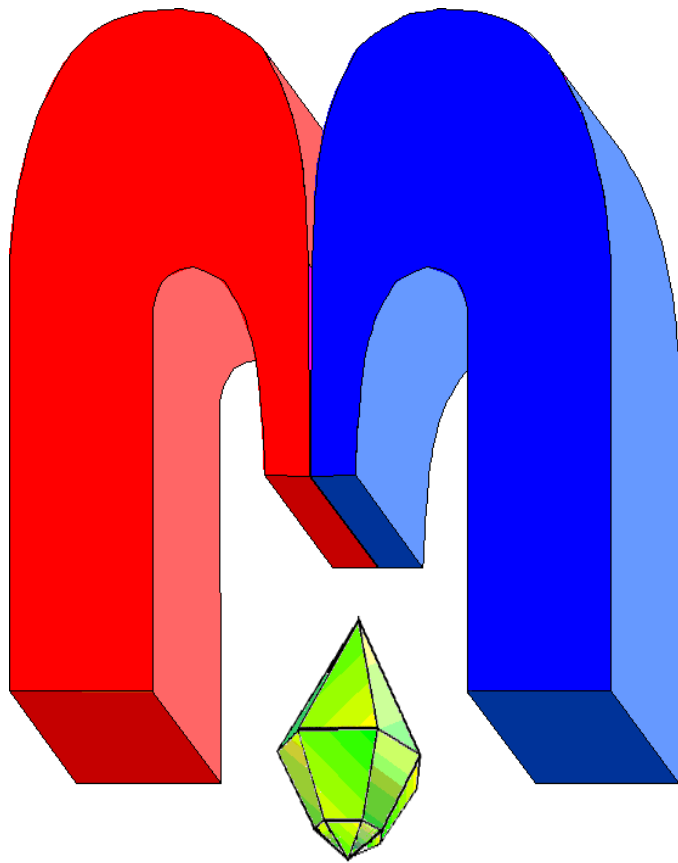


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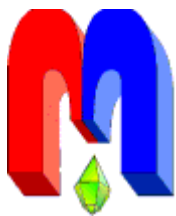
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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Dimer self-organization of ^{53}Cr impurity ions in synthetic forsterite

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Paramagnetic centers formed by isotopically pure impurity ^{53}Cr ions in synthetic forsterite (Mg_2SiO_4) are studied by continuous wave electron paramagnetic resonance. It is shown that chromium ions substitute magnesium ions as single ion with nonlocal charge compensation and dimer associate formed by two closely spaced Cr^{3+} ions. It is found that the integral intensity of resonance transitions belonging to the dimer associates is much higher than that to be expected for the statistical distribution of the impurity Cr^{3+} ions in the forsterite host. Therefore, there is a mechanism favoring the self-organization of the Cr^{3+} ions in dimer associates during the crystal growth.

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Keywords: forsterite, dimer self-organization of impurity ions, ^{53}Cr isotopes.

*This article is dedicated to the famous scientist and
the outstanding person professor Boris Malkin
on the occasion of his 80th birthday*

1. Introduction

Recently, much attention is attracted to the study of quantum systems that can serve as material basis for quantum computations. Two coupled quantum bits (qubits) are required to implement elementary quantum algorithms. In [1, 2] the possibilities of realization of qubits on the basis of electron spins of rare-earth ions in crystals and molecular clusters are analyzed. In [3] Cr^{5+} impurity ion in K_3NbO_8 has also been suggested and studied as a spin qubit system for quantum information processing based on transition metal ion.

To realize a long time of coherence memory in a two-qubit systems, it is necessary to use low concentration of these systems and to minimize the influence of neighboring electron spins. For this purpose, it is proposed to use dimers of rare earth ions localized in complex molecular systems as qubits on electronic spins [2]. The alternative way is to use dimer associates of impurity paramagnetic ions in dielectric crystals. At strictly statistical distribution of impurity ions over lattice sites, the ratio of the concentration of dimer associates C_{dimer} to that of single ions C_{single} is determined by [4]

$$C_{\text{dimer}}/C_{\text{single}} = 2c(1 - c)^2, \quad (1)$$

where c is the total mole fraction of the impurity ions in the crystal in respect to the substituted cation. To obtain long coherence time, value of c should be about 10^{-4} – 10^{-5} at.%. In this case, the concentration of the dimer associates should be several orders of magnitude lower than the concentration of the single impurity ions. Fortunately, there are dielectric crystals, where trivalent impurity ions substituting divalent cations in a quasi-one-dimensional cation chain have a tendency to the formation of dimer associates consisting of two closely situated impurity ions

with a divalent cation vacancy between them. The mechanism leading to this self-organization of the impurity ions into the dimers is related with the necessity to conserve the total cation charge during the heterogeneous substitution. In this case, three divalent cations are replaced by the two trivalent impurity ions. The decrease in the energy of the impurity dimer associate with respect to the energy of the two single impurity ions with a nonlocal charge compensation results in the high concentration of the dimer centers. The effect of the dimer self-organization of trivalent ions was observed by the electron paramagnetic resonance (EPR) for the Cr^{3+} [5], Gd^{3+} [6], Yb^{3+} [7], Ho^{3+} and Tm^{3+} [8] ions in CsCdBr_3 crystals and Ho^{3+} [9], Tb^{3+} [10], Yb^{3+} [11] and Er^{3+} [12] ions in synthetic forsterite (Mg_2SiO_4). Effect of dimer self-organization was observed also for Cr^{3+} ions in synthetic forsterite [13]. However, in [14] this result has been questioned. Our previous studies [8–10] have shown that single ions and dimer associates of ions with nonzero value of nuclear spin have essentially different hyperfine structure of resonance transitions. In order to clarify the question about the existence of dimer self-organization of Cr^{3+} ions in forsterite, we grown forsterite single crystal doped with monoisotopic ^{53}Cr (97.7 %) with nuclear spin $I = 3/2$ and studied EPR spectra of this sample. Naturally occurring chromium is composed of four stable isotopes; ^{50}Cr (4.31 %), ^{52}Cr (83.76 %), ^{53}Cr (9.55 %) and ^{54}Cr (2.38 %).

2. Experimental

$\text{Mg}_2\text{SiO}_4\cdot^{53}\text{Cr}$ single crystals were grown from the melt with 0.14 wt. % of chromium by the Czochralski technique in slightly oxidizing atmosphere (argon + 2 vol. % of oxygen). Sample for EPR studies was cut from the middle part of the grown crystal in the cubic form of $3\times 3\times 3$ mm with the faces oriented in the crystallographic planes. EPR measurements were carried out in X-band at room temperature on Bruker ELEXSYS E680 spectrometer with a dielectric resonator ER4118X-MD5-W1.

3. Results and discussion

A unit cell of forsterite crystalline structure contains four formula units and has an orthorhombic symmetry (the lattice constants are $a = 0.4753$, $b = 1.019$, $c = 0.5988$ nm in the P_{bmn} notation). The Cr^{3+} ions substitute the Mg^{2+} ions located in the two crystallographically non-equivalent types of oxygen octahedra labeled as M1 and M2. M1 octahedra form quasi-one-dimensional chain elongated parallel to the crystal c -axis. The crystal field in the M1 position is characterized by the inversion symmetry with the C_i point group. There are four magnetically nonequivalent impurity centers in the M1 position with principal magnetic axes declined from the crystallographic planes. The crystal field in the M2 position is characterized by the mirror symmetry with the C_s point group. The mirror plane is perpendicular to the c axis. Therefore the principal magnetic axes of the paramagnetic center in this position should be parallel to the c -axis or lie in the ab -plane. Orientation dependencies of the EPR spectra of ^{53}Cr -doped forsterite at the rotation of magnetic field \mathbf{B} in the (bc) plane are presented in Figure 1. It is seen that all resonance transitions have hyperfine structure due to interaction of the Cr^{3+} electron spin with ^{53}Cr nuclear spin $I = 3/2$. There are the Cr^{2+} [15, 16] and Cr^{4+} [17, 18] impurity ions in forsterite, but resonance lines of these ions are not seen in EPR spectra recorded at room temperature. For the only transition marked by the blue line in Figure 1, extrema of orientation dependence of resonance magnetic field coincide with the crystal axes. This transition belongs to the Cr^{3+} ion in the M2 position. The other transitions are due to the Cr^{3+} ions in the M1 position. Red lines correspond to orientation dependences calculated using the EasySpin program package [19, 20] with the spin Hamiltonian parameters determined in [14] for the single Cr^{3+} ion in the M1

position. The doublet structure of electron transitions in our spectra is due to two magnetically non-equivalent centers and misalignment between axis of sample rotation and crystal c -axis. There is some discrepancy between our spectra and results obtained for the even chromium isotopes [14]. This discrepancy may be due to small deviations of the Cr^{3+} crystal environment under different growing conditions or due to the difference of chromium isotopic content.

Each electron level of the $^{53}\text{Cr}^{3+}$ ion is split into 4 electron-nuclear sublevels due to hyperfine interaction. The hyperfine structure of the EPR spectrum of the single Cr ion should consist of four allowed transitions between the nuclear sublevels with the same projections of nuclear

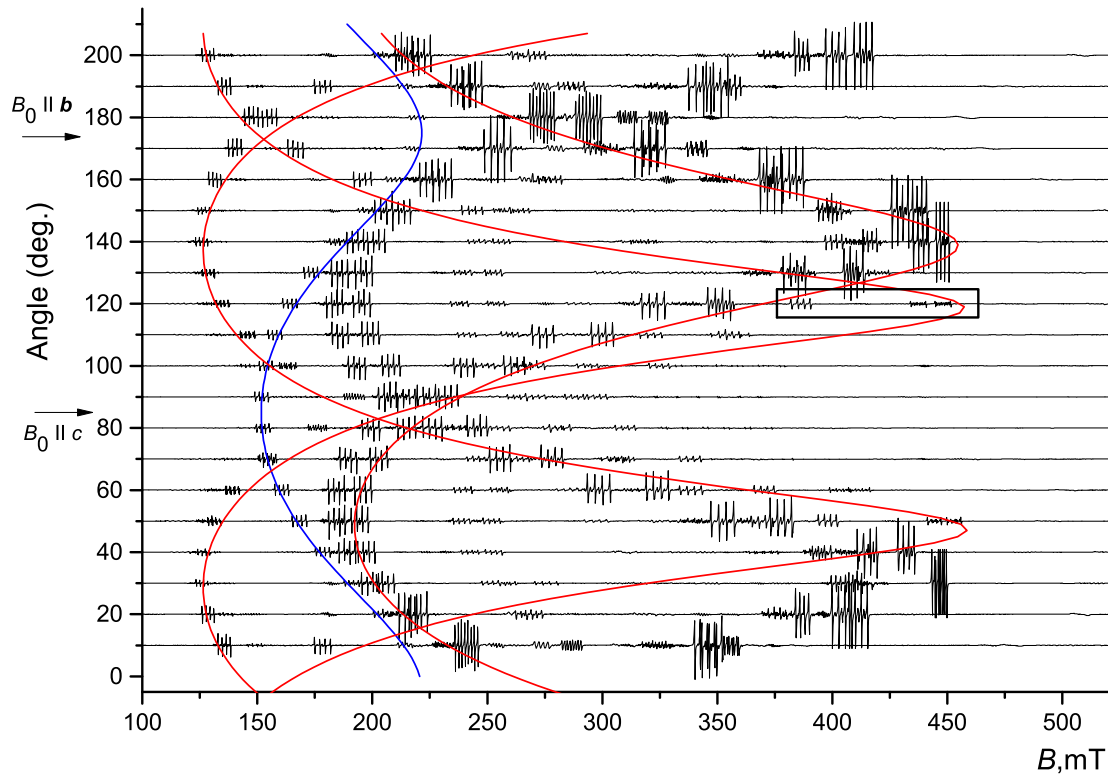


Figure 1. EPR spectra of the synthetic forsterite single crystal doped with chromium recorded at the rotation of the magnetic field around the crystallographic a -axis. The ordinate positions of spectra correspond to the orientation of the magnetic field \mathbf{B} during recording of the spectrum. The working frequency of the spectrometer is 9.77 GHz.

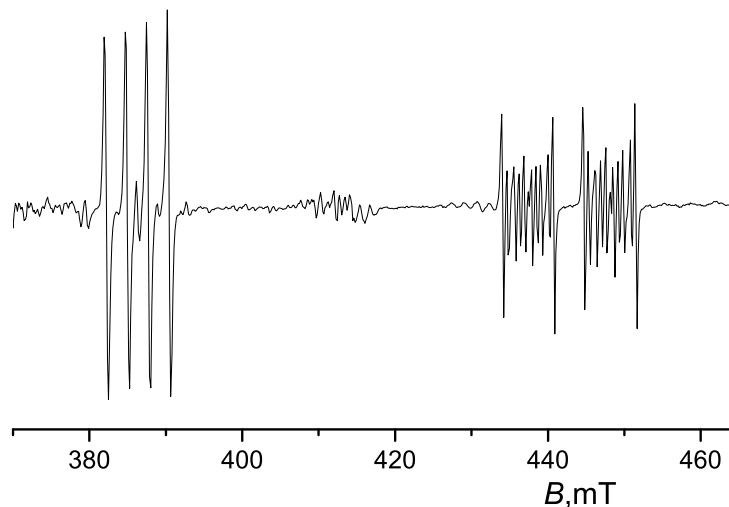


Figure 2. Part of the spectrum marked by the rectangle in Figure 1.

moment on the quantization axis ($\Delta I_z = 0$). Such structure is observed for the most of resonance transitions. For the dimer associates of the chromium ions, hyperfine structure of electron levels should consist of 16 sublevels, and up to 16 allowed transitions can be observed. To analyze the origin of paramagnetic centers formed by chromium ions in our sample, it is necessary to look at the Figure 2, which presents in more details the part of the spectrum marked by the rectangle in Figure 1. We see that, along with the transition having four-line hyperfine structure, there are transitions with more complicated structure. Obviously, these transitions are due to the dimer associate of the Cr^{3+} ion, but not to the single Cr^{3+} ion. Since partial crystal/melt distribution for the Cr^{3+} ion in forsterite is about 10^{-1} [21], real concentration of Cr^{3+} ion in the studied sample is about 1.4×10^{-4} . In accordance with (1), at statistical distribution of impurity ions over the lattice sites, concentration of Cr^{3+} dimer associates should be about 4 order of magnitude less than the concentration of the single Cr^{3+} ions. Probabilities of the resonance transitions of the Cr^{3+} ions in forsterite depend strongly on the origin of the transition and orientation of the external magnetic field. So, it is impossible to calculate real ratio $C_{\text{dimer}}/C_{\text{single}}$ on the basis of the EPR data. Nevertheless, taking into account relative intensities of the spectra presented in Figure 2, we can conclude that the distribution of Cr^{3+} ions in forsterite is not a statistical one. There is pronounced effect of self-organization of the Cr^{3+} ions in dimer associates during the crystal growth. Probabilities of formation of various Cr^{3+} cluster centers in forsterite were theoretically calculated in [22]. Cr^{3+} ions have electron spin $S = 3/2$. System of the Cr^{3+} ion electron levels in forsterite is presented by two Kramers doublets with large zero-field splitting Δ . For the single Cr^{3+} ion in the M1 positions, values of Δ calculated using spin Hamiltonian parameters of [14], [23] and measured experimentally [13] are 68.7, 67.7 and 66.7 GHz, respectively. Therefore only two intra-doublet transitions can be observed by X-band EPR. The Cr^{3+} dimer associates have 16 electron levels with multiple transitions between them. Large number of resonance transitions observed for Cr^{3+} ion in the M1 position may be a consequence of the dimer structure of the paramagnetic center.

4. Summary

Impurity trivalent chromium ions enter the crystal lattice of forsterite single crystals in the form of single ion with non-local compensation of excess cation charge under the heterovalent substitution of divalent magnesium ions and as a dimer associate. The concentration of the associates is much higher than it could be expected under the statistical distribution of Cr^{3+} ions in the crystal lattice.

References

1. Bertaina S., Gambarelli S., Tkachuk A., Kurkin I.N., Malkin B., Stepanov A., Barbara B. *Nature Nanotechnol.* **2**, 39 (2007)
2. Luis F., Repolles A., Martinez-Perez M.J., Aguila D., Roubeau O., Zueco D., Alonso P.J., Evangelisti M., Camon A., Sese J., Barrios L.A., Aromi G. *Phys. Rev. Lett.* **107**, 117203 (2011)
3. Nellutla S., Choi K.-Y., Pati M., van Tol J., Chiorescu I., Dalal N.S. *Phys. Rev. Lett.* **99**, 137601 (2007)
4. Motokawa M., Ohta H., Makita N., Ikeda H. *J. Phys. Soc. Jpn.* **61**, 322 (1992)
5. McPherson G.L., Heung W. *Solid State Comm.* **19**, 53 (1976)
6. McPherson G.L., Henling L.M. *Phys. Rev. B* **16**, 1889 (1977)

7. Malkin B.Z., Leushin A.M., Iskhakova A.I., Heber J., Altwein M., Moller K., Fazlizhanov I.I., Ulanov V.A. *Phys. Rev. B* **62**, 7063 (2000)
8. Tarasov V.F., Shakurov G.S., Malkin B.Z., Iskhakova A.I., Veber J., Altwein M. *JETP Lett.* **65**, 559 (1997)
9. Konovalov A.A., Lis D.A., Malkin B.Z., Nikitin S.I., Subbotin K.A., Tarasov V.F., Vorobieva E.N., Zharikov E.V., Zverev D.G. *Appl. Magn. Reson.* **28**, 267 (2005)
10. Konovalov A.A., Lis D.A., Subbotin K.A., Tarasov V.F., Zharikov E.V. *Appl. Magn. Reson.* **45**, 193 (2014)
11. Tarasov V.F., Sukhanov A.A., Dudnikova V.B., Zharikov E.V., Lis D.A., Subbotin K.A. *JETP Lett.* **106**, 92 (2017)
12. Zaripov R.B., Mingalieva L.V., Tarasov V.F., Zharikov E.V., Subbotin K.A., Lis D.A. *Phys. Solid State* **61**, 174 (2019)
13. Shakurov G.S., Tarasov V.F. *Appl. Magn. Reson.* **21**, 597 (2001)
14. Ryabov I.D. *Phys. Chem. Minerals* **38**, 177 (2011)
15. Tarasov V.F., Shakurov G.S., Gavrilenko A.N. *Phys. Solid State* **37**, 270 (1995)
16. Konovalov A.A., Tarasov V.F., Dudnikova V.B., Zharikov E.V. *Phys. Solid State* **51**, 1626 (2009)
17. Hoffman K.R., Casas-Gonzales J, Jacobsen S.M., Yen W.M. *Phys. Rev. B* **44**, 12589 (1991)
18. Whitmore M.H., Sacra A., Singel D.J. *J. Chem. Phys.* **98**, 3656 (1993)
19. Stoll S., Schweiger A. *J. Magn. Reson.* **78**, 42 (2006)
20. Stoll S., Schweiger A. *Biol. Magn. Reson.* **27**, 299 (2007)
21. Dudnikova V.B., Gaister A.V., Zharikov E.V., Senin V.G., Urusov V.S. *Geochem. Int.* **43**, 471 (2005)
22. Dudnikova V.B., Urusov V.S., Zharikov E.V. *Phys. Solid State* **51**, 1626 (2014)
23. Rager H. *Phys. Chem. Minerals* **1**, 371 (1977)