(3) Thermal aspects

In addition to the use of the pressure-dependence of the elastic constants to augment other investigations of cohesion in solids, the data are directly applicable to the study of certain aspects of anharmonicity of lattice vibrations. Consider the acoustic wave velocity and its pressure dependence in terms of the dispersion curves for lattice vibrations of a solid as revealed in the plot of the frequency vs. $|\bar{\mathbf{k}}|$ where $\bar{\mathbf{k}}$ is the wave vector for some direction of propagation in the crystal (see Fig. 8). The initial slope of such a curve is the velocity of an acoustic wave of frequency low compared to the cut-off frequency ν_{max}. Typical cut-off frequencies are $\sim 10^{13}$ cycles per second so that our 10-mc search wave is very near the origin on the scale of Fig. 8 and information derivable from it will only be applicable over the region of the ν vs. $|\bar{\mathbf{k}}|$ curve non-dispersive at all pressures considered. Consider now the behaviour of a normal mode i lying in the non-dispersive region (see Fig. 8), i.e. a plane standing-wave having a fixed number of nodes between two atom sites a distance L apart and a frequency ν_i. As the crystal volume is changed by application of pressure, the mode frequency will change for two reasons: (1) the sound velocity, hence the slope of the curve, will change, and (2) the value of $|\bar{\mathbf{k}}|$ will change because the reference lattice sites are compressed with the crystal. Analytically one can express this dependence in terms of $\gamma_i \equiv -\dfrac{\mathrm{d}\ln\nu_i}{\mathrm{d}\ln V}$, from which a connection may be made to the pressure dependence of the elastic constants by the relations: $\nu_i = v_i k_i$ where v_i is the wave velocity appropriate

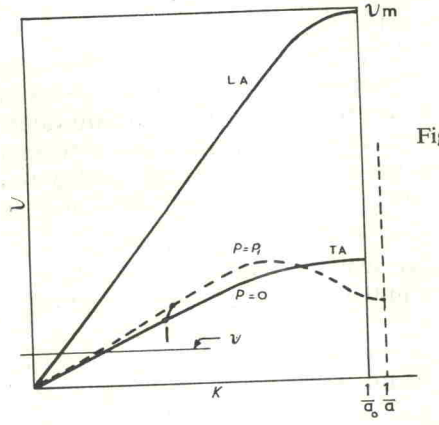

Fig. 8. *Acoustic lattice vibration dispersion curves for a longitudinal mode (LA) and a transverse mode (TA), showing change of the transverse acoustic (TA) curve caused by an applied pressure* P_1, *and the shift in frequency of the i'th normal mode*

The horizontal line, cutting off the frequency at $\nu = kT/h$ indicates the fact that at low temperatures, only the modes with less than this frequency are active

to type of wave, k_i is the reciprocal of the wavelength of the mode under consideration, $v_i = (C_i/\rho)^{\frac{1}{2}}$ where C_i is an elastic stiffness appropriate to the wave type, ρ the crystal density, and finally $\dfrac{\mathrm{d}\ln C_i}{\mathrm{d}\ln V} = -\dfrac{B\,.\,\mathrm{d}C_i}{C_i\,.\,\mathrm{d}P}$. Geometrically $\dfrac{\mathrm{d}\ln k_i}{\mathrm{d}\ln V} = -\dfrac{1}{3}$, $\dfrac{\mathrm{d}\ln\rho}{\mathrm{d}\ln V} = -1$. Performing the necessary derivatives and combining terms yields $\gamma_i = -\dfrac{1}{2}\cdot\dfrac{\mathrm{d}\ln C_i}{\mathrm{d}\ln V} - \dfrac{1}{6}$, an equation resembling the familiar expression* due to Slater,[5] but with C_i replaced by B_T, the bulk modulus, and derived under somewhat different restrictions: $\gamma_s = -\dfrac{1}{2}\cdot\dfrac{\mathrm{d}\ln B_T}{\mathrm{d}\ln V} - \dfrac{1}{6}$. Note that applicability of the Slater γ depends sensitively on independence of Poisson ratios on volume. If one has only a set of lattice vibrational modes γ_i contributing appreciably to the heat capacity of the crystal at the temperature under consideration, i.e. the electronic or other contributions may be neglected, a good approximation in insulators and semiconductors, one can, following Slater,[5] or Peierls[50] assume that the free energy of the crystal can be written:

$F = U_o(V) + kT\ln Z_{vib.}$ where $U_o(V)$ is the internal energy of the crystal at absolute zero,

* Slater's expression $\gamma_s = a_2/a_1^2 - 2/3$ may be shown to be identical to this expression. Consider a_1 and a_2 defined by $\Delta V/V_o = a_1P + a_2P^2$, a form in which many of Bridgman's experimental results are stated. Then by solving for P and evaluating $B_T = -V\left(\dfrac{\partial V}{\partial V}\right)_T$ and $\dfrac{\mathrm{d}\ln B_T}{\mathrm{d}\ln V}$ with care to differentiate $B_T(V) = -V\left(\dfrac{\partial P}{\partial V}\right)_T$, not $B_T(V) = V_o\left(\dfrac{\partial P}{\partial V}\right)_T$, $\left(\dfrac{a_2}{a_1^2} - \dfrac{2}{3}\right)$ and $\left(-1/2\,\dfrac{\mathrm{d}\ln B_T}{\mathrm{d}\ln V} - 1/6\right)$ are seen to be equivalent.

and is assumed to include the zero point energy. U_o is assumed to have no explicit temperature dependence. $Z_{vib.}$ is the quantum mechanical sum over states of the lattice vibrational energies. By elementary statistical mechanics, it can be shown that Grüneisen's gamma, defined by $\gamma_{Gr} = \alpha B_T V/C_v$ (where α is the volume coefficient of thermal expansion, B_T the bulk modulus and V and C_v the volume and heat capacity per mole), is given in terms of the γ_i by $\gamma_{Gr} = \dfrac{\Sigma\, C_{vi}\,\gamma_i}{\Sigma\, C_{vi}}$, where C_{vi} is the Einstein heat capacity of the i'th normal mode at the temperature under consideration and the summation is made over all modes. At temperatures $T \gg h\,\nu_{max}/k$, all modes will have heat capacity k and $\gamma_{Gr} = \bar{\gamma}$, the average of γ_i over all modes. In the limit of very low temperatures on the other hand, only the low-frequency acoustic modes will contribute to the heat capacity, the least stiff mode types being the most important contributors. In terms of the dispersion curves shown in Fig. 8, it is seen that if the occupation is cut off at $\nu = kT/h$, then for the lower stiffness modes (lower slope of ν vs. k), a larger number of states will be contributing to the heat capacity, hence the γ_i of these states will contribute relatively more heavily to γ_{Gr}. Experimentally (see Table V), it is most commonly observed that the lower stiffness modes have smaller γ_i, hence γ_{Gr} should decrease at low temperatures. This has been considered by Sheard[51] for a number of materials, and since one can show[29] that if the low-temperature limit of γ be γ_o, then $\gamma_o = -\dfrac{d \ln \Theta_o}{d \ln V}$. Then it is possible very simply to use deLaunay's tables[52] for Θ (C_{11}, C_{12}, C_{44}, ρ) together with values of the C's and d C/dP's in order to evaluate the γ_o, sometimes with surprising results,[53] as in the case of germanium and silicon[54] indicated in Fig. 9. Of course, one expects this value to be a valid one only in the case of materials in which one can assume negligible contribution of electronic heat capacity, i.e. in the case of non-metals. The generalisations of this are discussed by Bernardes & Swenson.[55] It is useful also to examine and compare values of γ derived with the assumption that the volume-dependence of the frequencies of a particular mode type, e.g. transverse acoustic, is the same in the dispersive region as that for the low-frequency modes. This involves averaging of three γ_i (one longitudinal, two transverse) over all directions in the crystal. Some values of $\bar{\gamma}$ are shown in Table V comparing γ_{Gr}, γ_s, and $\bar{\gamma}$ derived from shear and longitudinal acoustic measurements. Agreement of $\bar{\gamma}$ with γ_{Gr} is excellent in most cases, indicating that probably the gammas for modes in the dispersive region do not differ widely from those measured in the low frequency part of the lattice vibrational spectrum. A spectacular exception to the latter is provided by the temperature dependence of γ_{Gr} in the case of the diamond-like structures, e.g. Ge, Si, InSb, as shown in Fig. 9. In these a very pronounced dip in γ_{Gr} appears at about a tenth of the Debye temperature. The interpretation[56] of these negative anomalies is that the dispersive part of the spectrum of the transverse acoustic modes

Table V

$\gamma_i = -\dfrac{d \ln \nu_i}{d \ln V}$ *for various long wavelength acoustic mode types*

Values of the elastic constants appropriate to these modes are given in units 10^{12} dyne cm^{-2}. Comparison is made between the average γ_1 for these simple modes, the Slater γ and the Grüneisen γ, $\gamma_{Gr} = \alpha B_T V/C_v$, showing the better agreement between γ_{Gr} and γ_s. $\bar{\gamma}$ for NaCl and KCl are taken from Sheard[51] and represent an average of γ_i over all directions of propagation. Θ is the Debye temperature.

Crystal	C'_{11}	C_{44}	C'	γ'_{11}	γ_{44}	γ'	$\bar{\gamma}$	$\alpha B_T V/C_v$ $= \gamma_{Gr}$	Slater γ	γ_o	T/Θ
Na	0·11	0·42	0·0058	1·36	1·06	1·06	1·16	1·16	1·5		1·9
Cu	2·25	0·75	0·23	2·30	1·92	1·49	1·90	1·96	2·55	1·80	0·9
Ag	1·60	0·46	0·15	2·69	2·38	1·96	1·97	2·40	2·85		1·3
Au	2·30	0·42	0·15	3·00	3·38	2·31	2·34	2·90	2·93		1·8
Al	1·19	0·28	0·23	2·43	2·80	2·36	2·90	2·27	2·31	2·90	0·8
Ge	1·56	0·67	0·40	1·27	0·58	0·17	2·53 2·57H				
Si	2·11	0·79	0·50	1·35	0·33	−0·13	0·72	∼0·73	2·1	0·49	∼0·5
SiO_2 fused				−2·40	∼−2·08	∼−2·08	0·51	∼0·45	2·5	0·25	∼0·45
NaCl	0·486	0·128	0·184	1·99	0·14	2·89	−2·19 1·60S	∼0·00			
KCl	0·307	0·063	0·165	1·81	−0·87	3·03	1·57S	1·60	1·52	1·23	
RbI	0·171	0·028	0·112	—	−1·15	—		1·48	1·26	0·53	

S taken from Sheard[51] and H average by Houston's method