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Pressure dependence of the Grüneisen parameter and thermal expansion coefficient of solids

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Following the assumption of Jeanloz and Anderson, a computing model for the pressure dependence of the Grüneisen parameter and the thermal expansion coefficient has been proposed. Applying them to alkali metals and NaCl in different pressure ranges, the calculated results are found in good agreement with the experimental data. Finally, the flaw appears in other literatures have been corrected in this study.

Keywords: Grüneisen parameter, Thermal expansion coefficient, Second Grüneisen parameter

1 Introduction

Grüneisen parameter γ belongs to the most important characteristics of crystal lattice dynamics[1]. They enter into the equation of state, represent a measure of the anharmonicity of the forces acting in a crystal, and reflect the features and character of the distribution of the frequencies of the phonon spectrum and their variations under pressure.

It has both a microscopic and macroscopic definition, the former relating it to the vibrational frequencies of atoms in a material, and the latter relating it to familiar thermodynamic properties such as heat capacity, thermal expansion and isothermal bulk modulus[2]. Unfortunately, the experimental determination of γ, defined in either way, is extremely difficult; the microscopic definition requires a detailed knowledge of the phonon dispersion spectrum of a material, whereas the macroscopic definition requires experimental measurements of thermodynamic properties at high pressures and temperatures. As a result, a number of approximate expressions have been made[3–16] to study theoretically the variation of the Grüneisen parameter with high pressure and volume for several types of solids. In particular, it is worth mentioning that a self-consistent thermodynamic model has been developed by Filanovich and Povzner[17], which enables to calculate the Grüneisen parameter as a function of temperature even separately for acoustical and optical phonons.

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2 Theories

In 1996, Fang[4] assumed q to be a pressure-independent parameter, and got an expression for γ:

$$\gamma(T,P)=\gamma(T,0)\left(1+\frac{B_T'(T,0)}{B_T(T,0)}P\right)^{-\frac{q(T,0)}{B_T'(T,0)}} \quad \ldots (1)$$

where $\gamma(T,0)$ is the zero-pressure value of $\gamma(T,P)$. $B_T(T,0)$ and $B_T'(T,0)$ are the isothermal bulk modulus and its first pressure derivative at zero pressure, respectively. q is the second Grüneisen parameter, which is defined as:

$$q=\left(\frac{\partial \ln\gamma}{\partial \ln V}\right)_T \quad \ldots (2)$$

In 2003, Cui-Chen[8] made use of Chopelas approximation[18]:

$$\delta(T,P)+1=A\eta \quad \ldots (3)$$

and Anderson equation[19]:

$$\delta(T,P)=q(T,P)+B_T'(T,0)-1 \quad \ldots (4)$$

To obtain another expression of the Grüneisen parameter γ:

$$\gamma(\mathrm{T,P}) = \gamma(\mathrm{T},0)\left(1+\frac{\mathrm{B'T}(\mathrm{T},0)\mathrm{P}}{\mathrm{BT}(\mathrm{T},0)}\right)\exp\left\{\mathrm{A}\left[\left(1+\frac{\mathrm{B'T}(\mathrm{T},0)\mathrm{P}}{\mathrm{BT}(\mathrm{T},0)}\right)^{-\frac{1}{\mathrm{B'T}(\mathrm{T},0)}}-1\right]\right\} \quad \ldots (5)$$

where $\eta = V(T,P)/V(T,0)$. A is a constant, and equal to $\delta(T,0)+1$, $\delta(T,0)$ is the value of Anderson–Gruneisen parameter $\delta(T,P)$ at zero pressure.

Equations (1) and (5) have been derived by Fang[4] and Cui-Chen[8] for predicting the pressure (volume) dependence of γ of NaCl, Li, Na and K. But Jeanloz emphasized that assuming q to be a pressure-independent parameter is incompatible with the interpretation of shock wave experiment[20]. The curve of q versus V along various isotherms for MgO also shows the fallacy of expecting a single value of q to hold at all pressure regions, even for the same mineral[21]. From these considerations, Jeanloz and Anderson *et al* both suggested that q might be of the form[19, 21]:

$$q(T,P) = q(T,0)\eta^n \quad \ldots (6)$$

where n is a constant. Substituting Eq. (6) into Eq. (2) and integrating, we can obtain the following equation for Grüneisen parameter $\gamma(T,P)$ along isotherm:

$$\gamma(T,P) = \gamma(T,0)\exp\left\{\frac{q(T,0)}{n}\left[\eta^n - 1\right]\right\} \quad \ldots (7)$$

Equation (7) is a relation for the volume dependence of the Grüneisen parameter. The compression ratio $V(T,\ P)/V(T,0)$ in Eq. (7) can be calculated from the isothermal equation of state.

As a simple and phenomenological EOS, the Kumar EOS can be used to study the compressibility and the nonharmonic properties of different types of solids and show a good applicability in a wide range of pressure[22], which can be expressed as:

$$\eta = 1 - \frac{1}{B_T'(T,0)+1}\ln\left(1+\frac{B_T'(T,0)+1}{B_T(T,0)}P\right) \quad \ldots (8)$$

The Grüneisen parameter can also be indicated by:

$$\gamma = \frac{\alpha B_T V}{C_V} \quad \ldots (9)$$

where C_V is the specific heat at constant volume, α is the coefficient of volume thermal expansion. Assuming C_V is independent of volume compression and combining Eq. (7) and Eq. (9), we obtain:

$$\frac{\alpha(T,P)B_T(T,P)}{\alpha(T,0)B_T(T,0)} = \eta^{-1}\exp\left[\frac{q(T,0)}{n}\left(\eta^n - 1\right)\right] \quad \ldots (10)$$

where $\alpha(T,0)$ is the value of $\alpha(T,P)$ at zero pressure. If the following relationship[23]:

$$\frac{B_T(T,P)}{B_T(T,0)} = \exp\left(\frac{B_T'(T,0)}{s}\left(1-\eta^s\right)\right) \quad \ldots (11)$$

is substituted into Eq. (10) then the following expression for the volume compression dependence of thermal expansivity is obtained immediately:

$$\alpha(T,P) = \alpha(T,0)\eta^{-1}\exp\left[\frac{q(T,0)}{n}\left(\eta^n - 1\right) - \frac{B_T'(T,0)}{s}\left(1-\eta^s\right)\right] \quad \ldots (12)$$

In order to test the validity of Eqs (7) and (12), we apply them to the experimental data of four solids (NaCl, Li, Na, and K) in different pressure ranges. The input parameters are listed in Table 1. The values of q (T, 0) and n can be obtained by fitting the experimental data on the Grüneisen parameter under different pressure. We can get[23] S=1.078 for NaCl. Using the parameters mentioned above we calculate the values of the Grüneisen parameter and thermal expansion coefficient. The calculated results are shown in Tables 2-5, respectively. For convenience of comparison, the results given by other researcher are also listed together with our calculated results.

Table 1 — The parameters required for calculations

Crystal	T (K)	$B_T(T,0)$ (Ref. [3]) (kbar)	$B_T'(T,0)$ (Ref. [3])	$q(T,0)$	n
NaCl	300	238.41	4.999	1.806	5.049
	550	197.86	5.362	1.053	-9.519
	800	157.39	5.728	0.992	-7.096
Li	298	119.8	3.55	2.228	6.850
Na	298	64.0	3.62	2.746	10.381
K	298	34.0	2.99	1.972	1.996

Table 2 — Pressure dependence of the Grüneisen parameter of NaCl at 300 K

P (kbar)	*H*	(Ref.[8])	This work	Literature (Ref.[24])
0	1.000	1.6275	1.6275	1.6275
4.19	0.983	1.5816	1.5799	1.5590
8.35	0.968	1.5433	1.5416	1.5380
13.90	0.950	1.5008	1.4999	1.5130
19.33	0.934	1.4667	1.4663	1.4740
23.46	0.923	1.4445	1.4448	1.4410
29.18	0.909	1.4183	1.4195	1.4200
31.89	0.902	1.4073	1.4075	1.4030
RMSD		0.0099	0.0094	

3 Results and Discussion

3.1 Outcomes for NaCl

From Tables 2 and 3, we can see that, the calculated values are in good agreement with the experimental data in 300 K. The root mean square deviation (RMSD) is 0.0094. In the previous theoretical calculation, the RMSD of Cui-Chen[8] was minimum, which was 0.0099. The results of this paper are also slightly better than them. In 550 K, the RMSD is 0.0013 and in 800 K, the RMSD is 0.0016. This is a slight improvement compared with the previous best results[4].

From Table 4, among the four methods of calculating the coefficient of thermal expansion under high pressure, the RMSD of this work is also the smallest that is 0.00302.

Table 3 — Pressure dependence of the Grüneisen parameter of NaCl at 550 K and 800 K

P	550 K				800 K			
(kbar)	η	Fang[4]	This work	Literature (Ref.[25])	η	Fang[4]	This work	Literature (Ref.[25])
0	1.000	1.6581	1.6851	1.6851	1.000	1.7591	1.7591	1.7591
2	0.9894	1.6638	1.6653	1.6661	0.9879	1.7339	1.7370	1.7363
4	0.9807	1.6438	1.6475	1.6470	0.9768	1.7108	1.7150	1.7143
6	0.9720	1.6250	1.6282	1.6277	0.9656	1.6893	1.6911	1.6923
8	0.9632	1.6073	1.6070	1.6077	0.9563	1.6693	1.6697	1.6698
10	0.9555	1.5905	1.5869	1.5867	0.9470	1.6506	1.6467	1.6464
RMSD		0.0025	0.0013			0.0027	0.0016	

Table 4 – Pressure dependence of the thermal expansion coefficient ($10^{-4}K^{-1}$) of NaCl at T = 300 K

P (kbar)	Literature (Ref.[24])	This work	Literature (Ref.[26])	Literature (Ref.[28])	Literature (Ref.[29])
0	1.1752	1.1752	1.1752	1.1752	1.1752
2	1.1218	1.1219	1.1257	1.1234	1.1252
4	1.0737	1.0741	1.0804	1.0757	1.0801
6	1.0299	1.0310	1.0386	1.0318	1.0393
8	0.98997	0.99183	1.0001	0.9912	1.0021
10	0.95321	0.95609	0.9645	0.9535	0.9682
15	0.8900	0.8927	0.8862	0.8700	0.8948
20	0.8300	0.8315	0.8206	0.8000	0.8344
25	0.7900	0.7939	0.7650	0.7400	0.7838
30	0.7300	0.7374	0.7173	0.6900	0.7408
RMSD		0.00302	0.011	0.022	0.008

Table 5 – Pressure dependence of the Grüneisen parameter in Li, Na, and K at T = 298 K

P	Li				Na				K			
(kbar)	*H*	(Ref.[8])	This work	Literature (Ref.[30])	*H*	(Ref.[8])	This work	Literature (Ref.[30])	*H*	(Ref.[8])	This work	Literature (Ref.[30])
0	1.000	0.9800	0.98	0.9800	1.000	1.2100	1.21	1.2100	1.000	1.2700	1.27	1.2700
5	0.962	0.9173	0.9084	0.9000	0.933	1.0937	1.0563	1.0500	0.889	1.0125	1.0327	1.0200
10	0.929	0.8712	0.8614	0.8500	0.883	1.0258	0.9988	1.0000	0.820	0.8959	0.9193	0.9200
15	0.901	0.8361	0.8301	0.8400	0.842	0.9831	0.9709	0.9800	0.769	0.8329	0.8486	0.8600
20	0.876	0.8087	0.8072	0.8200	0.808	0.9550	0.9560	0.9600	0.729	0.7957	0.7999	0.8100
25	0.854	0.7870	0.7904	0.8000	0.779	0.9361	0.9473	0.9400	0.697	0.7728	0.7646	0.7600
30	0.834	0.7696	0.7774	0.7600	0.754	0.9234	0.9419	0.9400	0.671	0.7587	0.7382	0.7300
RMSD		0.0133	0.0111			0.0209	0.0053			0.0171	0.0083	

3.2 Outcomes for Li, Na and K

From Table 5, we can clearly see that the calculated Grüneisen parameters and the experimental results are in good agreement for the three kinds of crystals in 298 K. Compared with the best results of Cui-Chen[8]; it has been improved to some extent.

Finally, it should be mentioned that, Nie[6] and Chuan-Hui[7] misunderstood the meanings of Jeanloz[20] and Anderson *et al.*[21] and consider Eq. (6) as follows[6,7]:

$$q(T,P)=q(T,0)\left(\frac{V(T,P)}{V(T_R,0)}\right)^n \quad \ldots (13)$$

where T_R is reference temperature. Combining Eqs (13) and (2), Nie and Chuan-Hui got an expression as follows[6,7]:

$$\gamma(T,P)=\gamma(T,0)\exp\left\{\frac{q(T,0)}{n}\left[\left(\frac{V(T,P)}{V(T_R,0)}\right)^n-1\right]\right\} \quad \ldots (14)$$

All of the above process is flawed obviously, for the integration combining Eqs (13) and (2) should be along isotherm. But in Eq. (13), the expression of volume compression is $V(T,\ P)/V(T_R,0)$, so Eq. (14) cannot be obtained from the integration if T is not equal to T_R.

4 Conclusions

A simple computing model has been proposed for pressure dependence of the Grüneisen parameter and the thermal expansion coefficient. Calculated values with the model for NaCl, Li, Na and K in different pressure ranges under study were given. The calculated values are found to show fairly in good agreement with available experimental data. Due to the simplicity of the method, it may be extended to more complex solids like minerals of geophysical importance and application.

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