A new trapped-hole radiation defect in heavily Mg-doped $LiNbO_3$

1991 J. Phys.: Condens. Matter 3 8457

(http://iopscience.iop.org/0953-8984/3/43/012)

J. Phys.: Condens. Matter 3 (1991) 8457–8465. Printed in the UK

A new trapped-hole radiation defect in heavily Mg-doped $LiNbO_3$

I M Zaritskii†, L G Rakitina†, G Corradi‡, K Polgár‡ and A A Bugai†
† Institute of Semiconductors, Ukrainian Academy of Sciences, 252650 Kiev, USSR
‡ Research Laboratory for Crystal Physics, Hungarian Academy of Sciences, PO Box 132, H-1502 Budapest, Hungary

Received 18 June 1991

Abstract. In $LiNbO_3$ single crystals doped with 8 mol% Mg and γ irradiated at 77 K a new trapped-hole defect has been detected. The new defect is characterized by an anisotropic ESR spectrum with a nearly isotropic, partly resolved hyperfine structure due to a single Nb nucleus. The principal g-values are $g_1 = 2.029 \pm 0.010$, $g_2 = 2.049 \pm 0.010$ and $g_3 = 2.006 \pm 0.010$, the Nb hyperfine constant is $A = 1.5 \pm 0.2$ mT. The new spectrum is attributed to a hole localized on an oxygen ion and stabilized by a substitutional Mg^{2+} ion on the nearest-neighbour Nb site, with an appreciable spin density on the other close Nb neighbour of the oxygen. The new defect, called the $O^-(Mg)$ centre, appears in these crystals together with OH^{2-} trapped electron centres reported recently. The $O^-(Mg)$ centres can be produced in larger concentrations if the crystal contains, in addition to an over-threshold (6–8 mol%) amount of Mg, also the Fe dopant. This is attributed to the electron-trapping capabilities of Fe^{3+} centres. The $O^-(Mg)$ centre decays in the temperature range 170–230 K, i.e. is more stable than the O^- centre reported previously for undoped or weakly Mg-doped $LiNbO_3$.

1. Introduction

Mg doping above a concentration threshold ($c_{Mg} \geqslant 5$ mol% for congruent crystals) was found to change the properties of $LiNbO_3$ dramatically. The observed reduction in the photorefractive effect (Zhong *et al* 1980) and the increased photoconductivity (Bryan *et al* 1984) are apparently related to basic changes in the intrinsic and extrinsic defect structure (for a review see Schirmer *et al* (1991)). All these effects could be described consistently by assuming that, in the presence of over-threshold amounts of Mg during crystal growth, no antisite niobium defects (Nb_{Li}) are formed (Donnerberg *et al* 1989, 1991).

Defect formation during x-irradiation was also found to be affected by high-level Mg doping. The usual radiation defects in undoped $LiNbO_3$ are Nb^{4+} electron centres and O^- trapped holes first described by Schirmer and von der Linde (1978). None of these centres could be produced by x-irradiating over-threshold crystals (see the review by Schirmer *et al* (1991)). This could be understood as proof that the Nb^{4+} centres were electron polarons trapped at Nb_{Li}.

No detailed model going beyond the picture of a hole trapped on an oxygen ion has been suggested for the O^- centre yet. In particular the question about the existence and identity of an additional nearby defect stabilizing the hole remains open. A partly

0953-8984/91/438457 + 09 $03.50

resolved hyperfine (HF) structure in the ESR line of the O^- centre in γ-irradiated $LiNbO_3$, also observed by Miki *et al* (1989), has been tentatively attributed to close Nb and Li neighbours of the oxygen ion (Corradi *et al* 1989). In the $LiNbO_3$ lattice each oxygen ion has two close Nb (at 1.9 and 2.1 Å) and two close Li (at 2.1 and 2.2 Å) neighbours (see, e.g., Abrahams and Marsh 1986). An alternative explanation of the same HF structure was given by Miki *et al* (1989) in terms of three equivalent Nb nuclei. These workers proposed a model with C_3 symmetry involving three oxygen ions with the three HF-active Nb ions situated at about 5.1 Å from each other. However, this would involve a rather strong delocalization of the hole in the lattice, contradicting the usually observed well localized character and hopping-type behaviour of holes in oxides (see, e.g., Schirmer and von der Linde 1978, and references therein).

Recently another trapped-electron centre appearing after γ-irradiation and subsequent partial UV bleaching has been described as an OH^{2-} ion by Rakitina *et al* (1990a). The centre has been observed in undoped or magnesium-doped (2 or 5 mol%) $LiNbO_3$ and in larger concentrations in vanadium-doped (1 mol%) crystals. Arguments for the OH^{2-} model are the isotropic g-factor (2.0028 ± 0.0005) and a doublet HF splitting ($A = 3 \pm 0.5$ mT) of the ESR line.

Most transition-metal dopants, in contrast with Mg, influence the low-temperature defect formation processes already at low dopant concentrations. The absolute and relative intensities of γ-ray-induced Nb^{4+} and O^- ESR spectra were found to vary considerably if transition-metal dopants with changeable valencies were present (Corradi *et al* 1989). As shown by ENDOR (Corradi *et al* 1990a, b, 1991), EXAFS (Zaldo and Agulló-López 1989, Catlow *et al* 1990) and PIXE–channelling measurements (Rebouta *et al* 1991), and also by semiempirical computer simulation studies (Donnerberg *et al* 1990, 1991), divalent and trivalent transition-metal ions usually substitute for Li. However, in the presence of Mg near or over the concentration threshold the same ions may substitute also for Nb (for Cr^{3+} see Corradi *et al* (1990b, 1991), and for Fe^{3+} see Böker *et al* (1990) and Feng Huixian *et al* (1990)). According to the calculations of Donnerberg *et al* (1990, 1991) in over-threshold crystals all divalent and trivalent cations including Mg itself preferentially form self-compensating pairs on neighbouring Nb and Li sites.

In the present ESR study, radiation defects in $LiNbO_3$:Mg containing Mg in higher concentrations (up to 8 mol%) have been investigated. In these crystals a new trapped-hole defect has been observed which can also be described as an O^--type centre. However, for the new centre the hole has a more or less resolved HF interaction with only one Nb neighbour, indicating that one close Nb neighbour (out of two) of the oxygen ion is replaced by Mg. Accordingly we use the notation O^-(Mg) for the new defect. The results are confirmed in $LiNbO_3$ double doped with Mg and Fe.

2. Experimental procedures

$LiNbO_3$:Mg and $LiNbO_3$:Mg:Fe crystals with dopant concentrations in the ranges $c_{Mg} = 0$–8 mol% and $c_{Fe} = 0.05$–0.08 mol% in the samples have been grown in air from congruent melts in the Research Laboratory for Crystal Physics of the Hungarian Academy of Sciences in Budapest. The dopant concentrations in the samples have been determined by atomic absorption analysis. Merck Suprapure Li_2CO_3 and Starck Specpure or Grade I Johnson–Matthey Nb_2O_5 materials and a balance-controlled Czochralski growth method (Schmidt and Voszka 1981) were used. The crystals have

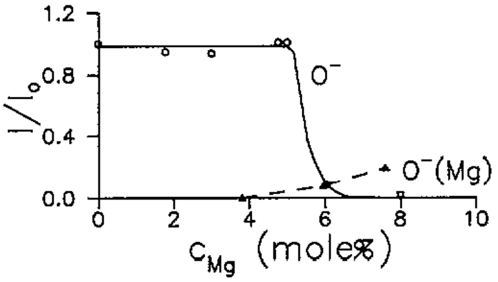

Figure 1. Dependence of the ESR intensities of trapped-hole centres at 77 K on the Mg concentration in γ-irradiated crystals: ○, O^- in $LiNbO_3$:Mg; □, $O^-(Mg)$ in $LiNbO_3$:Mg; △, $O^-(Mg)$ centres in $LiNbO_3$:Mg:Fe. The Fe concentration was 0.06 ± 0.01 mol%.

been exposed to a 10^5 Gy (10 Mrad) γ dose of a ^{60}Co source at 77 K and transferred without warming into the cold resonator of the ESR spectrometer. The latter was an SE/X-2544 Radiopan X-band spectrometer with 100 kHz modulation. The measurements were carried out in the temperature range between 15 and 300 K.

3. Experimental results

The dependence of the integral ESR intensity of O^- centres on the Mg concentration in γ-irradiated $LiNbO_3$:Mg crystals is shown in figure 1 (open circles). The O^- centres were accompanied by Nb^{4+} centres with an unchanged relative concentration. As seen in figure 1, after a plateau there is a sharp decrease in the ESR intensity (of both centres) near $c_{Mg} = 6$ mol%. The shapes of the ESR spectra were unchanged as long as these centres could be produced and were identical with those observed earlier in γ-irradiated undoped crystals (Corradi *et al* 1989). In crystals codoped with Fe, for $c_{Mg} < 4$ mol%, there was little change in the O^- production, however, instead of Nb^{4+} centres, Fe^{3+} centres assumed to be on the Li site were seen.

As indicated in figure 1, for $c_{Mg} = 8$ mol% in $LiNbO_3$:Mg and for $c_{Mg} \geqslant 6$ mol% in $LiNbO_3$:Mg:Fe new radiation-induced ESR spectra are observed. The (first-derivative) ESR spectra are shown for $LiNbO_3$:Mg in figure 2(*a*) for two special orientations of the magnetic field $\boldsymbol{B}$. (As usual, an x, y, z Cartesian coordinate system is used; the z axis is along the threefold c axis, and x is a non-piezoelectric direction perpendicular to c.) Apart from weak lines due to the Mn^{2+} impurity (Takeda *et al* 1968) the spectra are due to two different kinds of centre with overlapping ESR lines. At fields nearly corresponding to the free-spin g-value, transitions of the OH^{2-} centres (Rakitina *et al* 1990a) can be identified. All other lines belong to the new centre denoted $O^-(Mg)$.

The intensity of the $O^-(Mg)$ spectrum is much smaller than that of the O^- signal in undoped $LiNbO_3$ irradiated with the same dose. The estimated concentration of O^- centres corresponding to the plateau in figure 1 is of the order of 10^{20} cm^{-3}, and that of the $O^-(Mg)$ centres in $LiNbO_3$:Mg ($c_{Mg} = 8$ mol%) of the order of 10^{18} cm^{-3}. This is still too high for the new centre to contain some uncontrolled impurities.

The new lines can also be observed in γ-irradiated $LiNbO_3$:Mg:Fe, where they have a larger intensity (see figure 1) and the OH^{2-} spectrum does not appear. In this case, however, there is a strong interference from another spectrum (see the additional intense line in the central part of the spectrum shown in figure 2(*b*)) which can be ascribed to Fe^{3+} substituting for Nb (Sweeney *et al* 1985, Feng Huixian *et al* 1990, Böker *et al* 1990). This was the dominant Fe^{3+} defect in our over-threshold crystals both before and after γ-irradiation.

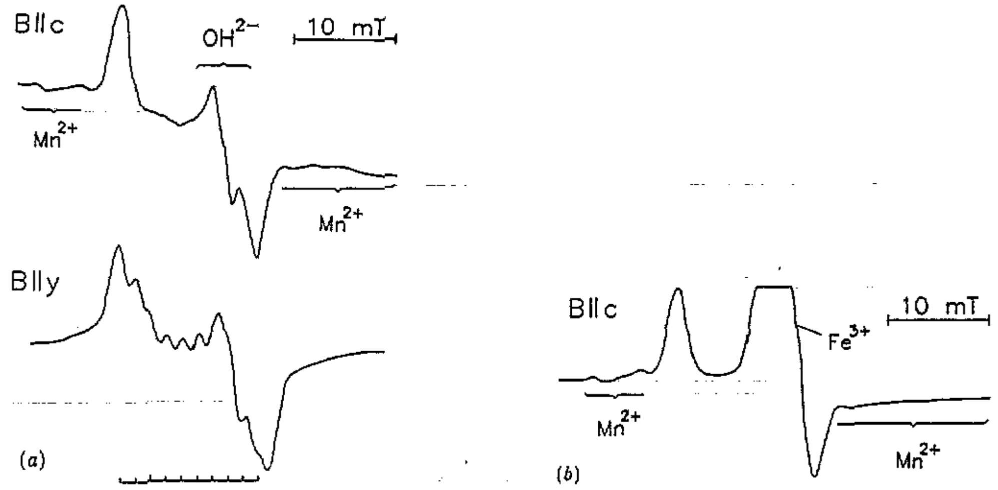

Figure 2. ESR spectra of the new trapped-hole centre measured at $T = 77$ K in (*a*) γ-irradiated $LiNbO_3$:Mg and (*b*) $LiNbO_3$:Mg:Fe for special orientations of the magnetic field $\boldsymbol{B}$. The Mg concentration in the samples was 8 mol% and 7.6 mol% respectively. The spectra of Mn^{2+}, OH^{2-} (also for $\boldsymbol{B} \parallel y$) and Fe^{3+} overlapping the O^-(Mg) signal and the partly resolved ^{93}Nb HF structure for the O^-(Mg) spectrum are indicated. Note that, for $\boldsymbol{B} \parallel y$, three different orientations of the centre yield spectra which are slightly shifted with respect to each other. This overlap prevents the exact assignment of HF components: the bars indicate the 1.5 mT periodicity of the structure.

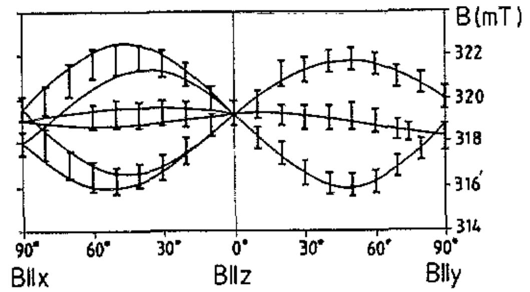

Figure 3. Angular dependence of ESR spectra of O^-(Mg) centres for the magnetic field rotating in the x–z and z–y planes in γ-irradiated $LiNbO_3$:Mg:Fe ($c_{Mg} = 7.6$ mol%). Each line position was determined as the average of the positions of the corresponding large maximum and minimum. For the x–z plane, only pairwise resolution of the lines was possible. The error bars represent experimental results; the full curves were simulated using the g-tensor data given in table 1.

The effect of the Fe codopant on the formation of radiation defects can be summarized as follows.

(1) Below the c_{Mg} threshold, Fe inhibits the production of Nb^{4+} centres.

(2) Above the threshold it enhances the concentration of O^-(Mg) centres and lowers the c_{Mg} threshold for their appearance but inhibits the production of OH^{2-} centres.

On the other hand, irradiation of over-threshold $LiNbO_3$:Mg:Fe crystals reduces the concentration of Fe^{3+} centres.

The ESR spectra clearly indicate that the O^-(Mg) centre is non-axial although the spectra corresponding to the six expected orientations of the centre are partly unresolved. The angular dependence of the corresponding field positions is shown in figure 3 for the magnetic field rotating in the x–z and z–y planes for the case of

Table 1. Eigenvalues and the direction cosines of the respective principal directions of the g-tensor and the splitting constant A due to the nearly isotropic hyperfine interaction of the hole with a ^{93}Nb nucleus for the new trapped-hole centre in over-threshold $LiNbO_3$: Mg. Estimated errors for g-values and direction cosines are ±0.01, and for the A-value ±0.2 mT.

		x	y	z
g_1	2.029	0.539	0.791	−0.290
g_2	2.049	−0.718	0.252	−0.648
g_3	2.006	0.440	−0.558	−0.704
A (mT)	1.5			

$LiNbO_3$: Mg : Fe. For the z–y-plane (which is a glide plane of the $LiNbO_3$ structure) the number of inequivalent orientations is reduced from 6 to 3. For $\boldsymbol{B} \parallel \boldsymbol{c}$ all orientations are equivalent. The same angular dependence is obtained also for over-threshold $LiNbO_3$: Mg. The angular dependence can be approximated by the spin Hamiltonian $H = \mu_B B g S$ with $S = \frac{1}{2}$ and C_1 symmetry. The eigenvalues of the g-tensor and the corresponding principal directions are given in table 1.

Each spectrum corresponding to a given defect orientation has a non-trivial shape and extends over a much larger region than the variations due to angular dependence. The main features are a sharp maximum at low fields and a similar minimum at high fields at about 14 mT apart (nearly independent of the orientation) whereas the central part remains flat (e.g. for $\boldsymbol{B} \parallel c$) or has a weak periodic structure (e.g. for $\boldsymbol{B} \perp c$). This non-trivial 'lineshape' can be understood to arise from the overlap of approximately ten weakly resolved equidistant HF components with equal intensities, each component having a simple first-derivative Gaussian-like lineshape. The positive half of the first component and the negative half of the last one are only weakly affected by the overlap and remain as sharp features, while the whole central part of the spectrum is smeared out with only some reminiscence of the HF structure, the resolution depending on the component linewidth. Such lineshapes have been simulated by Müller (1989) for various component linewidths.

In our case the overlap of lines belonging to different orientations and the presence of other ESR spectra make it still more difficult to discern the HF structure. Nevertheless in the cases where the periodic structure of the central part is observed (see the $\boldsymbol{B} \parallel y$ spectrum in figure 2(a)) a spacing of at about 1.5 mT of the HF components is indicated. The periodic structure is not affected by the HF lines of Mn^{2+} which have a different spacing and are weaker for the orientations in question. The observed spacing, compared with the spacing between the sharp features (14 mT), supports the assumption that the number of HF components is approximately ten (10 ± 1).

This HF structure may be due to a single nucleus with a natural abundance close to 100% and a nuclear spin of approximately $I = \frac{9}{2}$. The only reasonable choice is the ^{93}Nb nucleus ($I = \frac{9}{2}$, 100%) since all other candidates with $I = \frac{9}{2}$, i.e. ^{115}In and ^{209}Bi, are known to be present at most at the parts-per-million level and nuclei having $I = 4$ or 5 with appreciable natural abundances do not exist. The linewidth of the HF components can be estimated from the lineshape of the sharp features at both ends of the $\boldsymbol{B} \parallel \boldsymbol{c}$ spectra and is found to be 2 ± 0.5 mT. This broadening may be due to unresolved HF interaction with Li and further Nb nuclei.

The results of thermal annealing experiments for the O^-(Mg) centre in $LiNbO_3$: Mg : Fe are shown in figure 4. As seen, the centre decays in the interval

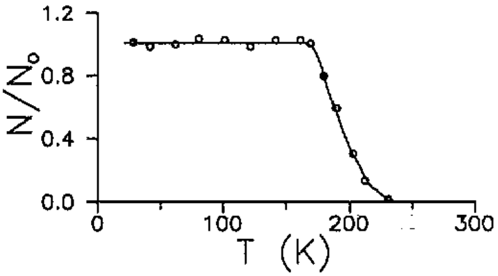

Figure 4. Isochronal thermal anneal results for the O^-(Mg) centre in $LiNbO_3$:Mg:Fe (c_{Mg} = 7.6 mol%) determined by ESR. The sample was kept for 10 min at each annealing temperature and quenched to T = 77 K for the measurements. The data points below 77 K are the results of measurements at those temperatures but are adjusted for the different Boltzmann populations of spin levels.

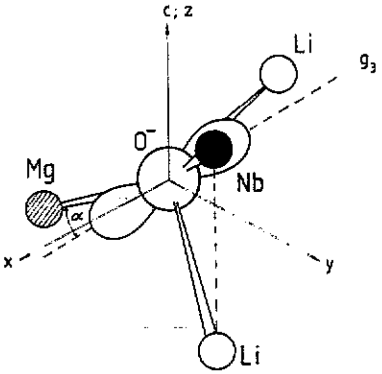

Figure 5. Model of the O^-(Mg) centre in over-threshold $LiNbO_3$:Mg.

170–230 K, i.e. it is more stable than the O^- centre which has been found to decay already near 150 K, almost independent of the energy of photons used for irradiation (Sweeney *et al* 1985, Miki *et al* 1989), or at still lower temperatures in crystals with c_{Mg} very close to the threshold (Sweeney *et al* 1985). The lineshape of the O^-(Mg) ESR signal is almost independent of the temperature up to the decay of the centre.

The O^-(Mg) centre was found to decay also as a result of UV irradiation at 77 K. There was a large decrease in the ESR intensity after UV irradiation for only a few minutes, similarly to the case of O^- centres (Rakitina *et al* 1990a). There was a much smaller decrease in the OH^{2-} intensity upon UV irradiation at 77 K.

4. Discussion

The positive *g* shifts of the new centre (see table 1) indicate that the involved radiation defect has a hole character. This is in agreement with the observation that they appear together with trapped-electron centres such as the OH^{2-} centres in $LiNbO_3$:Mg. In $LiNbO_3$:Mg:Fe, the generation of the new radiation defect is accompanied by the disappearance of some of the Fe^{3+} centres. This can be attributed to partial transformation into Fe^{2+} centres (still predominantly on Nb sites) again as a result of electron capture. The average *g*-value of the new centre is 2.028 which coincides within experimental error with the *g*-value of 2.03 found for O^- centres in $LiNbO_3$ (Schirmer and von der Linde 1978). Such a value, together with the observed anisotropy, is characteristic for O^- centres in oxides (for alkaline-earth oxides see the recent review of Chen and Abraham (1990) and for Al_2O_3 see Cox (1971)). Thus we conclude that the new centre is also a trapped hole essentially localized on a single oxygen ion.

For the O^-(Mg) centre an important HF interaction with only one Nb neighbour is observed. This should be contrasted with the case of the O^- centre where important HF interactions with two Nb neighbours have to be assumed (Corradi *et al* 1989). The width of the O^-(Mg) ESR signal (between the prominent features at both ends of the spectrum) is roughly equal to the half-width of the O^- ESR signal (which is approximately Gaussian). Therefore it is straightforward to assume that both centres have similar electronic structures; however, for the O^-(Mg) centre the Nb site nearest to the central oxygen is vacant or substituted by a non-magnetic impurity.

Nb vacancies or defect complexes comprising such vacancies are considered to be energetically unfavourable for over-threshold Mg concentrations (Donnerberg *et al* 1991). However, for Mg concentrations well above the threshold, Mg^{2+} is assumed to occupy not only Li^+ but also Nb^{5+} sites and partial self-compensation in the form of Mg_{Li}–Mg_{Nb} pairs is expected (Donnerberg *et al* 1990, 1991).

Accordingly, let us consider that the hole is trapped at Mg_{Nb}. Mg has only one isotope with non-zero nuclear spin (^{25}Mg; $I = \frac{5}{2}$; natural abundance, 10.12%), the majority of the Mg nuclei being non-magnetic. The effect of the ^{25}Mg isotope would be to add for each line of the ESR spectrum due to non-magnetic Mg a sextet of equidistant satellites 53 times smaller. These satellites are not expected to be resolved for several reasons. First ^{25}Mg has a nuclear g-factor four times smaller and a smaller spin than ^{93}Nb. No resolved ^{25}Mg HF splitting has been observed for the related Mg_{Al} trapped-hole centre in Al_2O_3 for an ESR half-width of approximately 4 mT either (Cox 1971, Du Varney *et al* 1985) and a ^{25}Mg HF constant of only 1.1 mT has been observed for the H^- centre in MgO (Orera and Chen 1987).

Thus for the new centre we propose the model of a hole trapped at an oxygen ion which has its nearest Nb neighbour replaced by a Mg^{2+} ion (figure 5) even if we have no direct evidence for the presence of Mg in this position.

Possibly another (or even two) Mg ions substituting for Li are also associated with the centre. For lack of information, only Mg_{Nb} is included in figure 5. The Li sites in the immediate vicinity of the hole would probably not be replaced by Mg owing to the positive effective charge of Mg_{Li}. Mg_{Nb} has a (nominal) threefold negative charge with respect to the perfect lattice which explains the high thermal stability of the centre even if other compensating defects, e.g. Mg_{Li}, are also present. Without additional Mg ions or other defects the usual notation of such a centre would be $[Mg_{Nb}]^{2-}$. As an alternative notation which avoids the problem of additional charge compensation we propose O^-(Mg).

For such a model the hole orbital is expected to point approximately towards the charge-compensating Mg_{Nb} defect, i.e. the angle α shown in figure 5 should be small. The orientation of the hole orbital is given by the g_3 direction (see, e.g., Tohver *et al* 1972). Starting from the g_3 direction given in table 1 and choosing out of the six possible defect orientations the one minimizing the angle α, we obtain $\alpha = 19 \pm 3°$. This value is reasonably small taking into account the C_1 symmetry of the defect and the fact that relaxational displacements have been neglected.

The role of the Fe dopant in the production of radiation defects seems to be partly changed in over-threshold crystals. Unlike the case of low magnesium levels, above the c_{Mg} threshold Fe enhances the formation of O^--type trapped holes, while electron trapping (at other than Fe sites) is inhibited in both cases. These facts indicate that in over-threshold crystals a new, more efficient hole trap, in our opinion Mg on Nb site, whose concentration may in addition be enhanced by Fe co-doping, is available. However, Fe^{3+} continues to be the most efficient electron trap above the threshold, notwithstanding its apparently changed substitution site. This seeming controversy may be resolved if charge compensating defects near to various Fe centres and/or Fe ions in higher charge states are taken into account.

An alternative model for the new trapped-hole centre where the O^- ion is stabilized by a nearest-neighbour Li vacancy has also been considered. This is the model originally discussed by Schirmer and von der Linde for trapped holes in undoped $LiNbO_3$. For that model to explain the new ESR spectrum, one had to assume that the Li vacancy oriented the hole orbital in such a way that for one of the two close Nb neighbours a cancellation of HF contributions took place. Moreover, for that model it is not clear why the centre is formed only for very high Mg concentrations where the concentration of Li vacancies is small compared with other regions of c_{Mg} (Donnerberg *et al* 1991).

The pronounced anisotropy of the *g*-tensor and the very weak temperature dependence of the ESR linewidth indicate that the hole in the new centre has a static behaviour. This is in contrast with the case of the O^- centre where an almost isotropic *g*-tensor (Schirmer and von der Linde 1978) and strong temperature broadening with a characteristic temperature of 10 K (Rakitina *et al* 1990b) is observed. This difference in behaviour can be explained as a motional effect for the O^- centre similarly to the case of O^- centres in alkaline-earth oxides (Tohver *et al* 1972). For the O^-(Mg) centre the hole is apparently more deeply trapped, and/or near to Mg_{Nb} there are possibly no equivalent oxygen sites for the hole. An isolated Mg_{Nb} would have C_3 symmetry but a specific oxygen site might be preferred owing to the presence of an additional defect, e.g. Mg_{Li}.

5. Conclusion

Radiation defects in heavily Mg-doped $LiNbO_3$ crystals have been found to be different from those observed in undoped or weakly Mg-doped crystals. One of the defects can be described as a new O^--type trapped hole centre where the hole is stabilized next to a magnesium ion substituting for Nb. Fe codoping is found to enhance the production of the new hole trap in contrast with the case of under-threshold crystals. Fe also inhibits the production of other trapped-electron centres both below and above the threshold.

Acknowledgments

This work was supported by the National Scientific and Research Fund of Hungary (OTKA). One of the authors (GC) is grateful to Professor Schirmer and Dr Donnerberg for discussions on related topics. Thanks are also due to Dr Watterich and Dr Kovács for useful suggestions concerning the manuscript.

References

Abrahams S C and Marsh P 1986 *Acta Crystallogr.* B **42** 61

Böker A, Donnerberg H, Schirmer O F and Feng Xiqi 1990 *J. Phys.: Condens. Matter* **2** 6865

Bryan D A, Gerson R and Tomaschke H E 1984 *Appl. Phys. Lett.* **44** 847

Catlow C R A, Donnerberg H, Schirmer O, Tomlinson S M and Cole M 1990 *Radiat. Eff. Defects Solids* at press

Chen Y and Abraham M M 1990 *J. Phys. Chem. Solids* **51** 747

Corradi G, Polgár K, Zaritskii I M, Rakitina L G and Deryugina N I 1989 *Fiz. Tverd. Tela* **31** 115 (Engl. Transl. 1989 *Sov. Phys.–Solid State* **31** 1540)

Corradi G, Söthe H, Spaeth J-M and Polgár K 1990a *J. Phys.: Condens. Matter* **2** 6603

—— 1990b *Radiat. Eff. Defects Solids* at press

—— 1991 *J. Phys.: Condens. Matter* **3** 1901

Cox R T 1971 *Solid State Commun.* **9** 1989

Donnerberg H, Tomlinson S M and Catlow C R A 1991 *J. Phys. Chem. Solids* **52** 201

Donnerberg H, Tomlinson S M, Catlow C R A and Schirmer O F 1989 *Phys. Rev.* B **40** 11909

—— 1990 *Radiat. Eff. Defects Solids* at press

Du Varney R C, Niklas J R and Spaeth J-M 1985 *Phys. Status Solidi* b **128** 673

Feng Huixian, Wen Jinke, Wang Huafu, Han Shiying and Xu Yunxia 1990 *J. Phys. Chem. Solids* **51** 397

Miki T, Hantehzadeh M R and Halliburton L E 1989 *J. Phys. Chem. Solids* **50** 1003

Müller H 1989 *Diplomarbeit* Osnabrück

Orera V M and Chen Y 1987 *Phys. Rev.* B **36** 5576

Rakitina L G, Zaritskii I M and Polgár K 1990a *Appl. Magn. Res.* **1** 149

Rakitina L G, Zaritskii I M, Corradi G and Polgár K 1990b *Fiz. Tverd. Tela* **32** 1112 (Engl. Transl. 1990 *Sov. Phys.–Solid State* **32** 652)

Rebouta L, Da Silva M F, Soares J C, Hage-Ali M, Stoquert J P, Siffert P, Sanz-Garcia J A, Diéguez E and Agulló-López F 1991 *Europhys. Lett.* **14** 557

Schirmer O F, Thiemann O and Wöhlecke M 1991 *J. Phys. Chem. Solids* **52** 185

Schirmer O F and von der Linde D 1978 *Appl. Phys. Lett.* **33** 35

Schmidt F and Voszka R 1981 *Cryst. Res. Technol.* **16** K127

Sweeney K L, Halliburton L E, Bryan D A, Rice R R, Gerson R and Tomaschke H E 1985 *J. Appl. Phys.* **57** 1036

Takeda T, Watanabe A and Sugihara K 1968 *Phys. Lett.* **27A** 114

Tohver H T, Henderson B, Chen Y and Abraham M M 1972 *Phys. Rev.* B **5** 3276

Zaldo C and Agulló-López F 1989 *Solid State Commun.* **71** 243

Zhong G G, Jin J and Zhong-Kang W 1980 *Proc. 11th Int. Quantum Electronics Conf.* (New York: IEEE) p 631