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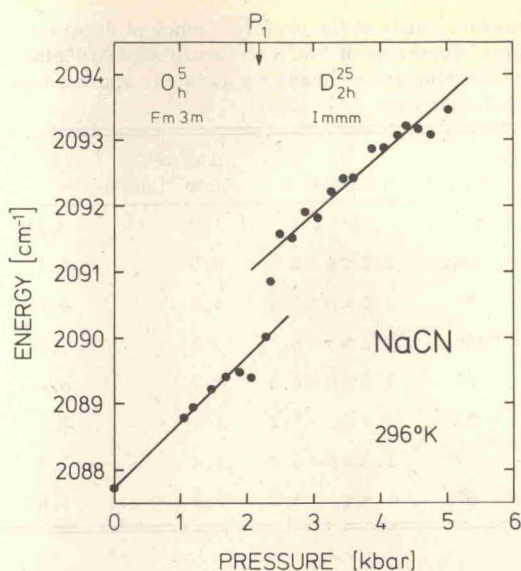

FIG. 5. The pressure shift of the CN⁻-stretching mode of NaCN at 296 °K.

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}.

line was crossed. By a linear extrapolation of the line up to room temperature ($\Delta T/\Delta P = 3.4 \,°K\,kbar^{-1}$) 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.

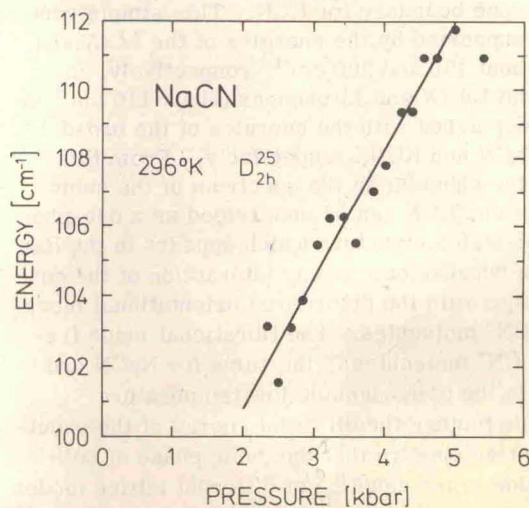| ω (cm⁻¹)	Phase	T (°K)	p (kbar)	$d\omega/dT$ (cm⁻¹/°K)
125	D_{2h}^{13}	$100 \leq T \leq 185$	3.0	0.08
150	D_{2h}^{13}	$100 \leq T \leq 185$	3.0	0.07
185	D_{2h}^{13}	$100 \leq T \leq 185$	3.0	0.11
250	D_{2h}^{13}	$100 \leq T \leq 185$	3.0	0.13
250	D_{2h}^{25}	$190 \leq T \leq 280$	0	0.23
250	D_{2h}^{25}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

FIG. 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 (°K)	p (kbar)	$\Delta\omega/\Delta P$ (cm^{-1}/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} [6] (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 ($\omega_{\text{LIB}} = 200$ 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 NaCN[13]) 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 $D_{2h}^{25} \rightarrow D_{2h}^{13}$ 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 $\mathbf{q}$ 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 $O_h^5 \rightarrow D_{2h}^{25}$ 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 $D_{2h}^{25} \rightarrow D_{2h}^{13}$ 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 $D_{2h}^{25} \rightarrow D_{2h}^{13}$ schematically. The two librational modes at the zone center of the phase D_{2h}^{25} are Raman active, but the libra-
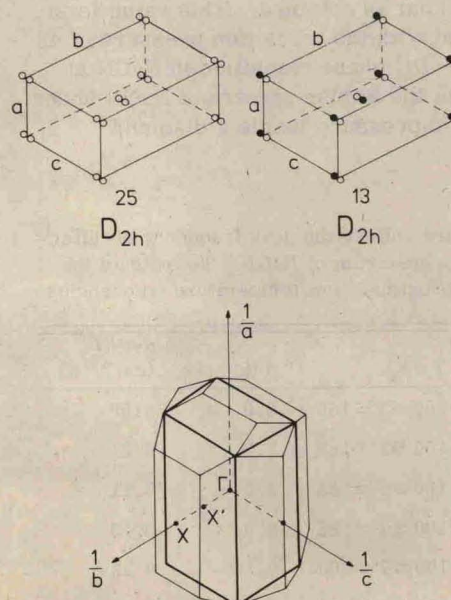

FIG. 7. Structures and Brillouin zones of the two orthorhombic low temperatures phases of NaCN.