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PHYSICAL REVIEW B

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Grüneisen Parameters of Cubic Metals

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The Grüneisen parameters of alkali metals, noble metals, and aluminum have been calculated at different temperatures from available pressure derivatives of elastic constants, using the Chéveau model for their lattice dynamics. The calculation is carried out by a modified Houston's method. The calculated Grüneisen parameters show reasonably satisfactory agreement with experimental measurements.

I. INTRODUCTION

The lattice dynamics of metals has been the subject of considerable theoretical and experimental literature. Early theoretical workers completely neglected the influence of conduction electrons. In the past few years, several models¹⁻³ have been worked out for studying the lattice vibrations in metals by introducing the influence of conduction electrons in Born-Von Kármán theory. Many of them, however, do not satisfy the periodic symmetry properties of the lattice. Lax⁴ has attributed this inadequacy to the neglect of translational invariance of the lattice. Recently, Krebs⁵ has propounded a model by incorporating the suggestion of Lax which meets the symmetry requirements of the lattice. However, this model suffers from a serious drawback of internal equilibrium. The derivative of long-range screened Coulomb interaction energy does not vanish in the equilibrium configuration. Quite recently, Chéveau⁶ has proposed a simple model for the lattice dynamics of cubic metals which satisfies the sym-

metry properties and preserves internal equilibrium without recourse to any external force. In this model, the ion-ion interaction is described by the first two terms in the Taylor expansion of the potential energy, as in the model of Bhatia.² The electronic contribution is, however, calculated from linearized Thomas-Fermi theory for the whole crystal.

In the present paper, we have utilized the Chéveau model to calculate the Grüneisen parameters of alkali metals, noble metals, and aluminum at different temperatures. The stimulus for this study was dictated by the recent appearance of thermal expansion and pressure derivative of elastic constants for these metals.^{7,8}

II. THEORY

The temperature variation of the thermal expansion is most conveniently represented by the dimensionless Grüneisen parameter $\gamma(T)$, defined by

$$\gamma(T) = \beta V B_T / C_v, \quad (1)$$

where β is volume thermal expansion coefficient, V the total volume, B_T the isothermal bulk modulus, and C_v the heat capacity at constant volume. In quasiharmonic approximation, the total Helmholtz free energy F of a crystal can be written as⁹

$$F = E_c + kT \sum_{\vec{q}, j} \ln[1 - \exp(-\hbar\omega_{\vec{q}, j}/kT)], \quad (2)$$

where $\omega_{\vec{q}, j}$ is the angular frequency of normal mode with wave vector \vec{q} and polarization j , T is the absolute temperature, k is the Boltzmann constant, and E_c is the internal energy of the crystal at absolute zero including the zero-point energy. Using the thermodynamic relation

$$\beta B_T = - \left(\frac{\partial^2 F}{\partial V \partial T} \right)_{T, V}, \quad (3)$$

and assuming that $\omega_{\vec{q}, j}$ is a function of the volume only, Eqs. (1) and (2) give

$$\gamma(T) = \frac{\sum_{\vec{q}, j} \gamma_{\vec{q}, j} E\left(\frac{\hbar\omega_{\vec{q}, j}}{kT}\right)}{\sum_{\vec{q}, j} E\left(\frac{\hbar\omega_{\vec{q}, j}}{kT}\right)}, \quad (4)$$

where $E(x)$ is the Einstein specific-heat function, and $\gamma_{\vec{q}, j}$ is the phonon Grüneisen parameter which measures the change in vibration frequency with values, defined by the relation

$$\gamma_{\vec{q}, j} = - \left(\frac{\partial \ln \omega_{\vec{q}, j}}{\partial \ln V} \right)_T. \quad (5)$$

Replacing the summation over \vec{q} by an integration within the first Brillouin zone, Eq. (4) reduces to

$$\gamma(T) = \frac{\sum_j \int d\Omega \int_0^{q_{\max}} d_q \gamma_j(q) E\left(\frac{\hbar\omega_j(q)}{kT}\right) q^2}{\sum_j \int d\Omega \int_0^{q_{\max}} d_q E\left(\frac{\hbar\omega_j(q)}{kT}\right) q^2}, \quad (6)$$

where Ω is solid angle in wave-vector space.

III. RESULTS AND DISCUSSION

The calculation of γ at different temperatures from Eq. (6) has been made by a modification of Houston's method.¹⁰ The integration over q was performed numerically and over Ω using a modified Houston spherical six-term integration method as developed by Betts *et al.*¹¹ The individual phonon Grüneisen parameters $\gamma_{\vec{q}, j}$ were obtained in terms of elastic constants and their pressure derivatives, using Chéveau⁶ secular determinant. In the calculation the elastic constants and lattice parameters were used corresponding to the temperature for which the computation is made. However, room-temperature values for the pressure derivative of elastic constants were used at all temperatures, as their temperature variation has not been studied. The sources of the temperature variation of the elastic constants together with their pressure derivatives at room temperature used in

the calculation are given in Table I. For sodium, potassium, and noble metals, we have used two sets of pressure-derivative data. In the case of alkali metals, one of the values is taken from recent theoretical calculations of Suzuki *et al.*⁸ using the model local pseudopotential of Ashcroft,¹² while the other is obtained from experimental measurements of Daniels,¹³ and of Smith and Smith.¹⁴ Jain¹⁵ has also measured the pressure derivative of elastic constants for lithium at room temperature, but his measurements are limited only to shear elastic constants. His values are, however, in good agreement with the theoretical values used in the present calculation. For noble metals, both sets of data refer to experimental measurements and are taken from the work of Hiki and Granato,⁷ and of Daniels and Smith.¹⁶ The two measurements agree reasonably well for copper, but differ considerably in the case of silver and gold. Daniels and Smith have measured the effect of hydrostatic pressure on elastic constants up to 10 000 bar, while Hiki and Granato have limited their measurements up to 60 bar. The latter workers claim to

TABLE I. Pressure derivatives and temperature variations of elastic constants for cubic metals. $C = C_{44}$, $C' = \frac{1}{2}(C_{11} - C_{12})$, and $B = \frac{1}{3}(C_{11} + 2C_{12})$.

Metal	Pressure derivatives			Source	Elastic constant data
	$\frac{\partial C}{\partial P}$	$\frac{\partial C'}{\partial P}$	$\frac{\partial B}{\partial P}$		
Li	1.034	0.085	3.173	Ref. 8	a
Na	1.567	0.226	3.629	Ref. 8	b
	1.63	0.226	3.60	Ref. 13	
K	1.539	0.253	3.819	Ref. 8	c
	1.62	0.251	3.97	Ref. 14	
Rb	1.565	0.253	3.832	Ref. 8	d
Cu	2.63	0.375	5.44	Ref. 7	e
	2.35	0.580	5.590	Ref. 16	
Ag	3.04	0.755	4.11	Ref. 7	f
	2.31	0.639	6.18	Ref. 16	
Au	1.52	0.380	5.21	Ref. 7	f
	1.79	0.438	6.43	Ref. 16	
Al	2.31	1.62	5.19	g	h

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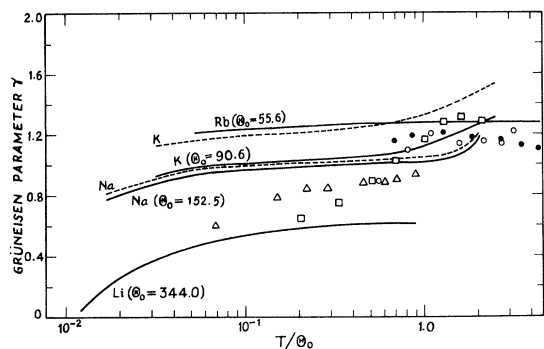


FIG 1. Grüneisen parameters of alkali metals as a function of temperature. The continuous curves are obtained from theoretical pressure derivative data and the dashed curves are based on experimental pressure derivatives. Experimental points; Li: \triangle Gray; Na: \square Siegel and Quimby; K: \circ Monfort and Swenson; \bullet Kelly and Pearson.

have achieved higher accuracy. In the calculation, the screening parameter of the electronic coupling coefficient was considered as an adjustable parameter. The best values of the parameter for the metals considered were determined from the data on experimental dispersion curves.

The calculated temperature variation of the Grüneisen parameter for alkali metals (Li, Na, K, Rb), noble metals (Cu, Ag, Au), and aluminum are depicted in Figs. 1 and 2. For comparison, we have also shown the values derived from experimental measurements of thermal expansion and

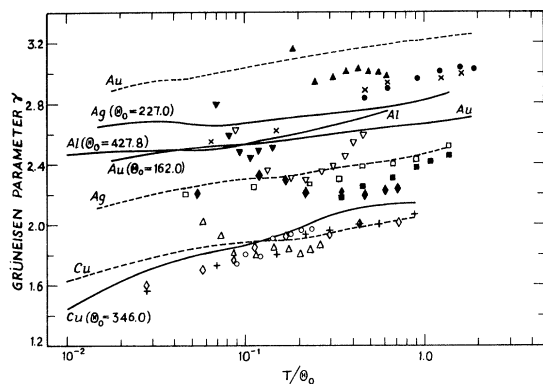


FIG 2. The Grüneisen parameters of noble metals and aluminum as a function of temperature. The continuous curves for noble metals are obtained by using pressure derivative data of Hiki and Granato, and the dashed curves are based on pressure derivatives of Daniels and Smith. Experimental points; Cu: + Rubin *et al.*; \circ Simmons and Balluffi; \diamond Leksina and Novikova; \triangle Fraser and Hollis-Hallett; Ag: \square Ebert, Nix, and MacNair; \blacksquare Leksina and Novikova; ∇ Fraser and Hollis-Hallett; Au: \times Ebert, Nix, and MacNair; \bullet Leksina and Novikova; \blacktriangle Fraser and Hollis-Hallett; Al: \blacklozenge Altman *et al.*; \blacktriangledown Fraser and Hollis-Hallett.

specific heat. The sources of the experimental thermal expansion and specific-heat data are sum-

TABLE II. Experimental thermal and specific-heat data for cubic metals.

Metal	Thermal expansion		Specific heat	
	Temperature range ($^{\circ}$ K)	Source	Temperature range ($^{\circ}$ K)	Source
Li	75-300	a	20-300	b
			3-30	c
Na	80-290	d	20-300	e
			2-30	c
K	20-320	f	12-300	g
			up to 30	h
Rb	77-297	i	up to 300	h
Cu	15-300	j	15-300	k
	8-100	l		
	20-1200	m		
	20-93	Ref. 17		
Ag	20-373	n	15-300	o
	85-300	p		
	20-1200	m		
	20-95	Ref. 17		
Au	20-373	n	15-300	q
	81-300	r		
	20-1200	m		
	11-95	Ref. 17		
Al	15-300	Ref. 18	15-300	k
	25-90	Ref. 17		

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marized in Table II. It will be seen from Fig. 1 that the general shape of the theoretical and experimental γ - T curves is similar, but they show large deviations in the high-temperature regions. Except for lithium, the calculated curves cross over the experimental data. For lithium, the theoretical curve is systematically lower than the experimental values and the discrepancy increases with the rise of temperature. In the case of potassium, it is disconcerting to find how much the theoretical results deviate from the experimental measurements due to large scatter in experimental values. The observed discrepancies at low temperature for Na are probably due to uncertainty in the temperature variation of the elastic constants.

Figure 2 shows that the calculated γ - T curves for silver and gold differ considerably for the two sets of pressure-derivative data. In fact, for silver the γ values obtained from the pressure-derivative data of Hiki and Granato⁷ are higher than for gold. This shows that the Grüneisen parameter is considerably changed by the change in the values of pressure derivatives. It is interesting to note that the calculations using old pressure-derivative data of Daniels and Smith¹⁶ show better agreement with experiments than the recent data of Hiki and Granato.⁷ The agreement is particularly striking in the case of copper and silver. It may be pointed out that the recent measure-

ments of Grüneisen γ for noble metals and aluminum by Fraser and Hollis-Hallett¹⁷ differ considerably from those of other workers. They show pronounced minima at intermediate temperatures. In the low-temperature regions, however, there is large uncertainty in their experimental measurements. It is interesting to note that their experimental values at the minima lie very close to the theoretical calculations. For aluminum, the measurements of Fraser and Hollis-Hallett are very close to our theoretical curve, but the experimental values of Altman *et al.*¹⁸ are much lower than the present calculations. The marked discrepancies in this case are not surprising and can be attributed to the assumption of short-range interionic interactions in the theory. From the present study, it emerges that the Chéveau model gives a reasonable description of temperature variation of Grüneisen parameters of alkali and noble metals. There is, however, a need for detailed measurements of the temperature dependence of the pressure derivatives of the elastic constants.

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