Table 4. Linearly extrapolated fractional changes over the temperature range 300–0°K of the bulk modulus and its pressure derivative in the alkali halides, from data by Bridgman

Material	$\frac{V(300^{\circ}) - V(0^{\circ})}{V(300^{\circ})}, (\%)$	$\frac{B_T(0^\circ) - B_T(300^\circ)}{B_T(300^\circ)}$ , (%)	$\frac{\frac{\mathrm{d}B_T}{\mathrm{d}P} (0^\circ) - \frac{\mathrm{d}B}{\mathrm{d}P} (300^\circ)}{\frac{\mathrm{d}B}{\mathrm{d}P} (300^\circ)}$	, (%)
LiF	3	6	13	
LiCl	3.7	20	49	
LiBr	4.2	25	65	
NaF	3.0	3	-10	
NaCl	3.5	26	39	
NaBr	3.6	23	60	
KF	3.0	4	10	
KCl	3.3	15	37	
KBr	3.5	18	48	
KI	3.7	18	48	
RbBr	3.1	5	14	
RbI	3.6	21	54	

8°K do reveal the minimum in Grüneisen's gamma which we expect will be a feature appearing in general in the alkali halides. Since the values of dC/dP can easily be measured at several temperatures to check this point quantitatively such measurements should and will be made. We have also used the Born-Mayer model to attempt to estimate that part of the temperature dependence of mode gammas due simply to change in the crystal volume with temperature. These calculations indicate fractional changes in mode gammas of the same order as the fractional change in volume. Thus the large changes in dB/dP measured by Bridgman must, if real, be due largely to an explicit temperature dependence.

The occurrence of a strong decrease of the mode gammas with increasing temperature would also force a revision of our ideas about the constant high temperature limit of the Grüneisen's gamma observed, for example, to remain unchanged over the entire range  $50-750 \,^{\circ}\mathrm{C}^{(15)}$  in KCl. The quasiharmonic oscillator model would predict a decrease in  $\gamma_G$  with increasing temperature if the mode gammas decrease. The observed constancy of  $\gamma_G$  could only come about if the anharmonic contribution to the entropy (e.g. from the "linear term" in  $C_v$ ) had a sufficiently

large-positive volume dependence to maintain a large value of the thermal expansion coefficient as the temperature was increased, or that a vacancy contribution to the expansion was present.

## GAMMAS OF DISPERSIVE MODES

The critical test of the Quasi Harmonic Oscillator model of the thermal expansion of non metallic crystals requires a knowledge of the values of  $\gamma_i$ , for dispersive as well as non-dispersive modes. We have attempted without success to date to obtain directly mode gammas of certain dispersive modes in silicon and germanium by examination of the effect of pressure on the energies of the "phonon kinks" in tunnel diode characteristics at liquid helium temperature. Neutron spectroscopy performed on crystals at high pressures will in principle provide all of the information desired. We are constructing a high pressure vessel for this purpose and it is to be hoped that such experiments prove feasible.

Acknowledgements—This work was supported in part by the Army Research Office, Durham. The author would like particularly to thank Professor Charles S. Smith for access to pre-publication results, and for many stimulating conversations.

## REFERENCES

- 1. SLATER J. C., Introduction to Chemical Physics, McGraw Hill, New York (1939).
- BARRON T.H.K., Ann. Phys. 1, 77 (1957); Phil. Mag. 46, 720 (1955).
- 3. LAZARUS D., *Phys. Rev.* 76, 545 (1949); McSHIMMIN H.J., *J. acoust. Soc. Amer.* 30, 314 (1957); DANIELS W.B. and SMITH Charles S., *J. Phys. Chem. Solids* 9, 100 (1959); DANIELS W.B. Phys. Rev. 119, 1246
  - 9, 100 (1959); DANIELS W.B., *Phys. Rev.* 119, 1246 (1960); CHAPMAN J.C., masters thesis, Case Institute of Technology, Cleveland, Ohio 1959, unpublished; DANIELS W.B., unpublished.
- 4. SHEARD F.W., Phil. Mag. 3, 138 (1958).
- 5. COLLINS J.G., Phil. Mag. 8, 323 (1963).
- 6. SCHUELE D.E. and SMITH Charles S., to be published.

of a said unperior of the foreign white a to

7. DANIELS W.B., Phys. Rev. Letters 8, 3 (1962).

- DE LAUNAY J., Solid State Physics, Vol. 2 (edited by SEITZ F. and TURNBULL D.) Academic Press, New York (1960).
- 9. WHITE G.K., Cryogenics 1, 1 (1961).
- DANIELS W.B., Proceedings of the International Conference on Semiconductors, Exeter, Institute of Physics and The Physical Society (1963).
- 11. MAYBURG S., Phys. Rev. 79, 375 (1950).
- BURSTEIN E. and SMITH P.L., Phys. Rev. 74, 229 (1948).
- Bridgman P.W., The Physics of High Pressure, Bell, London (1952).
- SWENSON C.A., CARR R.H. and SPARKS P.W., Private Communication.
- From high temperature thermal expansion data by ENCK F.D., ENGLE D.G. and MARKS K.I., J. Appl. Phys. 33, 2070 (1962).