Transactions of the Materials Research Society of Japan. Vol. 20

Temperature dependence of thermal expansion by phonon Virial pressure

Shigeo Kotake, Yasuyuki Suzuki and Masafumi Senoo

Department of Mechanical Engineering, Mie University,
1515 Kamihama Tsu city, 514, Japan

Under assumption of Virial pressure of phonon, temperature dependence of thermal expansion coefficients (TEC) in several materials were calculated in Debye model. Below Debye temperature, Virial pressure shows characteristic increase from zero. And above Debye temperature, Virial pressure saturates to constants ;2RT in unit molar. Calculated TEC of transition metals shows good agreement with experimental values. However, experimental TEC of simple metals are one half and those of semiconductor are twice as large as calculated values. Physical property of thermal expansion can be explained in the simple model.

1. INTRODUCTION

It is well-known that thermal phenomena of condensed matter, such as heat capacity, are successfully explained by Debye model and specific heats are common among various materials[1]. TEC is another important physical property under finite temperature. It shows characteristic temperature dependence like heat capacity. In former models, the characteristic temperature dependence of TEC was explained by inharmonic interatomic potentials[2],[3]. However, in these models, convergence of TEC above Debye temperature is not apparent. Since interatomic potential are consisted of many parameters, the models won't be simple.

Recently it has been noticed that TEC of various materials are inversely proportional to elastic constants at room temperature[4]. Since product of elastic constant and TEC is equal to the differentiation of thermal pressure with regard to temperature, the pressure can be constant in variety of materials.

Virial theorem has been successfully applied to ideal gas and free electron model to explain internal pressure and elastic moduli[5]. This theorem expresses the relation between pressure and (kinetic and potential) energy within the system. Since phonon is quasi-quantum particle, which represents atomic vibrations in solids, some disputations exist in treating them as momentum particle. Assuming that phonon is free particle under uniform flat potential and the quasi-momentum can be treated as real momentum, Virial theorem can be applied to phonon to deduce thermal pressure in materials.

In this paper we applied Virial theorem to phonon and electron under Debye and free electron model to discuss temperature dependence of TEC. Since Debye model is merely depended on Debye temperature, temperature dependence of TEC can be simply explained.

2. THEORY AND CALCULATION

2.1. Thermal pressure in solid

Assuming that thermal pressure is deduced from phonon and electron, it is the sum of Virial pressure of electron and phonon, as shown in eq. (1).

$$P_{thr} = P_{ele} + P_{pho} \cdots (1)$$

Since kinetic energy of electron is higher than phonon, thermal pressure is mainly caused by electron. However, since energy state of electron doesn't change with temperature elevation, besides that of phonon is keen to temperature condition, temperature dependence of thermal pressure is mainly caused by phonon pressure.

2.2. Thermal expansion coefficient of solid

Under assumption of constant volume and constant elastic moduli at various temperature, thermal strain is mostly equal to the ratio of thermal pressure to elastic constant, as shown in eq.(2). From differentiation of the equation with regard to temperature, TEC (α) is expressed in eq.(3).

$$\varepsilon_{thr} = P_{thr} / E \cdots (2)$$

$$\alpha_{thr} = \frac{\partial \varepsilon_{thr}}{\partial T} = \frac{1}{E}\left(\frac{\partial P_{ele}}{\partial T} + \frac{\partial P_{pho}}{\partial T}\right) \cdots (3)$$

Compared to the temperature dependence of TEC, volume and elastic constant is almost constant at various temperature, these assumption is fairly good. Gruneisen constant is ignored in the calculation.

2.3. Virial pressure of phonon

First, we will calculate phonon pressure in solid. Under uniform potential Virial theorem is expressed in eq.(4). Assuming free particles inside of cubic unit volume, phonon pressure; P is expressed with kinetic energy; T in eq. (5).

$$3P = 2T - \gamma U \cdots (4)$$

$$P = 2/3\ T \cdots (5)$$

Under Debye model, since wave number of phonon is quantized with 2π and total number of states is 3N (N is number of atoms), Debye wave frequency and Debye temperature are also defined in eq.(6,7).

$$\omega_D = v_s(6\pi^2 N)^{1/3} \cdots (6)$$

$$\theta_D = \hbar\omega / k_B \cdots (7)$$

To deduce Virial pressure of phonon, it is necessary to calculate total kinetic energy . At the chapter of specific heat, total energy of phonon is well described in many books on solid state physics[1]. Therefore we merely show the brief process of the calculations. Energy of each phonon is the product of density of state ($D(\omega)$) and Bose-Einstein distribution function ($\langle n(\omega)\rangle$). Since number of states is as much as Abogadro number, discrete summation to deduce total energy is replaced with integral from 0 to ED. Hence total kinetic energy of phonon is expressed in eq.(8).

$$E_{pho} = 3\int_0^{\omega D} D(\omega)\langle n(\omega)\rangle \hbar\omega\, d\omega$$

$$= \frac{3 k_B^4 T^4}{2\pi^2 v_s^3 \hbar^3}\int_0^{xD} \frac{x^3}{e^x - 1} dx \cdots (8)$$

Here, $x_D = \theta_D / T$.

Since kinetic energy of eq.(8) is the energy of N atoms, kinetic energy of unit volume is recalculated. According to Virial theorem, phonon pressure is expressed in eq.(9). Here ρ is the specific weight ad M is atomic quantity.

$$P_{pho} = \frac{2E_{pho}\rho}{3M} \cdots (9)$$

2.4. Virial pressure of electron

Secondary, we will calculate Virial pressure of electron. As same as phonon, total kinetic energy of electron is calculated from the summation of the energy of each electron. The kinetic energy of each electron is the product of density of state and the Fermi-Dirac distribution function. Total energy and Virial pressure of electron are expressed in eq.(10,11), in terms of Fermi energy ; E_f.

$$E_{ele} = 3/5\ N E_f + \frac{\pi^2}{6}(k_B T)^2 \frac{3N}{2E_f} \cdots (10)$$

$$P_{ele} = \frac{2E_{ele}\rho}{3M} \cdots (11)$$

From eq. (2,3) TEC is made of two facters; Temperature defferentiation of phonon pressure and electron pressure. Each TEC is expressed in eq. (12,13).

$$\alpha_{pho} = \frac{1}{E}\frac{\partial P_{pho}}{\partial T}$$

$$= \frac{6\rho R}{ME}\left(\frac{T}{\theta_D}\right)^3 \int_0^{xD} \frac{x^4 e^4}{(e^x - 1)^2} dx \cdots (12)$$

$$\alpha_{ele} = \frac{1}{E}\frac{\partial P_{ele}}{\partial T} = \frac{\pi^2 R^2 \rho}{3MEE_f} T \cdots (13)$$

Above Debye temperature, TEC of phonon pressure is converged to eq.(14).

$$\alpha_{pho} = \frac{2R\rho}{EM} \cdots (14)$$

3 . RESULTS AND DISCUSSION

3.1. Virial pressure of phonon at Debye temperature

According to eq.(12) we calculate Virial pressure of phonon in various pure materials. Debye temperature, which is determined from specific heat, and all the necessary material constants were obtained from AIPH[6].

Above Debye temperature, temperature coefficient of phonon pressure converged to constant, and at higher temperature, Virial pressure of electron much affects to thermal pressure. Therefore Debye temperature is appropriate condition to discuss quantitative

agreement between experimental and theoretical TEC. Table 1 shows the experimental and calculated values of TEC. Even though simple model was assumed, in conventional transition metals, most of calculated TEC were fit to experimental ones within 20% error. In lithium, experimental TEC is 2 times larger than calculated one. Meanwhile in some semiconductor, like silicon and germanium, experimental TEC is half of calculated one. Reasons of large disagreement of TEC in simple metals and semiconductors are not apparent. Even with some error thermal expansion is primarily well explained by Virial pressure of phonon.

3.2. Virial pressure of electron and thermal pressure of solid

According to eq.(13), TEC caused by electron pressure is proportional to temperature. Below Debye temperature, electron pressure is far lower than phonon pressure and thermal pressure will not be affected by electron pressure. However, above Debye temperature, Virial pressure of electron is not negligible. Linear increase of TEC above Debye temperature is the result of electron pressures.

3.3. Temperature dependence of thermal expansion coefficient

Fig.1, Fig.2, Fig.3 and Fig.4 show calculated and measured temperature dependence of TEC of diamond, aluminum, lead and lithium. Both calculated values agrees well with experimental values. Above Debye temperature, according to eq.(9), TEC of phonon shows convergence to constant; $2RM/\rho$. Below Debye temperature, TEC is gradually decreased until it converged to zero at absolute zero temperature. Since TEC in most of materials follows same tendencies, Virial pressure of phonon explains characteristic temperature dependence of TEC, which former model could not explain with ease.

Some anisotropic material, such as graphite, and some non-closed packed crystal like silicon show abnormal temperature dependence of TEC[7][8]. These abnormalities are believed to be caused from anisotropy of elasticity and extraordinal density of state of phonon. To discuss precise physical properties dispersion relation of phonon should be considered.

Table 1. Calculated and experimental TEC

	θ D (K)	α exp 10^-6 (1/K)	α cal 10^-6 (1/K)	ratio
Ag	225	18.6	16	0.84
Al	428	24.9	21	0.86
Au	165	14	11	0.80
Cu	343	17.3	16	0.92
Dia	2230	5.1	6.2	1.22
Fe	467	14.3	12	0.80
Ge	370	6.2	12	1.91
K	91	77	90	1.16
Li	344	46.6	24	0.51
Mo	450	5.2	62	1.19
Na	158	58	70	1.21
Ni	450	15.1	12	0.79
Pd	274	11.6	11	0.91
Pb	105	25.4	23	0.90
Si	640	3.8	11	2.79
Th	163	9.6	12	1.21
W	400	4.6	5.2	1.14

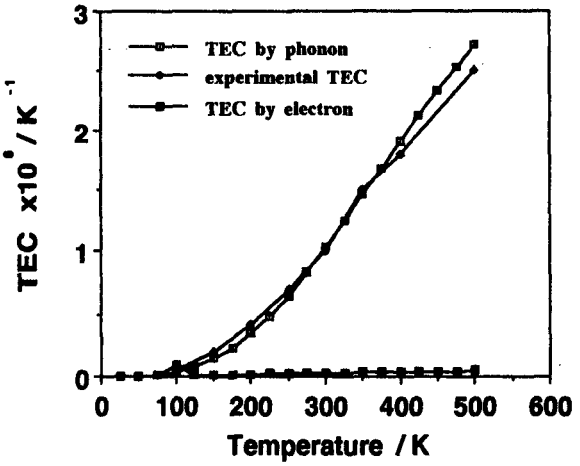

Fig.1 Thermal expansion coefficient of Diamond

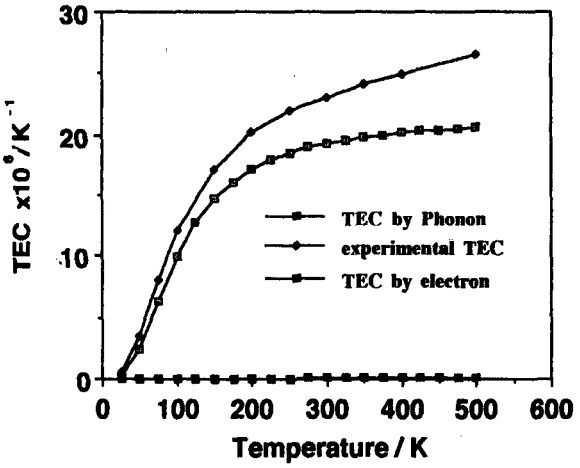

Fig. 2 Thermal expansion coefficient of Aluminum

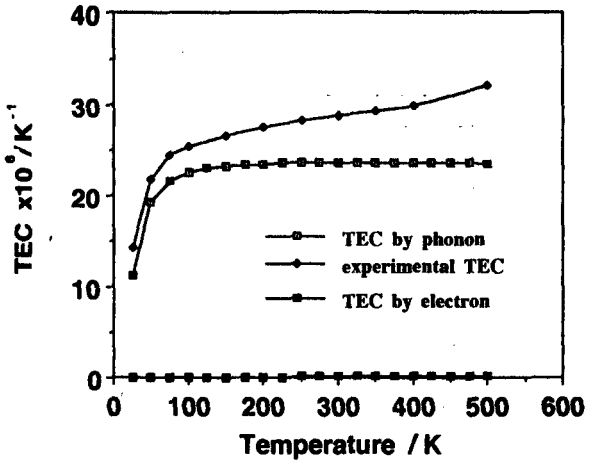

Fig. 3 Thermal expansion coefficient of Lead

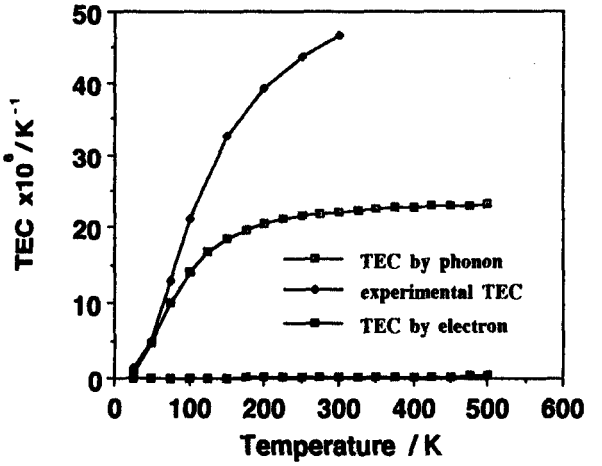

Fig. 4 Thermal expansion coefficient of Lithium

4. CONCLUSIONS

To explain thermal pressure, Virial theorem has been applied to phonon and electron in Debye model, and following results have been obtained.

1. Characteristic temperature dependence of thermal expansion coefficient (TEC) is explained by Virial pressure of phonon.
2. Calculated TEC shows fairly good agreement with measured values around Debye temperature.
3. Linear increase of TEC above Debye temperature is explained by electron pressure.

Same thermal phenomena, like melting, phase transition and crystal growth, can be also explained by Virial pressure of electron and phonon, in condensed matter.

REFERENCES

(1) Charles Kittel, Introduction to Solid State Physics, Wiley,New York, (1996)
(2) J.Mimkes, Phys.stat.sol. (b),148,91 (1988)
(3) R. Bhandari and V.K. Jindal, J. Phys. : Condens .Matter 3 899 - 907 (1991)
(4) S. Tamura and K. Hirota, J. Mater. Sci. Lett. 10 728-729 (1991)
(5) G. Marc and W.G.McMillan, The Virial Theorem, Mod. Prog. Phys. Chem.
(6) D. E. Gray (ed.), American Institute of Physics Handbook, McGraw-Hill, New York (1972)
(7) R. W. Munn, Adv. Phys., 18, 515 (1969)
(8) T.H.K. Barron and R.W.Munn, Phil. Mag., 15, 85 (1967)