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Richard Alan Lesar, Harvard University
R. G. Gordon, Harvard University

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Density-functional theory for the solid alkali cyanides

R. LeSar\textsuperscript{a)} and R. G. Gordon

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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Structural properties of the solid alkali cyanides were studied with a recently reported \textit{ab initio} theory based on the Gordon–Kim electron gas model. The low temperature crystal structures of LiCN, NaCN, KCN, RbCN, and CsCN were examined. The average error in lattice parameters is 2.6\% and in lattice dissociation energy 1.7\%. For the NaCN and KCN systems, the energy differences between the ferroelectric and antiferroelectric structures were examined and the antiferroelectric structure was found to be more stable at zero temperature by about 0.5–0.8 kcal/mol. The high pressure phases of KCN were studied and the phase diagram partially mapped out at 0 K. The crystal structure of RbCN at low temperatures was studied, and the orthorhombic \textit{Pmmn} structure found to be more stable than the monoclinic \textit{Aa} structure. The heat of formation of RbCN was calculated at 0 K to be about 31.4 ± 7 kcal/mol. The cyanide electron density was found to shift from the C atom towards the N atom in all crystals studied, when the free space \textit{CN}– ion is incorporated into a crystal.

I. INTRODUCTION

The alkali metal cyanides have long been used as examples of a general class of \textit{M}(\textit{AB})\textsuperscript{–} crystals, which, because of rotation of the (\textit{AB})\textsuperscript{–} molecules, show structures at high temperatures similar to that of the alkali halides. As the temperature is decreased, transitions to orientationally ordered phases occur. While there have been many studies on these systems, numerous questions concerning the structure, phase transitions, and dynamics remain.

The low pressure crystal structures for LiCN,\textsuperscript{1} NaCN,\textsuperscript{2–4} KCN,\textsuperscript{2,4,5} and CsCN\textsuperscript{6} are reportedly well determined, and some studies of the phase diagrams of NaCN\textsuperscript{1,4} and KCN\textsuperscript{5–11} are available at higher pressures. Theoretical studies on the structure of these systems have been limited to the use of empirical potentials,\textsuperscript{12} with little emphasis placed on the anisotropy of the pair interactions. Recently, there have been a number of studies of the dynamical properties of these crystals.\textsuperscript{13}

Recently we have presented an \textit{ab initio} electron gas theory of molecular crystals.\textsuperscript{14} Requiring no empirical parameters, the method can be applied to a wide variety of crystals involving linear molecules. Results on the alkali and alkaline earth hydroxides show that agreement with experiment is within 2\%, both in lattice parameters and dissociation energy. Here we examine the static properties of the alkali cyanides. The high pressure phases of KCN will be discussed, as well as the energy differences between the ordered and disordered phases in NaCN and KCN.

We give a brief outline of the theoretical model used to calculate the crystal dissociation energy as a function of crystal structure in Sec. II. In Sec. III we discuss the wave functions used here to calculate the cyanide ion electronic density. The choice of thermodynamic values used to find the experimental dissociation energy is also discussed. In Secs. IV–IV E we present results of calculations on LiCN, NaCN, KCN, RbCN, and CsCN crystals at low temperatures.

\textsuperscript{a)}Present address: Los Alamos National Laboratory, Los Alamos, NM 87545.

II. THEORY

In this section we briefly describe the theory used to calculate crystal lattice geometries and dissociation energy. Complete details are given in Ref. 14. We first assume that the total crystal charge density can be written as a superposition of the densities of the constituent individual ionic densities. The electronic density of a molecule is expanded in a sum of spherically symmetric densities located along the bond at \textbf{r} as

\[ \rho(\textbf{r}) = \sum_{\textit{j}=1}^{\textit{n}} \rho_{\textit{j}}(|\textbf{r} - \textbf{r}_{\textit{j}}|), \]

where

\[ \rho_{\textit{j}}(\textbf{r}) = \sum_{\textit{m}=1}^{\textit{m}_{\textit{j}}} C_{\textit{jm}} r_{\textit{jm}} \exp(-Z_{\textit{jm}} r), \]

and the parameters \( C_{\textit{jm}} \) are determined by fitting the electronic density from a molecular Hartree–Fock calculation.\textsuperscript{15} The total crystal charge density is then

\[ \rho(\textbf{r}) = \sum_{\textit{j}=1}^{\textit{n}} \sum_{\textit{m}=1}^{\textit{m}_{\textit{j}}} Z_{\textit{jm}} \delta(\textbf{r} - \textbf{r}_{\textit{j}}) - \rho_{\textit{j}}(|\textbf{r} - \textbf{r}_{\textit{j}}|), \]

where \( Z_{\textit{jm}} \) is the nuclear charge of the \textit{j}th function on the \textit{i}th molecule in the unit cell located at \( \textbf{r}_{\textit{ij}} = \textbf{r}_i + \textbf{r}_j + \textbf{r}_i \) and \( \textbf{r}_i \) is a lattice vector. The binding energy is written as the difference in energy between the crystal interaction energy per formula unit and the energy of the isolated atoms and molecules. The energy is divided into the short range electron gas terms, which include the kinetic, exchange, and correlation energies, and the electrostatic energy. The electron gas terms are described in Refs. 14 and 16, and can be written for a molecular crystal as

\[ W = \int_{V} \rho(\textbf{r}) \left\{ E\left[ \sum_{\textit{i}=1}^{\textit{i}_{\textit{p}}} \sum_{\textit{m}=1}^{\textit{m}_{\textit{p}}} \sum_{\textit{m}_{\textit{p}}=1}^{\textit{m}_{\textit{p}}} \rho_{\textit{ip}}(|\textbf{r} - \textbf{r}_{\textit{ij}}|) \right] - \sum_{\textit{i}=1}^{\textit{i}_{\textit{p}}} E\left[ \sum_{\textit{m}=1}^{\textit{m}_{\textit{p}}} \rho_{\textit{ip}}(|\textbf{r} - \textbf{r}_{\textit{ij}}|) \right] \right\}, \]

where \( E(\rho(\textbf{r})) \) is the appropriate energy density functional and \( V \) the volume of the unit cell. This equation gives the interaction term directly and includes the effects of many-body overlap. The electrostatic energy is
This term was split into a point Coulomb term (the Madelung energy) and a sum of short range pair interaction terms.

The molecular electronic charge densities are determined from Hartree–Fock self-consistent field wave functions. The effects of the crystal potential on the electronic distributions are approximated by the inclusion of a set of six bare external charges in the calculation of the wave function. The positions and total charges of these external point charges are determined by matching the calculated crystal potential along the molecular bond. This results in a contraction and shifting of the anion electron density. Because stabilization of this sort has little effect on the cation density, only the anions were treated in this manner. The calculations are repeated until the crystal potential and the electronic distributions are approximated by the molecular wave function consisted of the atomic double zeta basis functions. The effects of the crystal potential on the electronic densities are approximated by the wave function of Bonaccorsi et al., \cite{21} based on the electron affinity measured by Berkowitz et al. \cite{88} This value for the electron affinity is supported by recent Hartree–Fock calculations by Pacansky and Liu which have yielded an SCF electron affinity of about 75 kcal/mol. \cite{18} Correlation would be expected to increase this result, with an increase of about 10–12 kcal/mol being consistent with the results of Allen et al., on electron pair correlation. \cite{22} Using this electron affinity, the heat of formation of the cyanide ion is estimated as 15.2 ± 3 kcal/mol.

For all calculations using a gas phase cyanide wave function (the first step in the iteration process), the wave function of Bonaccorsi et al. was used. \cite{21} The wave function consisted of the atomic double zeta basis with added 3d polarization functions at a bond length of 2.1791 a.u. (1.15 Å). The exponents were not optimized. The molecular properties determined with this wave function are listed in Table I. As discussed in detail in the discussion of the calculations on NaCN.

### III. THE CYANIDE ION

An accurate value for the heat of formation of the cyanide ion is needed to calculate experimental lattice dissociation energies. Due to uncertainties in determining the electron affinity of the cyanide ion, there has been some question about the value for the heat of formation of CN\(^-\), with thermodynamic estimates ranging from about 15–30 kcal/mol. \cite{17} Attempts have been made to estimate the heat of formation by comparing calculated lattice dissociation energies of NaCN and KCN crystals, using empirical potentials, \cite{12} with experimentally determined heats of formation of NaCN(s) and KCN(s), with estimates of the heat of formation of the cyanide ion in the range from about 8–11 kcal/mol. We choose to adopt the thermodynamic value suggested by the JANAF tables, \cite{17} based on the electron affinity measured by Berkowitz et al. \cite{88} This value for the electron affinity is supported by recent Hartree–Fock calculations by Pacansky and Liu which have yielded an SCF electron affinity of about 75 kcal/mol. \cite{18} Correlation would be expected to increase this result, with an increase of about 10–12 kcal/mol being consistent with the results of Allen et al., on electron pair correlation. \cite{22} Using this electron affinity, the heat of formation of the cyanide ion is estimated as 15.2 ± 3 kcal/mol.

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crystals, the electronic density calculated with this wave function appears to be too contracted.

In performing the calculation of the wave function for the stabilized cyanide ion, only s and p type atomic orbitals were used; the double zeta basis of Bonaccorsi et al., without the 3d functions and with one more 2p per atom, with the exponent of the added function from atomic calculations. As a check of this basis set, we first considered a gas phase cyanide ion (no stabilization), where we optimized the exponents for the 2s functions and the two 2p functions with the smallest exponent for each atom. A list of the molecular properties calculated with this wave function is given in Table I, along with results from earlier ab initio calculations. Closer agreement with other reported values for the dipole moment and quadrupole moment are found with the present wave function than with that of Bonaccorsi et al. The reported moments are with respect to the center of mass of the cyanide ion with the orientation C–N. There seems to be some question on the direction of the dipole moment of CN−. Our results, as well as the results of Bonaccorsi et al. and Clementi and Klint, indicate a positive dipole moment with respect to the center of mass and orientation C–N. This implies, for instance for the result of Clementi and Klint, that one can assign a fractional charge of −0.53 on C (qC) and one of −0.47 on N (qN). The finite field SCF result of Gready et al., though reporting a result that is essentially the same as that of Clementi and Klint, reportedly has the opposite polarity.

The basis set used in finding stabilized wave functions was the same as that used on the gas phase ion. The exponents were optimized for one stabilization (about in the middle of the range of stabilizations) and for bond length 2.016 (the experimental bond length for the KCN mmm phase as discussed below), and were used for all other calculations. In Table I are given the electrostatic moments calculated with these wave functions.

The electronic densities found with the stabilized cyanide wave functions were fit to seven spherical functions located along the bond at, relative to the center of mass,

\[ C, -0.85, -0.45, 0.0, 0.4, 0.8, \text{and } N. \]

In all cases, fits to a relative standard deviation of about 0.5% were found. The "nuclear charges" on each center were adjusted to fit the monopole moments, given in Table I. In practice, only small changes in these "nuclear charges" were necessary to fit the moments.

IV. RESULTS

A. LiCN

Lithium cyanide is the exception to the trend that the alkali cyanides are cubic at room temperature. X-ray studies by Lely and Bijvoet have shown LiCN to have an orthorhombic structure at room temperature with four molecules per unit cell and a reported space group of \( Pbnm.\) Because of the low scattering from the Li+ ions, the C and N atoms could be distinguished and their positions determined. Each Li+ is surrounded by a distorted tetrahedron, consisting of three N atoms and one C atom at the corners. The atoms are in the special positions \( \{x, \frac{1}{2}, z\}, \{\frac{1}{2} - x, \frac{1}{2}, \frac{1}{2} + z\}. \) The structure is shown in Fig. 1, with the experimentally determined lattice parameters in Table II.

By fixing the structure in the known symmetry, the number of parameters to be varied in a minimization of the lattice binding energy can be reduced to nine \( (a, b, c, x_{Li}, y_{Li}, z_{Li}, x_{c.m.}, y_{c.m.}, z_{c.m.}) \) and two components of an orientation vector. The notation \( x_{c.m.} \) refers to the fractional position of the center of mass of the cyanide ions. The positions and orientations of all other ions are related by symmetry. In Table II, we compare with the experimental results the calculated crystal parameters for LiCN where we have converted the positions and orientations of the cyanide ions to fractional positions for the C and N atoms. In Table I we can find the molecular multipole moments associated with the cyanide ion in LiCN. The change in dipole moment indicates a shift in electronic density towards the nitrogen atom. This is consistent with the experimental results that indicate that most of the extra charge on the cyanide seems to be on the N atom. Only the converged result is given. The experimental bond length of the cyanide ion was 2.162 a.u., while the gas phase value of 2.1791 a.u. was used in our calculations.

Our calculations show excellent agreement with the experimental results. Neglecting the temperature differences (our model corresponds to 0 K and the experimental to room temperature), the average error in the structural parameters is about 2.8% and in the lattice dissociation energy about 0.9%. No other structures for LiCN were studied.
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special positions

\[ \text{Na}^+ : \ (0, 0, 0); \ (1/2, 1/2, 1/2), \]
\[ \text{C} \text{ or N} : \ (0, 1/2, z); \ (1/2, 0, z). \]

It was not possible experimentally to distinguish the C and N atoms. The experimental lattice constants are given in Table II. The structure is multidomained (ferroelectric) and the cyanide ions randomly ordered (head to tail disorder). The reported bond length of \( \text{CN}^- \) in this phase is appreciably shorter than the gas phase value (1.05 Å in NaCN and 1.15 Å in the gas phase). 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 the thermal disorder. Although the true structure is multidomained, we shall consider only the limiting structure of a crystal made up of repeating cells of ferroelectrically aligned cyanide ions.

Fontaine\(^3\) has reported the results of a neutron diffraction study on \( \text{NaCN} \) at low temperature (4.2 K). This phase \( \text{NaCN}_{II} \) has a primitive orthorhombic structure with space group \( Pmmn \). Rowe \textit{et al.} independently have determined the same structure for the low temperature phases of both \( \text{NaCN} \) and \( \text{KCN} \).\(^4\) The special positions of the atoms are

\[ \text{Na}^+ : \ (0, 0, z); \ (1/2, 1/2, z), \]
\[ \text{C(N)} : \ (0, 1/2, z); \ (1/2, 0, z). \]

The lattice constants are given in Table II and the structure is shown in Fig. 2. The essential difference in the reported structures of the II and III phases is the orientation of one of the cyanide ions in the unit cell. It is expected then that the phase transition from the I to II phase should show little change in lattice parameters, which is seen experimentally (Table II). Matsuo, Suga, and Seki\(^5\) found that the entropy change in this phase transition is about 2 Kln 2, which is consistent with an order–disorder transition of this type.

The experimental bond length reported for \( \text{CN}^- \) in \( \text{NaCN}_{II} \) is shorter than the gas phase value. In order to examine this result, and to illuminate the effects of stabilization by the crystal environment, we performed calculations on the \( \text{Immm} \) phase of \( \text{NaCN} \) with wave functions for \( \text{CN}^- \) with two bond lengths, \( r = 2.016 \) and the gas phase value \( r = 2.1791 \text{ a.u.} \). These results are summarized in Table II. With the shorter ion, the crystal can compress slightly, with a lower crystal binding energy \( E_b \) by about 1.4 kcal/mol. However, the energy to shorten the bond length (given by the difference in stabilization energies) is about 16.6 kcal/mol. Since the lattice dissociation energy depends on both the energy of the lattice as well as the atoms and molecules in the lattice, it is clear that the crystal with the longer cyanide ions is energetically more stable. This result is supported by the experimental structure determined for the \( Pmmn \) structure at 4.2 K (Table II) where the bond length was found to be 2.182 1.05 Å.

Listed in Table II are results from calculations on the \( \text{Immm} \) phase of \( \text{NaCN} \) with the \( \text{CN}^- \) wave function reported by Bonaccorsi \textit{et al.}\(^6\) The unit cell volume calculated with this wave function is smaller than with the stabilized wave function and the binding energy is greater in magnitude. Since the stabilization tends to shrink the size of the molecule it seems that the gas phase wave function reported by Bonaccorsi \textit{et al.} is too contracted. When the basis set was optimized for the gas phase wave function calculated here (essentially the same basis as Bonaccorsi \textit{et al.}), we found that the exponents in general got smaller, leading to a more diffuse electronic density. We did not repeat the crystal calculations with our gas phase wave function.

One way of determining an upper bound to the barrier to rotation of a cyanide ion in the \( \text{Immm} \) phase is to freeze the positions of all atoms and molecules but one and then find the energy as this molecule rotates. We calculated this energy for \( \text{NaCN} \) for two rotational paths, one with rotation in the \( ac \) plane (as shown in Fig. 2) and one with rotation in the \( bc \) plane. Due to the structure of our method, rotation of a molecule in only one unit cell is not possible and all equivalent molecules in other unit cells were rotated also. Since these other rotating molecules are not nearest neighbors, they should not greatly affect the results. We find a barrier to rotation in the \( bc \) plane of about 8 kcal/mol and in the \( ac \) plane of about 20 kcal/mol. About half of the barrier was due to the electrostatic forces and half was due to the short range forces, unlike the barriers found in \( \text{Mg(OH)}_2 \) reported previously,\(^7\) where the dipolar forces dominated. Vibrations and relaxations of the other molecules in this lattice would lead to a lower effective barrier. The minimum energy found was that with the cyanides oriented along the expected axis. Other theoretical estimates based on parametrized pair potentials have reported the barrier at about 6 kcal/mol.\(^8\)

The \( \text{NaCN}_{III} \) phase was also considered and the results given in Table II. Comparison of the dissociation...
energies of the II and III phases show that the Fmmm phase (low temperature phase) is energetically more stable. The difference in energy (about 0.5 kcal/mol) is of the limits of accuracy of the model, but does show the relative size of the energy difference. The overall agreement with experiment is quite good (a relative error of about 1%, in dissociation energy which is within experimental error and 3% in lattice constants). In Table II (footnote g) is given the calculated zero temperature pressure-volume relation for NaCN.

C. KCN

The phase diagram of KCN is shown in Fig. 3. At zero pressure, KCN behaves very much like NaCN, with a transition from a pseudocubic (NaCl-type) phase (with space group Fm3m) at high temperatures to an orientationally disordered orthorhombic structure (KCN A Immm) at 168 K, and a further transition to an ordered orthorhombic structure (KCN B, Pmmm) at 83 K. Parry has reported finding a form of KCN that has four molecules per unit cell in the special positions (x, y, z); (x + h, y, z); (x, y + h, z); (x + h, y + h, z); (x + h, y, z + h) (x + h, y + h, z + h). Given in Table III (footnote g) is the calculated zero temperature pressure-volume relation for NaCN. were determined, but no specific information about space group and molecular positions is available. At higher temperatures, the structure is reported to be Aa (KCN C), the same structure as reported by Parry in the small temperature range about 168 K. Decker et al. suggest that KCN has a monoclinic structure with space group Cm (KCN IV) at pressures higher than about 20 kbar, and at higher temperature (greater than 270 K) and pressures greater than 20 kbar, KCN has a disordered CsCl type cubic phase (KCN III). Here we shall consider the low temperature orthorhombic phases (A and B) and the high pressure monoclinic structures (C, D, and IV).

As for NaCN, we examined the high temperature NaCl type pseudocubic phase of KCN to see if certain orientations of the cyanide ions were preferred. Using the crystal parameters at -106 °C, we found that, as for NaCN, the structure with the cyanides aligned along the [001] direction is about 1.8 kcal/mol more stable than if they are aligned along the [111] direction and 2.5 kcal/mol more stable than if they are along the [110] direction. Comparison with the NaCN results shows that the energy differences between the three structures is much less for KCN.

KCN A and B are identical in structure to NaCN II and III discussed above. The results of calculations on these structures are given in Table II. The difference in energy between the two structures is 0.8 kcal/mol (with the ordered phase with lower energy) and the errors (relative to experiment) are 2.3% for the dissociation energy and 2.2% for the lattice constants.

The structure suggested for KCN C (space group Aa) has four molecules per unit cell in the special positions (x, y, z); (x + h, y, z); (x, y + h, z); (x + h, y + h, z); (x + h, y, z + h). Given in Table III are the experimental results of Dultz et al. for the C and D phases. The positional parameters for the C phase are also given in Table III. The cyanide ions are oriented in a head-to-tail ferroelectric pattern with slight distortions out of the ac plane (Fig. 4). The experimental structure considered here is surprising in that the cyanides are orientationally ordered in a ferroelectric manner. The lower temperature D phase has quite similar lattice parameters to the C phase, but with a smaller b axis and slightly larger a and c axes. The volumes of the two phases are about the same (within 0.32 cm^3/mole). Because the lattice parameters are so similar it suggests that the transition to the D phase involves only some change in the ordering of the cyanide ions as in the A-B transition. From our calculations on this (Immm-Pmmm) transition in NaCN and KCN we would expect an antiferroelectric ordering to be more stable by a small amount; however, we considered no other forms of the C phase, due to uncertainties in the proper molecular positions. The calculated structure is given in Table V, where we see that we get good agreement with the experimental results at 4.24 kbar.

The high pressure monoclinic form (Fig. 5) of KCN has been reported to have two molecules per unit cell with

FIG. 3. Phase diagram for KCN from Refs. 9 and 10(b).
TABLE III. KCN at high pressure. a

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a All notation and units as in Table II. P is the pressure in kbars, V the volume in cm³/mol, and G the free energy, \( G = -D_e + PV \). All calculations performed with wave function CN-(4) of Table I.

b The C phase of Fig. 3. The positional parameters are found to be: N (0.313, 0.001, 0.584) and C (0.209, -0.027, 0.414) with K fixed at the experimental positions. The higher pressure results were calculated with these center of mass positions and molecular orientations.

c From Ref. 10(b) (150 K). The positional parameters were reported as: K (0.0, -0.082, 0.0); N (0.254, 0.082, 0.494); and C (0.143, -0.086, 0.429).

d The KCN D phase from Ref. 10(b) at 100 K.

The B phase of Fig. 3. The positional parameters for calculations on the Pmmm phase were fixed at the zero pressure values of Table II.

The Cm structure is the reported Cm phase (phase IV of Fig. 3) while the Cm' phase is the antiferroelectric structure discussed in the text. At 25 kbar the positional parameters found for the two structures are (with the K positions fixed at the experimental values) Cm: N (0.551, 0.0, 0.635) and C (0.416, 0.0, 0.457); and Cm'N (0.070, 0.0, 0.121) and C (-0.070, 0.0, -0.049).

e From Ref. 11 (296 K).

The space group Cm and special positions \((x, y, z); \left(\frac{1}{2} + x, \frac{1}{2} + y, z\right)\). In the Cm structure, like the Immm phase (NaCN II), the cyanides presumably are orientationally disordered, with domains of unit cells with all cyanides aligned parallel to each other (ferroelectric). We considered two forms of this high pressure phase, one with the Cm ferroelectric ordering and one with an antiferroelectric ordering and positional parameters \((\frac{1}{2} + x, y, \frac{1}{2} + z); (x, \frac{1}{2} + y, \frac{1}{2} - z)\). The results for both the ferroelectric and antiferroelectric forms of the IV phase are shown in Table III, and compared with the experimental results at 25 kbar. The antiferroelectric form of the structure is generally more stable by about 0.2 kcal/
mol, which is similar to the energy differences found between the $Immm$ and $Pmmn$ phases of KCN and NaCN. Comparison of the present results with the experimental structure of Decker et al.\textsuperscript{11} shows only small differences in the lattice constants. The calculations at 40 kbar were checked with a more stabilized CN$^-$ ion, which matched the site potentials better, (the smaller the volume the higher the site potential), and it was found that the use of a more stabilized wave function changes the calculated molar volume of the $Cm\bar{m}$ phase by about 1.9%. All calculations reported in Table III were performed using the wave function found in the zero pressure calculation [CN(4)] of Table I.

Possible phase transition can be examined by comparing the free energy ($G = -D_s + PV$) of the phases of interest. The difficulty in making a prediction of the transition pressure from our present results is the uncertainty in the structures at low temperatures. Considering the difficulties in predicting the most appropriate structures to consider, as well as the errors due to lack of lattice vibrations or dispersion energy, the complete mapping out of the zero temperature phase diagram has not yet been done. However, in Table III we present results of calculations at high pressure (to 60 kbar) for the three phases of interest. We find that the $Cm\bar{m}$ phase (in its antiferroelectric version) has a smaller volume at high pressures which would favor this phase. At 60 kbar the $Cm\bar{m}'$ phase (antiferroelectric) is more stable than the $Pmmn$ phase by about 0.75 kcal/mol. The $Aa$ structure has a considerably larger volume at these high pressures. The calculations on this structure were performed without relaxing the molecule positions from those found at 4.24 kbar. It could be that a more complete minimization, including such relaxations, would lower the volume and so increase the magnitude of the free energy.

D. RbCN

Only a few experimental studies at normal pressures have been reported for RbCN. The first, an x-ray study,\textsuperscript{6} showed that like NaCN and KCN, RbCN has a pseudocubic (NaCl-type) structure at 300 K. It was also reported that RbCN has a pseudomonoclinic structure at 91 K with the CN$^-$ molecules oriented parallel to the [111] direction of the cubic phase. The reported low temperature phase only roughly explained the experimental intensities. Sugisaki et al.\textsuperscript{28} have reported the heat capacity of RbCN as a function of temperature (15–300 K), showing only one anomalous peak at 110 K with an entropy change of about 2 ln 2. This behavior differs considerably from the NaCN and KCN crystals which show two anomalous peaks. The investigators suggest that the low temperature phase of RbCN has a residual entropy of 2 ln 2, indicating incomplete ordering of the cyanide ions in this phase. Kondo, Schoemaker and Luty\textsuperscript{29} recently studied the RbCN crystal with dielectric and Raman techniques from about 5–300 K and report two large shifts in the real part of the dielectric constant of RbCN, at 132 K and a more gradual change in the 40–70 K range. They cannot account for the difference in reported transition temperatures (132 K for their result and 110 K for Sugisaki and co-workers), Kondo et al. also suggest that their results indicate that a gradual ordering process is taking place as the temperature is lowered above 47 K (lowest temperature dielectric loss measurement taken in their experiment), but feel that there is probably considerable orientational disorder at lower temperatures.

For RbCN, using the lattice parameters for $-100^\circ$ C,\textsuperscript{6} we find that the pseudocubic high temperature phase is more stable if the molecules are aligned along the [100] direction, as in KCN and NaCN. The structure with [111] alignment is less stable by about 1.0 kcal/mol and the [110] structure by about 1.4 kcal/mol. We then see that the energy differences between the structures decreases as we go from NaCN – KCN – RbCN. Molecular dynamics studies\textsuperscript{30} on small systems of KCN have shown that the [100] direction is favored for cyanide ions with a small quadrupole moment, but that a larger quadrupole causes the [111] structure to be favored.

The reported behavior of RbCN (by Kondo et al.) is similar to that of NaCN and KCN; however, there is neither a conclusive heat capacity measurement nor structural information available. By analogy with NaCN and KCN the low temperature phase may be an ordered (or disordered) orthorhombic structure; however, the x-ray results showing a pseudomonoclinic structure at 91 K are similar to the monoclinic structure found for KCN (Aa). Parry\textsuperscript{5} has suggested that the reported structure for RbCN is actually the same as that for the monoclinic phase of KCN.

The orthorhombic phase ($Pmmn$) has been described above for NaCN and KCN. The results of our calculations are given in Table IV. The $Aa$ phase is described above for KCN C. For RbCN, the $x$ and $z$ parameters for the metal atoms were taken as zero and the magnitude of the $y$ parameter varied. The initial positions of the cyanide ions was estimated at $(\frac{1}{4}, 0, \frac{1}{2})$ and the orientations to be approximately parallel to the [302] direction. The results from our calculations on this structure are given in Table IV.

Comparison of the binding energies in Table IV show the monoclinic phase (Aa) to be less stable than the orthorhombic ($Pmmn$) by about 2.8 kcal/mol. The $Aa$ phase as considered here has ferroelectric ordering. An antiferroelectric structure would be expected to have only slightly more binding.

Parry\textsuperscript{5} points out that the pseudomonoclinic phase of RbCN reported by early x-ray work\textsuperscript{30} may be related to the monoclinic structure he found for KCN and considered here for RbCN by taking new lattice vectors in the Aa structure

\[
d' = \frac{1}{2} [a], \quad c' = -\frac{1}{2} [102],
\]

we find new crystal parameters of

\[
d' = 5.17, \quad b = 4.43, \quad c' = 6.50 \text{ Å} \quad \text{and} \quad \beta = 112.1^\circ.
\]

The low temperature x-ray structure determination gave

\[
a = 4.78, \quad b = 4.88, \quad c = 6.67 \text{ Å} \quad \text{and} \quad \beta = 94.5^\circ.
\]

The structure found for the $Aa$ phase of RbCN is similar to that found for the C (D) phase of KCN except that the
TABLE IV. RbCN and CsCN at zero pressure. a

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>β(α)</th>
<th>V</th>
<th>D_e</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbCN Pmmn: b</td>
<td>7.900</td>
<td>12.003</td>
<td>10.214</td>
<td>...</td>
<td>43.21</td>
<td>0.2604</td>
</tr>
<tr>
<td>CN(5)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbCN Aa: c</td>
<td>19.551</td>
<td>8.364</td>
<td>14.095</td>
<td>121.35</td>
<td>43.91</td>
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</tr>
<tr>
<td>CN(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsCN: d</td>
<td>7.850</td>
<td>...</td>
<td>...</td>
<td>88.45</td>
<td>43.12</td>
<td>0.2471</td>
</tr>
<tr>
<td>experiment e</td>
<td>7.990</td>
<td>...</td>
<td>...</td>
<td>86.35</td>
<td>45.25</td>
<td>0.2406</td>
</tr>
</tbody>
</table>

aAll notation and units as in Table II. V is the volume in cm³/mol. Properties of the wavefunctions are given in Table I.

bStructure as discussed in text. The positional parameters are: zRb = 0.335 and zC = 0.122.

cStructure as described in text. The positional parameters are: N(0.337, 0.095, 0.526) and C(0.229, 0.013, 0.504).
dThe theoretical positional parameter is 0.522, which represents the fraction up the diagonal (with the nitrogen pointing up the diagonal) the center of mass is located.
eFrom Ref. 6 (150 K).
fFrom Refs. 17 and 31 at 298 K with an uncertainty of about ± 0.008.

cyanide ions are aligned more along the b axis. Considering the relatively close agreement between the transformed axes and the experimental ones, and the small energy difference between the calculated energies of the Aa and Pmmn phases, it is possible that at some temperature the Aa phase may be the most stable phase. At low temperatures, however, our results indicate that the Pmmn phase is clearly preferred.

To our knowledge, there has been no experimental determination of the heat of formation of RbCN(s) reported in the literature. Estimates have been made using empirical pair potentials to find the dissociation energy of RbCN and then subtracting the heats of formation of Rb⁺ and CN⁻, where the heat of formation of gas phase cyanide was calculated using empirical potentials to find the dissociation energies of KCN and NaCN and using the known heats of formation of these crystals. Since these empirical potentials do not necessarily adequately represent the true interactions, and considering the uncertainties in the value of ΔH₂[CN⁻(g)] used, their estimated value (~27.3 kcal/mol) is of uncertain accuracy. With our value for the lattice dissociation energy, for the Aa structure, and the heats of formation of CN⁻ and Rb⁺ (corrected to 0 K), we find the heat of formation of RbCN(s) at 0 K to be about ~31.4 kcal/mol. Taking into account the uncertainties in the structure, in our model, and in the values for the other thermodynamic quantities, this result should be good to about 5–7 kcal/mol.

E. CsCN

CsCN has a pseudocubic (CsCl-type) structure at room temperature. Below about 200 K, the structure is reported to be rhombohedral with a space group R₃m (one molecule per unit cell). No other structures have been reported. This structure is shown in Fig. 6. Sugisaki et al. have reported heat capacity measurements on CsCN from 15–300 K, where they found only one anomaly at 193.1 K with an entropy change of about R ln 4. They suggest that there may be a residual entropy of R ln 2 in the low temperature phase.

TABLE V. Summary of results. a

| Crystal | Δ% (|I|) | Δ% V | Δ% D_e |
|---------|------|------|--------|
| LiCN    | 2.9  | -4.3 | 0.5    |
| NaCN    | 3.1  | 8.8  | 0.9    |
| KCN(1)  | 2.2  | -3.5 | 2.5    |
| KCN(2)  | 2.0  | 4.7  | ...    |
| KCN(3)  | 2.0  | -1.5 | ...    |
| CsCN    | 2.0  | -4.9 | 2.7    |
| Absolute error | 2.6 | 5.0 | 1.7 |

aThe errors given are percent deviations from the experimental values reported in the text. The average of the errors in the unit cell parameters is (|I|), the molar volume is V, and the dissociation energy is D_e. The three structures for KCN are; (1) the low temperature Pmmn phase (phase B); (2) the Aa phase (C) and; (3) Cm phase (IV).
We performed calculations on the $R3m$ phase of CsCN. The results are reported in Table IV. The $u$ parameter represents the fraction up the diagonal the center of mass of the cyanide is located, where the nitrogen is pointed up the diagonal. An error of about 3.5% in dissociation energy (298 K) and 2.1% in lattice parameters (190 K) were found. There is a large uncertainty in the thermodynamic value for the dissociation energy.

V. DISCUSSION

In Table V is given a summary of the results for the cyanide crystals considered here. Given in this table are the percent errors in dissociation energy and lattice constants of our theoretical results as compared to experiment. The overall quality of the present results, with an absolute error of about 1.7% in energy and 2.6% in lattice constants, shows that the model does in fact give a good description of the forces acting between the molecules in the solids. The errors in the results are due to inadequacies in the electron gas model, lack of lattice vibrations and dispersion energies, and the simplified representation of the effects of the lattice on the electronic distributions.14 These errors make it especially difficult to map out possible phase transitions.

Probably the most intriguing aspect of the alkali cyanide crystals is the orientational disorder and molecular motions. Because of the small dipole moment of the CN$^-\text{ion relative to the hydroxide ion (0.14 vs 0.49 a.u. for the gas phase molecules), the behavior of these crystals is quite different. As discussed previously,14 the hydroxide systems are quite ordered (antiferroelectrically) and have rather simple morphology, with the orientational ordering due mainly to electrostatic dipolar forces. With the small dipole, cyanide crystals lack a strong ordering force (the barrier to rotation is about equally due to the short range repulsive forces as to the electrostatic forces) and entropic effects are important. The present theory is quite successful in showing the low barriers to rotation and in predicting the correct structures.

As in the hydroxide systems,14 there is a shift in the electronic distribution of the cyanide ions due to the interaction with the rest of the ions in the lattice. The dominant effect for the cyanide systems is the contraction of the electronic density, allowing for smaller and more bound lattices. There is, however, a shift in the electrons towards the N atom, as seen in how the dipole moments change (Table I). However, because of the smaller dipolar field in the cyanide systems, the change in dipole is not as great as in the hydroxide systems.

VI. SUMMARY AND CONCLUSIONS

Using an electron gas theory for molecular crystals we have examined the structures of the low temperature alkali cyanide crystals. The agreement between the calculated results and the experimental results is good. Approximating the effects of the crystalline environment on the electronic distributions by a simple electrostatic model is seen to give great improvement over calculations with a gas phase ionic distribution, leading to a more contracted and bound lattice. Inclusion of a more reasonable model for the crystalline environment, including Pauli repulsion, would be expected to improve the results.

The theory is successful in predicting the correct most stable low pressure, low temperature phases of NaCN and KCN, with the antiferroelectric structure favored over the ferroelectric structure by about 0.5–0.8 kcal/mol. NaCN and KCN were studied at high pressure, and a partial mapping of the low temperature phase diagram of KCN presented. The structure of RbCN, not yet observed experimentally at low temperature, was studied, with the orthorhombic $Pmmn$ structure favored over the monoclinic $Aa$ structure.

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