

CHARACTERISTICS OF METAL-LIGAND CHEMICAL BOND AND EFFECTS OF NONSTATISTICAL CATION DISTRIBUTION IN THE SPINELS BASED ON NONEMPIRICAL QUANTUM CHEMICAL CALCULATIONS

Yu.Shchapova, S.Votyakov*, E.Yuryeva**, A. Ivanovskii**

Ural State Technical University, Ekaterinburg

*Institute of Geology and Geochemistry, Ural Branch RAS, Ekaterinburg

**Institute of Solid-State Chemistry, Ural Branch RAS, Ekaterinburg

This study was supported by the Russian Fundamental Research Foundation (Project No. 00-05-64499)

Herald DGGGMS RAS № 5 (15) 2000 v.2

URL: http://www.scgis.ru/russian/cp1251/h_dgggms/5-2000/term23.eng

Study goals. The calculated crystallochemical formulas of the minerals form the basis for various petrological and geochemical studies. The ionic character of the metal-ligand chemical bond is always assumed in such calculations. However, this assumption is known to be rather approximate and rude for the most of the minerals, in particular, for oxides and silicates. The lack of alternative approach and the absence of actual calculations and experimental data concerning the covalence degree of the chemical bond in the minerals often lead to the contradictory results. The main goals of our study are the following: a) nonempirical quantum chemical analysis of the electronic structure and metal-ligand bond in the spinels ($\text{Mg}_x, \text{Fe}_{\text{IV}}(1-x)$) (Cr , Al , Fe_{VI}) $_2\text{O}_4$ ($x = 0\div 1$) with the normal distribution of cations, b) calculation of the electric field gradient at the core of Fe_{VI} in the octahedron position of the mineral, c) comparison of the calculated and experimental parameters of Mossbauer spectra of Fe_{VI} and verifying the calculation structural models. The mineral for investigation was chosen because of its wide applications in a number of olivine-spinel versions of geothermometers and oxybarometers [1]. The last ones have been used, in particular, for the estimating of the redox state and temperature of the upper mantle formation. However, the oxygen fugacity has been estimated with an error of three (four) orders of magnitude [1] while the stoichiometric model of the spinel and the ionic character of the chemical bond have been assumed. So the results obtained have to be tested and modified.

Calculation method. Calculations of the electronic structure and chemical bond of the ions in the spinel were based on the nonempirical quantum chemical cluster X_α -method of discrete variation. The calculation procedure has been described in details elsewhere [2-4]. The analysed structural fragments (clusters) contain the central octahedron $\text{Me}_{\text{VI}}\text{O}_6$ ($\text{Fe}_{\text{VI}}\text{O}_6$, $\text{Cr}_{\text{VI}}\text{O}_6$ or $\text{Al}_{\text{VI}}\text{O}_6$) surrounded by six tetrahedrons $\text{Me}_{\text{IV}}\text{O}_4$ ($\text{Mg}_{\text{IV}}\text{O}_4$ and $\text{Fe}_{\text{IV}}\text{O}_4$). The Mg-Fe cations distribution in the tetrahedral sites of the structure have been supposed to deviate from the statistical one. The variations of the mineral composition ($x = 0\div 1$) were assigned by the number of Mg_{IV} and Fe_{IV} cations in the clusters. To simplify calculations, the influence of Fe_{VI} , Cr_{VI} and Al_{VI} cations adjacent to the central octahedron in the structure has been neglected.

Electronic structure. Calculations demonstrated the main features of the electronic structure of

complex iron oxides, including the relative position of $\text{Fe}_{\text{VI}}3d$ and $\text{O}2s,2p$ valent levels in the spectrum, splitting of $3d$ levels in the crystalline field, and their spin polarization [2]. The energies of the valent states of oxygen and iron ions were found to overlap partially; considerable covalent mixing was observed for all the sample compositions studied. The overlap occupancy of $\text{Fe}_{\text{VI}}3d,4s,4p$ and $\text{O}2s,2p$ orbitals which can be used to characterize the degree of covalence was not equal to zero for all the clusters calculated. The maximum covalent effect was observed for $\text{O}2p$ and $\text{Fe}_{\text{VI}}3d,4s$ orbitals. In accordance with calculations, metal-ligand bonds were more ionic for oxygen in the $\text{Fe}_{\text{VI}}\text{-O-Mg}_{\text{IV}}$ coordination than in the $\text{Fe}_{\text{VI}}\text{-O-Fe}_{\text{IV}}$ coordination. Those bonds were found to be more ionic in character when Fe_{IV} was replaced by Mg_{IV} at tetrahedral sites in the neighborhood of Fe_{VI} ions.

Effective charges (Q) have been calculated according to [5]. They were shown to be equal to the following values for the various ions in the spinel: $+1.64\div 1.76$ (Fe_{VI}), $+1.22$ (Mg_{IV}), $+1.00$ (Fe_{IV}), $+1.80$ (Cr_{VI}), $+2.17$ (Al_{VI}) and $-1.17\div -1.47$ (O) (in the electron charge units). The charge values differ greatly from those used in the ionic model of the mineral. The effective charge of Fe_{VI} ions increased from $+1.64$ to $+1.76$ with the decreasing of Fe-amount in the samples. The oxygen ion charge value also changes considerably and depends on the nearest cation environment. The highest (-1.47) value corresponds to $\text{Al}_{\text{VI}}\text{-O-Mg}_{\text{IV}}$ coordination and the lowest one (-1.17) corresponds to $\text{Fe}_{\text{VI}}\text{-O-Fe}_{\text{IV}}$ coordination. This confirms the conclusion that the chemical bond is more covalent in the latter case.

Crystallochemical formula and cation distribution in the spinel. Based on the values of the effective ions charges for the several samples from the Ural ultramafites we calculated the charge values of their cation and anion sublattices [3]. Considering the assumptions on the normal distribution of the cations and the oxygen stoichiometry the lattice electroneutrality could be fulfilled only if oxygen ions in the samples had preferable coordinations conducive to the increase in the negative charge of the anion sublattice. This condition means that cations deviate from the statistical distribution in the spinel structure and cation associates are formed. It is shown that the inhomogeneity of the samples with the high Fe-content must be higher. This result is in qualitative agreement with the electron microprobe data accord-

ing to which high Fe-containing spinels are characterized by considerable inhomogeneous distribution of iron and magnesium in the grains.

Mossbauer parameters of Fe_{VI} ions. The electric field gradient (EFG) on the core of Fe_{VI} ion and the quadrupole splitting (QS) of its Mossbauer spectra are shown to be caused mainly by: a) the asymmetric distribution of the electronic density of 3d-orbitals of Fe_{VI} ions, b) the charge nonequivalence of the nearest oxygen ions [4]. Both contributions to EFG have the similar orders of magnitude. In accordance with calculations the dependence of QS on the sample composition is not additive and the maximum of QS (0.3 to 0.5 mm/s) for Fe_{VI} ions corresponds to compositions with $x = 0.17 \div 0.33$. The experimentally observed increase of QS with decreasing of Fe-amount in the samples [1] is probably due to the formation of cation associates of this composition in the region of intermediate iron concentrations. However, EFG on the iron core should be largely affected by distortions of iron-oxygen octahedrons, the vacancy concentration, etc. So, interpretation of Mossbauer parameters needs further investigation.

Conclusion. The metal-ligand chemical bond in the spinel is found to be characterised by a considerable degree of covalence; the latter depends on the local environment of oxygen octahedrons. The electronic structure and chemical bond specific features revealed indicate the deviation of cation distribution from statistical one and the formation of cation associates. The assumption on a nonstatistical cation distribution agrees with the results of experimental and theoretical analyses of Mossbauer spectra.

1. Chashchukhin I.S., Votyakov S.L., Uimin S.G., Borisov D.R., Bykov V.N. NGR Spectroscopy of Chromospinelides and Issues of Oxythermobarometry of Chromite-Bearing Ultramafites in the Ural Region. Ekaterinburg: Nauka, 1996, 136 p.
2. Blinov D.S., Shchapova Yu.V., Yurieva E.I., Ryzhkov M.V., Ivanovskii A.L., Votyakov S.L. The Effect of the Composition and the Structure of the Second Coordination Sphere on the Electronic Structure and Parameters of NGR Spectra of Fe^{3+} Ions in Complex Oxides. In: Problems of Spectroscopy and Spectrometry. Ekaterinburg: UGTU, 1999, No. 2, pp. 34-41.
3. Votyakov S.L., Shchapova Yu.V., Chashchukhin I.S., Yurieva E.I., Ryzhkov M.V., Ivanovskii A.L. On the Degree of Covalence of Metal-Ligand Chemical Bonds in Chromospinelide (Chemical Quantum Calculations). In: Yearbook-2000 of Institute of Geology and Geochemistry, Ural Branch RAS. Ekaterinburg: Izd-vo UrO RAN, 2000, in print.
4. Shchapova Yu.V., Yurieva E.I., Votyakov S.L., Ivanovskii A.L. The Electronic Structure and Parameters of NGR Spectra of Fe^{3+} Ions in Chromospinelides Determined from Nonempirical Chemical Quantum Calculations. In: Yearbook-1998 of Institute of Geology and Geochemistry, Ural Branch RAS. Ekaterinburg: Izd-vo UrO RAN, 1999, pp. 182-189.
5. Ryzhkov M.V. A New Method for Calculating Effective Charges of Atoms in Molecules, Clusters and Solids. Zhurnal Strukturnoi Khimii, 1998, v. 39, No. 6, pp. 1134-1140.