Electronic Structure and Dynamic Properties of Solid Alkali Cyanides

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The electronic structure of NaCN and KCN has been investigated by means of the periodic Hartree−Fock method. These calculations reveal a highly ionic character for both compounds. The analysis of the potential energy surfaces in the body-centered orthorhombic phases of both compounds indicates that rotation of the anions is severely hindered. Qualitatively different results were found for the high-temperature cubic structures. In KCN the small barriers allow almost free rotation of the cyanide anions, although shallow minima for the orientation of the CN^- ions along the [111] directions of the crystal are found. For NaCN the situation is quite different, with the CN^- units fixed in a random fashion in any of the equivalent positions with the molecular axis oriented along the [100] directions of the crystal.

Introduction

Sodium and potassium cyanides have been used for a long time as examples of a general class of M(XY) crystals that at high temperatures exhibit cubic crystal structures similar to those found for the alkali halides. These structures require that the linear CN^- anions assume effective cubic symmetry either because of orientational disorder or through rotation. In the past decades a considerable effort has been devoted to the study of the origin of the cubic average structures in the high-temperature phases and of the mechanisms of the phase transitions that yield orientationally ordered structures. Although there have been numerous experimental and theoretical studies devoted to these problems, several questions concerning the structure, phase transitions, and dynamics in these compounds remain still open.

In this contribution, ab initio calculations of the Hartree−Fock type have been employed in the study of the electronic structure of various phases of NaCN and KCN. The calculations presented in this paper were largely motivated by the aim of obtaining reliable first principles potential energy surfaces for the high-temperature phases of these compounds, a project that started previously with the study of the related CaC_2 structure.[1]

Methodology

All calculations reported in this paper have been performed using the CRYSTAL-92 program,[2] which provides self-consistent solutions to the Hartree−Fock−Roothan equations subject to periodic boundary conditions. Details of the mathematical formulation of this method have been previously described[3] and will be omitted here.

CRYSTAL-92 uses a set of Gaussian functions to construct a localized atomic basis from which Bloch orbitals are built up. As in molecular Hartree−Fock calculations, results can be quite sensitive to the choice of the basis set. Previous work has shown that the standard basis sets used in molecular calculations must be modified for their use on periodic systems.[3]

TABLE 1: Orbital Exponents ($bohr^{-2}$) for the Most Diffuse Gaussian Functions Used in Calculations on Crystalline NaCN and KCN

atom	type	α
Na	sp	0.5280
	sp	0.3030
	d	0.3500
K	sp	0.3890
	sp	0.1560
	d	0.2540
C	sp	0.1800
	d	0.8000
N	sp	0.2832
	d	0.8000

A double-ζ quality basis set with polarization functions on all atoms has been adopted in our calculations. The basis sets proposed in refs 4 and 5, slightly modified by reoptimization of the most diffuse functions using the experimental crystal structure of the *Immm* phase for NaCN, have been used for sodium, carbon, and nitrogen. For K, the basis set given in ref 4 has been modified according to a procedure analogous to that for Na but keeping the previously optimized functions for C and N fixed. The exponents for the most diffuse functions of each type obtained by this procedure are given in Table 1.

Computational parameters controlling the truncation of both the Coulomb and exchange infinite series have been chosen to provide a "good" level of accuracy defined in the sense of Pisani et al.[3]

Results

Crystal Structure. On cooling from room temperature, the ionic molecular crystals of NaCN and KCN display two successive phase transitions[6] (Figure 1). At high temperatures and ambient pressure they exhibit a phase of cubic symmetry (*Fm*3*m*). On lowering the temperature this phase undergoes a first-order transition to an intermediate body-centered orthorhombic phase (*Immm*). Critical temperatures for this transition are $T_c = 288$ K for NaCN and $T_c = 168$ K for KCN. The intermediate phase is characterized by long-range orientational order with the CN^- axis oriented along the [110] direction of

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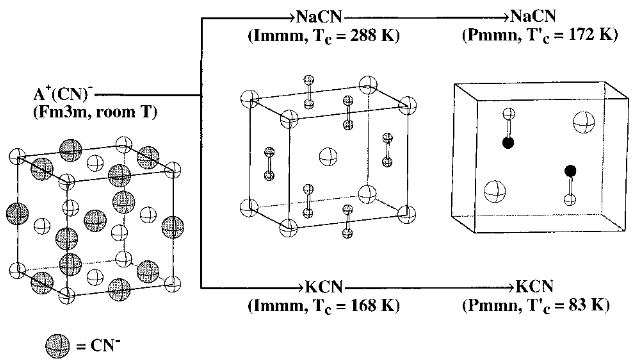


Figure 1. Crystal structures for the different phases of NaCN and KCN.

the high-temperature cubic phase. On further cooling, the residual head-to-tail disorder of the cyanide units is removed by a continuous order−disorder transition ($T_c' = 172$ K and $T_c' = 83$ K for NaCN and KCN, respectively) into an antiferroelectrically ordered orthorhombic ground state (*Pmmn*). The crystal structures of the different phases were determined by X-ray[7,8] and neutron powder diffraction studies[9−15] and have also been the subject of some theoretical work.[16] Transition temperatures for both compounds were determined by thermodynamic measurements.[17,18]

As mentioned above, the low-temperature phase has orthorhombic symmetry, space group *Pmmn* (no. 59), with the alkali atoms at 2a positions, C atoms at 2b positions, and N atoms at 2b positions. A total of six parameters (a, b, c and the internal coordinates z_A, z_C, z_N) are needed to fully describe the structure. The results obtained from the optimization of these six parameters together with their experimentally determined values are presented in Table 2. A good agreement between theory and experiment is observed.

The reported structure for the intermediate body-centered orthorhombic phase belongs to space group *Immm* (no. 71). The alkali atoms are located in 2a positions, while there are two CN$^-$ anions per unit cell oriented parallel to the [010] direction of the crystal and with their centers at the 2c positions. It was not possible experimentally to distinguish the C and N atoms. Although the real structure is multidomained (ferroelectric) with the cyanide anions randomly ordered, we shall consider only the limiting structure of a crystal made up of repeating cells of ferroelectrically aligned cyanide ions. This structure can be fully described using four parameters: a, b, c, and an internal coordinate y for the C (N) atoms. The calculated values for these four parameters are shown in Table 2 together with the experimentally determined data. A good agreement between calculations and experiment is also observed in this case.

For both compounds the low-temperature, antiferroelectrically ordered orthorhombic structure is predicted to be the most stable one. The calculated energy differences between both orthorhombic phases are 1.1 kcal/mol for NaCN and 1.8 kcal/mol for KCN. These values are of the same order as those found by LeSar and Gordon[16] (0.5 and 0.8 kcal/mol, respectively, with the ordered phase having lower energy) using a density functional based method.

C−N Stretching Frequency and Bulk Modulus. The calculated C−N distances (Table 2) agree well with the experimental data except for the intermediate orthorhombic phase of NaCN for which the experimental value is appreciably shorter than the calculated one. As noted by LeSar and Gordon,[16] it is most likely that the shorter bond length reported for this phase is due to uncertainties in the X-ray determination of the C and N positions and an averaging due to thermal disorder. The calculated C−N distances are only slightly shorter than the distance calculated for an isolated cyanide ion in the gas phase using the same level of theory ($d_{C-N} = 1.154$ Å), indicating that the surrounding environment has practically no effect on the geometry of these ions. This conclusion has also been reached in an earlier study on CaC_2.[1] In this case a property that has been found to change notably for the C_2^{2-} units when considering them in the crystal is the stretching frequency, which is almost 200 cm^{-1} higher than for the isolated dimer. To check if this trend is also found in the solid-state cyanides, we have calculated the C−N stretching frequencies for both low-temperature phases of NaCN and KCN.

To obtain the C−N stretching frequency in any of the four studied phases, the total energy of the solid has been calculated as a function of the displacement of the carbon and nitrogen atoms from their equilibrium positions, maintaining the symmetry of the crystal. The energy has been evaluated for nine different C−N distances and the harmonic vibration frequency obtained from the second derivative of a second-order polynomial least-squares fit of these data. The calculated frequencies are shown in Table 3.

Only a small increase in ν_{CN} is observed for all four crystals when compared to the stretching frequency of the isolated cyanide ion, $\nu = 2414$ cm^{-1}, evaluated at the same level of theory as in the crystal structures. Interaction of the cyanide anions with the surrounding environment in the crystal does not seem to be as important in the present case as in CaC_2 crystals. The different behavior can be attributed to electrostatic effects that are less important in the alkali cyanides because of the lower charges on the surrounding cations. Experience has shown that vibration frequencies obtained by the Hartree−Fock method with basis sets of similar quality as those employed in

TABLE 2: Structural Parameters Calculated for the Orthorhombic Phases of NaCN and KCN[a]

	a/Å	b/Å	c/Å	y(C, N)	d_{CN}/Å
			NaCN (*Immm*)		
calcd	3.550	5.071	5.4320	0.1135	1.151
exp[15]	3.760	4.700	5.6330	0.1110	1.043
			KCN (*Immm*)		
calcd	4.268	5.226	6.2175	0.1101	1.151
exp[15]	4.181	5.169	6.0730	0.1087	1.124

	a/Å	b/Å	c/Å	z_1 (Na, K)	z_2 (C)	z_3 (N)	d_{CN}/Å
				NaCN (*Pmmn*)			
calcd	3.620	5.542	4.762	0.2380	0.3434	0.1022	1.149
exp[14]	3.622	5.447	4.829	0.2190	0.3680	0.1280	1.159
				KCN (*Pmmn*)			
calcd	4.238	6.176	5.286	0.2083	0.3577	0.1397	1.152
exp[14]	4.192	6.083	5.257	0.2730	0.3600	0.1400	1.157

[a] Experimental data are provided for comparison.

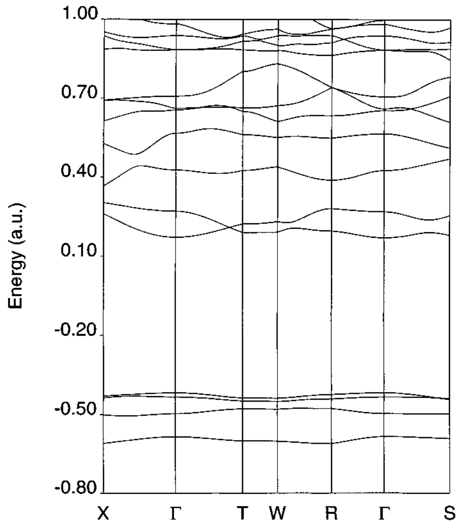


Figure 2. Electronic band structure for the *Immm* phase of NaCN.

TABLE 3: Harmonic Vibration Frequencies (in cm^{-1}) for the Low-Temperature Phases of NaCN and KCN

	Immm	*Pmmn*
NaCN	2439	2467
KCN	2441	2435

TABLE 4: Bulk Modulus (GPa) and Its Pressure Derivative for the Low-Temperature Phases of NaCN and KCN

	Immm		*Pmmn*	
	B	*B*′	*B*	*B*′
NaCN	93.8	3.9	97.1	6.8
KCN	66.1	5.0	66.8	4.9

our work are an average of 12.6% higher than the experimental ones.[19] If this trend is supposed to be valid for the present case, an estimated stretching frequency in the range 2128−2156 cm^{-1} is expected for the alkali cyanides in the solid state, in fair agreement with the experimental values of 2080−2085 cm^{-1} found in different experimental studies.[20−23] Both the calculated and the experimental values indicate that the replacement of Na by K does not induce significant differences in the vibrational stretching frequency of the cyanide anions.

The total crystal energy has been evaluated for nine different unit cell volumes obtained by an isotropic compression or expansion of the optimized crystal structure. The bulk modulus and its pressure derivative have been evaluated from a third-order polynomial fit to these data. The calculated values for these two properties will be an upper limit for them, since no reoptimization of lattice parameters and positions of the atoms has been performed for each fixed volume. This approximation seems to be reasonable in this case, since no important modifications of the crystal structure are expected for small deviations of the equilibrium crystal structure. The calculated values for these two properties are given in Table 4. Unfortunately, no experimental determination of these data has been reported in the literature to the best of our knowledge.

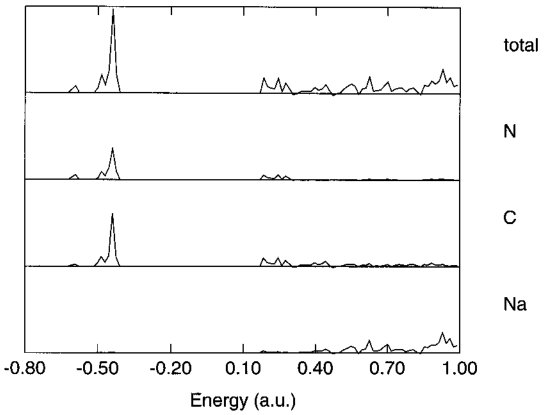


Figure 3. Atomic orbital projections of the density of states (DOS) obtained for the *Immm* phase of NaCN. The atomic orbital contributions have been evaluated using a Mulliken partition scheme.

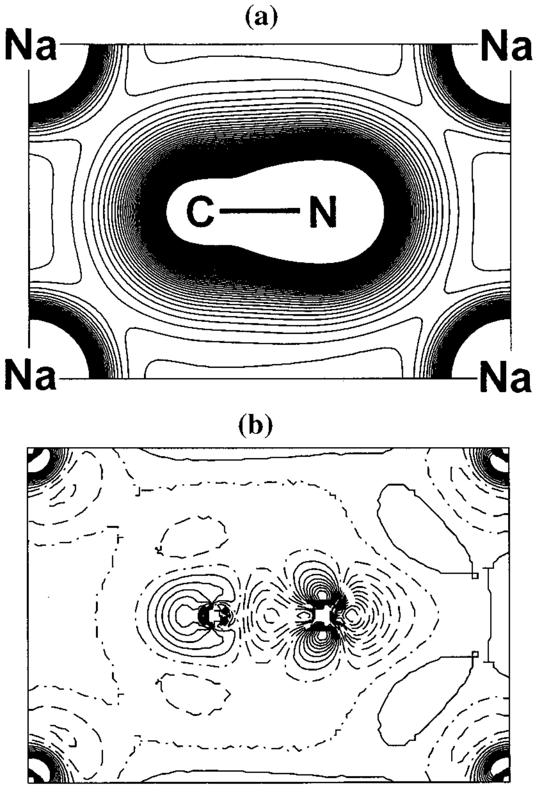


Figure 4. Electronic charge density maps calculated for the *Immm* phase of NaCN: (a) total electron density on the [001] plane; (b) electronic density difference between the crystal and the corresponding superposition of noninteracting ion densities on the same plane. The full and broken curves in the difference map indicate increase and decrease of electron density, respectively.

Band Structure and Density of States. The calculated band structure for the *Immm* phase of NaCN is presented in Figure 2. This compound is calculated to be a wide gap insulator with practically flat bands in all directions of the Brillouin zone. As can be appreciated from the different projections of the NaCN density of states (Figure 3), the upper zone of the valence band is divided into two parts. The lowest one is very narrow and arises from a single band of C−N σ bonding character. The topmost region is formed by one band of C−N σ bonding and two bands of C−N π bonding character. The two lowest unoccupied bands arise from the pair of C−N π antibonding orbitals. Participation of the sodium orbitals in the valence band and in the lowest zone of the conduction band is practically negligible. The band structures and density of states (DOS) plots calculated for the low-temperature phase of NaCN and those for both orthorhombic phases of KCN are very similar in their rough features to the ones described above for the *Immm* phase of NaCN and will not be discussed in further detail.

Electron Density Maps. The electron density map calculated for the *Immm* structure of NaCN in the [001] plane is shown in Figure 4a. The difference of the crystalline charge density and the superposition of the charge densities of the individual ions in the same plane is shown in Figure 4b. Complementary information is supplied in Table 5, where Mulliken population data are reported. As noted in earlier work, when periodic

TABLE 5: Mulliken Population Data for Isolated Cyanide Anions and CN$^-$ Anions in the Optimized Structure of NaCN (*Immm* Phase)

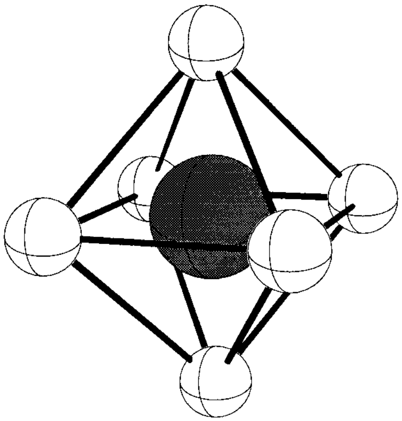
	total	1s	2s	2p$_\sigma$	2p$_\pi$	3d
			free ion			
C	6.383	1.997	1.630	1.095	1.602	0.058
N	7.617	1.997	1.698	1.547	2.330	0.040
			NaCN			
C	6.288	1.997	1.580	1.087	1.558	0.066
N	7.622	1.997	1.738	1.510	2.337	0.040

systems are dealt with, these values should be used in an even more qualitative way than for molecules.[3]

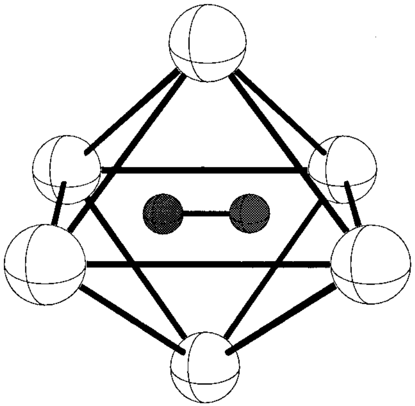
Figure 4a shows an almost perfect spherical charge density around the sodium atoms, indicating a strong ionic character for this compound. The charge density around the CN$^-$ units indicates a strong covalent bonding between both atoms with the expected polarization accumulating electron density around the more electronegative nitrogen atom. The population analysis reveals that on formation of the crystal from Na$^+$ cations and CN$^-$ anions, a little amount of charge (0.09 e) is transferred from the anions to the cations. This small transfer is, however, not important enough to imply any considerable departure from the ionic model in this compound. A closer look indicates that the larger part of this charge is supplied by the carbon atom. In the difference map one can observe a charge accumulation in the vicinity of this atom while donation of the charge to the cation array comes predominantly from its most diffuse orbitals. For the nitrogen atom, the charge loss in the orbitals of s type is almost completely compensated by the accumulation in the π type orbitals.

Dynamic Properties of the CN$^-$ Ions. As already mentioned above, the high-temperature phases of NaCN and KCN have cubic pseudo-NaCl crystal structures. It is well-known that spherical, octahedral, or tetrahedral symmetry is required for the ions of a compound to exhibit a cubic crystal structure. An interesting question that arises in this context is thus how a linear anion like CN$^-$ can achieve effective cubic symmetry in the crystal lattice. The qualitative explanation assumes that above the critical temperature the atomic groups are no longer restricted to adopt fixed orientations, the observed crystal structure being just an average of the atomic motion. Two viewpoints have been proposed concerning the nature of the group behavior. The first one, advanced by Pauling,[24] allows the groups to rotate freely. In the alternative hypothesis, due to Frenkel,[25] the groups still behave as torsion oscillators but may take any of several equivalent equilibrium positions. The dynamic structure of the high-temperature phases of the cyanides is still an open question despite the extensive research effort over several decades using a number of different methods, including X-ray[7,8] and neutron diffraction,[9–13,26–28] thermodynamic studies,[17,18,29] Raman scattering,[30] and nuclear magnetic resonance.[31] In this section we will present the ab initio potential energy surface for the rotation of the CN$^-$ units in both the cubic and the intermediate orthorhombic phases of NaCN and KCN. This information is used at a later stage to obtain orientational distribution functions of the cyanide ions and the contribution of the rotational movement of these units to the heat capacity of the solids.

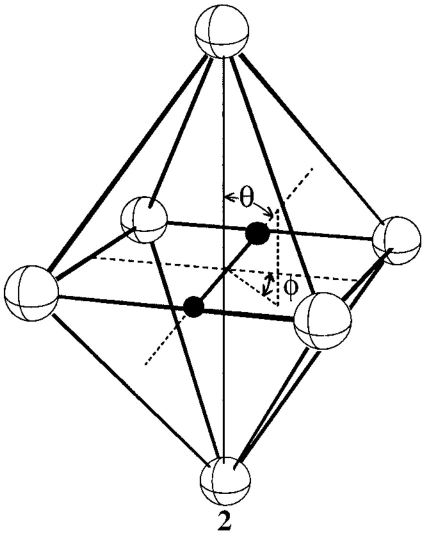
Taking a closer look at the coordination of the CN$^-$ units, one can see that for the cubic phase they are located in an octahedral environment formed by six alkali atoms (**1a**). Below the critical temperature, in the body-centered orthorhombic phase, these octahedra are elongated along the [100] direction with the CN$^-$ units aligned along the same direction (**1b**). The rotation of the cyanide anions within the octahedral environment can be described using two angles as shown in **2**. The experimental structure for the orthorhombic *Immm* phase corresponds to $\theta = 90°$ and $\phi = 0°$. In the cubic structure, the most relevant orientations of the cyanide anions are parallel to the [100] direction ($\theta = 90°$, $\phi = 45°$), parallel to the [110] direction ($\theta = 90°$, $\phi = 0°$), and parallel to the [111] direction ($\theta = 54.74°$, $\phi = 0°$).



1a



1b



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For the calculation of the potential energy surface associated with the rotation of the cyanide anions in the cubic phases of NaCN and KCN, a tetragonal supercell (space group *I*4/*mmm*) with $c = a\sqrt{2}$ has been considered. In all cases we have considered the rotation of the cyanides in a "frozen" crystal structure; i.e., no reoptimization of the cell constants is

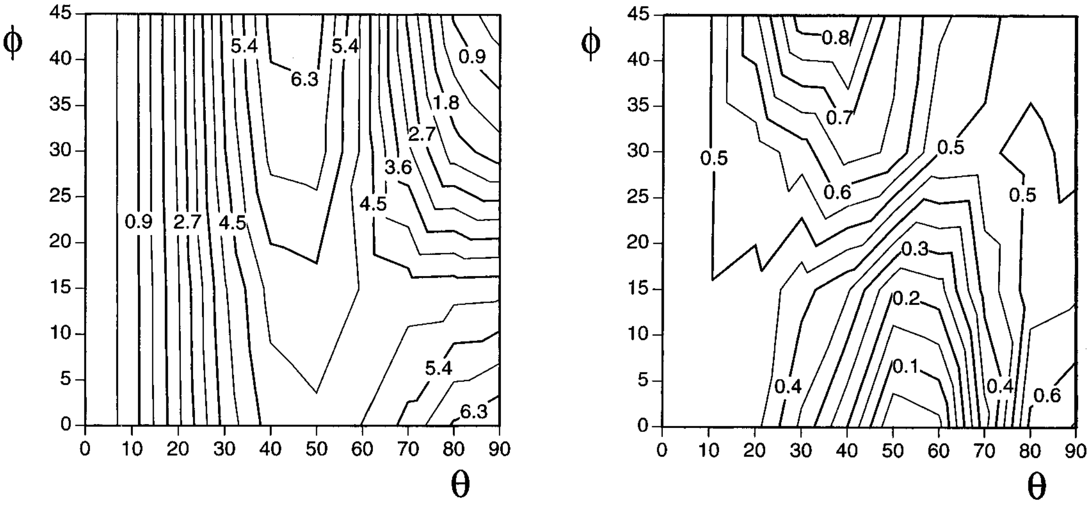

Figure 5. Relative potential energy for the rotation of the CN$^-$ anions in the cubic phases of NaCN (left) and KCN (right). The most relevant orientations of the cyanide anions are parallel to the [100] direction ($\theta = 90°$, $\phi = 45°$), parallel to the [110] direction ($\theta = 90°$, $\phi = 0°$), and parallel to the [111] direction ($\theta = 54.74°$, $\phi = 0°$). Energy values of the contour lines are given in kcal/mol.

performed for each orientation. The steep energy change calculated for small tilting angles (θ), for which no significant relaxation for the cationic subnet is expected, indicates that this frozen crystal approach can be applied to these crystals. To determine an upper bound to the rotation barrier of the CN$^-$ units, it is necessary to freeze the positions of all cyanide anions but one and then find the energy as this single anion rotates. Owing to the periodic boundary conditions imposed in our computational method, rotation of a single cyanide ion is not possible and all equivalent anions in other unit cells are rotated in the same sense. Since these other rotating molecules are not nearest neighbors, they should not greatly affect the results, as has been found for the rotation of dicarbide anions in CaC$_2$.[1]

The potential energy surfaces for the rotation of the cyanide anions in the high-temperature cubic phases of NaCN and KCN are presented in Figure 5. At a first glance one can see that both surfaces have very different shapes. In the case of NaCN one can observe two equivalent minima for the CN$^-$ units aligned along the [100] and [001] directions of the crystal ($\theta = 0°$, ϕ = any angle; $\theta = 90°$, $\phi = 45°$) with a barrier of 4.75 kcal/mol separating both minima. The surface for cubic KCN has a single minimum for the cyanide anions oriented along the [111] directions of the crystal. The calculated barrier between the symmetry equivalent structures with the cyanide anions oriented along the main diagonals of the cubic cell is only 0.45 kcal/mol, much lower than that found in NaCN. From these results it is clear that rotation should be much less hindered in KCN than in NaCN. The differences in the potential energy surfaces are also reflected in the calculated orientational distribution functions of the cyanide ions shown in Figure 6.

These results are in good agreement with the experimental data obtained by different experimental techniques. Coogan and Gutowsky, using ^{23}Na NMR spectroscopy,[31] were able to estimate a value of 6 kcal/mol for the barrier in NaCN. Matsuo et al.,[17] in a study of the thermodynamic properties of NaCN, suggest a barrier between 2 and 3 kcal/mol for the high-temperature cubic phase. The theoretical work of LeSar and Gordon[16] using density functional theory predicts an energy difference of about 4 kcal/mol between the structures with the CN$^-$ anions oriented along the [100] and the [111] direction, the first one being the most stable one. For KCN the only experimental estimate of the barrier is given by Suga et al. who obtained a value of 1.3 kcal/mol from thermodynamic measurements.[18] The theoretical study of LeSar and Gordon[16] predicts that in cubic KCN the [100] orientation should be about 1.8 kcal/mol more stable than the [111] orientation, a result that is in contradiction with our calculations and with the experimental data of Rowe et al.[10] who found in a neutron diffraction study that, in agreement with our results, the most favorable orientation of the CN$^-$ anions is different in both crystals: in NaCN the cyanide anions tend to align along the [100] directions of the crystal while in KCN they prefer to do it along the [111] directions. The experimental orientational distribution function obtained by these authors for KCN[10] agrees well with our calculations (Figure 6), while for NaCN a discrepancy between the experimental and the calculated results is observed: a relative maximum for the alignment along the [111] direction is not found in our calculated orientational distribution function. The discrepancy could arise from the model used by Rowe et al.[10] for obtaining the orientational distribution functions, since they used the same expressions for NaCN and KCN, although our calculations seem to indicate a very different dynamic behavior of the cyanide ions in both phases.

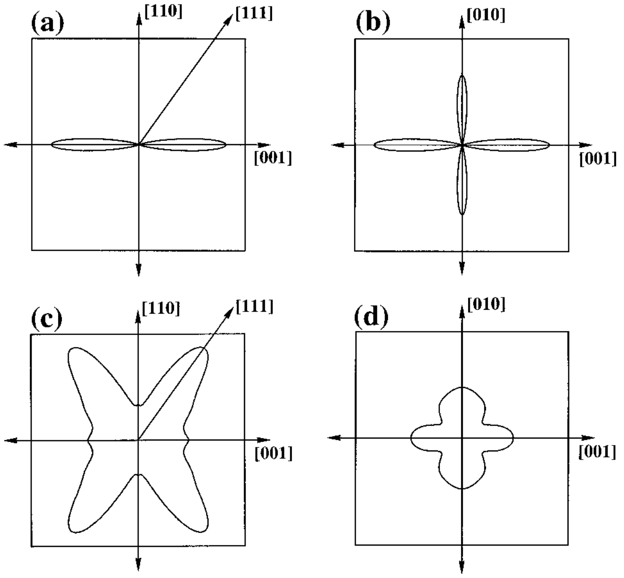

Figure 6. Orientational distribution functions for the cyanide anions in the [1$\bar{1}$0] plane (a) and [100] plane (b) of NaCN and in the [1$\bar{1}$0] plane (c) and [100] plane (d) of KCN.

The low barrier found for KCN seems to indicate that in this case the Pauling model[24] of nearly free rotating cyanide ions is adequate for describing the dynamic structure of the cubic high-

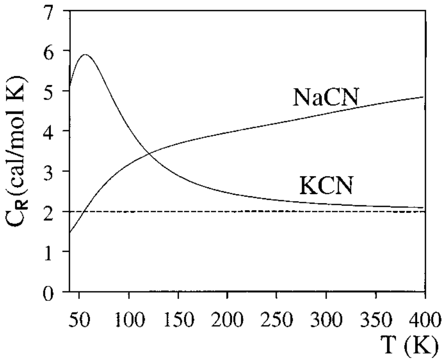

Figure 7. Rotational contribution to the total specific heat of the cubic phases of NaCN and KCN.

temperature phase. The Frenkel model[25] would be more appropriate for NaCN, where an orientational disorder with the cyanide anions oriented along the three equivalent [100] directions seems to be at the origin of the average cubic symmetry of the crystal. These conclusions are in good agreement with experimental and theoretical studies on $(KCN)_x(NaCN)_{1-x}$ solid solutions[32,33] that indicate the existence of two different CN^- populations, one more orientationally mobile than the other, corresponding to the statistical fractions of cyanide anions without and with sodium atoms as nearest neighbors, respectively.

To further investigate this question, we have performed the calculation of the contribution of the rotational motion of the CN^- anions (C_R) to the total specific heat of both crystals. For this purpose we have used the approximate technique proposed by Stepakoff and Coulter[34] for the construction of the quantum mechanical partition function of the hindered rotator that consists of the partition function for the hindered rotor in the form

$$Q_{hr} = Q_f\,(q_{qho}/q_{cho})$$

where Q_f is the classical phase integral for the rigid rotator in the hindering potential field, and q_{qho} and q_{cho} are the partition functions for a quantum mechanical and a classical harmonic oscillator, respectively. The classical phase integral has been obtained by numerical integration using the calculated potential energy surfaces for the hindering potential. The librational frequency used for the oscillators is obtained from the barriers V_0 in the potential energy surface using the relation $\nu = (1/\pi)(V_0/(2I))^{1/2}$ where I is the moment of inertia of the rotating anion. The contribution of the rotational motion of the CN^- anions to the total specific heat for both crystals is shown in Figure 7. In the case of potassium cyanide, C_R reaches the value of 2.18 cal mol^{-1} K^{-1} at 300 K, indicating that at room temperature the cyanide anions are rotating almost freely in the crystal. This is no longer the case for NaCN for which a value of C_R over 4 cal mol^{-1} K^{-1} reflects the severe hindrance for the rotational movement of the linear anions. These values are in fair agreement with the estimates of C_R obtained by Messer and Ziegler[29] from thermodynamic data: C_R (NaCN, 350 K) = 3.8 ± 1.0 cal mol^{-1} K^{-1} and C_R (KCN, 350 K) = 2.9 ± 1.0 cal mol^{-1} K^{-1}.

The potential energy surfaces for the rotation of the cyanide anions in the intermediate temperature body-centered tetragonal phases (Figure 8) are similar for both compounds, with deep minima corresponding to the experimental structures with the cyanide anions oriented along the [010] directions of the crystal. Rotation is severely hindered in both compounds with barriers between the different equivalent minumum energy orientations of 22.9 and 11.3 kcal/mol for NaCN and KCN, respectively. A similar ratio between these two values has been reported by Matsuo, Suga and Seki.[17,18] Their estimates for the rotational barriers in the low-temperature phases, obtained from experimentally determined thermodynamic data, are however somewhat lower: 13 and 7.5 kcal/mol, respectively.

These results show that the potential energy surfaces for the orthorhombic structures of the alkali cyanides are totally different from that found for CaC_2.[1] For this compound, a deep minimum is found for $\theta = 0°$ with the dicarbide anions aligned along the axis pointing to two of the calcium anions. This different behavior between the intermediate temperature phases of the alkali cyanides and that of calcium carbide may also have significant consequences in the dynamic behavior of the cubic high-temperature phase of the carbide, which is currently beeing studied in our group.

Concluding Remarks

The analysis of the electronic structure and bonding in NaCN and KCN reveals a highly ionic character for both compounds. One of the more interesting features of the alkali cyanides, the existence of high-temperature phases with cubic pseudo-NaCl structures, has been found to have a different origin in both compounds. The calculated potential energy surfaces for the rotation of the cyanide anions in the solid indicate that for KCN

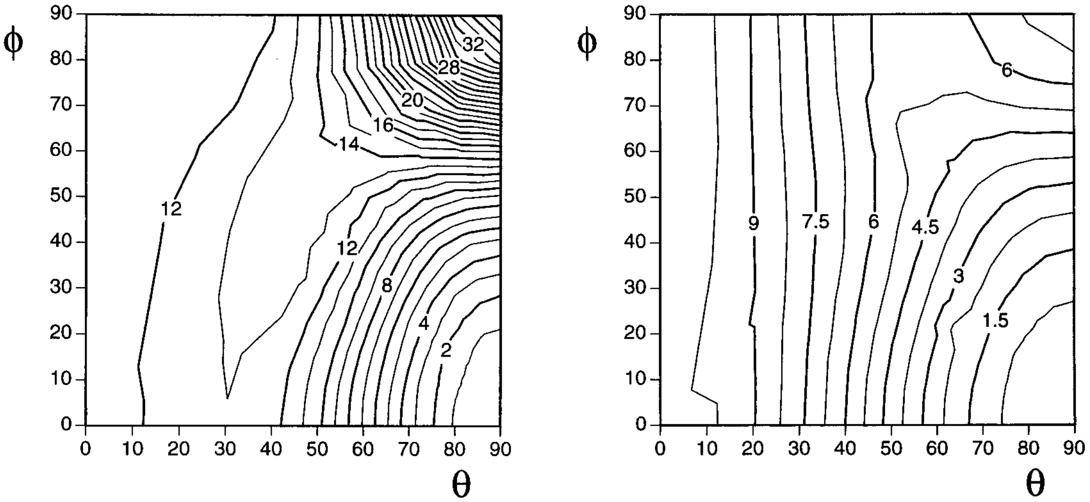

Figure 8. Relative potential energy for the rotation of the CN^- anions in the orthorhombic *Immm* phases of NaCN (left) and KCN (right). The experimental structures correspond to $\theta = 90°$and $\phi = 0°$ with the cyanyde anions oriented along the [010] directions of the crystal. Energy values of the contour lines are given in kcal/mol.

the Pauling model, with almost freely rotating anions, should describe properly the dynamic structure of the solid. A very different situation is expected for NaCN, where the Frenkel model, with static anions oriented randomly along the equivalent [100] directions of the crystal, seems to be more adequate for explaining the origin of the average cubic symmetry of the crystals.

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References and Notes

(1) Ruiz, E.; Alemany, P. *J. Phys. Chem.* **1995**, *99*, 3114.
(2) Dovesi, R.; Saunders, V. R.; Roetti, C. *CRYSTAL-92*; University of Torino and Landsbury Laboratory: Italy and U.K., 1992.
(3) Pisani, C.; Dovesi, R.; Roetti, C. *Hartree-Fock Ab-Initio Treatment of Crystalline Solids*; Springer-Verlag: Berlin, 1988.
(4) Dovesi, R.; Roetti, C.; Freyria-Fava, C.; Prencipe, M. *Chem. Phys.* **1991**, *156*, 11.
(5) Hehre, D. J.; Radom, L.; von Schleyer, P. R.; Pople, J. A. *Ab initio molecular orbital theory*; Wiley: New York, 1986.
(6) Lüty, F. In *Defects in Insulating Crystals*; Tuchkevich, V. M., Shvarts, K. K., Eds.; Springer-Verlag: Berlin, 1981; p 69.
(7) Verweel, H. J.; Bijvoet, J. M. *Z. Kristallogr.* **1938**, *100*, 201.
(8) Bijvoet, J. M.; Lely, J. A. *Rec. Trav. Chim. Pays-Bas* **1940**, *59*, 908.
(9) Fontaine, D. *C. R. Acad. Sci. Paris, Ser. B* **1975**, *281*, 443.
(10) Rowe, J. M.; Hinks, D. G.; Price, D. L.; Susman, S. *J. Chem. Phys.* **1973**, *58*, 2039.
(11) Rowe, J. M.; Rush, J. J.; Prince, E. *J. Chem. Phys.* **1977**, *66*, 5147.
(12) Rowe, J. M.; Rush, J. J.; Chester, N. J.; Michel, K. H.; Naudts, J. *Phys. Rev. Lett.* **1978**, *40*, 455.
(13) Rowe, J. M.; Susman, S. *Phys. Rev. B* **1984**, *29*, 4727.
(14) Schräder, T.; Loidl, A.; Vogt, T. *Phys. Rev. B* **1989**, *39*, 6186.
(15) Schräder, T.; Loidl, A.; Vogt, T. *Z. Phys. B: Condens. Matter* **1990**, *79*, 423.
(16) LeSar, R.; Gordon, R. G. *J. Chem. Phys.* **1982**, *77*, 3682.
(17) Matsuo, T.; Suga, H.; Seki, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 583.
(18) Suga, H.; Matsuo, T.; Seki, S. *Bull. Chem. Soc. Jpn.* **1965**, *7*, 1115.
(19) Hout, R. F.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234.
(20) Gordy, W.; Williams, D. *J. Chem. Phys.* **1935**, *3*, 664.
(21) Gordy, W.; Williams, D. *J. Chem. Phys.* **1936**, *4*, 85.
(22) Krishnamurti, P. *Indian J. Phys.* **1930**, *5*, 651.
(23) Pal; Gupta, S. *Indian J. Phys.* **1930**, *5*, 13.
(24) Pauling, L. *Phys. Rev.* **1930**, *36*, 430.
(25) Frenkel, J. *Acta Physicochim. URSS* **1935**, *3*, 23.
(26) Atoji, M. *J. Chem. Phys.* **1971**, *54*, 3514.
(27) Elliot, N.; Hastings, J. *Acta Crystallogr.* **1961**, *14*, 1018.
(28) Sequeira, A. *Acta Crystallogr.* **1965**, *18*, 291.
(29) Messer, C. E.; Ziegler, W. T. *J. Am. Chem. Soc.* **1941**, *63*, 2610.
(30) Mathieu, J. P. *Compt. Rend.* **1954**, *238*, 74.
(31) Coogan, C. K.; Gutowsky, H. S. *J. Chem. Phys.* **1964**, *40*, 3419.
(32) Adolphi, N. L.; Conradi, M. S. *Phys. Rev. B* **1992**, *45*, 13057.
(33) Cheng, A.; Klein, M. L.; Lewis, L. J. *Phys. Rev. B* **1991**, *44*, 13.
(34) Stepakoff, G. L.; Coulter, L. V. *J. Phys. Chem. Solids* **1963**, *24*, 1435.