

Ab Initio Calculations of the Energy Barriers in Potassium Thiocyanate

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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. In these systems the rotational modes are coupled to the strains. Additionally the vibrational modes, arising from deformations of the thiocyanate molecules, are coupled to the rigid body translations and rotations of the ions.

The order-disorder phase transition occurring in that crystals around 400 K still remains mysterious while there is no clear microscopic picture of transition. Experimental data give contradictory mechanism of disordering. Namely, Raman scattering suggest that linear SCN dumbbells flip by reorientation around crystallographic c-axis while X-ray scattering indicate reorientation around axis from (a,b) plane.

We performed *ab initio* calculations of potassium thiocyanate [1] on the supercell consisting of a single unit cell of KSCN with *Pbcm* symmetry (16 atoms) and with periodic boundary conditions to get some insight into the microscopic mechanism of the phase transition in thiocyanates, especially on the nature of couplings between torsional and internal vibrations of SCN groups. Our method of calculations of rotational barriers for SCN anions rely on the frozen phonon approach. Briefly speaking we allowed rotation of single thiocyanate dumbbell and full relaxation of elastic strains.

The calculations yield the information that for small amplitudes the rotations around axis from (a,b) crystallographic plane is energetically favorable. As the amplitude of rotation increases the rotation around c-axis requires less energy as presented on the figure.

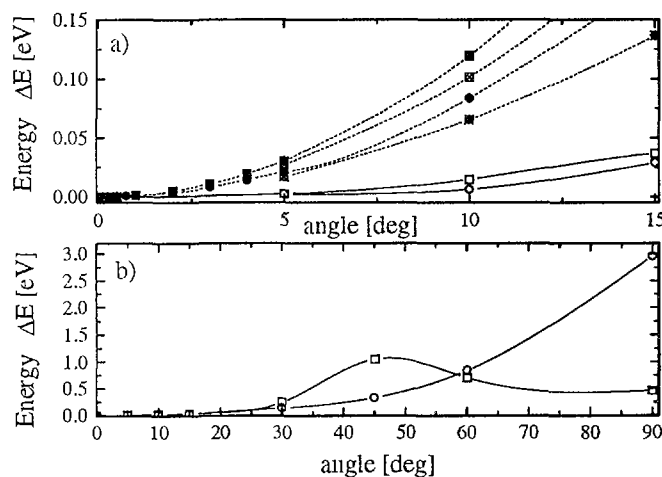


Fig. 1. Dependence of the total energy of the system on the angle of rotation of a single SCN molecule. a) the dependence for small angles, squares and circles denote c-axis and (a,b)- plane axis rotations, respectively. The full symbols indicate energies of strained cell, the hashed symbols – relaxed strain energy and the open ones are for fully relaxed case. b) total energy of the system with fully relaxed strains. Symbols as in a). Lines are guides to the eye.

The calculations within DFT approach yield the following picture for 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. For this mode the lattice distortions becomes significantly lower as the rotation angle approaches 90° . The relaxed configurations indicate strong rotation–translation coupling for all calculated modes and angles of rotation.

Reference:

1. Z. Lodziana, W. Schranz and K. Parliński, "Computational Investigations of Inhomogeneous Elastic Effects near Phase Transitions", *Phase Transitions*, **69** (1999) 147.



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Lattice Dynamics of Copper Indium Diselenide by the First Principle Calculations

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The copper indium diselenide (CIS) is one of the I–III–VI₂ semiconductors representative crystallizing in chalcopyrite structure (I $\bar{4}$ 2d). It is indebted its popularity because of its high absorption coefficient and good chemical stability. It is used in high-efficiency thin-film solar cells. The aim of this work was to determine phonon dispersion relations and phonon density of states for CuInSe₂ from the first principle calculations. Particular encouragement to undertake the present work was that recently the inelastic neutron scattering data for CIS [1] has appeared.

The crystal structure of CIS was determined by *ab initio* pseudo-potential method within the local density approximation (LDA) using CASTEP package [2]. The norm conserving, non-local pseudo-potentials for Cu, In and Se were used. A plane wave basis set was applied with 650 eV cutoff. The integration over the Brillouin zone has been performed with weighted summation over two wave vectors generated by Monkhorst-Pack scheme. The finite plane wave basis set correction was included in total energy. All calculations were done for 1×1×1 supercell (crystallographic unit cell) with 16 atoms.

From HF forces the phonon dispersion curves were calculated with the direct method. According to the direct method, 1×1×1 supercell gives exact phonon frequencies at Γ and Z points. Seven separate displacements are required by the symmetry of chalcopyrite structure, to obtain a complete set of HF forces. We used 0.03 Å displacements in OX and OZ directions. To minimize anharmonic effects the displacements in both positive and negative directions were used. We obtain following structural parameters of CIS: $a_0 = 5.832$ Å, $c_0 = 11.622$ Å and $u = 0.222$, which could be compared with experimental data [4]: 5.782, 11.620 and 0.235, respectively. The differences are very small and do not exceed 1%.

In the Fig. 1 we compare our results with those measured by inelastic neutron scattering for [100] and [001] directions. One can see that in Γ –Z ([001]) direction, the agreement with experiment is a little better then for Γ –M direction. Along both Γ –Z and Γ –M lines some optical branches are overestimated. Our result includes LO–TO splitting, which is determined by the effective charges taken from Ref. [4] (0.475, 1.255 and -0.865 for Cu, In and Se, respectively). The primitive unit cell of chalcopyrites contains 8 atoms, which produced 24 dispersion curves. The small softening of one acoustic mode near the Γ point comes from finite size of supercell. Long-range Coulomb interaction, which dominates in this region requires infinite summation unreachable in the direct method. This