

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.

Acknowledgements—This work was initiated at the University of Pavia, Italy and carried out at the Argonne National Laboratory. It is a pleasure to acknowledge the comments that we have received from T. H. K. BARRON, M. BLACKMAN, R. O. DAVIES, C. DOMB, E. A. GUGGENHEIM and J. A. MORRISON, and to thank G. K. HORTON and A. A. MARADUDIN for allowing us to see their papers prior to publication.

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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:

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

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

$$\frac{S}{3Nk} = -\ln \left[\frac{h}{kT} \left(\prod_j \nu_j \right)^{1/3N} \right]$$

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

$$\frac{W_{\text{vib.}}}{3NkT} = \frac{W_{\text{th.}}}{3NkT} + \frac{1}{2} \frac{h}{kT} \mu_1 = 1$$

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

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