Radiation Measurements 90 (2016) 122–126

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Luminescence and EPR spectroscopy of neutron-irradiated single crystals of magnesium aluminium spinel

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HIGHLIGHTS

- Photo-, cathodo- and thermally stimulated luminescence; conventional and pulse EPR.
- In irradiated spinel Mn^{2+} ions are moved from tetrahedral to octahedral interstices.
- An electron from an F^+ centre is in superhyperfine interaction with ^{27}Al nuclei.

ARTICLE INFO

Article history:
Received 30 October 2015
Received in revised form
21 December 2015
Accepted 22 December 2015
Available online 25 December 2015

Keywords:
Magnesium aluminium spinel
Photo- and cathodo-luminescence
EPR

ABSTRACT

Neutron irradiated single crystals of stoichiometric $MgAl_2O_4$ and $MgAl_2O_4$:Mn^{2+} (0.15 wt. %) were studied using the methods of luminescence spectroscopy and versions of electron paramagnetic resonance. In stoichiometric $MgAl_2O_4$:Mn^{2+} single crystals, the transition of a part of manganese impurity ions from tetrahedral to octahedral coordination, caused by irradiation with fast fission neutrons, is detected using photoluminescence spectra. This fact confirms the partial inversion of a normal spinel due to neutron-irradiation. Using pulse EPR technique it is shown that an electron in the field of oxygen vacancy (i.e. from neutron-irradiation induced F^+ centres, which are spatially separated from each other) is in hyperfine interaction only with neighbouring ^{27}Al nuclei with nuclear spin 5/2.

1. Introduction

Insufficient radiation resistance is a serious limitation for many wide-gap materials possessing other necessary properties to be used for various applications. For instance, radiation-induced structural defects strongly affect the functionality of various optical components and, therefore, the understanding of the mechanisms of defect creation and annihilation is of fundamental importance. Now it is widely accepted that magnesium aluminium spinel exhibits a very high tolerance to irradiation with fast neutrons and swift ions as well as a very little swelling even to high doses (see, e.g., Sickafus et al., 2000; Uberuaga et al., 2007, 2015). Therefore, $MgAl_2O_4$ single crystals and ceramics can be exploited for different applications, including their use as radio-frequency and optical windows or insulating materials in future deuterium-tritium fusion reactors as inert matrices for nuclear fuel and the forms for nuclear waste (Bacorisen et al., 2006) and as an inert matrix target material in the nuclear transmutation of radioactive actinides (Konings et al., 2000).

$MgAl_2O_4$ is a mixed oxide with high melting temperature at 2410 K. It has good thermal and mechanical properties, a high hardness and a low electrical loss. The spinel belongs to double oxides of the $A^{2+}(B^{3+})_2O_4$ type, where A^{2+} is Mg^{2+}, Fe^{2+}, Mn^{2+} or other bivalent ions, and B^{3+} is Al^{3+}, Fe^{3+}, Cr^{3+}, Mn^{3+} or other trivalent ion. The unit cell of spinel $AO \cdot nB_2O_3$ (if stoichiometric, $n = 1$) consists of 8 formula units AB_2O_4 arranged in an almost-perfect cubic close-packed body of oxygen ions with 64 tetrahedral and 32 octahedral interstices (*Fd*3*m* space group). In the case of "normal" spinel ($MgAl_2O_4$) with no cation disorder, A^{2+} (Mg^{2+}) ions occupy only eight fourfold coordinated interstices (A-sites), while

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http://dx.doi.org/10.1016/j.radmeas.2015.12.020
1350-4487/

B^{3+} (Al^{3+}) ones – a half of sixfold coordinated interstices (B-sites). So, the spinel contains a huge density of so-called structural vacancies in the crystalline lattice (56 and 16 unoccupied A and B sites per unit cell, respectively).

Under certain conditions (e.g., under neutron irradiation), Mg and Al ions are able to swap A and B sites and occupy a "wrong" cation position, thus forming cation disorder via so-called antisite defects – Mg^{2+} in octahedral coordination ($Mg|_{Al}$) and Al^{3+} in tetrahedral coordination ($Al|_{Mg}$). It was shown (see, e.g., Gilbert et al., 2009) that the formation energy for an antisite in $MgAl_2O_4$ is much lower than that for all other elementary lattice defects. The disorder processes in a cation sublattice of spinels were simulated by atomistic technique (Sickafus et al., 2000; Bacorisen et al., 2006; Uberuaga et al., 2007, 2015). In the case of the "inverse" spinel, a half of $B^{3+}(Al^{3+})$ ions are located in the tetrahedral interstices (instead of A^{2+} in the normal spinel), the other part of B^{3+} and $A^{2+}(Mg^{2+})$ and ions are usually statistically distributed between the octahedral B-positions. If we use an inversion parameter i, the chemical formula of magnesium aluminium spinel may be expressed as $^{IV}(A_{1-i}B_i)^{VI}[A_iB_{2-i}]O_4$, where $^{IV}(\cdot)$ and $^{VI}[\cdot]$ represent fourfold (A) and sixfold coordinated (B) sites. Assuming $i = 1$, we obtain a formula A[AB]O_4 for the inverse spinel, where all A^{2+} cations are located in B-sites, i.e. they are antisite defects. The optical and EPR characteristics of F-type centres (one or two electrons in the field of an oxygen vacancy) were studied in virgin and neutron-irradiated $MgAl_2O_4$ crystals (see, e.g., Ibarra et al., 2005; Sawai et al., 2012 and references therein).

Transition metal Mn ions introduced into $MgAl_2O_4$ were studied extensively (Reed et al., 1969; Gritsyna et al., 1983, 2005; Mironova et al., 1993, 1996; Jouinia et al., 2006; Skvortsova et al., 2011; Riekstina et al., 2013), and their optical spectra in the infrared and visible regions are satisfactorily understood. However, the influence of these impurities on photoluminescence and electron paramagnetic resonance (EPR) spectra of magnesium aluminium spinel is not yet completely understood, particularly, in relation to the radiation-induced effects in this material.

The present study is devoted to the processes induced by irradiation of $MgAl_2O_4$ and $MgAl_2O_4$:Mn^{2+} single crystals with fast fission neutrons. Photo-, cathodo- and thermally stimulated luminescence as well as conventional and pulse EPR methods were used for characterization of virgin and neutron-irradiated samples.

2. Experimental

In the present study, we used stoichiometric $MgAl_2O_4$ as well as $MgAl_2O_4$ doped with Mn^{2+} (0.15 wt. % in a crystal bulk) single crystals grown by the Verneuil method. The irradiation by fast neutrons (energies more than 0.1 MeV) with a fluence up to10^{20} cm^{-2} was performed using the Latvian research reactor in Salaspils. The irradiation temperature was below 370 K.

The spectra of photoluminescence (PL) were measured at 295 K in the region of 2–5.5 eV with the use of a double prism monochromator DMR-4 and a photomultiplier tube R-6358-10 Hamamatsu in a photon counting mode. The excitation by 5.2-eV photons was performed using a deuterium discharge lamp DDS-400 and the second DMR-4 monochromator.

The spectra of cathodoluminescence (CL) were measured in the region of 1.6–6 eV at the excitation by a steady electron beam (5–10 keV, 100–300 nA) at 78 K. After the electron irradiation was stopped, the thermally stimulated luminescence (TSL, heating rate of $\beta = 10$ K/min) was measured at 78–420 K for a spectrally integrated signal (see for details Nakonechnyi et al., 2006).

Standard X-band spectrometer Bruker Elexsys E580 operating in continuous wave and pulse modes was used for EPR measurements. A version of pulsed EPR – hyperfine sublevel correlation spectroscopy (HYSCORE) was used to analyse the interaction between a spin of an electron (from an F^+ centre that is an electron in the field of an oxygen vacancy) and nuclear spins of neighbouring atoms. This type of two-dimensional EPR spectroscopy is based on the electron spin-echo envelope modulation effect, where a sequence of four microwave pulses is applied to the sample and the produced stimulated spin-echo is measured (see for details Schweiger et al., 2001).

3. Results and discussion

Photoluminescence spectra of $MgAl_2O_4$:Mn^{2+} crystals irradiated by fast neutrons to three different fluences are shown in Fig. 1. PL spectra were measured at 295 K under steady excitation by 5.2-eV photons in the absorption region of manganese-containing complex centres (see, e.g., Gritsyna et al., 2005). In the case of low fluence of $\Phi = 10^{13}$ cm^{-2} (Fig. 1b), the PL spectrum exhibits two bands with the maxima at 2.41 (514 nm) and 1.89 eV (656 nm). With the rise of neutron fluence, the relative intensity of the ~1.9 eV band increases (Fig. 1*a*) and at $\Phi = 10^{20}$ cm^{-2} even exceeds that for the ~2.4 eV band (Fig. 1*c*).

According to Klick et al., 1952, a Mn^{2+} ion emits green light when it is tetrahedrally (fourfold) coordinated in the solids, while it emits orange-red light in a more spacious octahedral (sixfold) coordination. For Mn^{2+} ions ($3d^5$-configuration) in $MgAl_2O_4$, the net stabilization energy is zero, therefore, the manganese ions with equal probability can occupy tetrahedral and octahedral sites (Reed et al., 1969). Green emission was observed by Mironova et al. (1993) for synthetic stoichiometric and non-stoichiometric $MgAl_2O_4$ crystals containing manganese impurity ions. According to Mironova et al. (1996), such luminescence is typical of the divalent manganese ions in fourfold tetrahedral coordination. Unlike synthetic single crystals, a luminescence band peaked at 625 nm (1.98 eV), and associated with the emission of the manganese ions in sixfold coordination, was detected in the natural spinel with high concentration of manganese (Mironova et al., 1993). So, the emission bands presented in Fig. 1 can be attributed to Mn^{2+} ions which occupy either tetrahedral (2.4 eV) or octahedral sites (1.9 eV). Considering the foregoing, it can be concluded that the irradiation with fast neutrons leads to the transition of impurity ions from tetrahedral to octahedral positions, thus increasing the spinel inversion. The similar process was earlier observed in neutron-irradiated chromium-containing spinel crystals (Skvortsova et al., 2002).

It is generally accepted that fast neutrons cause the creation of

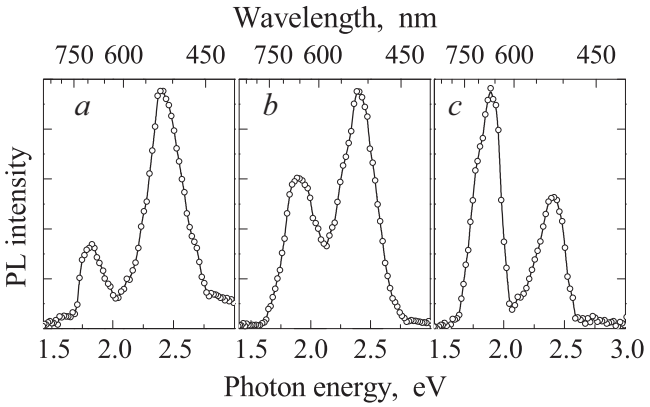

Fig. 1. Photoluminescence spectra measured at the excitation with 5.2-eV photons at 295 K for $MgAl_2O_4$:Mn^{2+} single crystals previously irradiated by fast neutrons at a fluence of $\Phi = 10^{16}$ cm^{-2} (*a*), $\Phi = 10^{13}$ cm^{-2} (*b*) and $\Phi = 10^{20}$ cm^{-2} (*c*).

the so-called anion Frenkel defects (neutral and charged vacancy–interstitial pairs) in solids via the rapid impact (knock-out) mechanism connected with the elastic collisions of high-energy incident neutrons with the crystal nuclei, providing the displacement of atoms from their regular sites into interstices. In a normal spinel crystal, Mn^{2+} impurity ions mainly substitute for Mg^{2+} cations and are located in tetrahedral positions. Under irradiation of $MgAl_2O_4$:Mn^{2+} with fast neutrons, fourfold coordinated Mn^{2+} impurity ions undergo collisions with incident neutrons resulting in their displacement from tetrahedral positions and the subsequent partial location of Mn^{2+} in octahedral ones.

It is worth noting that the observed PL bands are asymmetric ones (see Fig. 1), that indicates to their complex structure due to the presence of other luminescence centres. According to Sviridov et al. (1979), an additional emission band can belong to Mn^{4+} ions. Moreover, the emission at ~1.9 eV in a virgin spinel crystal is triggered by the band edge excitation and is assigned to the charge-transfer process associated with the manganese ions (Tomita et al., 2004).

In a neutron-irradiated $MgAl_2O_4$:Mn^{2+} single crystal ($\Phi = 10^{16}$ cm^{-2}), the spectrum of recombination luminescence excited at 78 K by a steady 5-keV electron beam contains the dominant and slightly asymmetric band peaked at ~2.4 eV (Fig. 2*a*). This emission band belongs to the fourfold coordinated Mn^{2+} ions in an $MgAl_2O_4$ spinel. It has been shown already that the CL spectrum of Mn^{2+} ions in $MgAl_2O_4$ depends on the stoichiometry and the concentration of Mn^{2+} in the sample (Mironova et al., 1996). The spectrum of recombination CL, measured at 78 K for a neutron-irradiated nominally pure $MgAl_2O_4$ is also shown in Fig. 2*a*.

Fig. 2*b* shows the CL spectra measured for virgin and proton-irradiated nominally pure $MgAl_2O_4$ single crystals. CL spectrum of a virgin sample consists of three-four overlapping bands in the range from 2 to 6 eV, but to the best of our knowledge only one of these (at ~2.7 eV) is reliably interpreted as F^+ centre luminescence (Sawai et al., 2012). The irradiation by 100-keV protons ($\Phi = 10^{17}$ cm^{-2}) was performed using the KIIA 500 kV implanter at Helsinki University, Finland. The penetration depth of 10 keV electrons approximately fits the thickness of proton-irradiated layer (~0.5 μm) – so the CL excited within the damaged layer was examined. Similar to the case of fast neutrons, the irradiation with 100-keV protons causes a huge drop of CL intensity (up to two orders of magnitude) compared to that measured under the same conditions for a virgin sample. It is worth noting that heavy irradiation completely suppresses the UV band at ~5 eV. The position and relative intensity of this UV band varies in different virgin samples being probably dependent on the content of "as-grown" antisite defects or impurities. The radiation-induced suppression of the UV band can be partly connected with the luminescence reabsorption by radiation-induced F-type centres, but, in our opinion, is mainly caused by the inversion process of spinel lattice, i.e. the efficient creation of antisite defects.

Fig. 3 shows the curves of spectrally integrated TSL measured up to 420 K (our limit for CL setup) for neutron irradiated $MgAl_2O_4$ spinel crystals after an additional irradiation with 5-keV electrons at 78 K. The TSL curves exhibit weak peaks at ~130 and ~250 K for a nominally pure sample (curve 1) and the significantly more intense peaks at 105 and 310 K for $MgAl_2O_4$:Mn^{2+} (curve 2). Both spinel samples were irradiated with fast fission neutrons ($\Phi = 10^{16}$ cm^{-2}) and additionally with 5-keV electrons at 78 K during 15 min. The TSL peak at 210 K accompanies the release of charge carriers captured at manganese-containing trapping centres (filled during additional electron-irradiation).

The EPR spectrum of a neutron-irradiated $MgAl_2O_4$ typically consists of a single singlet with *g*-factor close to 2.00. Nevertheless, Ibarra et al. (1998) reported on the occurrence of two signals (a narrow sharp derivative line and a wide weak signal close to $g = 2.083$, the both of which do not depend on applied magnetic field orientation, i.e. they are the isotropic ones. In contrast to the sharp EPR line, the wide signal was detected only in the samples

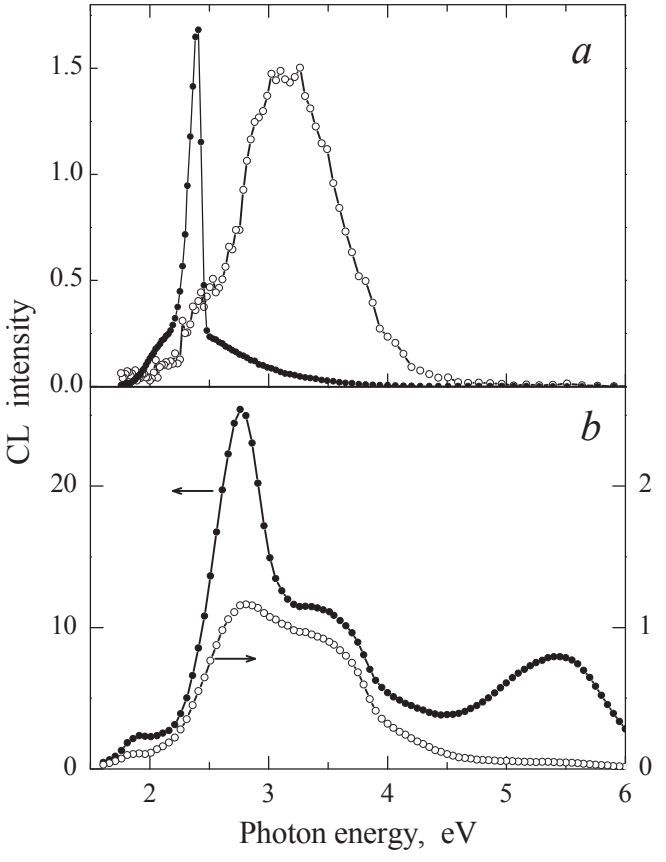

Fig. 2. The cathodoluminescence spectra measured for spinel single crystals under excitation by 5-keV electrons at 78 K. (*a*) for neutron-irradiated ($\Phi = 10^{16}$ cm^{-2}) $MgAl_2O_4$ (empty circles) and $MgAl_2O_4$:Mn^{2+} crystals (filled circles); (*b*) for virgin (filled circles) and proton-irradiated ($\Phi = 10^{17}$ cm^{-2}, empty circles) nominally pure $MgAl_2O_4$.

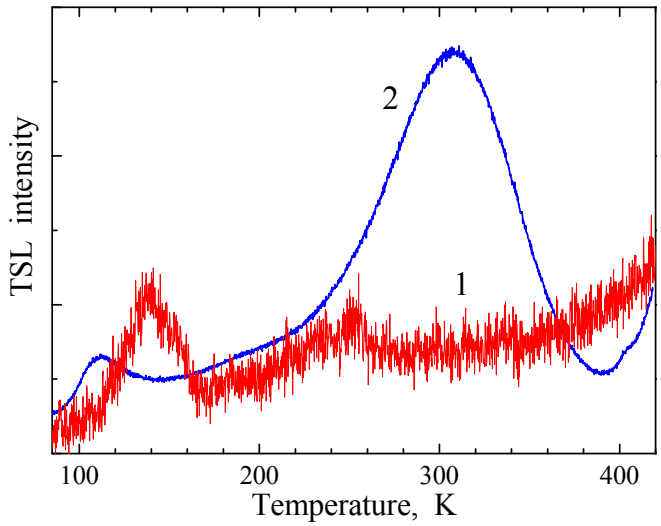

Fig. 3. The TSL curves of neutron-irradiated $MgAl_2O_4$ (curve 1) and $MgAl_2O_4$:Mn^{2+} (curve 2) single crystals after additional irradiation by an electron beam (5 keV, 0.3 μA, 15 min, 78 K). Curve 2 is multiplied by a factor of 15. $\beta = 10$ K/min.

irradiated with a high neutron dose ($\Phi > 10^{23}$ cm^{-2}) and high irradiation temperature of (~1000 K). So, the wide EPR signal was attributed to dislocation clusters or other extended defects (e.g., metal colloids). According to Ibarra et al. (2005), the narrow isotropic EPR signal with $g = 2.0005$ was related to radiation-induced F^+ centres (an electron in the field of an oxygen vacancy). The structure, optical and EPR characteristics as well as the process of thermal annealing of F^+ centres in neutron-irradiated $MgAl_2O_4$ were discussed in literature (see Ibarra et al., 2005 and references therein).

Fig. 4 presents the EPR spectrum of F^+ centres measured in our neutron-irradiated nominally pure $MgAl_2O_4$ sample at 295 K. In $MgAl_2O_4$:Mn^{2+} sample, EPR spectrum contains also a band at $g = 2.00$ with six-line hyperfine structure typical for a Mn^{2+} paramagnetic centre (Mironova et al., 1996). It is worth noting that the EPR signal of F^+ centres was not detected in virgin $MgAl_2O_4$ samples.

In the present study, Electron Nuclear Double Resonance (ENDOR) pulse induced EPR technique has been also applied to study radiation paramagnetic defects in spinel. Pulse EPR spectrometers work at a fixed magnetic field. The T_1 and T_2 relaxation time measurements were carried out by the inversion recovery spin-echo pulse sequence at 295 K T_1 ascribing spin-lattice relaxation was measured by a standard two pulse sequence $\pi/2 - \pi$, while for T_2 (spin–spin relaxation) three pulse sequence $\pi - \pi/2 - \pi$ was used. The relaxation times were determined to be $T_1 = 324$ ns and $T_2 = 1802$ ns for our stoichiometric $MgAl_2O_4$ crystal irradiated with fast neutrons. So, the interaction of F^+ centres with a crystal field is much stronger than that between F^+ centres which, tentatively, are spatially separated from each other.

The HYSCORE spectrum of a neutron irradiated $MgAl_2O_4$ has been recorded in the magnetic field of 0.3382 T (i.e. at the EPR resonance for F^+ centres). Fig. 5 presents two symmetric peaks of the highest intensity of the ENDOR signal in lower left and upper right quadrants, which are detected at Larmor frequency of 3.755 MHz. According to Bruker tabular data such value is typical of ^{27}Al nucleus with nuclear spin $J = 5/2$. Only ^{25}Mg nuclei possess non-zero spin $J = 5/2$, but they have lower nuclear magnetic moment and only 10% of abundance. Therefore, it can be concluded that the nearest nuclei to the radiation-induced F^+ centre are octahedrally coordinated ^{27}Al, and that an electron in the field of an oxygen vacancy is in a hyperfine interaction only with neighbouring ^{27}Al nuclei.

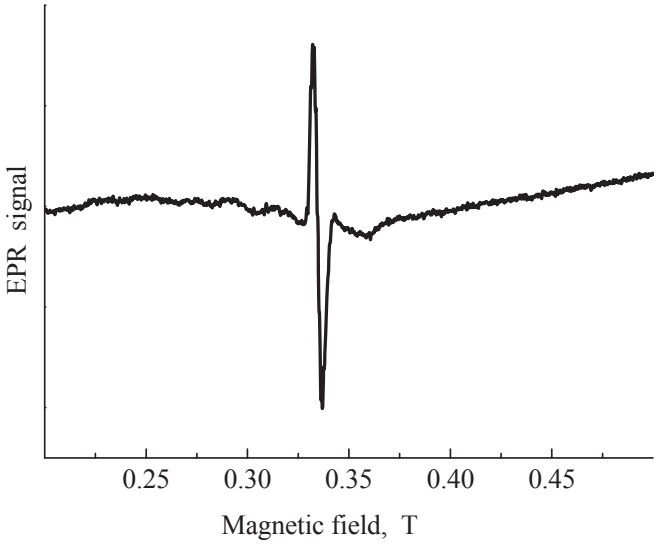

Fig. 4. EPR spectrum of F^+ centres in a neutron irradiated $MgAl_2O_4$ crystal. $T = 295$ K.

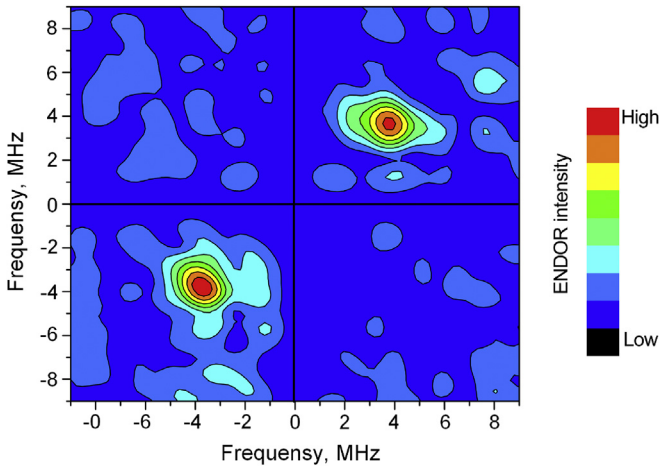

Fig. 5. HYSCORE spectrum (version of pulsed EPR) for a neutron irradiated $MgAl_2O_4$ crystal (see text for details). $T = 295$ K.

4. Conclusions

In stoichiometric $MgAl_2O_4$:Mn^{2+} single crystals irradiated with fast neutron, the transition of the manganese impurity ions from tetrahedral to octahedral coordination (more spacious) is detected using luminescence methods. Heavy irradiation also strongly attenuates cathodoluminescence of a nominally pure $MgAl_2O_4$ spinel and completely suppresses the UV band at ~5 eV. All these data can be interpreted as the partial inversion of a normal spinel due to elastic collisions of incident fast fission neutrons with cation nuclei. Using pulse EPR technique, hyperfine sub-level correlation spectroscopy (HYSCORE) it is shown that an electron from a neutron-irradiation induced F^+ centre is located in a hyperfine interaction only with neighbouring octahedrally coordinated ^{27}Al nuclei.

Acknowledgements

The research leading to these results has received funding from the Latvian Science Council Grant No. 402/2012 and the Estonian Research Council–Institutional Research Funding IUT02-26. This work was partially supported by the Center of Excellence "Radiation and Nuclear Technologies" (Competitiveness Enhancement Program of Ural Federal University, Russia).

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