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DOI <http://dx.doi.org/10.1016/j.jpcs.2011.10.008>

**Volume-Based Thermoelasticity:**  
**Thermal expansion coefficients and the Grüneisen Ratio**

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**2 Figures**

**1 Supplementary Table**

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## Abstract

In an extension of our current studies of volume-based thermodynamics and thermoelasticity (VBT), we here consider the parameters at ambient temperature of the dimensionless Grüneisen ratio (or Grüneisen parameter),  $\gamma_{th}$ , which is a standard descriptor of the thermophysical properties of solids:

$$\gamma_{th} = \alpha K_T V_m / C_v = \alpha V_m / \beta C_v$$

It has earlier been established that the isothermal volume compressibility,  $\beta$  (which is the reciprocal of the bulk modulus,  $K_T$ ), and the ambient-temperature heat capacity,  $C_p$ , are strongly linearly correlated with the molar volume,  $V_m$ , among groups of materials with similar structures. Here, we examine possible correlations between the volumetric thermal expansion coefficient,  $\alpha$  (the remaining Grüneisen parameter), and molar volume. Using the high-temperature limiting value,  $\alpha^\circ$ , as a surrogate for  $\alpha$ , we find that  $\alpha$  is essentially uncorrelated with volume among a range of materials.

As a consequence of the lack of correlation through volume of  $\alpha$  with the other Grüneisen parameters, we conclude that the dimensionless Grüneisen ratio at ambient temperatures itself is thereby poorly constant across materials and cannot be reliably used for predictive purposes. It is noted that, for thermodynamic reasons, the values of  $\gamma_{th}$  generally range from about 0.5 to 3, clustering around 2.

## 1. Introduction

Thermodynamics is fundamental to understanding of the behaviour of materials, both chemical and physical. Experimental thermodynamics is, however, not much practised because it is demanding and difficult; as a consequence, thermodynamic data is unavailable for many materials. This data absence can, at least partially, be filled by theoretical methods but these, too, are demanding and require specialist expertise. This provides the opportunity for the use of empirical predictive methods based upon extrapolations from the behaviour of related materials. While the resulting values may be approximate, they fill important data gaps.

Over recent years, colleagues and I have developed empirical volume-based thermodynamic (VBT) correlations by which thermodynamic quantities, such as entropies, heat capacities, lattice enthalpies and formation enthalpies, may be reliably estimated by linear correlation with molar (or formula unit) volume,  $V_m$ , across ranges of generally ionic materials, independent of structural details.[1-4] Extending beyond standard chemical thermodynamics, we have lately also examined thermoelastic relations, observing that compressibility,  $\beta$ , is proportional to formula volume within groups of materials of similar structure and with a common anion (for example, silicate clinopyroxenes ( $ABSi_2O_6$ ), chalcopyrites ( $ABX_2$ ) and perovskites ( $ABO_3$ )).[5, 6]

The thermodynamic and thermoelastic parameters of a solid are conveniently related through the dimensionless Grüneisen ratio (or Grüneisen parameter):[7-10]

$$\gamma_{th} = \alpha K_T V_m / C_v = \alpha V_m / \beta C_v$$

where  $C_v$  = heat capacity under conditions of constant volume

and

$$C_v = C_p - \alpha^2 V_m K_T T = C_p - \alpha^2 V_m T / \beta$$

with  $C_p$  = heat capacity under conditions of constant pressure

$$\alpha, \text{ the coefficient of cubic thermal expansion, } = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_p$$

while the compressibility,  $\beta$  or  $\kappa$ , is defined by

$$\beta, \kappa = -\frac{1}{V} \left( \frac{\partial V_m}{\partial p} \right)_T = \frac{1}{B}, \frac{1}{K_T}$$

Here, the bulk modulus,  $B$  or  $K_T$ , which is the reciprocal of the coefficient of isothermal compressibility, represents the resistance to bulk compression of the material (also known as the incompressibility) and is the form generally favoured by geophysicists.

The Grüneisen ratio, which relates thermophysical constants of solid ionic materials, sets limitations on the thermophysical properties of materials.[7, 10] It is variously defined: in particular it has definitions both in the microscopic domain and in the macroscopic domain. In the microscopic domain it relates to vibrational frequencies within the solid while in the macroscopic version (which is the form under consideration here),  $\gamma_{th}$  measures the change in pressure resulting from an increase in energy density at constant volume. In its macroscopic form, it enters into equations of state (EoS) for matter in condensed phases and thus is of particular value in respect of high-temperature and -pressure conditions, for example in the study of the earth's interior and, more generally, in the study of the extra-terrestrial planets. Its value at ambient pressure is generally close to 2, lying roughly between 0.5 and 3. It is very approximately independent of

temperature and generally decreases in value as the volume decreases under pressure.[7-9]

Since the linear relations between  $\beta$  and  $V_m$  and between  $C_p$  and  $V_m$  under ambient conditions have previously been established,[1, 5, 6] it becomes worthwhile to consider whether a further relation can be established between the thermal quantities,  $\alpha$  and  $V_m$ , which would then illuminate the behaviour of the Grüneisen ratio across materials. (Note: the difference between  $C_p$  and  $C_v$  is small for solids and graphs of  $C_p$  and  $C_v$  versus  $V_m$  show very similar behaviour, so that they will be considered to be equivalent for present purposes.)

There are established thermodynamic reasons (which are noted elsewhere[11, 12]) which explain the clustering of the Grüneisen ratio around a value of 2, as follows:

$$\gamma_{th} = \frac{1}{2} \left( \frac{\partial K_T}{\partial p} - 1 \right) \approx \frac{1}{2} (5 - 1) = 2$$

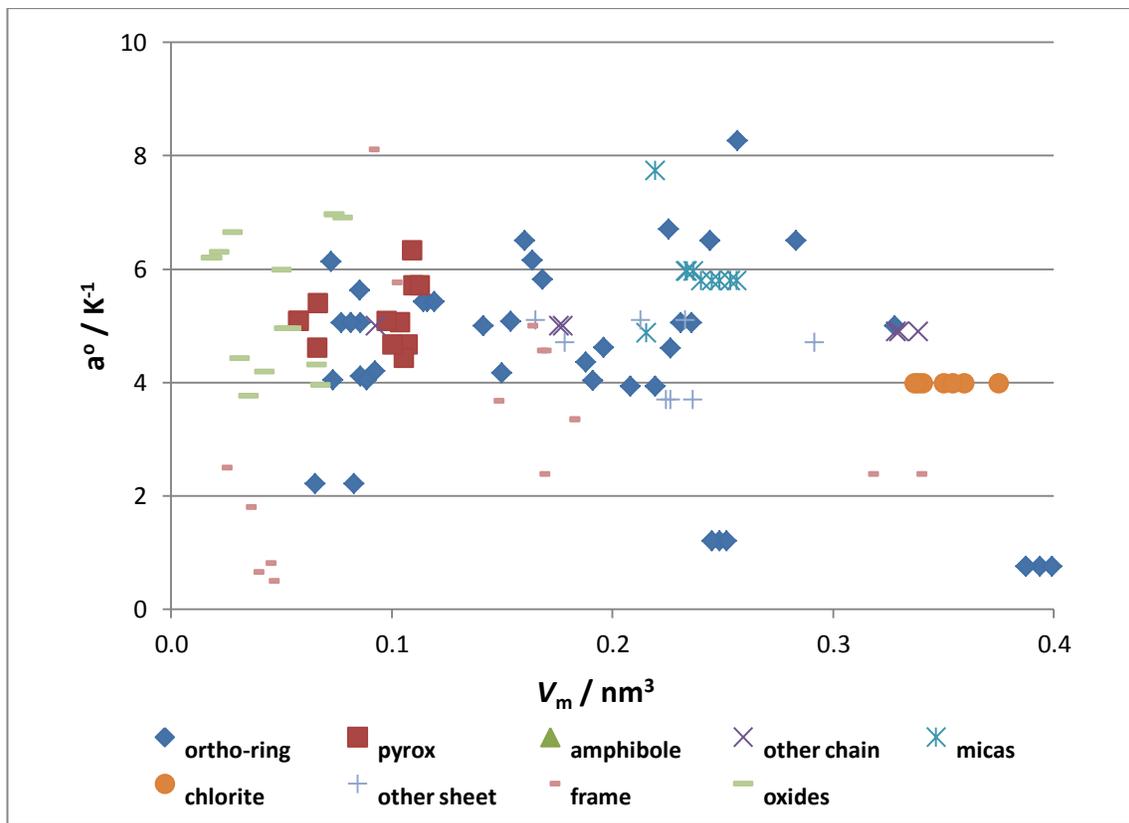
$$\text{using the relation [13]: } \left( \frac{\partial K_T}{\partial p} \right) \approx 5$$

## 2. Results

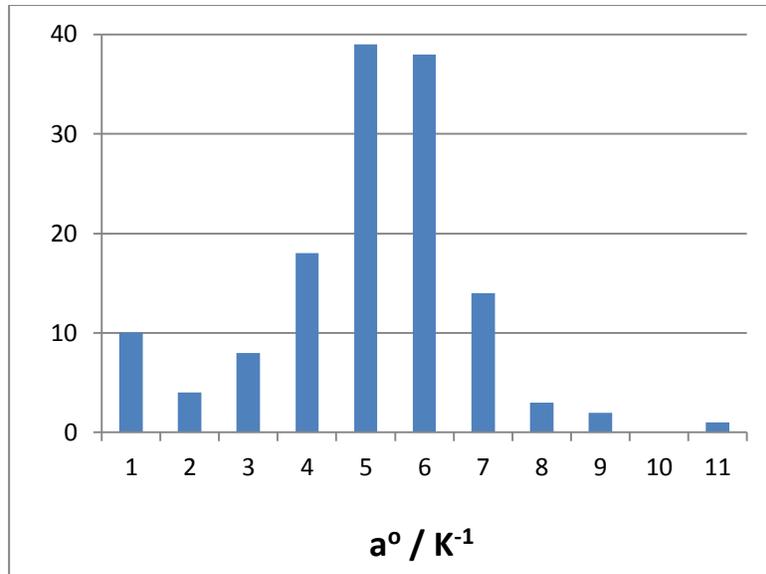
In the extensive compilation of Holland and Powell,[14] the cubic thermal expansion coefficient,  $\alpha_T$ , is represented by a thermal expansion parameter,  $a^o$  (with the equivalent units,  $K^{-1}$ ), which corresponds to its high-temperature limit. While this is not the exact quantity required for the Grüneisen ratio, it will serve as a suitable surrogate and, indeed,

has the useful feature that it provides values at the equivalent corresponding state for all the materials here considered.

Fig. 1 is a plot of this thermal expansion parameter,  $a^0$ , versus  $V_m$  for a wide range of inorganic materials. There is no reasonable correlation discernible. It may be observed in Fig. 2 that  $a^0$  ranges in value from about 1 to 10, centred quite strongly around 5 and 6.



**Figure 1:** Plot of the thermal expansion parameter,  $a^0$ , versus formula unit volume,  $V_m$ , for a wide range of inorganic materials. No reasonable correlation can be discerned.



**Figure 2:** Frequency distribution of the thermal expansion parameter,  $a^\circ$ . The ten materials with the lowest values of  $a^\circ$  are quartzes (classified as framework structures) and 6-member ring magnesium aluminium cyclosilicates (cordierites and osumilites).[14]

### 3. Discussion and Conclusion

Since the cubic thermal expansion parameter,  $a^\circ$ , does not show any reasonable correlation with volume, in contrast with the compressibility,  $\beta$ , and heat capacity,  $C_V$  or  $C_P$ , we can conclude that the Grüneisen ratio itself is thereby poorly correlated with volume across different materials. The small variability which is observed may be ascribed to the range in values of the thermal expansion parameter seen in Fig. 1, from about 1 to 10, quite strongly centred around 5 and 6.

As a consequence of these observations, we may conclude that simple empirical relations will be unsuitable for prediction of values of the Grüneisen ratio among ionic solids.

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**Table S1:** Thermal expansion parameter,  $a^{\circ}$ , versus formula unit volume,  $V_m$ , for a wide range of inorganic materials, from the extensive compilation of Holland and Powell.<sup>1</sup>

<b>End-member<sup>a</sup></b>	<b>V</b> <b>/ nm<sup>3</sup></b>	<b><math>a^{\circ}</math></b> <b>/ K<sup>-1</sup></b>
<b>Ortho-Ring</b>		
akermanite	0.1537	5.08
almandine	0.1911	4.03
andalusite	0.0856	4.11
andradite	0.2193	3.93
clinohumite	0.3278	5.00
clinozoisite	0.2263	4.60
epidote	0.2310	5.05
fayalite	0.0769	5.05
Fe-chloritoid	0.1159	5.42
Fe-cordierite	0.3937	0.76
Fe-epidote	0.2356	5.05
Fe-staurolite/3	0.2484	1.20
ferrosumilite	0.6363	0.80
forsterite	0.0725	6.13
gehlenite	0.1499	4.17
grossular	0.2082	3.93
hydrous cordierite	0.3873	0.76
kyanite	0.0733	4.04
larnite	0.0857	5.05

lawsonite	0.1682	5.82
merwinite	0.1635	6.15
Mg-chloritoid	0.1142	5.42
Mg-cordierite	0.3873	0.76
Mg-staurolite/3	0.2450	1.20
Mn-chloritoid	0.1191	5.42
Mn-cordierite	0.3990	0.76
Mn-staurolite/3	0.2516	1.20
monticellite	0.0855	5.63
osumilite(1)	0.6292	0.76
osumilite(2)	0.6383	0.76
phase A	0.2564	8.26
pumpellyite	0.4907	5.00
pyrope	0.1879	4.36
rankinite	0.1603	6.50
sillimanite	0.0828	2.21
spessartine	0.1958	4.62
sphene	0.0924	4.20
spurrite	0.2441	6.50
tephroite	0.0814	5.05
tilleyite	0.2829	6.50
hydroxytopaz	0.0887	4.04
vesuvianite/10	0.1415	5.00
zircon	0.0652	2.22
zoisite	0.2254	6.70
<b>Pyroxenes</b>		
acmite	0.1073	4.66
Ca-schermak pyroxene	0.1055	4.43
diopside	0.1099	5.70
enstatite	0.1040	5.05
ferrosilite	0.1095	6.32
hedenbergite	0.1128	5.70
jadeite	0.1003	4.66
Mg-schermak pyroxene	0.0978	5.08
pseudowollastonite	0.0666	5.39
pyroxmangite	0.0577	5.08
rhodonite	0.0580	5.08
wollastonite	0.0663	4.60
<b>Amphiboles</b>		
anthophyllite	0.4407	5.00
cummingtonite	0.4372	5.00
Fe-glaucophane	0.4415	5.30
Fe-anthophyllite	0.4628	5.00
ferroactinolite	0.4696	5.34
gedrite	0.4284	4.80
glaucophane	0.4326	5.30

grunerite	0.4623	5.00
pargasite	0.4515	5.34
riebeckite	0.4565	5.30
tremolite	0.4528	5.34
tschermakite	0.4450	5.34
<b>Other</b>		
deerite/10	0.0926	5.00
Fe-carpholite	0.1775	5.00
Fe-sapphirine	0.3386	4.90
Mg-carpholite	0.1759	5.00
sapphirine(221)	0.3300	4.90
sapphirine(793)	0.3284	4.90
<b>Micas</b>		
annite	0.2563	5.79
celadonite	0.2331	5.96
eastonite	0.2450	5.79
Fe-celadonite	0.2366	5.96
margarite	0.2153	4.87
Mn-biotite	0.2535	5.79
muscovite	0.2339	5.96
Na-phlogopite	0.2400	5.79
paragonite	0.2194	7.74
phlogopite	0.2485	5.79
<b>Chlorites</b>	0.0000	
Al-free chlorite	0.3597	3.98
amesite	0.3408	3.98
clinochlore	0.3502	3.98
daphnite	0.3544	3.98
Fe-sudoite	0.3388	3.98
Mn-chlorite	0.3751	3.98
sudoite	0.3371	3.98
<b>Other</b>	0.0000	
antigorite/10	0.2914	4.70
chrysotile	0.1784	4.70
Fe-talc	0.2362	3.70
kaolinite	0.1650	5.10
prehnite	0.2329	5.10
pyrophyllite	0.2127	5.10
talc	0.2263	3.70
tschermaks talc	0.2243	3.70
<b>Oxides</b>		
baddeleyite	0.0351	3.76
corundum	0.0425	4.19
geikielite	0.0512	4.95
hematite	0.0503	5.99
hercynite	0.0677	3.95

ilmenite	0.0526	4.95
lime	0.0278	6.65
magnesioferrite	0.0740	6.96
magnetite	0.0739	6.96
manganosite	0.0220	6.30
nickel oxide	0.0182	6.20
periclase	0.0187	6.20
pyrophanite	0.0546	4.95
rutile	0.0313	4.43
spinel	0.0661	4.31
ulvospinel	0.0777	6.90
<b>Hydroxides</b>		
brucite	0.0409	13.00
diaspore	0.0295	7.97
goethite	0.0346	7.97
<b>Framework</b>		
albite	0.1662	4.56
analcite	0.1617	5.00
anorthite	0.1674	2.38
coesite	0.0343	1.80
cristobalite	0.0433	0.81
heulandite	0.5281	2.38
high albite	0.1679	4.56
kalsilite	0.1003	5.76
laumontite	0.3383	2.38
leucite	0.1466	3.67
meionite	0.5643	3.16
microcline	0.1809	3.35
nepheline	0.0900	8.10
quartz	0.0377	0.65
sanidine	0.1810	3.35
stilbite	0.5458	2.38
stishovite	0.0233	2.50
tridymite	0.0448	0.50
wairakite	0.3162	2.38

<sup>a</sup> The formulae of very complex materials have been divided by an appropriate factor, for example vesuvianite/10, in order that their weighting in fitting processes is not excessive.

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