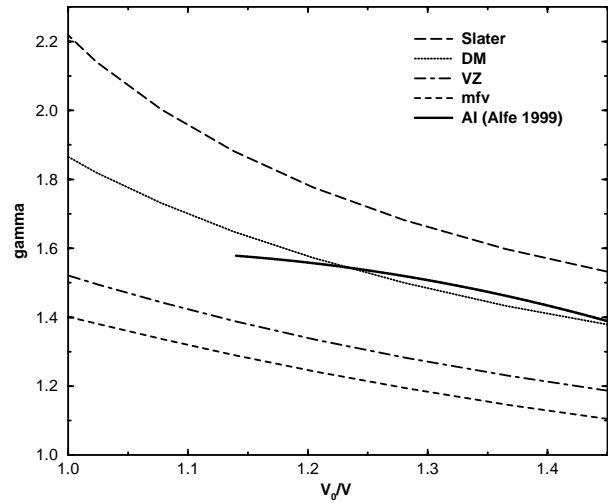
which the thermodynamic γ is based include higher anharmonic effects (Alfè et al. in preparation). However, the effect of this temperature dependence is not expected to be significant because it is thought that $\partial \gamma / \partial T$ is such that the error in γ would only be ~10% at 4000 K and $P = 0$ (and therefore less at lower T); this error would also decrease significantly with increasing pressure (Stacey 1995). (2) None of the various formulations of the analytical gamma include the electronic effects present in the ab initio calculations. However, at low temperatures (<2000 K) the contribution to γ from the thermal excitations of the electrons is negligible (Alfè et al. in preparation) and therefore provided that T is above the Debye temperature and below ~2000 K, γ can be determined entirely from the harmonic phonon spectrum. (3) All of the analytical formulations of γ, excepting the modified free-volume γ, are derived from a model whereby a solid is described in terms of independently vibrating harmonic oscillators interacting via pairwise central forces; this is not a realistic description. (4) Although the modified free-volume theory does take into account the correlated motions of atoms, it effectively reduces the entire force constant matrix of a material to a single effective force constant; this, too, is not a realistic description of a material.

Our conclusion, therefore, is that although the Dugdale-MacDonald Grüneisen parameter appears to lie closest to that determined directly from ab initio calculations, this is likely to be merely fortuitous, because all analytical γ are based on approximations that rely upon a number of unjustified assumptions. In the past, such an approach was the only way forward, but these analytical methods are now being superceded by ab initio techniques. We believe, therefore, that, in the absence of reliable high P-high T experimental data, thermoelastic parameters, such as the Grüneisen parameter, cannot be reliably obtained from approximate descriptions, rather they should now be derived from rigorous, highly accurate, quantum mechani-

cal free-energy calculations. Finally, we also note that from the analysis of our example data set (hcp-Fe), of the EOS considered, both the fourth order logarithmic and the Vinet EOS should be the formulations of choice.

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