Vol. XVII, 3 REVISTA MEXICANA DE FISICA 1968

GRÜNEISEN PARAMETERS OF CUBIC METALS

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(Received: August 11, 1968)

ABSTRACT

The Grüneisen parameters of cubic metals copper, silver, gold, aluminium, sodium and potassium are determined from the measured elastic constants and their pressure derivatives, using de Launay and Sharma-Joshi's models of electron-ion interaction. The calculation makes use of Houston's six-term approximation. The results of the calculations are compared with available experimental information. It is found that Sharma-Joshi's model yields a better agreement with experiment.

RESUMEN

A partir de las determinaciones experimentales de las constantes elásticas y sus derivadas respecto a la presión y mediante el uso de los modelos de interacción electrón-ion propuestos por de Launay y Sharma-Joshi, se determinan en *este trabajo los parámetros de Grüneisen para cobre, plata, oro, aluminio, sodio y potasio. Los cálculos se hacen con una aproximación de Houston a seis términos y se comparan con la información experimental disponible. Se encuentra que el modelo de Sharma-Joshi está en mejor concordancia con los valores experimentales.*

I. INTRODUCTION

In the theory of the thermal expansion of crystals, an important part is played by the Grüneisen parameter γ defined by the relation

$$\gamma = \frac{\alpha V K_T}{C_v} \tag{1}$$

where K_T is the isothermal bulk modulus, α the volume thermal expansion coefficient, V the crystal volume and C_v the specific heat at constant volume of the material. This quantity provides a measure of the anharmonicity in a crystal and is related to the variation of lattice frequencies with volume. Grüneisen's theory assumes γ to be a constant, independent of lattice frequency and temperature. This picture has now been shown to be inadequate.

In recent years the expansion coefficients of crystals have been the subject of a considerable theoretical and experimental literature. The various experiments on thermal expansion at low temperatures provide strong evidence that the parameter γ varies with temperature. The theoretical work of Barron[4] and Blackman[5] on thermal expansions using idealized models for the lattice dynamics shows that drastic variations in the value of γ with temperature occur in the temperature region $T = 0.2\Theta$. Sheard[6] has related the volume dependence of the normal-mode frequencies with the pressure dependence of the elastic constants for an anisotropic elastic continuum. From the suitably weighted average of $\gamma_{q,p}$ over the phonon spectrum, he has obtained the values of γ for the two extreme cases of high enough ($T > \Theta$) and very low temperatures ($T << \Theta$), respectively. Though the anisotropic continuum model is an oversimplification, Sheard's results for noble metals show a reasonable agreement with the experimental data. The same model has also been used by Collins[7] to compute the temperature dependence of γ for a number of materials of cubic structure. Horton[8] investigated the temperature dependence of γ by incorporating the observed temperature variation of the elastic constants into a central nearest and next nearest model. The agreement between theory and experiment is quite satisfactory.

Sharma and Joshi[9,10] have propounded a model for studying the lattice vibrations in metals taking congnizance of electrons as a compressible gas. In this model the effect of the gas of valence electrons on ionic vibrations is taken into account by attributing to it a bulk modulus. The model is found to give a plausible explanation of temperature variation of heat capacities and Debye-Waller factors of a number of cubic alkali and noble metals[11]. De Launay[12] has also proposed a simple phenomenological model in which conduction electrons are assumed to behave like an ordinary gas supporting no shear stress. This model has been successfully used for the calculation of the frequency spectra and the temperature dependence of the specific heats of a number of cubic metals by Dayal and his coworkers[13]. In both models the contribution of ions to the elements of the dynamical matrix is exactly the same. The electronic contribution is, however, different.

In this paper we have utilized the models of de Launay and Sharma-Joshi for the calculation of the temperature variation of γ for some cubic metals from the experimental values of the pressure derivatives of elastic constants. The results for copper, silver, gold, aluminium, sodium and potassium are presented and compared with the available experimental information.

II. THEORY

The general method of computing the volume expansion coefficient α is to use the thermodynamic relation

$$\alpha = - \frac{1}{K_T}\left(\frac{\partial^2 F}{\partial V \partial T}\right), \qquad (2)$$

where F is the Helmholtz free energy. In the quasi-harmonic approximation the temperature-dependent part of the free energy is given by[14]

$$F = k_B T \sum_{\mathbf{q},p} \ln \left[2 \sinh (\hbar\omega_{\mathbf{q},p} / 2 k_B T) \right] , \tag{3}$$

where $\omega_{\mathbf{q},p}$ is the angular frequency of normal mode of wave vector $\mathbf{q}$ and polarization p, k_B the Boltzmann constant, and the summation is taken over all the normal vibrations of the crystal. From Eqs. (2) and (3), it follows that

$$\alpha V K_T = k_B \sum_{\mathbf{q},p} \gamma_{\mathbf{q},p} \, E (h\omega_{\mathbf{q},p} / k_B T) , \tag{4}$$

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

$$E(x) = x^2 e^x / (e^x - 1)^2 , \tag{5}$$

and

$$\gamma_{\mathbf{q},p} = - (\partial \ln \omega_{\mathbf{q},p} / \partial \ln V)_T . \tag{6}$$

Equation (4) gives the Grüneisen relation (1), when γ is the mean of $\gamma_{\mathbf{q},p}$ defined by

$$\gamma = \frac{\sum_{\mathbf{q},p} \gamma_{\mathbf{q},p} \, E (h\omega_{\mathbf{q},p} / k_B T)}{\sum_{\mathbf{q},p} E (h\omega_{\mathbf{q},p} / k_B T)} . \tag{7}$$

The quantity γ so defined is a parameter which will vary with the temperature. Replacing the summations over $\mathbf{q}$ by integration over the allowed values of $\mathbf{q}$ within the first Brillouin zone, Eq. (7) becomes

$$\gamma = \frac{\sum\limits_{p} \int_{0}^{q_{\max}} \int_{\Omega} \gamma_p(q)\, E(\hbar\omega_p(q)/k_B T)\, q^2\, dq\, d\Omega}{\sum\limits_{p} \int_{0}^{q_{\max}} \int_{\Omega} E(\hbar\omega_p(q)/k_B T)\, q^2\, dq\, d\Omega} \tag{8}$$

where Ω is the solid angle in wave-vector space.

III. NUMERICAL COMPUTATIONS

The calculation of γ at different temperatures has been carried out by using a modification of Houston's method. The integration over q was performed numerically and the integration over Ω was carried out by using the modified Houston's spherical six-term integration procedure as elaborated by Betts et al.[15] Horton and Schiff[16] have discussed the applicability of Houston's method in the calculation of specific heat, and Collins[7] and Ganesan and Srinivasan[17] have shown that this method may give reliable temperature dependence of γ. The six directions used in the present calculation are: [100], [110], [111], [210], [211] and [221].

In order to use Houston's method, the secular equations[9,10] for the determination of the angular frequencies of lattice waves in fcc and bcc metals were solved in each of the six directions. The limiting values of **q** along the six directions for both types of structure are given in Table I. The quantities $\gamma_{\mathbf{q},p}$ were expressed in terms of the three elastic constants C_{11}, C_{12} and C_{14} and their pressure derivatives. The values of these quantities were taken from experiment. In the calculation we used the measured temperature variations of the elastic constants and the lattice parameter. The elastic constants in the high-temperature region were extrapolated from the existing experimental values. For the pressure derivative we have used their room-temperature values because experimental data for them below room temperature have not yet been reported.

IV. RESULTS AND DISCUSSIONS

Figs. 1-6 show the calculated values of γ as a function of reduced temperature (T/Θ_0) from de Launay's and Sharma-Joshi's models for copper, silver, gold, aluminium, sodium and potassium for which data on pressure derivatives of the elastic constants are available. For comparison we have also shown the value of γ derived from the experimental measurements of the thermal expansion. The sources of the elastic constants and thermal expansion date together with the experimental values of the pressure derivatives of elastic constants are summarized in Table **II**. The lattice-parameter values at various temperatures were taken from Pearson[18]. Because of the considerable variation in the values of pressure derivatives of elastic constants for noble metals as reported by Daniels and Smith[19], and Hiki and Granato,[20] our calculated curves for new and old elastic data do not coincide.

A survey of Figs. 1-6 reveals that the calculations based on Sharma and Joshi's model yield a better agreement with the experimental values of γ for copper and silver. A possible source of discrepancy at low temperatures seems to be the use of room-temperature values of the pressure derivatives of elastic constants. In view of insufficient experimental data for sodium, potassium and gold, it is difficult to draw any definite conclusion for these metals. In the case of aluminium, though the shape of theoretical and experimental curves is similar, it is disconcerting to find how widely the calculations deviate from the experimental measurements. The discrepancies observed in this case are not so surprising and can be attributed to the approximate description of the electron-lattice interaction and to the assumption of short-range interatomic interaction in both the models. Recent experimental investigations of phonon dispersion relations in aluminium[21] show that the interatomic forces in this metal are of a fairly long-range and noncentral nature.

ACKNOWLEDGEMENTS

We are grateful to the Council of Scientific and Industrial Research and the University Grants Commission for financial assistance. Part of the work was supported by the Department of Atomic Energy, Bombay.

TABLE I

Maximum values of wave vector **q** for body-centred and face-centred cubic crystals

Direction	Maximum values	
	body-centred	face-centred
[100]	$\frac{\pi}{a}$	$\frac{\pi}{a}$
[110]	$\frac{1}{\sqrt{2}} \frac{\pi}{a}$	$\frac{3}{2\sqrt{2}} \frac{\pi}{a}$
[111]	$\frac{\sqrt{3}}{2} \frac{\pi}{a}$	$\frac{\sqrt{3}}{2} \frac{\pi}{a}$
[210]	$\frac{\sqrt{5}}{3} \frac{\pi}{a}$	$\frac{\sqrt{5}}{2} \frac{\pi}{a}$
[211]	$\frac{\sqrt{6}}{3} \frac{\pi}{a}$	$\frac{3\sqrt{6}}{8} \frac{\pi}{a}$
[221]	$\frac{3}{4} \frac{\pi}{a}$	$\frac{9}{10} \frac{\pi}{a}$

Table II

Elastic and thermal-expansion data for cubic metals.

	Pressure derivatives of the elastic constants				
Metal	$\partial C_{11}/\partial P$	$\partial C_{12}/\partial P$	$\partial C_{44}/\partial P$	Elastic constants	Thermal expansion
Copper	[a] 6.363	5.203	2.350	Overton and Gaffney[f]	Rubin et al.[m]
	[b] 5.940	5.190	2.630		
Silver	[a] 7.032	5.754	2.310	Neighbours and Alers[g]	Corruccini and Gniewek[n]
	[b] 5.117	3.607	3.040		
Gold	[a] 7.014	6.138	1.790	Neighbours and Alers[g]	Corruccini and Gniewek[n]
	[b] 5.717	4.957	1.520		
Aluminium	[c] 7.350	4.110	2.310	Sutton[h] Kamm and Alers[i]	Corruccini and Gniewek[n]
Sodium	[d] 3.901	3.449	1.630	Quimby and Siegel[j] Diederich and Trivisonno[k]	Corruccini and Gniewek[n]
Potassium	[e] 4.305	3.803	1.620	Marquardt and Trivisonno[l]	Monfort and Swenson[o]

NOTES TO TABLE II

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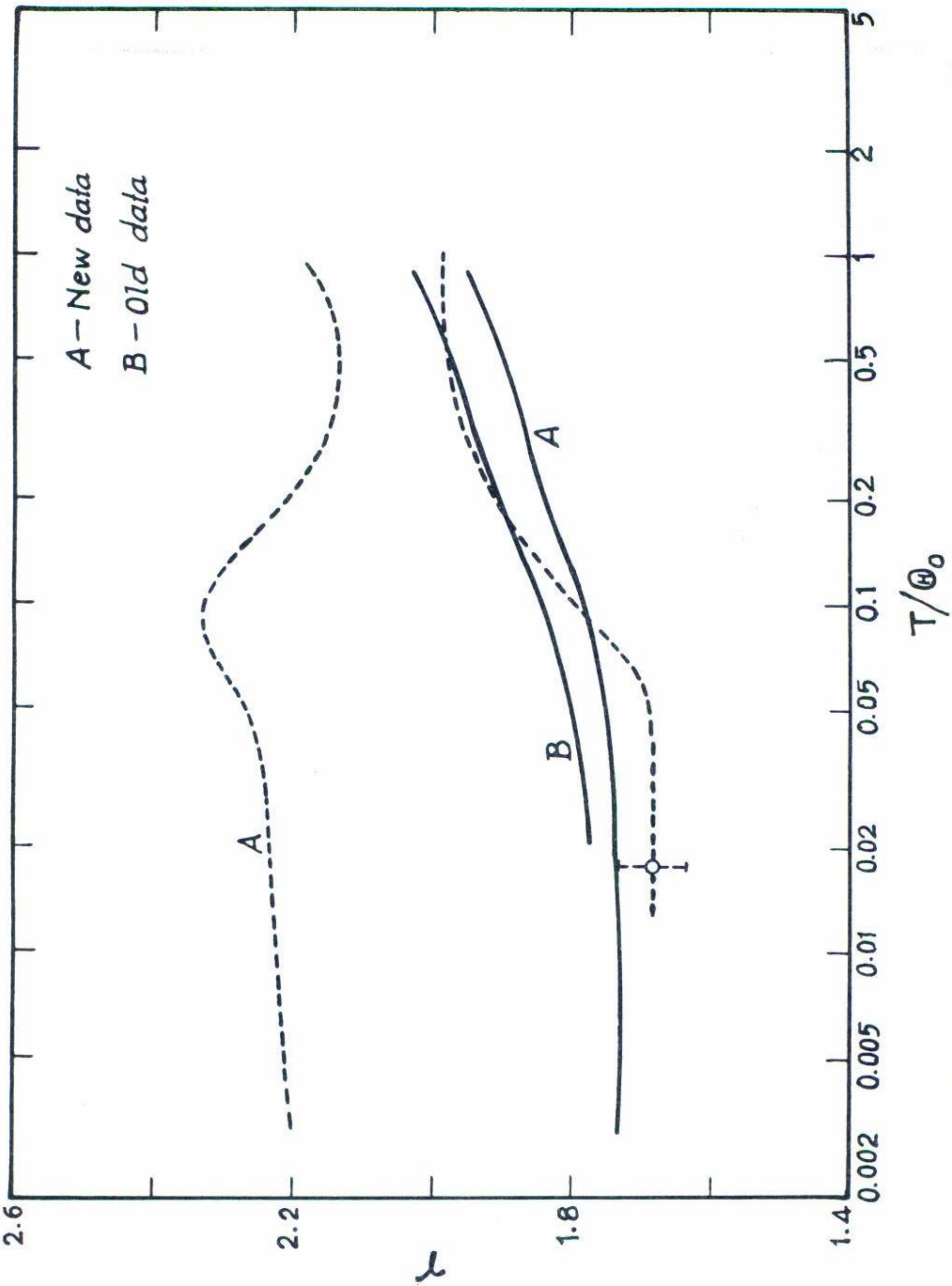

Fig. 1. γ as a function of reduced temperature (T/Θ_0) for copper ($\Theta_0 = 331$ °K). The solid curve is obtained from Sharma and Joshi's model and the dashed curve shows the calculation using de Launay's model. The curve with a circle shows the experimental behaviour.

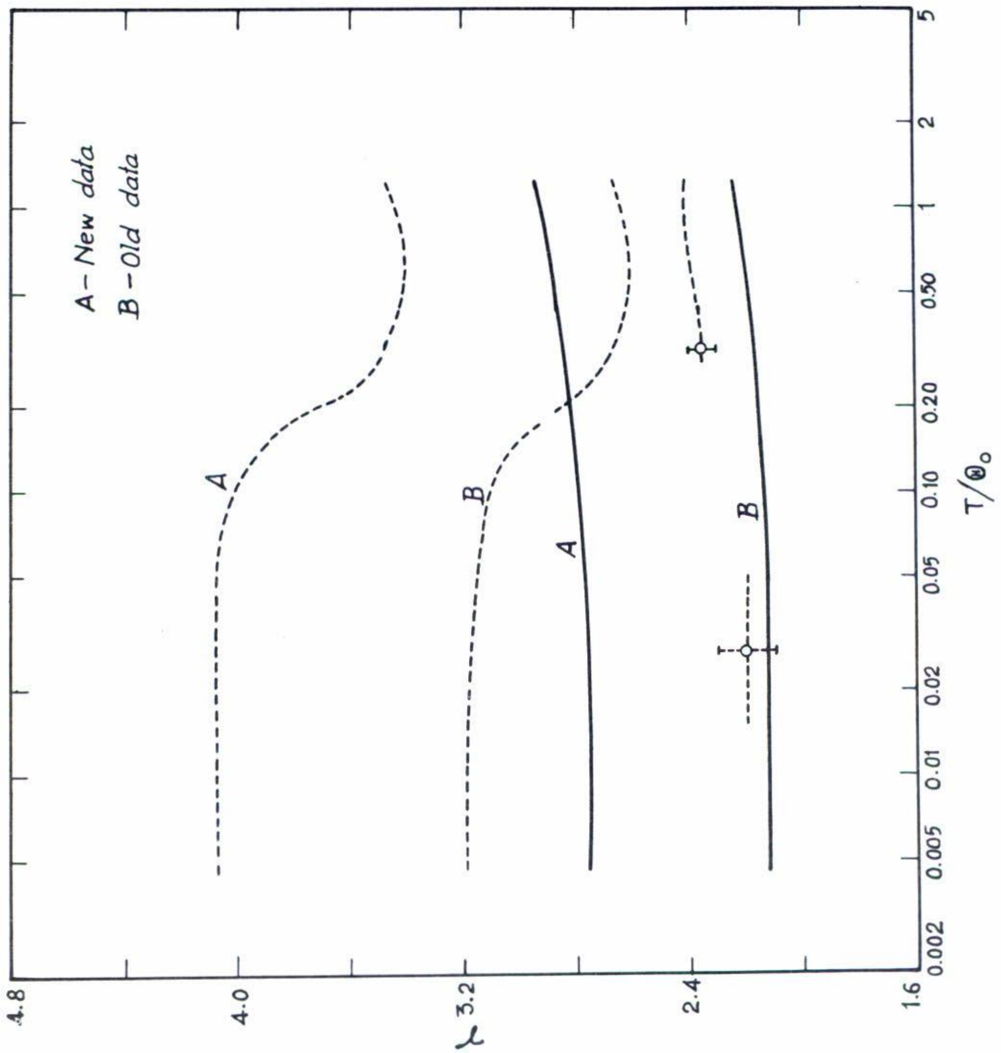

Fig. 2. γ as a function of reduced temperature (T/Θ_0) for silver ($\Theta_0 = 217°K$). The solid curves show calculations from Sharma and Joshi's model and the dashed curve is obtained from de Launay's model. The curve with a circle shows the experimental behaviour.

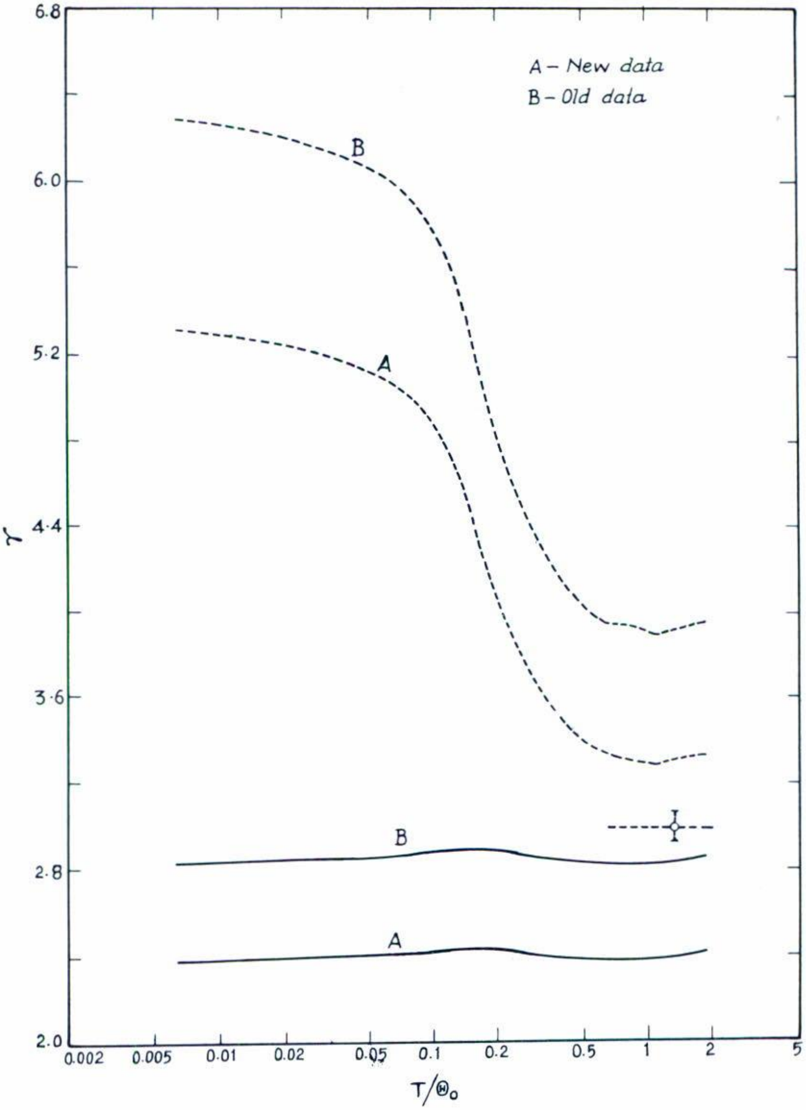

Fig. 3. γ as a function of reduced temperature (T/Θ_0) for gold (Θ_0 = 156°K). The solid curves are based on Sharma and Joshi's model and the dashed curves show calculations using de Launay's model. Circle is the experimental point.

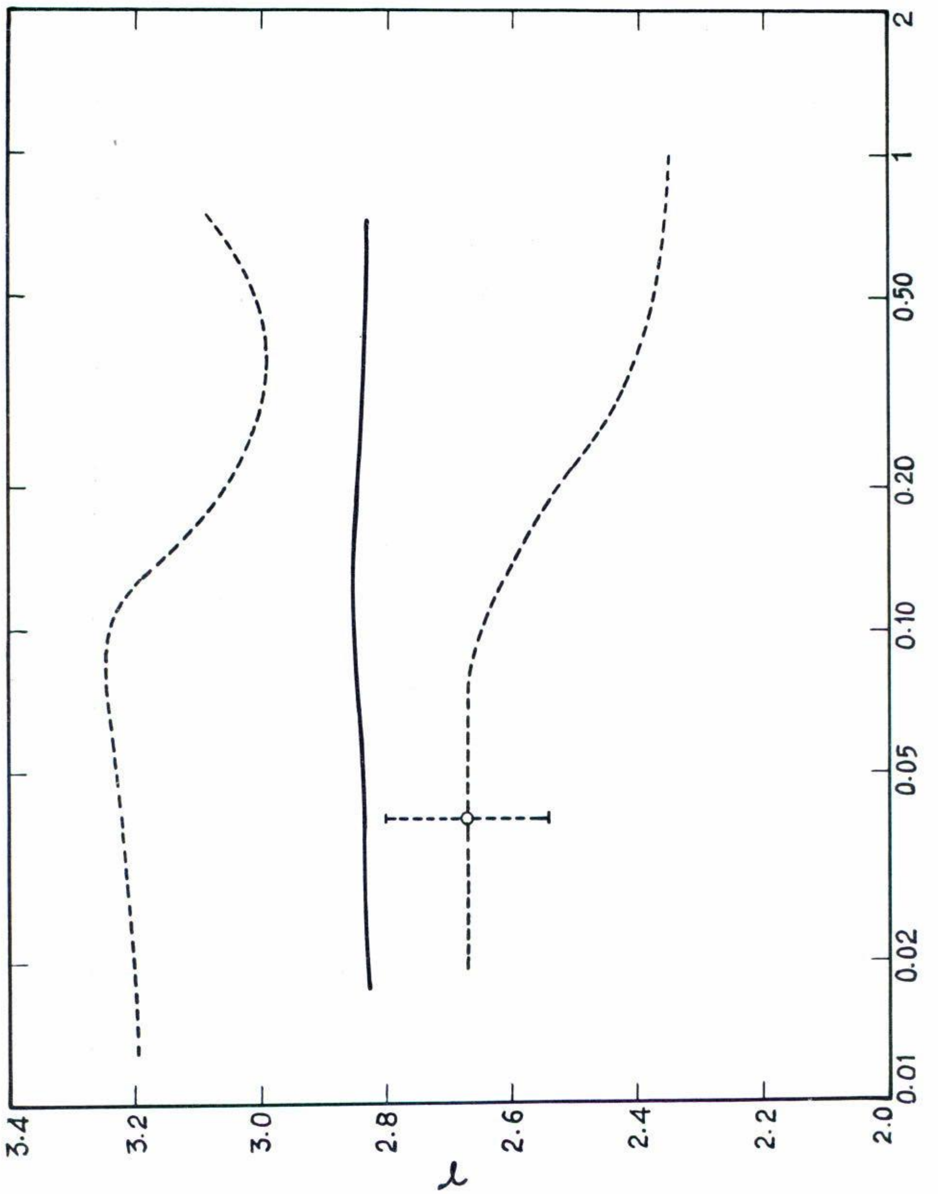

Fig. 4. γ as a function of reduced temperature (T/Θ_0) for aluminium. ($\Theta_0 = 407$°K). The solid curve is obtained from Sharma and Joshi's model and the broken curve represents calculation from de Launay's model. The curve with a circle shows the experimental behaviour.

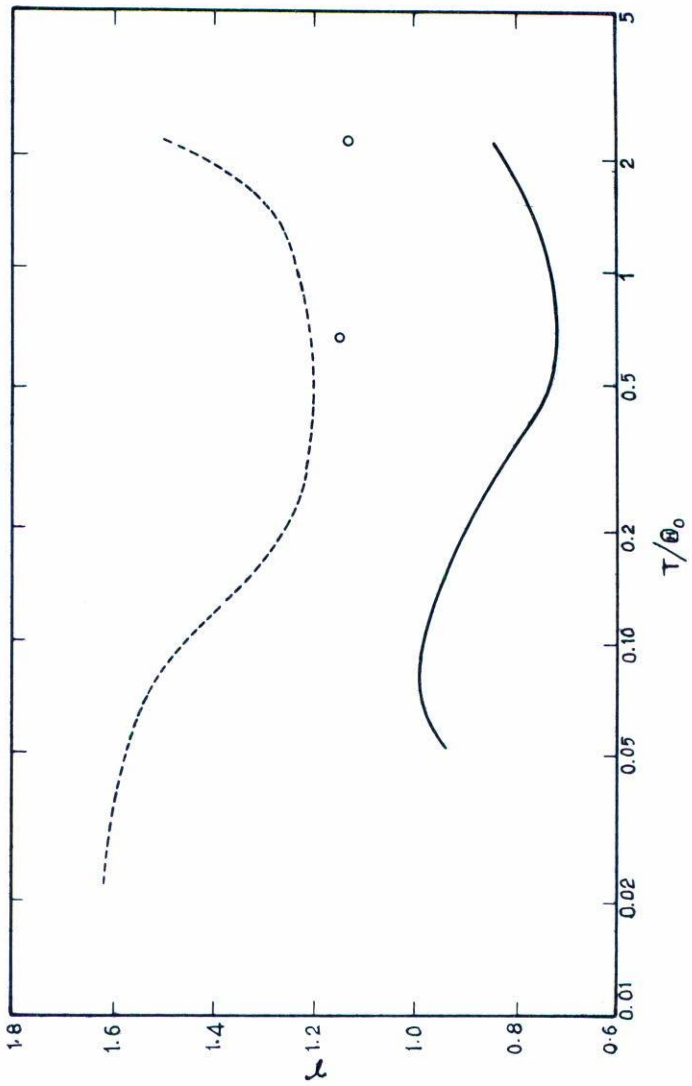

Fig. 5. γ as a function of reduced temperature (T/Θ_0) for sodium (Θ_0 = 134°K). The solid curve depicts calculations from Sharma and Joshi's model and the dashed curve is obtained from de Launay's model. Circles are experimental points.

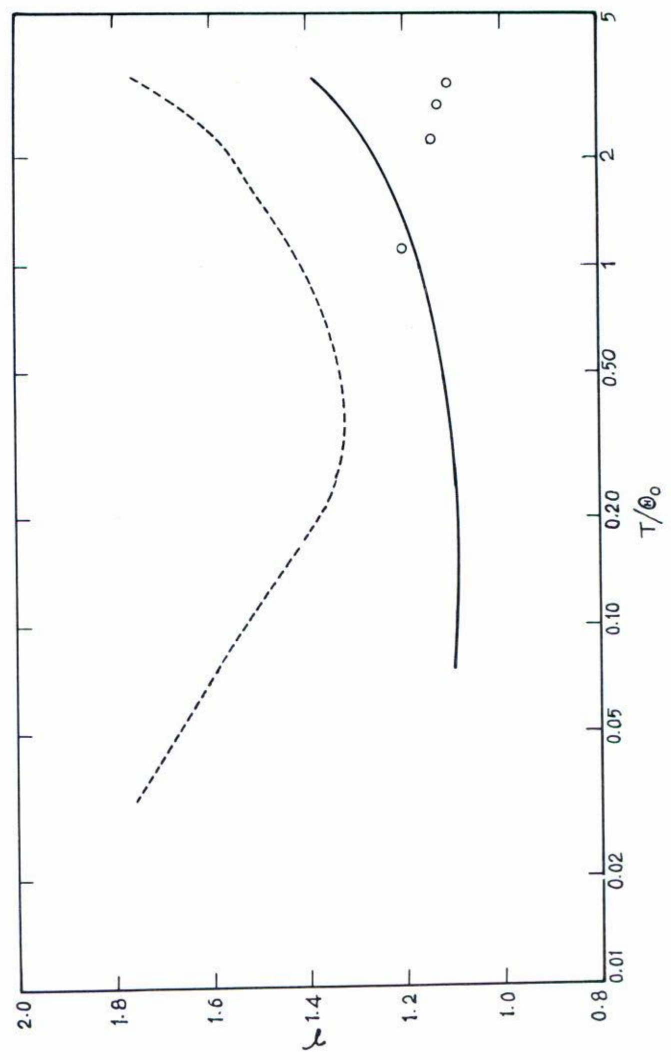

Fig. 6. γ as a function of reduced temperature (T/Θ_0) for potassium (Θ_0 = 92°K). The solid curve is obtained from Sharma and Joshi's model and the dashed curve depicts calculation using de Launay's model. Circles are the experimental values.