# Simple Point-Ion Electrostatic Model E plains the Cation Distrib tion in Spinel O ides

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The $A_2$ $_4$ spinel oxides are distinguished by having either a normal ( ) or an inverse ( ) distribution of the $A$, cations on their sublattices. A point-ion electrostatic model parametrized by the oxygen displacement parameter and by the relative cation valencies $_A$ vs provides a simple rule for the structural preference for or : if $_A >$ the structure is normal for $> 0.25$ 2 and inverse for $<$ 0.257 , while if $_A <$ the structure is normal for $< 0.2550$ and inverse for $> 0.257$ . This rule is illustrated for the known spinel oxides, proving to be $\sim$ % successful.

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The $A_2$ $_4$ spinel oxides form a family of ~120 compounds [1] spanning a range of physical properties including ferromagnetism [2], coexistence of transparency, and -type conductivity [3], superconductivity [4], and ferroelectricity [5]. The spinel structure consists of face-centered cubic (fcc) lattice of oxygen anions within which $A$ and cations occupy octahedral and tetrahedral interstitial sites arranged in one of two possible patterns: - ( ) and ( ). In the normal spinel structure ( 3 space group) the tetrahedral sites are occupied exclusively by the cations while the octahedral sites are occupied exclusively by $A$ cations. The inverse spinel structure represents a class of configurations in which tetrahedral sites are occupied exclusively by $A$ cations but the octahedral sites can be occupied by both $A$ and cations possibly in a random fashion. The ~120 known oxide spinel compounds are classified experimentally into Normal or Inverse types [1,6]. This includes also dual ( ) spinels which are classified according to their degree of inversion (relative concentration of A on tetrahedral sites) that can be intermediate between ( = 0) and ( = 1). Despite the importance of versus cationic distribution there is still no complete agreement on the nature of the physical and chemical interactions responsible for or cationic distributions [1,6–12]. Here we offer a deductive approach based on revisiting the previously discredited [7,13,14

measured values for these should perhaps be revisited experimentally.