*American Mineralogist, Volume 87, pages 1113–1120, 2002*

# Intersite distribution of $Fe^{2+}$ and Mg in the spinel (sensu stricto)–hercynite series by single-crystal X-ray diffraction

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## ABSTRACT

The influence of composition on $Fe^{2+}$-Mg intracrystalline distribution was studied in eleven synthetic crystals belonging to the spinel (sensu stricto)–hercynite series $(Mg_{1-y}Fe^{2+}_y)Al_2O_4$, with $0 \le y \le 1$, produced by flux-growth at 800 °C. Samples were analyzed by single-crystal X-ray diffraction and electron microprobe methods, and found to be chemically homogeneous with only minor $Fe^{3+}$, which substitutes for Al and increases up to 0.09 atoms per formula unit with total Fe. Structural parameters *a*, *u*, T-O, and M-O increase with hercynite content and, among bond distances, T-O shows the maximum change, from 1.920 to 1.968 Å. The *a* variation from 8.0855 to 8.1646 Å is essentially caused by the T-O increase that, in turn, is due to the cooperative effects of (1) $Fe^{2+} \rightarrow Mg$ substitution and (2) decrease of inversion from 0.23 to 0.15 along the series.

Intracrystalline cation distribution was obtained by a minimization procedure that takes into account structural and chemical data. The T site is mainly populated by Mg and $Fe^{2+}$ but, at a given temperature, $Fe^{2+}$ shows a marked preference for tetrahedral coordination with respect to Mg. The influence of composition and temperature on Fe-Mg intracrystalline distribution was modeled within the framework of the general thermodynamic model of O'Neill and Navrotsky for spinel binary solid solutions. The inversion values observed in our samples agree very well with those calculated by the model. Both measured and calculated amounts of octahedral $Fe^{2+}$ ($^{VI}Fe^{2+}$) show a non-linear increase from spinel s.s. to hercynite. Consequently, the $^{VI}Fe^{2+}/Fe^{2+}_{tot.}$ ratio is not constant along the join, but increases from zero to 15% toward the hercynite end-member. This behavior explains the very limited $Fe^{2+}$ inversion observed in natural spinels, which usually belong to the hercynite-poor part of the join.