Analysis of paramagnetic centers for threerelent iron in aluminosilicates

D Apushkinskaya¹, E Apushkinskiy², B Popov², V N Romanov², V Saveliev² and V Sobolevskiy²
¹ Department of Mathematics, Saarland University, Saarbrücken, Germany
² St. Petersburg Polytechnical University, St. Petersburg, Russia
E-mail: darya@math.uni-sb.de, apushkinsky@hotmail.com

Abstract. We present the results of investigation of the defects in fluorine aluminosilicates from the Volyn-field Al₂[SiO₄][F,OH]₂ by the Electron Paramagnetic Resonance (EPR) method. The studies were carried out on the spectrometer Bruker ER 220D. Three types of EPR spectra of single centers were obtained. Their angular dependence was also investigated. The obtained EPR spectra correspond to the paramagnetic ion Fe³⁺ in the high-spin state S = 5/2. Three types of paramagnetic centers were found: one with cubic-symmetry and two with orthorhombic-symmetries.

1. Introduction
The processes of minerals formation in geological environments are still not quite understood because of their complexity and diversity. A complex multi-stage evolution of natural materials causes to formation of various defects in the crystal lattice, i.e., to deviations from the ideal crystal structure.

Studying of local defects in the minerals-silicates formed in the process of their growth is of great interest. Recent investigations [1] show that the local defects arising during the minerals growth are stable. Such defects define the optical, electrical and magnetic properties of the silicates [1,2].

On the other hand, there are so called radiation defects of the minerals. They arise after irradiation of the mineral that upset the crystalline structure energy balance. In this case, opening of separate chemical bonds, redistribution of free electrons between the lattice ions and impurities as well as formation of short-lived isotopes of chemical elements are possible. This type of defects is unstable. It manifests itself by degradation of mechanical, electrical and other properties of silicates that limits probable application of such materials.

Unfortunately, there are no reliable criteria to identify the defects of natural or radiation origin. In the main, this is due to our insufficient knowledge about the nature of point defects in aluminosilicates.

Embedding of the iron ions in the state ⁶S (3d⁵) into the crystalline lattice of a mineral can provide data accessing about its structure [2]. As a brilliant representative of aluminosilicates one can point to topaz. Its chemical formula is Al₂[SiO₄][F,OH]₂, and the crystal structure is built with silicon-oxygen tetrahedra (SiO₄) and aluminum octahedra surrounded by four oxygen ions and two fluoride ions. Defects formed by the substitutional ions are of most practical
interest. In the topazes there are two types of defects: octahedral and tetrahedral. The type of defect depends on the substitutional ions location. If silicon in silicon-oxygen tetrahedra (SiO$_4$) is replaced by aluminum (Al$^{3+}$ → Si$^{4+}$), as well as by impurity ions such as chromium (Cr$^{3+}$) or iron (Fe$^{3+}$), we observe luminescence in different spectral regions. For example, luminescence in aluminosilicates can be caused by tetrahedrally coordinated impurity ions Cr$^{3+}$, Fe$^{3+}$ and Mn$^{2+}$ which isomorphically replaced Si$^{4+}$ in silicon-oxygen tetrahedra [1].

2. Experiment / Calculation / Theory
The intrinsic defects in fluorine aluminosilicates (topazes) were investigated by the EPR method. The studies were carried out with spectrometer “Bruker” ER 220D. We have obtained three types of EPR spectra of single centers (Fig. 1) and studied their angular dependence (Fig. 2).

Three types of spectra of iron centers with different symmetry were observed. Each spectrum consists of 5 lines of the fine structure and corresponds to high-spin state $S = 5/2$. However, the ratios of the intensities of the individual transitions are different. The ratios of intensities in the spectrum of Fe (I) equal 8 : 5 : 9 : 5 : 8. The intensity ratios for similar transitions for Fe (II) and Fe (III) are 5 : 8 : 9 : 8 : 5.

Thus, it can be assumed that the center of Fe (I) corresponds to the octahedral coordination of the oxygen, while the centers of Fe (II) and Fe (III) correspond to the tetrahedral one. In order to prove the assumption about the symmetry of location centers we made numerical calculations and simulation of the EPR spectrum of ion Fe$^{3+}$ using the model of the spin Hamiltonian. This
Hamiltonian for the ground state \( ^6S \) has the form [3]:

\[
H = g\beta HS + \frac{a}{6} \left\{ [Sx^4 + S_y^4 + S_z^4] - \frac{1}{5} [S(S + 1)(3S^2 + 3S + 1)] \right\}
\]

where \( g \) is the spectroscopic splitting factor, \( b \) is the Bohr magneton, \( H \) is the strength of the constant magnetic field, and \( a \) is the constant of the level splitting for the ground state by a crystal field of cubic symmetry. Energy levels determining the position of the EPR lines are calculated in the second-order perturbation theory in a strong magnetic field with direction cosines \( l, m \) and \( n \) with respect to the axis of the fourth order:

\[
\begin{align*}
E_{\pm 5/2} &= \pm \frac{5}{2} g\beta H + \frac{1}{2} pa \pm \left( 212 - 24p - 113p^2 \right) \frac{a^2}{240 g\beta H} \\
E_{\pm 3/2} &= \pm \frac{3}{2} g\beta H - \frac{3}{2} pa \pm \left( 12 + 8p - 15p^2 \right) \frac{a^2}{16 g\beta H} \\
E_{\pm 1/2} &= \pm \frac{1}{2} g\beta H + pa \pm \left( -2 - 3p + p^2 \right) \frac{a^2}{3 g\beta H}
\end{align*}
\]

where \( p = l - 5(l^2m^2 + m^2n^2 + l^2n^2) \).

Extreme values of \( p \) are equal to +1 for the direction \( <001> \), -2/3 for the direction \( <111> \) and -1/4 for the direction \( <110> \). Consequently, the angular dependence let us to determine the direction of chemical bonds in the complex. All the measurements were carried out in high magnetic fields \( (g\beta H \gg a) \). The values of the second order with respect to \( a \) were neglected. In this case, the EPR spectrum consists of 5 lines of the fine structure, for those the magnetic quantum number \( m \) is changed to 1. The latter corresponds to transitions:

\[
\begin{align*}
\Delta E_{(5/2\rightarrow 3/2)} &= g\beta H + 2pa \\
\Delta E_{(3/2\rightarrow 1/2)} &= g\beta H - \frac{5}{2} pa \\
\Delta E_{(1/2\rightarrow -1/2)} &= g\beta H \\
\Delta E_{(-1/2\rightarrow -3/2)} &= g\beta H + \frac{5}{2} pa \\
\Delta E_{(-3/2\rightarrow -5/2)} &= g\beta H - 2pa
\end{align*}
\]

The following values of parameters of the spin Hamiltonian for Fe (I) in an octahedral encirclement of oxygen were obtained: \( g = 2.004 \pm 0.003; \) \( a = 120 \cdot 10^{-4} \) cm\(^{-1}\). In addition, the central transition width measured between the peaks of the first derivative points, \( \Delta H = (11 \pm 1) \) Oe is established as well. The parameters of EPR spectra for Fe (II) and Fe (III) in tetrahedral symmetry are shown in Table 1.

**Table 1.** The parameters of the EPR spectra.

| \( g \)-factor | \( \Delta H \) [Oe] | \( a \) [cm\(^{-1}\)] |
|----------------|---------------------|---------------------|
| 2.004          | 11                  | 120 \cdot 10^{-4}   |
| 2.022          | 14                  | 620 \cdot 10^{-4}   |
| 2.040          | 17                  | 700 \cdot 10^{-4}   |
3. Discussion
Thus, it can be concluded that three types of paramagnetic iron centers in the S-state are formed in aluminosilicates, the total spin of centers equals 5/2, but the fine structure parameters as well as the symmetry of centers are different. The analysis of the angular dependence shows that centers such as Fe (I) are formed by iron ions in the state 3d^5 replacing aluminum in a cubic lattice surrounded by four oxygen ions and two fluoride ions. This is also confirmed by the presence the lines of the superhyperfine structure of low intensity of the nuclear magnetic moments of fluorine (I = 1/2) in the EPR spectrum of Fe (II) center. The centers of Fe (II) and Fe (III) occur in tetrahedras of SiO\textsubscript{4} with one (center Fe (II)) or two (center Fe (III)) oxygen vacancies by substituting Fe\textsuperscript{3+} → Si\textsuperscript{4+}. The fragment of the aluminosilicate lattice with a tetrahedral iron center and one oxygen vacancy is shown in Fig. 3.

![Figure 3. Fragment of the center Fe\textsuperscript{3+} with oxygen vacancies at the angle ϕ = 10°.](image)

It is important to note that the presence of vacancies implies a significant distortion the symmetry of the center [4]. Substituting ion is displaced from its equilibrium position at a distance \(d = 0.544L \tan \phi\). The displacement for the center Fe (II) is equal 0.17 Å, while the center of Fe (III) is shifted to 0.27 Å from the center of the tetrahedron.

4. Conclusion
The above-described centers were observed in non-irradiated topaz crystals. So, their structure and electron states are stable. In addition, the study of the temperature dependence of EPR spectra in the temperature range 77-300 K showed that the intensity of the EPR signal is well described by the Curie-Weiss law.

References
[1] Lazarenko E K, Pavlishin V I, Lett V T and Sorokin Y G 1973 Mineralogy and Genesis Chamber Pegmatites of Volyn (Lviv)
[2] Pleshakov I V, Klekhta N S and Kuzmin Yu I 2012 Technical Phys. Letters 38 60-66
[3] Abragam A and Bleaney B 1970 Electron Paramagnetic Resonance of Transition Ions (Oxford)
[4] Vasiukov V N, Chabanenko V V, Kochkanyan R O et all 2004 Low Temp. Phys. 30 1272-78