TABLE IX. Thermal Grüneisen's first and second parameters for α-Al_2O_3.

Temperature (°K)	β ($\times10^{-6}$/°K)	C_p (cal/mol·°K)	V (cm^3/mol)	B^s ($\times10^{11}$ dyn/cm^2)	$\gamma_{G(\text{thermal})}$	$(1+T\beta\gamma_G)$
4.2	?	0.0021	25.538	25.747	...	...
77	1.08	1.50	25.539	25.727	1.13	1.000094
100	2.40	3.07	25.540	25.691	1.23	1.000294
150	6.15	7.64	25.545	25.638	1.26	1.001162
200	10.23	12.22	25.555	25.593	1.31	1.002677
273	14.88	17.482	25.578	25.512	1.33	1.005389
298	16.41	18.98	25.580	25.507	1.35	1.006636
400	20.10	23.38	25.631	25.270	1.33	1.010698
500	22.05	25.55	25.689	25.053	1.33	1.014632
600	23.55	26.85	25.748	24.833	1.34	1.018935
700	24.69	27.75	25.820	24.602	1.35	1.023340
800	25.65	28.44	25.885	24.396	1.36	1.027926
900	26.55	28.99	25.950	24.162	1.37	1.032787
1000	27.42	29.47	25.022	23.950	1.39	1.037993
1100	28.14	29.90	26.097	23.700	1.39	1.043054
1200	28.68	30.29	26.164	23.470	1.39	1.047815
1300	29.34	30.66	26.235	23.197	1.39	1.053077

of volume is evidently invalid (especially in the case of the longitudinal and shear moduli), since the last term in Eq. (5.2) vanishes if $M=M(V)$.

5.2. Grüneisen's Parameters and Equation of State for Alumina

Essentially, there are two Grüneisen's parameters; one given by

$$\gamma_G=\beta V/C_p\chi^s=\beta VB^s/C_p=\gamma_{G(\text{thermal})} \tag{5.4}$$

and the other

$$\begin{aligned}\psi_G&=-[\partial(\ln B^s)/\partial T/\partial(\ln V)/\partial T]_p\\&=-(1/\beta B^s)(\partial B^s/\partial T)_p=\psi_{G(\text{thermal})},\end{aligned} \tag{5.5}$$

where β is the coefficient of volume thermal expansion, V is the volume, B^s is the adiabatic bulk modulus, C_p is the specific heat at constant pressure, and χ^s is the adiabatic compressibility. These parameters give a *measure* of the anharmonicity of the interatomic potential, and they are useful in the study of the solid equation of state.[26–30] In Table IX, these parameters are tabulated as a function of temperature. The data on thermal expansion are due to Wachtman *et al.*[3] and Schauer.[4] The data on specific heats were taken from tables presented by the National Bureau of Standards.[5] It is seen here that the first Grüneisen parameter, often termed Grüneisen's ratio, remains almost constant with temperature above 200°K (which is about $0.2\theta_D$). This constancy supports the Grüneisen theory of solids.

The parameters defined by Eqs. (5.4) and (5.5) are *thermal* Grüneisen's ratio and *thermal* Grüneisen's anharmonic parameter, respectively, and it can be shown easily that they are related to the pressure derivatives of the elastic moduli. The relationship between γ_G and (dB/dp), with two simplifying assumptions,[27] was given first by Slater. The Slater relation[27] is

$$\gamma_{\text{Slater}}=\tfrac{1}{2}(\partial B^T/\partial p)_T-\tfrac{1}{6} \tag{5.6}$$

and from our data $\gamma_{\text{Slater}}=1.95$. The general relationship between γ_G and (dM/dp) is based on a correspondence relation that, within the quasiharmonic approximation,[29]

$$\gamma_{G(\text{thermal})}=\gamma_{G(\text{acoustic})}, \tag{5.7}$$

where

$$\gamma_{G(\text{acoustic})}=\sum\gamma_iC_i(\nu_i)/\sum C_i(\nu_i), \tag{5.8}$$

where

$$\gamma_i=-d(\ln\nu_i)/d(\ln V), \tag{5.9}$$

and $C_i(\nu_i)$ are Einstein's specific heats of the ith mode having the frequency ν_i. In terms of the single-crystal elastic constants and their first pressure derivatives, Smith and his collaborators[31] presented the corresponding expression for Eq. (5.9). For isotropic solids (like a strain-free glass and a polycrystalline aggregate), the equivalent expression for Eq. (5.9) is

$$\bar{\gamma}_j=-\tfrac{1}{6}+(B^T/2)(\partial\ln M_j^s/\partial p)_T, \tag{5.10}$$

---

[26] E. Grüneisen, in *Handbuch der Physik*, H. Geiger and K. Scheel, Eds. (Springer-Verlag, Berlin, 1926), Vol. X, Pt. I. For an English translation, see NASA Tech. Rept. No. RE2-18-59W (Feb. 1959).

[27] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Co., New York, 1939).

[28] F. Birch, Phys. Rev. **71,** 809 (1947); J. Geophys. Res. **57,** 227 (1952).

[29] T. H. K. Barron, Phil. Mag. **7(46),** 720 (1955); Ann. Phys. (New York) **1,** 77 (1957).

[30] J. J. Gilvarry, J. Appl. Phys. **28,** 1253 (1957); J. Appl. Phys. **33,** 3595 (1962).

[31] C. S. Smith, D. E. Schuele, and W. B. Daniels, in *Physics of Solids at High Pressures*, C. T. Tomizuka and R. M. Emrick, Eds. (Academic Press Inc., New York, 1965). See also D. E. Schuele and C. S. Smith, J. Phys. Chem. Solids **25,** 801 (1964).

where the subscript j refers to either longitudinal or transverse modes so that

$$\bar{\gamma}_l = -\tfrac{1}{6} + (B^T/2L^s)(\partial L^s/\partial p)_T \tag{5.11}$$

and

$$\bar{\gamma}_t = -\tfrac{1}{6} + (B^T/2G)(\partial G/\partial p)_T. \tag{5.12}$$

The bar over the gammas indicates $\bar{\gamma}_j = \gamma_j(\phi, \theta)$, and these $\bar{\gamma}_j$ are *isotropic*. The physical implication of Eqs. (5.11) and (5.12) is that there are acoustic longitudinal modes with the longitudinal velocity v_l and a corresponding longitudinal Grüneisen mode-gamma $\bar{\gamma}_l$, and acoustic transverse modes with transverse velocity v_t and a corresponding Grüneisen mode-gamma $\bar{\gamma}_t$.[31] Thus, the *total* Grüneisen parameter $\bar{\gamma}$ is given by (as T approaches zero)

$$\bar{\gamma} = (\bar{\gamma}_l/3)(v_m/v_l)^3 + (2\bar{\gamma}_t/3)(v_m/v_t)^3 = \bar{\gamma}_0. \tag{5.13}$$

At high temperatures, we find a similar expression to that of Smith *et al.*[31] to be

$$\bar{\gamma}_\infty = \tfrac{1}{3}(\bar{\gamma}_l + 2\bar{\gamma}_t). \tag{5.14}$$

However, it is noted that since at high temperatures the optical and short-wave acoustic modes are excited the mode-gammas corresponding to these vibrations will be affected by these modes. Equation (5.14) does not take into account these modes; therefore, $\bar{\gamma}_\infty$ obtained by Eq. (5.14) will not give the exact value of the high-temperature limit of the Grüneisen parameter, but instead it gives an approximate value which is accurate only in a first-order approximation.

Using our acoustic data, the calculated mode-gammas are as follows: $\bar{\gamma}_l = 1.58$ and $\bar{\gamma}_t = 1.22$. And the limiting values are: $\bar{\gamma}_0 = 1.26$ and $\bar{\gamma}_\infty = 1.58$, and these may be compared with $\gamma_{G(\text{thermal})}$ tabulated in Table IX.

The second Grüneisen parameter $\psi_{G(\text{thermal})}$ can be found from the acoustic data also. It has been shown by Birch[28,32] that

$$-(1/\beta B^T)(\partial B^T/\partial T)_p = (\partial B^T/\partial p)_T = \psi'_{G(\text{acoustic})}, \tag{5.15}$$

where

$$(\partial B^T/\partial p)_T = (\partial B^s/\partial p)_T + C = \psi_{G(\text{acoustic})}. \tag{5.16}$$

The dimensionless constant C is given by Overton's relation[2]

$$\begin{aligned} C = {} & [(A-1)/A][(2/\beta)(\partial \ln B^T/\partial T) - 1] \\ & + [(A^2-1)/A^2](\partial B^s/\partial p)_T \\ & + [(A-1)/A]^2[1 + (1/\beta)(\partial \ln\beta/\partial T)_p], \end{aligned} \tag{5.17}$$

where $A = C_p/C_v = B^s/B^T = 1 + \beta T\gamma_G$ and for alumina at room-temperature $C = 0.04$. Since $(dB^s/dp)_{T=298^\circ\text{K}} = 4.19$. $\psi_{G(\text{acoustic})} = 4.23$ according to Eq. (5.16); this is in good agreement with $\psi_{G(\text{thermal})} = 4.1$ but it disagrees with 3.6 found for the Lucalox.[13]

It is frequently assumed by some authors[33] that the ratio of specific heats (i.e., C_p/C_v) is unity. The implication of this assumption is that the lattice vibrations of solid under consideration are *harmonic* and that the quantity given by $(\beta T\gamma_G)$ and its temperature dependence is zero. This is a misleading assumption, and because of this assumption inconsistent formalisms are often found in the literature. Aluminum oxide is a relatively incompressible material (thus relatively low expansivity). However, as evident from Table IX, the value of $(\beta T\gamma_G)$ at room temperature is 6.6×10^{-3} and at $T \cong \theta_D$, $(\beta T\gamma_G)$ is 33.4×10^{-3}. At higher temperatures, β and γ_G approach a constant value; thus, the quantity $(\beta T\gamma_G)$ is proportional to temperature. Since $(\beta T\gamma_G)$ is inversely proportional to the lattice thermal conductivity, the high-temperature conductivities of alumina can be understood from the data.

Figure 5 shows a plot of experimental compression points of Bridgman (0–30 kbar)[9] and also those of Hart and Drickamer (0–300 kbar).[10] Also included are the shock-wave data of McQueen and Marsh[11] on both single-crystal (500–1500 kbar) and polycrystalline (300–1300 kbar) aluminas. The lines drawn in the figure are the results of the Murnaghan equation of state[24] using the acoustic parameters defined at different boundary conditions. A similar curve to Fig. 5 has been given by Anderson,[34] but Anderson used the acoustic parameters derived from the Lucalox material. What is apparent in Fig. 5 is that the Murnaghan parameters evaluated from both the single-crystal and polycrystalline acoustic data give a reasonable description of the pressure–volume relation for the experimental compression points including the shock-wave data. Finally, it may be mentioned that the Murnaghan equation of state and effects of evaluating the Murnaghan parameters at different thermodynamic boundary conditions[2] can not be seen in the scale of a plot of the kind shown in Fig. 5. Thus, on the basis of this consideration and following Murnaghan,[24] the most probable equation of state for alumina is

$$V/V_0 = (1 + 1.653\times10^{-3}p)^{-0.2364} \tag{5.18}$$

and this will describe the pressure–volume relation to pressures of a few megabars.

5.3. The Debye Temperature

Values of the Debye temperature as a function of temperature were calculated from the elastic moduli, and these have been tabulated in the last column of Table VII. The low-temperature limit of the Debye

---

[32] F. Birch, J. Geophys. Res. **73**, 817 (1968).

[33] Y. A. Chang, J. Phys. Chem. Solids **28**, 697 (1967).

[34] O. L. Anderson, J. Phys. Chem. Solids **27**, 547 (1966).