

**MgAl₂O₄-MgCr₂O₄-FeAl₂O₄-NATURAL SPINELS FROM THE URALS
ULTRAMAFITES: MÖSSBAUER STUDY, QUANTUM-CHEMICAL SIMULATION
OF THE LOCAL ATOMIC AND ELECTRONIC STRUCTURE**

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Crystal chemistry of MgAl₂O₄-MgCr₂O₄-FeAl₂O₄ natural spinels from the Urals ultramafites has been investigated by means of Mössbauer spectroscopy and microprobe analysis. The Urals ultramafites are represented by the main massifs of the alpine-type and dunite-clinopyroxenite-gabbro complexes. They characterize the redox state evolution of ultramafites from their formation up to the early serpentinization process. The oxidation state of the iron atoms in the minerals has been estimated and the site distributions of Fe³⁺ and Fe²⁺ ions has been analyzed. The Mössbauer parameter variations in 150 samples of the spinels have been discussed. The *ab initio* quantum-chemical cluster calculations of the short-range order structure relaxation and the electronic state spectrum for normal and partially inverse spinel solid solutions MgAl₂O₄-MgCr₂O₄-FeAl₂O₄ was carried out. The relaxed atomic positions were found by the cluster total-energy minimization within the GAMESS program; the electronic structure of relaxed clusters were analyzed by DVM program by discrete-variation X_α-method. Spinel was simulated by the cluster [^{VI}Me_{cent}^{IV}(Mg,Al)₆^{VI}(Mg,Al)₆O₃₈] containing the central octahedron ^{VI}Me_{cent}O₆ (Me_{cent} = Al, Mg, Fe, Cr) surrounded by six tetrahedra (^{IV}MgO₄ or ^{IV}AlO₄) and six octahedra (^{VI}MgO₆ or ^{VI}AlO₆). To find the total energy minimum, the coordinates of six oxygen atoms nearest to the central cation were varied. The equilibrium distances ^{VI}Me_{cent}-O were found to be 1.93 Å for Me_{cent} = Al, 2.03 Å for Mg, 2.00 Å for Fe, and 1.97 Å for Cr, that were in satisfactory agreement with structure refinement data for natural spinels. The central octahedron was shown to be trigonally distorted. The deviations from the cubic symmetry of the nearest oxygen surrounding were obtained to increase at the substitutions Al→Cr→Fe→Mg. The local values of the oxygen parameter *u* were calculated and compared with the experimental averaged values of *u*. The electronic structure and effective atomic charges were calculated both for “idealized” clusters and those with relaxed structure. The influence of relaxation effects on the changing of the spatial distribution of electronic density and integral atomic charges was considered. In particular, effective cation charges increase as the interatomic distances decrease; the ionicity of bonding between cations and the surrounding oxygen atoms increases. The theoretical results were used for evaluation of the spectroscopic parameters of the spinel solid solutions, such as electric field gradient at the iron core (or the quadrupole splitting of Mössbauer spectra) and the transition energies of the optical absorption spectra. Comparable analysis of the data obtained on the base of “idealized” and relaxed models showed that the octahedra distortions should be taken into account when interpreting spectroscopic parameters of natural spinels.

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