

**ELECTRONIC ABSORPTION SPECTROSCOPY OF NATURAL
(Fe²⁺, Fe³⁺)-BEARING SPINELS OF MAGNESIO-SPINEL-HERCYNITE AND
GAHNITE-HERCYNITE SOLID SOLUTIONS AT DIFFERENT TEMPERATURES
AND HIGH PRESSURES**

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Natural Fe²⁺, Fe³⁺-bearing spinel solid solutions from the magnesiospinel-hercynite and gahnite-hercynite series were analyzed and studied by electronic absorption spectroscopy in the spectral range 30000-3500 cm⁻¹ in the temperature and pressure ranges 77 ≤ T_K ≤ 600 and 10⁻⁴ ≤ P_{GPa} ≤ 11.0. Two crystals were light-violet in color (type I) and six green or bluish-green (type II). The spectra of both types of spinel are dominated by an UV-absorption edge near 28000 to 24000 cm⁻¹, depending on the iron contents, and a very intense band system in the NIR centered around 5000 cm⁻¹, which is caused by spin-allowed *dd*-transition of tetrahedral Fe²⁺, derived from ⁵E → ⁵T₂. The strong band is split into four sub-bands, which can only be observed in very thin platelets. Between the UV-edge and the high-energy wing of the NIR-band there occur a number of very weak bands in type I spinels while the green type II spinels show some of these with significantly enhanced intensity. The intensity of the very weak bands is nearly independent on temperature. Such bands are attributed to spin-forbidden electronic transitions of ^{IV}Fe²⁺. Temperature and pressure dependence of the intensity enhanced bands of spinels type II indicate that they are caused by ^{IV}Fe²⁺ and ^{VI}Fe³⁺. By temperature and pressure behaviors they are attributed to spin-forbidden transitions ⁶A_{1g} → ⁴A_{1g}, ⁴E_g → ⁴T_{2g} and → ⁴T_{1g} of ^{VI}Fe³⁺, the two latter being strongly intensified by exchange-coupling interaction with adjacent ^{IV}Fe²⁺. The pressure dependence of ^{IV}Fe²⁺ *dd*-band system in the NIR caused by spin-allowed ⁵E → ⁵T₂ transition noticeably differs from that of octahedral Fe²⁺, an effect which is attributed to a dynamic Jahn-Teller effect of ^{IV}Fe²⁺ in the spinel structure. In difference to ^{VI}Fe²⁺ in many oxygen-based minerals, the splitting of the spin-allowed bands derived from ⁵E → ⁵T₂ transition of ^{IV}Fe²⁺ in spinels does not decrease with pressure. On the contrary, it markedly increases showing that values of vibronic coupling coefficients of ^{IV}Fe²⁺ are rising. Also, the values of tetrahedral moduli of Fe²⁺ in spinel, evaluated from high-pressure spectra and X-ray diffraction structural refinements, are significantly different that again may be caused by a dynamic Jahn-Teller effect of ^{IV}Fe²⁺ in the spinel structure.