

Table 4. Comparison of experimental and theoretical values of $\partial \ln \gamma / \partial \ln V$ and δ_s at 295°K

	γ_{th}			$\frac{\partial \ln \gamma}{\partial \ln V}$			δ_s			
	Theory	Experiment	Theory	[13]	Experiment	[b]	Theory	Experiment	[b]	[c]
		[a]	This paper							
LiBr	2.48	1.94	3.5		2.0[d]		8.7	4.1[d]		
LiI	2.38	2.19	3.4		1.9[e]		8.4	4.0[e]		
NaF	1.86	1.51	2.3		1.22		5.3	3.75		
NaCl	1.69	1.62	2.0		1.40		4.8	3.87		
NaBr	1.75	1.65	1.9		1.75		4.8	4.13		
NaI	1.72	1.71	1.9	1.44	0.05[f]	1.77	0.67[f]	4.6	2.58[f]	3.22
KF	1.71	1.52	2.4		1.57		5.3	4.12		
KCl	1.59	1.49	2.1	1.64	1.77		4.9	4.41		
KBr	1.69	1.50	2.0		1.37		5.1	4.05		
KI	1.27	1.54	2.0	1.37	-0.40[f]	1.26	0.47[f]	4.7	2.14[f]	2.94
RbF	1.66	1.40	2.9		2.07		5.7	5.05		
RbCl	1.45	1.39	2.2	1.82	1.44[f]	2.14	1.92[f]	5.0	4.06[f]	4.68[f]
RbBr	1.37	1.42	2.2	1.86	1.09[f]	1.99	1.58[f]	4.9	3.74[f]	4.44[f]
RbI	1.32	1.56	2.4	1.91	0.12[f]	1.91	1.34[f]	5.1	3.05[f]	4.35
NaCl (i)	1.70						4.8			
NaCl (ii)	1.82						5.1			
NaCl (iii)	1.70						4.8			

[a] Tabulated in Refs. [43, 45, 48].

[b] Tabulated in Ref. [12].

[c] Tabulated in Ref. [13].

[d] Calculated from data in Refs. [43, 42].

[e] Calculated from data in Refs. [43, 44].

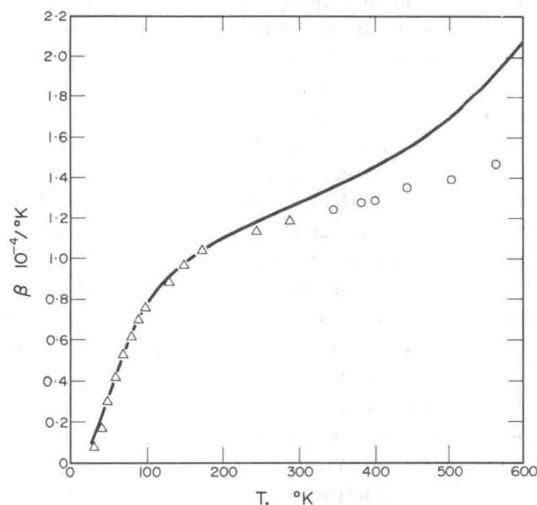
[f] Calculated at $V(P=0, T=0)$.

Fig. 1. Coefficient of thermal expansion in NaCl as a function of temperature. — lattice model calculation. Experimental data: ○ Ref. [58], △ Ref. [57].

amount which increases with temperature. The inclusion of higher order anharmonic terms would help to correct this problem[7].

The predictions of $\partial \ln \gamma / \partial \ln V$ are in general better than those of Barsch and Achar[13], but somewhat worse than those of Roberts and Rupp[12]. The large errors for LiBr, LiI, NaF and NaCl are probably a result of the neglected anharmonic terms. While this correction would also improve the calculated results for the other alkali halides, it is unlikely to be large enough to bring them into agreement.

δ_s does not depend as strongly on thermal effects as does $\partial \ln \gamma / \partial \ln V$. The present calculation is in better agreement with experiment than that of Ref. [13], although the error is somewhat larger than expected.

Most of the experimental and theoretical values for $\partial \ln \gamma / \partial \ln V$ and δ_s from Ref. [13] refer to a slightly contracted volume corresponding to $P=0$ at $T=0$. The correction back to zero pressure at room temperature is smaller than the experimental error in these quantities.

6. CALCULATIONS AT HIGH PRESSURE

6.1 The behavior of γ at high pressure

Uncertainty as to the variation of the Grüneisen parameter with volume is a major problem in high pressure physics. Figure 2 plots the present model calculation of γ along the Hugoniot as a function of volume for fourteen alkali halides. The different plots are displaced vertically for clarity on this log-log graph.

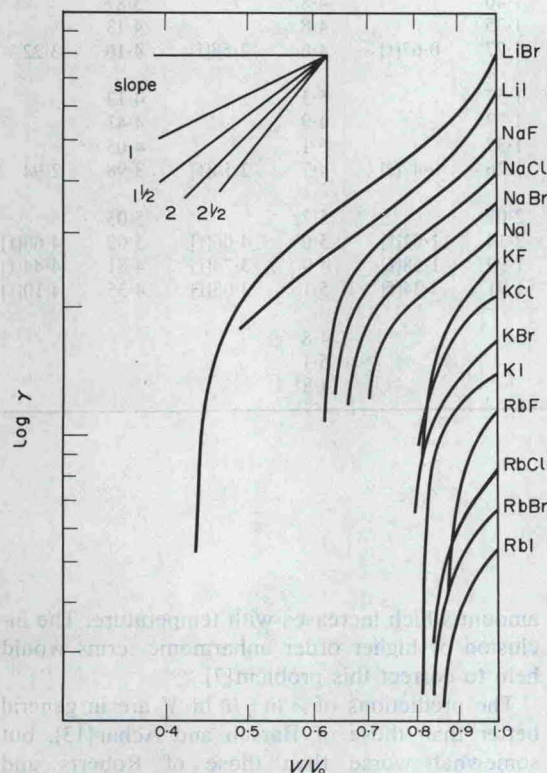


Fig. 2. Model calculation of the Grüneisen parameter as a function of volume for fourteen alkali halides. Graphs are displaced vertically for clarity.

Three different types of behavior of $\gamma(V)$ can be seen. They are:

- (i) An initial steep slope caused essentially by the fact that under pressure the coulombic forces increase less rapidly than the short range forces. This effect is most noticeable in LiBr, LiI and NaF, but is mostly canceled by other factors in the other alkali halides.
- (ii) A region of nearly linear decrease, with a relatively shallow slope.
- (iii) Another region of sharp decrease, arising from soft modes.

The third region is a precursor of an instability caused by a zero frequency transverse acoustic mode occurring, in the present model calculation, in the (1, 0, 0) direction at the Brillouin Zone boundary. In actual practice, a phase transition to the B2(CsCl) structure occurs before this steep dip is too pronounced. However, the soft modes are also important in determining the slope in region (ii) and in counteracting the coulomb effect in region (i).

The calculated instabilities are generally consistent with known transitions that occur under pressure, although the calculated instabilities in NaBr ($P \approx 265$ kbar, $V/V_0 \approx 0.65$) and NaI ($P \approx 150$ kbar, $V/V_0 \approx 0.69$) seem suspiciously low, and it is unlikely that there exist undiscovered transitions at such easily accessible pressures in such common compounds.

It is interesting to note that according to the present model, for all alkali-halides the assumption that $\gamma = \gamma_0(V/V_0)^q$ with $q = 1.75$ or 2.0 would only be in error by about 10%, from zero pressure up to the region of a transition. Other simple assumptions such as that made by finite strain theory[24, 27] may be equally valid. However setting q equal to the zero pressure slope of γ in LiBr, LiI, and NaF might lead to a serious underestimation of γ at high compression.

Previous calculations of this type used a six-twelve anion-anion interaction[23]. In these calculations, there was no instability at high pressure in the sodium halides, and $\gamma(V)$ decreased to a minimum and then increased under pressure. This strange behavior of $\gamma(V)$ was a result of two related factors: a lack of mode softening under pressure, and an anion-anion force of the power law form, which increased in strength faster than the anion-cation exponential force.

While the present model calculations are more likely to be valid than the previous ones, there may exist crystals in which there are no soft modes over a wide pressure range, and in which one type of short-range force gradually becomes dominant over another. Although γ probably behaves monotonically in all the NaCl type alkali halides, it may have a local minimum in some crystals. It has generally been assumed that $\gamma(V)$ is a smooth monotonic function. A more fundamental assumption is that the potential function be composed of terms which are smooth functions of interatomic separation. This type of assumption does not necessarily imply that $\gamma(V)$ will behave monotonically. A $\gamma(V)$ which has a local minimum may be unusual, but it is not unreasonable.