

## 1.4.34

### Quantum-chemical simulation of the local atomic and electronic structures for MgAl<sub>2</sub>O<sub>4</sub>-MgCr<sub>2</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub> solid solution

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The *ab initio* quantum-chemical cluster calculations of the short-range order structure relaxation and electronic state spectrum for normal and partially inverse spinel solid solutions MgAl<sub>2</sub>O<sub>4</sub>-MgCr<sub>2</sub>O<sub>4</sub>-FeAl<sub>2</sub>O<sub>4</sub> 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<sub>α</sub>-method. Spinel was simulated by the cluster [VI Me<sub>cent</sub><sup>IV</sup>(Mg,Al)<sub>6</sub>VI(Mg,Al)<sub>6</sub>O<sub>38</sub>] containing the central octahedron VI Me<sub>cent</sub>O<sub>6</sub> (Me<sub>cent</sub>=Al,Mg,Fe,Cr) surrounded by six tetrahedra (IV MgO<sub>4</sub> or IV AlO<sub>4</sub>) and six octahedra (VI MgO<sub>6</sub> or VI AlO<sub>6</sub>). To find the total energy minimum, the coordinates of six oxygen atoms nearest to the central cation were varied. The equilibrium distances VI Me<sub>cent</sub>-O were found to be 1.93Å for Me<sub>cent</sub>=Al, 2.03Å for Mg, 2.00Å for Fe, and 1.97Å 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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### Quantum-mechanical and Monte Carlo simulations of Fe-As-S solid solution properties and the energetics of Au incorporation into arsenian pyrite

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In Carlin-type and epithermal deposits, “invisible” gold is structurally bound exclusively to arsenic-rich pyrite (arsenian pyrite, Fe(As,S)<sub>2</sub>). Previous analytical results support this Au-As relation, although spectroscopic evidence is not conclusive about the structural setting of Au and As at the atomic scale. In order to test the most energetically favorable atomic configurations for Au and As in pyrite, we have performed *ab-initio* quantum mechanical calculations. Different geometric configurations were used as a starting point, in which one of the Fe atoms was replaced by a Au atom in an octahedral site, and one S atom was replaced by an As atom in a tetrahedral site. S atoms were then progressively replaced by As atoms in all possible sites. Results show that the total energy of the system varies with respect to the Au-As distance. Different atomic configurations of Au and As within the pyrite structure show that the defect energy for replacing one Fe atom by a Au atom is lowered by ~1 eV if two or more As atoms are in the near vicinity. In a more general way, configurations in which As atoms are clustered around a Au atom are more energetically favorable.

Although these results predict the relative stability for certain Au-As configurations, they do not represent thermodynamic stabilities for Au-rich arsenian pyrite. Furthermore, calorimetric data are not available for this phase due to experimental difficulties to reach thermodynamic equilibrium at low temperatures (<300C°). In order to fully understand the stability (or metastability) of arsenian pyrite in nature, we are calculating the thermodynamic properties of the Fe-As-S system within the framework of pyrite and marcasite-arsenopyrite-loellingite structures. The As-S interaction parameters, determined from our quantum-mechanical total-energy results, were incorporated into Monte Carlo simulations. This method was used to calculate the free energy, enthalpy, and entropy of mixing and to construct a phase diagram of the solid solution.