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Elastic neutron scattering investigations of new high-pressure phases of KCN

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Two recently discovered high-pressure phases of KCN were studied with elastic neutron scattering techniques. For phase *C* we found the space group *Aa* which is the space group of strained KCN at 165 K at zero pressure as expected, but the orientations of the CN^- molecules follow a staggered and ordered pattern pointing in between [100] and [110] directions of the original NaCl-type structure. We determined the lattice parameters of phase *D*, of the cubic phase *Fm*3*m* under pressure, and of the well-known orthorhombic low-temperature phase *Immm*. Our measurements excellently confirm the phase diagram of KCN which was determined earlier by Raman spectroscopy.

I. INTRODUCTION

From a physical standpoint the alkali cyanides behave very similarly to the alkali halides, but contrast by their variety of temperature-, pressure-, and material-dependent ordered and disordered phases, owing to more or less correlated orientations of the CN^- molecules in the crystal lattice. Hydrostatic pressure drives the alkali cyanide crystal into a higher coordinated phase analogously to the alkali halide crystal where simple geometric considerations describe the stability limits of a crystalline structure and explain the equivalence of increasing pressure and increasing cation radius as structure determining parameters.[1] It comes as a surprise that the same correspondence exists in the noncubic ordered low-temperature phases of the alkali cyanides, allowing the discovery of new high-pressure phases of KCN by using Raman spectroscopy as a probe for phase transformations.[2]

The Raman spectrum of a crystal is sensitive to changes in the structure of the crystal. A drastic first-order reduction of the symmetry or changes in the size of the unit cell are especially easily determinable. The different phases of KCN perfectly fulfill these conditions, and it was possible to obtain the detailed phase diagram by this method (see Fig. 1). In addition to the cubic disordered high-temperature phase *Fm*3*m* and the two orthorhombic low-temperature phases *A* (*Immm*) and *B* (*Pmmn*) at zero pressure, two new high-pressure phases *C* and *D* were found. Hatching indicates the possible coexistence region for two adjacent phases but note that pure phases can be obtained in these regions by a suitable sample treatment. X-ray investigations[3,4] of highly strained KCN crystals had shown the existence of a new phase of space group *Aa* in a small temperature region around 165 K at zero pressure and it was obvious to identify the new high-pressure phase *C* of KCN with this phase. From cell dimensions the orientation of the CN^- molecules was concluded to be a body diagonal ([111] direction) of the original cubic lattice in contrast to a [110] orientation in the orthorhombic zero-pressure phases. To obtain certainty about the crystal structure of the new phases of KCN, scattering investigations with neutrons were made, since neutron scattering techniques are particularly able to give complete information about the orientation of the CN^- molecules. In this work we

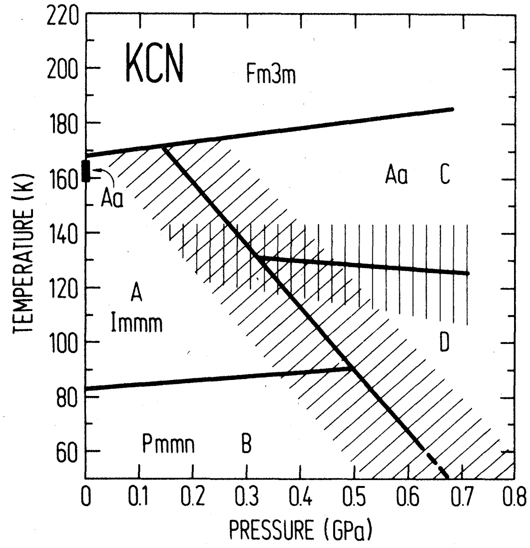

FIG. 1. Phase diagram of KCN (Ref. 2).

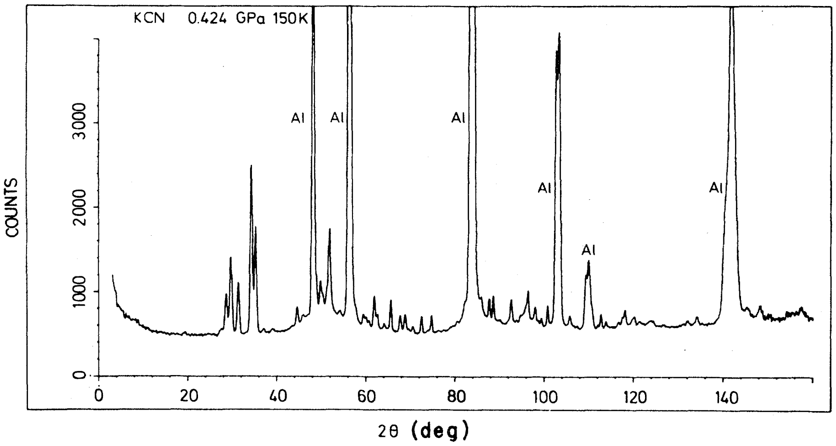

FIG. 2. Debye-Scherrer diagram of KCN in phase *C*.

report on Debye-Scherrer elastic neutron measurements of KCN under hydrostatic pressure and at low temperatures. We established the existence of the two new high-pressure phases *C* and *D*, see Fig. 1, and found the space group of phase *C* to be *Aa* as expected. For phase *D* we have some indications about the structure. Additional refined data on the lattice parameters of the cubic disordered NaCl-type phase *Fm*3*m* as well as on the orthorhombic phase *Immm* of KCN were obtained.

II. EXPERIMENTS

We measured the Debye-Scherrer diagrams using the D1*A* spectrometer of the Laue-Langevin Institute (ILL) at Grenoble. Our high-pressure equipment consisted of an aluminum cell which we built after plans given in Ref. 5 and the He-gas compressor and a cryostat of the ILL. The sample was precipitated from aqueous solution by ethanol. Temperatures down to 90 K and pressures up to 0.45 GPa were reached. The scattering density was measured in 0.1° steps of the scattering angle 2θ between 5° and 160° in about 10–15 h with neutrons of a wavelength of 1.9073 Å. Figure 2 shows the Debye-Scherrer diagram of KCN in phase *C* as an example. Major parts of the diagram are covered by the pressure-dependent strong peaks of the Al cell which also produces a less prominent but disturbing background. To illustrate the structural difference of the phases of KCN, Fig. 3 shows the first group of reflections in the range $2\theta < 40°$. The reflections 111 and 200 of the cubic phase (space group *Fm*3*m*) split into four well-separated reflections in the orthorhombic low-temperature phase (space group *Immm*), but into five more or less overlapping reflections in the new phases *C* and *D*. We think that the simplicity of the diagrams rules out the possibility of a mixture of two phases at these temperatures and pressures. A well-expressed mixture between phase *C* and *D* was indeed found in the coexistence region of the phase diagram, Fig. 1.

Intensities and scattering angles of the different reflections were determined by line-fitting techniques from the powder diagrams and corrected with respect

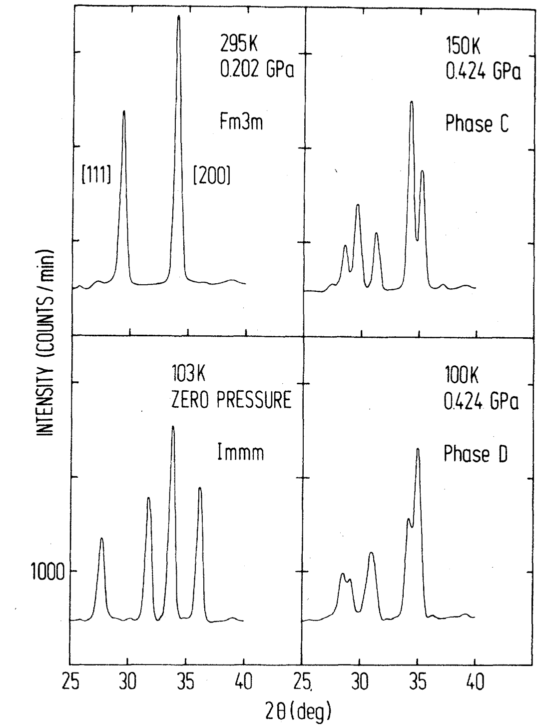

FIG. 3. Debye-Scherrer diagrams of the different phases of KCN in the range $25° < 2\theta < 40°$.

TABLE I. Crystal data for different phases of KCN.

Phase	P (GPa)	T (K)	Space group	a(Å)	b (Å)	c (Å)	β (deg)	Z	V/Z (Å^3)	D_x (Mg m^{-3})
				Neutron data, this work						
KCN I	0.2	295	$Fm3m$	6.495(2)				4	68.50	1.579
			monoclinic setting	9.185	4.593	7.955	125.26	4	68.50	1.579
C	0.424	150	Aa	9.103(6)	4.606(3)	7.433(4)	122.22(12)	4	65.915	1.641
D	0.424	100	?	9.464(10)	4.269(2)	7.943(8)	125.4(2)	4	65.388	1.654
KCN V (A)	0	103	$Immm$	4.221(1)	5.205(2)	6.136(3)		2	67.405	1.604
				Earlier x-ray data						
KCN I[a]	0	293	$Fm3m$	6.51				4		1.57
Strained KCN (I)[b]	0	163	Aa	8.97	4.53	7.47	122.32	4		
KCN V (A)[a]	0	167	$Immm$	4.23	5.08	6.14		2		1.64
				Earlier neutron data						
KCN V (A)[c]	0	90	$Immm$	4.21(1)	5.20(1)	6.11(1)		2	66.9	
KCN V (B)[c]	0	6	$Pmmn$	4.18(1)	5.24(1)	6.07(1)		2	66.5	
KCN III[d]	2.2	347	$Pm3m$	3.8080				1		1.64
KCN IV[d]	2.2	339	Cm	5.5166	5.2662	3.7579		2	54.49	1.985

[a] Reference 7.

[b] Reference 4.

[c] Reference 8.

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

to the usual diffraction angle-dependent factors. Starting from an indexing of the first five reflections, the parameters of the unit cell were refined by a least-squares method using the program PULVER.[6] For phase D we only used the first five reflections to derive the lattice parameters since the diagram is quite diffuse at higher scattering angles. Some caution has to be taken with respect to a possible cell doubling or to a slight reduction of the symmetry in this case. Technical details of the analysis and structure determination are specified in the following sections. Table I summarizes our results for the lattice parameters of KCN in various phases including some earlier data for comparison. V/Z denotes the volume per KCN molecule in the lattice. The numbers in parentheses indicate the standard deviations associated with the last digits throughout this work. Our lattice parameters for the cubic phase $Fm3m$ and the orthorhombic phase $Immm$ agree with earlier x-ray data, showing only a slightly larger $b = 5.205$ Å in the latter case. The lattice parameters of our high-pressure phase C are very similar to those of highly strained KCN at zero pressure. Only for phase D were we unable to derive a space group so far.

III. CRYSTAL-STRUCTURE ANALYSIS

A. Phase C: 0.424 GPa, 150 K

About 40 reflections were used to refine the lattice parameters [mean error of the angle $\sigma(2\theta) = 0.025°$] and to determine the crystal structure. The systematic absences: hkl for $k+l$ odd, $h0l$ for h odd, and $0k0$ for k odd restrict the possible space groups to Aa and $A2/a$. The space group $A2/a$ is structurally improbable because the four carbon and nitrogen atoms in the unit cell would be in a special position in this case, which would not allow the physically true C—N bond length of about 1.1 Å.[4] Thus the space group must be Aa, which is noncentrosymmetric and has only the general fourfold position.

Starting from a distorted NaCl structure, the crystal structure of phase C was successfully determined in subsequent refinement cycles using Fourier and full matrix least-squares techniques. The final reliability factor was $R = 0.058$. Scattering lengths of $\bar{b}_K = 35$, $\bar{b}_C = 66.1$, and $\bar{b}_N = 94.1$ pm/atom were assumed for the respective nuclei. For iostropic thermal parameters for all atoms and using the physically

TABLE II. Positional and thermal parameters for phase *C*.

Atom	x/a	y/b	z/c	U (Å^2)
K	0.0^a	−0.082(6)	0.0^a	0.002(7)
C	0.143(4)	−0.086(8)	0.429(5)	0.065(8)
N	0.254(3)	0.082(6)	0.494(5)	0.068(6)

^{a}Restricted.

plausible condition of their equality for carbon and nitrogen, we find a site occupation of C and N which shows a preference of 89% for a definite position. This means that the structure is ordered and distinguishes head and tail of the CN$^-$ molecules which is also indicated by the different bond lengths K$^+$—C and N—K$^+$. The mean distance between the K$^+$ ion and C is 2.80 Å compared to that between K$^+$ and N being about 3.12 Å. Carbon has four nearest neighbors (3K + N), and the bond distances and angles suggest a high degree of covalency. The resulting positional and thermal parameters as well as selected bond distances are listed in Tables II and III. The form of the isotropic temperature factor is $T = \exp(-2\pi^2 U/d^2)$, where U is the mean-squared atom displacement perpendicular to the reflecting plane of interplanar distance d.

The crystal structure of phase *C* is shown in Fig. 4. Treating the CN$^-$ groups as a single entity, K$^+$ is coordinated to six CN$^-$ as is expected for a distorted NaCl-type structure. *A*-face-centered sheets of K$^+$ ions are alternately displaced from the origin of the unit cell by an amount of ∓0.38 Å along [010], which corresponds to a [110] direction of the original cubic KCN structure. This is an essential result already qualitatively proposed earlier[4] for the crystal structure of strained KCN at zero pressure. The displacements of the K$^+$ ions lead to different cation separations of 6.101 and 7.151 Å in the (001) plane giving space for the CN$^-$ groups to arrange in between the more distant K$^+$ ions in a staggered orientation by means of the *a* glide plane. With regard to the original cubic KCN lattice, each CN$^-$ group lies in a (100) plane and is tilted about 20° out of a [100] direction in this plane. We feel that the structure of strained KCN (Ref. 4) is different from the structure of phase *C* in this respect. The rms vibrational amplitude of 0.26 Å for the CN$^-$ group is quite large, but very small for the K$^+$ ion. We think that this supports the absence of dynamic disorder in phase *C* since large uncorrelated orientational jumps of the CN$^-$ ions would cause a relaxing of the K$^+$ ions and result in a considerable movement of these ions.

TABLE III. Bond lengths in Å for phase *C*.

Atom	C	N
K	2.727(31)	2.801(26)
	2.815(40)	3.189(33)
	2.844(40)	3.196(33)
	[3.369(27)]	3.197(33)
		3.218(26)
C	· · ·	1.155(22)
N	1.155(22)	· · ·

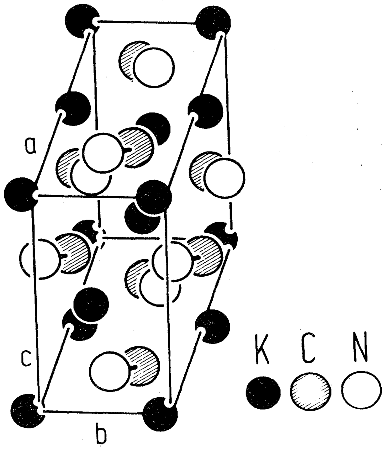

FIG. 4. Structure of KCN in phase *C*.

B. Phase *D*: 0.424 GPa, 100 K

The density of phase *D* calculated from the lattice parameters on the basis of four molecules per unit cell is much smaller than the density of the eightfold coordinated phases of KCN with a CsCl-type or distorted CsCl-type structure, respectively called KCN III and KCN IV in the literature, see Table I. This shows undoubtedly that phase *D* has a distorted NaCl-type structure with a sixfold coordination as was already concluded from light scattering experiments.[2] The small period of translation $b = 4.269$ Å indicates that the ordering of the CN$^-$ molecules occurs not in [100] directions as in phase *C* but probably in a [110] direction as in phase *A* (*Immm*) or perhaps in a body diagonal of the original cubic cell as was proposed for the strained crystal. The Raman band of the CN$^-$ stretching vibration shows a Davidov-splitting in phase *D*. Thus a relatively strong interaction between two CN$^-$ molecules per unit cell must occur.

TABLE IV. Positional and thermal parameters for phase *Immm* (*A*).

Atom	Position	x/a	y/b	z/c	U (Å^2)
K	2(*a*)	0	0	0	0.016(5)
C or N	4(*h*)	0	0.1088	$\frac{1}{2}$	0.030(2)

TABLE V. Bond lengths of phase *Immm* in Å.

Atoms	Bond length
C− N	1.133(14)
K−C or N	2.933(1) (4×)
	3.120(1) (2×)

C. Phase *A*: KCN V (*A*), zero pressure, 103 K

We refined the structural parameters of the orthorhombic low-temperature phase of KCN at zero pressure from the intensity data of our neutron-diffraction powder diagram measured at 103 K. We confirmed the crystal structure to have the space group *Immm*. Only four parameters had to be refined because C and N statistically occupy a fourfold position, for which we used the average scattering length of $\bar{b}_{CN} = 80.1$ pm. The final reliability factor for 31 reflections was $R = 0.053$. The result of the structure analysis is summarized in Tables IV and V. Our results are in excellent agreement with earlier x-ray[7] and neutron scattering[8] results of this phase, see Table I.

IV. CONCLUSIONS

Comparing earlier speculations[4] about the CN$^-$ molecular orientations in strained KCN with the staggered orientation in the high-pressure phase *C*, we feel sure that both phases have the same structure. Apparent differences are not great enough to lie outside the uncertainty range of postulates depending only on the analysis of cell dimensions from x-ray data. Neutron spectroscopy is highly suitable in this case, since the scattering intensity in the Debye-Scherrer diagrams is very sensitive to the orientation of the CN$^-$ molecules. The head-to-tail order in phase *C*, which is a "ferro" order came as surprise to us and the neutron scattering technique was essential for its discovery.

The complete order and the staggered orientation of the CN$^-$ molecules in phase *C* raises the question again as to what orientation the CN$^-$ molecules in the low-temperature phase (or phases) of RbCN may have. The phase diagram of the alkali cyanides suggests ordering as in phase *C* and/or *D* of KCN.[2] It should be easy to determine the structure of RbCN below 130 K with neutrons at zero pressure, and we are confident that it will agree with our suggestion, especially since agreement is indicated by Raman measurements.[9]

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