PHYSICAL REVIEW B VOLUME 18, NUMBER 1 1 JULY 1978

Light-scattering studies of the polymorphism of potassium cyanide under hydrostatic pressure

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(Received 13 February 1978)

We measured the Raman spectrum of potassium cyanide under hydrostatic gas pressures up to 7 kbar at temperatures down to 75 K and found two new high-pressure phases with characteristic Raman spectra. The topology of the phase diagram of the alkali cyanides suggests that the orientation of the CN^- molecules in these phases is probably a [111] direction of the original cubic lattice. We discuss possible structures of new phases and correlate them with the intermediate phase *Aa* in potassium cyanide at zero pressure. From the pressure shift of the Raman bands, we estimate the Grüneisen parameters of the lattice modes and compare them with the temperature-dependent bulk Grüneisen parameter of KCN and the Grüneisen parameter of the soft TA phonon above the cubic to orthorhombic phase transition.

I. INTRODUCTION

The alkali cyanides have recently gained increasing attention because they exhibit orientational disorder of the CN^- molecules similar to a molecular crystal together with the cubic symmetry and the ionic character of the alkali halides. The ellipsoidal CN^- molecules rotate more or less free and uncorrelated on the anion sites of the cubic lattice and their different orientation from cell to cell breaks the translational invariance of the crystal. Since this disturbance of the symmetry is weak, the concept of an ideal ionic crystal can be used as a basis for the understanding of the lattice dynamics of the disordered cyanide crystal. Shell-model calculations for NaCN and KCN give an overall agreement with inelastic neutron measurements of the phonon dispersion curves but show also principal deviations where the orientational movements of the CN^- molecules affect the phonon branches.[1-3]

At lower temperatures or under hydrostatic pressure, the CN^- molecules freeze in with a uniform orientation all over the crystal and the alkali cyanide undergoes an order-disorder transition to an ordered phase. The relatively low symmetry of the CN^- molecules inside a high-symmetry lattice cell gives rise to a variety of partly and completely ordered phases. The phases of the different alkali cyanides can be classified by arranging them in a single P-T phase diagram (see Fig. 1). The net of phase lines in this diagram is cut by vertical temperature axes which mark the zero-pressure point at the pressure axis for each material. Using an individual scaling of the temperature axes, the diagram is supposed to exhibit the topography of the P-T phase diagram for the respective alkali cyanide. In analogy to the phase diagram of the alkali halides the phases on the left-hand side have a fourfold coordination similar to the wurtzite structure; in the middle of the diagram the phases are NaCl-type with the coordination number six and on the right-hand side we find phases with eightfold coordination and a structure similar to the CsCl-type. The additional phase lines describe phase transitions due to the orientational disorder of the cyanides. The solid-state phases in Fig. 1 are characterized by a space-group symbol, by the direction of orientation of the CN^- molecules with respect to the axes of the corresponding cubic lattice, and by two dumb-bells which describe the order of the CN^- molecules. Broken phase lines or temperature axes indicate features which are proposed but up to now not experimentally verified beyond all doubt. Figure 2 gives the relevant references[4-18] for the different features of the phase diagram of Fig. 1.

KCN is the best studied alkali cyanide because it is relatively easy to obtain in crystalline form and

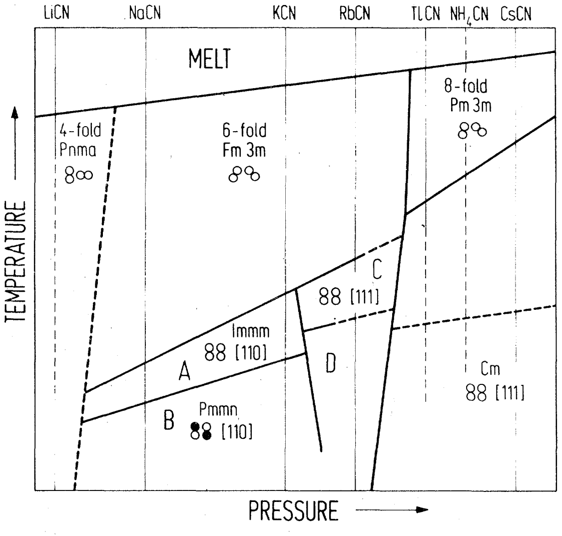

FIG. 1. Phase diagram of the alkali cyanides.

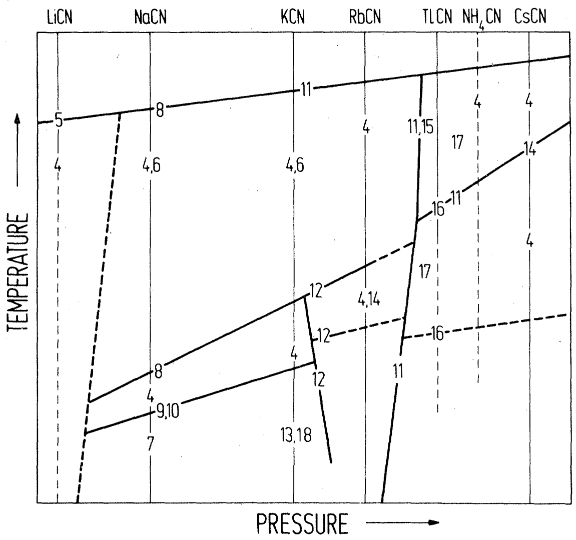

FIG. 2. References to Fig. 1.

shows nearly all the phase transitions of the diagram, Fig. 1, at reasonable temperatures and pressures. The structures of TlCN, NH_4CN, and CsCN with eightfold coordination on the right-hand side of Fig. 1, for instance, were not studied very much and the phase lines and space groups of the diagram mainly describe features of the known high-pressure phases of KCN above 20 kbar; these were investigated with caloric inelastic-neutron-scattering, and with Raman techniques.[11,17,19] In this work we study the high-pressure phases *C* and *D* (Fig. 1) of KCN which have a sixfold coordination and which appear at temperatures below 170 K and at pressures above 0.3 kbar. We can predict the existence of these new phases from the different orientations of the CN^- molecules in the ordered low-temperature phases of KCN and RbCN at zero pressure with the help of the *P*-*T* diagram (Fig. 1).

From the change of the Raman spectra of KCN with temperature and pressure we obtain the actual phase lines. The intermediate phase *Aa* which was found by thermal cycling of a KCN crystal around the phase transition at 168 K and zero pressure[20] seems to be a high-pressure phase which is stabilized by internal stresses in the multidomain crystal. We estimate the mode Grüneisen parameters from the pressure shift of the corresponding Raman bands and discuss the possible structures of the new phases.

II. EXPERIMENTS

We have measured the Raman spectrum of KCN at temperatures down to 75 K under He-gas pressures up to 7 kbar. The solution grown KCN-crystals were cleaved into platelets of $3 \times 4 \times 5$ mm^3 and measured inside an optical high-pressure cell[21] using a 2-W Ar laser, a 1-m double monochromator, and photon counting equipment. The accuracy of the temperature and pressure measurements was ±1 K and ±0.1 kbar, respectively. At the phase transition from the cubic room-temperature phase to the partly ordered low-temperature phases the crystal becomes multidomain and opaque and no polarized Raman spectra could be obtained. Figure 3 shows the Raman spectrum of KCN in the region *A*-*D* of the phase diagram (Fig. 1). The band at 2080 cm^{-1} is due to the CN^- stretching vibration. For comparison we also show the Raman spectrum of the cubic phase of KCN as we obtain it with the crystal inside the high-pressure cell and no polarizers used. The Raman spectra of KCN at zero pressure are shown in Ref. 13 and 22.

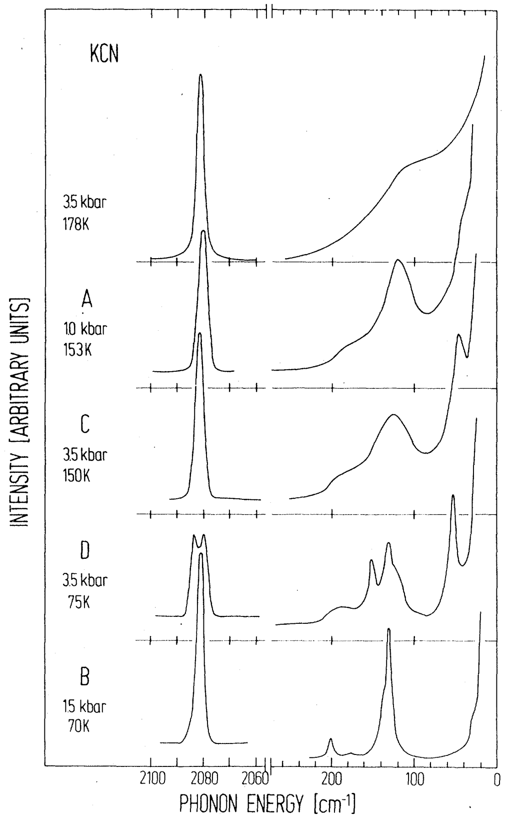

FIG. 3. Raman spectra of KCN in the different low-temperature phases.

The broad shoulder in the spectrum of the cubic phase disappears in the low-temperature phases *A* and *C* and a broad band appears at about 120 cm^{-1} which was assigned to be the librational mode of the CN^- molecules in phase *A*.[22] The agreement in energy of this band and the shoulder in the spectrum of the cubic phase seems to be accidental.[10] The spectra of the low-pressure phase *A* and the new high-pressure phase *C* differ only in the inten-

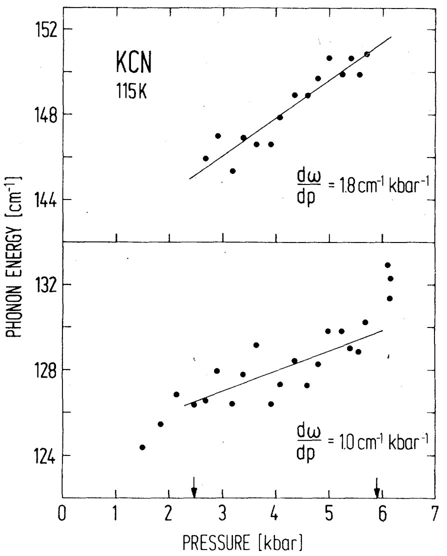

FIG. 4. Pressure shift of two Raman bands in the high pressure phase *D*.

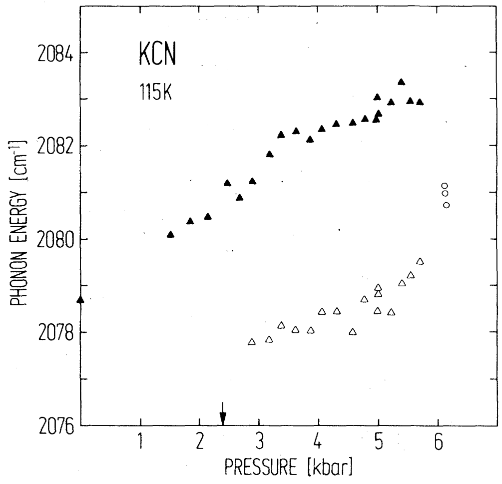

FIG. 5. Peak energies of the CN^- stretching mode in phase *D*.

sity of the low-frequency band at 50 cm^{-1}, which is larger in phase *C* but never disappears completely in phase *A*.

Both low-temperature phases *C* and *D* show a number of new bands. At the phase line between $C \rightarrow D$ the low-frequency band shifts up from 48 to 52 cm^{-1} (115 K, 6 kbar); the same band shifts down from 50 to 47 cm^{-1} (115 K, 2.4 kbar) at the transition $D \rightarrow B$. At this transition the peak energy of the band at 190 cm^{-1} jumps up from 184 to 194 cm^{-1} (115 K, 2.4 kbar). Figure 4 shows the pressure shift of two bands in the Raman spectrum of phase *D*. The phase appears suddenly if phase *C* is cooled down far enough or if at sufficiently low temperature the pressure is reduced. For the latter case Fig. 5 shows the extraordinary behavior of the band of the CN^- stretching mode at 2080 cm^{-1}. In phase *C* at 115 K and 6.2 kbar the band is single (open circles) but splits symmetrically when pressure is reduced. The intensity of the two bands together is about as large as for the single band. After a region of hindered relaxations, due to the first-order transition, the two components shift towards each other when the pressure is further reduced. At the phase transition to phase *B* the low-frequency component disappears and the remaining component overtakes its intensity. The splitting of the band is smaller when phase *C* collapses into phase *D* at higher temperatures, thus it depends on the amount of supercooling of phase *C*.

Table I shows the pressure shift of the different Raman bands of KCN in various phases. The corresponding Grüneisen parameters γ_i were determined using the bulk modulus from elastic constants[23] of the cubic phase at zero pressure just above the phase line at 168 K.[10] The bands are characterized by their average peak energy in the corresponding phase. The last column of the Table gives a tentative assignment of the different modes (see Refs. 10 and 13 and the discussion).

Figure 6 shows the phase diagram of KCN as we obtained it from our Raman measurements. Arrows at the points indicate the direction in which a phase line was crossed. The phase line between the two low-temperature phases *Immm* (*A*) and *Pmmn* (*B*) was proposed to be of second order at zero pressure,[13,24] all other phase lines are of first order. Details of the experimental points are given in Table II. Note the large hysteresis between the phases *A* and *C* and the high-pressure phases *C* and *D* and between *B* and *D*. To obtain phase *C* and *D* it needs therefore less pressure if the phases are reached by lowering the temperature under pressure than by increasing the pressure at low temperatures. It is remarkable that a triple point lies at about 170 K and 0.3 kbar very near to the zero-pressure transition from the cubic to the orthorhombic phase.

III. PHASE DIAGRAM AND RAMAN SPECTRA

New features in the phase diagram of KCN (see Fig. 6) were not surprising. An "intermediate phase" had already been reached by cooling the crystal over the cubic to orthorhombic phase transition at 168 K and zero pressure.[20] The structure of this phase which is only stable within an interval of a few degrees (see Fig. 6) was determined to be *Aa* with a unit cell twice as large as the normal zero-pressure phase *Immm*; the CN^- molecules are uniformly oriented in a [111] direction

TABLE I. Pressure shifts and approximate mode Grüneisen parameters of the Raman-active modes in KCN.

ω_i (cm^{-1})	Phase	T (K)	$\frac{d\omega_i}{dP}$ $\frac{\text{cm}^{-1}}{\text{kbar}}$	γ_i	Assignment with respect to the cubic phase
118	C	155	1.7	2.2	liberation
50	D	115	0.5	1.5	acoustical mode from L point
128	D	115	1.0	1.2	liberation?
148	D	115	1.8	1.9	
2078	D	115	0.42	0.031	CN$^-$ stretching vibration
2082	D	115	0.60	0.044	
125	B	82	1.3	1.6	liberation
134	B	82	1.2	1.4	LA(X)[10]
175	B	82	1.2	1.1	TO(X)[13]
198	B	82	1.9	1.5	LO(X)[13]
2078	B	82	0.72	0.053	CN$^-$ stretching vibration

of the cubic lattice. The doubling of the cell is due to alternating shifts of the potassium ions along a [110] direction and not a result of an antiparallel ordering of the CN$^-$ molecules as for the zero-pressure phase *Pmmn* (*B*). Raman measurements by Winchester at zero pressure showed that the intensity of the 50-cm^{-1} band could be increased by the thermal cycling process around the 168 K phase transition but no additional bands could be generated.[25]

From the phase diagram of the alkali cyanides (see Fig. 1) a steep phase line between KCN and RbCN can be expected since the orientation of the CN$^-$ axes in the ordered phase of the two materials is different. The existence of the intermediate phase *Aa* with the right CN$^-$ orientation shows that the moderate pressure from internal stresses of the multidomain crystal can change the structure of the KCN crystal just below 168 K. Our Raman measurements of KCN at low temperatures under hydrostatic pressure show the expected new high-pressure phases (see Fig. 6).

The triple point near 170 K and 0.3 kbar suggest the possibility of reaching phase *C* in a highly stressed multidomain KCN crystal; the negative slope of the phase line between the low-and high-pressure phases explains the small stability region of this "intermediate phase" at zero pressure. On the other hand the Raman spectrum of phase *C* does not show particular signs of a cell doubling compared to the orthorhombic phase *Immm* (*A*). Since this result is in agreement with Winchester's measurements (see above) and since a unit-cell doubling due to large shifts of the potassium ions should show up in the Raman spectrum, we propose a structure for phase *C* which has half the unit cell of the intermediate phase *Aa* and possibly inversion symmetry, i.e., *A*2/*m*. This space group would explain the similarity of the Raman spectra of the phases *A* and *C*. The 50 cm^{-1} band can be assigned to a one-phonon density-of-states maximum which appears in the Raman

TABLE II. Description of the measured points in Fig. 6.

●↑ ●↓	crystal becomes opaque or gets transparent
↓	band at 175 cm^{-1} appears
×	sudden doubling of the CN$^-$ stretching mode
↑ ←⊖	doubling of CN$^-$ stretching mode disappears
⊖→	doubling of CN$^-$ stretching mode appears
△→	band at 50 cm^{-1} appears
△↕ ←△	band at 50 cm^{-1} disappears
□→	band at 50 cm^{-1} starts to grow

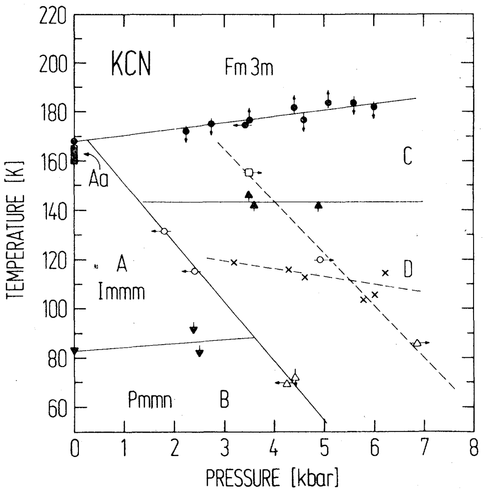

FIG. 6. Phase diagram of potassium cyanide.

spectrum because of the head-tail disorder of the CN^{-1} molecules in phase *A* and *C*.[13,21] The different intensity of this band in the two phases can be explained by a different coupling strength of the relevant lattice modes from the zone boundary to the head-tail disordered but uniformly in a [110] (*A*) or [111] (*C*) direction oriented molecules.

The splitting of the CN^- stretching mode in phase *D* looks very much like a Davydov splitting and indicates, as do the new low-frequency Raman bands a doubling of the unit cell. It is not very likely that phase *D* can be assigned to the space group *Aa* of the intermediate phase of KCN since the stability regions of both phases are quite far apart (see Fig. 6). Recent Debye-Scherer measurements of KCN under hydrostatic pressure with neutrons show no obvious correlations between the spectra of the phase *A*, *C*, and *D* indicating that phase mixtures are unprobable.[26] The jump of the Raman band at 50 cm^{-1} at the phase transition $C \rightarrow D$ is in agreement with our assumption that this band is a disorder allowed one-phonon density-of-states maximum of an acoustical-phonon branch in phase *C* which folds into the Γ point and becomes Raman allowed in phase *D*. This density maximum cannot be at the *X* point of the original cubic zone since it would be Raman allowed in phase *Pmmn* (*B*). We think that the cubic *L* point is more likely, also because this point folds into Γ at a transition $A2/m \rightarrow Aa$.

IV. THE GRÜNEISEN PARAMETERS

The mode Grüeneisen parameters γ_i of a lattice mode describes the volume dependence of the mode frequency ω_i:

$$\gamma_i = -\frac{d\ln\omega_i}{d\ln V}\,. \tag{1}$$

Force constant anharmonicities contribute to γ_i as well as other volume dependent parameters of ω_i as the crystal mass density and the wave vector $\vec{q}_i$. For a direct measurement of γ_i inelastic neutron and light scattering techniques or infrared absorption can be used; the crystal is pressurized inside a suitable cell. More indirect information about special mode Grüneisen parameters can be obtained from macroscopic physical properties: the γ_i of the ferroelectric soft mode in $NaNO_3$, for instance, was obtained from the dielectric constant and the thermal expansion coefficient α of the crystal.[27]

The mode Grüneisen parameters γ_i can be compared with the bulk Grüneisen parameter γ_{th}. This quantity is defined as the average of all the γ_i of the crystal. In the harmonic approximation γ_{th} can be derived from the free energy *F* in the high-temperature limit

$$\alpha K_T = -\frac{\partial}{\partial T}\frac{\partial F}{\partial V} = \frac{1}{V}\frac{\partial}{\partial T}\sum_i \epsilon_i\gamma_i = \frac{1}{V}\sum_i c_i\gamma_i\,, \tag{2}$$

and for $\hbar\omega_i \lesssim kT$,

$$\alpha K_T = \frac{k}{V}\sum_i \gamma_i = \frac{C_V}{V}\gamma_{th}\,. \tag{3}$$

K_T is the isothermal bulk modulus, ϵ_i the energy, and c_i the specific heat of the *i*th oscillator, *N* is the number of oscillators and C_V the specific heat at constant volume.

Usually, the Grüneisen parameters γ_i and γ_{th} depend only weakly on temperature, but near a phase transition some mode frequencies, $\omega_i = \omega_i(V,T)$ and the corresponding γ_i, depend explicitly on temperature. In this case, we obtain from Eq. (2) in the high-temperature limit

$$\gamma_0(T) \equiv \frac{\alpha K_T V}{C_V} = \gamma_{th} + T\,\frac{\partial\gamma_{th}}{\partial T}\,. \tag{4}$$

If $\gamma_0(T)$ is known, $\gamma_{th}(T)$ can be determined from (4) by numerical integration; for a boundary condition $\gamma_{th}(T \gg T_c) = \gamma_0(T)$ may be used. $\gamma_{th}(T)$ should exhibit the temperature dependence of the mode Grüneisen parameter which is most sensitive to temperature changes. In many cases, this will be the Grüneisen parameter of the soft mode. For NaCN and KCN we obtain $\gamma_0(T)$ if we determine K_T from the elastic constants.[23,28] Figure 7 shows $\gamma_0(T)$ and $\gamma_{th}(T)$ for KCN in the cubic phase. Note the opposite temperature behavior of $\gamma_0(T)$ and $\gamma_{th}(T)$. For comparison the bulk Grüneisen parameter γ_{th} of KCl (see Ref. 29) is also shown in Fig. 7. The temperature dependence of $\gamma_0(T)$ is mainly due to the increasing thermal expansion coefficient of KCN near the transition temperature. NaCN shows qualitatively the same behavior but $\gamma_{th}(T \gg T_c)$ is only about 0.7 due to an abnormal low bulk

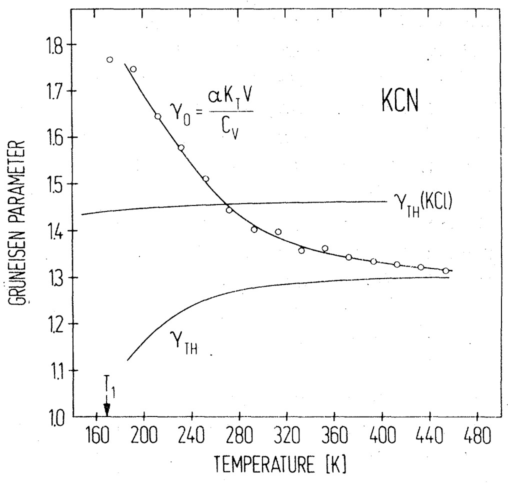

FIG. 7. Temperature dependence of the bulk Grüneisen parameter γ_{th} in KCN.

modulus of this material in the cubic phase.

From the moderate decrease of the bulk Grüneisen parameter $\gamma_{\text{th}}(T)$ we expect a strongly decreasing Grüneisen parameter γ_{TA} of the soft mode which is a TA mode in NaCN and KCN.[23,28] A decreasing soft mode Grüneisen parameter above the transition is also expected from the positive slope dT_1/dP of the phase line between the cubic and the orthorhombic phase of NaCN and KCN. Since γ_{TA} is given by

$$\gamma_{\text{TA}} = \frac{K_T}{2c_{44}} \frac{\partial c_{44}}{\partial P} - \frac{1}{6}, \tag{5}$$

and since $\partial c_{44}/\partial P = -0.35$,[30] for NaCN we find $\gamma_{\text{TA}}(350\text{K}) = -3.0$ and $\gamma_{\text{TA}}(290\text{ K}) = -8.4$ as expected. The relevant elastic constant c_{44} in NaCN can be well described as a linear function of temperature near the phase transition temperature at $T_1 = 288$ K which passes zero at $T_0 = 256$ K.[28] The slope $\partial T_0/\partial P = 3.4$ kbar (Ref. 30) is in fair agreement with the slope of the transition temperature $\partial T_1/\partial P = 5.4$ kbar (Ref. 8); thus, for NaCN the picture is at least qualitatively consistent.

In KCN the slope of the phase line $\partial T_1/\partial P = 2.56$ kbar^{-1} (see Fig. 6) is positive as in NaCN and the same considerations should hold: γ_{th} should decrease above the transition (see Fig. 6) and $\partial T_0/\partial P$ should be positive. Brillouin scattering measurements of KCN under hydrostatic pressure show that c_{44} and T_0 are nearly pressure independent[31] and consequently γ_{TA} is constant. On the other hand, c_{44} stiffens in KCN-KCl mixed crystals.[23] Small amounts of KCl doped into KCN act as a negative pressure (1-at. % KCl shifts T_1 1.9 K down) and we may calibrate the KCl concentration as an effective pressure. Assuming $\partial T_0/\partial P \approx \partial T_1/\partial P = 2.56$ K/kbar^{-1} we find 1-at.% KCl corresponds to a pressure of -0.75 kbar and from the change of c_{44} with concentration[23] $\partial c_{44}(\text{KCN})/\partial P_{\text{eff}} = -0.25$ which is comparable to NaCN (see above). It seems that this pressure dependence of c_{44} cannot be extrapolated to positive pressures. The triple point in KCN at 170 K and small positive pressures (see Fig. 6) is no obvious explanation for this discrepancy since an ordering of the CN$^-$ molecules in [111] direction of the cubic lattice should also lead to a softening of c_{44}.

The Grüneisen parameters of the different modes which appear in the Raman spectrum of KCN (see Table I) are comparable to the corresponding modes in NaCN.[10] The band at 118 cm^{-1}, which was assigned to librational modes of the CN$^-$ molecules,[21] has a rather high Grüneisen parameter γ_i near the phase transition at 168 K but γ_i decreases with increasing distance from the phase line. This effect is more substantial in NaCN where the complicated phase structure at low temperatures is missing.

V. SUMMARY

Raman spectroscopy of crystals under high hydrostatic pressure provides an effective method to measure the phase lines in the P-T phase diagram of the material and to obtain informations about the structure of high-pressure phases. Using this method we found two new high-pressure phases of potassium cyanide. The symmetry of the phase diagram of the alkali cyanides suggests a [111] orientation of the CN$^-$ molecules in these new phases corresponding to the low-temperature phase in RbCN. The intermediate phase *Aa* of KCN with a stability interval of only a few degrees near 165 K is probably a high-pressure phase which is stabilized by internal stresses in the multidomain crystal.

The pressure shift of the different bands in the Raman spectrum allows us to estimate the Grüneisen parameters of the corresponding phonon modes. The bulk Grüneisen parameter of NaCN and KCN is temperature dependent just above the cubic to orthorhombic phase transition. This is consistent with the pressure dependence of the elastic constant c_{44} of NaCN and with the concentration dependence of c_{44} in KCN-KCl mixed crystals, but in the present stage it seems to disagree with the finding that c_{44} in KCN is pressure independent.

ACKNOWLEDGMENTS

The authors thank Professor S. Haussühl for the KCN crystal, E. Rehaber for many helpful discussions, and J. Ploner for his technical help. This work was supported by the Deutsche Forschungsgemeinschaft.

[1] J. M. Rowe, J. J. Rush, N. Vagelatos, D. L. Price, D. G. Hinks, and S. Susman, J. Chem. Phys. 62, 4551 (1975).

[2] C. J. Bill, H. Jex, and M. Müllner, Phys. Lett. A 56, 320 (1976).

[3] J. Daubert, K. Knorr, W Dultz, H. Jex, and R. Currat, J. Phys. C 9, L389 (1976).

[4] Struct. Rep. 9, 137 (1942-1944).

[5] A. Perret and R. Perrot, Helv. Chim. Acta 15, 1165 (1932).

[6] J. M. Rowe, D. G. Hinks, D. L. Price, and S. Susman, J. Chem. Phys. 58, 2039 (1973).

[7] D. Fontaine, C. R. Acad. Sci. (Paris) B 281, 443 (1975).

[8] C. W. F. T. Pistorius and J. C. A. Boeyens, J. Chem. Phys. 48, 1018 (1968).

[9] W. Dultz, M. Stock, and L. W. Winchester, *Proceedings of the Fifth International Conference on Raman Spectroscopy* (Schulz, Freiburg, 1976) p. 604.

[10] W. Dultz, H. Krause, and L. W. Winchester, J. Chem. Phys. 67, 2560 (1977).

[11] C. W. F. T. Pistorius, J. B. Clark, and E. Rapoport, J. Chem. Phys. 48, 5123 (1968).

[12] W. Dultz and H. Krause, this work.

[13] W. Dultz, J. Chem. Phys. 65, 2812 (1976).

[14] M. Sugisaki, T. Matsuo, H. Suga, and S. Seki, Bull. Chem. Soc. Jpn. 41, 1747 (1968).

[15] J. B. Clark and C. W. F. T. Pistorius, Solid State Commun. 7, 787 (1969).

[16] T. Matsuo, M. Sugisaki, H. Suga, and S. Seki, Bull. Chem. Soc. Jpn. 42, 1271 (1969).

[17] D. L. Decker, R. A. Beyerlein, G. Roult, and T. G. Worlton, Phys. Rev. B 10, 3584 (1974).

[18] J. M. Rowe, J. J. Rush, E. Prince, and N. J. Chesser, Ferroelectrics 16, 107 (1977).

[19] M. Stock and W. Dultz (unpublished).

[20] G. S. Parry, Acta Cryst. 15, 601 (1962).

[21] W. Dultz, H. Krause, and J. Ploner, Proceedings of the Sixth AIRAPT International High Pressure Conference, Boulder, Colorado, 1977 (unpublished).

[22] W. Dultz, Solid State Commun. 15, 595 (1974).

[23] S. Haussühl, Solid State Commun. 13, 147 (1973).

[24] W. Rehwald, J. R. Sandercock, and M. Rossinelli, Phys. Status Solidi A 42, 699 (1977).

[25] L. W. Winchester, thesis (University of Illinois, 1975) (unpublished).

[26] W. Dultz (unpublished).

[27] G. H. Wegdam and J. v. d. Elsken, Solid State Commun. 9, 1867 (1971).

[28] C. H. Wang and S. K. Satija, J. Chem. Phys. 67, 851 (1977).

[29] D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972), p. 368.

[30] H. D. Hochheimer (private communication).

[31] H. D. Hochheimer, W. F. Love, and C. T. Walker, Phys. Rev. Lett. 38, 832 (1977).