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Ab initio calculations of the phase-transition mechanism in potassium thiocyanate

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We present the density-functional theory calculations of the microscopic mechanism of the order-disorder phase transition in potassium thiocyanate. The original method of calculations indicates that all molecules from the unit cell are taking part in the reorientation process. The leading phase-transition mechanism should involve both pure torsions of SCN dumbbells around the **c** axis and around the axis in the (a,b) plane. With increasing amplitude of rotations, torsional vibrations around the **c** axis become energetically favorable. The calculations also yield a considerable coupling between the reorientation of SCN molecules and the lattice strains. The present results explain previous contradictory experimental data concerning the mechanism of structural phase transition in thiocyanates.

Thiocyanate crystals have been of special interest for a long time. At room temperature some members of the family MSCN ($M=$K,Rb,Tl) possess an orthorhombic *Pbcm* structure with $Z=4$ molecular units in the unit cell.[1] The structure is formed by alternate layers of M cations and SCN anions, aligned along the **c** direction. The thiocyanate dumbbells are perpendicular to each other on the adjoining layers and in the low-temperature phase possess head-tail ordering along the base diagonals. At temperatures above 400 K all mentioned systems undergo a structural phase transition to the tetragonal phase $I4/mcm$. Above the transition temperature T_c the SCN anions lose their orientational order and take two opposite orientations with equal probability. The previous investigations[2] demonstrate that in these systems a strong coupling between the orientational degrees of freedom and lattice strains occurs. Recent NMR studies[3] suggest that the dynamics of the order parameter is rather slow, both in the low- and the high-temperature phase. Just below T_c the neutron diffraction experiments[4] show a peculiar behavior of KSCN. The shape of the diffuse peak suggests that fluctuations of the order parameter appear 30 K below T_c and grow in number but not in size as approaching the transition temperature.

The interest that has been shown in the alkali thiocyanates is due to their structure, which consists of spherical metal cations and linear molecular SCN anions.[5] In these systems the rotational modes are coupled to the lattice strains. Additionally, the vibrational modes, arising from deformations of the thiocyanate molecules, are coupled to the rigid-body translations and rotations of the ions. Several groups studied the interplay between lattice distortions and the internal modes of SCN. The investigations of the ν_3 C-N stretching mode (2060 cm^{-1}) and the sideband frequency above this mode suggest the existence of two phonon processes and a substantial anharmonic coupling between C-N internal mode and lattice vibrations.[6] On the other hand, there are studies of the external vibrations of the SCN group as a whole. The Raman data show two types of rotatory modes in the lattice frequency region. One mode is the reorientation of thiocyanate group around the **c** axis and the another one involves the reorientation around the axis laying in the (a,b) plane. In both cases the amplitude of vibrations grows larger with increasing temperature until the molecules can attain opposite orientations with equal probability. According to the literature this reorientational process can occur in two possible ways. Studies by Hassan Ali and Talaat[7] suggest that the energy barrier for the reorientation around the **c** axis (0.19 eV) is lower than the barrier for the reorientation around an axis in the (a,b) plane (0.27 eV). On the other hand, x-ray diffraction study[8] of the temperature behavior of the thermal parameters B_{33} indicate that torsional vibrations around the axis in the (a,b) plane are a dominant mechanism of the disordering process. These obviously contradictory statements, together with unusual behavior of fluctuations close to T_c, indicate that the phase transition mechanism in thiocyanates is far from comprehension. The main motivation of the present work is to give some insight into the microscopic mechanism of the phase transition in thiocyanates, especially to identify which molecular motions are associated with the structural changes. Another aim is to check the nature of coupling between torsional and internal vibrations of SCN groups and lattice distortions. In this paper we performed *ab initio* calculations of KSCN, looking for the energy increase and relaxed atomic configurations resulting from different assumed orientations of the single thiocyanate anion.

The present *ab initio* calculations were performed on the supercell consisting of a single unit cell of KSCN with *Pbcm* symmetry (16 atoms) and with periodic boundary conditions. For calculations we used the package CASTEP.[9] The density-functional theory (DFT) functional was minimized with nonlocal norm-conserving pseudopotentials[9,10] available within this package. The pseudopotentials were parametrized in reciprocal space with cutoff energy of 780 eV. The exchange-correlation energy term was calculated within local-density approximation (LDA) and generalized gradient approximation (GGA). The integration over the Brillouin zone has been done on the mesh generated by the Monkhorst-Pack procedure,[11] using from 0.1 Å^{-1} up to 0.07 Å^{-1} grid size, resulting in 2–9 k-points. There were no significant differences found between 4 and 9 k-points sampling, i.e., equilibrium lattice constants differ by less than 0.05%. Therefore, the 4 k-points sampling was used in further calculations.

The ground state of the crystal obtained in the LDA approximation yields the following lattice parameters: $a_0 = 6.4758$ Å, $b_0 = 6.4219$ Å, and $c_0 = 7.1295$ Å as compared with the experimental values[2,8] extrapolated to $T = 0$ K ($a_0 = 6.598$ Å, $b_0 = 6.576$ Å, and $c_0 = 7.233$ Å). Such agreement is quite reasonable. We have also used the GGA approximation for which the agreement is better for the a_0 and b_0 constants, but the c_0 lattice constant disagrees considerably. The use of approximation of the exchange-correlation energy is a crucial point of DFT calculations. Since GGA is considered to be more suitable to the calculations of the cohesive energy or chemical reactions,[12] the LDA works equally well for the bulk properties of crystals.[13,14] The following results are presented for calculations within LDA; however, as we checked, the GGA approximation gives qualitatively similar results with quantitative differences of energy by less than 1% for the angles of 60° and 45°. The calculated geometry of the thiocyanate molecule yields the following values of the bond lengths in the ground state: C-S, 1.612 Å; C-N, 1.180 Å and the bending angle Θ, 179.9° while the experimental[1] values are 1.647 Å, 1.171 Å, and 180°, respectively.

The procedure of calculations of the rotational barriers comes from the frozen phonon method.[15] Having the system in the optimized ground-state configuration we have chosen one of the SCN molecules and rotated it in the first stage. As a rotation axis, we used either the axis along the **c** direction crossing SCN at its center of mass, or the axis in the (a,b) plane perpendicular to the selected thiocyanate anion. After rotating the molecule to a new fixed orientation, in the second stage, all other atoms in the unit cell and the cell parameters were allowed to relax to reach minimum of energy. In the third stage, we fixed the cell parameters and the relaxed atoms in their new positions and allowed the rotated molecule to adjust to the new internal structure of the supercell. The last step of this procedure does not change the orientation of the rotated molecule only, if the relaxed atomic configuration obtained in the second stage provides a local minimum for the rotated molecule. This procedure allowed us to adjust the geometry of all SCN dumbbells. It is worth mentioning that by the third step one can lower the total energy of the system by a considerable amount [as seen on Fig. 1(a)]. The repetition of the second stage after the third step reduces the total energy by about 1%, thus, we decided to stop calculations after step three. After such a procedure the total energy, the cell parameters and atomic configuration were recorded for the angles of rotation 5°, 10°, 15°, 30°, 45°, 60°, 90° and the antiphase (180°) configuration.

Figure 1 presents the dependence of the supercell total energy with respect to the rotation angle of SCN dumbbell. On Fig. 1(a) we see the details for small angles of rotation after each stage of calculation. For small angles of rotation, the energy increases so much in the nonrelaxed case that it becomes nonrealistic,[16] and we did not continue these calculations above 15°. The energy barriers are significantly smaller in the relaxed case. The significant difference in the energy between stages two and three comes from the fact that, in general, the rotation axis does not go through the center of mass of the SCN molecules. The relaxation of the rotated molecule itself, besides relaxing the molecular geometry, allows us to find the proper rotation axis and the translation of the molecule. As presented on Fig. 1(b) the out of (a,b) plane torsions are favored for the rotational angles below 60°, while above 60° the rotations around the **c** axis are more expected. Notice also that the pure rotation around the **c** axis goes over the energy barrier around 50°. This suggests that at low temperatures the out-of-plane torsions are dominant. At higher temperatures larger rotational amplitudes lead to the excitations of the rotations around the **c** axis. The calculated energy barriers are $\Delta E = 2.95$ eV for pure (a,b) plane axis rotation, $\Delta E = 1.04$ eV for **c** axis rotation. The height of the barriers suggests that the results in the vicinity of the ground state and the antiphase configuration are noteworthy. The configurations of particles in the unit cell resulted from the **c** axis and axis from the (a,b) plane cannot be easily mapped to each other for angles greater than a few degrees. It appears that the general axis of rotation changes from perpendicular to the **c** axis for the small angles to parallel to it. In the intermediate state the axis of rotation shall move in space from one orientation to another and is a combination of both considered axes. The another reason of the overestimation of the barrier height comes from the long-range nature of the elastic strains, which can be relaxed on the mesoscopic scale. The relaxed configuration in which the SCN dumbbell is rotated by 90° around the **c** axis corresponds to a local minimum of the energy. This configuration consists of rotated and displaced ions, and we found that it possesses the *Pnma* space group symmetry. In *Pnma* space group the remaining members of the thiocyanate family, namely, NaSCN and CsSCN, crystallize. One has to remember that the rotation of the single molecule causes rotations of all other thiocyanates in the unit cell. The rotation of only a single molecule would require much more energy (as after stage one). It is interesting that independently on the rotation axis the induced rotations of the remaining dumbbells are

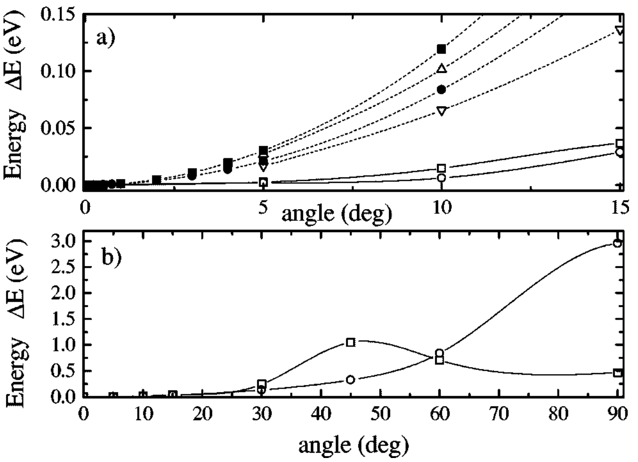

FIG. 1. Dependence of the total energy of the system on the angle of rotation of a single SCN molecule. (a) The dependence for small angles and □ (△), ○ (∇) denote the **c** axis and the (a,b) plane axis rotations, respectively, the full symbols indicate energies after stage one, triangles are for energies after stage two, and open symbols denote energies after the final stage of calculations. (b) Total energy of the system after third stage of calculation. Symbols as in (a). Lines are guides to the eye.

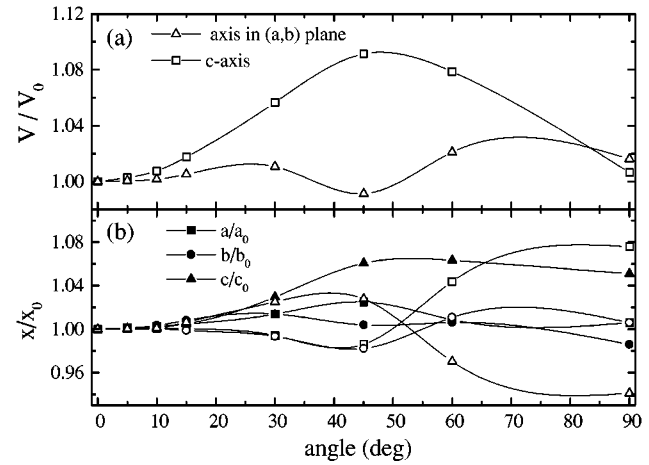

FIG. 2. (a) Change of the volume of the unit cell vs angle of SCN anion rotation. (b) Variation of particular cell parameters. Open symbols are for **c** axis rotations and full symbols for axis in the (a,b) plane, respectively. Lines are guides to the eye.

limited to the (a,b) plane. When the system is in local minimum, corresponding to the $Pnma$ symmetry, it can return to the initial configuration or the SCN dumbbell may flip to an opposite (180°) orientation. In the case when one of the SCN anions is rotated by 180° the energy of the unrelaxed cell is $\Delta E = 0.262$ eV higher than the ground-state energy and $\Delta E = 0.249$ eV higher for the relaxed cell parameters, respectively. For the case of the relaxed cell the elongation along the **c** axis is dominant (2.7%) and strains in (a,b) plane are below 1%.

The rotations of SCN molecules are accompanied by the lattice distortions. They involve variations of the unit cell volume, the cell parameters, and are depicted in Fig. 2. The changes of the unit cell volume can be positive or negative for different angles of rotation [Fig. 2(a)]. Notice that the volume change of the unit cell is larger for the rotations around the **c** axis. The individual cell parameters depicted on Fig. 2(b) change within almost 7%. Such large lattice distortions can be overestimated, since close to the ground state and antiphase configurations they are considerably smaller, about 1%. This result again gives an indication that there exists an axis of rotation for intermediate angles that is a combination of both perpendicular axes.

The discussed structural changes involve also the geometrical changes of the thiocyanate molecule itself. As the system is out of equilibrium, since rotations are assumed, forces from the surrounding area influence the internal structure of SCN, which is the static manifestation of the coupling between internal modes and lattice strains. During the rotations around the **c** axis all SCN anions remain straight within 0.5% accuracy, and the bond lengths change. The C-S bond length contracts up to 0.3% for angles below 45° and stretches by 0.7% for angles from 45° to 90°. The C-N bond length only contracts with maximal change of 0.42% for the angle of 45°. The reorientation around the axis in the (a,b) plane leaves the shape of the molecules practically unaltered, with minor influence on the C-N bond length only.

To summarize, the calculations within the DFT approach yield the following picture of the microscopic mechanism of the structural changes in potassium thiocyanate: the disordering is a collective phenomenon in the sense that all molecules in the unit cell are taking part in the reorientation process to minimize the strains. The transition cannot be performed by pure in- or out-of-plane reorientations of the SCN dumbbells. Only if the reorientation is composed from both modes, the calculations yield reasonable values of the energy barriers. Pure out-of-plane rotations involve smaller energy changes for small angles of rotations and the induced strains are also smaller for this mode. As the amplitude of torsional vibrations increases the mode of torsion around the **c** axis dominates. The lattice distortions are high for this mode; however, as the rotation angle approaches 90° lattice strains become significantly lower. This behavior suggests the axis of rotation of the SCN anions transforms from one laying in the (a,b) plane to the axis parallel to the **c** axis. The linear distortion of SCN anions resulting from the coupling between internal modes and lattice strains indicate that C-N bond is influenced in both modes of rotation. The relaxed configurations indicate strong rotation-translation coupling for all calculated modes and angles of rotation. This may explain the suppression of the collective behavior close to T_c, i.e., the first-order nature of the phase transition.

The calculated energy of antiphase configuration is equal $\Delta E = 0.249$ eV for the antiphase configuration of SCN, which is between the experimental value given in Ref. 7.

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