

# Volume variation of Gruneisen parameters of *fcc* transition metals

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**Abstract.** The volume variation of the Gruneisen parameters of ten *fcc* transition metals, up to 40% compression, has been studied on the basis of a model approach proposed by Antonov *et al.* The results are reasonably good for six metals except for Rh, Ag, Au and Ni when compared with available experimental and other theoretical values. The model requires an appropriate modification for Rh, Ag, Au and Ni.

**Keywords.** *fcc* transition metals; pseudopotential; Gruneisen parameter; volume variation of Gruneisen parameter.

## 1. Introduction

The nuclear Gruneisen parameter  $g$  is an important thermodynamic quantity. The study of the pressure (volume) dependence of  $g$  is an interesting problem from theoretical as well as experimental point of view, particularly, due to the lack of a proper theory and enough experimental data (Fang 1996).

In the reduction of shock-wave data to isothermal data, the knowledge of pressure dependence of the Gruneisen parameter is very useful. The volume variation of  $g$  is central in theoretical equation of state, geophysical models, ultrasonic measurements and melting of solids (Mulargia and Boschi 1978, 1979; Boehler *et al* 1979; Godwal *et al* 1979, 1983; Walzer *et al* 1979; Soma *et al* 1983; Bratkovskii 1984; Moriarty *et al* 1984; Nagara and Nakamura 1984; Schlosser *et al* 1989; Erikson *et al* 1992).

For ordinary metals where anharmonicity is small, the entropy can be analysed at atmospheric pressure. To do this it is necessary to correct  $q_D$  (Debye temperature at 0 K) for the effects of thermal expansion by using the Gruneisen parameter defined by  $g_0 = d \ln q_D / d \ln r$ . Here  $r$  is the density (Erikson *et al* 1992; Wallace 1992).

The experimental values of Gruneisen parameters are mostly available at normal pressure (Gschneidner 1964). The volume variation of  $g$  can be obtained from experimental measurements of change of temperature with small adiabatic pressure changes (Ramakrishnan *et al* 1978). In such an experiment a substance is generally compressed by about 10% and for higher compressions,  $g$  values are extrapolated by using the relation

$$g = g_0(\Omega/\Omega_0)^q, \quad (1)$$

where  $q$  is a parameter.  $\Omega_0$  and  $\Omega$  are volumes at zero

pressure and the pressure under consideration, respectively. Gruneisen parameter can also be determined by an electric discharge under pressure (Parshukov and Batsanov 1984). But this method cannot be used to determine  $g$  at zero pressure. The values of  $g$  determined from thermodynamic constants, shock-wave, ultrasonic and some other experiments are usually not accurate (Parshukov 1985).

Several expressions have been proposed, in the literature to calculate this parameter (Grover *et al* 1969; Godwal *et al* 1983; Kumari and Das 1986).

It has been noted that, to a good approximation, the ratio ( $g/\Omega$ ) of Gruneisen parameter to volume is a constant for some solids (Boehler 1983). Fang and Rong (1994) have calculated the melting temperatures under high pressures for seven metals Al, Ag, Au, Cu, Na, K and Rb, with the assumption that  $g/\Omega$  is constant, using Lindemann's law and Debye model. This empirical approximation,  $g/\Omega = \text{constant}$ , has been used frequently in the work on shock compression of metals. However, experiments show that for several metals  $g/\Omega = \text{constant}$  is not a good approximation (Parshukov 1985). Moreover, none of the widely used expressions of the type

$$g(\Omega) = [a/2 - 2/3] - \Omega/2[(d^2(P\Omega^a)/d^2\Omega)/(d(P\Omega^a)/d\Omega)], \quad (2)$$

with  $a = 0, 2/3$  or  $4/3$  could describe the experimental results satisfactorily. Quite often, the volume dependence of  $g$  is given by the relation  $q = d \ln g / d \ln \Omega$ . The value of  $q$  is generally not equal to unity. Recently, Nie (2000) has suggested the following form for the volume dependence of  $g$ :

$$g = g_0[q_0/n(h^n - 1)], \quad (3)$$

where  $g_0$  is the zero pressure Gruneisen parameter,  $q_0$  is a pressure independent but temperature dependent parameter and  $h = \Omega(P, T)/\Omega(O, T_R)$ .  $T_R$  is the room temperature.

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Attempts have also been made to compute  $g$  and its volume dependence using model approaches. Moriarty *et al* (1984) and Soma *et al* (1983) have computed the volume variation of  $g$  for Al and alkali metals, respectively using the pseudopotential approach (Godwal *et al* 1979, 1983). Nagara and Nakamura (1984) have used the Thomas–Fermi–Dirac statistical model to compute  $g$  of Al and Fe as function of volume. Bratkovskii *et al* (1984) have also carried out similar studies for several metals. It should be noted that a pseudopotential which describes satisfactorily the pressure dependence of several physical properties of given metals would be most appropriate to compute  $g(\Omega)$  relations. Such a model has been recently proposed by Antonov *et al* (1990a,b). This model was found to be quite useful to compute cold equation of state up to several  $M$  bar pressure, the pressure derivatives of elastic constants and other lattice properties of ten transition metals. The model also predicts Debye–Waller factor and mean square displacement of *fcc* transition metals reasonably well (Vyas *et al* 2001a).

Looking at the uncertainties in the measured and estimated dependence of  $g$  on volume and also noting that the above mentioned model is well suited for the study of the pressure dependence of physical properties, we, in the present paper, compute the volume variation of Gruneisen parameters of ten transition metals by using this model.

## 2. Theory

In the model proposed by Antonov *et al* (1990a,b), the contribution to energy due to *s*-like electrons is calculated by second order perturbation theory for the local model pseudopotential while that due to *d*-like electrons is taken into account by introduction of repulsive short range interatomic potential. The details of different contributions to the energy of a transition metal, in this model, may be found in the original papers of Antonov *et al* (1990a,b).

The Gruneisen parameters, in the present work, were determined as follows.

It is convenient to write

$$g = -1/2 \, d \ln \bar{n}^2 / d \ln \Omega, \quad (4)$$

where  $\bar{n}^2$  is the second moment of phonon frequency spectrum. Since  $\bar{n}^2$  is related to the coordinate derivatives of interatomic potential,  $\Phi(R)$ , we find for the pairwise central interaction (Liebfried and Ludwig 1969),

$$g = \frac{-1/6 \left[ \sum_l C_l [-(2/R)\Phi'(R) + 2\Phi''(R) + R\Phi'''(R)] R = R_l \right]}{\left[ \sum_l C_l [(2/R)\Phi'(R) + \Phi''(R)] R = R_l \right]}, \quad (5)$$

where  $C_l$  is the coordination number for the  $l$ th coordination sphere of radius  $R_l$  and  $\Phi'$ ,  $\Phi''$  and  $\Phi'''$  are derivatives of the interatomic potential. (4) contains the third derivative of the potential function, and hence it provides a severe test of the given potential function. The effective pair potential  $\Phi(R)$  can be computed from the following expression

$$\Phi(R) = 2Z^2/R \left[ 1 - 2/p \int_0^\infty F_N(q) \sin qR/q \, dq \right] + Ae^{-aR}, \quad (6)$$

where  $F_N(q)$  (the normalized energy wave number characteristic) can be calculated from the model pseudopotential and the dielectric function for electron gas. For  $F_N(q)$ , we have taken the model proposed by Antonov *et al* (1990a).  $A$  and  $a$  are the Born–Mayer parameters. These are given in Antonov *et al* (1990a). For each metal,  $\Phi(R)$  was computed at different volumes and using (4)  $g$  were computed for different volumes. The summation in (4) was carried out up to the 65th coordinate sphere in order to obtain proper convergence.

## 3. Results and discussion

First, we compare the presently computed values of  $g$  at normal volume with the corresponding experimental ones in table 1. It can be seen from this table that the experimental values are fairly scattered. Rice *et al* (1958) carried out a partial analysis of data on  $g$  and found a 15% average discrepancy between the values of  $g$  measured by various methods for 23 metals. Experimentally only the total Gruneisen parameter can be measured. The total Gruneisen parameter is the sum of lattice, electronic and probably magnetic contribution. The latter term is present in palladium (White and Pawlok 1970) and nickel (White 1973). Thus the procedure of the extraction of the lattice contribution is always connected with the errors arising for example from taking electronic  $g$  from the free electron model. Such error in the experimental data is of the order of 0.1.

The model based computed values of  $g$  contain uncertainty arising from the following sources: (i) The errors in the experimental values of the physical quantities which are used to determine the model parameters, (ii) the error associated with the use of particular form of exchange and correlation effects, in the dielectric function of electron gas, which enters in the calculation of energy wave number characteristic,  $F_N(q)$  and (iii) the errors associated with the method of computation of  $g$ .

Several studies in the past based on model pseudopotential suggest that all such factors will introduce an uncertainty of about 10 to 15% in the physical properties calculated from the given model.

The present value for Cu is in good agreement with the experimental values. Also, the presently obtained value agrees well with those computed by Barrera and Batana (1993b) and Pal and Sengupta (1979). For Ag and Au the present values fall far from the range of values reported in the literature. However, our value for Au matches with that reported by Harrison and Wills (1983), who used a more sophisticated model. The present value of Ni is also high. However,  $g$  values of Pd, Pt, Co, Ir and Rh are quite reasonable compared to experimental and other theoretical values (Barrera and Batana 1993a; Katsnelson *et al* 1997).

The volume variation of  $g$  for ten transition metals is displayed in figure 1. There are very few experimental measurements. Ramakrishnan *et al* (1978) measured changes of sample temperature associated with

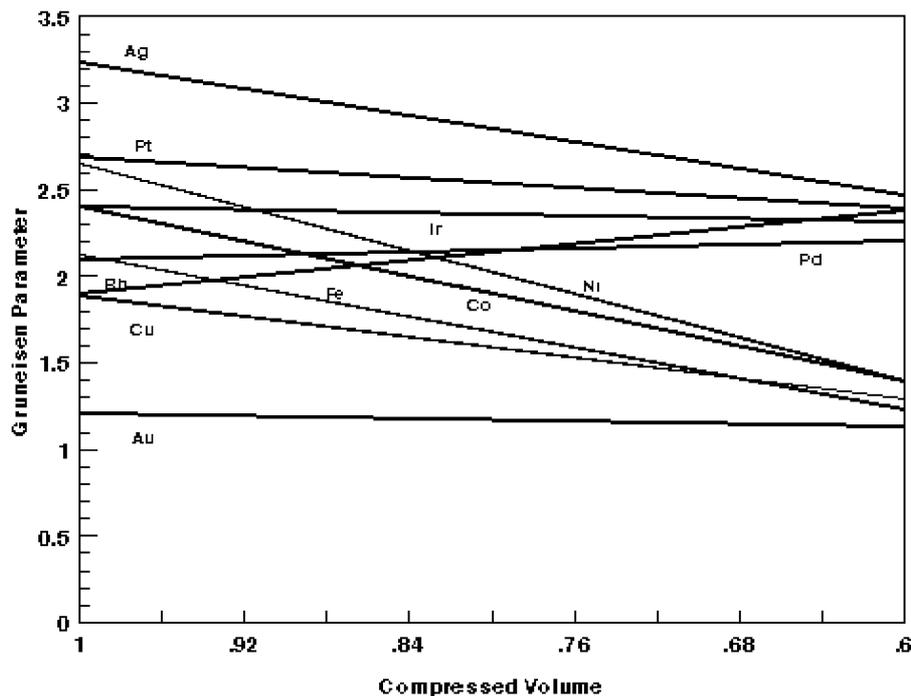
small adiabatic pressure changes of Cu and Fe along with three other metals. From the values of  $\Delta T/\Delta P$ , the volume dependence of  $g$  was found. They also found that relation (1) for the volume dependence of  $g$  holds good.

For Cu, the  $q$  value reported by them is 1.33 and for Fe,  $q$  was found to be 0.6. In the present study we find  $q(\text{Cu}) = 1.085$  and  $q(\text{Fe}) = 0.783$ . It may be noted that Ramakrishnan *et al* (1978) compressed the sample only by 10% and the results were extrapolated up to 40% compression.

A number of authors, in their high pressure studies, have used the approximation  $g/\Omega = \text{constant}$  (Altshuler *et al* 1987; Ob *et al* 1991). Our calculations show that the relation  $(g/\Omega) = \text{constant}$  holds good for fcc transition metals.

**Table 1.** Comparison of  $g$  at normal volume with corresponding experimental and theoretical values.

Metal	Present	Experimental (Gschneidner 1964)	Other	Theoretical results
Cu	1.93	1.97, 1.96, 2.00 $\pm 0.08$ , 2.93, 2.00 $\pm 0.06$	1.84 1.73 1.19 1.90 2.15 2.16	(Barrera and Batana 1993b) (Daniels and Smith 1958) (Harrison and Wills 1983) (Pal and Sengupta 1979) (Pal and Sengupta 1979) (Pal and Sengupta 1979)
Ag	3.28	2.46, 2.44, 2.36 $\pm 0.12$ , 0.32, 2.29	2.22 2.14 1.26	(Barrera and Batana 1993b) (Daniels and Smith 1958) (Harrison and Wills 1983)
Au	1.19	3.09, 3.06, 3.04 $\pm 0.04$ , 1.84, 2.22	2.77 2.47 1.31 3.03 2.71 2.713	(Barrera and Batana 1993b) (Daniels and Smith 1958) (Harrison and Wills 1983) (Pal and Sengupta 1979) (Pal and Sengupta 1979) (Pal and Sengupta 1979)
Ni	2.77	2.0, 1.83, 1.88 $\pm 0.08$ , 1.28, 2.0 $\pm 0.19$	1.32 1.62 1.6	(Barrera and Batana 1993a) (Barrera and Batana 1993a) (Barrera and Batana 1993a)
Pd	2.18	2.47, 2.18, 2.28 $\pm 0.1$ , 7.35, 2.84	2.18 2.03 2.25	(Barrera and Batana 1993a) (Barrera and Batana 1993a) (Barrera and Batana 1993a)
Pt	2.64	2.92, 2.69, 2.56 $\pm 0.12$ , 0.05, 1.81	2.33 2.50	(Barrera and Batana 1993a) (Barrera and Batana 1993a)
Co	2.47	2.07, 1.95, 1.93 $\pm 0.06$ , 1.14, 2.01		
Fe	2.18	1.81, 1.76, 1.66 $\pm 0.06$ , 1.69, 1.60		
Ir	2.32	2.49, 2.39, 4.58	1.73 1.99	(Katsnelson <i>et al</i> 1997) (Katsnelson <i>et al</i> 1997)
Rh	1.94	2.43, 2.29, 2.23 $\pm 0.03$ , 0.71, 2.29	1.54 2.05	(Katsnelson <i>et al</i> 1997) (Katsnelson <i>et al</i> 1997)



**Figure 1.** Volume variation of  $g$  for Cu, Ag, Au, Ni, Pd, Pt, Co, Fe, Rh and Ir.

However, the results of volume variation of  $g$  for Ni, Ag, Au and Rh are not satisfactory. This point is worth discussing.

There are two important assumptions in the model proposed by Antonov *et al* (1990a,b): (i) The model assumes a separation between  $s$ -electrons and  $d$ -electrons. Then the pseudopotential for  $s$ -electrons is taken as Heine–Abarenkov (1964) type model potential which has been used extensively for simple  $s$ – $p$  bonded metals and (ii) it is also assumed in this model that the effects of higher order perturbation terms and some components of  $d$ -electron effects cancel each other. The remaining  $d$ -electron components are the two centred radial  $d$ – $d$  interactions which are simulated by a short range Born–Mayer type potential energy function.

It seems from the presently obtained results for Ni, Ag, Au and Rh that these assumptions are not true for these metals. In fact, it has been known that for Ni (Upadhyaya and Prakash 1986) and also for Ag and Au, the three body forces do play an important role in determining phonon frequencies (Vyas *et al* 2001b). This fact also shows that some of the components of  $d$ -electron effects which were assumed to be cancelled by many body force terms, have to be included in the form factor. In other words, a simple model potential of Heine–Abarenkov (1964) type, as used by Antonov *et al* is not adequate atleast for Ag, Au, Ni, and Rh. In fact, recently Katsnelson *et al* (1997) have carried out an extensive study of phonon spectra and specific heat of Rh with Heine–Abarenkov type model potential. These authors found that the form factor obtained from Heine–Abarenkov model requires modification in certain region of  $q$ -space. Thus, a model with a more

appropriate form factor and with some scheme to account for many body forces for transition metals is required.

#### 4. Conclusions

We have calculated the volume variation of Gruneisen parameter of ten  $fcc$  transition metals. We used a model approach proposed by Antonov *et al* (1990a), which was found to be quite successful previously for other pressure dependent properties. Except for Rh, Ag, Au and Ni, the results obtained in the present study are reasonably good. For Rh, the observation of Katsnelson *et al* (1997) that the form factor is required to be modified is confirmed from the present study. Thus the present study brings out the fact that the lattice mechanical model proposed by Antonov *et al* (1990a) is not quite good for the computation of volume variation of Gruneisen parameter of atleast four of these ten transition metals. The Gruneisen parameter is a higher order quantity involving third order derivative of interatomic potential. Hence, this quantity provides a stringent test of any model for lattice mechanical properties. The present study is such a test of the model due to Antonov *et al* (1990a,b). The present study suggests that an appropriate modification of form factor for Rh, Ag, Au and Ni is necessary.

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