

## Gruneisen's gamma function for liquid iron at the Earth's outer core conditions

E. BOSCHI (\*) - F. MULARGIA (\*)

Received on July 15<sup>th</sup>, 1977

**SUMMARY.** - We derive the Gruneisen's gamma as a function of temperature and pressure for liquid iron at the temperature and pressures of the Earth's outer core taking into account the anharmonic and electronic contributions in a self-consistent way. We obtain numerical values definitely different from those generally quoted in the geophysical literature, but in agreement with recent experimental determinations.

**RIASSUNTO.** - Si ottiene un'espressione per il gamma di Gruneisen in funzione della temperatura e della pressione per il ferro liquido nell'intervallo di pressioni e temperature del nucleo esterno della Terra tenendo anche conto, in maniera consistente, dei contributi anarmonici ed elettronici. Si ottengono valori numerici nettamente diversi da quelli generalmente riportati nella letteratura geofisica, ma in accordo con i risultati di recenti esperimenti.

It is generally accepted that the Earth's outer core is mainly composed by liquid iron. In this work we assume it composed by pure liquid iron and we shall evaluate the Gruneisen's gamma values in the outer core range of pressures and temperatures. The Gruneisen's gamma is derived taking into account all the known possible physical effects according to recent achievements in solid state theory. Furthermore, instead of extrapolating with dubious rigour values relative to solid crystals, as it is generally made in the geophysical literature, we apply our theory to liquid state. The problem of the determination of the Gruneisen's gamma for liquids has had scarce attention (<sup>4, 11</sup>).

---

(\*) Istituto di Geofisica, Università di Bologna.

By liquid state, at the Earth's core conditions, we mean a lattice with a simple cubic structure in which transverse waves have a transmission coefficient irrelevant in comparison with the longitudinal transmission coefficient. This liquid model arises from experimental diffraction data on liquid metals (<sup>7, 15</sup>) which show a nearest-neighbour pattern much more randomly located than for solids. This gives the reasons to support for liquids a lower coordination number than for solids (<sup>17</sup>) and a very low transverse « constant » in order to allow nearly free shear movements in the lattice. According to DOMB et al. (<sup>5</sup>), by force constants we mean the spring constant  $\partial F/\partial r$  of the intermolecular forces  $F$ . We believe that at the present stage of knowledges this is the best way to tackle the problem since neither the cell model (<sup>12</sup>), nor the distribution function model can be profitably used in the lattice calculations (<sup>11</sup>).

An explicit expression for the Gruneisen's gamma can be found following the general procedure of considering a solid as a system of  $3N$  strongly anharmonic oscillators. The hamiltonian function of the system may then be splitted into its harmonic (in the Leibfried-Ludwig sense (<sup>13</sup>)) and anharmonic parts

$$H = H_H + H_A$$

which can be solved separately. Considering the harmonic term, we find the normal modes of vibration of the system as eigenvalues of  $H_H$  and then, from the energy spectrum, compute the Gruneisen's gamma according to the definition

$$\gamma = \sum_i (\partial \ln \nu_i / \partial \ln V)$$

It must be noted that the high temperatures of the core allow us to use a Thirring's series expansion (<sup>18</sup>) to express the harmonic Gruneisen's without passing through the explicit frequency spectrum, but just considering its statistical moments. Then the harmonic Gruneisen's gamma turns out to be

$$\gamma_H = V (\partial E_{VIB} / \partial V)_T (TC_V - E_{VIB})^{-1} \quad [1]$$

where

$$E_{VIB} = E(T) - U \quad [2]$$

$$C_V = (\partial E_{VIB} / \partial T)_V$$

$U$  is the static lattice potential and  $E(T)$  the internal energy of the system.  $E_{VIB}$  can be written as

$$E_{VIB} = 3 N k T \left\{ 1 - \sum_{n=1}^{\infty} (-1)^n [B_{2n}/(2n)!] \mu_{2n} (\bar{h}/kT)^{2n} \right\} \quad [3]$$

where  $B_{2n}$  are Bernoulli numbers and  $\mu_{2n}$  are the static even moments of the frequency distribution. The very high temperatures we are treating allow us to consider only the first few moments since the Thirring's series is strongly convergent up from the Debye temperature. These moments have been calculated for any lattice structure to the 20-th order (<sup>2, 5, 16, 13</sup>) (BHATIA) and HORTON, 1955, DOMB et al., 1959; MONTROLL, 1943; LEIGHTON, 1948). We shall use the septenary partition model (<sup>4</sup>), which gives the momenta of a simple cubic 3  $d$  lattice. The first two moments can be written as

$$\mu_2 = (K_p + 2 K_t) M_A^{-2} \quad [4]$$

$$\mu_4 = 2 (K_p^2 + 2 K_t^2) M_A^{-2} + 4 (K_p + 2 K_t) M_A^{-2} \quad [5]$$

where  $K_p$  and  $K_t$  are the longitudinal and transverse constants, respectively. We employ an intermolecular potential of Rydberg type, namely

$$\varphi = -D [1 + b (r_{ij} - r_v)] \exp [-b (r_{ij} - r_v)] \quad [6]$$

where  $r_v$  is the static distance of approach of the molecules,  $r_{ij}$  is the instantaneous distance.  $D$  and  $b$  are constants, and namely,  $D = 74.69 \times 10^{-14}$  ergs,  $b = 2.0534 \times 10^{-8} \text{ \AA}^{-1}$ . This potential shows a very good agreement with experimental data for iron and nickel compression (<sup>21</sup>) (VARSHNI and BLOORE, 1963). The force constants are then given by

$$K_p = Db^2 [1 - b (r_{ij} - r_v)] \exp [-b (r_{ij} - r_v)] \quad [7]$$

$$K_t = C K_p \quad [8]$$

where  $C$  is arbitrarily taken  $10^{-2}$  and  $10^{-3}$ .

This choice will appear irrelevant for our aims as it will be evident from the following. If we consider in detail equation [2], we see that all the terms can be immediately calculated. In particular we note that the term  $V (\partial E_{VIB}/\partial V)_T$  can be expressed by

$$V (\partial E_{VIB}/\partial V)_T = -5 N k T \sum_{n=1}^{\infty} (-1)^n [B_{2n}/(2n)!] (\partial \mu_{2n}/\partial V) (\bar{h}/kT)^{2n} \quad [9]$$

which is easily computed by

$$V (\partial K_p / \partial V) = D b^2 \exp [-b (r_{ij} - r_e)] [-(2/3) b r_{ij} + b^2 (r_{ij} - r_e) / 3]$$

$$V (\partial K_i^2 / \partial V) = (2/3) D^2 b^5 r_{ij} [-2 - b^2 (r_{ij} - r_e)^2 + b r_{ij} - b r_e / 2 + \\ + 2 b (r_{ij} - r_e)] \exp [-2 b (r_{ij} - r_e)].$$

Using the above equations we determine the harmonic Gruneisen's gamma for various compressions. The volume dependence is directly taken into account by changing the value of  $r_{ij}$  in the intermolecular potential equation. Results are shown in Fig. 1. The values of  $C$  of equation [8] turn out to be immaterial for the values of  $\gamma_H$ .

The anharmonic part of the hamiltonian function is then written in the framework of the self-consistent phonon theory <sup>(16)</sup> as

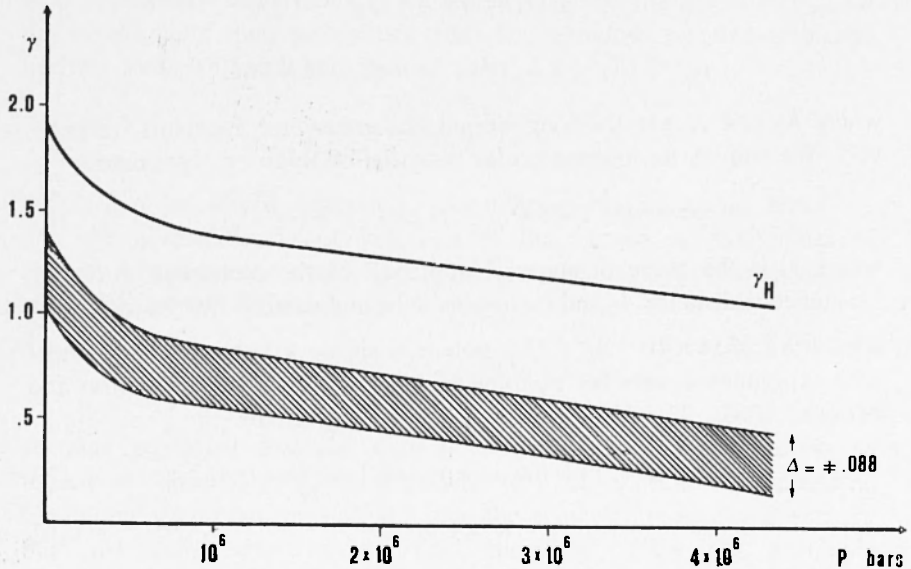


Fig. 1 — The Gruneisen's harmonic gamma and the total gamma function are plotted versus pressure. The total gamma is taken along an isotherm at 5800° K.

$$H_A = 12 k^2 h^2 \sum_{KK'} \Phi_{K, -K, K', -K'} (\omega_K \omega_{K'})^{-1} - 24 k^2 \bar{h}^{-3} \sum_{KK'K''} \\ [(\Phi_{K, K', K''})^2 + (3/2) \Phi_{K, -K, -K''}] (\omega_K \omega_{K'} \omega_{K''})^{-1} \quad [10]$$

where  $\Phi_{K,K',\dots}$  is the total lattice potential intended as a pair potential and  $G, K', \dots$  accounting for the summation pairs <sup>(1)</sup>.  $\omega_K$  are the eigenvalues of the dynamical matrices.

Since we are treating a metal we must also account for the electronic contributions to the free energy of the system. Let us write them as

$$H_{el} = \Gamma T^2/2 \quad [11]$$

where  $\Gamma$  is the electronic specific heat divided by  $T$ . We incorporate all the electronic effects in the anharmonic hamiltonian function. The electronic contributions for liquid iron can be evaluated from the density of the states relatively to the non-ferromagnetic phase because of the high temperatures we are considering. Up to now, no experimental data are available for these quantities, but there is physical evidence that liquid iron density of the states values should slightly differ from the solid iron ones <sup>(1)</sup>. Furthermore, a physically reliable theoretical approach, based on the cluster model <sup>(10)</sup>, shows that electronic bands for liquid iron differ for no more than 5% from those relative to the solid state. We shall use values computed for solid non-ferromagnetic iron which have been tested with good accordance with experimental data <sup>(23)</sup>. The effects of pressure on this term were computed by HENRY <sup>(9)</sup> by using a Fermi-Thomas atom model, with the result that electronic specific heat decreases by a factor smaller than 3 for pressures of  $10^2$  Megabars. Therefore we shall suppose that the electronic contribution is not affected by the pressures we consider. In any case the error is much less than the uncertainty in the anharmonic term. Then the Gruneisen's gamma function is evaluated by the equation

$$\gamma = \gamma_H + \gamma_A \quad [12]$$

which leads to

$$\begin{aligned} \gamma = \gamma_H \{ 1 + (1/12) [ \langle \bar{h} \omega_K / kT \rangle^2 - \gamma_H^{-1} \langle (\bar{h} \omega_K / kT)^2 \rangle ] - (3NnkT^{-1})^{-1} \times \\ \times \{ (\Gamma - 2 A_2) - 2 \gamma_H^{-1} V [d(\Gamma - 2 A)/dV] \} \} \quad [13] \end{aligned}$$

where the averages are performed over the normal modes,  $A_2$  is the anharmonic leading term of the free energy <sup>(1)</sup>, and  $n$  is the number of particles in a cell. Equation [13], in the high temperature conditions of the Earth's core, simplifies to

$$\gamma = \gamma_H - (3NknT^{-1})^{-1} \{ (\Gamma - 2 A_2) - 2 \gamma_H^{-1} V [d(\Gamma - 2 A_2)/dV] \} \quad [14]$$

Concluding, by means of the above equations, we computed the Gruneisen's gamma function for liquid iron versus pressure along an isotherm at  $5800^{\circ}\text{K}$ , temperature that most recent theories <sup>(7)</sup>, quote as the inner core outer core boundary temperature in the assumption of a pure iron core. The corresponding results are plotted in Fig. 1. We computed also the isobars at 1.4 and 3.1 Megabars, i. e. at the pressures of the mantle-core and the inner core-outer core boundaries. The uncertainty on the anharmonic gamma leads to an average uncertainty on the values of the gamma function of 0.09. The results are plotted in Fig. 2, where the zone corresponding to the outer core is shaded. Gruneisen's gamma ranges from 1.0, at the mantle-core boundary, to 0.5, at the inner core-outer core boundary.

BOHELER, RAMAKRISHNAN, and KENNEDY <sup>(3)</sup> have recently measured the Gruneisen's gamma at high pressures for iron and our results are in agreement with theirs. Therefore the values of the Gruneisen's gamma generally assumed for iron at core conditions, 1.7, are definitely

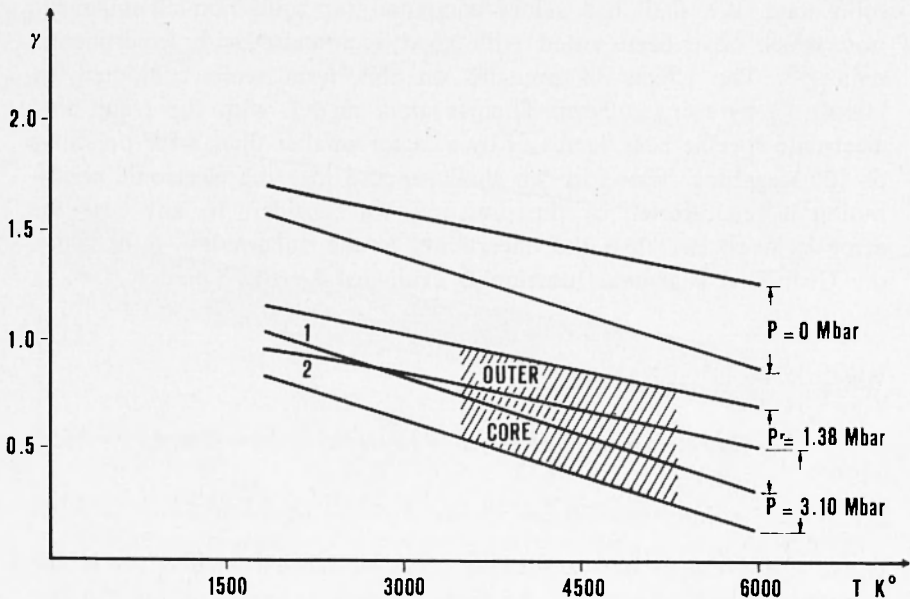


Fig. 2 — The total Gruneisen's gamma function is plotted versus temperature along the isobars at 0, 1.4, and 3.1 Megabars.

unacceptable. Finally we wish to emphasize the fact that, for the first time, the temperature effects have been accounted for in a self-consistent way.

#### ACKNOWLEDGMENTS.

We wish to thank R. BOEHLER for letting us use his data prior to publication. Thanks are due also to V. LELLI and G. MOLINARI for their kind assistance.

This work has been performed with a contribution from Consiglio Nazionale delle Ricerche.

#### REFERENCES

- (<sup>1</sup>) BAER, Y., et al., 1970. *Band structure of transition metals studied by ESCA*. Phys. Scripta, **1**, p. 55.
- (<sup>2</sup>) BHATIA, A. B., and G. K. HORTON, 1955. *Vibration spectra and specific heats of cubic metals, Applications to silver*. Phys. Rev., **98**, p. 1715.
- (<sup>3</sup>) BOEHLER, R., J. RAMAKRISHNAN, and G. C. KENNEDY, 1977. *Gruneisen's gamma for metals at high pressures*. J. Appl. Phys..
- (<sup>4</sup>) BRADELY, J. C., 1961. *Vibrational frequency spectrum of random crystal lattices*. Ann. Phys., **15**, 411.
- (<sup>5</sup>) CHAN, T., H. A. SPETZLER, and M. D. MEYR, 1976. *Equation-of-state parameters for liquid metals and energetics of the Earth's core*. Tectonophys., **35**, p. 271.
- (<sup>6</sup>) DOMB, C., et al., 1959. *Vibrational spectra of disordered lattices*. Phys. Rev., **115**, p. 18.
- (<sup>7</sup>) FAZIO, D., F. MULARGIA, and E. BOSCHI, 1977. *Melting of iron temperature distribution in the Earth's outer core*. Nuovo Cimento B. **40**, p. 206.
- (<sup>8</sup>) FABER, T. E., 1972. *Introduction to theory of liquid metals*. Cambridge University Press.
- (<sup>9</sup>) HENRY, J. F., 1962. *Equation of state and conduction bands of iron at high pressures*. J. Geophys. Res., **67**, p. 4845.
- (<sup>10</sup>) KELLER, J., and R. JONES, 1973. *The density of states of liquid transition metals*. J. Phys. F, **45**, p. 753.

- (11) KIRKWOOD, J. G., 1935. *Statistical mechanics of fluid mixtures*. J. Chem. Phys., **3**, p. 300.
- (12) KNOPOFF, L., and J. N. SHAPIRO, 1970. *Pseudo-Gruneisen parameter in liquids*. Phys. Rev., B **1**, p. 3893.
- (13) LEIBFRIED, G., and LUDWIG, W., 1961. *Theory of anharmonic effects in crystals*. Solid State Phys., **12**, p. 275.
- (14) LEIGHTON, R. B., 1948. *The vibrational spectrum and specific heat of a face-centered-cubic crystal*. Rev. Mod. Phys., **20**, p. 165.
- (15) LENNARD-JONES, J. E., and A. F. DEVONSHIRE, 1937. *Critical phenomena in gases*. Proc. Roy. Soc., **163**, p. 58.
- (16) LUDWIG, W., 1958. *The effects of the anharmonicity on the properties of crystals*. J. Phys. Chem. Solids, **4**, p. 283.
- (17) MADEIN, R., et al., 1958. *Liquid metals and solification*, *Proceedings of the American Society for Metals*. New York.
- (18) MONTROLL, E. W., 1943. *Frequency spectrum of crystalline solids general theory and applications to simple cubic lattices*. J. Chem. Phys. **11**, p. 481.
- (19) STISHOV, S. M., 1969. *Melting at high pressures*. Sov. Phys. Usp. **11**, p. 816.
- (20) THIRRING, H., 1913. *Zur theorie der raumgitterschwingungen und der spezifischen wärme fester körper*. Phys. Z., **14**, p. 867.
- (21) VARSHNI, Y. P., and F. J. BLOORE, 1965. *Rydberg function as an interatomic potential for metals*. Phys. Rev., **129**, p. 115.
- (22) WALLACE, D. C., 1965. *Thermal expansion and other anharmonic properties of crystals*. Phys. Rev., **139**, p. 877.
- (23) WOOD, J. H., 1962. *Energy bands in iron via augmented plane waves method*. Phys. Rev., **126**, p. 517.