

Na₃O(CN): *Ab initio* calculations on a multidomain structure

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The structure and properties of Na₃O(CN) have been studied using parameter-free model calculations based on density functional theory. The results suggest that, unlike in pure alkalicyanides, the CN anions are orientationally disordered in the ground-state structure. The calculations show that in the fully disordered structure, the global strain is minimized.

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I. INTRODUCTION

In past decades alkali cyanides, *MCN*, with $M = \text{Na, K, Rb, and Cs}$, have been studied intensively in an effort to understand temperature-induced order and disorder phase transitions.¹⁻⁷ These crystals are cubic at high temperatures, where they are isostructural to alkali-halide structures [NaCl type for NaCN, KCN, and RbCN; CsCl type for CsCN (Refs. 8-11, respectively)]. In these compounds the observed macroscopic cubic symmetry is caused by a dynamical orientational disorder. Therefore, cooling below a critical temperature leads to a long-range ordering of the CN anions with a concomitant reduction of the lattice symmetry. While RbCN and CsCN undergo just one phase transition to a monoclinic¹² or rhombohedral¹³ structure, respectively, with disordered electric dipoles, NaCN and KCN undergo two phase transitions: first to a structure with space group *I**mmm*, in which a long-range order of the CN anions parallel to [010] occurs, while on further cooling the residual head-to-tail disorder of the CN anions is removed by a continuous order-disorder transition.¹⁴

In contrast to the multitude of studies carried out on alkali cyanides, only few studies have been directed to understand whether trialkali oxide cyanides, where the structural aspects are quite similar, show a related behavior. According to single-crystal x-ray structure determinations Na₃O(CN)¹⁵ and K₃O(CN)¹⁶ crystallize in the antiperovskite structure-type with space group symmetry *Pm* $\bar{3}$ *m* (Fig. 1). Similar to the alkali cyanides, there is an inconsistency between the point symmetry of the CN anion (∞ *m*) and the point symmetry of the site it occupies in the cuboctahedron (Wyckoff position 1b with point symmetry $m\bar{3}m$). Therefore, the CN anions have to be either dynamically or statically disordered over six equivalent orientations, so that a volume and/or time average gives a cubic space group.¹⁵ Contrary to the pure alkali cyanides, no temperature-induced phase transition has been observed in the temperature range from ambient conditions down to 120 K. As the observed atomic displacement factors of C and N were small, static disorder has been assumed.¹⁵

The local symmetry breaking by static disorder raises the question of how the structure responds locally. This is a commonly encountered question, which cannot be investigated by diffraction techniques, but requires atomistic models, either on their own or for the interpretation of spectroscopic data. Here we address the question of the local structural response to disorder by parameter-free quantum-mechanical modeling. Reliable and accurate models are available whose only input information is the chemical composition of the material. However, in some respects the available approaches are not well suited to study static disorder due to the use of

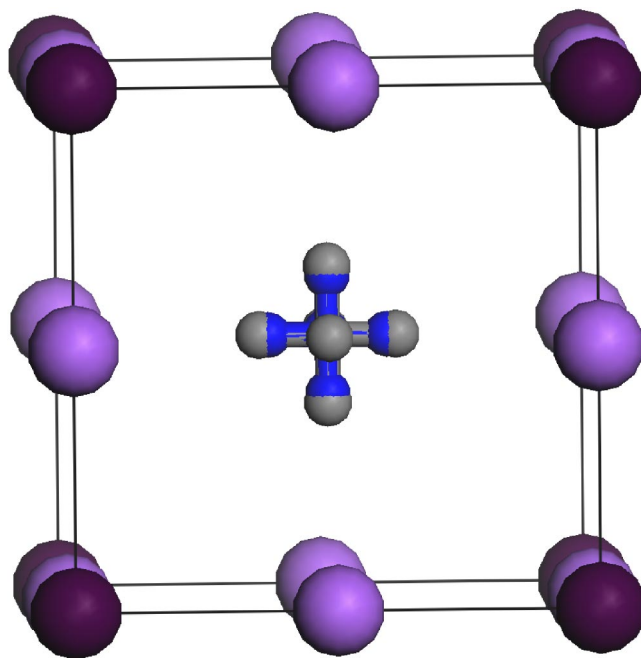


FIG. 1. (Color online) Experimentally determined crystal structure of Na₃O(CN)¹⁵ with the CN anion disordered over six equivalent orientations. Oxygen atoms are located at the corners of the unit cell. Sodium atoms are located on the centers of the edges. The CN anions are located in the center of the unit cell.

periodic boundary conditions, which always impose a long-range order. This can only partially be alleviated by the use of supercells, as highly accurate calculations of low-symmetry structures generally are restricted to supercells with volumes not significantly exceeding 1000 \AA^3 . Nevertheless, the use of supercells allows one to study local structural effects and this has been exploited here.

II. COMPUTATIONAL DETAILS

The quantum-mechanical calculations performed here are based on density functional theory (DFT). While DFT itself is exact,¹⁷ practical calculations require an approximation for the treatment of the exchange and correlation energies. Here we use the “generalized gradient approximation” (GGA),¹⁸ in the PBE version.¹⁹ Results based on GGA calculations are generally in better agreement with experiment than those obtained with the local density approximation (LDA).^{20–23}

Total energy differences between polymorphs are usually small, and their evaluation requires precise calculations of the total energies. The computational scheme that we use here allows such accurate calculations for low-symmetry crystal structures. It is based on an expansion of the charge density and electronic wave functions in a basis set of plane waves. However, as it is impractical to consider tightly bound core electrons explicitly when using a plane-wave basis set, pseudopotentials have to be used to mimic the screening of the Coulomb potential of the nucleus by the core electrons. A number of approaches for the construction of pseudopotentials have been presented in the literature.^{24,25} The state of the art is the efficient “ultrasoft” pseudopotential, leading to calculations that require a comparatively small number of plane waves.^{26,27} Such ultrasoft pseudopotentials were used here, with a maximum cutoff energy of the plane waves of 410 eV. In addition to the cutoff energy, only one further parameter determines the quality of the calculations, namely, the density of points with which the Brillouin zone is sampled. Here, we use a sampling of reciprocal space such that distances between grid points are less than 0.05 \AA^{-1} . This gives a BZ sampling error smaller than $1e-4$ eV. This is a rather strict criterion for obtaining ground-state properties of an insulator. Full geometry optimization calculations were performed. After the final self-consistency cycle, the remaining forces on the atoms were less than $0.005 \text{ eV \AA}^{-1}$, and the remaining stress was less than 0.001 GPa. The present calculations are restricted to the athermal limit, in which temperature effects and zero-point motions are neglected. For all calculations we used academic and commercial versions of the CASTEP program, which has been described elsewhere.^{28–31}

As has been mentioned above, the present study is based on a comparison of several supercells, which, by virtue of the long-range order imposed by the periodic boundary conditions, correspond to domain structures. The smallest possible unit cell—which we will call “initial model”—includes one formula unit and is identical with the experimentally determined structure, except that the CN anion was placed onto one of the six possible orientations (Fig. 2). In comparison to a disordered macroscopic crystal, the structure mod-

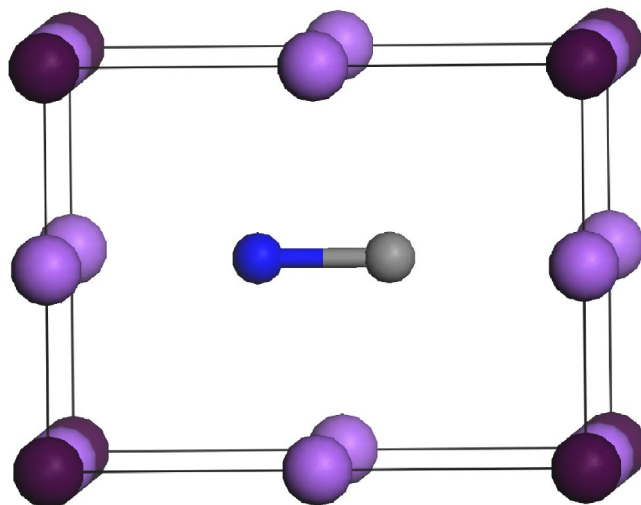


FIG. 2. (Color online) Initial $\text{Na}_3\text{O}(\text{CN})$ model. Here, just one of six equivalent CN orientations was chosen (in this case, parallel to the a axis) in order to create a crystal in which all CN anions are oriented equally (corners: O, centers of the edges: Na, CN in the center of the cell).

eled in such a way may be described as a single domain in which all CN anions have the same orientation. We introduce a naming scheme to facilitate the comparison of different domain structures, where this structure is called “3dd.”

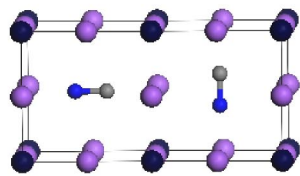
Commencing from this structure we constructed a variety of supercells with increasingly complex orientation patterns of the CN anions. Two of these supercells are shown in Figs. 3 and 4. These structures have different kinds of domains. For example, unit cells in which two adjacent CN anions are oriented perpendicular to each other ($\uparrow\leftarrow$) would produce a crystal with alternating layers of cells in which the anions are oriented parallel to a - (\uparrow) and c -axis (\leftarrow), respectively. This is equivalent to a crystal built of alternating domains whereby each layer represents one domain (Fig. 3) and, therefore, called two-dimensional domains (2dd). The arrangement of domains in crystals consisting of cells like Fig. 4 can be described as columnar [therefore, labeled one-dimensional domain (1dd)], and finally, a completely randomized distribution of the anions, where no adjacent CN anions are oriented the same way, shall be called zero-dimensional domain (0dd).

Due to limitations of computational resources, the largest supercell was $2 \times 2 \times 2$ times larger than the smallest cell (Fig. 5), but as will be shown below, this was sufficient to determine the preferred orientation of the CN anions in Na_3OCN .

III. RESULTS AND DISCUSSION

The optimized data of all trial structures are given in Table I. In all relaxed structures, the calculated values for the C—N bond lengths, $d(\text{C—N})$, range between 1.187 and 1.200 \AA , while the experimentally determined value of the disordered structure [$d(\text{C—N})_{\text{exp}} = 1.099(9) \text{ \AA}$] is about 10% smaller.¹⁵ It is most likely that the shorter bond length re-

Cell:



Crystal:

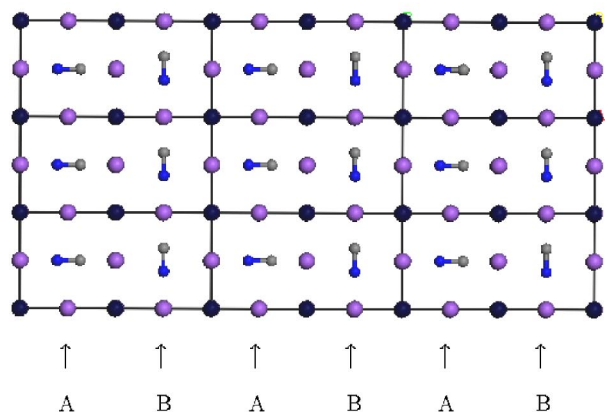


FIG. 3. (Color online) A unit cell in which two adjacent CN anions are oriented perpendicular to each other produces a crystal with alternating layers of domains. Within each domain, all CN anions are oriented equally, while the domains differ from each other by perpendicular alignment of the CN anions.

ported 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 as it has been noted earlier for NaCN.³² The Mulliken population analysis gave an expected large value of 1.66(2) *e* for the covalent C—N bonds in all struc-

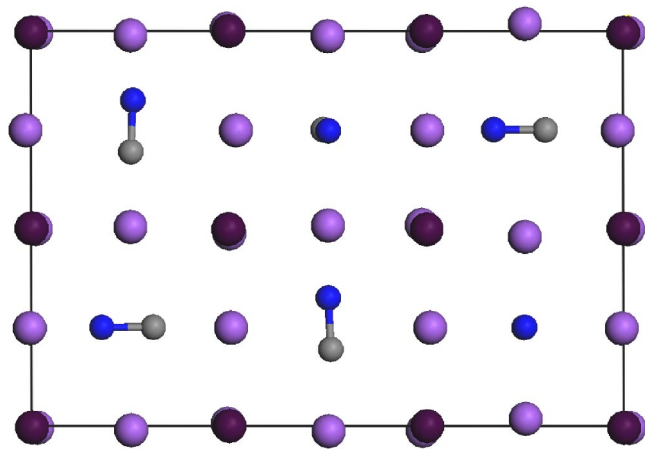


FIG. 4. (Color online) In a more complex cell, the domains consisting of adjacent CN anions with equal orientation are reduced from layers to columns (in direction of sight).

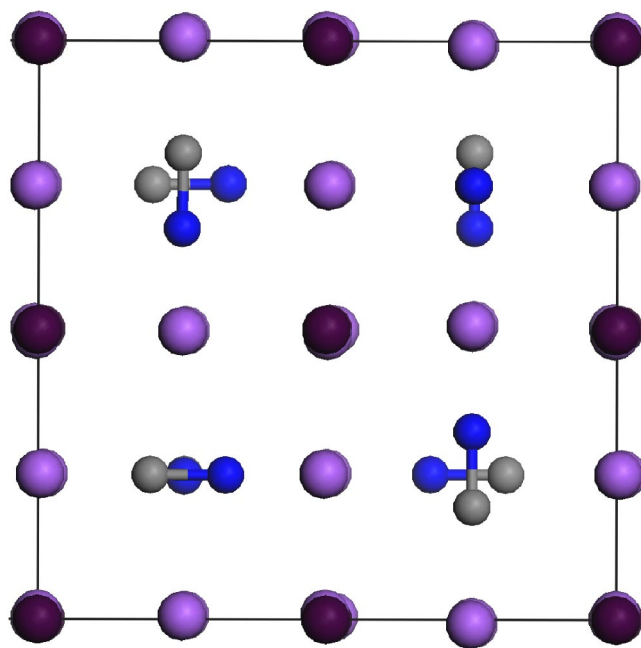


FIG. 5. (Color online) The biggest and most complex unit cell which was used as trial structure. Here, all adjacent CN anions are oriented perpendicular to each other.

tures. The atomic populations show negative charges for both C (−0.24 *e*) and N (−0.52 *e*). The next largest bond populations are significantly smaller (0.20–0.35 *e*) and occur between the positive Na (0.49–0.61 *e*) and negative O (−0.90 *e*) ions that build the cages in which the CN anions are located. Populations between C/N and Na/O can get as large as 0.19 *e*, but seem not to be correlated with the relative stabilities of the structures, which will be discussed now.

The geometry optimization of the initial model results in a tetragonal unit cell with $c/a=1.0439$ as long as the CN anion is aligned parallel to one of the crystal axis in the trial structure (\leftarrow). If one rotates the CN anion in the trial structure by a few degrees out of the high symmetry orientation, the geometry optimization results in a monoclinic cell with the CN anion in a face diagonal position (\swarrow , see Fig. 6). This cell is by ≈ 3.6 kJ/mol more stable than the tetragonal cell. The structural data are given in Table II where they are compared with the experimental structure.

As a next step, a 2dd supercell with $P1m1$ symmetry ($\uparrow \leftarrow$, Fig. 3) was used as a trial cell for the geometry optimization. Here, the full geometry optimization gave only a slight rotation of the CN anions out of their initial position, while the symmetry of the structure remained monoclinic (i.e., the mirror plane was conserved as the molecules rotated only within the mirror planes). The total energy of this structure is ≈ 6 kJ/mol lower than that of the tetragonal structure, and, therefore, the stability is also higher than that of the 3dd monoclinic cell. In consideration of the results for the initial model, we also tried to optimize a 2dd supercell with $P1$ symmetry, in which both CN anions are in a face diagonal position. Here, a rotation of the CN anions out of their initial position can be observed as well, leading to a structure that has—within the numerical errors—the same total energy as

TABLE I. Optimized $\text{Na}_3\text{O}(\text{CN})$ trial structures in order of increasing complexity of the unit cells. Arrows denote the orientation of the CN anions in the a (\uparrow), b (\cdot), and c (\leftarrow) directions in order of appearance. Arrows that are separated by commas denote that CN anions are distributed in the unit cell in the corresponding orientations. The given volume has been normalized to that of one formula unit.

Cell	Orient.	Space Group	V (\AA^3)	a (\AA)	b (\AA)	c (\AA)	α ($^\circ$)	β ($^\circ$)	γ ($^\circ$)	ΔE (kJ/mol)	ϵ_{ss}
$1 \times 1 \times 1$	\leftarrow	P4mm	96.73	4.525	4.525	4.724	90	90	90	-0.12	0.0353
$1 \times 1 \times 2$	$\uparrow \downarrow$	Pcmm	96.37	4.710	4.523	9.046	90	90	90	0	0.0334
$1 \times 1 \times 1$	\swarrow	P1	97.84	4.602	4.615	4.614	93.08	90	90	-3.60	0.0381
$1 \times 1 \times 2$	$\uparrow \cdot$	Ama2P	97.50	4.631	4.631	9.091	90	89.80	90	-6.77	0.0154
$1 \times 1 \times 2$	$\uparrow \leftarrow$	P1m1	97.93	4.662	4.554	9.226	90	90.60	90	-5.92	0.0182
$1 \times 1 \times 2$	$\swarrow \uparrow$	P1	98.02	9.255	4.611	4.596	91.83	89.82	90.56	-6.56	0.0242
$1 \times 1 \times 3$	$\uparrow \cdot \leftarrow$	P1	96.50	4.606	4.591	13.693	89.48	90.20	89.98	-6.92	0.0094
$1 \times 2 \times 3$	$\uparrow, \cdot, \leftarrow$	P1	95.99	4.616	9.129	13.668	90.06	90.07	90.01	-9.76	0.0101
$2 \times 2 \times 2$	\uparrow, \cdot	P4mcc	95.38	9.172	9.172	9.070	90	90	90	-9.38	0.0109
$2 \times 2 \times 2$	$\uparrow, \cdot, \leftarrow$	C1c1P	95.45	9.155	9.155	9.111	90.09	90.09	90.00	-11.49	0.0042

the one described above, with a $P1m1$ supercell but different atomic positions of C and N. Therefore, the geometry optimization gave distinct relaxed structures with very similar total energies depending on the initial orientation of the C—N group. This implies the presence of local minima in the Born-Oppenheimer total energy hypersurface. While our calculations show that a tilted alignment may correspond to a local energy minimum, the amount of tilting seems to decrease with increasing supercell volume. Due to the limitations imposed by the available computing resources, this could not be investigated for the largest supercell. However, as the discussion below will show, the energetics of the system are dominated by the dimensionality of the domains, and

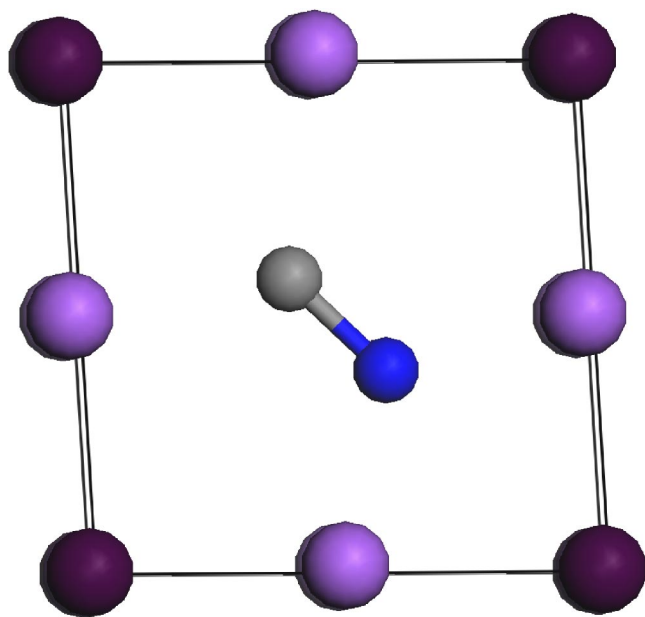


FIG. 6. (Color online) If the CN anion in the trial structure is rotated by a few degrees out of the high symmetry orientation, the geometry optimization results in a monoclinic cell with the CN anion in a face diagonal position.

not by the exact orientation of the CN anions. This is evident from Fig. 7, where an increasing disorder leads to an increasing stability. All calculated 2dd trial structures in which two adjacent CN anions are oriented perpendicular to each other ($\uparrow \leftarrow$, $\uparrow \cdot$, $\uparrow \leftarrow$) have a total energy 6–7 kJ/mol lower than the tetragonal structure and are therefore also more stable than the monoclinic cell. On the other hand, an antiparallel ($\uparrow \downarrow$) orientation of CN anions does not significantly change the total energy with respect to a parallel alignment. Technical difficulties prevented full optimization of cells in which adjacent CN anions are antiparallel and pointing toward each other ($\rightarrow \leftarrow$), leaving a residual stress of ≈ 1 GPa on the corresponding axis. Consequently, the most complex cell in which *all* adjacent CN anions are oriented perpendicular to each other and which, therefore, consist of a 0dd arrangement of the CN anions (Fig. 5) turned out to build the most stable structure of all investigated cells.

To verify that there is no artificial dependence of the energy on the volume of the supercell, two test calculations were performed: first, a single-point energy (SPE) calculation on a $2 \times 2 \times 2$ supercell in which all CN anions are aligned parallel and which has the same symmetry as the

TABLE II. The optimized initial models (Relaxed Tetragonal and Relaxed Monoclinic) in comparison with the experimental structure found by.¹⁵ In the theoretical models, all CN anions are aligned parallel.

	Experiment	Relaxed Tetr	Relaxed Mon
Space Group	$\text{Pm}\bar{3}\text{m}$	P4mm	P1m1
a (\AA)	4.543	4.5226	4.6142
b (\AA)	4.543	4.5226	4.6015
c (\AA)	4.543	4.7245	4.6146
c/a	1	1.045	
β ($^\circ$)	90	90	93.08
Volume (\AA^3)	93.76	96.64	97.84

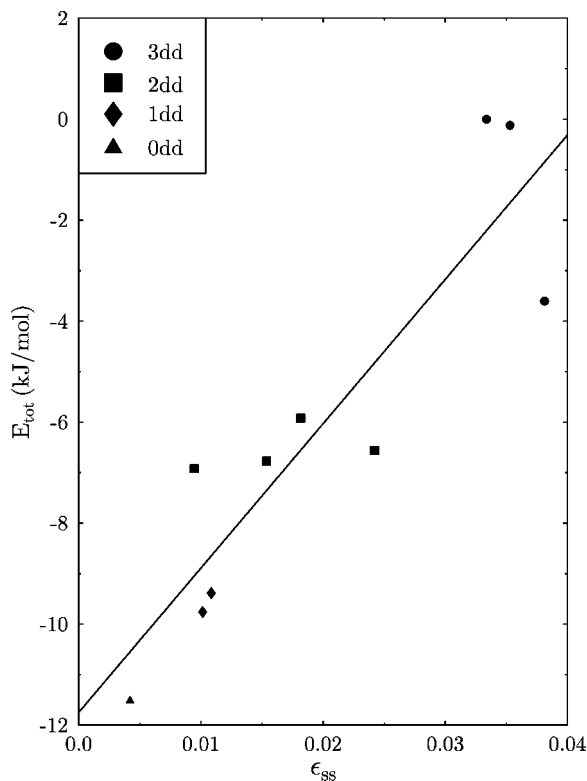


FIG. 7. Linear dependence of the total energy E_{tot} on the scalar spontaneous strain ϵ_{ss} of the relaxed structures from a pseudocubic cell. The straight line is a least-squares fit to all data points and shows that a fully disordered structure is about 11.7 kJ/mol more stable than a fully ordered structure.

initial cell ($P4mm$). The total energy achieved for this structure differs by 0.022 kJ/mol from the total energy of the initial cell. Second, a set of SPE calculations with increasingly dense k-point grids was performed on the optimized initial cell to estimate the absolute convergence error. This error was also smaller than 0.02 kJ/mol, far less than the energy differences between the particular domain groups (≈ 3 kJ/mol), and less than the energy differences of particular structures within one group of domains (≈ 0.3 kJ/mol). Therefore, the obtained results can be considered as reliable.

To investigate to what extent the statistical distribution of the CN anions leads to a reduction of the deviation from the pseudocubic unit cell, we calculated the scalar spontaneous strain ϵ_{ss} for all optimized structures³³

$$\epsilon_{\text{ss}} = \sqrt{\sum_{i,j} e_{ij}^2}. \quad (1)$$

The individual strain components e_{ij} were calculated on the basis of the equations from Refs. 34 and 35. The lattice parameter a_0 of the cubic high-symmetry phase was taken as the cubic root of the molar volume for each domain structure. As the high-symmetry phase is cubic, the formulas for the e_{ij} simplify to

$$e_{11} = \frac{a \sin \gamma}{a_0} - 1 \quad (2)$$

$$e_{22} = \frac{b}{a_0} - 1 \quad (3)$$

$$e_{33} = \frac{c \sin \alpha \sin \beta^*}{a_0} - 1 \quad (4)$$

$$e_{23} = \frac{c \cos \alpha}{2a_0} \quad (5)$$

$$e_{13} = \frac{-c \sin \alpha \cos \beta^*}{2a_0} \quad (6)$$

$$e_{12} = \frac{a \cos \gamma}{2a_0}. \quad (7)$$

Figure 7 shows that the dependence of the total energy on ϵ_{ss} can be described well as linear. Figure 7 also demonstrates that the variation of the total energy within one group of domains with the same dimensionality is much smaller than the difference between structures with domains with differing dimensionality as has been pointed out above when discussing the deviation of the CN orientation from an alignment parallel to the crystal axes. An interpolation of the curve to $\epsilon_{\text{ss}}=0$ would give an energy difference of 11.7 kJ/mol between a fully disordered cell (Fig. 1) and the smallest fully ordered structure (Fig. 2). Phase transition temperatures may be predicted using Landau-Ginzberg models,³⁶ or estimated more crudely from a rough equivalence of the ordering energy with the thermal energy from the equipartition theorem of classical statistical mechanics. The latter approach would predict an ordering transition at roughly 1400 K for Na₃OCN. Consequently, we conclude that the disorder observed at 120 K is likely to be frozen in domains similar to the structures we have calculated.

In summary, the present study has shown that the ground-state structure is statically disordered in agreement with the experimental observation. This result is unexpected in the view of the behavior of the pure alkali cyanides.³⁷ The disordered CN sublattice can be viewed as orientational glass with no long-range order. This disorder seems to be stabilized by the minimization of the local strain. The existence of the ground-state disordered structure of Na₃O(CN) is also distinct for the case of K(CN, Br) mixed crystals, which remain cubic on cooling.³⁸ Regrettably, only high-temperature studies of the thermal and electric properties of Na₃O(CN) have been performed until now.^{15,39} In these studies it was shown that there is an endothermic phase transition in Na₃O(CN) at 220 °C. This phase transition, which leads to a significant increase in the ionic conductivity, is thought to be associated with a dynamic disorder and a “partial melting” of the sodium sublattice.³⁹ However, this interpretation has not been independently verified yet. A disordered structure, which has been shown here to be the ground state, is

unlikely to result from a well-defined endothermic transition at relative high temperatures. We would rather expect a continuous, glasslike freezing in of dynamically disordered CN anions. To detect this, however, either very sensitive experimental investigations or molecular dynamics simulations are required.

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