Grüneisen Parameter along Hugoniot and Melting Temperature of ε-Iron: a Result from Thermodynamic Calculations*

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Based on the available data of specific heat C_v at constant volume and the Grüneisen parameter γ of both lattice and electron contributions, we present a consistent method for simultaneously calculating the effective or synthesized Grüneisen parameter along Hugoniot, γ_{eH}, covering solid, mixed, and liquid states, and the melting temperature T_m for ε-iron. The rationality validation for this method is confirmed as compared with the experimental data, including the measured T_m and Hugoniot bulk sound velocities C_b. The calculated γ_{eH} and T_m for ε-iron at the Earth's inner-core boundary (330 GPa) are 1.58 and 5930 K, respectively, which are close to the values of 1.53 and 6050 K given by Anderson [J. Phys. Chem. Solids 64 (2003) 2125]. This method for determination of γ_{eH} could be, in principle, also applicable to any thermodynamic state calculations, e.g., along isothermal and isentropic paths, other than the Hugoniot locus.

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Iron is considered as the major component constituting the core of Earth, therefore the properties of iron at elevated pressures and temperatures are crucial to model the temperature profile and the dynamics of the core.[1] For this reason, the Grüneisen parameter γ is one of the important thermodynamic quantities in geophysics since it often appears in equations that describe the thermophysical behaviour of Earth's core at relevant pressures and temperatures. The available data of γ for iron, especially in the Hugoniot, are limited and are not in complete agreement with each other. For example, four different γ representations for iron along the Hugoniot, though using the same parametrization $\gamma = \gamma_0(\rho_0/\rho)^q$ but different values of γ_0, ρ_0 and q, were suggested by different authors. Here ρ is the density and the subscript 0 refers to a reference state. They are $\gamma_0 = 2.2$, $q = 1.62$, and $\rho_0 = 8.31\,\mathrm{g/cm^3}$ for ε-phase;[2] $\gamma_0 = 1.7$, $q = 0.7$, and $\rho_0 = 8.28\,\mathrm{g/cm^3}$ for ε-phase;[3] $\gamma_0 = 2.53$, $q = 1$, and $\rho_0 = 7.856\,\mathrm{g/cm^3}$[4] (deduced from the values suggested by the other authors); and $\gamma_0 = 1.945$, $q = 1$, and $\rho_0 = 7.856\,\mathrm{g/cm^3}$.[5] The latter two are without comment on phase. The above results with such a dispersion manner (Fig. 1) make it difficult to assess which one is usable. Again, when we further pay attention to the recent experimental γ contributed simply from phonon vibrations,[6] denoted by γ_N, as shown in Fig. 1, more puzzles arise spontaneously for us.

In this Letter, an attempt of finding a way to accurate γ determination will be discussed. For iron, just as all metals, its thermophysical properties are affected cooperatively by lattice and electron contributions, and thus the Grüneisen parameter γ_{eff} and the specific heat at constant volume, C_V, can be defined as[7]

$$\gamma_{\mathrm{eff}} = (C_{VN}\gamma_N + C_{Ve}\gamma_e)/C_V, \quad (1)$$

$$C_V = C_{VN} + C_{Ve}, \quad (2)$$

where subscripts N and e refer to the lattice (phonon) and electron contributions, respectively. For iron, we adopt $C_{VN} = 446.65$ (J kg^{-1} K^{-1}) according to the Dulong-Petit value, $C_{Ve} = 0.091\ (8.298/\rho)^{1.34}T$ (J kg^{-1} K^{-1}),[8] $\gamma_e = 2$,[7] and γ_N from Ref. [6]. In order to calculate γ_{eff} of iron along the Hugoniot, hereafter denoted by γ_{eH}, two-step calculations will be performed as follows.

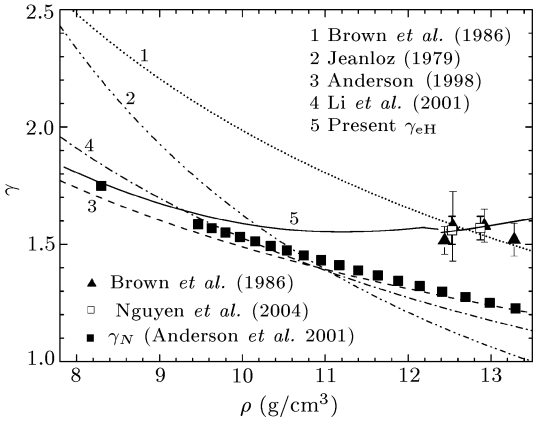


Fig. 1. Grüneisen parameter of iron along the Hugoniot.

First, we make the estimation of the melting tem-

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perature T_m in advance, due to the need for discriminating solid, mixed, and liquid regions along the Hugoniot when the γ_{eH} calculation is performed. For this purpose, a latest reported Hugoniot data of iron,[9] centred at α-phase and ambient pressure, up to 442 GPa was given by

$$D = C_0 + \lambda u, \text{ in units of km/s},$$
$$C_0 = 3.935\,\text{km/s},\ \lambda = 1.578,\ \rho_0 = 7.850\,\text{g/cm}^3, \tag{3}$$

where D and u are the shock wave velocity and the particle velocity, respectively. Therefore, the shock pressure P_H and the Rankine-Hugoniot energy E_H, via the conservation relation, can be expressed by

$$P_H = \rho_0 C_0^2 \eta/(1-\lambda\eta)^2, \tag{4}$$
$$E_H = 0.5 P_H \eta/\rho_0 + (E_0 + E_{tr}), \tag{5}$$

where $\eta = 1-(\rho_0/\rho)$, E_0 is the energy increment of ε-iron at ambient pressure from 0 K to 300 K and equals 76.2684 kJ kg^{-1} determined from the Debye temperature θ_0,[6] E_{tr} represents the phase transition energy of $\alpha \to \varepsilon$ phase at 300 K and at the ambient pressure, which is deduced from the recent experimental phase diagram of iron to be 10.910 kJ kg^{-1}.[10] On the other hand, a 300-K isothermal of ε-iron was given in Ref. [6], from which the 0-K isothermal compression curve $P_x(\rho)$ and energy $E_x(\rho)$ can be deduced accordingly. A recent Hugoniot sound velocity experimental data[11] revealed that the shock-induced melting begins at 225 GPa (corresponding to the so-called superheating meting pressure, $P'_m = 225$ GPa, and temperature, $T'_m = 5100$ K) and completes at 260 GPa (corresponding to the equilibrium melting pressure P_m and temperature T_m[12]). Here we use energy conservation relation to directly calculate T_m from P_m, instead of the methods[12,13] in which T_m was found from T'_m by superheating corrections, by the equation

$$E_H = E_X + \int_0^{T_m} C_V dT + T_m \Delta S. \tag{6}$$

Combining Eq. (6) with Eqs. (2), (4) and (5), and substituting the melting entropy $\Delta S = 0.79R$[14] and other above-mentioned proper parameters into, we can obtain the result $T_m = 5300$ K at $P_m = 260$ GPa, as shown in Fig. 2. It should be noted that this data (260 GPa, 5300 K) is only one point on the whole melting curve for ε-iron, whereas it could be utilized as a reference point to deduce the high pressure melting curve, $T_m(\rho)$, using the Lindemann law,

$$\Delta T_m = 2T_m(\gamma_{\text{eff}} - 1/3)\frac{\Delta\rho}{\rho}. \tag{7}$$

The calculated result is given in Fig. 2 by a dashed line, demonstrating that the result is in agreement well with the two newly static high-pressure data reported in Refs. [15,16]. Therefore, this calculation is of rationality.

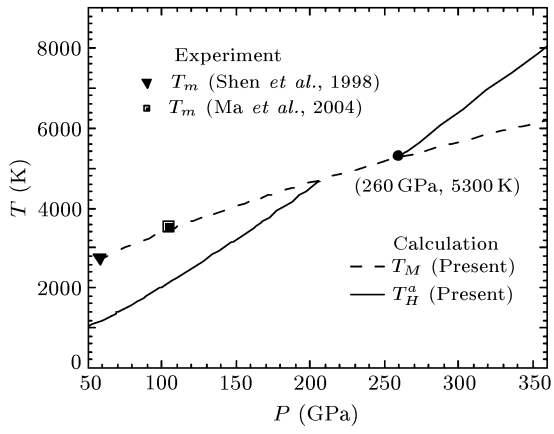


Fig. 2. High-pressure melting curve of ε-iron.

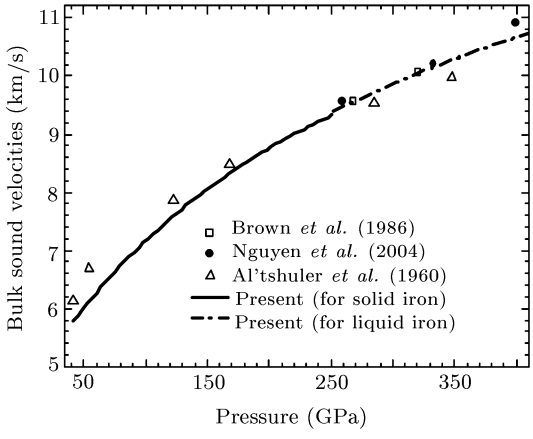


Fig. 3. Comparison of the measured bulk sound velocities with the calculated Hugoniot data for ε-iron.

The second step is to compute γ_{eH}. To do this, we should compute the solid ε-iron Hugoniot temperature T_H^S firstly, which is used in comparison with T_m at the same density for differentiating solid, mixed, and liquid regions. We adopt

$$dT_H^S = (T_H\gamma_{eH}/\rho)d\rho + \lfloor(\eta/\rho_0)dP_H - (P_H/\rho^2)d\rho\rfloor/C_V. \tag{8}$$

Therefore, we could compute the actual Hugoniot temperature T_H^a, since it is not only in solid state, but also passing through mixed and liquid states under the Earth's core pressure condition. The used equations are

$$E_H = E_X + \int_0^{T_H^a} C_V dT,$$
$$\text{(in solid state for } T_H^a = T_H^S \le T_m), \tag{9}$$
$$E_H = E_X + \int_0^{T_H^a} C_V dT + T_{mc}\Delta S\frac{T_{mc}-T_m}{T_{Hc}^S - T_H^S},$$

$$\text{(in mixed state for } T_H^S \geq T_m = T_H^a\text{)}, \tag{10}$$

$$E_H = E_X + \int_0^{T_m} C_V dT + \int_0^{T_H^a} C_V^l dT + T_m \Delta S, \quad \text{(in liquid state for } T_H^S \geq T_H^a \geq T_m\text{)}, \tag{11}$$

where the subscript c refers to the state variable at 260 GPa along the Hugoniot, $C_V^l = C_V - 0.15(RT/T_m)$[17] is the specific heat at constant volume in liquid state. Substituting the calculated T_H^a into Eqs. (2) and (1), we can obtain γ_{eH} as shown in Fig. 1, which also illustrates the data of γ_{eH} indirectly deduced from the measured Hugoniot bulk sound velocity C_b,[11] in liquid state using Eq. (12) for comparison. It is noted that between the calculated C_b using Eq. (12) according to γ_{eH} is in good agreement with the measured C_b in both solid[18] and liquid[4,11] states, as shown in Fig. 3, which may be regarded as an additional support for the rationality of the direct thermodynamic calculation method proposed here for γ_{eH}.

$$C_b^2 = \frac{dP_H}{d\rho}\left[1 - \frac{\gamma_{eH}}{\rho_0}\frac{\rho - \rho_0}{2}\right] + \frac{\gamma_{eH}}{\rho}\frac{P_H}{2}. \tag{12}$$

In summary, we have presented a consistent method for simultaneously calculating the Grüneisen parameter along the Hugoniot and the melting temperature for ε-iron. We also present some rationality validations by the experimental data. It is interesting to note that the calculated γ_{eH} and T_m at the inner-core boundary (330 GPa) are 1.58 and 5930 K, respectively, which are close to the estimation values given in Ref. [19]. In principle, this proposed method for the $\gamma_{\rm eff}$ calculation is also applicable for other thermodynamic states, e.g. isothermal and isentropic compressions, other than the Hugoniot locus.

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