Study of Polytypism in Z_nS

Scholar
Mohd. Ajmal Khan

Supervisor
Prof. M. A. Wahab
Department of Physics
Jamia Millia Islamia

Co-Supervisor
Dr. Shandar Ahmad
Department of Physics
Jamia Millia Islamia

A lot of work has been done in this mysterious and exciting field of polytypism since its discovery by Baumhauer in 1912. ZnS is the most widely investigated polytypic compound besides SiC and CdI_2. ZnS occurs in basically two crystallographic form viz. cubic and hexagonal. Polytypism has been exhibited by both natural and artificially grown ZnS crystals.

In our study, we have chosen close packed polytypic compounds in general and ZnS in particular to understand the phenomenon of polytypism in them. For this purpose, one-dimensional Ising model and Molecular dynamics techniques have been used.

Towards the ANNNI model study of close packed sequences, we modified the Ising Hamiltonian and removed the discrepancies in the assignment of isospins vis a vis Ising model. So far, the spin assignment to different interacting double layers (close packed planes) has been considered to be based on relative orientations of the two constituent layers, which does not seem to be appropriate for two reasons. (i) The interaction between the pairs of double layers AB and BC turns out to be positive and that of AB and AC turns out to be negative without a plausible physical reason, (ii) the orientation of a layer relative to the preceding layer does not contain any information about the interacting layers. In the present work, we have removed this discrepancy by following a new and more realistic criterion. The proposed Hamiltonian according to new spin criterion, can be written as

where $\square$'s are the interaction parameters similar to those used in the ANNNI model and $\square$ is $+1$ if the i–th and $(i+k)$–th layers are in the same orientation and -1 if they are in different orientations and m is the farthest neighbour whose interaction is included and is significant. In fact, we do not replace the individual layers by isospins but in the calculation of every interaction we add or subtract the corresponding amount depending

on if the two layers are in the same or different orientations. Thus, interactions become more clearly dependent on the relative orientations of the interacting layers instead of double layers.

Simulations have been performed for third neighbour and fourth neighbour interactions and the corresponding phase diagrams have been obtained in each case. In case of fourth neighbour interactions, stabilization of polytypic phases are observed but with a lesser degree. However, its contribution cannot be ignored as far as the stability of observed polytypes are concerned. Results obtained from inverse square type potential and exponential type potential based on infinite range simulations indicate that the long-range interactions stabilize a particular polytype, under normal thermodynamic conditions. These results confirms the correctness of our model based on new spin criterion formulated by us.

Beside the above work, we have also carried out the study of the basic properties of ZnS using constant temperature molecular dynamics simulations, employing the Columbic interactions. We have chosen Lennard-Jones potential and it was optimized to calculate the forces of interaction between atoms. To create our MD unit cells, we have chosen coordinates of a tetrahedral structure of ZnS. Beeman algorithm has been used to integrate the equation of motion of the interacting atoms and the temperature has been controlled using Nose Hoover thermostat. A second order phase transformation has been observed in ZnS. We also tested effect of degree of disorderness in ZnS by calculating mean square displacement for Zn and S only. The MSD data confirms the existence of a metastable phase between 1100-1400 K.

Finally, to check the correctness of our MSD values we also plotted lnD vs 1/T curves each for Zn and S atoms from the obtained data. The resulting curves represent perfect straight lines, confirming a well-known Arrhenius plot. This also confirms the correctness of our MSD data.