mode gap is obscured in Fig. 6, but weaker samples, with better cyanide to cyanate ratios, showed no evidence of in-gap features of comparable intensity to those found for NCO⁻ [see Fig. 2 and the ν_{ext} (NCO⁻) spectrum plotted with respect to $\nu(CN^{-})$ for comparison in Fig. 6]. Figure 6 is further complicated in this "gap" region by the presence of concentration-dependent satellites on $\nu_3(\text{NCO})$ (see Ref. 3). For this sample, with a cyanide to cyanate ratio of about 10:1, the bulk of their structure is due to cvanide-cvanate pairs and is therefore different to that found in cyanate-only-doped crystals. In the present case, the satellites show increased structure at very low temperatures (below 20°K), which might be expected because the cyanide ion becomes frozen into some specific orientation with respect to the cyanate neighbor. Careful study of the available spectra leads us to believe that none of this absorption is due to $\nu(CN^{-}) + \nu_{ext}$ in-the-gap modes. The growing of better crystals is under investigation, but even if it proves impossible to grow cyanate-free crystals with high-cyanide concentrations, the use of high-purity isotopic species would make it possible to investigate absorptions at this separation. [C13 shifts v3(NCO-) 57 cm-1 and v(CN-) 43 cm-1; N15 shifts ν_3 (NCO⁻) 18 cm⁻¹ and ν (CN⁻) 32 cm⁻¹.]

The most striking difference between the ν_{ext} spectra of NCO⁻ and CN⁻ each isolated in KBr is the absence in the CN⁻ spectrum of the four sharp lines which dominate the NCO⁻ spectrum. Since these have been assigned as localized torsional modes for the NCO-, they were not expected for the CN⁻, where the torsional restoring force is so small that bands of these energies cannot be obtained. Each spectrum shows basically two broad maxima within the acoustic band of KBr: at 44 and 80 cm⁻¹ for NCO⁻ and at 12.3 and 75 cm⁻¹ for CN⁻. The feature at 12.3 cm⁻¹ in the cyanide spectrum has been reported¹⁷ to sharpen considerably in going down to 2°K and is interpreted as the summation band involving the torsional oscillation of the CN-, or, equivalently, as the $T_{1u}(J=1)(v=0) \rightarrow T_{2g}(J=2)(v=1)$ transition of a vibrating hindered rotator obeying a Devonshire²⁰ model. Although this is a reasonably satisfactory explanation of the sharp band at 2°K (see, however, Ref. 15), the general broad absorption extending about 30 cm⁻¹ from the main line in Fig. 6 cannot be explained on the same model. Note also a residual absorption at about -12 to -15 cm⁻¹ from the main band which appears to be simply a thermally suppressed difference band equivalent (suggesting a sample temperature of about 6.5°K). The bulk of this absorption must, we believe, be due to combination with acoustic-type lattice vibrations in which the CN⁻ ion plays an energetically minor part. This is to be contrasted with the above models for the sharp band seen at 2°K at about ν (CN⁻)+(12 cm⁻¹), where the energy is assumed to reside on the ion performing a specific motion within an infinitely massive containing potential well. If an analogy is to be drawn between the lowseparation absorption in the cvanide spectrum with the absorption showing a maximum at 44 cm⁻¹ in the cyanate spectrum, then the possible reasons for its changed position might be (i) different mass of impurity, (ii) different force constants between impurity and lattice, and (iii) different orientation of impurity within the lattice. The impurity mass is certainly not the dominant factor, since the heavier mass has the greater frequency. Also, since only a small fraction of the total energy is to be associated with the impurity in these essentially delocalized acoustic-type modes, the impurity mass is a parameter to which they might be expected to be insensitive. Calculations on the force constants operative in the two cases certainly show the NCO⁻ ion to be held more securely in a transverse and particularly a torsional sense, but both are held comparably longitudinally, and the transverse and longitudinal force constants are comparable to, or larger than, the host-lattice force constants. Again the proposed delocalized acoustic nature of the proposed modes would render them relatively insensitive to the local force constants,^{21,22} although here at least the change from CN⁻ to NCO⁻ gives an effect in the observed direction, particularly for torsional motion. The effect of orientation is hard to assess, but it seems inevitable that if a given impurity ion were to be rotated into a different orientation within the crystal, then this would (a) change the local density of states, and (b) change the relative activity of the various modes as they appear in binary combination with ν_{int} . It should be re-emphasised that the ν_{ext} spectra observed here represent only a selection of the external modes involving the impurity, governed by the relative activity of these modes in binary combination with ν_{int} . Similarly, the direct observation of external modes in the far infrared samples the total external-mode motion in terms of the fundamental infrared activity of these modes. Thus we believe that the orientation (111) for NCO⁻ and (001) for CN⁻ may well represent the overriding consideration for these low-energy

²⁰ A. F. Devonshire, Proc. Roy. Soc. (London) A153, 601 (1936).

²¹ Note the difference here between our low-energy broad bands and the sharp-resonance type of low-energy band observed for certain monatomic impurities (e.g., Li⁺ in KBr). (See Ref. 22.) Benedek and Nardelli (Ref. 11) have made a theoretical investigation of the monatomic-impurity case and found that the sharpresonant band part of the absorption is very sensitive to small changes in the force constant between the impurity and its nearest neighbors. The resonant mode is only so sensitive to forceconstant changes because of the very small net-force constant which is operative in the examples which they quote, and the corresponding high degree of localization of the motion associated with this resonance which is shown by the large isotopic shift. In the NCO⁻ and CN⁻ cases, the force constants are comparable to, or larger than, those operative between host-lattice ions, and the observed low-energy absorption in these cases is more like the nonresonant part of the monatomic-impurity absorption, which on the Benedek and Nardelli model is described as "structures due to the host-lattice dynamics," which, not surprisingly, they find is insensitive to changes in the impurity ion's nearest-neighbor force constant.

²² A. J. Sievers and S. Takeno, Phys. Rev. 140, A1030 (1965).

acoustic-type ν_{ext} . This being so, it may be relevant to mention that zone-boundary values for the TA mode in pure KBr (see Ref. 13) vary from 40 to 74 cm⁻¹ for different reciprocal lattice directions. The LA, TO, and LO of pure KBr do not show such a marked directional dependence in the energies at which their dispersion curves show regions, where their slopes tend to zero, which may be considered to tie in with the fact that the CN⁻ and NCO⁻ ν_{ext} spectra show maxima in the same general regions at greater separations from the main line.

We have dealt at some length with the ν_{ext} spectra observed for NCO⁻ and CN⁻ in KBr in order to establish the importance of torsional motion and to introduce the idea of directional dependence. We now consider other spectra in the light of these two concepts.

$v_3 \pm v_{ext}$ SPECTRA FOR NCO- IN 12 ALKALI HALIDES

Figure 7 shows the ν_{ext} spectra observed in combination with ν_3 of NCO⁻ when this ion was isolated in 12 alkali halides. Although many of our observed ν_{ext} peak absorption energies have already been published,⁵ Table II contains for completeness the relevant NCO⁻ values for all lattices. The four most extensive spectra in Fig. 7 (NaCl, NaBr, KCl, and RbCl) show an additional band at about 2400 cm⁻¹. This is the lowestenergy component of a fermi triplet, $2\nu_1$, $\nu_1+2\nu_2$, $4\nu_2$, and it is quite possible that the concentration-dependent broadening of this line in NaBr is in fact obscuring some relevant ν_{ext} structure. The best available calculated density-of-state curves for the various pure host lattices have been included in Fig. 7 (from models



FIG. 7. $\nu_3 + \nu_{ext}$ spectra at 100°K for NCO⁻ isolated in various alkali halides, compared with the integrated density of states where available (see Refs. 13, 23, and 24)