

Mg-Al cation exchange in MgAl_2O_4 spinel and its short-range ordering

XI LIU¹, YUNLU MA¹, XUWEI ZHAO¹, ZHIGANG ZHANG²

¹ School of Earth and Space Sciences, Peking University,
Beijing 100871, China (xi.liu@pku.edu.cn)

² Key Laboratory of Earth and Planetary Physics, Institute of
Geology and Geophysics, Chinese Academy of Sciences,
Beijing 100029, China

MgAl_2O_4 -spinel shows substantial amounts of intersite Mg-Al cation exchange (denoted by the inversion parameter x), which modify the structural features and influence the physical and chemical properties. Here we first critically reviewed the kinetics studies on the Mg-Al cation exchange reaction, and then reviewed all thermodynamics experiments. With further necessary temperature correction and data removal, we have obtained a generally reliable x - T dataset (71 data pairs in total) at ambient P . Fitting these x - T data to three most commonly used thermodynamic models, we have obtained more accurate model parameters. The model-fitting results suggest that the $T\Delta S_D$ might be important. We consequently evaluated the experimental results from different research fields. The same conclusion that the $T\Delta S_D$ should not be neglected has been obtained.

To understand the origin of the $T\Delta S_D$ and constrain its value, we additionally performed theoretical simulations using the DFT technique. Calculations were conducted using the VASP code, with the exchange-correlation interaction approximated by the LDA method. We considered all the possible cation configurations at the x values of 0, 0.125, 0.25, 0.375 and 1 (~1000 different configurations). The results clearly show that there is indeed short-range Mg-Al cation ordering, which significantly reduces the residual entropy. Our observation is in good agreement with some reversed phase-equilibrium data in the literature.

Cation order-disorder phenomenon is very common in important rock-forming minerals such as olivine, pyroxene, garnet and ringwoodite. The evidence to the existence of short-range cation ordering observed in the MgAl_2O_4 spinel has profound effects on the thermodynamic properties of these minerals.