

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 NaCN³ as in KCN⁴ 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.

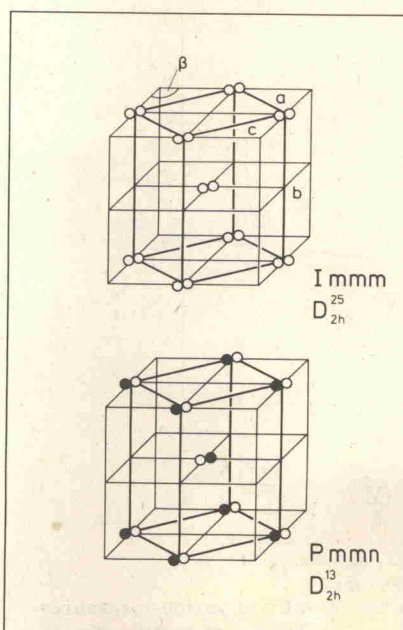


FIG. 1. The structures of the two orthorhombic low temperature phases of NaCN.

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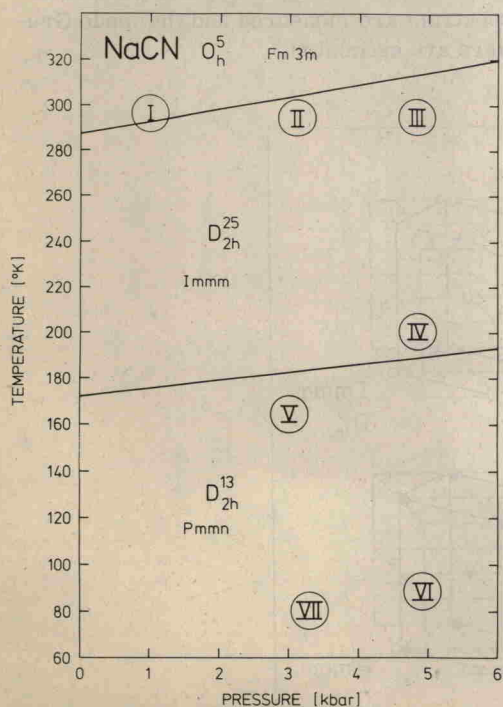
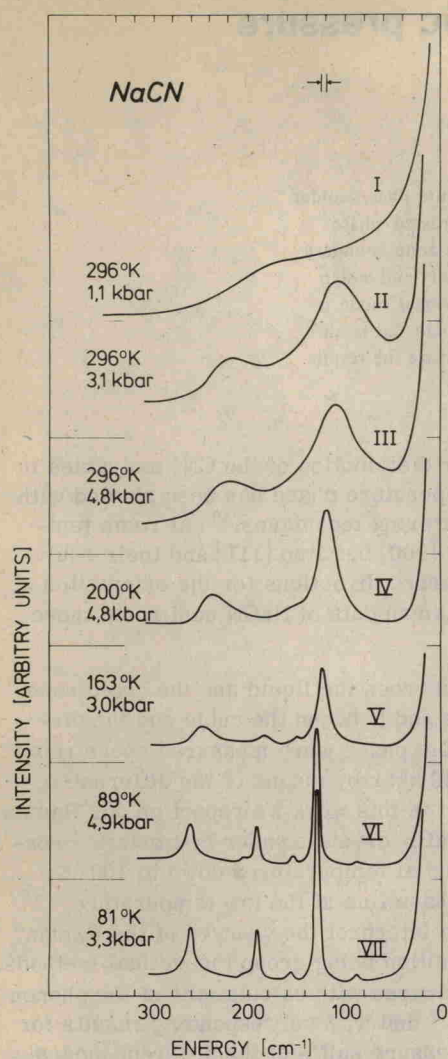


FIG. 2. The Raman spectrum of NaCN at various pressures and temperatures. (a) The phase diagram of NaCN. The numbers mark pressure and temperature at which the spectra of Fig. 2 were taken.

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

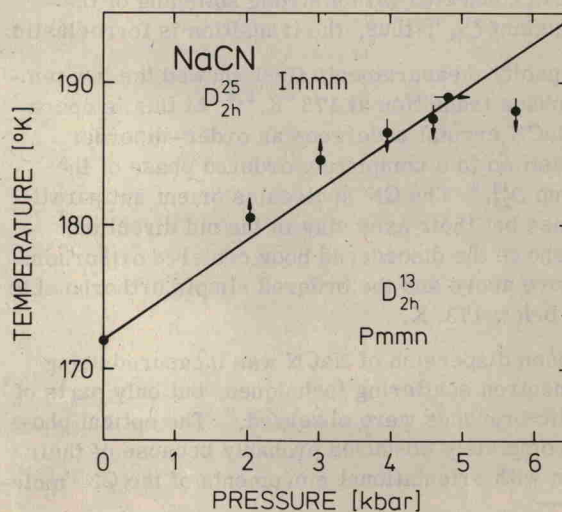


FIG. 3. The phase line of the low temperature phase transition of NaCN.