Identification of environment symmetry for iron centers in aluminosilicates by EPR

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Abstract. We study an angular dependence of EPR spectra of the own defects in topaz (Al[SiO4][F,OH]). The topaz crystal structure is built of silicon-oxygen tetrahedral (SiO4) and octahedral aluminum surrounded by four oxygen ions and fluorine ions or a hydroxyl group. There are two types of substitution defects in topaz, such as octahedral and tetrahedral, depending on the location of the impurity ion. The point defects with octahedral symmetry arise on local substitution of aluminum (Fe3+ → Al3+), while tetrahedral coordinated centers are formed by substitution of silicon (Fe3+ → Si4+) in the silicon-oxygen tetrahedral (SiO4). To determine the symmetry of the impurity centers, the angular dependence of the EPR spectrum is calculated. The excited energy states for defects are determined by the magnitude of the g-factor shift. These states equal 1.6 eV and 3.2 eV, respectively. A super-hyperthin structure (SHTS) of the EPR lines of iron has been observed. This SHTS is determined by the magnetic moments of the fluorine nuclei F19 located in the first coordination sphere of the paramagnetic iron center. The models of the three new paramagnetic centers in topazes are suggested, one of them being of orthorhombic symmetry for aluminum substitution and the two others being of tetragonal symmetry for silicon substitution with oxygen vacancies.

1. Introduction

The research into natural minerals shows that the local defects occurring in the course of growth are stable [1,2]. The impact of radiation on the mineral leads to the rupture of chemical bonds, to the redistribution of free electrons between the lattice ions and impurities, and to the formation of short-lived isotopes of chemical elements. The irradiation of minerals disturbs the energy balance of the crystal structure and, thereby, contributes to the formation of defects within the structure. The defects of this type are not stable and mainly determine the degradation of electrical, optical and other properties of silicates, which in turn limit their practical use.

Polyvalent elements available in aluminosilicates, in particular iron-group transition elements and rare earth elements, prevent the formation of the centers under the action of radiation. Thus, fluorine aluminosilicates can be considered as promising materials for radiation dosimetry and protective coating of solar elements against radiation.

The interest in the research of aluminosilicates doped with transition of the iron group is also associated with the search for new materials for laser physics. They are promising also for the development on their basis of light emissive devices. The compounds of fluorine aluminosilicates have good luminescent properties. The optical properties have been partially studied in [1,2,3]. However, the characteristics of the centers responsible for radiation are not available in the literature. There have not been any reliable criteria...
for identification of defects with natural and radioactive origins. To a large extent, this is due to the insufficient knowledge about the nature of point defects in the aluminosilicates.

It is well-known that a brilliant representative of aluminosilicates is topaz Al$_2$[SiO$_4$],[F,OH]$_2$. The topaz crystal structure is built of silicon-oxygen tetrahedral (SiO$_4$) and octahedral aluminum surrounded by four oxygen ions and fluorine ions or a hydroxyl group. The topaz crystal lattice is shown in Fig. 1. In our view, the defects formed by substitution ions of the iron transition group are of great practical interest. They have an unfilled 3d-shell. It means that they can play the role of cations with variable valence. A significant magnetic moment of these centers allows to use them as spin labels [4,5] and investigate the electronic configuration and symmetry of the defects.

![Figure 1 Structure of topaz projected on the plane (001).](image)

For example, Fe ions in 6S (3d$^5$) state are paramagnetic. These Fe ions, embedded in the crystalline lattice of the mineral, can provide a rather important information on the lattice structure. There are two types of substitution defects in topaz, such as octahedral and tetrahedral, depending on the location of the impurity ion. The point defects with octahedral symmetry arise on local substitution of aluminum (Fe$^{3+} \rightarrow$ Al$^{3+}$), while tetrahedrally coordinated centers are formed by substitution of silicon (Fe$^{3+} \rightarrow$ Si$^{4+}$) in the silicon-oxygen tetrahedral (SiO$_4$). The topaz composition can vary from Al$_2$[SiO$_4$],F$_2$ to Al$_2$[SiO$_4$],[F$_{0.7}$,(OH)$_{0.3}$]$_2$. In accordance with this change, its optical properties are changed, too. According to [2,5], the luminescence attributed to the defects formed by the ions of tetrahedrally coordinated centers is observed in the spectra of luminescence of natural topaz. For example, the appearance of brown-orange coloration is associated with the oxygen vacancies, which formed by substitution of silicon chromium by Cr$^{3+}$ (640 nm wavelength) or Fe$^{3+}$ (710 nm wavelength).

In studies of centers formed by 3d-elements, the electron paramagnetic resonance method (EPR) plays a significant role. It is an indispensable tool for investigation the electronic structure of the paramagnetic center, that is, for determining the symmetry of the center, its charge state, the total magnetic moment, the interaction between the defects and the host lattice ions. Our aim is to investigate by the EPR method the new Fe centers with local cubic symmetry embedded in Al$_2$[SiO$_4$],[F,OH]$_2$ (this was announced in [6]).

2. Experiment / Calculation / Theory

An important aspect of the interpretation of EPR spectra of ions in 6S- state is the explanation of the difference between the values of $g$-factor and the pure spin state ($g_0 = 2.0023$). Unlike to other magnetic centers with the number of d-electrons $n_d = 5$, the energy difference $\Delta = E_{t2} - E_e$ can not be considered as the excited energy state of the local center. This is due to the fact that any electron exchange between the energy levels of $e$ and $t_2$ states leads to a change in total spin of the center.
The levels of unpaired 3d-electrons located in the band gap are not pure d-levels in view of a delocalisation of the corresponding wave functions. The "resonances" in the valence band, which do not affect the total magnetic moment of the center, are of explicit character. In this case, a state formed as a result of the transition of a hole from the bottom of d-levels in the forbidden zone to $d_0$ (the level in the valence band) should be considered as the first excited state. Indeed, the neutral iron atom has the electron configuration $3d^6 4s^2$. Substituting a silicon atom with the electron configuration $3s^23p^2$ gives two 4s-electrons and one 3d-electron for the formation of chemical bonds with neighboring atoms (the electron configuration $3d^5$).

The structure of the levels in the one-electron approximation is shown in Figure 2. A characteristic feature of this structure is the presence of filled d-resonance states in the valence band. The excited state is a state $|d_0\rangle$ in the valence band, which corresponds to the occupied states $|d_0\rangle$ in the forbidden zone. Hence, the difference between the energies of the states $|d_0\rangle$ and $|d_0\rangle$ is to be taken as the energy difference $\Delta'$ for ground and excited states, which determines the $g$-factor shift (see Fig. 2). The $g$-factor shift may be calculated as follows [7]:

$$\Delta g = 8K_{\sigma\pi} \frac{H_{ij}}{\Delta' H_0} ,$$

(1)

where $K_{\sigma\pi}$ is the factor determining the change in the spin-orbit interaction due to the d-state delocalization, $\lambda$ is the constant of spin-orbit coupling to the atomic state, $H_{ij}$ and $H_0$ are the one-electron matrix elements of spin-orbit coupling for the states involved in the formation of covalent bonds and purely atomic ones, respectively. Since the values of the matrix elements of spin-orbit interaction are never precisely known, the relationships $H_{ij}/H_0$ are considered as parameters.

Assuming a change of spin-orbital communication center with respect to a free atom insignificant, we set the parameter $H_{ij}/H_0$ equal to 1. We do not take into account the electron delocalisation of local centres as in the ground state as in the excited one. Therefore, we assume $K_{\sigma\pi} = 1$. The constant of spin-orbit coupling to the Fe atom is 0.008 eV [7]. Thus, the expression for the $g$-factor shift ($\Delta g = g - g_0$) can be rewritten as: $\Delta g = \delta \lambda / \Delta'$. From the last equality one can find the value of the excited state energy of the center: $\Delta' = \delta \lambda / \Delta g$. For Fe(III), the $g$-factor shift is $\Delta g = 0.038$, which corresponds to the energy $\Delta' = 1.6$ eV. This electronic transition should define a certain luminescence of topaz in 710 nm bands [1,2]. For the center of Fe (II) we have $\Delta g = 0.020$, while the corresponding excitation energy is equal to 3.2 eV.
Taking into account the proximity of the used model crystal field, we can observe the reasonable agreement between the estimated value of the excited energy state and the experimental one \([4,6]\).

The calculation of the EPR line width, measured between the inflection points, is also quite important for the interpretation of the EPR spectrum of \(Al_2[SiO_4][F,OH]_2\). Note that the transfer of the charge density of d-electrons in ligands and the associated interaction of unpaired electrons of the center with the magnetic moment of ligands, i.e. the so-called super-hyperthin interaction (SHTI), should lead to a broadening of the EPR line. In the EPR spectrum of the center of Fe(II), shown in \([6]\), we distinctively see a group of three lines of the super-hyperthin structure (SHTS). The EPR lines for SHTS are clearly resolved for transitions (-3/2→-1/2) and (5/2→3/2). The SHTS lines for centers such as Fe(III) are actually not observed.

To determine the EPR line widths, it is sufficient to consider the interaction of the d-electron of paramagnetic center with the nuclear magnetic moments of ligands. In our case these ligands are the nuclei of \(F^{19}\) located in the vicinity of a 3d-ion. The distance between the adjacent lines of the EPR spectrum is equal to a constant \(A_{SHTS}\), which is determined from the EPR spectrum. For Fe(II) center we have \(A_{SHTS} = 5\) Oe \([6]\). Now one can determine the width of the central transition line between the points of maximum curvature \((\Delta H_{pp})\) as follows. Due to SHTS, each electronic transition is split into \(2n + 1\) lines of equal intensity. Here \(I\) is the nucleus ligand spin which equals to 1/2 for fluorine, while \(n\) is the number of ligands with spin \(I\). Thus, the width of the EPR line taken between the inflection points of the absorption line is \(\Delta H_{pp} = A_{SHTS}(2I+1)\).

Since the width of the EPR line of center Fe(II) is equal to 14 Oe \([6]\), we claim that in a vicinity of Fe\(^{3+}\) there are two fluorine ions \((n = 2)\). The width of the EPR line of center Fe(III) is \(\Delta H_{pp} = 17\) Oe \([6]\). It should be assumed that both the SHTI and the spin-lattice interaction give the contribution to the line width of the EPR of center \([8]\). In this case \(K_{ss}\) factor, which is responsible for the change in the spin-orbit interaction due to delocalization of d-state, is different from 1. It should be taken into account in the corresponding calculation of the EPR line width.

3. Discussion

It is shown in \([6]\) that the constants \(a\) of the fine structure (FS) of centers Fe(II) and Fe(III) differ from the constant of FS for Fe(I). The latter indicates a significant difference in the magnitude of low-symmetric component of crystal field acting on Fe ions. This conclusion is also supported by the absence of the SHTS lines for centre Fe(III).

The super-hyperthin structure is usually permitted only for certain orientations of the magnetic field, when the ligands (in our case fluoride) form a group of magnetically equivalent centers and the magnetic field is directed along one of the crystal axes. However, the availability of the vacancy leads to a significant distortion of the center’s symmetry \([6]\). The substitution of silicon by the Fe\(^{3+}\) ions implies the displacement of the latter from the center of tetrahedron. The replacement ion is displaced from its equilibrium position by a distance \(d = 0.544 L \cdot \tan \phi\) in the direction <110>. According to the angular dependence for the EPR spectra for Fe(II) and Fe(III) \([6]\), the angle \(\phi\) is equal to 6° and 10°, respectively. The corresponding displacements from the center of tetrahedron equal to 0.17Å for Fe(II) and 0.27Å for Fe(III).

4. Conclusions

The structure of the new local centers based on the trivalent Fe has been discovered and studied for the first time. It has been shown that the center of Fe(II) is formed through the substitution of silicon by Fe accompanied by the oxygen vacancy formation in the presence of two fluorine ions. This centre of Fe(II) is responsible for the luminescence in the region 710-720 nm. The resolved hyper-thin EPR line structure is not observed near Fe(I) and Fe(III). It should be noted that in the EPR spectra of the studied crystals one can observe the signals of Cr\(^{3+}\), Ti\(^{3+}\) and, probably, other impurities of the low intensity.
The above-mentioned centers Fe$^{3+}$ have been observed for the first time in the non-irradiated crystals of topaz [6]. The electronic state and structure defects are stable. Magnetic interactions between paramagnetic impurities have not been detected.

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