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THE ANOMALOUS g -FACTOR VALUE OF PARAMAGNETIC IRON CENTERS IN THE TOPAZ LATTICE WITH STRONG TETRAGONAL DISTORTION

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The theoretical and experimental results of analyzing the electron paramagnetic resonance (EPR) spectra of iron impurity paramagnetic centers in the topaz (aluminum fluorosilicate) lattice are presented. Characteristic defects of the system exhibiting some lines with abnormally large values of g -factor (4.33 and 2.66) in the EPR spectra have been found. The experimental results were discussed within the framework of a previously developed model describing a defect involving an impurity iron ion replacing the Al^{3+} or Si^{4+} ion. The “ Fe^{3+} – an oxygen vacancy” model is a special case of the complexes with strong tetragonal distortion. The g -factors were calculated taking into account the covalent nature of the bonds.

Keywords: EPR spectrum, center symmetry, Hamiltonian, g -factor, topaz, tetragonal distortion

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АНОМАЛЬНОЕ ЗНАЧЕНИЕ g -ФАКТОРА ПАРАМАГНИТНЫХ ЦЕНТРОВ ЖЕЛЕЗА В РЕШЕТКЕ ТОПАЗА С СИЛЬНЫМ ТЕТРАГОНАЛЬНЫМ ИСКАЖЕНИЕМ

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Представлены результаты теоретических и экспериментальных исследований спектров электронного парамагнитного резонанса (ЭПР) примесных центров железа в решетке фторосиликата алюминия $Al_2SiO_4(OH,F)_2$ – топаза. Обнаружены характерные дефекты системы, приводящие к появлению линий с аномально большими значениями g -факторов (4,33 и 2,66) в спектрах ЭПР. Результаты эксперимента обсуждаются в рамках ранее разработанной модели с дефектом при участии примесного иона железа, замещающего ион Al^{3+} или Si^{4+} . Модель « Fe^{3+} – кислородная вакансия» является частным случаем модели комплексов с сильным тетрагональным искажением. В работе приведен расчет g -факторов с учетом ковалентного характера химической связи.

Ключевые слова: спектр ЭПР, симметрия центров, топаз, спин-гамильтониан, g -фактор, тетрагональное искажение

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Introduction

Topaz is an aluminum fluorosilicate with the chemical formula $\text{Al}_2\text{SiO}_4(\text{OH},\text{F})_2$. The structure of topaz consists of SiO_4 groups connecting $\text{Al}[\text{O}_4(\text{F},\text{OH})_2]$ octahedral chains. Four of the six anions surrounding the Al^{3+} ion belong to oxygen (O^{2-}), and the remaining two to the fluoride ion (F^-) or the hydroxyl group (OH^-).

Topaz has the following lattice parameters, Å:

$$a = 4.6499, b = 8.7969, c = 8.3909.$$

The color of the crystals can be changed by irradiating them or adding transition metal impurities [1]. However, the coloring mechanisms of topaz are not entirely clear. Irradiation induces complex defects that are unstable. Iron group transition elements present in aluminosilicates prevents the formation of centers generated by ionizing radiation. For this reason, aluminum fluorosilicates appear to be promising materials for radiation dosimetry and radiation-resistant coatings. Since Al_2SiO_4 compounds have good luminescent properties, aluminosilicates with iron group impurities are also interesting as novel materials for laser devices [2]. Furthermore, study of impurity centers in topaz is potentially valuable for fundamental research. Impurity ions can take different charge states due to strong internal electric fields [3, 4]. Considering intrinsic defects in aluminosilicates, we earlier observed an unusual spectrum of electron paramagnetic resonance (EPR) [1, 5]. We discovered three types of iron centers: a Fe(I) center in state S ($3d^5$ electron configuration) with $g = 2.004$ and two Fe(II) and Fe(III) centers with anomalous values of g equaling 4.33 and 2.66. EPR spectra obtained at room temperature for the X band (the frequency $\nu \approx 9.4$ GHz) using a Bruker ER 220D spectrometer are given in [1, 5]. The high intensity of the spectra collected for the samples at room temperature pointed to high concentration of iron impurities ($n \approx 10^{19} \text{ cm}^{-3}$). A model of the centers that can form with the participation of iron was proposed.

This is primarily the center with the g -factor equal to 2.004. Such an iron ion substitutes

aluminum, occupying an octahedral site coordinated by oxygen (Fe(I) center). The iron atom donates its three electrons to bond formation, acquiring the electron configuration $3d^5$ (Fe^{3+}), ground state 6S . The position of energy levels, their angular dependence and calculation of the g -factor for this center are given in [5]. The angular dependences of EPR spectra for Fe(II) and Fe(III) centers suggest their tetrahedral symmetry. The centers are formed when silicon ions are substituted by iron ions. The Fe(II) center with the g -factor equal to 2.66 was an iron–oxygen vacancy complex: $\text{Fe}^{5+} - V_{\text{O}}$. Interacting with an oxygen vacancy, the substituting Fe^{3+} ion ($3d^5$) is shifted from its equilibrium position by $d = 0.544L \cdot \text{tg}\varphi$ in the $\langle 110 \rangle$ direction. It was found from analysis of the angular dependence of the EPR spectrum for Fe(II) that the angle φ equals 6° . As a result, the Fe(II) center is shifted by 0.17 Å from the center of the tetrahedron.

The Fe(III) center with $g = 4.33$ is formed by the Fe^{4+} ion in $3d^4$ state, substituting silicon at the Si^{4+} site. However, theoretical calculations of anomalous values of the g -factor were not performed in [5].

Our study presents calculations of anomalous values of the g -factor for Fe(II) and Fe(III) centers in a strong crystal field, taking into account bond covalence.

Theoretical calculation of EPR spectra

Following Abragam and Bleaney's classical work [6, 7], let us consider the theory of paramagnetic resonance of iron ions in a cubic field. The angular dependence of EPR spectra [1] indicates that local paramagnetic Fe(II) and Fe(III) centers are located in a crystal field with tetrahedral symmetry. Experimental results confirm that CF splitting exceeds the electron interaction energy. Hund's rule is violated in this case, and the ion is in a low spin configuration. Splitting diagrams for iron ions in a tetrahedral crystal field, taking into account the spin-orbit coupling and tetragonal distortion of the crystal lattice, are shown in Fig. 1.

We use the equivalent spin Hamiltonian to describe the EPR spectrum. In contrast to the spin Hamiltonian used in [5], we take into account the distortion of cubic symmetry of the crystal field due to its axial distortion [8, 9] along the tetragonal axis; the degree of distortion depends on the fine-structure parameter D . In this case, the spin Hamiltonian H is written as follows:

$$H = \beta(\mathbf{H}g\mathbf{S}) + \frac{1}{6}a\{S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)\} + D\{S_z^2 - \frac{1}{3}S(S+1)\} + \lambda\mathbf{L}\mathbf{S}, \quad (1)$$

where \mathbf{H} is the applied magnetic field; \mathbf{S} is the full spin of the center, S is its quantum number; \mathbf{L} is the orbital angular momentum, L is the quantum number of the total orbital momentum; β is the Bohr magneton; a , D are the crystal field parameters determining the fine structure of the EPR spectrum; λ is the spin-orbit coupling constant.

The energy levels of allowed transitions were calculated in [5]. Accounting for tetragonal distortion, characterized by the parameter D , generates a change in the energies by $\pm 2D$, $\pm D$. The parameters of the spin Hamiltonian are given in the table.

The structure of the Fe(II) center (includes the Fe³⁺ ion) is determined by the fact that the energy level of d electrons in the crystal field with tetrahedral symmetry is split into a lower doublet (e states) and an upper triplet (t_2 states) with the energy difference denoted as $10Dq$ (see Fig. 1). The positions of resonance transitions in the EPR spectrum of the Fe(II) center indicate that the CF splitting is greater than the spin-spin interaction energy, i.e., $D \gg g\beta H$. The lower doublet in the ligand field with tetragonal distortion splits into an orbital triplet with an effective angular momentum $l = 1$, $S = 1/2$. Spin-orbit coupling causes the triplet to split into a series of levels with an effective total momentum

$$J_{eff} = S + 1, J, S - 1.$$

The diagram for energy level splitting in a crystal field with tetrahedral symmetry taking into account axial distortion is shown in Fig. 1, a . It is assumed for iron group transition elements in a strong crystal field [1] that

$$\lambda^2/D \approx 1 \text{ cm}^{-1}.$$

In this case, the energy difference between sublevels with the effective momentum J_{eff} is described by the effective g -factor g_{eff} , which is determined by the expression equivalent to the Landé g -factor [6]:

Table

Parameters of spin Hamiltonian of paramagnetic iron centers in crystal lattice of topaz

Center	g -factor	$a, 10^{-2} \text{ cm}^{-1}$	$D, 10^{-2} \text{ cm}^{-1}$
Fe(II) $\{3d^5 - V_O\}$	2.66	6.2	3.2
Fe(III) $\{3d^4\}$	4.33	7.0	3.5

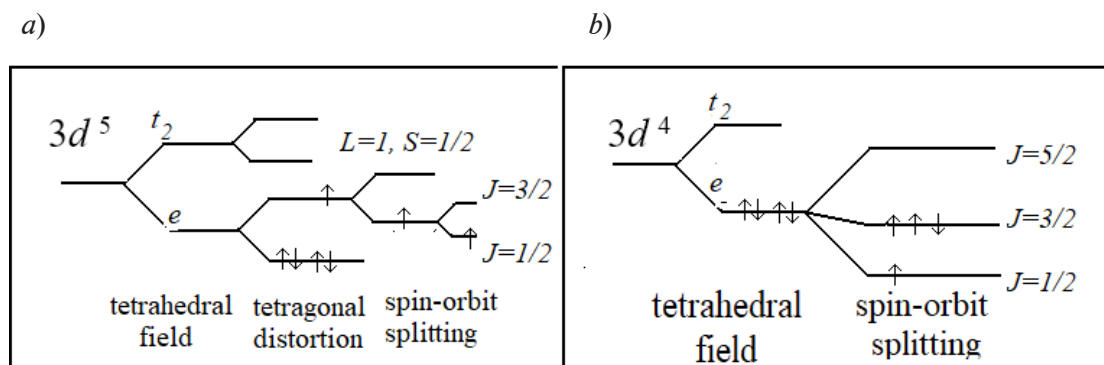


Fig. 1. Energy levels of Fe³⁺ ions in $3d^5$ configuration (a) and Fe⁴⁺ ions in $3d^4$ configuration (b) in strong crystal fields with tetrahedral symmetry in the presence of tetragonal lattice distortion (a) and spin-orbit interaction (a, b)



$$g_{eff} = \frac{1}{2}(g_s + g_l) + \frac{l(l+1) \pm s(s+1)}{2J(J+1)(g_s - g_l)}. \quad (2)$$

Substituting the values $g_l = 1$ and $g_s = 2$ into the formula

$$g_{eff} = \frac{4}{3}g_l + \frac{2}{3}g_s,$$

we obtain the value $g_{eff} = 2.67$, which is in good agreement with the experiment.

The diagram for energy level splitting in a crystal field with tetrahedral symmetry taking into account spin-orbit interaction is shown in Fig. 1, *a*.

The structure of the F(III) center (Fe^{4+} ion) is determined by the fact that it is energetically favorable for electrons to occupy the lower e level for the $3d^4$ ion in a strong crystal field, as long as this is allowed by the Pauli principle. Consequently, the Fe^{4+} ion is non-magnetic and its EPR spectrum should not be observed. However, strong spin-orbit coupling can remove spin degeneracy [9, 10]. Three pseudo- J -multiplets form, which are characterized by the effective momenta

$$J_{eff} = 1/2, 3/2, 5/2.$$

The doublet with $J_{eff} = 1/2$ is the ground state because the parameter $\alpha\lambda$ (spin-orbit coupling constant accounting for chemical bond covalence) is positive. The energy splitting diagram of the Fe^{4+} ion in the $3d^4$ configuration is shown in Fig. 1, *b*. Accounting for spin-orbit interaction changes the gaps between energy levels by

$$\Delta E\left(\frac{5}{2} \rightarrow \frac{3}{2}\right) = \frac{5}{2}\alpha\lambda,$$

$$\Delta E\left(\frac{3}{2} \rightarrow \frac{1}{2}\right) = \frac{3}{2}\alpha\lambda.$$

Using the effective total angular momentum allows to calculate the g -factor by expression (2), replacing the orbital value of $g_l = 1$ with $g_l = \alpha = -3/2$ [3, 6]. We have for the ground state with $J_{eff} = 1/2$:

$$g_{eff} = \frac{5g_s - 2g_l}{3} = \frac{13}{3} = 4.33.$$

Conclusion

Studying iron impurity centers of iron in topaz by EPR spectroscopy, we found that strong crystal fields make it possible to observe and identify transition ions in different charge states even at room temperature. Iron ions can substitute both Al^{3+} and Si^{4+} ions. The paramagnetic Fe(I) center substitutes aluminum and is located in an oxygen-coordinated octahedral site; the paramagnetic Fe(II) and Fe(III) centers substitute Si_{4+} ions in SiO_4 tetrahedra. The Fe(II) center with oxygen vacancies (V_o) is formed by substituting $Fe^{3+} \rightarrow Si^{4+}$, and the Fe(III) center is formed by substituting $Fe^{4+} \rightarrow Si^{4+}$. A fragment of the aluminosilicate lattice with tetrahedral oxygen coordination of the iron center and one oxygen vacancy was considered in [5]. Applying procedure for calculating EPR spectra based on representation of the model spin Hamiltonian and effective angular momenta greatly simplified the calculations, yielding good agreement between the experimental data and the theoretical description.

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