

## THERMAL EXPANSION OF STOICHIOMETRIC AND VACANCY-CONTAINING MG, AL SPINEL

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A single-crystal X-ray investigation was performed on three synthetic Mg, Al spinels (A, B, C). A and B are stoichiometric  $\text{Mg Al}_2\text{O}_4$ , equilibrated at 600 and 800°C respectively. The chemical formula of crystal C, synthesized with the Verneuil method, is  $\text{Mg}_{0.40} \text{Al}_{2.40} \square_{0.20} \text{O}_4$ . A single set of non equivalent 88 reflections was collected in steps of 100° up to 1000°C. Several reversal runs were performed down to room temperature, and again some data were collected up to 1000°C. The main results are as follows. As a mean, the  $a_0$  increase is about 0.006 Å for 100°C, but it is not linear. Crystal C shows values of positional oxygen parameter  $u$  equal at all temperatures within one or two standard deviations. As a consequence of  $a_0$  and  $u$  behaviour, both T-O and M-O increase regularly with increasing temperature. In crystals A and B  $u$  remains constant up to the equilibration temperatures, and then strongly decreases as a consequence of Mg-Al disordering. This causes shortening of the T-O bond which, at 1000°C, returns to values equal to or lower than those at 25°C. Consequently, the increase in  $a_0$  is only due to the higher rate of the M-O increase during the disordering reaction. Up to 600-700°C, the T-O thermal behaviour of crystal C is very similar to that of stoichiometric samples A and B. This is surprising, since the Pauling bond strength of T site is much greater for C (0.65) than for A and B samples (0.55).