these two satellite bands, increased by the relative abundance ratio of about 90, which give the main band its much increased width in the upper phase. However, the high-energy side of the line is fairly sharp, and this has allowed the $\nu_3 + \nu_{\text{ext}}$ spectrum to be seen reasonably clearly to within about 20 cm^{-1} of the main line.

On going through the phase change, the prominent low-separation band peaking at about $\nu_3 + 31$ cm^{-1} disappears and is replaced by a less intense though more clearly resolved band at about $\nu_3 + 55$ cm^{-1}. The superoptic doublet becomes much wider spaced in the upper phase and is found closer to the main line. These changes are probably seen more clearly in Fig. 13, where the three most prominent ν_{ext} energies in each phase are plotted as a function of pressure.

Since, as discussed earlier, the lower component of the superoptic doublet is always found close to the maximum optic-mode frequency of the pure lattice, Figs. 12 and 13 show that this maximum optic-mode frequency decreases as RbBr is compressed through its NaCl to CsCl structure phase change. The interpretation of the low-separation absorption is less clear, but the marked increase (31–55 cm^{-1}) of its maximum suggests a marked increase in the relevant acoustic-lattice modes. Although this would be the expected result of the increased density of the high-pressure phase, the initial negative slope of the $\nu_3 + 31$ cm^{-1} line suggests that such an explanation is oversimplified.[29-31]

EXTERNAL MODES OF NCO⁻ IN RbBr AS
FUNCTION OF PRESSURE AT 100°K
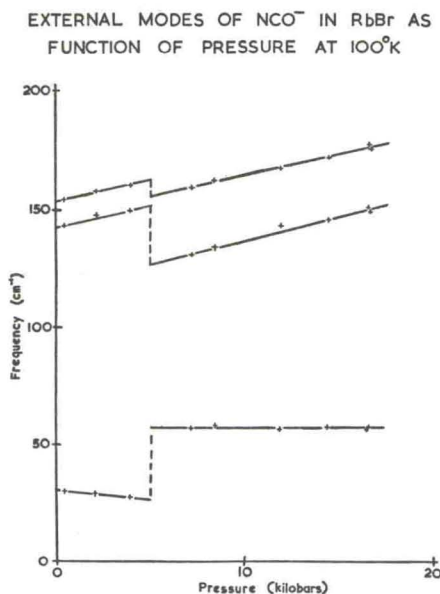
FIG. 13. Pressure dependence of the frequencies of the prominent features in the lattice-sideband structure to ν_3(NCO⁻) isolated in RbBr at 100°K (cf. Fig. 12).

EXTERNAL MODES OF NCO⁻ IN KBr AT 140°K
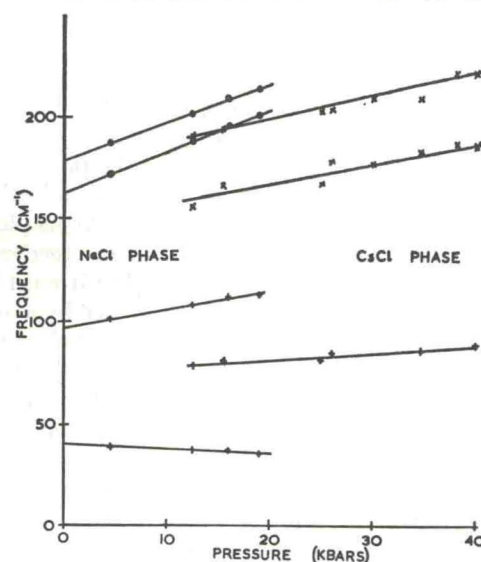
FIG. 14. Pressure dependence of the frequencies of the prominent features in the lattice-sideband structure on ν_3(NCO⁻) isolated in KBr at 140°K (cf. Fig. 2). The in-gap doublet (NaCl phase) had to be plotted as a single line on this scale, although the two components could still be distinguished up to the phase change in spite of a slight broadening of the spectral features under pressure.

Since no sharp features appear near the center of the ν_{ext} spectrum of the upper phase, it seems fair to conclude that there is no gap in the integrated phonon density of states of the CsCl-structured RbBr.

Figure 14 shows the pressure dependence of the most prominent ν_{ext} features in the $\nu_3 \pm \nu_{\text{ext}}$ spectrum of NCO⁻ in KBr. All the effects noted above for RbBr are seen again in this case. The strong sharp in-gap doublet, plotted as a single line in Fig. 14, has no analogous feature in the CsCl-structured high-pressure phase, suggesting that here again there is no gap in the integrated phonon density of states of the high-pressure phase.

The $\nu_3 \pm \nu_{\text{ext}}$ spectra for NCO⁻ in both RbI and KI have also been recorded as a function of pressure at low temperature. In these two cases also the same general trends were observed at the phase change, i.e., (i) a lowering in energy and widening of separation of the superoptic doublet, (ii) the replacement of the broad

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[29] The difference between these bands and the monatomic-impurity low-energy resonance bands discussed by Benedek and Nardelli (Ref. 11) must again be underlined here. The general differences were discussed earlier in the section on CN⁻ in KBr, but the difference in behavior under pressure should be noted at this point. (i) In the low-pressure phase, the band shows a definite decrease in frequency as the pressure is raised, which is the

opposite behavior to that of the monatomic-impurity resonance mode. (ii) In the upper phase the band appears at a much higher energy, which takes it very much closer to the reststrahlen frequency which has dropped in energy during the phase change (see above and Refs. 30 and 31), and yet it is a much sharper band in marked contrast to the findings of Benedek and Nardelli (Ref. 11) for the monatomic resonance bands which broaden very rapidly when pushed under pressure towards the reststrahlen frequency.

[30] S. S. Mitra, J. N. Plendl, and L. C. Mansur, in Proceedings of the Ninth European Congress on Molecular Spectroscopy, Madrid, 1967 (unpublished). See also Phys. Rev. Letters 18, 455 (1967).
[31] W. G. Fateley, N. T. McDevitt, and R. E. Witkowski, in Proceedings of the Ninth European Congress on Molecular Spectroscopy, Madrid, 1967 (unpublished).

very-low-energy absorption by a sharper feature at almost twice the energy, and (iii) the absence of any in-gap structure in the high-pressure phase.

Before leaving the topic of effects due to the NaCl-type to CsCl-type phase change, some consideration should be given to the low-separation band in the NaCl structure, which decreases in energy as the pressure is raised. This decrease, in marked contrast to all other bands, even the feature which appears to take its place in the CsCl structure, may be indicating a tendency towards instability at the phase change, but it must be emphasized that this band had only decreased by about 15% in each case (see, e.g., Figs. 13 and 14) before the phase change occurred. In general, the steady shifts which the various bands show as a single phase is compressed indicate the changes in the relevant force constants with pressure. Although for any one particular localized mode this information is of fairly limited interest, in those cases where the band can reasonably be associated with a point in the dispersion curve of the pure host lattice these shifts carry information about the anharmonicity of the host-lattice forces, and this is a topic of more general concern.

PRESSURE DEPENDENCE OF IN-GAP LOCALIZED MODE

KBr has such a narrow gap that in following the sharp in-gap modes one is effectively monitoring this parameter of the host crystal. Figure 15 shows the pressure dependence of the in-gap modes observed in the $\nu_3 + \nu_{ext}$ spectra of NCO$^-$ and N$_3^-$ isolated in KBr. As expected, the results for the two different ions are virtually identical. The continued presence of sharp

bands shows that the gap still exists at elevated pressures, and the absence of noticeable divergence of the two NCO$^-$ lines suggests that the gap does not widen appreciably. Thus it is suggested that both the LA and TO at $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ (the modes limiting the gap; see Ref. 13) increase at the rate shown by the gap modes in Fig. 15. The TO at the band center is expected to rise slightly faster than this.[32]

Not all the external-mode features show the straight-line-frequency–versus–pressure type of graph illustrated in Figs. 13–15. The 105-cm^{-1} line of the NCO$^-$ in NaI external-mode spectrum has a very curved appearance, as shown in Fig. 16. At pressures above about 12 kbar this line is seen to be straight to within the experimental accuracy and this portion of the graph extrapolates back to an intercept of about 111 cm^{-1}, which is fairly close to the lowest-energy optic mode (TO$\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ ≈ 117).[13] The first impression that this gives is that the localized acoustic-torsional mode of the NCO$^-$ isolated in an oversize iodide site, being very sensitive to pressure, rises rapidly until it meets the bottom of the optic band, whereafter it is constrained to move more slowly with the main lattice modes. However, the band center TO frequency has been calculated to fair accuracy at zero pressure, using the rigid-ion model,[33–35]

NCO$^-$ IN NaI : PRESSURE DEPENDENCE OF EXTERNAL MODE AT 100°K

FIG. 16. Observed pressure dependence of the strongest in-gap mode for NCO$^-$ in NaI (cf. Fig. 7) compared with the calculated change in the TO band-center frequency.
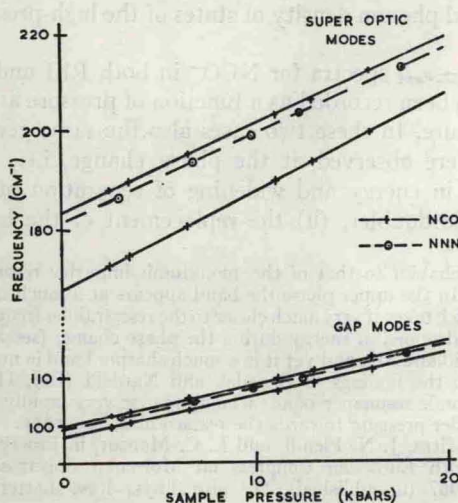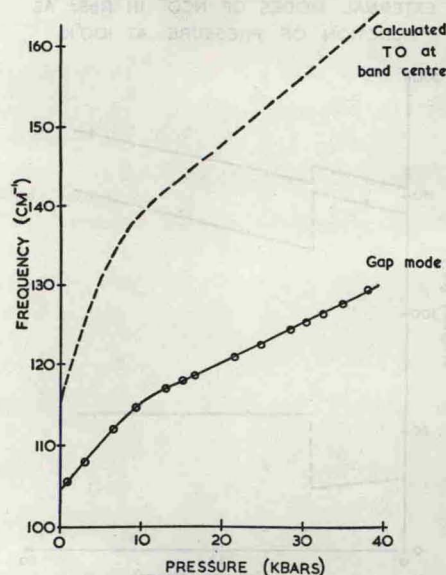
LOCAL MODES IN KBr AS A FUNCTION OF PRESSURE AT 100°K

FIG. 15. Comparison of the pressure dependence of the local-mode frequencies of NCO$^-$ and N$_3^-$ in the low-pressure phase of KBr at 100°K.

[32] The temperature dependence of the in-gap modes (Fig. 10) is very close to that of the TO at the band center (see, e.g., Ref. 13).

[33] B. G. Dick and A. W. Overhauser, Phys. Rev. 112, 90 (1958).
[34] M. Born and K. Huang, *Dynamic Theory of Crystal Lattices* (Oxford University Press, Oxford, England, 1954).
[35] B. Szigeti, Trans. Faraday Soc. 45, 155 (1945).