



Fig. 6. Plot of $\Delta\nu/\nu\Delta p$ vs mole fraction for $\text{KCl}_{1-x}\text{Br}_x$. For comparison, experimental hardness data¹⁹ after Smakula (solid circles) and Vorobev *et al.* (crosses) are also included.

mental data exist. Since the compressibility of many mixed crystal systems may not be a linear function of the mixing ratio, a point which we shall elaborate upon later, Fig. 5 should only be taken qualitatively; (2) although Fig. 5 establishes that $\nu_{\text{TO}} \approx \text{const}/V^n$, not much significance can be attached to the exponent n of this plot because of the large scatter of points. Furthermore, if at any fixed value of x one follows the change of ν due to change of r_0 (nearest-neighbor distance) one may encounter different slopes than the average slope of the line drawn on Fig. 5.

The pressure dependence of the long wavelength TO frequency may be discussed in terms of a mode Gruneisen parameter defined as

$$\gamma_{\text{TO}} = -d \ln \nu_{\text{TO}} / d \ln V. \quad (4)$$

Since the measurements were done at a constant temperature, this equation may be rewritten as

$$\gamma\chi = \frac{1}{\nu_{\text{TO}}} (\partial \nu_{\text{TO}} / \partial P)_T \quad (5)$$

where χ is the isothermal compressibility. Measurements on pure KCl and KBr crystals showed⁶ that the experimental values of γ obtained from this relation compared very well with values calculated from a rigid ion model using a Born-Mayer potential.

A plot of $(1/\nu)(\Delta\nu/\Delta P)$ for the TO mode in the pressure range of 0.001 kbar to 10 kbar is shown in Fig. 6. This curve has a distinct minimum around $x = 0.5$. An examination of Eq. (5) reveals that the ordi-

nate of Fig. 6 is proportional to $\gamma_{\text{TO}}\chi$. The Gruneisen parameter for the TO mode of most ionic crystals of the NaCl type is known to be around 3. For KCl and KBr, γ_{TO} is, respectively, 2.9 and 2.6, and appears¹⁸ to depend on the effective ionic charge, which is $0.81e$ and $0.76e$, respectively, for these two crystals. The effective ionic charge for the mixed system is known to vary linearly with composition between these two limits. Thus the nonlinear behavior of $(1/\nu)(\Delta\nu/\Delta P)$ displayed in Fig. 6 may be understood largely in terms of a nonlinear behavior of χ . However, since χ and γ are related to the second and third derivative of the cohesive energy with respect to volume, it is entirely possible that both these quantities vary nonlinearly. For comparison, the hardness variation¹⁹ of KCl-KBr system as a function of the mixing ratio is also shown in Fig. 6. It may be noted that hardness, which may be compared²⁰ to the bulk modulus (reciprocal of compressibility), goes through a maximum in the intermediate mixing range.

This paper is based on work performed under the auspices of the U.S. Atomic Energy Commission. It was supported in part by the U.S. Air Force In-House Laboratory, Independent Research Fund under Contract AF19(628)-6042.

S. S. Mitra of the University of Rhode Island, Department of Electrical Engineering, is a consultant to Argonne National Laboratory. C. J. Hoskins was a CSUI student, September-December 1968.

References

1. J. R. Ferraro, S. S. Mitra, and C. Postmus, *Inorg. Nucl. Chem. Lett.* **2**, 269 (1966).
2. C. Postmus, J. R. Ferraro, and S. S. Mitra, *Inorg. Nucl. Chem. Lett.* **4**, 55 (1968).
3. C. E. Weir, E. R. Lippincott, A. Van Valkenburg, and E. N. Bunting, *J. Res. Nat. Bur. Std.* **63A**, 55 (1959). The diamond cell is commercially available from High Pressure Diamond Optics, Inc., McLean, Va.
4. C. Postmus, V. Maroni, J. R. Ferraro, and S. S. Mitra, *Inorg. Nucl. Chem. Lett.* **4**, 269 (1968).
5. S. S. Mitra, C. Postmus, and J. R. Ferraro, *Phys. Rev. Lett.*, **18**, 455 (1967).
6. C. Postmus, J. R. Ferraro, and S. S. Mitra, *Phys. Rev.* **174**, 983 (1968).
7. I. F. Chang and S. S. Mitra, *Phys. Rev.* **172**, 924 (1968).
8. A. Mitsuishi, in U.S.-Japan Cooperative Seminar on Far Infrared Spectroscopy, Columbus, Ohio 1965 (unpublished).
9. S. S. Mitra, in *Optical Properties of Solids*, S. Nudelman and S. S. Mitra, Eds. (Plenum Press, Inc., New York, 1969), pp. 413.
10. R. H. Lyddane, R. B. Sachs, and E. Teller, *Phys. Rev.* **59**, 673 (1941).
11. K. Rao and A. Smakula, *J. Appl. Phys.* **36**, 2031 (1965).
12. F. Matossi, *J. Chem. Phys.* **19**, 161 (1951).
13. Y. S. Chen, W. Shockley, and G. L. Pearson, *Phys. Rev.* **151**, 648 (1966).
14. L. Nordheim, *Ann. Physik* **9**, 607, 641 (1931). T. Muto, *Sci. Papers Inst. Phys. Chem. Phys. (Tokyo)* **34**, 377 (1938).

15. R. Brout, *Phys. Rev.* **113**, 43 (1959).
16. S. S. Mitra and R. Marshall, *J. Chem. Phys.* **41**, 3158 (1964).
17. L. Vegard, *Skrifter Norske Videnskaps. Akad, Oslo I. Mat. Naturv. Klasse* 1947, No. 2, 83 pp. *Chem. Abstracts* **43**, 4073h (1949).
18. S. S. Mitra, O. Brafman, W. B. Daniels, and R. K. Crawford, *Phys. Rev.* to be published.
19. A. A. Vorobev, E. K. Zavodoskaya, and M. S. Ivankina, *Izv. Vysshikh Uchebn. Zavedenii Fiz.* **6**, 162 (1959). A. Smakula, *Quart. Progr. Repts.* AF19(628)-395 and AF19(628)-2418, (1962-1967).
20. J. N. Plenol, S. S. Mitra, and P. J. Gielisse, *Phys. Stat. Solidi* **12**, 376 (1965).