tions from the X point of D_{2h}^{25} are inactive in the ordered low temperature phase.

From this we expect two bands—the two librations of the CN^- molecules—in the Raman spectrum of the phase D_{2h}^{25} and eight bands—the two librations and six lattice modes—in the spectrum of the phase D_{2h}^{13}. Since the NaCN crystal is multidomain and opaque in the ortho-rhombic phases, no polarized Raman spectrum could be obtained and the polarization selection rules are useless for further assignment.

The Raman spectrum of NaCN in the phase D_{2h}^{25} shows two very broad bands at about 110 and 220 cm^{-1} (see Fig. 4). For KCN the corresponding lines lie at 115 and 185 cm^{-1}, respectively. It is likely that the band at 115 cm^{-1} in KCN is due to the Raman active librational modes of the CN^- molecules.[18] The band at 185 cm^{-1} probably is a disorder allowed one-phonon density maximum of the LO phonon from the X point of the Brillouin zone. This assignment explains the temperature dependence of the intensity of this band in KCN.[4] Moreover, from an extrapolation of the frequency shift of the 185 cm^{-1} band up to room temperature into the cubic phase we obtain about 155 cm^{-1}, in good agreement with calculations of the LO-phonon energy at the X point of O_h^5.[13] For NaCN the same extrapolation for the band at 250 cm^{-1} gives 200 cm^{-1} (160 cm^{-1} calculated[13]). The poorer agreement may be due to the stronger first order character of the transition $O_h^5 \to D_{2h}^{25}$ which is destructive in NaCN but not in KCN. We
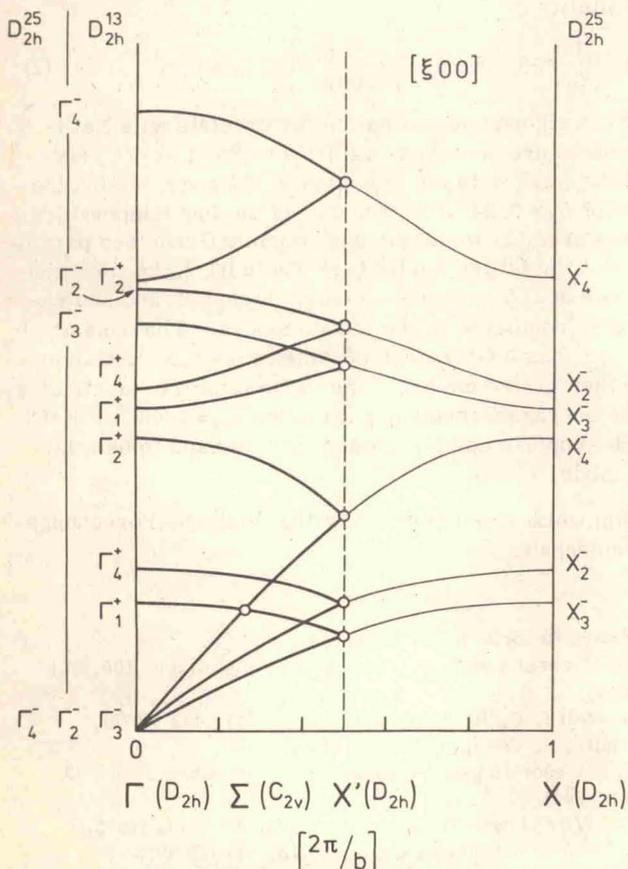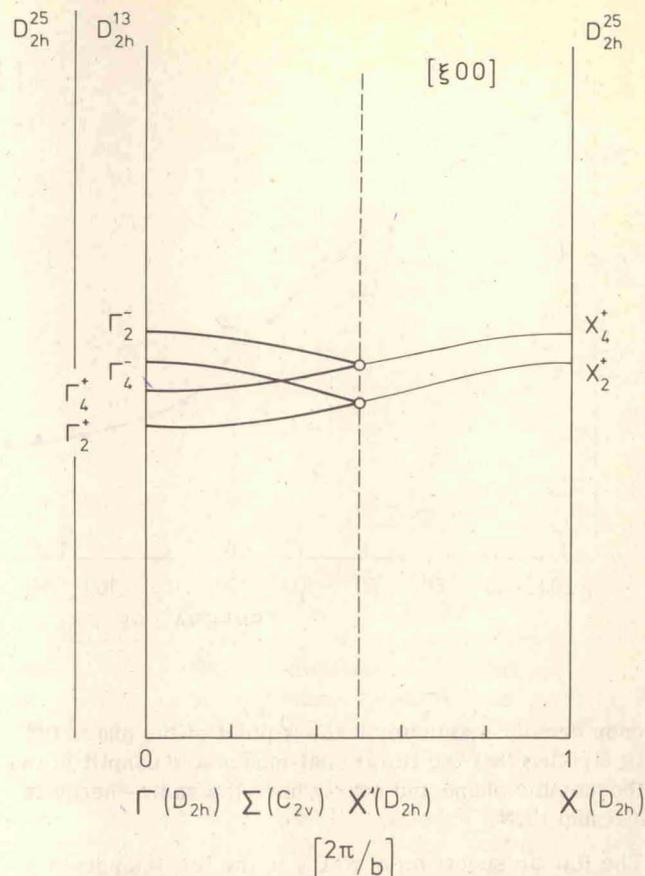

FIG. 9. The dispersion of the CN^--librational mode at the low temperature phase transition of NaCN.

do not think that the Raman band at 185 cm^{-1} in KCN can be one component of the librational modes. This assignment cannot explain the temperature dependence of the band which is different from the librational modes at 115 cm^{-1} in KCN.[4,18] The continuous shift from 160 to 190 cm^{-1} of this band with increasing amounts of KCN in the mixed crystal system KCN_xKCl_{1-x}[21] may indicate an equivalent shift of the LO phonon at the X point of the mixed crystal. This phonon lies at 160 cm^{-1} in pure KCl.

NaCN and KCN have the same low temperature phases and very similar Raman spectra; thus, we assign the band at 110 cm^{-1} in NaCN to the unsplit librational modes of the CN^- molecules and the band at 220 cm^{-1} to the LO

FIG. 8. The phonon dispersion of NaCN at the low temperature phase transition $D_{2h}^{25} \to D_{2h}^{13}$.

TABLE III. Assignment of the Raman bands of NaCN in the two low temperature phases.

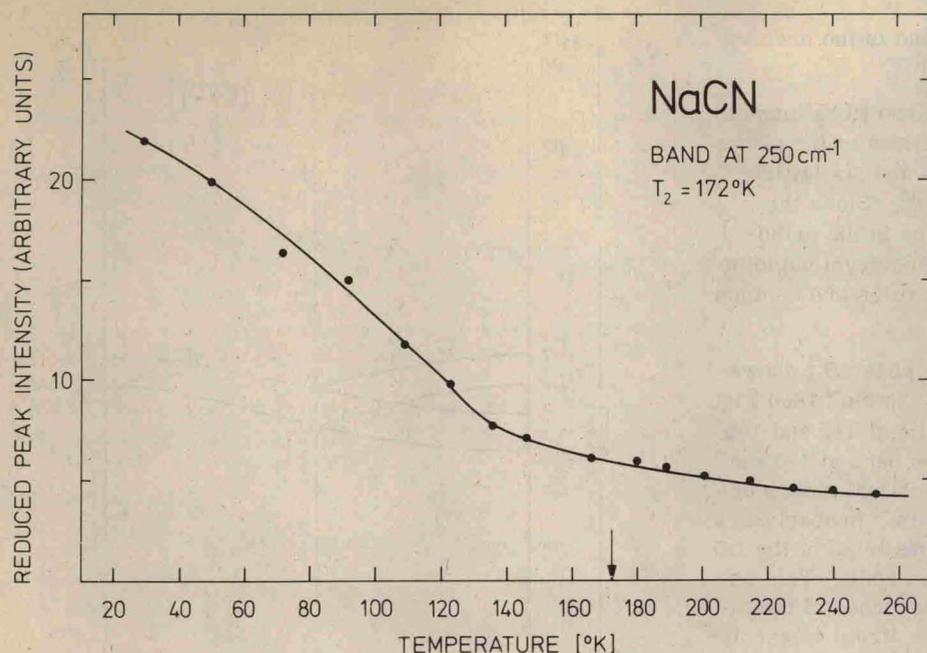| ω (cm^{-1})	Symmetry in the phase D_{2h}^{25}	Symmetry in the phase D_{2h}^{13}
80	TA(X_2^- or X_3^-)	Γ_1^+ or Γ_4^+
125	Librations Γ_2^+, Γ_4^+	Librations Γ_2^+, Γ_4^+
150	TA(X_2^- or X_3^-)	Γ_1^+ or Γ_4^+
180	LA(X_4^-)	Γ_2^+
190	TO(X_2^- or X_3^-)	Γ_1^+ or Γ_4^+
250	Density maximum LO(X_4^-)	Γ_2^+

FIG. 10. The reduced peak intensity of the Raman band at 250 cm⁻¹ in NaCN.

phonon density maximum at the X point of the phase D_{2h}^{25}. It is striking that the librational modes are unsplit in the orthorhombic phase and nearly have the same energy in NaCN and KCN.

The Raman spectrum of NaCN in the low temperature ordered phase D_{2h}^{13} has six bands. If we assume that the librations are unsplit, we expect seven bands from group theory. We tentatively assign the different bands as shown in Table III using the calculated dispersion curves of NaCN. The temperature dependence of the intensity of the band at 185 cm⁻¹ in KCN was quantitatively explained by the assumption that fluctuating clusters of the ordered low temperature phase D_{2h}^{13} appear in the disordered phase D_{2h}^{25} near the phase transition. Below the transition temperature an increasing order parameter is due to the increasing intensity of the band.[4] For the band at 220 cm⁻¹ in NaCN we expect a similar temperature dependence. Figure 10 shows the reduced peak intensity $\omega_p^*[n(\omega_p)+1]^{-1}I(\omega_p)$ of this band versus temperature. $n(\omega_p)$ is the Bose occupation number. The quantitative behavior of the reduced peak intensity is the same as in KCN but the curve is much more smeared out. We believe that this is due to the stronger first order character of the cubic to the orthorhombic phase transition in NaCN which can produce highly stressed domains in the low temperature phases. The structure of the band around 150 °K which disappears at lower temperatures (see Fig. 4) shows that several density-of-states maxima from different points of the Brillouin zone of NaCN overlap in the frequency region. The different temperature dependence of the contributing density maxima explains the large shift of the peak maximum in phase D_{2h}^{25} (see Table I) and obscures expected temperature dependence of $I(\omega_p)$.

The pressure shift of the frequency of the CN⁻-stretching mode in NaCN at 97 °K (Table II) is nearly the same as the corresponding pressure shift of a CN⁻ impurity in sodium chloride ($d\omega/dP = 0.54$ cm⁻¹/kbar at 90 °K).[22]

From the pressure shift of the lattice modes in NaCN the mode Grüneisen parameters γ_i can be obtained by

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V} = \frac{K_T}{\omega_i}\frac{\partial \omega_i}{\partial P}. \tag{1}$$

Since the isothermal bulk modulus K_T is unknown for NaCN, we estimate K_T from the formula for the compressibility κ[23]:

$$\kappa = \frac{1}{K_T} \approx 0.193 \times 10^{-12}\, r^3 \left[\frac{cm^2}{dyn}\right] (r \text{ in Å}), \tag{2}$$

which is a good approximation for crystals with NaCl-type structure and single valent ions, and works very well for KCN; r is the interatomic distance. Using the value of $K_T \approx 0.24 \times 10^{12}$ dyn/cm² in the low temperature phases of NaCN we obtain approximate Grüneisen parameters of the lattice modes (see Table II).[24] The librational mode at 125 cm⁻¹ has a clearly higher Grüneisen parameter compared to the lattice modes. The band at 250 cm⁻¹ has a Grüneisen parameter $\gamma \approx 1.5$ similar to the other lattice modes. The value is nearly identical to the average Grüneisen parameter $\gamma_{av} = 1.43$[25] of NaCl which supports our assignment of this band to be a lattice mode.

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