Review on Gruneisen Theory of Thermal Expansion Coefficient.

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Abstract: *It is known that property of Thermal expansion is directly related to the anharmonicity of atomic vibrations. If the vibrations are harmonic, the crystal would not expand at all. Any theory of thermal expansion of solids must take into account of anharmonic nature of the lattice. Gruneisen considered the vibrations as harmonic but brings anharmonicity into the picture by making the frequencies of vibrations are volume dependent. The data on Gruneisen parameter is too large and too scattered in the literature. We made an account to review some of the important aspects Gunnison constant.*

I.   Introduction

The Gruneisen Parameter γ The Grüneisen parameter, γ, named after Edward Gruneisen, describes the effect that changing the volume of a Crystal has on its vibration properties, and, as a consequence, the effect that changing temperature has on the size or dynamics of the lattice Theory of thermal expansion of solids was proposed by Gruneisen in terms of the interatomic forces and atomic vibrations in the solid. Al though several developments have been taken place since then in our understanding of crystal physics, Gruneisen's theory continues to dominate in the field of thermal expansion. In this article, certain aspects of Gruneisen's theory are considered. Before taking up a discussion of these aspects a brief resume of Gruneisen's theory is presented.

Resume of Gruneisen Theory Gruneisen (1912) proposed a theory of thermal expansion of solids almost simultaneously with Debye's (1912) theory of specific heat of solids. Although much sophistication have taken place in lattice dynamics, Guneisen theory still provides the basic frame work as far as thermal expansion is concerned. A detailed account of Gruneisen theory is provided by Gruneisen (1926), Parrington (1952) and Anderson (1967). Brief accounts are given by Krishnan (1958), Yates (1972) and Krishnan et al. ,(1974). A brief resume of Gruneisen theory is presented here.

It is known that property of Thermal expansion is directly related to the anharmonicity of atomic vibrations. If the vibrations are harmonic, the crystal would not expand at all. Any theory of thermal expansion of solids must take into account of anharmonic nature of the lattice. Gruneisen considered the vibrations as harmonic but brings anharmonicity into the picture by making the frequencies of vibrations are volume dependent. Thus his treatment may be considered as a quasi – harmonic approximation.
The lattice energy of the crystal is presented by

$$U = -\left(\frac{a}{r^m}\right) + \left(\frac{b}{r^n}\right) \qquad (1)$$

Where **r** is the interatomic distance, **a** and **b**, **m** and **n** are the constants of a crystal.
The free energy **F** is given by

$$F(V,T) = U(V,T) + \frac{1}{2}\sum^{3N} h\nu_I + Kt\sum^{3N}\log\left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right] \qquad (2)$$

Where U(V,T) associated with lattice second term on right hand side is zero poin and last term represents for thermal energy.
Using thermodynamic relations
$$P = (\partial F/\partial V)_T \text{ and} \qquad (3)$$
$$\frac{\beta}{\psi} = (\partial^2 F /\partial v^2) \qquad (4)$$

The following equations are obtained.

$$P = \left(\frac{\partial U}{\partial T}\right)_T - \frac{1}{V}\sum^{3N}\left[\frac{1}{2}h\nu_i + \frac{h\nu_i}{\left(\frac{\exp h\nu_i}{kT-1}\right)}\right] \cdot \frac{d\log \nu_i}{d\log v} \qquad (5)$$

$$C_{v=K} \sum \frac{3N(hvi/kT)^2 exp\,(hvi/kT)}{(\frac{exp\,hvi}{kT-1})^2} \qquad (6)$$

Here β is volume coefficient of expansion and compressibility.

The dimension less quantity $\frac{dlog\,vi}{dlogv}$ represents the volume dependence of frequencies.

When referred to particular frequency it is called as mode Gruneisen constant and it is denoted by (γ_i). However, Gruneisen assumed this parameter to be same for all frequencies. The average value is called the Gruneisen constant and denoted by (v).

Equation (5) may be written as

$$PV + G\,(V) = \gamma\,E \qquad (7)$$

Where
$$G(V) = V\,(\frac{\partial U}{\partial V})_T \qquad (8)$$

and
$$E = \int_0^T Cv\,dT \qquad (9)$$

equation (7) is known as Mie Gruuneisen equation of state.

At P = 0 equation (7) becomes

$$G(V) = \gamma E \qquad (10)$$

Representing the increase in volume (V-$V_{0)}$ by Δ.

Then G(V) may be expanded as Taylor series as follows:

$$G(V) = G(V_0) + G^{'}(V_0) + \frac{1}{2}\Delta^2\,G^{''}(v_0) + \text{------------} \qquad (11)$$

It can be shown that

$$G(v_0) = 0 \qquad (12)$$

$$G^{'}(V_0) = \frac{1}{\Psi} \qquad (13)$$

$$G''(V_0) = -\left[\frac{(m+n+3)}{6}\right]\frac{1}{\Psi V_0} \qquad (14)$$

Where Ψ is the compressibility. Substituting equations (11) to (14) in equation the following equation may be obtained.

$$\frac{V_T - V_0}{V_0} = \frac{E}{Q-KE} \qquad (15)$$

$$Q = \frac{V_0}{\gamma\Psi} \qquad (16)$$

and
$$K = \gamma + \frac{2}{3} \qquad (17)$$

Differentiating equation (4.15), we get

$$\alpha = \frac{1}{3v_0}\left(\frac{\partial V}{\partial T}\right)_P = \frac{QC_v}{3(Q-KE)^2} \qquad (18)$$

It can also be shown that

$$\gamma = \frac{3\alpha V}{\Psi C_v} \qquad (19)$$

The Gruneisen constant defined in equation (19) is often called as thermal gamma.

As shown above, Gruneisen's theory provides an expression for the coefficient of thermal expansion (equation 19)in terms of the specific heat (C_v) and the heat content (E).

(C_v) can be obtained from experimental values of C_p and E is$\int C_v dT$.

Alternately C_v and E may be calculated from the Debye model or any other model.

Nix and Mc Nair (1941, 1942)calculated the thermal expansion of number of metals using equation (18) and observed satisfactory agreement with experimental data. Blackman (1955) suggested that equation 18 may be used for estimating the Debye temperature of the crystal. Fischmiester (1956)rearranged equation 15 as follows :

$$\frac{a_0}{a_{T-a_0}} = \frac{Q}{3E} - \frac{K}{3} \qquad (20)$$

Plotting the experimental values of $\frac{a_0}{a_{T-a_0}}$ against the value of 1/E he obtained the linear plots for several crystals and thus verified the equation (15).

At low temperature the contribution of E becomes small and one get

$$\frac{\alpha}{C_p} = \text{constant} \qquad (21)$$

This relation is sometimes referred as the Gruneisen rule and has been used by (Claytor and Marshall 1960) to predict thermal expansion at low temperature from specific heat data. The volume dependence of atomic frequency is the real conceptual, contribution of Gruneisen. Although he assumed the common Gruneisen constant for all modes, very soon it was shown by many workers that there is there is considerable variation in the mode γ's corresponding different modes. The maximum information has come from studies on pressure and temperature variation of Raman spectra, I.R Spectra, neutron inelastic scattering and lattice dynamics.

The average Gruneisen parameter is equally important as solid stat parameter. Harris and Avarami (1972) have discussed the various aspects of Physics of the Gruneisen parameter. The data on Gruneisen parameter of crystals are too large too scattered to be cited. Apart from the thermal Gruneisen constant, several methods of calculating the Gruneisen constant have evolved. Slater (1939) showed the Gruneisen constant the pressure variation of bulk modulus.

$$s\gamma = -\frac{1}{6} + \left(\frac{1}{2}\right)\left[\frac{dB}{dP}\right] \qquad (22)$$

Where (B) is the bulk modulus and this known as Slater formula. Dugdale and McDonald (1953) modified this relation as follows:

$$\gamma = -\frac{1}{2} + \frac{1}{2}\left(\frac{dB}{dp}\right) \qquad (23)$$

Knopff and Shapro (1969) showed that the pressure variation of shear modulus is important and gave the following relation.

$$\gamma = -\frac{1}{6} + 0.024\left(\frac{dB}{dp}\right) + 0743\left(\frac{dG}{dp}\right) \qquad (24)$$

Wher G is the shea modulus. In recent years the melting of crystal ubder the high pressure has been studied. Knopoff and Shapiro (1969) showed that the Gruneisen constant may be estimated pressure variation of melting temperature from the following relation

$$\gamma = \left(\frac{1}{3}\right) - \left(\frac{1}{2}\right)\left[\frac{d\log T_m}{d\log V}\right] \qquad (25)$$

Slater also has shown that the Gruneisen constant can be evaluated from the inter atomic potential of a crystal and used this method to evaluate the Gruneisent constants of several metals from the Morse Potential and several alkali halides Born potential. Sirdeshmukh and Rao (1972, 1975) used this method to calculate the Gruneisen constant od CaF_2 type crystals and some oxides respectively.

In recent years, considerable amount of experimental data has been generated on second order elastic constant (SOEC), their pressure derivative and the third order elastic constant (TOEC). Burger (1965) and same year Mason (1965) developed the expression for the estimation of the mode gammas and average gamma the SOEC and TOEC, but their method has not received sufficient attention. A modified method of evaluation of average Gruneisen constant from Third order elastic constant (TOEC) was proposed by Ramji Rao (1974) ; this method also remained practically unexplored. It is also possible to estimate Gruneisen constant from pressure variation of Debye temperature (Kumari and Das 1986) but unfortunately data on pressure variation are not available. We are working on the following aspects of Gruneisen's theory.

i) Evaluation of Gruneisen constant using third order elastic constant employing the Mason Burger method.
ii) Evaluation of Gruneisen constant using third order elastic constant employing the
    Ramji Rao's method.

Acknowledgements

References

[1]. Anderson O L (1965)
[2]. Physical Acoustic vol IIIB, (Academic press)
[3]. Blackman M (1955)
[4]. Phys.Rev.137,1826
[5]. Burger K(1965)
[6]. Phys. Rev. 137, 1826
[7]. Claytor R c and Marshall B J (1960)
[8]. Phys. Rev. 120,3327
[9]. Debye P (1912)
[10]. Ann. Phys.(4) Bd,39,789.

[11].   Dugdale J S and McDonald (1955)
[12].   Phys. Rev. 102, 331
[13].   Fischmieser HF (1956)
[14].   Acta Crysallogr.9, 416.
[15].   Gruneisen E (1912)
[16].   Ann.d.Phys.Bd.39, 257
[17].   Gruneisen E (1926)
[18].   Handbuch der Phys.Bd. 10, 1
[19].   Haris P and Avarami (1972)
[20].   Technical Report no 4423. Picctinny Arsnel Dover NJ
[21].   Knopoff L and Shapiro J N (1969)
[22].   J. Geo. Phys. Res. Tech.21, 1583
[23].   Krishnan R S (1958)
[24].   Progrss in Crystl. Physics (Vishwanatham Madras)
[25].   Kumari M and Dass N (1986)
[26].   Phys. Stat. Sol (b) 133
[27].   Mason M P (1965)
[28].   Physical Acoustics, Vol. IIIB (Academic Press, NY).
[29].   Nix F C anD Mc Nair D (1941)
[30].   Phys. Rev. 60, 597
[31].   Nix F C anD Mc Nair D (1942)
[32].   Phys. Rev. 61, 74
[33].   Partington J R (1952)
[34].   An Advanced Treatise on Physical Chemistry (Logman S, London).
[35].   Ramji Rao (1974)
[36].   Phys. Rev. 10. 4173
[37].   Sirdeshmukh D B and Rao B K (1972)
[38].   J.Chem.phys.57
[39].   Sirdeshmukh D B and Rao B K (1975)
[40].   j.Phys.Chem. Solids, 36,395