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Equation Of State And Thermoelastic Properties Of Some Binary Solids And Geophysical Minerals

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Abstract

The Holzapfel equation of state based on the adapted polynomial of second order and the Thomas-Fermi model has been used in the present study to predict pressure-volume relationship, bulk modulus and its pressure derivatives for some binary solids and geophysical minerals viz. NaCl, NaF, LiF, CaF_2, SiC, MgO, CaO, $MgSiO_3$, $CaSiO_3$ and $Mg_3Al_2Si_3O_{12}$. The results thus obtained have been used in the reciprocal gamma relationship between the Grüneisen parameter and the ratio of pressure and bulk modulus. Values of Grüneisen parameter and its volume derivatives have been computed in the present study which are useful for investigating high derivative thermoelastic properties of materials.

Keywords : Equation of state, thermoelastic properties, Grüneisen parameter, Binary solids, Geophysical minerals, Reciprocal gamma relationship.

1. Introduction

The adapted polynomial of second order (AP2) equation of state (EOS) due to Holzapfel (1996, 1998) has been used in the present study to determine thermoelastic properties of some binary solids and geophysical minerals. The Grüneisen parameter γ is an important property related to thermal and elastic properties of materials (Anderson, 1995; Stacey and Davis, 2004; Stacey and Hodgkinson, 2019). We make use of the reciprocal gamma relationship between $1/\gamma$ and P/K, the ratio of pressure and bulk modulus. We determine first-and second order volume derivatives of γ with the help of the relationship between $1/\gamma$ and P/K (Shanker et al., 2017). In the present study we report also the results for higher order pressure derivatives of bulk modulus for the solids under study.

2. Method of Analysis

The Holzapfel AP2 EOS can be written as follows

$$P = 3K_0 x^{-5}(1-x)[1+C_2 x(1-x)]\exp[C_0(1-x)] \quad (1)$$

where $x = (V/V_0)^{1/3}$, V_0 is the volume V at P = 0. K_0 is the bulk modulus K at P = 0, and

$$C_0 = -\ln\left(\frac{3K_0}{P_{FG0}}\right) \quad (2)$$

where P_{FGO} is the pressure of Fermi gas written as follows

$$P_{FGO} = a_{FG}\left(\frac{Z}{V_0}\right)^{5/3} \quad (3)$$

Here a_{FG}=0.02337 GPa nm^5, Z is the total number of electrons per molecule multiplied by the Avogadro number, V_0 is the volume in cm^3/mol. The parameter C_2 is determined using the relationship

$$C_2 = \frac{3}{2}(K'_0 - 3) - C_0 \tag{4}$$

Here K'_0 is the pressure derivative of bulk modulus $K' = dK/dP$ at zero pressure. An expression for bulk modulus and its pressure derivatives can be obtained from Eq. (1) using the relationships

$$K = -V\frac{dP}{dV} = -\frac{x}{3}\frac{dP}{dx} \tag{5}$$

$$K' = \frac{dK}{dP} = -\frac{x}{3K}\frac{dK}{dx} \tag{6}$$

and

$$KK'' = K\frac{d^2K}{dP^2}$$
$$= \frac{x^2}{9K}\left(\frac{d^2K}{dx^2}\right) - K'\left(K' + \frac{1}{3}\right) \tag{7}$$

Equation (5) yields the following expression for K as a function of x

$$K = K_0\left[5x^{-5} + (C_0 + 4C_2 - 4)x^{-4} + (C_0C_2 - C_0 - 6C_2)x^{-3} + (2C_2 - 2C_2C_0)x^{-2} + C_0C_2x^{-1}\right]\exp C_0(1-x) \tag{8}$$

Values of dK/dx and d^2K/dx^2 can be determined by differentiating Eq. (8) with respect to x. Finally, we have determined values of P, K, K' and KK" for different solids at changing values of volume compression V/V_0. The input parameters used in calculations are given in Table 1 and the results are given in Table 2. For determining γ and its volume derivatives, we use the following relationships (Shanker et al., 2017).

$$\frac{1}{\gamma} = A + B\frac{P}{K} \tag{9}$$

where A and B are material dependent constant given below

$$A = \frac{1}{\gamma_0} \tag{10}$$

and

$$B = K'_\infty\left(\frac{1}{\gamma_\infty} - \frac{1}{\gamma_0}\right) \tag{11}$$

The subscripts 0 and ∞ present values at zero-pressure and infinite pressure, respectively. We have used the following identity (Knopoff, 1963)

$$\left(\frac{P}{K}\right)_\infty = \left(\frac{1}{K'_\infty}\right) \tag{12}$$

where K'_∞ is the value of pressure derivative of bulk modulus $K' = dK/dP$ at infinite pressure. The second order Grüneisen parameter q is defined as

$$q = \frac{d\ln\gamma}{d\ln V}$$
$$= B\gamma(1 - K'P/K) \tag{13}$$

and the third order Grüneisen parameter

$$\lambda = \frac{d\ln q}{d\ln V}$$
$$= \frac{(KK'')P/K}{(1 - K'P/K)} + K' + q \tag{14}$$

We have used equations (9) - (14) to find values of γ, q and λ using the results given in Table 2. We have taken $\gamma_\infty = 1/2$ and $K'_\infty = 5/3$ according to the model due to Burakovsky and Preston (2004) and recently supported by Anand (2025). Values of γ, q and λ as a function of V/V_0 are shown in Figures 1-10.

3. Discussion and Conclusions

Values of pressure P and bulk modulus K increase with decreasing V/V_0 down to 0.60 for all the solids under study such that P/K incrases with the increase in volume compression $(1-V/V_0)$. On the other hand, K' decreases with the increase in pressure such that Eq. (12) is satisfied in the limit of extreme compression (V→0) or infinite pressure. The second pressure derivative of bulk modulus, $K''=d^2K/dP^2$ is found to be negative for all solids at different values of compression V/V_0. It should be mentioned that K" is negative since K' decreases with the increase in pressure. The magnitude of K'' decreases with the increase in pressure, and tends to zero in the limit of infinite pressure. The results given in Figures 1-10 reveal that γ, q and λ all decrease with decreasing volume ratio V/V_0 or increasing pressure. The extreme values of γ, i.e. $\gamma_\infty = 1/2$, q_∞ tends to zero and $\lambda_\infty = 1/3$ for all the materials under study (Shanker et al., 2007).

Table 1
Values of input parameters used in computational work (Anderson, 1995; Shim et al., 2000; Sunil et al 2024; Yongtao et al. 2012)

	V_0 (cm^3/mol)	K_0(GPa)	K'_0	C_0	C_2	γ_0
NaCl	27.02	24.0	5.35	2.70	0.83	1.59
NaF	16.41	46.5	5.28	2.30	1.12	1.72
LiF	9.84	66.5	5.30	1.95	1.50	1.63
CaF_2	24.55	81.7	5.22	2.14	1.19	1.90
SiC	12.48	241	2.84	1.20	–1.44	1.06
MgO	11.25	162	4.15	1.69	0.04	1.54
CaO	16.75	111	4.85	1.96	0.81	1.35
$MgSiO_3$	23.85	261	4.0	1.48	0.02	1.50
$CaSiO_3$	27.45	232	4.80	1.61	1.09	1.92
$Mg_3Al_2Si_3O_{12}$	112.61	173	4.0	2.79	–1.29	1.19

Table 2

Results for pressure P (GPa), bulk modulus K (GPa), pressure derivatives of bulk modulus K' and KK" at different values of volume compression V/V_0 determined from the Holzapfel AP2 EOS

	V/V_0	P	K	K'	KK"
NaCl	1.00	0	24.00	5.35	-9.10
	0.95	1.41	31.24	4.95	-6.97
	0.90	3.34	40.44	4.61	-5.47
	0.85	5.98	52.20	4.33	-4.37
	0.80	9.59	67.37	4.09	-3.55
	0.75	14.55	87.14	3.89	-2.92
	0.70	21.43	113.2	3.70	-2.42
	0.65	31.06	148.0	3.54	-2.03
	0.60	44.72	195.3	3.39	-1.71

	V/V_0	P	K	K'	KK"
NaF	1.00	0	46.50	5.28	-9.24
	0.95	2.73	60.29	4.87	-7.06
	0.90	6.44	77.69	4.53	-5.53
	0.85	11.50	99.81	4.25	-4.41
	0.80	18.38	128.1	4.01	-3.57
	0.75	27.79	164.8	3.80	-2.93
	0.70	40.76	212.8	3.61	-2.43
	0.65	58.80	276.3	3.45	-2.03
	0.60	84.22	362.0	3.30	-1.71

	V/V_0	P	K	K'	KK"
LiF	1.00	0	66.50	5.30	-9.90
	0.95	3.903	86.25	4.86	-7.49
	0.90	9.216	111.0	4.50	-5.81
	0.85	16.43	142.4	4.21	-4.60
	0.80	26.24	182.3	3.96	-3.71
	0.75	39.60	233.6	3.74	-3.02
	0.70	57.95	300.4	3.55	-2.49
	0.65	83.35	388.3	3.38	-2.07
	0.60	119.0	505.9	3.23	-1.74

	V/V_0	P	K	K'	KK"
CaF_2	1.00	0	81.70	5.22	-9.16
	0.95	5	105.6	4.81	-7.00
	0.90	11	135.7	4.47	-5.48
	0.85	20	173.8	4.19	-4.37
	0.80	32	222.4	3.96	-3.54
	0.75	48	285.2	3.75	-2.91
	0.70	71	367.0	3.57	-2.41
	0.65	102	475.0	3.40	-2.01

0.60	145	620.0	3.26	-1.69

SiC

V/V_0	P	K	K'	KK"
1.00	0	241.0	2.84	-1.64
0.95	13.30	278.2	2.76	-1.40
0.90	29.51	322.4	2.69	-1.19
0.85	49.42	375.4	2.63	-1.01
0.80	74.08	439.5	2.57	-0.86
0.75	104.9	518.0	2.52	-0.72
0.70	143.9	615.5	2.48	-0.61
0.65	194.0	738.3	2.44	-0.51
0.60	259.2	895.8	2.40	-0.42

MgO

V/V_0	P	K	K'	KK"
1.00	0	162.0	4.15	-4.88
0.95	9.241	199.3	3.93	-3.98
0.90	21.22	245.0	3.73	-3.28
0.85	36.80	301.7	3.56	-2.73
0.80	57.18	372.6	3.41	-2.29
0.75	84.04	462.2	3.27	-1.93
0.70	119.8	576.7	3.15	-1.64
0.65	167.8	725.2	3.04	-1.40
0.60	233.4	920.9	2.93	-1.19

	V/V_0	P	K	K'	KK"
CaO	1.00	0	111	4.85	-7.54
	0.95	6.443	141	4.51	-5.90
	0.90	15.05	179	4.22	-4.70
	0.85	26.57	226	3.98	-3.80
	0.80	42.01	285	3.77	-3.12
	0.75	62.82	362	3.59	-2.58
	0.70	91.10	461	3.43	-2.16
	0.65	130	591	3.28	-1.81
	0.60	184	764	3.15	-1.53

	V/V_0	P	K	K'	KK"
$MgSiO_3$	1.00	0	261	4.00	-4.48
	0.95	14.83	319	3.79	-3.68
	0.90	33.92	389	3.61	-3.05
	0.85	58.59	476	3.45	-2.55
	0.80	90.65	584	3.31	-2.15
	0.75	133	720	3.18	-1.82
	0.70	188	894	3.07	-1.55
	0.65	262	1117	2.96	-1.32
	0.60	363	1410	2.86	-1.13

	V/V_0	P	K	K'	KK"
$CaSiO_3$	1.00	0	232	4.80	-7.75
	0.95	13.45	294	4.45	-6.04
	0.90	31.37	371	4.16	-4.79
	0.85	55.24	467	3.91	-3.87
	0.80	87.11	588	3.70	-3.16
	0.75	130	742	3.52	-2.61
	0.70	188	940	3.35	-2.17
	0.65	267	1199	3.20	-1.82
	0.60	376	1541	3.07	-1.53

V/V_0	P	K	K'	KK"

$Mg_3Al_2Si_3O_{12}$	1.00	0	173	4.00	-4.17
	0.95	9.820	211	3.81	-3.40
	0.90	22.47	258	3.64	-2.80
	0.85	38.85	316	3.49	-2.32
	0.80	60.18	390	3.37	-1.93
	0.75	88.23	482	3.25	-1.61
	0.70	125	601	3.15	-1.35
	0.65	176	757	3.06	-1.13
	0.60	244	964	2.98	-0.95

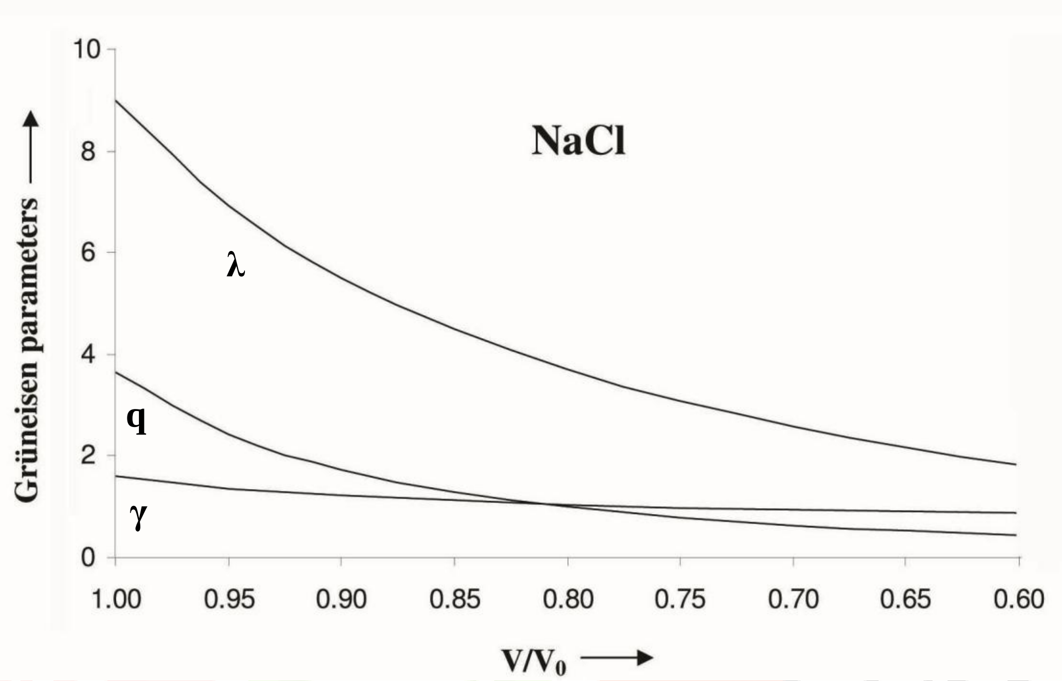

Figure 1 : Plots of Grüneisen parameters γ, q and λ versus volume compression (V/V_0) for NaCl

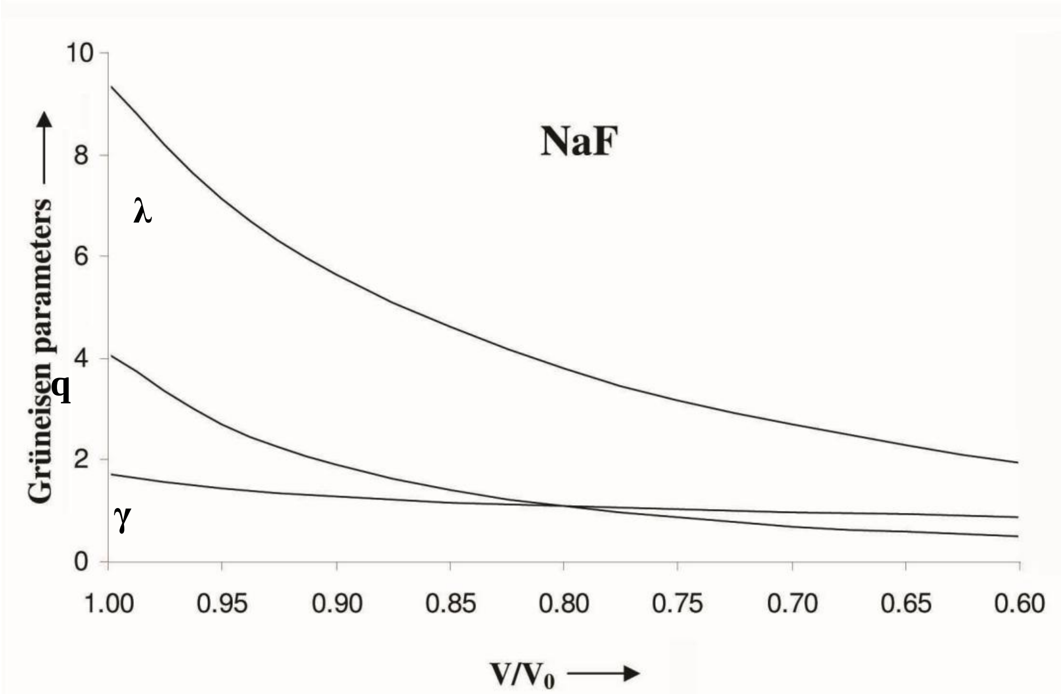

Figure 2 : Plots of Grüneisen parameters γ, q and λ versus volume compression (V/V_0) for NaF

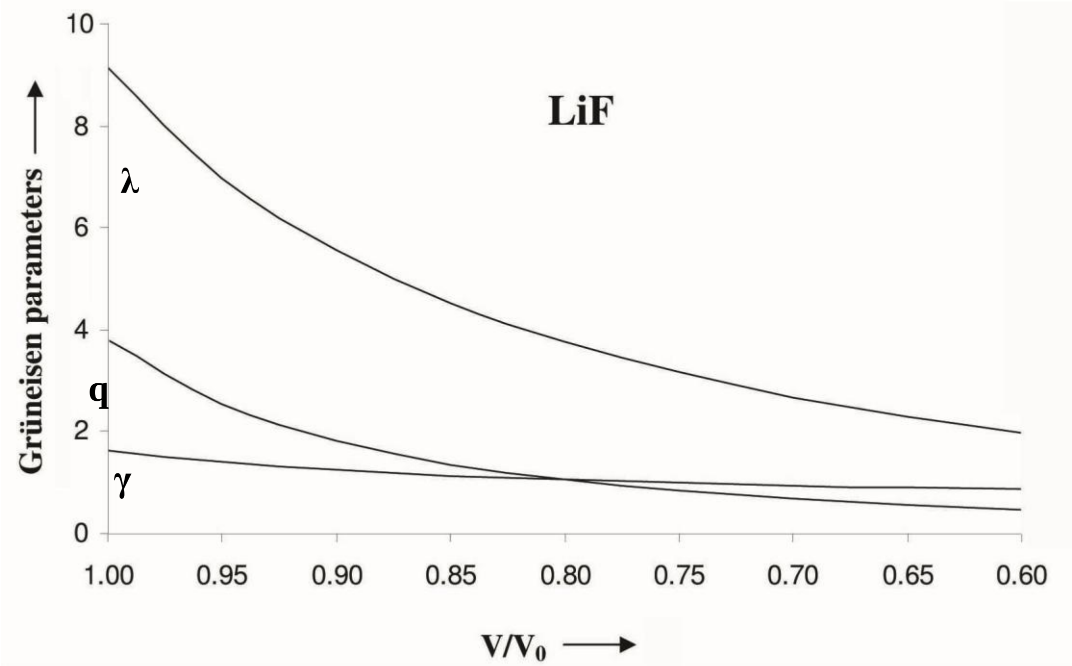

Figure 3 : Plots of Grüneisen parameters γ, q and λ versus volume compression (V/V_0) for LiF

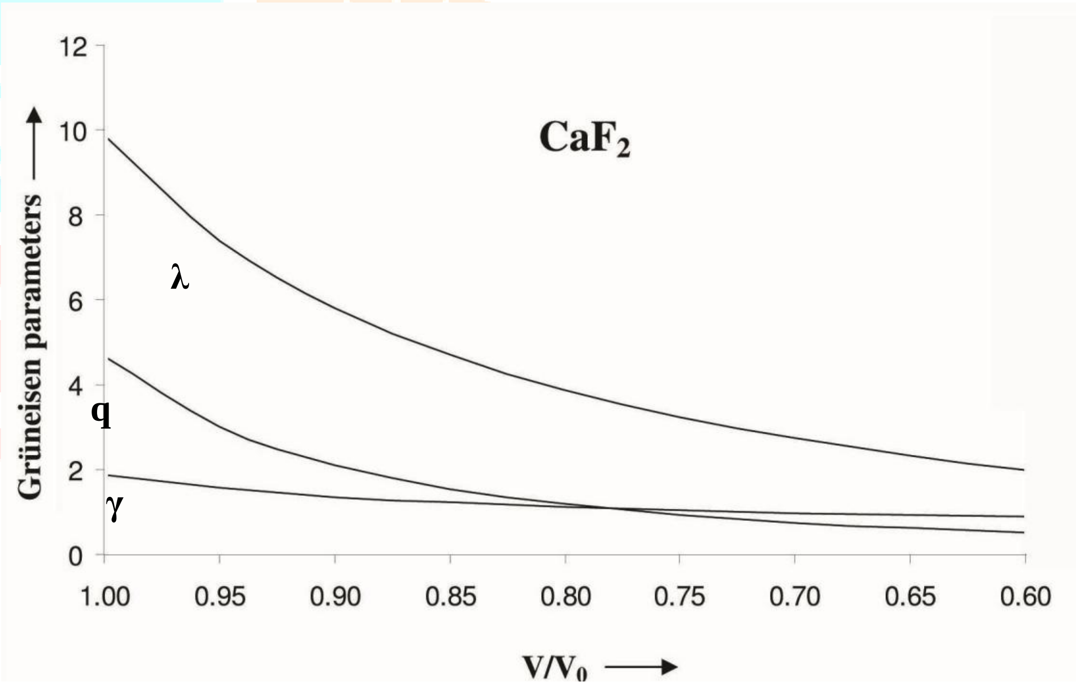

Figure 4 : Plots of Grüneisen parameters γ, q and λ versus volume compression (V/V_0) for CaF_2

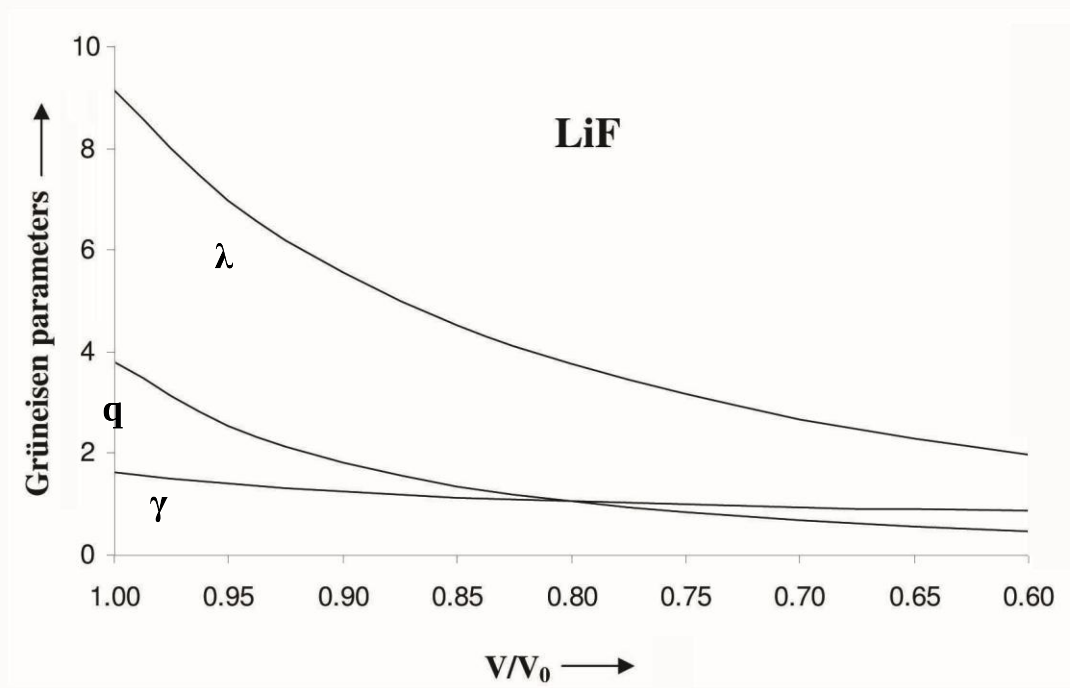

Figure 5 : Plots of Grüneisen parameters γ, q and λ versus volume compression (V/V_0) for LiF

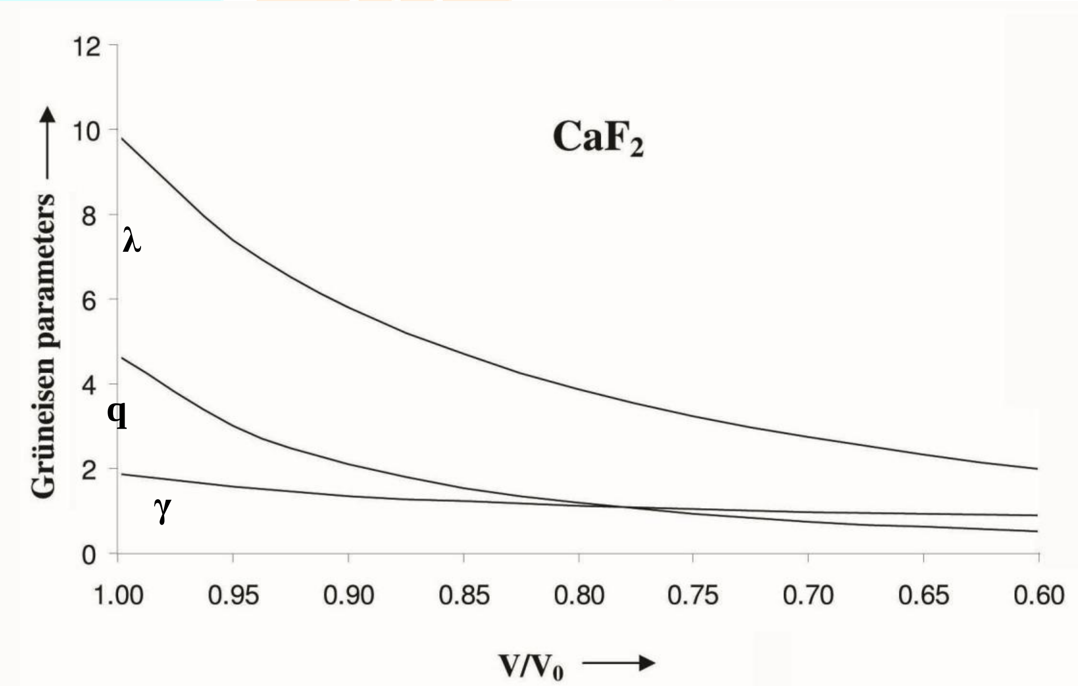

Figure 6 : Plots of Grüneisen parameters γ, q and λ versus volume compression (V/V_0) for CaF_2

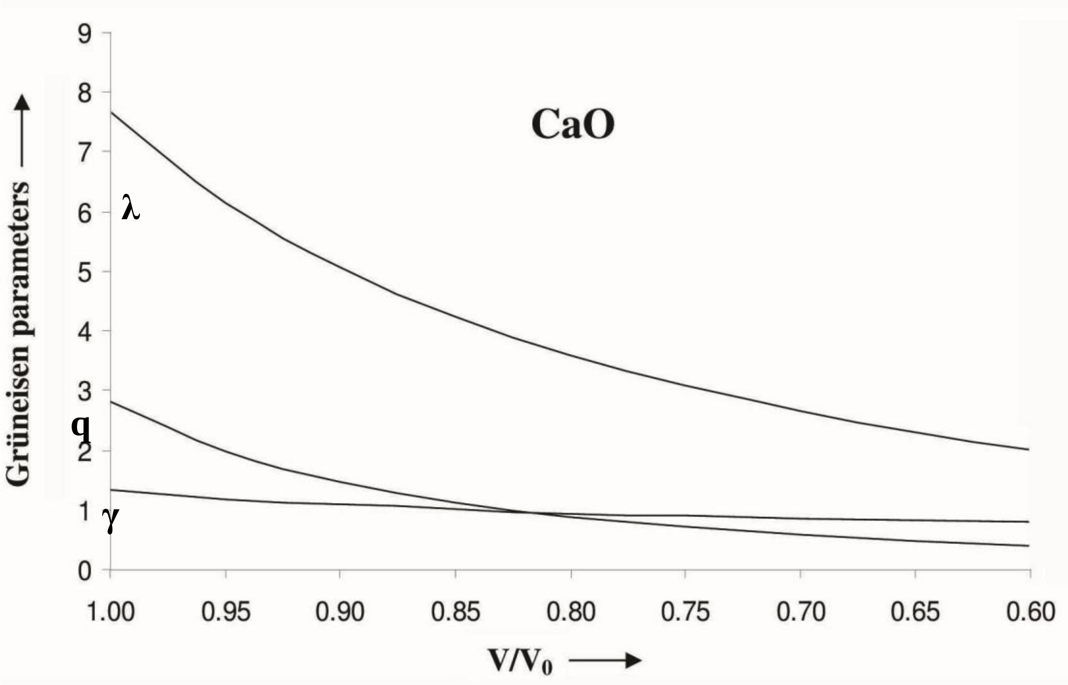

Figure 7 : Plots of Grüneisen parameters γ, q and λ versus volume compression (V/V_0) for CaO

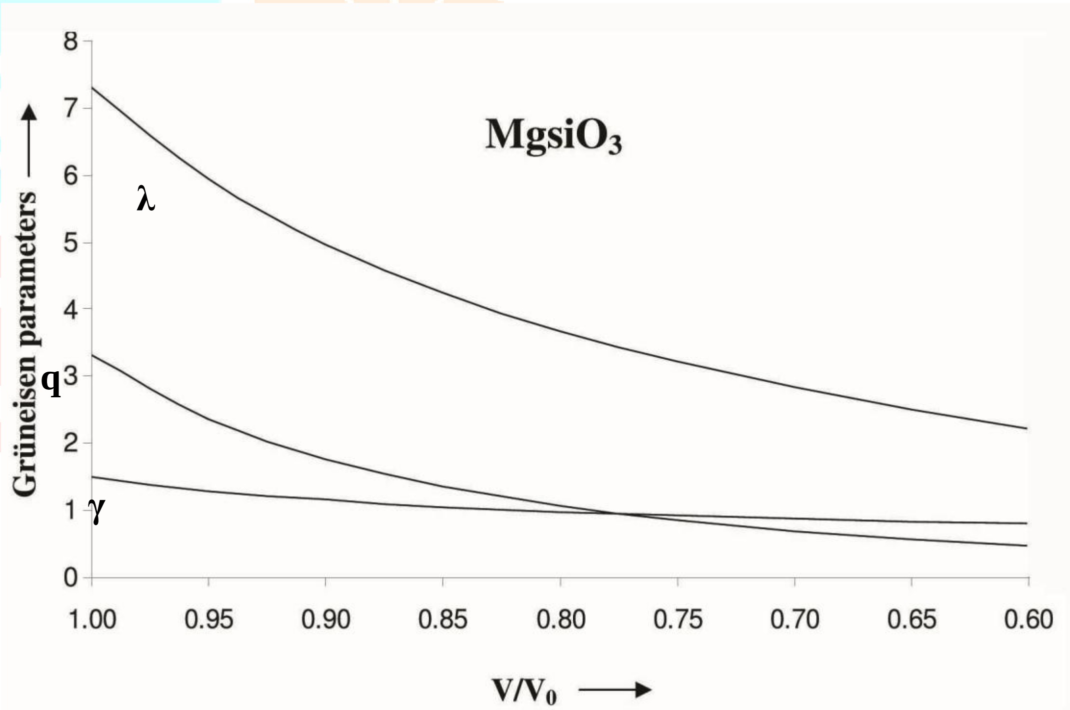

Figure 8 : Plots of Grüneisen parameters γ, q and λ versus volume compression (V/V_0) for $MgSiO_3$

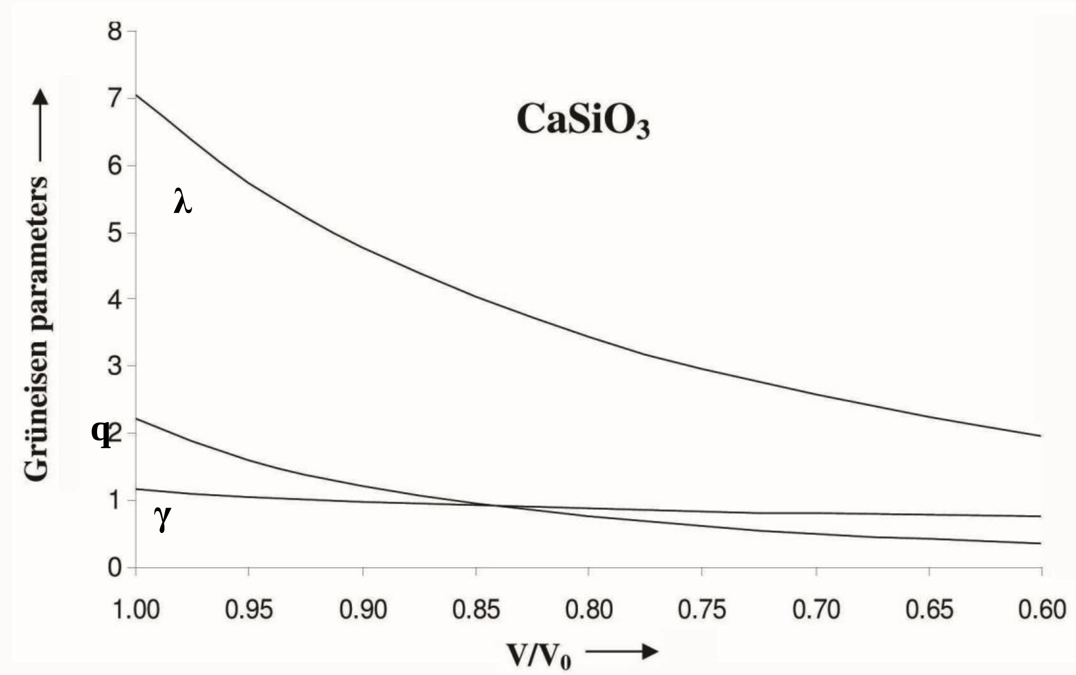

Figure 9 : Plots of Grüneisen parameters γ, q and λ versus volume compression (V/V_0) for $CaSiO_3$

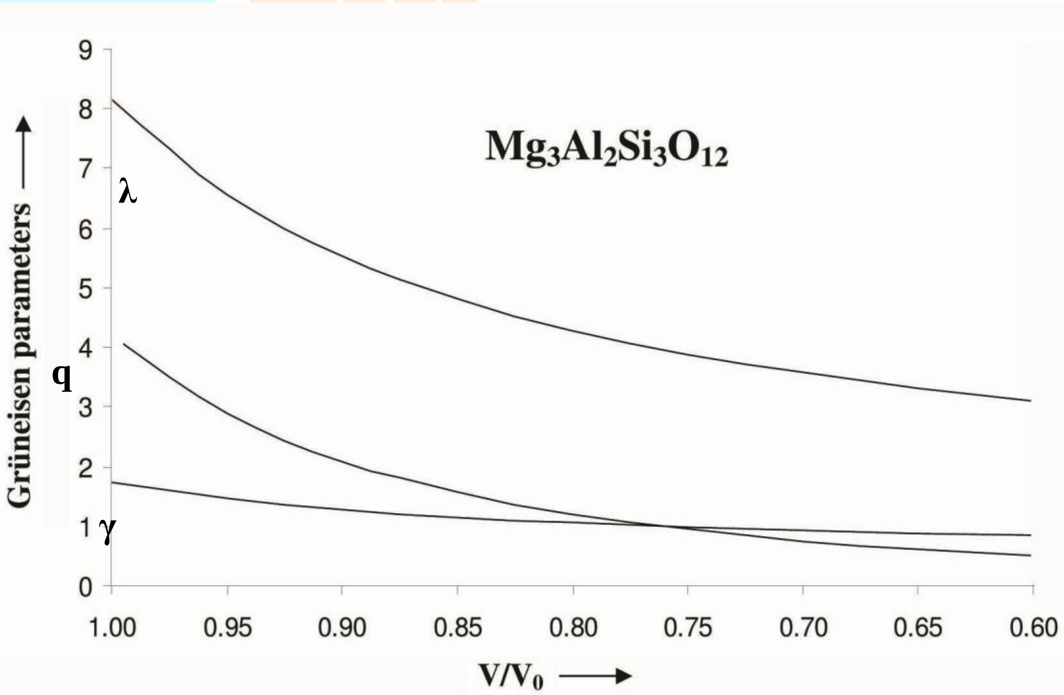

Figure 10 : Plots of Grüneisen parameters γ, q and λ versus volume compression (V/V_0) for $Mg_3Al_2Si_3O_{12}$

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