



Anion interstitials in neutron-irradiated MgO single crystals

T. Kärner^{a,*}, S. Dolgov^a, N. Mironova-Ulmane^b, S. Nakonechnyi^a, E. Vasil'chenko^a

^a*Institute of Physics, University of Tartu, Riia 142, 51014, Tartu, Estonia*

^b*Solid State Physics Institute of Latvian University, Kengaraga Str. 8, LV-1063 Riga, Latvia*

Received 20 August 2000; received in revised form 1 February 2001; accepted 10 February 2001

Abstract

Electron paramagnetic resonance (EPR) and high-temperature (300–775 K) thermoluminescence of neutron-irradiated MgO single crystals were studied. Spin-hamiltonian parameters of the observed anion interstitial centres (O_2^- molecular ion in an oxygen site by a cation vacancy—H centre) were determined. The thermal stability of anion interstitials (H centres) and other EPR-active centres was investigated. It is shown that the thermal decay of H centres is attended by a TL peak due to hole recombination luminescence at 700 K. A possible mechanism for the thermal destruction of anion Frenkel defects in MgO is discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thermoluminescence; Radiation defects; Anion interstitial; Simple oxide

1. Introduction

Defects in the MgO single crystals, containing anion or cation vacancies, and the processes, involving these defects (their formation, migration, localization and clustering, trapping and thermal release of charge carriers, luminescence etc.) have been widely investigated. However, we know little about the role of interstitials in these crystals. The properties of anion interstitials have been studied in several theoretical papers (Brudevoll et al., 1996; Evarestov et al., 1996; Kotomin and Popov, 1998). The calculations showed that charged interstitials are unstable at room temperature. For a neutral oxygen interstitial it was found that a $O^- - O^-$ dumb-bell configuration on an anion lattice site is energetically the most favourable one. The calculated equilibrium distance between two atoms of the dumb-bell is close to that of a free O_2^- molecule, yet the data about the chemical bonding between these atoms are controversial. The only experimental work in which anion interstitials have

been directly recorded, is that of Halliburton and Kappers (1978). In a neutron-irradiated MgO crystal they observed electron spin resonance (ESR) spectra of O_2^- molecules localized near cation vacancies and interpreted this centre as an analogue of H-centres in alkali halide crystals—a radiation-produced oxygen interstitial combined with an indigenous oxygen ion, with the cation vacancy acting as the stabilizing site. There is also some indirect data concerning radiation-produced anion interstitials: the effect of neutron irradiation on the d-transitions in MgO: Mn²⁺ crystals was attributed to the presence of interstitial-impurity-F-centre complexes (Okada et al., 1987). In our previous paper (Kärner et al., 2001), we described a high temperature thermoluminescence (TL) peak at ~700 K coinciding with the thermal decay of H centres, which was interpreted as the result of a radiative recombination of anion interstitials with F⁺ centers. A drastic difference was observed in the behaviour of TL peaks in a region of 400–550 K and 630–750 K before and after a thermal destruction of H centres, measured in neutron-irradiated MgO crystals immediately after a control X-irradiation. Heating a crystal to 775 K enhances the TL peaks in a low-temperature region and reduces the 700 K high-temperature peak. In the same temperature region, we registered an abrupt drop of the frequency factor

* Corresponding author. Tel.: +372-7-428-946; fax: +372-7-383-033.

E-mail address: tiit@fi.tartu.ee (T. Kärner).

of the thermoluminescence recombination process that was ascribed to the hopping diffusion of anion interstitials.

In this work, we present additional data concerning anion interstitials and their recombination process in MgO.

2. Experimental

The ESR and TL (up to 775 K) of neutron-irradiated undoped and aluminium-doped MgO single crystals have been measured. The MgO crystals were grown at the Institute of Physics, University of Tartu, by a variation of the arc fusion technique. For the growth of aluminium-doped crystals the concentration of Al_2O_3 in the starting powder was 10 000 ppm (the so-called MgO M6 crystals) or 5000 ppm (MgO M4) that resulted in a concentration of V_{Al} centres of about 10^{18} cm^{-3} . The MgO crystals were neutron irradiated in a nuclear reactor of Latvian Nuclear Research Center, Salaspils. The irradiation doses were 10^{14} – 10^{17} neutron/cm².

The EPR spectra were measured with an X-band (9.9278 GHz) ERS 231 spectrometer. A continuous-flow helium cryostat (Oxford Instruments, ESR900) was used to keep the samples at the necessary temperature (typically 100 K). Pulse annealing of the samples was carried out to determine the thermal stability of the observed EPR-active centres. On pulse annealing the crystals were kept, after a fast heating up, for a certain time (2 min) at the required temperature and then cooled to the measurement temperature. All the EPR spectra of H centres were analysed using the computer program EPR-NMR (Department of Chemistry, University of Saskatchewan, Canada, 1993).

High-temperature thermally stimulated luminescence of the MgO crystals was measured at a heating rate of 2.86 K/s in the atmosphere of flowing nitrogen, using a System310 TLD Reader. A method of control colouration (X-irradiation, dose 100 Gy) was used before every TL measurement. The construction of the TLD Reader ruled out the possibility of using a monochromator in the TL measurements, therefore, optical light filters were used to determine the spectral distribution of the luminescence in the TL glow peaks.

3. Results and discussion

The EPR spectra of the MgO M4 crystals revealed two types of H-centre. Their spin-hamiltonian parameters ($g_x = 2.0059$, $g_y = 2.0011$, $g_z = 2.0767$, $\theta = 30.46^\circ$ and $g_x = 2.0061$, $g_y = 2.0011$, $g_z = 2.0761$, $\theta = 31.24^\circ$, where θ —angle between the axis of a O_2^- molecule and $\langle 100 \rangle$ direction in the crystal) are somewhat lower than those determined earlier (Halliburton and Kappers, 1978), but an almost uniform shift of the components of the g tensor and, especially, an equal difference between the spin-hamiltonian parameters for two centres in both cases, leaves little doubt that the observed centres are the centres H_I and H_{II} seen

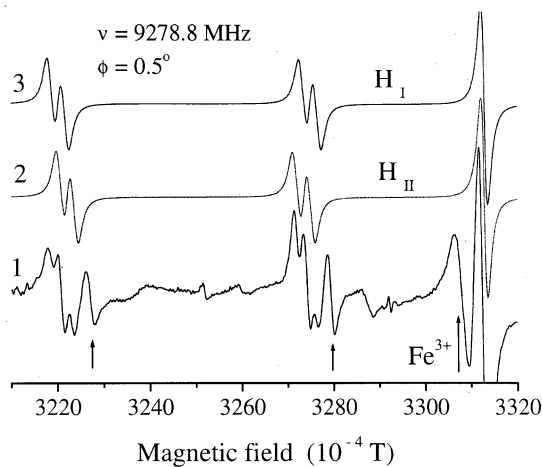


Fig. 1. EPR spectra of the neutron-irradiated (10^{17} n/cm^2) MgO:Al (MgO M4) single crystal. 1—experimental spectrum, 2 and 3—computer simulated spectra for H_{II} and H_I centres, respectively. Short arrows mark the spectral lines, visible only at small angles between the magnetic field and $\langle 100 \rangle$ crystal directions (see text).

by these earlier authors. The concentrations of H_I and H_{II} centres were roughly equal. In the MgO M6 crystal with a higher dopant content we observed only an H_I centre. However, its concentration was about 10 times as high as that in MgO M4.

Besides the spectra of H_I and H_{II} centres we observed another EPR spectrum, the intensity of which was so orientation-dependent that it could be observed only at small angles between the magnetic field and $\langle 100 \rangle$ direction (see Fig. 1). In Fig. 1 the measured EPR spectrum of a MgO M4 crystal and computer-simulated spectra of H_I and H_{II} centres for an angle 0.5° are given. The spectral lines of the above-mentioned orientation-dependent EPR spectrum are marked with arrows. The angular dependence of the position of these lines, as far as they can be observed, and their thermal stability is close to that for the H centres, therefore, it is reasonable to assume that the nature of this centre is similar.

In Fig. 2 are shown the pulse annealing curves of the centres, observed by EPR in a MgO M4 crystal. All the EPR spectra were measured at 100 K, the spectra of H centres were recorded at a microwave power of 125 mW, F^+ centres were measured at $\sim 8 \mu\text{W}$, and the other impurity centres were measured at 0.2 mW. The H centres decay in a relatively narrow temperature region from 650 to 725 K, whereas the decay of F^+ centres begins at ~ 500 K and is not finished by 775 K. According to Halliburton and Kappers (1978), the destruction temperature of the H_{II} centres is about 30 K lower than that of the H_I centres, and their decay is accompanied with a simultaneous growth of the EPR signal of the H_I centres. Due to the low intensity of the EPR signals and difficulties in the orientation of the crystal we

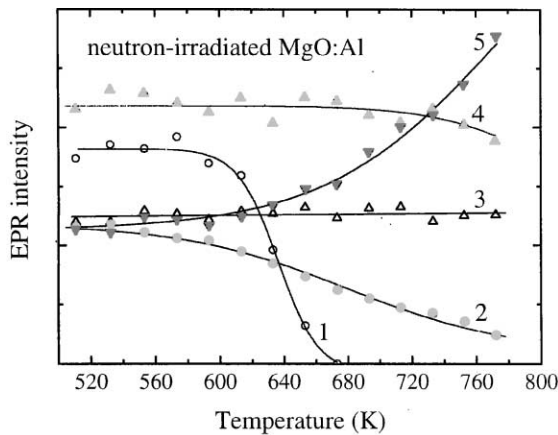


Fig. 2. The intensity of EPR signals of the neutron-irradiated MgO M4 crystal versus the pulse annealing temperature. All spectra were measured at 100 K. 1—the pulse annealing curves for H, 2— F^+ , 3— Mn^{2+} , 4— Fe^{3+} , 5— Cr^{3+} centres.

could not separate the thermal decay of the H_I and H_{II} centres. During the thermal decay of the F^+ and H centres, we observed a significant growth of the intensity of the EPR signal at $g = 1.9800$ that belongs to Cr^{3+} centres with an essentially octahedral symmetry, whereas the intensities of the EPR spectra of other common impurities with a variable charge state (Mn^{2+} , V^{2+} , Fe^{3+}) remain unchanged.

The luminescence spectrum of MgO at high temperatures consists of two main bands. One of them is of a complex origin and is centred in the blue spectral region at ~ 2.9 eV. The luminescence is dominantly recombinational and arises as a result of the thermal release of both electrons and holes. The other band of red luminescence belongs to Cr^{3+} in sites with different symmetry; the R-line is situated at 1.776 eV. To determine the spectral composition of the TL peak at 700 K, we measured TL using additional optical filters. In Fig. 3 for an undoped MgO crystal, the changes in the TL curves induced by heating of the neutron-irradiated crystal to 775 K (the difference between the second and the first TL measurements of the same neutron-irradiated crystal), registered without and with filters, spectral transmittance of which is given in the inset, are depicted. As can be seen, the glow in the 700 K peak is mainly due to Cr^{3+} luminescence.

The ESR spectrum of the H centres was observed in all the investigated crystals, neutron-irradiated with doses 10^{17} n/cm², but we did not find H centres in the unirradiated, X-irradiated or even plastically deformed and X-irradiated crystals. This makes MgO quite different from another simple oxide—SrO, in which a large variety of O_2^- centres have been observed in unirradiated SrO crystals (Seeman et al., 1980). O_2^- molecular ion–cation vacancy complexes (H centres) seem to be a well-established form of anion interstitials in MgO. From a slightly different point of view, they may be regarded as interstitial atoms, trapped by V centres,

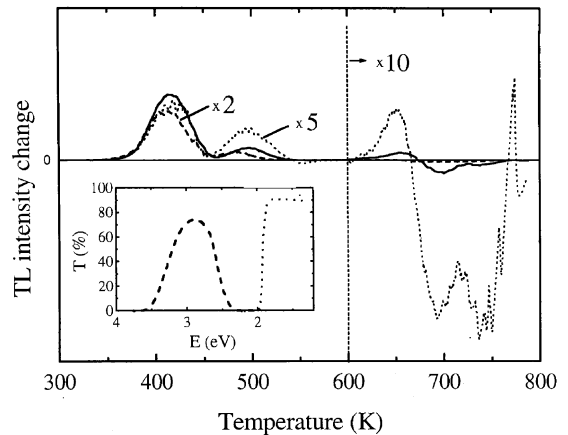


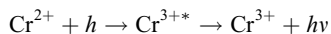
Fig. 3. The change in the TL intensity of a neutron-irradiated undoped MgO crystal between the first two consecutive measurements (difference between the second and the first measurements): without filter (solid line); filter CC5, transmitting light in a band, centred at $\lambda = 430$ nm (dashed line); filter KC15, cutting light with $\lambda \leq 650$ nm (dotted line). In the inset the spectral transmittance of the filters is depicted.

and we can expect a family of H centres with somewhat different spin-hamiltonian parameters analogous to those of V centres. In MgO all the identified V centres, because of the dominant influence of the cation vacancy, have close g -factors (identical in the case of V^- and V_{Al} centres); apparently such is the case for H centres, too. Therefore, the close agreement between the spin-hamiltonian parameters of the H centres reported earlier and the one measured by us is not unexpected. The exact correspondence between various members of the families of V and H centres needs further investigation.

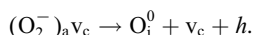
The curve of the thermal decay of F^+ centres measured by EPR (Fig. 2) is quite similar to that recorded by the fall of an optical absorption of F and F^+ centres at 5.0 eV (Halliburton and Kappers, 1978). This agrees with the result that in neutron-irradiated crystals anion vacancies are normally in the F^+ state (González et al., 1999). We tried to estimate by EPR the relative number of F^+ and H centres in a MgO M4 crystal and found that the total number of H_I and H_{II} centres (neglecting the observed “phantom” H centre) was about one half of that for F^+ centres. That means that the H centres are the dominant form of anion interstitials, at least in this particular crystal. This result raises a number of issues and must be carefully checked to draw any conclusions. The issues raised include: how can the gently sloping decay curve of F^+ centres be explained on the ground of a relatively sharp drop of the number of H centres; how can the dominant part of anion interstitials be associated with cation vacancies.

The growth of the number of Cr^{3+} centres is observed in the same wide temperature range where the decay of F^+

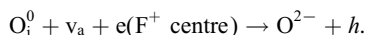
centres occurs. With rising temperature (in Fig. 3) we can follow the increasing importance of red chromium luminescence in the TL peaks. The red luminescence arises according to the following reaction (in which * depicts the excited state):



and indicates an occurrence of hole release processes. The low-temperature TL peak at about 420 K arises during the thermal destruction of V centres. According to Luthra and colleagues (Luthra et al., 1977) all TL peaks up to 550 K are due to hole-trapped centres. But the most interesting, for us, is the dominant role of red luminescence in the TL peak at 700 K ascribed to the thermal destruction of H and F^+ centres (Fig. 3). The thermal destruction of H centres can be described by the reaction:



In this process holes are created, but the recombination of these holes cannot explain the decrease of the frequency factor of the recombination process (Kärner et al., 2001) since it requires the hopping diffusion of an interstitial ion as an essential limiting part of the recombination process. It implies the following final step of the oxygen interstitial— F^+ centre recombination process:



The thermoluminescence, observed at 700 K, is supposedly a mixture of two recombination processes with the participation of these two kinds of holes.

4. Conclusion

The anion interstitials in MgO can be trapped by various V centres, forming a family of H centres, homomorphic with the family of V centres. The annealing of H centres in n -irradiated MgO is connected with the destruction of the O_2^- molecules localized near cation vacancies. The hopping diffusion of released O_i^0 brings about their recombination with F^+ centres, decreasing the optical absorption at 5 eV.

The recombination of the released holes with the electrons, trapped at impurity centres, during the destruction of H centres and during the $\text{O}_i^0 - \text{F}^+$ interaction, causes the TL peak at $T = 700$ K.

Acknowledgements

We would like to thank Prof. Ch.B. Lushchik for helpful discussions. This work was supported in part by the Estonian Science Foundation (Grant 3867) and by the Latvian Council of Science (Grant no. 96.0412).

References

- Brudevoll, T., Kotomin, E.A., Christensen, N.E., 1996. Interstitial-oxygen-atom diffusion in MgO. *Phys. Rev. B* 53, 7731–7735.
- Evarestov, R.A., Jacovs, P.W.M., Leko, A.V., 1996. Oxygen interstitials in magnesium oxide: a band-model study. *Phys. Rev. B* 54, 8969–8972.
- González, R., Monge, M.A., Muñoz Santiuste, J.E., Pareja, R., Chen, Y., Kotomin, E., Kukla, M.M., Popov, A.I., 1999. Photoconversion of F-type centers in thermochemically reduced MgO single crystals. *Phys. Rev. B* 59, 4786–4790.
- Halliburton, L.E., Kappers, L.A., 1978. Radiation-induced oxygen interstitials in MgO. *Solid State Commun.* 26, 111–114.
- Kärner, T., Dolgov, S., Lushchik, A., Mironova-Ulmane, N., Nakonechnyi, S., Vasilchenko, E., 2001. High-temperature thermoluminescence manifestations of anion interstitials in neutron-irradiated pure and doped single crystals of MgO. *Radiat. Eff. Def. Solids*, to be published.
- Kotomin, E.A., Popov, A.I., 1998. Radiation-induced point defects in simple oxides. *Nucl. Instr. and Meth. B* 141, 1–15.
- Luthra, J.M., Sathyamoorthy, A., Gupta, N.M., 1977. A thermoluminescence study of defect centres in MgO. *J. Lumin.* 15, 395–404.
- Okada, M., Kawakubo, T., Seiyama, T., Nakagawa, M., 1987. Enhancement of 3d-electron transitions in neutron-irradiated MgO:Mn^{2+} crystals. *Phys. Stat. Sol. (B)* 144, 903–909.
- Seeman, V., Reifman, S., Lehto, T., Haldre, U., 1980. Family of O_2^- centres in SrO crystals. *Phys. Stat. Sol. (B)* 102, 459–465.