

The Raman spectrum of NaCN under hydrostatic pressure

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We have measured the Raman spectrum of NaCN in the two orthorhombic low temperature phases under hydrostatic pressure up to 6 kbar. At the order-disorder phase transition from the disordered phase D_{2h}^{25} to the ordered phase D_{2h}^{13} the unit cell doubles and new phonon bands fold from the zone boundary to the center and appear in the Raman spectrum. We analyze the transition group theoretically and assign the different phonon bands in the Raman spectrum. The pressure shift of the CN^- librational mode is larger than the shift of the lattice modes, which supports our band assignment. We estimate the mode Grüneisen parameters using an approximated value for the bulk modulus of NaCN and compare the results with the averaged Grüneisen parameter of NaCl.

INTRODUCTION

Single crystals of the alkali cyanides exhibit the high symmetry and the ionic character of the alkali halides together with the disorder of the plastic phases of molecular crystals. At room temperature the different alkali cyanides are isomorphic with the corresponding alkali chlorides.¹ The ellipsoidal CN^- molecules are oriented independently in their lattice cells and because of the different orientation from cell to cell the translational symmetry of the cyanide crystal is destroyed; the crystal is disordered. At lower temperatures the CN^- dumbbells freeze in with a uniform orientation and the crystal undergoes an order-disorder phase transition to an ordered low temperature phase.²

In $NaCN$ ³ as in KCN ⁴ the ordering of the CN^- molecules is established in two steps: at 288 °K the disordered room temperature phase with NaCl-type structure undergoes an order-disorder transition to an orthorhombic phase (space group D_{2h}^{25}) in which the CN^- molecules are oriented in one [110] direction of the cubic phase, but there is still disorder with respect to the C-N sequence (head-tail disorder).^{2,5} Because of the high symmetry of the cubic room temperature phase the orthorhombic phase consists of different domains which strongly scatter the light and the NaCN crystal is opaque below 288 °K. In contrast to KCN it does not become transparent when heated up again into the cubic phase.⁶ In KCN this phase transition is connected with a strong softening of the elastic constant C_{44} ⁷; thus, the transition is ferroelastic.

Heat capacity measurements first showed the low temperature phase transition at 173 °K.^{5,8} At this temperature the NaCN crystal undergoes an order-disorder phase transition to a completely ordered phase of the space group D_{2h}^{13} .³ The CN^- molecules orient antiparallel in this phase but their axes stay in the old direction. Figure 1 shows the disordered body centered orthorhombic structure above and the ordered simple orthorhombic structure below 173 °K.

The phonon dispersion of NaCN was measured using inelastic neutron scattering techniques, but only parts of the acoustic branches were observed.⁹ The optical phonons are completely obscured probably because of their interaction with orientational movements of the CN^- mole-

cules. The angular distribution of the CN^- molecules in the cubic room temperature phase has been studied with elastic neutron scattering techniques.¹⁰ At room temperature especially [100] but also [111] and their equivalents are the preferred directions for the orientation of the CN^- axes. Raman data of NaCN confirmed these results.^{6,11}

The phase lines between the liquid and the cubic room temperature phases and between the cubic and the disordered orthorhombic phase were measured above room temperature up to 40 kbar by means of the differential thermal analysis.¹² In this work we report on our Raman measurements of NaCN crystals under hydrostatic pressure up to 6 kbar and at temperatures down to 100 °K. We determine the phase line at the low temperature phase transition and interpret the changes of the Raman spectra at this transition using group theoretical methods. The results are compared with calculations of the phonon dispersion of NaCN¹³ and with corresponding results for KCN.⁴ The high pressure shifts of the different modes in the Raman spectrum are measured and the mode Grüneisen parameters are estimated.

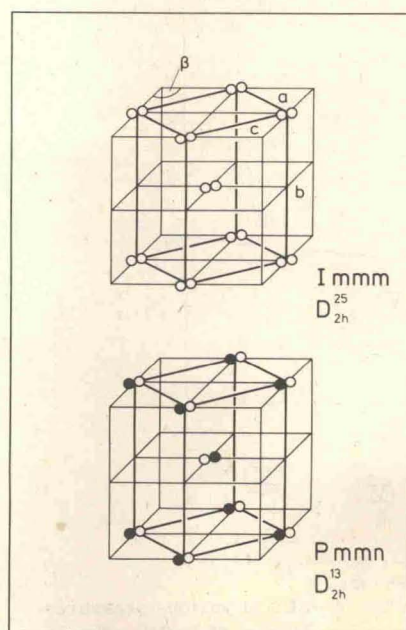


FIG. 1. The structures of the two orthorhombic low temperature phases of NaCN.

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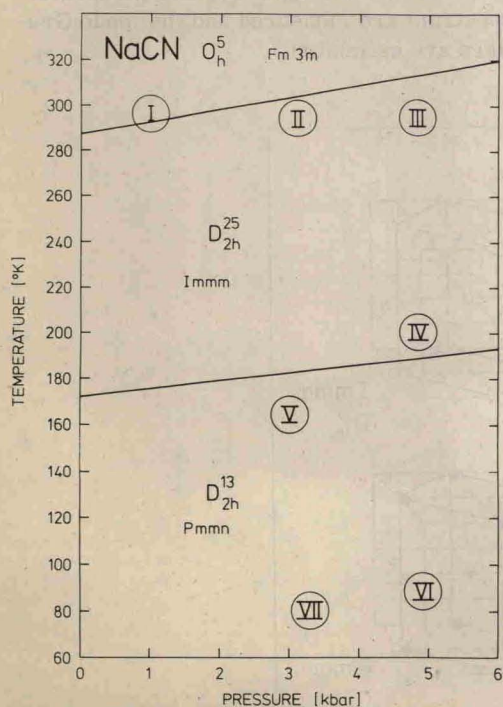
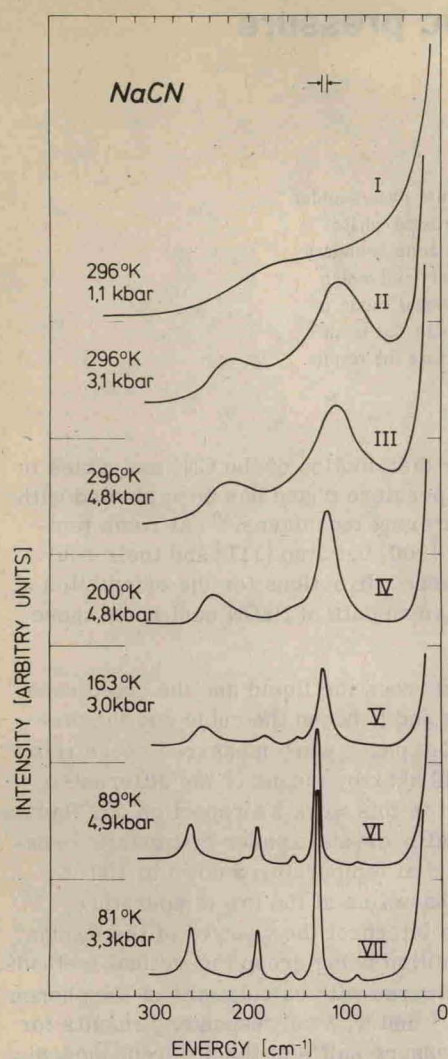


FIG. 2. The Raman spectrum of NaCN at various pressures and temperatures. (a) The phase diagram of NaCN. The numbers mark pressure and temperature at which the spectra of Fig. 2 were taken.

EXPERIMENTS

The Raman spectra of melt grown NaCN crystals under hydrostatic pressure were measured using a He-gas operated high pressure cell with two coaxial sapphire windows of 7 mm free aperture.¹⁴ Right angle scattering geometry is established with two 90° glass prisms inside the cell. The cell is clamped to the liquid nitrogen bath of the cryostat. We measure the temperature by means of thermocouples on the outer surface of one of the sapphire windows and in bores on the surface of the cell body. Several heaters allow the stabilization of intermediate temperatures. The accuracy of the temperature and pressure measurement at the sample is ± 1 °K and ± 0.1 kbar, respectively. The Raman apparatus consists of a 2 W Ar laser, a 1 m double monochromator, and a channeltron detector with photon counting equipment.

Since NaCN is multidomain and opaque in the orthorhombic phases, no polarized Raman spectrum can be obtained below 288 °K.¹⁵ Figure 2 shows selected Raman spectra of NaCN in the different phases; the location of the spectra in the phase diagram is shown in Fig. 2(a). At room temperature the broad feature at about 170 cm^{-1} shows no notable change up to a pressure of 2.2 kbar at 23 °C, where the phase transition to the orthorhombic phase D_{2h}^{25} occurs. The crystal becomes opaque and the Raman spectrum changes abruptly. Two broad bands at 110 and 220 cm^{-1} appear which shift to higher energies with increasing pressure.

The phase transition from the cubic to the orthorhombic phase $O_h^5 - D_{2h}^{25}$ is of first order. Because of the hysteresis at this transition we can not determine the slope of the phase line from the transition pressure and compare it with previous measurements.¹²

The appearance of several new bands in the Raman spectrum below 180 °K shows that the crystal has changed to the ordered low temperature phase D_{2h}^{13} . Figure 3 shows the phase line of this transition. The new band at 185 cm^{-1} was used to indicate the transition temperature. Small arrows indicate the direction in which the phase

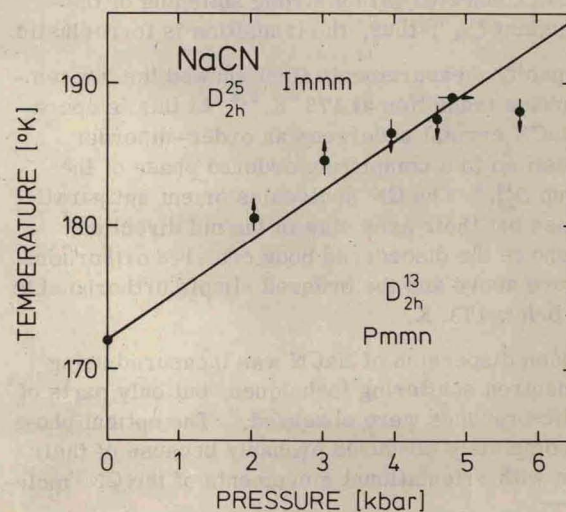


FIG. 3. The phase line of the low temperature phase transition of NaCN.

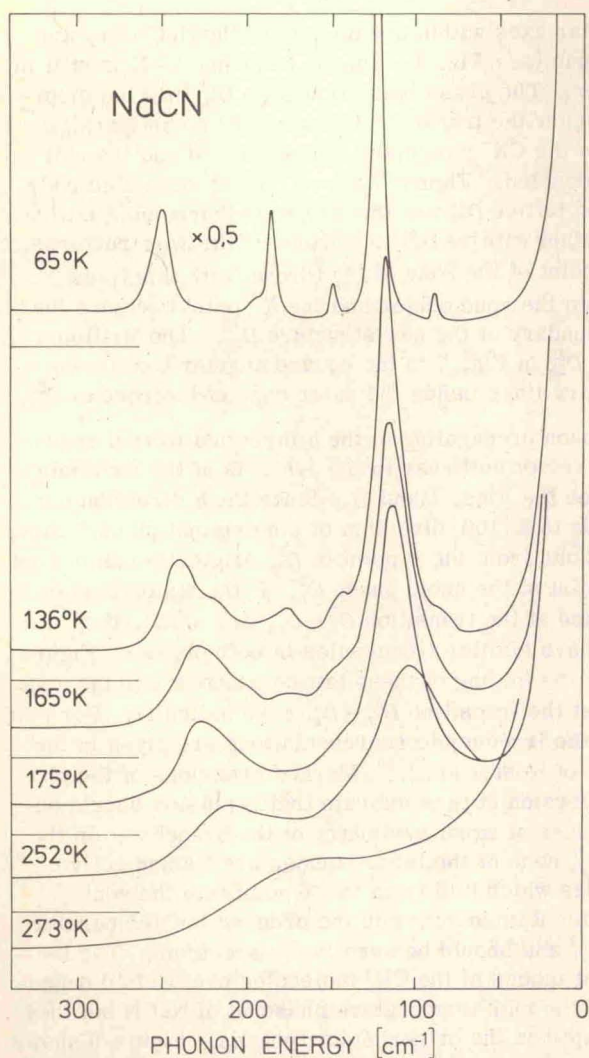


FIG. 4. The temperature dependence of the Raman spectrum of NaCN at zero pressure.

line was crossed. By a linear extrapolation of the line up to room temperature ($\Delta T/\Delta P = 3.4^\circ\text{K kbar}^{-1}$) a transition pressure of 40 kbar is obtained. This value is in very good agreement with the transition pressure of 42 ± 5 kbar for the $D_{2h}^{25} \rightarrow D_{2h}^{13}$ phase transition in NaCN at 298°K obtained from the Raman spectra of NaCN under very high hydrostatic pressure inside a diamond squeezer.¹⁶

TABLE I. Temperature shift of the peak frequency of different bands in the Raman spectrum of NaCN. To indicate the bands we use their approximate low temperature frequencies.

ω (cm^{-1})	Phase	T ($^\circ\text{K}$)	p (kbar)	$d\omega/dT$ ($\text{cm}^{-1}/^\circ\text{K}$)
125	D_{2h}^{13}	$100 \leq T \leq 185$	3.0	0.08
150	D_{2h}^{13}	$100 \leq T \leq 185$	3.0	0.07
185	D_{2h}^{13}	$100 \leq T \leq 185$	3.0	0.11
250	D_{2h}^{13}	$100 \leq T \leq 185$	3.0	0.13
250	D_{2h}^{25}	$190 \leq T \leq 280$	0	0.23
250	D_{2h}^{25}	$190 \leq T \leq 280$	5.8	0.23

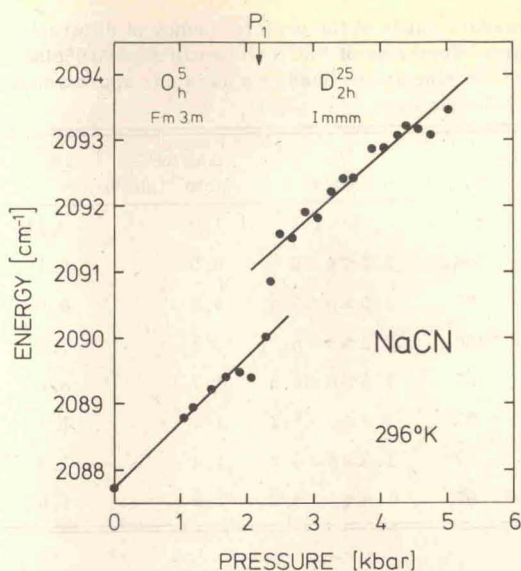


FIG. 5. The pressure shift of the CN^- -stretching mode of NaCN at 296°K .

The Raman spectra of NaCN at zero pressure are shown in Fig. 4. These spectra are similar to the spectra at high pressures in Fig. 2; at lower temperatures the different bands sharpen and become more distinct. The temperature shifts of the different low frequency Raman bands of NaCN at various temperatures and pressures are given in Table I. Note the relative large temperature shift of the band at 250 cm^{-1} in the phase D_{2h}^{25} .

The pressure induced frequency shift of the CN^- -stretching mode at 2088 cm^{-1} is shown in Fig. 5. The frequency of this mode jumps about 1 cm^{-1} at the first order phase transition $O_h^5 \rightarrow D_{2h}^{25}$. The low frequency Raman bands slightly shift with pressure to higher energies (see Fig. 6). The values of the pressure shift of the different bands are given in Table II. The main band of the spectrum which shifts from about 100 cm^{-1} at 280°K to about 125 cm^{-1} at low temperatures is very pressure sensitive, especially in the disordered phase D_{2h}^{25} .

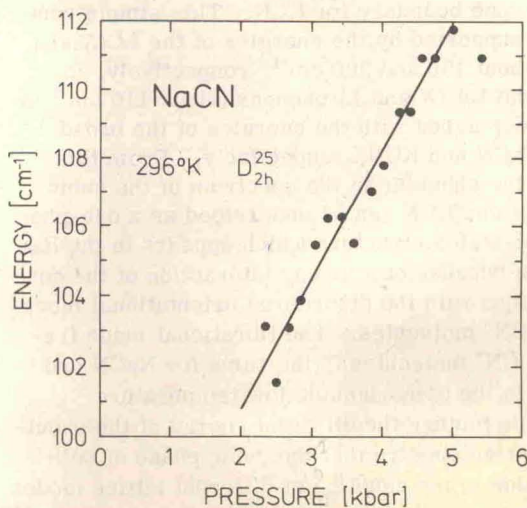


FIG. 6. The pressure shift of the main low frequency Raman band of NaCN at 296°K .

TABLE II. Pressure shifts of the peak frequency of different bands in the Raman spectrum of NaCN and estimated Grüneisen parameters γ_i . To indicate the bands we use their approximate low temperature frequencies.

ω (cm^{-1})	Phase	T ($^{\circ}\text{K}$)	p (kbar)	$\Delta\omega/\Delta P$ ($\text{cm}^{-1}/\text{kbar}$)	γ_i
2088	O_h^5	296	$0 \leq p \leq 2.2$	1.0	0.11
2088	D_{2h}^{25}	296	$2.2 \leq p \leq 5$	0.9	0.10
2088	D_{2h}^{13}	97	$1.5 \leq p \leq 5$	0.5	0.06
125	D_{2h}^{25}	296	$2.2 \leq p \leq 5$	3.5	7.6
125	D_{2h}^{13}	97	$1.8 \leq p \leq 5.2$	1.7	3.3
150	D_{2h}^{13}	97	$1.8 \leq p \leq 5.2$	1.0	1.4
180	D_{2h}^{13}	97	$1.8 \leq p \leq 5.2$	1.4	1.8
250	D_{2h}^{13}	97	$1.8 \leq p \leq 5.2$	1.6	1.5

DISCUSSION

In the cubic room temperature phase of NaCN no lattice phonons should be Raman active. The Raman spectrum shows a central component with a broad shoulder at about 170 cm^{-1} (see also Fig. 2 and 4). These features are believed to come from combinations of librational and orientational diffusive movements of the CN^- molecules.^{6,11} The assignment agrees fairly with calculations of the librational mode frequencies with the help of a Devonshire model from specific heat data ($\omega_{\text{LIB}} = 200 \text{ cm}^{-1}$ for NaCN)¹⁷ and corresponds to a similar interpretation of the shoulder at 110 cm^{-1} in the room temperature phase O_h^5 of KCN.¹⁸

To make room for the orientational movements of the CN^- ions the Na^+ ions shift randomly from the ideal lattice sites of the cubic crystal.¹ From this a strong coupling of the librational and orientational movements of the CN^- molecules with short wavelength lattice modes which are characterized by large vibrational amplitudes of the cations is expected. Since the Na^+ ion is lighter and the K^+ ion heavier than the CN^- molecule, we find from a linear chain model that these modes are the optical modes at the zone boundary for NaCN and the acoustic modes at the zone boundary for KCN. This simple consideration is supported by the energies of the LO(X and L) phonons (about 160 and 220 cm^{-1} , respectively, in NaCN¹³) and the LA (X and L) phonons (about 110 cm^{-1} in KCN^{13,19}), which agree with the energies of the broad shoulder in NaCN and KCN, respectively. From this point of view the shoulder in the spectrum of the cubic phase of NaCN and KCN can be understood as a one-phonon density-of-states structure which appears in the Raman spectrum because of a strong interaction of the contributing phonons with the disordered orientational movements of the CN^- molecules. The librational mode frequency of the CN^- molecules is the same for NaCN and KCN at least in the orthorhombic low temperature phases. In this picture the different energy of the shoulders in the Raman spectrum of the cubic phase of both materials is due to the coupling of different lattice modes to the disorder.

In the disordered phase D_{2h}^{25} the orientation of the CN^-

molecular axes within one domain of the NaCN crystal is uniform (see Fig. 1); but the sequence C-N is still in disorder. The phase transition $D_{2h}^{25} - D_{2h}^{13}$ lifts the disorder: Below the transition temperature an antiparallel order of the CN^- molecules is established and the unit cell is doubled. Figure 7 shows the orthorhombic body centered lattice D_{2h}^{25} and the simple orthorhombic lattice D_{2h}^{13} together with the Brillouin zones of the two structures. The X point of the zone of D_{2h}^{25} (drawn with thin lines) folds into the zone center and the X' point becomes the zone boundary of the new structure D_{2h}^{13} . The Brillouin zone of D_{2h}^{13} in Fig. 7 is the square angular box drawn with heavy lines inside the outer cage of the zone of D_{2h}^{25} .

A phonon propagating in the b direction in real space has a q vector collinear to the $1/b$ axis of the Brillouin zone (see the Figs. 1 and 7). Since the b direction corresponds to a $[100]$ direction of the original cubic lattice, the phonons from the X point of D_{2h}^{25} originally came from the X point of the cubic phase O_h^5 . If the distortions of the lattice at the transition $O_h^5 - D_{2h}^{25}$ are small, they should have similar frequencies in both phases. Figure 8 shows the folding of these lattice phonons into the zone center at the transition $D_{2h}^{25} - D_{2h}^{13}$ schematically. For both phases the irreducible representations are given in the notation of Koster *et al.*²⁰ Marked crossings of the phonon dispersion curves indicate that repulsion should occur because of equal symmetry of the branches. In the phase D_{2h}^{25} none of the lattice modes are Raman active. All modes which fold from the X point into the zone center are Raman active in the ordered low temperature phase D_{2h}^{13} and should be seen in the spectrum. The librational modes of the CN^- molecules are twofold degenerate in the high temperature phase O_h^5 of NaCN but they should split in the orthorhombic phases. Figure 9 shows the dispersion of the librations at the transition $D_{2h}^{25} - D_{2h}^{13}$ schematically. The two librational modes at the zone center of the phase D_{2h}^{25} are Raman active, but the libra-

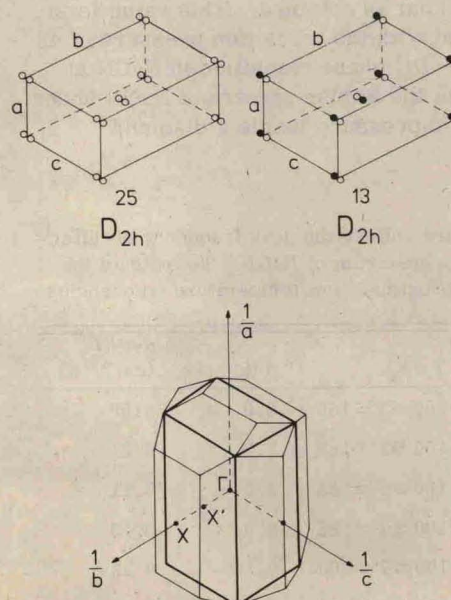


FIG. 7. Structures and Brillouin zones of the two orthorhombic low temperatures phases of NaCN.

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 orthorhombic 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} calculated¹³). The poorer agreement may be due to the stronger first order character of the transition $O_h^5 - D_{2h}^{25}$ which is destructive in NaCN but not in KCN. We

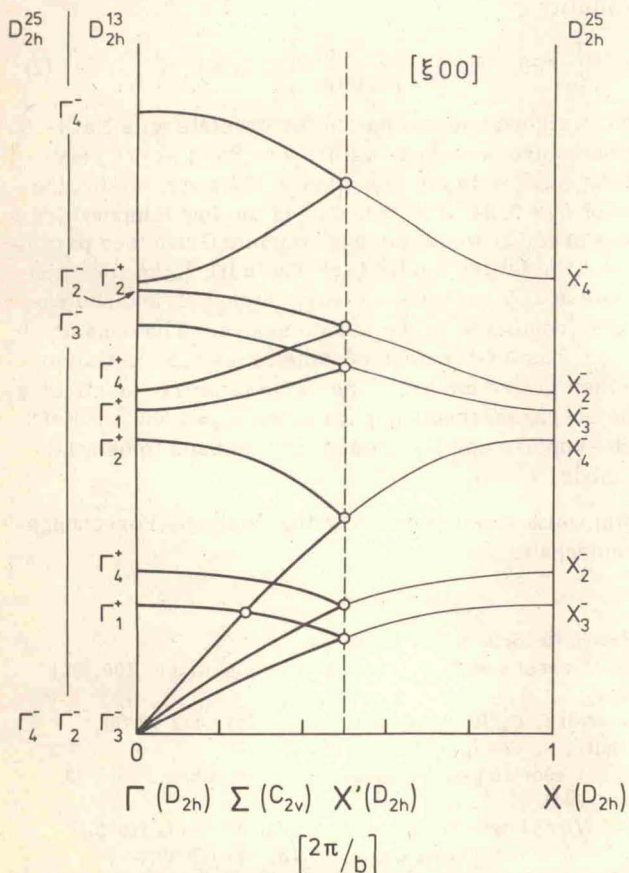


FIG. 8. The phonon dispersion of NaCN at the low temperature phase transition $D_{2h}^{25} \rightarrow D_{2h}^{13}$.

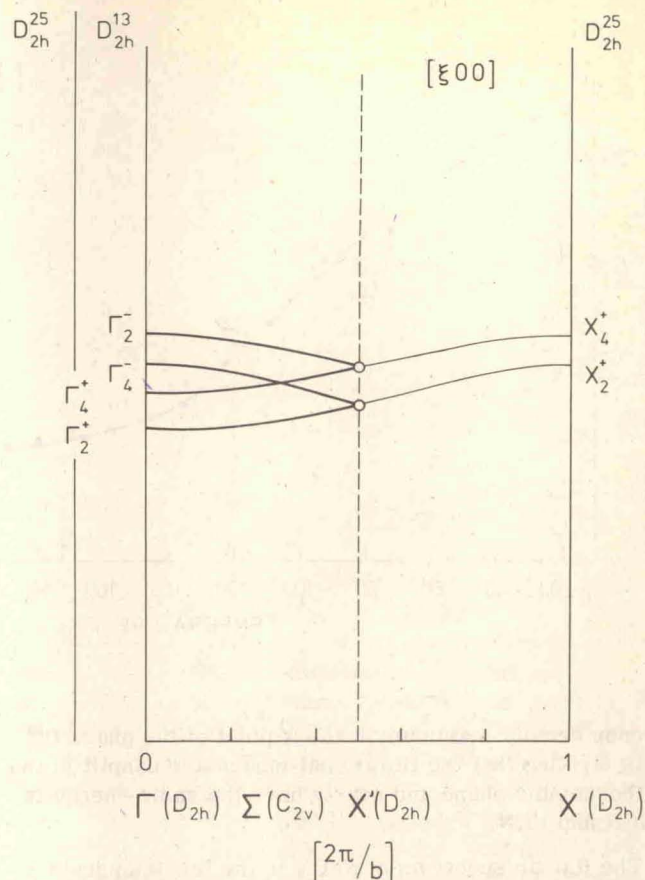


FIG. 9. The dispersion of the CN^- librational mode at the low temperature phase transition of NaCN.

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 $\text{KCN}_x\text{KCl}_{1-x}$ 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

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^+

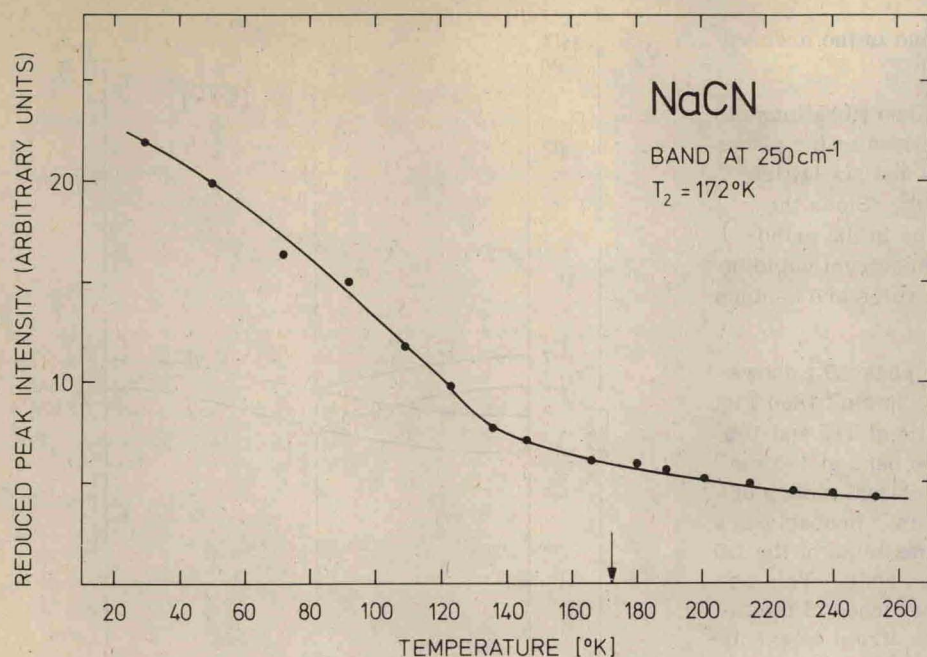


FIG. 10. The reduced peak intensity of the Raman band at 250 cm^{-1} in NaCN.

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 $\omega_p^n [n(\omega_p) + 1]^{-1} I(\omega_p)$ 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 ($d\omega/dP = 0.54 \text{ cm}^{-1}/\text{kbar}$ at 90°K).²²

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

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V} = \frac{K_T}{\omega_i} \frac{\partial \omega_i}{\partial P} \quad (1)$$

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

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

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 $K_T \approx 0.24 \times 10^{12} \text{ dyn/cm}^2$ 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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