TEMPERATURE DEPENDENCE OF THE GRÜNEISEN PARAMETERS OF SOME CUBIC METALS

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The temperature dependence of the Grüneisen parameters of cubic metals sodium, potassium, copper, silver, gold and aluminium is studied from the experimentally measured pressure derivatives of elastic constants, using Bhatia's electron gas model. Formidable integrals over the phonon wave vectors are evaluated from Houston's six-term interpolation procedure. The calculated γ values are compared with available experimental data. The agreement of the theoretical values with experiments is satisfactory for silver, but not in the case of other metals.

1. *Introduction*

The effect of anharmonicity on thermal expansion of crystals is usually expressed in terms of a dimensionless parameter γ, called the Grüneisen parameter, defined by the relation

$$\gamma = \frac{\beta V}{\chi C_v}, \tag{1}$$

where β is the volume thermal expansion coefficient, χ the compressibility, V the volume and C_v the specific heat at constant volume. This quantity is related to the variation of lattice vibration frequencies with volume. GRÜNEISEN's theory [1] assumes γ to be a constant, independent of temperature and lattice frequency.

Recent experimental and theoretical investigations on thermal expansions of crystals have shown inadequacy of Grüneisen's theory. The experiments of RUBIN *et al.* [2], WHITE [3], and CARR *et al.* [4] on thermal expansions of metals at low temperatures show that γ varies with temperatures. BLACKMAN [5] and BARRON [6] have made detailed calculations of γ for ionic crystals by using idealized models for their lattice dynamics and have found that drastic variation in γ values occure at temperatures about 0.3Θ (Θ: Debye temperature). Since then many calculations on the temperature variation of γ of cubic metals have been carried out, notably by SHEARD [7], HORTON [8], COLLINS [9] and TOYA [10].

In the present paper, we report a calculation of temperature dependence of Grüneisen parameter for some cubic metals on the basis of BHATIA's model of electron-lattice interaction [11, 12]. It has been shown by JOSHI and HEMKAR [13, 14] that this model offers a fairly reasonable decription of vibration spectra and heat capacities of alkali and noble metals. In a recent study [15], we found thet this model provides a plausible explanation of gross features of temperature variation of Debye—Waller factors and resistivities of these metals. It was therefore thought proper to use this model to compute the thermal expansion of some cubic metals.

The results for sodium, potassium, copper, silver, gold and aluminium, for which data on pressure dependence of elastic constants are available, are presented in this paper and compared with available experimental values.

2. *Theory*

The volume thermal expansion coefficient β of a solid is given by the relation

$$\beta = -\chi \frac{\partial^2 F}{\partial V \partial T}, \tag{2}$$

where F is the Helmholtz free energy. In the quasi-harmonic approximation, the temperature dependence of the Free energy can be written as [16]

$$F = kT \sum_{\mathbf{q},j} \ln[1 - \exp(-\hbar\omega_{\mathbf{q}j}/kT)] + E_0, \tag{3}$$

where E_0 is the cohesive energy at absolute zero including the zero point energy, $\omega_{\mathbf{q},j}$ the angular frequency of lattice waves of wave vector $\mathbf{q}$ and polarization j, k the Boltzmann constant and the summation over $\mathbf{q}$ is taken over all the normal modes of the crystal. Combining Eqs. (2) and (3), we get

$$\frac{\beta V}{k\chi} = \sum_{\mathbf{q},j} \gamma_{\mathbf{q},j} E(\hbar\omega_{\mathbf{q},j}/kT), \tag{4}$$

where $E(x)$ is the Einstein specific heat function and

$$\gamma_{\mathbf{q},j} = -(\partial \ln \omega_{\mathbf{q},j}/\partial \ln V)_T. \tag{5}$$

The formula (4) gives the Grüneisen parameter γ as

$$\gamma = \frac{\beta V}{\chi C_v} = \frac{\sum_{\mathbf{q},j} \gamma_{\mathbf{q},j} E(\hbar\omega_{\mathbf{q},j}/kT)}{\sum_{\mathbf{q},j} E(\hbar\omega_{\mathbf{q},j}/kT)}. \tag{6}$$

Replacing the summation over allowed values of $\mathbf{q}$ within the first Brillouin zone by integrations over $\mathbf{q}$ and solid angle Ω in the wave vector space, Eq. (6) can be written as

$$\gamma(T) = \frac{\sum_j \int_\Omega d\Omega \int_0^{q_{\max}} dq\, \gamma_j(q) E(\hbar\omega_j(q)/kT) q^2}{\sum_j \int_\Omega d\Omega \int_0^{q_{\max}} dq\, E(\hbar\omega_j(q)/kT) q^2}. \tag{7}$$

3. *Numerical calculations*

The Grüneisen parameter at different temperatures is calculated using the expression (7). To evaluate the integrals, we have employed HOUSTON's method, as developed by BETTS *et al* [17]. The integration over q was performed numerically and the integration over Ω was carried out by using modified Houston's spherical six-term integration procedure. The applicability of Houston's method for evaluating various physical properties of a crystal has been discussed by several authors [18—20]. In this method, the integrand which is invariant under the operations of the complete cubic symmetry is expanded in cubic harmonics and the series is averaged analytically over the complete solid angle. The six directions used in the calculation are: [100], [110], [111], [210], [211] and [221].

To use HOUSTON's integration method, the secular equations determining the vibration frequencies of body-centred and face-centred cubic metals [11, 12] were solved for q vectors lying along the above six directions. The quantities $\gamma_j(q)$ were obtained in terms of the elastic constants C_{ij} and their pressure derivatives $\partial C_{ij}/\partial P$. In the calculation we took account of the variation of elastic constants and lattice parameters with temperature. In high temperature regions, these were obtained by extrapolation from the existing measurements.

4. *Results and Discussion*

The calculated values of the Grüneisen parameters for sodium, potassium, copper, silver, gold and aluminium, for which data on pressure derivatives of elastic constants are available have been plotted as a function of reduced temperature (T/Θ_0) in Figs. 1—4. Here Θ_0 is the Debye temperature deduced from the elastic constants. For comparison, the values of γ derived from experiments on thermal expansions have also been shown. The values of the pressure derivatives of elastic constants along with sources of the temperature variation of elastic constants and thermal expansion data needed in the calculation are listed in Table I. The lattice parameter values at different temperatures were obtained from PEARSON [21].

A survey of Figs. 1—4 shows that the agreement between theory and experiment is reasonably satisfactory for silver throughout the temperature range studied, for potassium at temperatures neither very low nor very high, for copper and aluminium at low temperatures only, and for gold at a particular temperature at which experimental value is known. In view of nonavailability of sufficient experimental data for sodium, potassium and gold, no definite conclusions can be drawn for these metals. The marked discrepancies in the case of sodium are probably caused by large uncertainties in the values of elastic constants reported by QUIMBY and SIEGEL [22] and also by the change in crystal structure. In our calculation we have taken no account of the fact that sodium undergoes martensitic type of phase transformation [23, 24] from a *bcc* to a mixture of *bcc* and *hcp* phases at about 37 °K. In potassium, the anharmonic effects are quite predominant because of low melting point. Hence a good agreement between theory and experiment is not possible at higher temperatures. For copper, the disagreement at high temperatures is due to the fact that BHATIA's theory gives a poor representation of frequency distribution of this metal in the high frequency region. The discrepancies in the case of aluminium

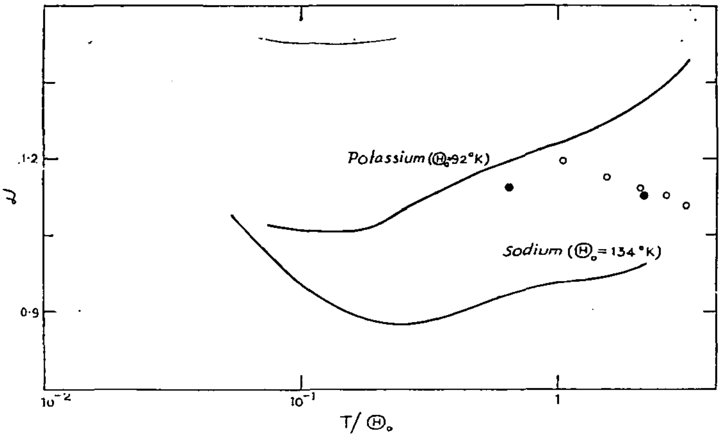

Fig. 1. Variation of γ with temperature for sodium and potassium. Experimental data: 0 potassium; sodium

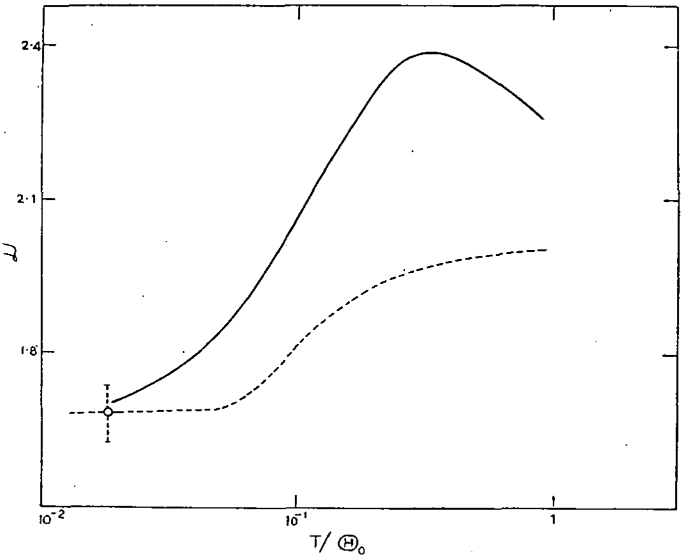

Fig. 2. Variation of γ with reduced temperature for copper ($\Theta_0 = 331$ °K). The solid curve shows present calculations and the broken curve corresponds to experimental measurements

are not unexpected and may be attributed to the approximate description of electron-lattice interaction and to the assumption of short range interionic interaction in the theory.

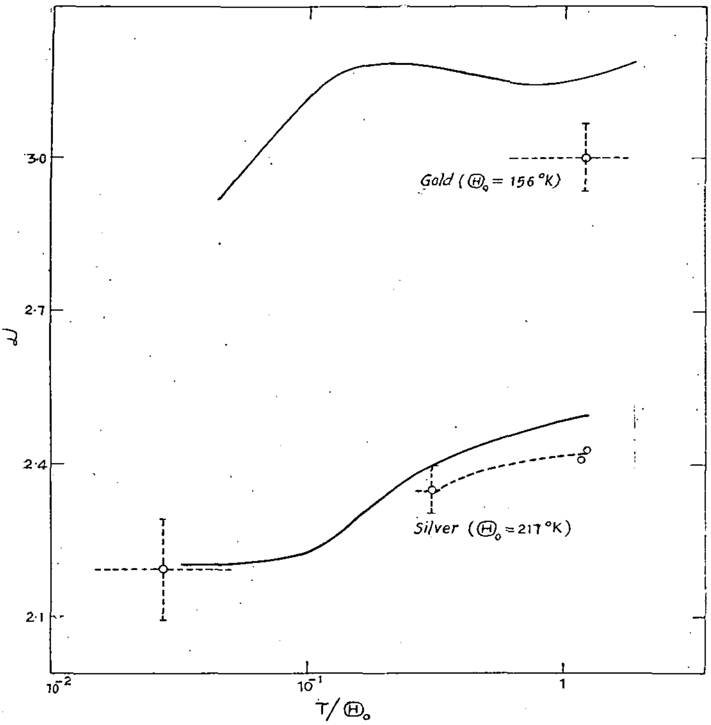

Fig. 3. Variation of γ with reduced temperature for silver and gold. Circles show experimental values

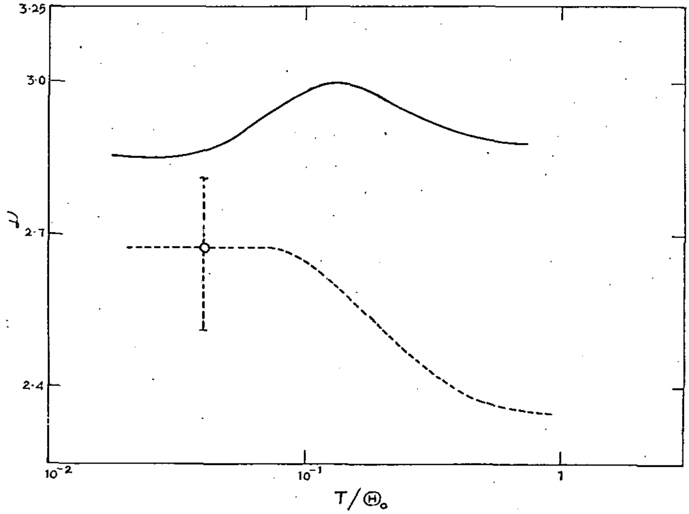

Fig. 4. Variation of γ with reduced temperature for aluminium ($\Theta_0=407$ °K). The solid curve is based on present calculations and the dashed curve shows experimental measurements

Table I

Material	Pressure derivatives of elastic constants			Reference for pressure derivative	Reference for elastic constants	Reference for thermal expansion
	$\partial C_{11}/\partial P$	$\partial C_{12}/\partial P$	$\partial C_{44}/\partial P$			
Sodium	3.901	3.449	1.630	Daniels [a]	Quimby and Siegel [e]	Corruccini and Gniewek [j]
Potassium	4.305	3.803	1.620	Smith and Smith [b]	Marquardt and Trivisonno [f]	Monfort and Swenson [k]
Copper	6.363	5.203	2.350	Daniels and Smith [c]	Overton and Gaffney [g]	Rubin et al. [l]
Silver	7.032	5.754	2.310	Daniels and Smith [c]	Neighbours and Alers [h]	Corruccini and Gniewek [j]
Gold	7.014	6.138	1.790	Daniels and Smith [c]	Neighbours and Alers [h]	Vorruccini and Gniewek [j]
Aluminium	7.350	4.110	2.310	Schmunk and Smith [d]	Sutton [i]	Corruccini and Gniewek [j]

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