PHYSICAL REVIEW VOLUME 167, NUMBER 3 15 MARCH 1968

Thermal Expansion of Alkali Halides at Low Temperatures

T. H. K. BARRON AND ALICIA BATANA
Department of Theoretical Chemistry, University of Bristol, Bristol, England

(Received 3 August 1967)

A previous calculation of the temperature variation of the Grüneisen function $[\gamma(T)=\beta V/\chi_S C_p]$ for rigid-ion models of NaCl indicated a rather deep minimum at low temperatures. No such minimum has been observed for shell models of NaI and KBr. It is here pointed out that approximations employed in the calculations on the rigid-ion model were particularly unsatisfactory at low temperatures, and that the error resulting from these approximations can be assessed independently by calculating the low-temperature limits γ_0 from the volume derivatives of the elastic constants. Such calculations indicate that there can be no deep minimum in $\gamma(T)$ for these models, in general agreement both with the shell-model calculations and with experiment. Dispersion curves for both frequency and Grüneisen parameter as a function of wave vector suggest that $\gamma(T)$ is probably monotonic at low temperatures, but the possibility of a shallow minimum (depth ~0.01) cannot be excluded.

I. INTRODUCTION

BECAUSE the thermal expansion of alkali halides becomes very small at low temperatures, its detailed behavior as $T\rightarrow 0°\text{K}$ is hard to determine experimentally. This behavior is conveniently represented by the temperature variation of the dimensionless Grüneisen function, defined by

$$\gamma(T)=3\alpha V/\chi_S C_p. \quad (1)$$

Here α is the coefficient of linear expansion, V the volume, χ_S the adiabatic compressibility, and C_p the heat capacity at constant pressure. As we shall see in Sec. II, the most precise experimental data published still leave it uncertain whether for these salts $\gamma(T)$ flattens off monotonically at low temperatures or passes through a minimum.

Evidence from theoretical models is at first sight also inconclusive. Arenstein, Hatcher, and Neuberger,[1] with rigid-ion models for NaCl, found a relatively deep minimum in γ at $T\sim 11°\text{K}$. On the other hand, Cowley and Cowley,[2] with shell models for KBr and NaI, found no such minimum. In this paper, we show that the qualitative difference between these results is due only to approximations used in the rigid-ion model calculations and not to differences between the salts or the models used for them. Although neither type of model is wholly adequate, the theoretical evidence thus suggests that there is no pronounced minimum in $\gamma(T)$ for the sodium and potassium halides. The possibility of a shallow minimum is not excluded.

II. EXPERIMENTAL EVIDENCE

The two most precise sets of measurements of the thermal expansion of alkali halides are those of White[3] and of Meincke and Graham.[4] White measured α for eight salts (LiF, NaCl, NaI, KCl, KBr, KI, RbI, and CsBr) down to helium temperatures, using a variable capacitance method with a sensitivity able to detect a change in length of about 1 part in 10^9. Meincke and Graham measured α for four salts (NaCl, NaI, KCl, and KBr) down to 7°K, using an interferometric method with a sensitivity lower by almost an order of magnitude than White's. For our present purposes we need consider only the behavior at the lowest temperatures, for $T<0.07\ \Theta_0^C$; here Θ_0^C is the equivalent Debye temperature representing the heat capacity as $T\rightarrow 0$. The two sets of measurements are in quite good agreement over this range,[5] but the fairly large experimental uncertainty allowed some difference in the interpretation of the results, particularly for NaCl.

In displaying his results White[3] made the simplest possible assumption compatible with his data, namely, that there is no minimum and that for $T\lesssim 0.03\ \Theta_0^C\ \gamma(T)$ has flattened off to its limiting low-temperature value γ_0. Since χ_S is effectively constant in this range and C_p is known accurately for most alkali halides, this assumption provides the simplest extrapolation of α down to the lowest temperatures. However, White[3] also pointed out that his accuracy did not exclude the possibility of a significant minimum in $\gamma(T)$ for $T\lesssim 0.03\ \Theta_0^C$ and suggested that values of γ_0 calculated from the pressure derivatives of experimental elastic constants might help to resolve the question. Unfortunately, experimental accuracy is not quite good enough for this purpose. For some alkali halides (including NaCl, but not KCl[6]) the values of γ_0 calculated in this way are greater than White's extrapolated values, giving some support for the existence of a minimum (see Fig. 1); but after a careful consideration of the accuracy of the elastic constants, which affects both values, Smith, Schuele, and Daniels[7] concluded that the discrepancy could be due to experimental error.

---

[1] M. Arenstein, R. D. Hatcher, and J. Neuberger, Phys. Rev. **132**, 73 (1963).

[2] E. R. Cowley and R. A. Cowley, Proc. Roy. Soc. (London) **A287**, 259 (1965).

[3] G. K. White, Proc. Roy. Soc. (London) **A286**, 204 (1965).

[4] P. P. M. Meincke and G. M. Graham, Can. J. Phys. **43**, 1853 (1965).

[5] Disagreement for KCl below about 0.04 Θ_0^C was ascribed by Meincke and Graham (Ref. 4) to a systematic error in their own results due to a high heating rate for this salt.

[6] R. A. Bartels and D. E. Schuele, J. Phys. Chem. Solids **26**, 537 (1965).

[7] C. S. Smith, D. E. Schuele, and W. B. Daniels, in *Proceedings of the First International Conference on the Physics of Solids at High Pressure*, edited by C. Tomizuka (Academic Press Inc., New York, 1965), p. 496.

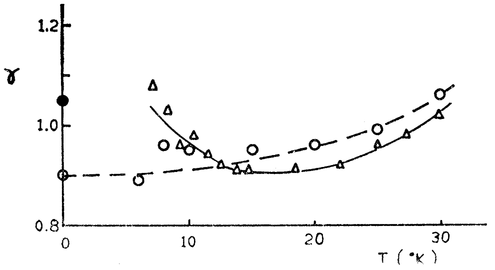

FIG. 1. Experimental values of $\gamma(T)$ for NaCl at low temperatures (Refs. 3 and 4). —○—, White; —△—, Meincke and Graham; ●, Bartels and Schuele.

The most explicit evidence for a minimum in $\gamma(T)$ was found in NaCl by Meincke and Graham[4]; instead of flattening off, $\gamma(T)$ appeared to rise again for $T \lesssim 0.04$ ($\Theta_0^C = 321°\text{K}$), although accuracy was not enough to make this certain (Fig. 1). No evidence was available for the other three salts, because the reduced temperatures (T/Θ_0^C) reached for KBr and NaI were not low enough and the results for KCl were unreliable at the lowest temperatures. The results for NaCl were compatible with a depth of the minimum equal to about one third of the total drop of $\gamma(T)$ from its high-temperature value. It was pointed out that this agreed qualitatively with the theoretical results of Arenstein *et al.*[1]

In summary, then, the experimental evidence for a significant minimum in $\gamma(T)$ for NaCl at low temperatures is slight. It consists mainly of measurements made by Meincke and Graham at the low extremity of their temperature range, which are not supported by the more precise measurements of White.

III. THEORETICAL MODELS

The rigid-ion model used by Arenstein *et al.*[1] for NaCl had Coulomb forces between the ionic charges and a central force repulsion between nearest neighbors. The shell model used by Cowley and Cowley[2] for NaI and KBr allowed also for ionic distortion.

The results of Cowley and Cowley[2] for KBr and NaI were obtained by calculating individual values of the angular frequencies $\omega(\mathbf{k},j)$ and the Grüneisen parameters,

$$\gamma(\mathbf{k},j) = -d\ln\omega(\mathbf{k},j)/d\ln V, \tag{2}$$

for normal modes with wave vectors $\mathbf{k}$ at 47 independent points of reciprocal space and replacing the integrals over reciprocal space by sums over these points. They calculated γ_0 independently from the volume dependence of sound velocities by averaging over all directions in space and extrapolated their $\gamma(T)$ curves so that they flattened off at these limiting values. The curves show no minimum at low temperatures, but this is not conclusive; averaging over a coarse mesh in reciprocal space does not give reliable estimates for γ at low temperatures. But from their dispersion curves of frequency[8] and Grüneisen parameter[2] against wave number in different directions of reciprocal space, it seems almost certain that the depth of a minimum in $\gamma(T)$ at very low temperatures will not be greater than about 0.01 and rather unlikely that there exists a minimum at all.

For NaCl, Arenstein *et al.*[1] calculated $\gamma(T)$ for a number of rigid-ion models with different force constants and interionic distances. The results for three typical models are displayed in Fig. 2, where the extrapolation to the value at $T=0°\text{K}$ has been made to satisfy the requirement that $d\gamma/dT=0$ at $T=0$. These were obtained by calculating values of $\omega(\mathbf{k},j)$ and $\gamma(\mathbf{k},j)$ for normal modes with wave vectors at 73 independent points of reciprocal space and averaging in the same way as Cowley and Cowley.[2] At high temperatures, when most of the modes are excited, this should be a good approximation; but it must break down at sufficiently low temperatures. In particular, at the temperature of the supposed minimum ($\sim 11°\text{K}$) there are only 12 modes at these points with values of $\hbar\omega/kT < 7$, and most of the points contribute negligibly to the thermodynamic properties. The mesh of points, although finer than that used by Cowley and Cowley,[2] is still not fine enough to give an accurate estimate of thermodynamic properties at these temperatures. The shape of the $\gamma(T)$ curve may therefore be unreliable in this range.

The limiting values γ_0 may be subject to even greater error. They were estimated from the relation $\gamma_0 = \gamma(-3)$, where $\gamma(-3)$ is the limiting value of

$$\gamma(n) = \sum_{\mathbf{k},j} \gamma(\mathbf{k},j)[\omega(\mathbf{k},j)]^n \Big/ \sum_{\mathbf{k},j} [\omega(\mathbf{k},j)]^n \tag{3}$$

as $n \to -3$ from above.[9] Since the frequency distribution is proportional to ω^2 at low frequencies, the sums in both the denominator and the numerator tend to infinity as $n \to -3$, although their ratio remains finite. As $n \to -3$, the contribution to both sums of long-wave acoustic modes becomes dominant, and the limiting ratio thus depends only on the elastic properties of the solid. The approximation of Arenstein *et al.*[1] was to calculate

$$\sum_{\mathbf{k},j} \gamma(\mathbf{k},j)[\omega(\mathbf{k},j)]^{-3} \Big/ \sum_{\mathbf{k},j} [\omega(\mathbf{k},j)]^{-3}$$

by taking the sums over their mesh of points in reciprocal space.[10] This can give at best only a crude estimate of γ_0, because the long-wave acoustic modes which wholly determine γ_0 all belong to an infinitesimal region about the origin $\mathbf{k}=0$.

To investigate whether the minimum in $\gamma(T)$ is a genuine property of the model it is therefore necessary to recalculate γ_0 more accurately. This can be done by

---

[8] R. A. Cowley, W. Cochran, B. N. Brockhouse, and A. D. B. Woods, Phys. Rev. **131**, 1030 (1963).

[9] T. H. K. Barron, Phil. Mag. **46**, 720 (1955).

[10] M. Arenstein, R. D. Hatcher, and J. Neuberger, Phys. Rev. **131**, 2087 (1963).

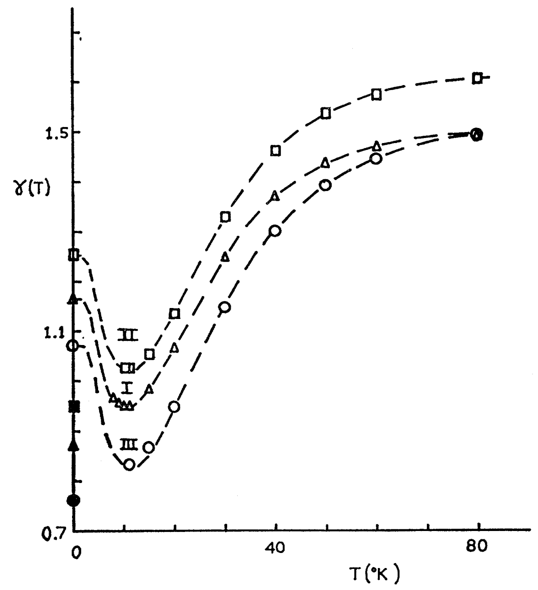

FIG. 2. $\gamma(T)$ for three rigid-ion models of NaCl (see Table I). △, ○, □, Arenstein *et al.*; ▲, ●, ■, present calculations.

taking the known volume dependence of the elastic constants $c_{\lambda\mu}$ for the model and performing a calculation essentially equivalent to that of Cowley and Cowley.[2] We have[11]

$$\gamma_0=-d\ln\Theta_0{}^C/d\ln V \tag{4}$$

$$=-\frac{1}{6}-\frac{1}{6}\frac{d\ln c_{44}}{d\ln r_1}-\frac{r_1}{9f}\left(\frac{\partial f}{\partial s}\frac{\partial s}{\partial r_1}+\frac{\partial f}{\partial t}\frac{\partial t}{\partial r_1}\right), \tag{5}$$

where r_1 is the nearest-neighbor distance and

$$s=(c_{11}-c_{44})/(c_{12}+c_{44}),\quad t=(c_{12}-c_{44})/c_{44}; \tag{6}$$

the function $f(s,t)$ is tabulated by de Launay[12,13] at sufficiently close intervals to estimate the partial derivatives to within 1 or 2%. The interionic potentials in the models of Arenstein *et al.*[1] consisted of a Coulomb potential $\pm e^2/r$ between all neighbors and a repulsive potential Ae^{-Br} between nearest neighbors. This gives for the elastic constants of the static lattice

$$c_{11}=(1/2r_1{}^4)[(3\beta+\tfrac{1}{3}\alpha)e^2+2AB^2r_1{}^3e^{-Br_1}], \tag{7}$$

$$c_{12}=(1/2r_1{}^4)[(3\eta-\tfrac{1}{3}\alpha)e^2+2ABr_1{}^2e^{-Br_1}], \tag{8}$$

$$c_{44}=(1/2r_1{}^4)[(3\eta+\tfrac{1}{3}\alpha)e^2-2ABr_1{}^2e^{-Br_1}], \tag{9}$$

where e is the electronic charge and α, β, and η are the Coulomb lattice sums:

$$\alpha=-\sum_{j\neq i}\frac{e_ie_j/e^2}{(r_{ij}/r_1)}=1.7476, \tag{10}$$

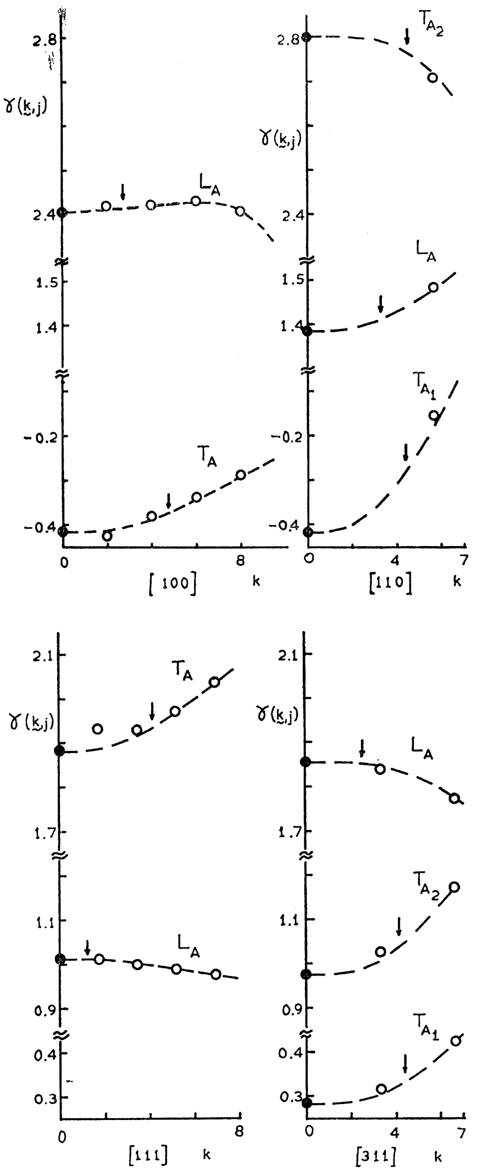

FIG. 3. Variation of $\gamma(\mathbf{k},j)$ with k for acoustic modes propagating in four different directions in model I. ○, Arenstein *et al.*; ●, present calculations. The arrows indicate modes with angular frequencies $\omega(\mathbf{k},j)\simeq10^{13}$ sec^{-1}.

$$\beta=\sum_{j\neq i}\frac{e_ie_j/e^2}{(r_{ij}/r_1)}\left(\frac{x_{ij}}{r_{ij}}\right)^4=-1.0461, \tag{11}$$

$$\eta=\sum_{j\neq i}\frac{e_ie_j/e^2}{(r_{ij}/r_1)}\frac{x_{ij}{}^2y_{ij}{}^2}{r_{ij}{}^4}=0.2318, \tag{12}$$

with the summations taken over all neighbors of the ion i.

These elastic constants are defined from the stress-strain relations rather than from the second derivatives of the Helmholtz energy, so as to give the correct

---

[11] W. B. Daniels, Phys. Rev. Letters **8**, 3 (1962).
[12] J. de Launay, J. Chem. Phys. **24**, 1071 (1956).
[13] J. de Launay, J. Chem. Phys. **30**, 91 (1959).

TABLE I. Potential parameters, interionic distances, and γ_0 values for three rigid-ion models of NaCl.

Models	$10^9 A$ (erg)	$10^{-8} B$ (cm^{-1})	$10^8 r_1$ (cm)	γ_0
I	1.474	3.048	2.814	0.87 ± 0.01
II	2.550	3.291	2.814	0.95 ± 0.02
III	2.550	3.291	2.7886	0.76 ± 0.02

velocities of long waves in a crystal under isotropic stress.[14]

Calculations were made for the three models of Fig. 2, which differ only in the values of A, B, and r_1 (see Table I). The resulting values of γ_0 are also displayed in Fig. 2. For each model, they are lower than the previous estimates by about 0.3. For models I and II, they are also inconsistent with the sharp curvature in $\gamma(T)$ found by Arenstein *et al.*[1] at low temperatures, which is thus confirmed to be seriously misleading.

Because the low-temperature values of γ (except for γ_0 itself) are uncertain, we still need to investigate the possibility of a significant minimum in $\gamma(T)$ with lower values of γ than those suggested by Arenstein *et al.* As with the shell-model calculations, we can do this by examining the variation of acoustic normal mode frequencies and Grüneisen parameters with wave vector $\mathbf{k}$. Calculated values of $\omega(\mathbf{k},j)$ and $\gamma(\mathbf{k},j)$ are available for the model I of Table I, at 73 points of reciprocal space,[15] enabling us to obtain points on dispersion curves for several different directions of $\mathbf{k}$. To supplement this information, limiting values as $\mathbf{k}\rightarrow 0$ of the velocities $\omega(\mathbf{k},j)/k$ and the Grüneisen parameters can be calculated from the elastic constants and their volume dependence,[16] and are given for four different directions of $\mathbf{k}$ in Table II; these values are accurate to at least three significant figures.

TABLE II. Limiting velocities and $\gamma(\mathbf{k},j)$ values of elastic waves in model I as $\mathbf{k}\rightarrow 0$.

Direction of propagation	L_A branch $\omega(\mathbf{k},j)/k$ (10^6 cm sec^{-1})	$\gamma(\mathbf{k},j)$	T_{A_2} branch $\omega(\mathbf{k},j)/k$ (10^6 cm sec^{-1})	$\gamma(\mathbf{k},j)$	T_{A_1} branch $\omega(\mathbf{k},j)/k$ (10^6 cm sec^{-1})	$\gamma(\mathbf{k},j)$
[100]	0.4532	2.406	0.2424	−0.416	0.2424	−0.416
[110]	0.4367	1.385	0.2709	2.800	0.2424	−0.416
[111]	0.4311	1.009	0.2617	1.881	0.2617	1.881
[311]	0.4435	1.854	0.2545	0.975	0.2478	0.283

A low-temperature minimum in $\gamma(T)$ could be due either to high dispersion in those branches of the acoustic spectrum which have low values of $\gamma(\mathbf{k},j)$ or to a decrease in $\gamma(\mathbf{k},j)$ with increasing $\mathbf{k}$. For a minimum at 11°K, only modes with $\omega(\mathbf{k},j)<10^{13}$ sec^{-1} are relevant. In this range, the calculations of Arenstein *et al.*[1] show very little dispersion in the plots of $\omega(\mathbf{k},j)$ against $\mathbf{k}$, in agreement with the independent rigid-ion model calculations of Karo and Hardy[17]; a significant minimum could therefore only arise because of strong variation of $\gamma(\mathbf{k},j)$ with $\mathbf{k}$.

Figure 3 displays the calculated values of $\gamma(\mathbf{k},j)$ for acoustic modes with four different directions of propagation. The error in the results of Arenstein *et al.*[1] is not explicitly stated, but it is likely to be greatest for low values of $\mathbf{k}$ where the small acoustic frequencies are obtained from differences between much larger quantities. The curves of $\gamma(\mathbf{k},j)$ against $\mathbf{k}$ have been drawn so as to flatten off to the values at $\mathbf{k}=0$ obtained from the elastic constants, because at sufficiently low values of $\mathbf{k}$ the velocities $\omega(\mathbf{k},j)/k$ and hence also the $\gamma(\mathbf{k},j)$ can be expanded as power series in k^2.

From these curves a low-temperature minimum in $\gamma(T)$ of depth 0.1 appears to be almost impossible. For most branches, for frequencies lower than 10^{13} sec^{-1} the variation in $\gamma(\mathbf{k},j)$ is less than 0.1; the only curve in which the variation is greater than 0.1 is the T_{A_1} mode propagating in the [110] direction, where $\gamma(\mathbf{k},j)$ is increasing with $\mathbf{k}$. These curves therefore suggest that $\gamma(T)$ is probably a monotonically increasing function of T at low temperatures, although a shallow minimum cannot be ruled out. To obtain the detailed shape of the $\gamma(T)$ curve at low temperatures more accurate calculations would be needed.

We may conclude that there is no theoretical support for the existence of an appreciable minimum in the $\gamma(T)$ curves for alkali halides at low temperatures and that consequently White's extrapolation of his experimental $\gamma(T)$ values to 0°K is probably valid to within a few percent.

ACKNOWLEDGMENT

One of us (A. B.) gratefully acknowledges a scholarship given by Consejo Nacional de Investigaciones Científicas y Técnicas of the República Argentina.

---

[14] T. H. K. Barron and M. L. Klein, Proc. Phys. Soc. (London) **85**, 523 (1965).

[15] We thank Dr. M. Arenstein for sending us these values.

[16] S. L. Quimby and P. M. Sutton, Phys. Rev. **91**, 1122 (1953).

[17] A. M. Karo and J. R. Hardy, Phys. Rev. **141**, 696 (1966).