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Submillimeter ESR Spectra of Fe²⁺ Ions in Synthetic and Natural Beryl Crystals

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Abstract—Electron spin resonance spectra of non-Kramers bivalent iron (Fe²⁺) ions have been detected in synthetic and natural beryl crystals with an iron impurity. The observed ESR spectra have been attributed to resonance transitions of Fe²⁺ ions from the ground (singlet) state to excited (doublet) levels with the splitting $\Delta = 12.7 \text{ cm}^{-1}$ between the levels. The experimental angular and frequency dependences of the resonance field of the ESR signal have been described by the spin Hamiltonian with the effective spin $S = 1$. The analysis of the ESR data and optical absorption spectra indicates that the Fe²⁺ ions are situated in tetrahedral positions and substitute Be²⁺ cations in the beryl structure.

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1. INTRODUCTION

Electron spin resonance spectroscopy of Fe²⁺ ions in crystals is currently represented by a few works. Information available in literature does not allow predicting the possibility of the observation of Fe²⁺ ESR in various structures. The ESR signals for the positions of rhombic and a lower symmetry as a rule cannot be observed with the use of the standard X- and Q-band apparatus. This is associated with the fact the spin states of non-Kramers Fe²⁺ ions in these cases are singlets, the energy intervals between which are greater than the energy quanta of standard spectrometer. This situation takes place, e.g., in ammonium Tutton's salt crystals [1] and forsterite (Mg₂SiO₄) [2]. In the case of axial and cubic symmetry, the ground energy level of a Fe²⁺ ions is often singlet as well, and degenerate levels lie too far from it to observe the resonance between these levels. Such systems are exemplified by α -Al₂O₃ [3] and ZnS [4]. The ESR signal can be detected only if the ground state is degenerate in the magnetic field, as in, e.g., MgO crystal [5]. In this case, interpretation of the spectra on the basis of a single observed transition requires serious theoretical analysis.

Obviously, to extend the number of crystals in which the observation of the ESR spectra of Fe²⁺ ions is possible, higher resonance frequency and, accord-

ingly, the magnetic field of the ESR spectrometers are required. Tunable sources of the subterahertz range can also be used in relatively weak magnetic fields. In these cases, resonance transitions from the ground state to the excited states of Fe²⁺ ions can be observed for both low-symmetry and high-symmetry crystals. However, the power of microwave sources decreases with an increase in frequency and, in addition, an additional absorption associated with the phonon spectrum of the crystal appears in the terahertz range, which also restricts the possibility of observing the ESR spectra. Thus, the ESR spectroscopy of Fe²⁺ ions in crystal is a challenging experimental problem.

In this work, we present the results of the experimental investigation of submillimeter ESR spectra of Fe²⁺ ions in a synthetic beryl (Be₃Al₂Si₆O₁₈) and natural colorless goshenite crystals. To compare the found results with the literature data we also measured the optical spectra of the crystals under investigation.

The beryl crystal has a hexagonal symmetry (space group *P6/mcc*) and trivalent aluminum cations in its structure are surrounded by oxygen anions forming octahedra, whereas bivalent beryllium and tetravalent silicon ions are surrounded by oxygen tetrahedra, respectively. The point symmetry of the Al, Be, and Si positions is *D*₃, *D*₂ and Cs, respectively. The first works [6, 7] devoted to the investigation of iron ions in beryl