

INTERPRETATION OF ADIABATIC DECOMPRESSION MEASUREMENTS  
OF THE GRÜNEISEN PARAMETER

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**Abstract.** The most direct measurement of the thermodynamic Grüneisen parameter  $\gamma$  of a material is by observation of temperature changes accompanying sudden (adiabatic) compressions or decompressions. Measurements over a wide pressure range permit the dependence of  $\gamma$  upon density  $\rho$  to be inferred, but if measurements are made below the Debye temperature of the material, interpretation of the results may be confused by the temperature dependence of  $\gamma$ . If the temperature dependence is measured for the same samples, the density dependence may be adjusted to refer to a specimen held at a constant fraction of its Debye temperature  $\theta$ , instead of constant temperature, by the equation  $[-(\partial \ln \gamma / \partial \ln \rho)_{T/\theta}] = [-(\partial \ln \gamma / \partial \ln \rho)_T] \times [1 + \alpha T (d \ln \theta / d \ln \rho)] - (\partial \ln \gamma / \partial \ln T)_P (d \ln \theta / d \ln \rho)$  where  $(\partial \ln \gamma / \partial \ln \rho)_{T/\theta}$  is the more fundamental quantity and for crystals with high Debye temperatures, will commonly be smaller in magnitude than  $(\partial \ln \gamma / \partial \ln \rho)_T$  (both being negative) because  $(\partial \ln \gamma / \partial \ln T)_P$  is positive at  $T < \theta$ . Ideally, for geophysical purposes, we are interested in  $(\partial \ln \gamma / \partial \ln \rho)_{T > \theta}$  which is probably not very dependent on  $T$  and for which  $(\partial \ln \gamma / \partial \ln \rho)_{T/\theta}$  at  $T < \theta$  appears to be a good approximation, but  $(\partial \ln \gamma / \partial \ln \rho)_T$  for  $T < \theta$  is not. However, the difference appears to be small for Cu, NaCl, CaF<sub>2</sub> and  $\alpha$ -SiO<sub>2</sub>.

Introduction

The thermodynamic definition of the Grüneisen parameter of a material is

$$\gamma = \frac{\alpha K_T}{\rho C_V} = \frac{\alpha K_S}{\rho C_P} \quad (1)$$

where  $\alpha$  is volume expansion coefficient,  $K_T$ ,  $K_S$  are the isothermal and adiabatic incompressibilities,  $\rho$  is density, and  $C_V$ ,  $C_P$  are the specific heats at constant volume or pressure. This definition implies directly an identity

$$\gamma = \left[ \frac{\partial \ln T}{\partial \ln \rho} \right]_S \quad (2)$$

for changes of temperature  $T$  due to adiabatic density changes. Equation (2) is the basis of the most direct measurements of  $\gamma$ . Boehler et al. [1977, 1979] and Ramakrishnan et al. [1978] reported data from sudden adiabatic decompression of a number of metals and minerals, extending their measurements to a sufficient range of pressures to deduce the pressure dependence of  $\gamma$ . They represented this by a simple power law dependence on density

$$\gamma = \gamma_0 (\rho_0 / \rho)^q \quad (3)$$

where subscript zero indicates a zero pressure value and  $q$  is a positive index, representing a decrease in  $\gamma$  with increasing  $\rho$ . There is no reason to suppose that such a power law has any fundamental significance or can be extended to compressions corresponding to the earth's deep interior, but it is satisfactory as a representation over the laboratory pressure range. Validity of (3) is not necessary for representation of the density dependence of  $\gamma$  in terms of  $q$  if we define  $q$  as

$$q = -(\partial \ln \gamma / \partial \ln \rho)_T \quad (4)$$

at  $P \rightarrow 0$ , as in the data referred to here.

It is the purpose of this note to point out that if the temperature  $T$  at which measurements are made is laboratory temperature, which may be well below the Debye temperature  $\theta$  of the materials investigated, then  $q$  as defined by (4) is not the fundamental quantity that is of geophysical interest. Rather we wish to know the value of

$$q^* = -(\partial \ln \gamma / \partial \ln \rho)_{T/\theta} \quad (5)$$

that is, the variation of  $\gamma$  with  $\rho$  at a fixed point on the characteristic specific heat curve. Since  $\theta$  increases with compression, constant  $T/\theta$  means increasing  $T$ , and the normal behavior is an increase in  $\gamma$  with  $T$  (for  $T < \theta$ ) so that  $q^*$  is less than  $q$ . The logic of the preference for  $q^*$  is that for geophysical purposes we are really interested in properties at high temperatures, well above  $\theta$ , at which  $\gamma$  becomes more nearly independent of  $T$ . The parameter  $q^*$  is a much better representation of  $(\partial \ln \gamma / \partial \ln \rho)_{T > \theta}$  than is  $q$ .

Although at high temperatures, mode interactions make the definition of  $\gamma$  as a weighted sum of mode gammas erroneous, it is convenient to refer to this model. In the deep interior of the earth we are interested in temperatures that are sufficiently high for all lattice modes to be excited, and in this state the weighting of mode gammas is independent of  $T$  or  $P$ . Although, in general, individual mode gammas have somewhat different density dependences, more serious is the fact that the values of mode gammas are very different, some being negative in many materials. Thus at low temperatures, at which some modes are not excited, the weighting of mode gammas that contribute to the total  $\gamma$  may be quite different. This explains the strong temperature dependences of  $\gamma$  for many materials. The variations of the mode frequencies with pressure also change the weighting of mode gammas when a material is compressed at constant temperature, so that the pressure (or density) dependence of  $\gamma$  is not simply a weighted sum of

TABLE 1. Parameters of Four Materials

| Crystal                    | $\theta(K)$ | $d \ln \theta / d \ln \rho$ | $(\partial \ln \gamma / \partial \ln T)_P$ | Maximum                                    | $q$  | $q^*$ |
|----------------------------|-------------|-----------------------------|--|--|------|-------|
|                            |             |                             | at $T = 290K$                              | $(\partial \ln \gamma / \partial \ln T)_P$ |      |       |
| Cu                         | 345         | 1.9                         | 0.02                                       | 0.3  | 1.33 | 1.32  |
| NaCl                       | 290         | 2.3                         | 0.02                                       | 1.1  | 1.29 | 1.35  |
| CaF <sub>2</sub>           | 508         | 2.8                         | 0.15                                       | 1.1  | 4.6  | 4.4   |
| $\alpha$ -SiO <sub>2</sub> | 615         | 2.1                         | 0.06                                       | 2.3  | 1.7  | 1.6   |

the pressure dependences of the mode gammas but reflects also the change in weighting. We wish to separate these effects and the observed temperature dependence of  $\gamma$  gives us the only observational basis for doing so. If one cannot work conveniently at high temperatures the simplest approximate way of compressing a material so that the same lattice modes are excited at all pressures is to maintain the temperature at a fixed fraction of the Debye temperature  $\theta_D$ . To the extent that this approximation is valid, the mode weighting problem is removed by considering  $q^*$  rather than  $q$ .

It must be admitted that the mode approach to  $\gamma$  is unsatisfactory except below about  $0.02 \theta_D$  because of nonlinear mode interactions that disallow the identification of discrete modes in the atomic motions of a lattice. Nevertheless, we expect the nature of lattice motion to remain sensibly similar in a material that is compressed at fixed  $T/\theta_D$ . Indeed the blurring of lattice modes improves the validity of this assumption.

#### Relationship Between $q$ and $q^*$

Writing  $\gamma$  as a function of  $\rho$  and  $T/\theta$ , so that

$$d\gamma = \left(\frac{\partial \gamma}{\partial \rho}\right)_{T/\theta} d\rho + \left(\frac{\partial \gamma}{\partial (T/\theta)}\right)_{\rho} d(T/\theta) \quad (6)$$

we obtain the differential identity

$$\left(\frac{\partial \gamma}{\partial \rho}\right)_{T/\theta} = \left(\frac{\partial \gamma}{\partial \rho}\right)_T - \left(\frac{\partial \gamma}{\partial (T/\theta)}\right)_{\rho} \left(\frac{\partial (T/\theta)}{\partial \rho}\right)_T \quad (7)$$

Now  $\theta$  is taken to be independent of  $T$  at fixed  $\rho$ , so that (7) simplifies to

$$\left(\frac{\partial \gamma}{\partial \rho}\right)_{T/\theta} = \left(\frac{\partial \gamma}{\partial \rho}\right)_T + \frac{T}{\theta} \cdot \left(\frac{\partial \gamma}{\partial T}\right)_{\rho} \cdot \frac{d\theta}{d\rho} \quad (8)$$

where  $(\partial \gamma / \partial T)_{\rho}$  is not directly observable but is related to  $(\partial \gamma / \partial T)_P$  by another identity

$$\begin{aligned} \left(\frac{\partial \gamma}{\partial T}\right)_{\rho} &= \left(\frac{\partial \gamma}{\partial T}\right)_P + \left(\frac{\partial \gamma}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_{\rho} \\ &= \left(\frac{\partial \gamma}{\partial T}\right)_P + \left(\frac{\partial \gamma}{\partial \rho}\right)_T \cdot \left(\frac{\partial \rho}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_{\rho} \\ &= \left(\frac{\partial \gamma}{\partial T}\right)_P + \alpha \rho \left(\frac{\partial \gamma}{\partial \rho}\right)_T. \end{aligned} \quad (9)$$

Making this substitution in (8), multiplying by appropriate factors to convert the equation to a relationship between logarithmic derivatives, and noting the definitions of  $q$  and  $q^*$ , we obtain the result

$$q^* = q \left[ 1 + \alpha T \cdot \frac{d \ln \theta}{d \ln \rho} \right] - \left( \frac{\partial \ln \gamma}{\partial \ln T} \right)_P \frac{d \ln \theta}{d \ln \rho} \quad (10)$$

where  $d \ln \theta / d \ln \rho$  is identified as the "Debye gamma", not identical to the thermodynamic  $\gamma$  but readily calculated from the pressure dependences of elastic constants and having a value of about 2 for most materials of interest. The square bracketed factor is relatively unimportant because  $\alpha T$  is no more than 7%, even at the melting point of a solid. We expect the difference between  $q$  and  $q^*$  to be due primarily to the last term, that is, to the temperature dependence of  $\gamma$ .

#### Examination of Laboratory Data

Values of  $q$  for several metals were reported to Ramakrishnan et al. [1978], for NaCl by Boehler et al. [1977], and for quartz, quartzite, and fluorite by Boehler et al. [1979]. Some surprisingly high values, especially 4.6 for fluorite, prompted the present analysis. Data for calculating  $(\partial \gamma / \partial T)_P$  and  $(d \ln \theta / d \ln \rho)$  have a disturbingly large scatter, so that there remains considerable uncertainty in the calculation of  $q^*$  for crystals for which  $q$  data have been obtained. Values for Cu, NaCl, CaF<sub>2</sub>, and  $\alpha$ -SiO<sub>2</sub>, estimated from tabulations of the component parameters in (1) by Touloukian et al. [1970] and from high pressure ultrasonic data, are given in Table 1, with the resulting values of  $q^*$ .

When  $\gamma(T)$  is plotted on a log  $T$  scale, the curves for many materials show a steep rise in the temperature range  $0.1\theta$  to  $0.2\theta$ , flattening to more nearly constant values  $\gamma_{\infty}$  at high temperatures and  $\gamma_0$  at low temperatures (Figure 1). For NaCl there may be a shallow minimum at about  $0.05\theta$ . The data for  $\alpha$  quartz show a very pronounced minimum at a higher than normal temperature but are especially unreliable at low temperatures. For all four materials,  $(\partial \ln \gamma / \partial \ln T)_P$  happens to be reasonably small at laboratory temperatures, so that the differences ( $q - q^*$ ) are small. However, the values of the gradient are not very secure, depending upon the calculation of small differences between much larger quantities with

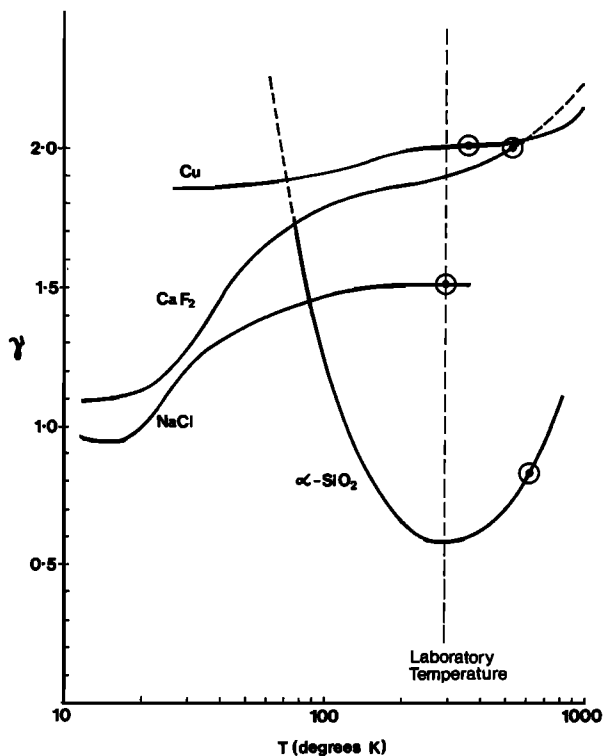


Fig. 1. Dependences of  $\gamma$  upon temperature for four materials. Circled points on curves indicate Debye temperatures.

appreciable uncertainties, especially in the cases of  $\text{CaF}_2$  and  $\alpha\text{-SiO}_2$ . It would be useful to obtain  $(\partial \ln \gamma / \partial \ln T)_p$  directly by decompression measurements at different temperatures. The maximum values of  $(q - q^*)$  that would be found at lower temperatures are 2.4 for  $\text{NaCl}$  and 2.9 for  $\text{CaF}_2$  or 4.6 for quartz at higher temperatures but only 0.55 for  $\text{Cu}$ . Evidently, the small  $(q - q^*)$  differences found for the four materials considered here are fortuitous consequences of the fact that laboratory temperature appears at points of slight gradients on the  $\gamma(T)$  curves.

#### Conclusion

The argument presented here is based on the supposition that if it were possible to make direct measurements of  $q^*$  (equation (5)), it

would be found to be almost independent of the value of  $T/\theta$ , whereas  $q$  (equation (4)) is temperature-dependent. It is important to the interpretation of adiabatic decompression measurements that this be verified. Only then can we estimate reliably from measurements at laboratory temperature the density dependence of  $\gamma$  at high temperatures ( $T > \theta$ ).

The parameter  $q^*$  is readily estimated from  $q$  if  $\gamma$  is a known function of temperature, and the estimates in Table 1 are based on available data. Although the  $\gamma(T)$  data are indirect and the gradient very uncertain, it appears to be small for the four materials considered, so that in these cases,  $q$  is a good approximation to  $q^*$ . The difference is greatest for  $\text{CaF}_2$ , for which the reported value of  $q$  is remarkably high but is not dramatically reduced by these considerations. The difference  $(q - q^*)$  would be greater if measurements were made at different temperatures. For close-packed materials (of which metallic copper is representative) we expect the difference to be small in any case, but for open crystals such as quartz,  $(q - q^*)$  may be sufficiently large that it is not obvious just what is being measured. The most certain way of making geophysically relevant observations would be to measure the density dependence of  $\gamma$  at high temperatures, but, failing this, correction to constant  $T/\theta$  gives the best available parameter, i.e.,  $q^*$ .

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