

grown. (See Ref. 26 for more detail on this point.) The internal-mode frequency for the crystal used to obtain the spectrum in Fig. 9 is such as to suggest an orientation of the NCS^- different to that of the NCO^- which gave the spectrum of Fig. 7. So far we have not grown a high-concentration NCS^- -doped CsI crystal with the alternative orientation.

The in-gap doublets shown by the NaI and KI spectra occur at energies close to those observed in the NCO^- spectra, re-emphasizing the extent to which the host lattice dictates these frequencies. The more localized superoptic frequencies show a greater disparity between the NCS^- and NCO^- numbers, as might be expected for bands which are more dependent on impurity mass and localized-force constants than on host-lattice dispersion curves.

ν_{ext} IN COMBINATION WITH DIFFERENT INTERNAL MODES

The ease with which good NCO^- -doped crystals can be produced has led to this ion's being used only in this part of the investigation. Figure 7 showed ν_{ext} as observed in combination with $\nu_3(\text{NCO}^-)$. The other internal modes which are strong enough to give a reasonable chance of observing $\nu_{\text{int}} \pm \nu_{\text{ext}}$ spectra are ν_2 (the doubly degenerate bending mode at about 630 cm^{-1}) and the $\nu_1, 2\nu_2$ fermi doublet (at about 1200 and 1300 cm^{-1} , with ν_1 being the more symmetric of the two stretching modes). All these three bands are down by a factor of about 30 in intensity compared with the ν_3 mode, and the external modes in combination with them are down by about the same factor when compared with ν_3 sidebands. Thus even the strongest samples so far used have only shown the most intense features in ν_{ext} in combination with ν_2, ν_1 , and $2\nu_2$. Although the first, and strongest, sample (1 cm of RbBr having about 1.5% NCO^- for Br^- replacement) that we used to investigate these other bands appeared to show extra structure in combination with ν_2 , our subsequent spectra have shown these bands to have been due to other impurities.

In all cases so far investigated, the strongest lattice sidebands found on ν_3 have also been found on all three of the other bands (ν_2, ν_1 , and $2\nu_2$) at separations which were the same within the experimental reliabilities. Thus, so far we have failed to find evidence from this part of the investigation to support the idea of directional selection of ν_{ext} modes which show strong binary combination with ν_{int} . This is not to say that the idea must be rejected, since it was only postulated to apply to the broader, delocalized structure which has yet to be recorded in these other regions. It is hoped to continue this part of the investigation with larger, more heavily doped crystals, since only a factor of about 5 in sample absorption is estimated to be required before a positive assessment of the more intense broad features could be made.

TEMPERATURE EFFECTS

All the $\nu_{\text{int}} \pm \nu_{\text{ext}}$ spectra were recorded at 300 and 100°K , many were also recorded at about 30°K , using a Norelco-Cryogem sample cooler, and some were studied over the whole temperature range from 7 – 450°K . The sharp features on each side of the internal mode always appeared, within the experimental accuracy, to have intensities relative to one another which were simply determined by the thermal populations of the respective lower levels. Superoptic features were found to broaden and decrease in separation from ν_{int} more rapidly with increasing temperature than in-gap features (see, e.g., Fig. 10). Broad features, though less easy to measure, seemed to show intensity changes over and above those associated with binary combinations having thermally controlled populations in their lower levels. An example of such behavior is the lowest-separation broad band in $\nu_3(\text{NCO}^-)$ spectra, where at lower temperatures there appeared a definite reduction of intensity in the summation band feature. It would seem that the presence of other phonons, playing an energetically neutral part, increase the transition probability of this combination.

Two particular temperature-induced changes seem to warrant individual comment. Firstly, the relatively broad band observed for CN^- in NaBr at 90°K at 154 cm^{-1} . At temperatures below 25°K this band sharpens quite markedly, until at 7°K it dominates the ν_{ext} spectrum and is seen in Fig. 8 to be a sharp band situated almost in the center of the optic band as calculated by Karo and Hardy.²⁴ This is the only absorption clearly within the optic band of the host lattice that has been found to show this dramatic sharpening.

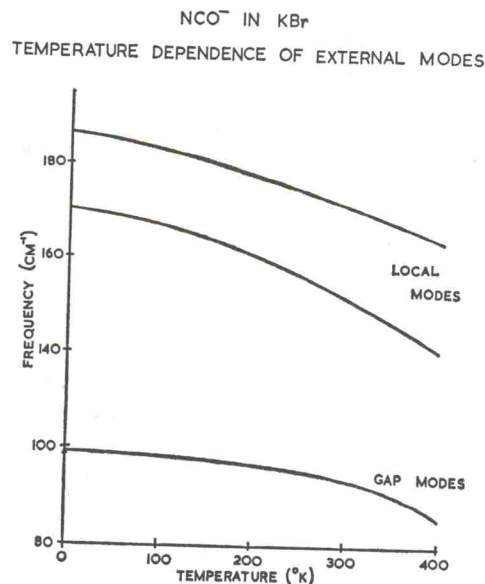


FIG. 10. Temperature dependence of the frequencies of the sharp external-mode features found in combination with $\nu_3(\text{NCO}^-)$ in KBr .

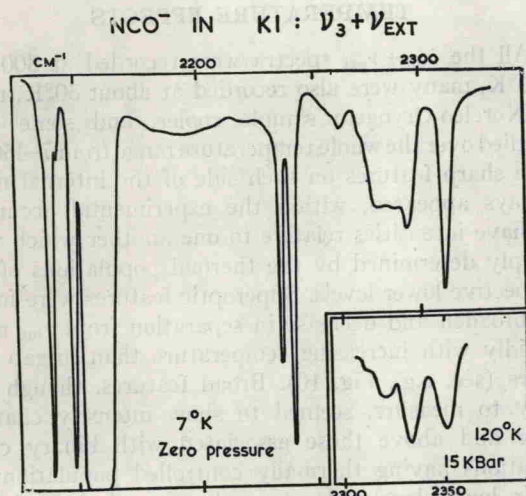


FIG. 11. $\nu_3 + \nu_{\text{ext}}$ spectrum of NCO^- in KI at 7°K and zero pressure with insert showing the superoptic doublet region at 120°K and 15 kbar pressure. The strength of the main ν_3 line at 2157 cm^{-1} can be judged from the intensities of the O^{18} and N^{15} isotopic species seen to slightly lower frequencies. Note the reduced intensity of the low-energy broad external-mode band when compared with the 100°K spectrum of Fig. 7 and the more clearly resolved lower component of the superoptic doublet.

The $\langle 001 \rangle$ orientation of the ion is believed to be significant, as is the fact that this energy coincides with a clearly marked minimum in the ν_{ext} spectrum found in combination with ν_3 of the $\langle 111 \rangle$ -oriented NCO^- ion. Secondly, the effect of lowering the temperature of $\text{KI} + \text{NCO}^-$ to 7°K is shown in Fig. 11. If this spectrum is compared with the 90°K spectrum of Fig. 7, the relative intensity of the lowest-separation broad band is seen to have decreased (as was found generally to be the case; see above), but of particular interest is the super-optic region. Here the 152- cm^{-1} band has sharpened further, and moved out to 155 cm^{-1} , and the 133- cm^{-1} band has moved out to 137 cm^{-1} and can be seen to be sharper and almost resolved from the general optic-band absorption. The description of these two bands as the optic-torsional doublet can be seen to look much more reasonable in this very-low-temperature spectrum. Also included as an inset in Fig. 11 is the 15-bar 120°K spectrum, which shows the band originally at 133 cm^{-1} even more clearly resolved from the general optic-band absorption.

PRESSURE EFFECTS

The effects of high pressures on absorption bands which show lattice sideband structure have been investigated, using a modified Drickamer type²⁷ of high-pressure optical cell working up to 50 kbar at temperatures in the range 90–500°K.²⁸ Some of the spectra recently recorded have been obtained, using later modifications to the high-pressure cell design in

which samples up to $\frac{1}{2}$ in. along the radiation path may be investigated at about 120°K up to pressures above 40 kbar. All spectra included an internal pressure calibrant²⁸ which allowed sample pressures to be quoted to within a fraction of a kbar with respect to our primary pressure calibrant, the shift of $\nu_3(\text{NCO}^-)$ in NaCl as quoted by Drickamer *et al.*²⁷

PRESSURE-INDUCED PHASE CHANGES

Perhaps the most interesting change to observe as the pressure is increased is the change that takes place when a potassium or rubidium halide changes from its low-pressure NaCl-type structure to its high-pressure CsCl-type structure. Even at the relatively great impurity-ion concentrations ($\approx 1\%$) required for the observation of lattice-sideband spectra, no meaningful changes are observed in the pressures at which the phase changes take place, but the onset of the change becomes increasingly sluggish as the doping increases.

Figure 12 shows the $\nu_3 \pm \nu_{\text{ext}}$ spectrum for NCO^- isolated in RbBr at two different pressures in the low-pressure phase and two different pressures in the high-pressure phase. The lowest-pressure spectrum is somewhat inferior to that shown in Fig. 7, due partly to the temperature of the high-pressure cell being slightly above that obtainable with a standard cold cell, and partly to the disrupting effect of pressing the sample into the pressure cell. The center frequency of the main band is indicated at each pressure by a vertical dashed line.

Using the C^{13} isotopic line as a guide to the effect of pressure on the internal mode, the phase change can be seen to have caused a noticeable increase in frequency and also to have produced an unfortunate pair of satellite lines on the low-energy side of the band. It is

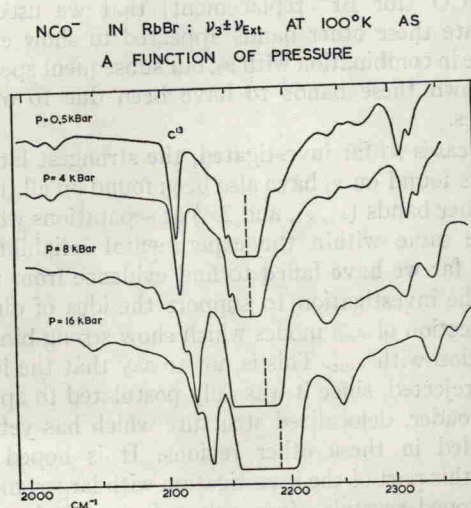


FIG. 12. Effect of pressure at 100°K on the $\nu_3 \pm \nu_{\text{ext}}$ spectrum of NCO^- in RbBr. The center frequency of the main line is indicated by a vertical dashed line and its intensity can be gauged from that of the 1.1% natural abundance NC^{13}O^- line.

²⁷ H. G. Drickamer, R. A. Fitch, and T. E. Shykhov, *J. Opt. Soc. Am.* 47, 1015 (1957).

²⁸ W. F. Sherman, *J. Sci. Instr.* 43, 462 (1966).