

limiting high temperature value of the γ s more slowly than γ . Of course this theorem leads one further to anticipate that γ'' for copper and aluminum should not be independent of temperature in the entire range in which this holds for γ . For the alkali halides for which BARRON *et al.*⁽²¹⁾ have proved the accuracy of the quasi-harmonic approximation to the thermal thermodynamic functions at moderate temperatures, one would again expect that γ at atmospheric pressure should not vary significantly with temperature in a region around and below the pertinent Θ_2 . The measurements of RUBIN *et al.*⁽²⁵⁾ prove that this is true for sodium chloride.

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APPENDIX

The Quasi-Harmonic Approximation at Moderate Temperatures and the Debye Model

At temperatures above $h\nu_m/2\pi k$, where ν_m is the highest vibrational frequency of the solid, the thermodynamic functions of a quasi-harmonic non-metal are represented by their Thirring-Stern expansions⁽¹⁰⁾ in inverse powers of the absolute temperature:

$$\begin{aligned} \frac{F_{\text{vib}}}{3NkT} &= \frac{F_{\text{th}}}{3NkT} + \frac{1}{2} \frac{h}{kT} \mu_1 \\ &= \ln \left[\frac{h}{kT} \left(\prod_j \nu_j \right)^{1/3N} \right] \end{aligned} \quad (\text{A.1})$$

$$- \sum_{n=1}^{\infty} (-1)^n \frac{B_{2n}}{2n(2n)!} \left(\frac{h}{kT} \right)^{2n} \mu_{2n}$$

$$\begin{aligned} \frac{S}{3Nk} &= -\ln \left[\frac{h}{kT} \left(\prod_j \nu_j \right)^{1/3N} \right] \\ + 1 - \sum_{n=1}^{\infty} (-1)^n \frac{B_{2n}}{(2n)!} \frac{2n-1}{2n} \left(\frac{h}{kT} \right)^{2n} \mu_{2n} \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned} \frac{W_{\text{vib.}}}{3NkT} &= \frac{W_{\text{th.}}}{3NkT} + \frac{1}{2} \frac{h}{kT} \mu_1 = 1 \\ - \sum_{n=1}^{\infty} (-1)^n \frac{B_{2n}}{(2n)!} \left(\frac{h}{kT} \right)^{2n} \mu_{2n} \end{aligned} \quad (\text{A.3})$$

$$\frac{C_V}{3Nk} = 1 + \sum_{n=1}^{\infty} (-1)^n B_{2n} \frac{2n-1}{(2n)!} \left(\frac{h}{kT}\right)^{2n} \mu_{2n} \quad (\text{A.4})$$

Here the B_s are the Bernoulli numbers⁽²⁶⁾ and $\mu_n = \sum_j v_j^n / 3N$ is the n^{th} moment of the frequency distribution of the $3N$ normal modes of the solid and depends only on its (homogeneous) strain state. The expansion of the thermal free energy, whence the other expansions follow straightforwardly, is obtained quite easily by integration of the Taylor expansion of the function $d/dx \{\ln[(1-e^{-x})/x]\}$, and this involves the Bernoulli expansion⁽²⁶⁾ of the function $x/(1-e^{-x})$, which converges for $|x| < 2\pi$. The region of convergence of the Thirring-Stern expansions extends to below 80°K even for a value of ν_m equal to 10^{13} sec^{-1} .

Each term of the Thirring-Stern expansions is a function of the ratio between the absolute temperature and an appropriate (purely strain-dependent) characteristic temperature. We define the characteristic temperature appropriate to the logarithmic term of the entropy, Θ_0 , and the characteristic temperature for the term of the expansions containing the n^{th} moment of the frequency distribution, Θ_n , as follows:

$$\Theta_0 = \exp\left(\frac{1}{3}\right) \frac{h}{k} (\prod_j \nu_j)^{1/3N} \quad (\text{A.5})$$

$$\Theta_n = \left(\frac{n+3}{3}\right)^{1/n} \frac{h}{k} \mu_n^{1/n} \quad (n = 1, 2, 4, 6, \dots) \quad (\text{A.6})$$

This choice of the numerical factors, which are *a priori* arbitrary, ensures that when all these characteristic temperatures are taken as equal the expansions (A.1) to (A.4) reduce to the well-known Debye expansions.

For each thermodynamic function there is clearly a high-temperature region, generally of different width for different functions, where only the leading strain-dependent term of its Thirring-Stern expansion is relevant. Thus the correct quasi-harmonic expression coincides with the Debye expression at these classical or nearly classical temperatures. However, the appropriate Debye characteristic temperatures for the entropy and for the heat capacity are different (see, for example, Ref. 12) and differ also from the one appropriate for the thermal energy, being given by Θ_0 , Θ_2 and Θ_1 respectively;

on the other hand, the appropriate Debye characteristic temperatures for the (vibrational and thermal) free energies and for the vibrational energy coincide, respectively, with those for the entropy and for the heat capacity. Numerical values of these Θ s for some alkali halides, referred to the volume at 0°K and atmospheric pressure, are given in the paper by BARRON *et al.*⁽²¹⁾; e.g. for potassium iodide one has $\Theta_0 = 142.8^\circ\text{K}$, $\Theta_1 = 152.9^\circ\text{K}$ and $\Theta_2 = 162.5^\circ\text{K}$. The experimental Debye temperatures, obtained by fitting the appropriate Debye formulae to the measured values of the entropy, thermal energy and heat capacity of a non-metal, will not actually tend to Θ_0 , Θ_1 and Θ_2 at high temperatures, owing to the presence of anharmonic contributions. However, while these affect the experimental Debye temperature for the heat capacity by a percentage much larger than their fractional weight in the heat capacity, as BARRON *et al.*⁽²¹⁾ have dramatically illustrated for some alkali halides, they affect the experimental Debye temperature for the entropy only by a percentage comparable to that fractional weight.

At lower temperatures, where several strain-dependent terms of the Thirring-Stern expansion of a given thermodynamic function are relevant, the Debye temperature appropriate to this function, determined by fitting the truncated Debye expansion to the truncated Thirring-Stern expansion, will depend explicitly on temperature whenever the values of the characteristic temperatures pertinent to the relevant terms of the Thirring-Stern expansion are numerically different, because the relative weights of these terms change with temperature. DOMB and SALTER⁽¹⁵⁾ have expressed this temperature dependence for the Debye temperature for the heat capacity analytically, as an expansion in inverse powers of the absolute temperature, and analogous expansions can be easily obtained for the Debye temperatures pertinent to the other thermodynamic functions. These expansions are of course different for different thermodynamic functions, and should represent rather accurately the temperature dependence of the experimental Debye temperatures for the various functions in the region of relatively low temperatures. As yet, this has been shown to be the case only for the DOMB and SALTER expansion.⁽²¹⁾ A final remark, of some interest, is that even if the numerical values of the characteristic temperatures (A.5) and (A.6) pertinent to the relevant terms of the Thirring-Stern expansion of a given thermodynamic function are different, so long as their strain dependence is the same, the function depends only on the ratio between the absolute temperature and a unique (purely strain-dependent) characteristic temperature, but the dependence on this variable is not of the Debye form.