PS-08.04.48 STUDY ON THE LAW OF MINUTE CHANGE IN CRYSTAL STRUCTURE. By Zhang Haining, Institute of Mineral Deposits of Chinese Academy of Geological Sciences, He Zhenwen and Yu Li, China University of Science and Technology.

The crystal structure varies minutely with the change of its composition and the environment which it is situated in. These changes could be indicated in different ways. Researchers previously proposed a lot of expressing methods with which they compared these structures, such as unit cell parameters, volume of tesseract cell, bond lengths and bond angles, deformation of ligands, the change of thermal parameters of each ion, and so on. Based on the study of the minute variation of some type structures in recent years, the authors find that: (1) The change of coordinates of characteristic ions or the relative value of each parameter can be used to indicate the law of minute change in crystal structure. (2) On condition that the space group is unchanging, no matter how the tiny the change of crystal structure is, the ligand form can become different but the symmetry of ligand can be unchanged. In this paper, we discuss the law of the minute change in crystal structure, taking the examples spinel, wurtzite, nickelite, rutile, calcium, and cubic type structure etc.

Spinel (AB₂O₄) The space group of spinel is Fd-3m. In its crystal structure, the O⁺ ion cumulate and arrange closely with each other, and produce octahedral and tetrahedral void. A ion occupy the tetrahedral voids with coordinates (1/4, 1/4, 1/4) and B ions are located in the (1/2, 1/2, 1/2) octahedron. The coordinates of O⁺ ions are (u, v, w). Because of the specialities of A and B ions, their symmetry and coordinates are not changing when composition, temperature and pressure vary. However, O⁺ ions may move along the 3 axes (i.e., will possess different values). Thus, A₁O₄tetrahedral and B₂O₈octahedral will react differently. The four O⁺ ions will move (in or out) along the four A→O directions of an A₁O₄tetrahedron at the same time, and form a regular tetrahedron, only the ligand size will change. The six O⁺ ions of a B₂O₈octahedron will move along the [111] direction of the unit cell simultaneously. Thus, the regular octahedron will distort and become a flat tetrahedron or elongated trigonal antiprism. The relation between each parameter and the U value is as indicated in the blood diagram (Fig.1). From this we can see that there are two main points (u=0.373 and w=0.375) which influence the crystal structure as the U value is changing. So, the structure can be divided into five regions, the main characters of each and is as in figure 1.

Conclusion: (1) The coordination polyhedron of ions in structure can be used to discuss the law of minute change in crystal structure. (2) The nature of ions in crystal structure should follow the symmetry rules of the space group. (3) The form and size of ligand in structure can change, but its symmetry is consistent. That is to say, the minute change in crystal structure is the adjusted result of form and size of each ligand. The law of minute change in crystal structure can be reflected from the locus of ion movement.