Abstract of Ph.D. Thesis

Theoretical Study of Polymorphic and Polytypic Compounds

Scholar
Sohail Ahmad

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

To understand the phenomenon of polymorphism and polytypism an extensive theoretical and experimental work has been carried out in the past few decades, covering different aspects of the problem. However, there remain certain aspects which needed immediate attention for further understanding the two phenomena. In the present work, we have tried to answer the questions like (i) What is the general nature of distribution of elements/compounds based on crystal structure (symmetry)? (ii) Why only certain elements/compounds exhibit polymorphism, polytypism or both at the same time? (iii) How to verify the nature of phase transformations in polymorphic and polytypic elements/compounds?

Thus the investigations made in the course of present study can be broadly divided into three parts.

1. Analyses of the available crystallographic data of elements, MX and MX_2 type compounds on different basis in order to know the general nature of distribution of elements/compounds based on crystal structure (symmetry).

2. Cohesive energy calculations for all polymorphic modifications of elements and MX type compounds and their analyses to know that why only certain polymorphic elements/compounds exhibit polytypism.

3. Molecular Dynamics Simulation of polymorphic and polytypic elements and MX- type compounds to verify the nature of phase transformation in them.

The analysis of the crystallographic data of elements existing at room temperature or above on different basis i.e. the crystal system (crystal symmetry), axial ratio and efficiency shows that majority of the elements acquire close packed configuration (either

hcp or ccp) and the number decreases with the decrease in crystal symmetry. A similar classification of MX- type compounds shows that there is a non-linear shift in the distribution of compounds from high to low symmetry side. A comparison of the crystallographic data of elements, MX- and MX_2 - type compounds have also been made to know the nature of general distribution of elements/compounds with crystal symmetry and to infer some important conclusions.

The analysis suggests that 22 elements and 20 MX- type compounds are polymorphic. In order to know which of the polymorphic elements/compounds will likely to behave as polytypic, we made the calculation of cohesive energies using 6 – 12 potential energy equation for elements and Born's point charge model for MX- type compounds. The energy difference between the polymorphic forms has been measured in each case. The total energies and stacking fault energies measured by other workers have also been analyzed and compared with the calculated values to explore the possible reason/condition for a polymorphic element/compound to exhibit polytypism.

Besides, we have also carried out the constant temperature molecular dynamics simulation to study the basic properties employing the Coulombic interactions using Lennard - Jones potential. In order to verify the nature of structural transformation in Nickel and Cobalt chosen as the representative of polymorphic and polytypic elements, respectively. The Lennard - Jones parameters ε and σ have been chosen from the nearest inert gas L-J parameter and optimized by performing many simulations at 300 K for different timesteps. The basic structure for these elements has been reproduced successfully to validate the value of potential parameters. Constant temperature molecular dynamics simulations have been performed at different temperatures in NVT ensemble. 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.

The radial distribution function during MD simulations at different temperatures, gives the basic structural properties quite satisfactorily. Energy temperature graph shows a break at 440 K with the regular increase in case of Nickel indicating the existence of first order phase transformation. A sharp and continuous increase in the specific heat curve at the same temperature is also observed. This indicates that the transformation in Nickel is of the first order type. While the energy temperature graph does not show any

break in case of Cobalt. However, a break in the specific heat curve at around 700 K and a λ type transformation are observed. This indicates that the transformation in Cobalt is of the second order type and hence proves polytypic nature.

Further, we repeated constant temperature molecular dynamics simulation to study the basic properties of polymorphic and polytypic MX- type compounds (Copper Bromide and Silver Iodide) using the same Lennard-Jones potential. At room temperature, RDF peaks successfully reproduce the atomic distances between a lattice point and its neighboring sites of the structures. We plotted the RDF at different temperatures in order to study the nature of their structural change with the temperature. Energy temperature graph shows a break at around 660 K with the regular increase in case of CuBr and a sharp increase in the specific heat curve at the same temperature indicates that phase transformation in CuBr is of the first order type and hence proves polymorphic nature.

In case of AgI, in addition to the decrease in height of peaks with temperature, we also observe that the first peak suddenly decreases from 2.825 A^0 to 2.775 A^0 at 410 K and remains the same beyond this temperature. The decrease in the Ag-I separation brings the pair close to each other. Consequently the Ag-I bond becomes stronger and more molecular in nature, an important conclusion to be taken into account in AgI polytypic transformation. The energy temperature graph does not show any break. However, a break in the specific heat curve at 410 K as well as a λ type transformation are observed. This indicates that the transformation in AgI is of the second order type and hence proves polytypic nature.