CHAPTER 8

ELASTIC GRÜNEISEN PARAMETERS OF CUBIC ELEMENTS AND COMPOUNDS

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Contents

ABSTRACT

From a material's second-order elastic-stiffness coefficients C_{ij} and its third-order elastic-stiffness coefficients C_{ijlmn}, we calculated the scalar dimensionless Grüneisen parameter γ, the single most important property of an anharmonic solid. We give γ for elements and compounds including halides, oxides, and covalent compounds.

Introduced by Grüneisen in 1912 [1], the Grüneisen parameter γ has come to mean many things to many people because it represents the most important parameter of an *anharmonic* solid. (For the harmonic case, $\gamma = 0$.) Harmonic theories of solids fail to explain such common phenomena as thermal expansion, elastic-constant temperature and pressure dependences, finite thermal conductivity, and finite internal friction. Grüneisen himself used γ in many ways (reviewed in reference 2). His basic definition was

$$\gamma = (\partial P/\partial u)_V \tag{8.1}$$

Here P denotes pressure and $u = U/V$ the internal energy per unit volume V. In the Mie–Grüneisen potential energy

$$\phi = -\frac{a}{r^m} + \frac{b}{r^n} \tag{8.2}$$

Handbook of Elastic Properties of Solids, Liquids, and Gases, edited by Levy, Bass, and Stern
Volume II: Elastic Properties of Solids: Theory, Elements and Compounds, Novel Materials, Technological Materials, Alloys, and Building Materials

ISBN 0-12-445762-2 / $35.00

Table 8.1. Elastic Grüeisen parameters γ for some cubic elements and compounds. C_{ij} and C_{ijk} units are gigapascals.

	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	γ_L	γ_H	C_{ijk} Ref.
Elements											
Al	106.75	60.41	28.34	−1076	−315	36	−23	−340	2.277	2.224	1
Ar	2.77	1.37	0.98	(−30.9)	(−18.6)	(0.47)	(0.14)	(−18.3)	3.802	3.988	2
Ca	16	8	12	(−118)	(−41)	(−6.5)	(−43)	(−24.5)	0.673	0.764	3
C(d)	1076	125	575.8	−6260	−2260	112	−674	−2860	0.986	1.010	4
Cs	2.47	1.48	2.06	−19.1	−2.6	−4.0	−5.1	−2.0	0.294	0.268	5
Cr	350.0	67.80	100.8	(−804)	(−140)	(−184)	(−184)	(−140)	−0.291	−0.278	6
Cu	169.68	122.55	74.493	−1271	−814	−50	−3	−780	1.646	2.011	7
Ge	128.53	48.26	66.80	−732	−290	216	−8	−304	0.775	0.778	8
Au	192.9	163.8	41.5	−1729	−922	−233	−13	−648	2.580	2.579	9
Fe	231.4	134.7	116.4	−2705	−626	−575	−836	−531	1.803	1.795	10
Kr	4.52	2.55	2.60	(−26.3)	(−16.7)	(0.64)	(0.37)	(−16.5)	1.119	1.110	11
Pb	49.66	42.31	14.98	(−624)	(−382)	(86)	(43)	(−405)	6.200	6.307	12
Li	13.5	11.44	8.78	(−148)	(−32)	(−47)	(−51)	(−35)	1.534	1.497	13
Mo	463.7	157.8	109.2	(−3557)	(−1333)	(−617)	(−269)	(−893)	1.379	1.392	14
Ni	248.1	154.9	124.2	−2030	−1040	−220	−138	−910	1.593	1.583	15
Nb	240.19	125.58	28.22	−2560	−1140	−467	−343	−168	1.586	1.613	16
Pd	227.1	176.04	71.73	(−1349)	(−414)	(−70)	(−497)	(−371)	0.884	0.903	17
Pt	346.7	250.7	76.50	(−1775)	(−194)	(−262)	(−826)	(−253)	0.294	0.316	18
K	3.70	3.14	1.88	−38.7	−5.7	−9.1	−11.4	−5.8	1.264	1.207	19
Si	165	64	79.2	−825	−451	−64	12	−310	0.266	0.503	20

Parentheses indicate *theoretical* third-order elastic-stiffness coefficients.

We used Hearmon's recommended C_{ij} values for 8-N compounds: R. Hearmon (1979, 1984) in *Landolt-Börnstein Zahlenwerte und Funktionen aus Naturwissenschaften und Technik*, Neue Series, Group III, volumes 11 and 18, Springer, Berlin, p. ix.

(Letters "a" and "b" denote references for the C_{ij} and C_{ijk}, respectively.)

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Table 8.1. (continued)

	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	γ_L	γ_H	C_{ijk} Ref.
Ag	122.2	90.7	45.4	−843	−529	189	56	−637	2.485	2.503	21
Na	7.39	6.22	4.19	(−93.5)	(−14.4)	(−23.0)	(−29.8)	(−17.2)	1.950	1.888	22
Sr	14.7	9.9	5.74	(−126)	(−60.3)	(−123)	(−26.9)	(−14.1)	3.049	4.316	23
W	522.39	204.37	160.83	(−546)	(−164)	(−102)	(−102)	(−164)	−0.773	−0.728	24
Xe	2.98	1.40	1.48	(−39.9)	(−24.2)	(0.68)	(0.42)	(−24.1)	4.193	4.195	25
Halides											
LiF	112	46	63.5	−1420	−264	156	85	−273	1.413	1.250	26
LiCl	49.1	22.0	24.8	(−637)	(−90.6)	(31.4)	(37.4)	(−93.6)	1.232	1.073	27
LiBr	39.4	18.9	19.1	(−598)	(−66.7)	(22.7)	(28.7)	(−69.8)	1.533	1.256	28
LiI	29.1	14.2	14.1	(−539)	(−44.4)	(14.5)	(20.5)	(−47.6)	1.967	1.534	29
NaF	97	24.2	28.1	−1480	−270	280	46	−114	1.099	1.471	30
NaCl	49.1	12.8	12.8	−864	−50	9	7	−59	1.202	1.545	31
NaBr	40.0	10.6	9.96	−659	−49	48	50	−74	1.206	1.532	32
NaI	30.2	9.0	7.36	(−478)	(−29.8)	(8.9)	(14.9)	(−33.2)	0.852	1.220	33
KF	65.0	15.0	12.5	−1078	−54	15	123	−92	0.439	1.092	34
KCl	40.5	6.9	6.27	−701	−22	13	13	−24.5	0.366	1.178	35

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Table 8.1. (continued)

	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	γ_T	γ_H	C_{ijk} Ref.
KBr	34.5	5.5	5.10	−532	−49	69	22	28	0.411	1.221	36
KI	27.4	4.3	3.70	−499	5	−95	54	−41	0.293	1.149	37
RbF	55.1	14.5	9.24	−671	−18	5	11	−17	−0.321	0.338	38
RbCl	36.4	6.3	4.70	−617	−67	87	25	−26	0.273	1.359	39
RbBr	31.5	4.8	3.82	−580	−30	28	30	−27	0.262	1.368	40
RbI	25.6	3.7	2.79	−463	−20	20	24	−22	0.193	1.335	41
CsCl	36.6	9.0	8.07	(−333)	(−42.7)	(−31.5)	(−23.5)	(−39.5)	0.770	0.942	42
CsBr	30.7	8.4	7.49	(−287)	(−40.1)	(−31.0)	(−23.0)	(−36.6)	0.846	1.012	43
CsI	24.5	6.6	6.31	(−230)	(−36.3)	(−29.8)	(−21.7)	(−32.3)	0.965	1.120	44
CuCl	45.4	36.3	13.6	−264	−172	−112	0	−21	−1.390	−0.544	45

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Table 8.1. (continued)

	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	γ_L	γ_H	C_{ijk} Ref.
AgCl	59.6	36.1	6.22	−947	−301	159	61	−64	0.653	1.862	46
AgBr	56.3	32.8	7.25	−948	−286	130	46	−68	1.325	2.194	47
TlBr	37.6	14.8	7.54	(−328)	(−140)	(−97)	(−144)	(−166)	5.679	4.687	48
TlCl	40.3	15.5	7.69	(−325)	(−154)	(−106)	(−156)	(−180)	6.029	4.845	49
CaF_2	165	46	33.9	(−1246)	(−400)	(−254)	(−124)	(−214)	0.936	1.119	50
SrF_2	124	45	31.7	−821	−309	−181	−95	−175	0.674	0.895	51
BaF_2	90.7	41.0	25.3	(−584)	(−299)	(−206)	(−121)	(−89)	0.320	0.705	52
PbF_2	88.8	47	24.5	(−239)	(−405)	(−292)	(34)	(−72)	−0.288	0.074	53
$RbMnF_3$	116	42	32	−1840	−240	40	−60	−180	1.662	1.856	54
$CsCdF_3$	108	40	25.0	−1340	−445	240	−310	−70	1.893	2.137	55

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continues

Table 8.1. (continued)

	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	γ_L	γ_H	C_{ijk} Ref.
Oxides											
MgO	294	93	155	−4900	−95	−69	113	−659	1.513	1.375	56
CaO	224	60	80.6	(−3020)	(−76)	(95)	(122)	(−340)	0.990	1.009	57
SrO	172.2	46.87	55.42	(−2630)	(−141)	(74)	(87)	(−233)	1.171	1.212	58
BaO	125.1	48.87	34.13	(−2246)	(−223)	(87)	(87)	(−223)	1.891	1.931	59
MnO	224	114	78	(−2510)	(−710)	(255)	(255)	(−710)	1.745	1.750	60
CoO	260.6	147.7	82.31	(−2412)	(−843)	(301)	(301)	(−843)	1.657	1.657	61
NiO	334.6	148.1	27.40	(−2326)	(−930)	(331)	(331)	(−930)	2.746	2.544	62
$SrTiO_3$	318.7	103.4	123.0	−4960	−770	20	−810	−300	1.775	1.803	63
$BaTiO_3$	214.0	139.5	119.1	(−2410)	(−280)	(−90)	(−90)	(−280)	0.829	0.784	64

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Table 8.1. (continued)

	C_{11}	C_{12}	C_{44}	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	γ_L	γ_H	C_{ijk} Ref.
Covalent compounds											
CdS	76	55	23	−250	−280	−190	30	−60	−1.654	−0.710	65
GaP	142	63	71.6	−737	−474	−131	−107	−234	0.251	0.565	66
GaAs	118	53.5	59.4	−622	−387	−57	2	−269	0.389	0.672	67
ZnTe	71.5	40.8	31.1	−707	−121	−412	183	−217	0.059	0.484	68
HgTe	53.2	36.8	20.8	−260	−170	−77	−17	−57	−0.518	0.002	69
PbTe	107	8.1	13.1	−1850	35	−97	44	−98	0.762	1.400	70
ZnSe	85.0	50.2	40.7	−827	−136	−511	222	−265	−0.039	0.414	71
ZnP	102	58	46	−860	−185	−510	−650	160	−0.123	0.315	72
InAs	84.4	46.4	39.6	−560	−300	−240	−140	−90	0.076	0.532	73
InSb	66.0	35.8	30.1	−314	−210	−48	9	−118	0.026	0.366	74
GaSb	88.4	40.3	43.4	−475	−308	−44	50	−216	0.377	0.672	75
Others											
KCN	19.4	12.0	1.45	−129	−55	−101	16	−27	−1.106	−0.282	76
NaCN	22.7	12.6	0.35	−162	−97	−68	24	−27	−5.920	−1.129	77

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Grüneisen related it to the repulsive-energy exponent n:

$$\gamma = \frac{n+2}{6} \tag{8.3}$$

Here, r denotes interatomic spacing and $m(<n)$ the attractive-energy exponent. Grüneisen also realized the connection of γ to θ, the characteristic temperature $h\nu/k$:

$$\gamma = -\frac{d\log\theta}{d\log V} \tag{8.4}$$

Perhaps the most familiar relationship is

$$\gamma = \frac{B\beta V}{C_P} \tag{8.5}$$

Here B denotes bulk modulus, β volume thermal expansivity, V volume, and C_P constant-pressure heat capacity.

In distinguishing adiabatic (constant entropy S) and isothermal (constant temperature T) quantities, Grüneisen showed that

$$\frac{B_S}{B_T} = \frac{C_P}{C_V} = 1 + \gamma\frac{T}{V}\frac{\partial V}{\partial T} \tag{8.6}$$

Further discussions of the thermodynamics of γ appear elsewhere [3–5].

The main purpose here is to calculate γ for a variety of cubic-symmetry elements and compounds from the second- and third-order elastic-stiffness coefficients:

$$C^S_{ijkl} = (1/V)(\partial^2 U/\partial\epsilon_{ij}\partial\epsilon_{kl})_{S,\epsilon'} \tag{8.7}$$

$$C^S_{ijklmn} = (1/V)(\partial^3 U/\partial\epsilon_{ij}\partial\epsilon_{kl}\partial\epsilon_{mn})_{S,\epsilon'} \tag{8.8}$$

We use the usual Voigt contraction scheme so that the second- and third-order elastic stiffnesses are written C_{ij} and C_{ijk}. We calculated both high- and low-temperature limits of the thermodynamic Grüneisen parameter [6, 7]:

$$\gamma_H = \frac{1}{3N}\sum_{i=1}^{3N}\gamma_i \tag{8.9}$$

$$\gamma_L = \sum_{i=1}^{3N}\frac{\gamma_i}{v_i^3}\Big/\sum_{i=1}^{3N}\frac{1}{v_i^3} \tag{8.10}$$

Here, v_i denotes wave velocity of the ith mode, and γ_i denotes the mode Grüneisen parameter, which we can calculate from [6, 7].

$$\begin{aligned}\gamma_j = -\left(\frac{1}{6w}\right)\{&2w + C_{11} + 2C_{12} + (C_{111} + 2C_{112})(N_1^2U_1^2 + N_2^2U_2^2 + N_3^2U_3^2)\\ &+ (C_{144} + 2C_{166})[(N_2U_3 + N_3U_2)^2 + (N_3U_1 + N_1U_3)^2 + (N_1U_2 + N_2U_1)^2]\\ &+ 2(C_{123} + 2C_{112})(N_2N_3U_2U_3 + N_3N_1U_3U_1 + N_1N_2U_1U_2)\}\end{aligned} \tag{8.11}$$

Here

$$\begin{aligned}w = &C_{11}(N_1^2U_1^2 + N_2^2U_2^2 + N_3^2U_3^2)\\ &+ C_{44}[(N_2U_3 + N_3U_2)^2 + (N_3U_1 + N_1U_3)^2 + N_1U_2 + N_2U_1)^2]\\ &+ 2C_{12}^S(N_2N_3U_2U_3 + N_3N_1U_3U_1 + N_1N_2U_1U_2)\end{aligned} \tag{8.12}$$

The vectors **N** and **U** denote propagation and polarization vectors of the jth normal mode. The elastic constants are expressed in Voigt's contracted notation. To calculate γ for intermediate temperatures, one uses the temperature variation of the specific heat.

Table 8.1 shows the input information and the calculated gammas. Table 8.2 shows comparisons between our results and those given by Gschneidner [8]. For unclear reasons, the γ_B values seem especially unreliable. Otherwise, agreement is fair to good.

Table 8.1 shows that the Grüneisen parameter changes little from low to high temperatures. Also, the material-to-material variation is small: γ ranges usually between 1 and 3, clustering around 2. The cluster around 2 is easily understood because, by using general thermodynamic arguments, one can show that [9]

$$(\partial B/\partial P) = 5 \tag{8.13}$$

By simply rearranging Chang's Eq. (24) [10], we can show that

$$\gamma = \tfrac{1}{2}(\partial B/\partial P - 1) \tag{8.14}$$

Then $\gamma = 2$ follows immediately.

Pearson [11] argued that the Grüneisen gamma is determined by the coordination number or the number of bonds per atom n. For covalent solids (he includes metals), he derived the relationship

$$\gamma = n/3 \tag{8.15}$$

Thus, he predicts $\gamma = 0.67$ for the zincblende structure, $\gamma = 1.33$ for the b.c.c. structure, and $\gamma = 2.00$ for the f.c.c. structure. From Table 8.1, we see that the average value for the covalent elements is $\gamma = 0.78$, for b.c.c. elements $\gamma = 1.56$ (excluding obviously wrong values), for f.c.c. elements $\gamma = 2.19$ (again excluding obviously wrong values). The covalent compounds such as GaAs also cluster around $\gamma = 0.67$.

To treat ionic solids, Pearson derived the relationship

$$\gamma = Mn/3 \tag{8.16}$$

Here M denotes the Madelung constant. Thus, for BeO ($CN = 4$) he predicts $\gamma = 1.10$. For NaCl-structure alkali halides, he predicts $\gamma = 1.75$, somewhat higher than the values in Table 8.1. For CsCl-structure alkali halides, he predicts $\gamma = 2.34$, more than double the average value ($\gamma = 1.02$) in Table 8.1 for CsCl, CsBr, and CsI obtained from *theoretical* third-order elastic stiffnesses C_{ijk}.

Table 8.2. Comparisons with previous reports.

Element	γ_H	γ_C	γ_B	γ_{SW}	γ_{lit}
Al	2.224	2.14	1.96	1.96	2.09
C(d)	1.010	0.89	1.53	—	1.18
Cu	2.011	1.96	2.93	1.93	2.00
Ge	0.778	0.80	1.56	—	—
Au	2.579	3.06	1.84	2.22	3.04
Fe	1.795	1.70	1.69	1.69	1.66
Li	1.497	0.89	1.53	—	1.18
Si	0.503	0.57	1.81	—	—
Ag	2.503	2.44	−0.32	−2.29	2.36
Na	1.888	1.31	1.16	—	1.31

γ_H = high-temperature limit, present study; γ_C = from specific heat [8]; γ_B = from bulk modulus, specific heat, thermal expansivity [8]; γ_{SW} = from shock waves [8]; γ_{lit} = average literature value [8].

Many gamma values in Table 8.1 look physically suspect. Although negative values are possible, they imply irregular physical properties, which provide a way to check the predicted gamma. Large values are hard to understand; they probably imply wrong third-order elastic-stiffness coefficients.

In summary, we showed that one can calculate the Grüneisen gamma from only the second- and third-order elastic-stiffness coefficients. Because gamma relates strongly to so many anharmonic phenomena, these same phenomena must connect with the elastic constants.

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