Computer Molecular Dynamics and Phase Transitions in Alkali Azides and Thiocyanates

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ABSTRACT

An account is presented of our studies of the order-disorder phase transitions in KN_3, RbN_3, CsN_3, KSCN, RbSCN and CsSCN. These are based on parameter-free inter-ionic potentials based on the Gordon-Kim modified electron gas formalism extended to molecular ions.

With these potentials we performed static structural relaxations and supercell molecular dynamics and predict with reasonable accuracy the temperatures for the onset of the transitions. In particular we address the question of how the N_3^- and SCN^- ions reorient to yield the transitions.

It was found that in case of azides we observed hindered rotations of the anions about all three crystallographic axes, in all three systems. However, in the thiocyanates only CsSCN yielded hindered rotations about all three axes. In KSCN and RbSCN the order-disorder transition appears rather to involve large amplitude librations of the SCN^- ions, primarily about the **c** axis.

Keywords: Azides; Thiocyanates; Ionic molecular solids; Phase transitions

I. INTRODUCTION

Alkali azides (AN_3) and alkali thiocyanates (ASCN) belong to a class of molecular ionic solids. Unlike alkali halides they have an internal molecular structure, the linear anions. That makes them an interesting subject to study after alkali halides. In this work we concentrate on order-disorder phase transitions in some of these systems. In particular, we identify the mechanism of these transitions in KN_3, RbN_3, CsN_3, KSCN, RbSCN and CsSCN by means of Computer Molecular Dynamics (CMD).

In recent years the dramatic increase in computer speed has enabled the density-functional theory (DFT) to be used extensively in condensed matter physics to investigate the potential-energy surfaces of a variety of materials. DFT methods, which include exchange-correlation correction to the Hartree energy, in connection with CMD, yield accurate *ab-initio* predictions of the behavior of solids and liquids on the atomic scale [1]. The approach used in this work is based on the Gordon-Kim (GK) modified electron gas theory [2] used in conjunction with molecular charge densities obtained from the GAUSSIAN94 [3] quantum chemistry program. Our fast and versatile method is capable of predicting the observed values of physical quantities for a variety of systems and is of more general interest since it can be applied to any interaction between a polyatomic unit (molecule) and a solid system, e.g., a surface.

II. CALCULATION OF THE INTER- AND INTRAMOLECULAR POTENTIALS

In prior work [4] we have developed a first-principles approach to study ionic molecular crystals by means of CMD, based on the GK modified electron gas formalism. This method starts from *ab-initio* quantum chemistry calculations for the whole molecular ion (in this case N_3^- and SCN^-) performed with the GAUSSIAN94 quantum chemistry program to obtain the electron charge distribution and subsequently treats the inter-molecular pair interactions within the GK approximation. Intramolecular interactions are treated within a harmonic expansion whose coefficients are also determined by the GAUSSIAN94 program.

Calculation of the GK potentials requires that individual charge densities be extracted from the charge density of the whole molecular ion. This, along with other details of our approach, has been described in detail previously [4].

For charge densities of alkali ions we used Clementi tables [5]. The long-range Coulomb interactions were computed from the fractional ionicities within the molecular N_3^- and SCN^- anions obtained from Mulliken population analysis [6] and the ionicity of +1 for alkali cations.

III. LOW-TEMPERATURE STRUCTURES AND THE ORDER-DISORDER PHASE TRANSITIONS IN KN_3, RBN_3, CSN_3, KSCN, RBSCN AND CSSCN

The room-temperature phase of KN_3, RbN_3 and CsN_3 has a body-centered tetragonal structure of space group *I4/mcm* in which the azide ions are perfectly ordered along two distinctive crystallographic directions [7,8]. As the temperature is raised, at ambient pressure, RbN_3 and CsN_3 transform at 588 K and 424 K, respectively, into orientationally disordered cubic phase. This phase was reported as optically isotropic [9] and thus it has been concluded that the linear azide ions are in this phase either randomly oriented or they rotate freely. However, steric hindrance would appear to rule out free rotations and thus the azide

Table 1: Prototypic atomic positions in the relaxed structures of selected azides and thiocyanates. Experimental values [15] are given in parentheses.

Prototype	x / a	y / b	z / c	Wyckoff
N(2) in KN$_3$	0.1414(0.1365)	0.5+0.1414(0.1365)	0	8(h)
N(2) in RbN$_3$	0.1376(0.1310)	0.5+0.1376(0.1310)	0	8(h)
N(2) in CsN$_3$	0.1334(0.1260)	0.5+0.1334(0.1260)	0	8(h)
K in KSCN	0.2142(0.2059)	0.25	0	4(c)
S in KSCN	0.6066(0.6033)	0.3099(0.2919)	0.25	4(d)
C in KSCN	0.7938(0.7737)	0.3099(0.2919)	0.25	4(d)
N in KSCN	0.9227(0.8934)	0.4365(0.4139)	0.25	4(d)
Rb in RbSCN	0.2166	0.25	0	4(c)
S in RbSCN	0.6104	0.1303	0.25	4(d)
C in RbSCN	0.7941	0.3108	0.25	4(d)
N in RbSCN	0.9204	0.4340	0.25	4(d)
Cs in CsSCN	0.1907(0.1781)	0.25	0.0863(0.1060)	4(c)
S in CsSCN	0.0267(0.0187)	0.25	0.6878(0.6899)	4(c)
C in CsSCN	0.1788(0.1724)	0.25	0.5369(0.5588)	4(c)
N in CsSCN	0.2864(0.2849)	0.25	0.4366(0.4681)	4(c)

ions are most likely oriented at random with respect to the edges of the cubic unit cell in the high-temperature phase. This was later supported by Raman scattering studies in these two systems [10,11]. No transition to a high-temperature cubic phase was found in KN$_3$.

KSCN and RbSCN have orthorhombic *Pbcm* symmetry in their low-temperature phase. This is a modification of the low-temperature tetragonal *I4/mcm* phase of KN$_3$, RbN$_3$ and CsN$_3$ which arises from the fact that the three atoms that form the linear SCN$^-$ ion are all different. CsSCN has an orthorhombic *Pnma* phase in which the Cs$^+$ cations are displaced into the SCN$^-$ layers because of their larger sizes. As in the azides, in these low-temperature phases of KSCN, RbSCN and CsSCN the SCN$^-$ ions are perfectly ordered.

As the temperatures are raised, at ambient pressure, to 413 K, 435 K and 470 K, respectively, these systems undergo order-disorder phase transitions to rotationally disordered phases characterized by random orientation of the SCN$^-$ ions with respect to the edges of the high-temperature unit cell [12-14].

The detailed nature of the disordering of the N$_3^-$ and SCN$^-$ ions at the transition is ambiguous [15] and it is the aim of this work to address this question.

IV. STATIC RELAXATION OF THE LOW-TEMPERATURE STRUCTURES

We began our simulations by deriving *ab-initio* potential surfaces for our systems using the procedure outlined in Section II. This produced a set of short-range intermolecular and intramolecular pair-potentials as well as fractional charges within N$_3^-$ and SCN$^-$ molecular groups to be used for the long-range Coulomb interactions. For the N$_3^-$ ion we obtained the charges of +0.3022e and –0.6511e on the center and end nitrogens, respectively. For the SCN$^-$ ion the calculated charges were –0.5526e on S, +0.1022e on

C and –0.5496e on N. For the Hartree-Fock optimization the standard 6-31G basis set with single first polarization functions were used for S, C and N atoms.

From these potentials we first performed static relaxations for the low-temperature phases of KN$_3$, RbN$_3$, CsN$_3$, KSCN, RbSCN and CsSCN. This procedure determines the positions of atoms and the axial vectors that correspond to the minimum of the theoretical potential-energy surface, where the generalized forces associated with atoms and lattice vectors are zero. For each case this is performed for an infinite lattice by applying periodic boundary conditions. The standard Ewald summation is used to calculate the lattice energy and forces and the minimization uses a Newton-Raphson algorithm.

For each system we used supercells equal to the crystallographic unit cells and relaxed them within appropriate symmetry constraints. The agreement of the relaxed structures with experiment is excellent. In case of all six compounds the calculated lattice constants are on average 5% shorter than their experimental counterparts. This overall shortening of the lattice constants is a rather general feature for simulations using GK potentials, which we have observed in our other work [4]. Table 1 lists prototypic atomic positions for the three azides and the three thiocyanates and compares them with experimental values. In case of the azides the theoretical and experimental *x/a* parameters of the end nitrogens in the relaxed structures differ for KN$_3$ by 0.005, for RbN$_3$ by 0.007 and for CsN$_3$ by 0.007, which combined with the differences in the lattice constants amounts to 2%, 1% and 1% shortening of the N-N bond lengths. These discrepancies in atomic positions are well within the thermal fluctuations of the atoms at room temperature. For KSCN the largest difference in fractional coordinates between theory and experiment is in the *x/a* parameter for the nitrogen atom. This difference of 0.0293 in the fractional coordinate corresponds to 0.197 Å in the

Table 2: Calculated and experimental values of T_c and experimental melting points for the selected azides and thiocyanates. Experimental values are taken from Ref. [15] and references thereof.

	KN$_3$	RbN$_3$	CsN$_3$	KSCN	RbSCN	CsSCN
T_c theory (K)	600	620	480	420	435	655
T_c experiment (K)	-	588	424	413	435	470
Melting experiment (K)	618	590	599	445	457	479

atomic position. For CsSCN the largest difference is in the z/c parameter for the nitrogen atom. This difference of 0.0315 corresponds to 0.264 Å in the atomic position. In both cases this is, again, within the thermal fluctuations of the atoms at room temperature.

The comparison of atomic positions for the third of the thiocyanates, RbSCN, is not included in Table 1. To the best of our knowledge, the atomic positions for RbSCN have not yet been experimentally determined. However, it is known that RbSCN has the same low-temperature symmetry as KSCN. We therefore initialized our relaxa-tion from atomic coordinates of KSCN. In general, this proce-dure does not reproduce the "true" low-temperature phase of RbSCN because multiplying "incorrect" fractional atomic coordinates by "correct" lattice constants introduces deformations to the structure. However, since the differ-ences in experimental a, b and c between RbSCN and KSCN are only +1.3%, +3.2% and +5.9%, respectively, we hoped that in course of relaxation the structure smoothly reached the global potential-energy minimum, thus repro-ducing the "true" *Pbcm* low-temperature phase of RbSCN. Indeed, the convergence in this run was excellent and the residual stresses left by the program were negligible.

Finally we also performed static relaxations for all six systems without the respective symmetry constraints. In all cases the resultant structures were exactly those given by relaxations with the constraints.

V. MOLECULAR DYNAMICS SIMULATION OF THE PHASE TRANSITIONS

This successful reproduction of the low-temperature phases of KN$_3$, RbN$_3$, CsN$_3$, KSCN, RbSCN and CsSCN serves as a validation of our theoretical potential-energy surface. The structures produced in static relaxations were used to initiate CMD runs aimed at reproducing the order-disorder phase transitions in the six systems.

Among selected azides only RbN$_3$ and CsN$_3$ are known to undergo structural transformation from the low-temperature tetragonal phase to the high-temperature cubic phase. However, it is likely that KN$_3$ would also undergo a similar phase transition if it did not first melt at 618 K.

For all but KSCN we used supercells of 64 ions formed by doubling the low-temperature cells in all three directions and followed the motions of the atoms in real time as we "heated" the supercells incrementally until they transformed to high-temperature phases and further "melted". For KSCN we used larger supercells of 96 ions necessary to obtain a "clean" transition. As in case of static relaxation we used periodic boundary conditions and standard Ewald summation for the long-range interactions. At each tem-perature step we added kinetic energy equivalent to 5 K and let the atoms equilibrate for 12 ps. The molecular dynamics step used was 0.001 ps. A typical run on one R10000® CPU took about two weeks.

The first system studied was KN$_3$. Figure 1 shows the lattice constants as a function of temperature for the CMD simulation. There is a sharp change in the lattice constants at T ≈ 600 K indicating an onset of a structural transformation of the supercell. Indeed, the cross sections of the supercell in Figure 2 below and above this temperature reveal unlocking of azide ions from the ordered state and show the new rotationally disordered phase. It is signifi-cant that these hindered rotations of the azide anions appear about all three crystallographic directions. The large
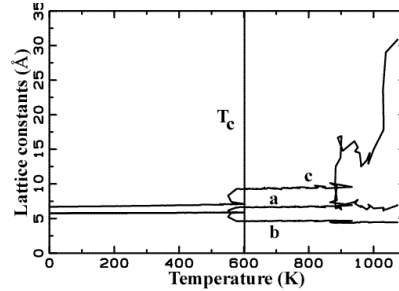

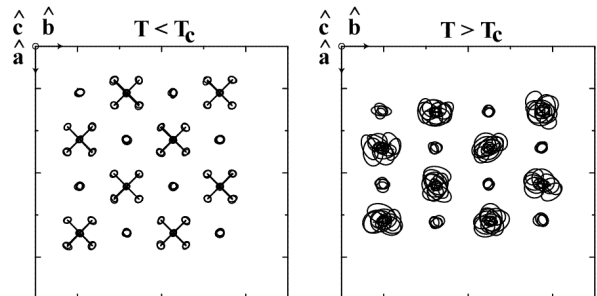Figure 1: Lattice constants as a function of temperature for the CMD run on KN$_3$.

Figure 2: Projections below and above T_c along **c** of the average atomic positions in the 2x2x2 supercell of KN$_3$ obtained from CMD. Thermal ellipsoids indicate RMS deviation of atoms from their average positions.

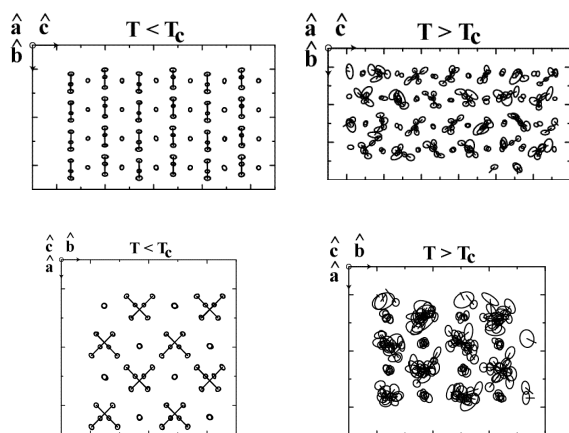Figure 3: Projections below and above T_c along **a** and **c** of the 2x2x3 supercell of KSCN obtained from CMD.

thermal hysteresis associated with this transition, which is visible in Figure 1, is due to absorption of the thermal kinetic energy as internal potential energy reflecting the strong first-order nature of this transition.

The similar picture of the onset of the order-disorder transition was found for RbN_3 as well as for CsN_3. Table 2 lists the critical temperatures T_c for all cases.

The data for thiocyanates is also included in Table 2. Figures 3 and 4, respectively, show cross sections for the KSCN and CsSCN supercell below and above T_c. In case of KSCN and RbSCN we do not observe hindered rotations about all three axes. Instead we see large librations of the SCN^- ions, predominantly in-plane. This may reflect the fact that in the SCN^- anion the center of mass does not co-incide with the geometric center of the ion (as in N_3^-) but lies ⌐30% of the distance from the central carbon to the sulfur atom. In CsSCN, whose low-temperature phase is different from that of KSCN and RbSCN we again observe hindered rotations about all three axes.

VI. CONCLUSIONS

We have successfully tested our *ab-initio* potentials by reproducing low-temperature phases of KN_3, RbN_3, CsN_3, KSCN and CsSCN. In addition we determined the unreported low-temperature structure of RbSCN. We also predict with reasonable accuracy the temperatures for the onset of the order-disorder phase transitions and found a novel
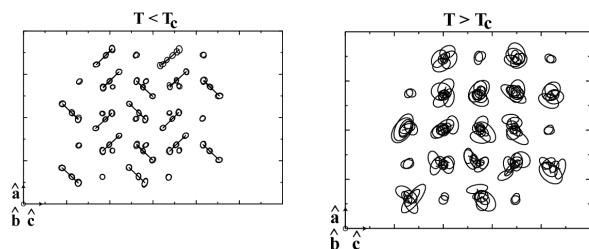

Figure 4: Projections below and above T_C along **b** of the 2x2x2 supercell of CsSCN obtained from CMD.

high-temperature phase in KSCN. In one case, CsSCN, we found the T_c significantly higher (~40%) than the experimental value. This probably arises from the fact that CsSCN had the largest thermal hysteresis in our CMD runs.

For the first time our technique gave us a microscopic view of the order-disorder phase transitions in these materials. Most significantly, we found that the transitions to the high-temperature phases in these systems are driven by rotational disordering of the linear anions. In the case of all the azides we observed hindered rotations of the anions about all three crystallographic axes. However, in the thiocyanates only one system, CsSCN, yielded hindered rotations of this kind. In KSCN and RbSCN the order-disorder transition appears rather to involve large amplitude librations of the SCN^- ions, primarily about the **c** axis.

The further account of this work is in progress. This will include a detailed description of the high-temperature phases of KN_3, RbN_3, CsN_3, KSCN, RbSCN and CsSCN.

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