New axial Fe^{3+} centres in stoichiometric lithium niobate crystals

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Abstract. Two new axial Fe^{3+} centres, arising after reduction of stoichiometric lithium niobate crystals grown from melts containing K_2O, were discovered and investigated by EPR. Their b_2^0 crystal field parameters are equal to 495 and 688 ($\times 10^{-4}$ cm^{-1}) and are thus much smaller than b_2^0 for the axial Fe_{Li}^{3+} centre, 1660×10^{-4} cm^{-1}, which had been studied before. The models of Fe^{3+} centres in lithium niobate and lithium tantalate crystals are compared and the possible structures—Fe_{Nb}^{3+} and Fe_{Nb}^{3+}–K_{Li}—of the new centres are discussed.

1. Introduction

It is known that iron plays a key role in the photorefractive effect of lithium niobate (LN) and its applications [1–3]. Therefore Fe has been investigated intensively, mostly with EPR, in undoped LN crystals as well as in LN codoped, for instance, with Mg [4] or Zn [5]. The centre studied in most detail is axial Fe^{3+} in pure LN [6–11], called Fe1 in the following. Its spectroscopic parameters at room temperature ($g = 1.995$, $b_2^0 = 1660$, $b_4^0 = -43$, $b_4^3 = 560$ ($\times 10^{-4}$ cm^{-1})) were obtained long ago [6]. Several attempts have been made to determine the location of Fe^{3+} in the lattice [7, 9–11]. Here the difficulty arises that there are three positions in the LN structure with the same axial C_3 symmetry: the Li and Nb sites and the structural vacancy. EPR and optical methods cannot distinguish these positions. Only recently it was proved that Fe^{3+} substitutes for Li^+ [12–14], slightly perturbed by some local disorder among the neighbours of this site, most probably an unknown defect being present in the first Li sphere [14].

Pure LN grown from a melt with congruent or even stoichiometric composition contains a high concentration of intrinsic defects, n_{def}, and it is possible to find among them an intrinsic compensator for the excess (Fe_{Li+}^{3+})˙ charge, for example an Li vacancy, $(V_{Li+})'$. With respect to the existence of V_{Li+} in LN see, e.g. [15] and [16]. The situation is changed when we deal with LN heavily doped with Mg, which after replacing all Nb_{Li} antisite defects of the lattice enters at Li as well as at normal Nb sites [16]. In such crystals another more complicated spectrum of Fe^{3+} arises (labelled Fe2 in the following) [4], which for $B \parallel c$ and 34 GHz shows crystal-field splittings about half as large as those of Fe1 [17]. However, the symmetry of this centre is lower than C_3 [18], and its complete structure has not yet been determined.

Recently we discovered [19, 20] that crystals which were grown from a congruent melt, to which 6 wt% K_2O had been added (such crystals will be called LN 6K in the following) have the following surprising features [20]. (1) K enters the crystals only in very small

quantities. Its concentration in the crystal is about 10^{-2} wt%. (2) The Li content of such crystals, $x_c = [Li]/([Li]+[Nb])$, is 0.500 ± 0.0015. They thus can be considered to be stoichiometric†. Consequently n_{def} is much smaller than in material grown in the conventional way. This leads to essential changes of the Fe1 spectra: the intensities of the forbidden lines decrease; the allowed ones become much more narrow, and the asymmetry of all lines is lowered. Because of these reasons finer details of the spectra can be resolved than has been possible so far.

The present work is devoted to the EPR investigation of two new axial Fe^{3+} centres, which arise in LN 6K after slight reduction.

2. Crystals

The specimens studied had been grown, using the Czochralski method, from melts with a nearly congruent composition, $x_m = 48.6\%$, to which 6 wt% K_2O had been added. The K content [K] of these specimens was determined with an electron microprobe to be 0.022 $\pm$ 0.004 wt% [20]. The error range represents the limit of K detectivity. This newly determined K concentration is in accord with that found previously [19] using different methods: $[K] \lesssim 10^{-2}\%$. All crystals studied here were nominally pure, but as usual, they contain Fe as a trace impurity. The reduction was performed by embedding the crystals into Li_2CO_3 powder and heating in vacuum for 6 h at 500 °C. It is remarkable that only a faint greyish tint of the crystals is caused by these conditions, whereas they lead to almost black coloration in congruent specimens, having a high n_{def}. This is in accord with the model [21] that reduction of congruent material proceeds by filling cation vacancies of the lattice with the Li and Nb ions left over when O leaves the crystal. Such intrinsic defects are absent in stoichiometric material. All EPR spectra were measured with a Bruker ER 200 spectrometer at about 9 GHz and 25–30 K. The Fe^{3+} ESR signals could also be observed at room temperature. We chose the indicated low temperatures because the lines then were about 20% narrower. Care was taken not to saturate the resonances.

3. The EPR spectra and their evaluation

After reduction the EPR spectra of defects in LN crystals generally differ from those before; most of the Fe_{Li}^{3+} ions (Fe1) are recharged to Fe_{Li}^{2+}. Using conventional spectrometers, the EPR of this charge state is not observed. Recently it was identified, however, using the technique of thermally detected EPR [22]. Also in LN 6K Fe1 centres were found before reduction. After this treatment they had partly vanished. Instead new signals arose, their spectra being exhibited for $B \parallel c$ in figure 1.

Figures 2 and 3 show the angular dependences of the resonance fields of Fe1 as well as of these two new centres, designated Fe3 and Fe4. Using the program package 'R-spectr', developed by one of the authors (VG), the angular patterns were reproduced by assuming two $S = 5/2$ centres described by the spin Hamiltonian

$$\mathcal{H} = \beta(g_{00}\{BS\}_0^0 + g_{20}\{BS\}_2^0) + b_2^0 O_2^0 + b_4^0 O_4^0 + b_4^3 O_4^3 + c_4^3 \Omega_4^3. \tag{1}$$

† Such crystals have to be distinguished from specimens grown from melts with $x_m > 0.5$, which are often claimed to be stoichiometric. This is not the case, as has recently been shown [20], e.g. for a crystal produced from a melt with $x_m = 0.545$, x_c was found to be only 0.495.
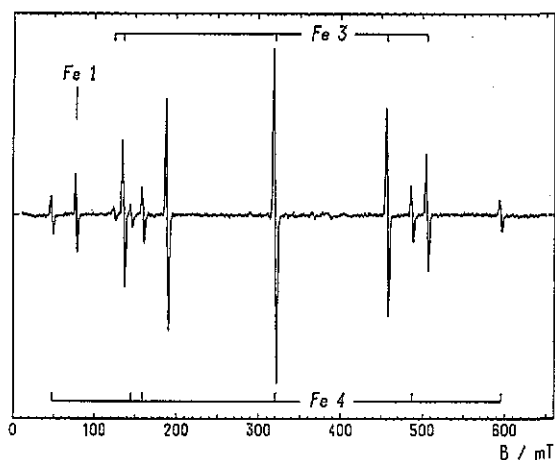
Figure 1. EPR spectra of Fe^{3+} in an LN 6K crystal after reduction. $B \parallel c$; microwave frequency 9.018 GHz; $T = 25$ K. Only the strongest line of Fe1 is indicated.
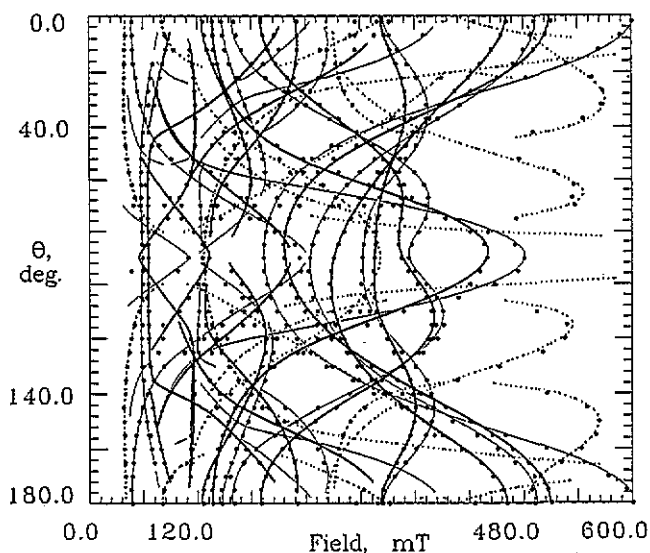

Figure 2. Angular dependence of the Fe^{3+} EPR lines in reduced LN 6K. ZX plane. Points, experimental data; dotted (Fe1), bold (Fe3) and fine (Fe4) curves, dependences calculated using the spin-Hamiltonian parameters of table 1.

Here the isotropic and axial parts of the $\mathbf{g}$ tensor are defined by $g_{00} = (g_{xx} + g_{yy} + g_{zz})/3$ and $g_{20} = (2g_{zz} - g_{xx} - g_{yy})/6$. The $\{BS\}_k^q$ are the corresponding irreducible tensor operators; x, y, z, the orthohexagonal crystallographic axes.

We point out that LN (space group symmetry $R3c$) has two LiNbO$_3$ molecules in its elementary cell. They are transformed into each other by reflection in the glide mirror plane of the structure (zy plane). This means that each axial centre, say I, has an electrically, but not magnetically equivalent partner, II. The spin-Hamiltonian parameters of these centres are equal with respect to their absolute values, but b_4^3 (I) $= -b_4^3$ (II), because the x axis of I is turned into $-x$ for II by reflection in the zy plane. The presence of two magnetically non-equivalent centres in the LN structure leads to a splitting of the EPR lines in the zx plane if the magnetic field deviates from the z axis. In the zy plane the lines of both centres always coincide, but the c_4^3 term creates some asymmetry of the angular dependences, related to the change of polar angle from ϑ to $180° - \vartheta$. The knowledge of these features of the EPR spectra in LN helps to identify the lines of different centres, if simultaneously present in the same crystal. These circumstances have often been ignored in EPR studies of LN because
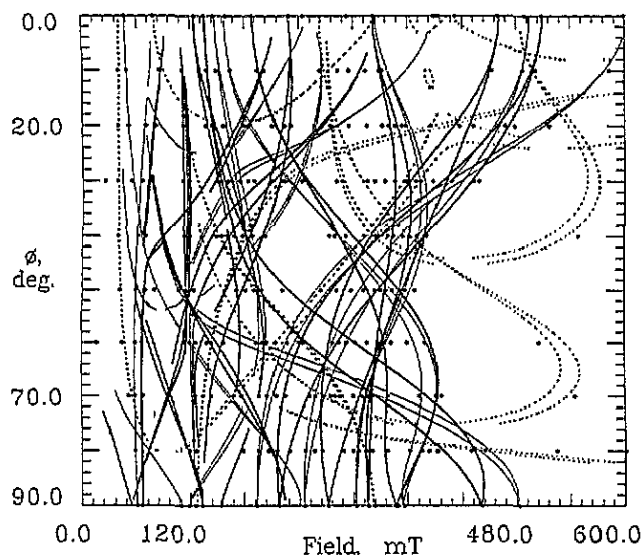
Figure 3. Angular dependence of the Fe^{3+} EPR lines in reduced LN 6K. ZY plane. Points, experimental data; curves, theory for Fe1 (dotted), Fe3 (bold) and Fe4 (fine).

so far all observed lines have been rather wide, and therefore it was difficult to distinguish these splittings and the very small asymmetry of their angular dependences. In LN 6K we have lines up to ten times narrower than in congruent LN [20]; for this reason the splittings and asymmetries are clearly seen (figures 2 and 3). All new lines have been accounted for by assuming the presence of two axial centres, Fe3 and Fe4. The corresponding spin-Hamiltonian parameters are listed in table 1 together with those of the old Fe1 centre. It should be noted that the latter has only partly been determined previously at the low temperatures used here, 25–30 K [17]. The EPR parameters differ considerably from those found at room temperature.

Table 1. Spin-Hamiltonian parameters of Fe^{3+} centres in LN 6K at 25 K (crystal-field parameters in 10^{-4} cm^{-1}; the sign of b_2^0 was not determined). For the mirror partner b_4^3 has the opposite sign.

Centre	Parameter					
	g_0^0	g_2^0	b_2^0	b_4^0	b_4^3	c_4^3
Fe1	1.995	0.012	1768	−49	650	−380
	±0.002	±0.002	±20	±5	±50	±50
Fe3	2.005	−0.001	495	−59	−1400	860
	±0.002	±0.002	±2	±2	±50	±50
Fe4	2.004	−0.004	688	−41	420	380
	±0.002	±0.002	±2	±2	±50	±50

4. Discussion

Both new centres contain Fe^{3+} ions as indicated by their spin, $S = 5/2$, and by the omnipresence of Fe even in undoped LN crystals. All differences between their characteristics must be caused by variations in the arrangement of the ions in the first or second shell around Fe^{3+}. For at least one of the centres an additional defect must be

present on the same crystal axis as the Fe^{3+} ion. These new centres were observed for the first time in the crystals LN 6K investigated here; they were not present in LN specimens grown in the convential way, independent of their reduction or other treatments. Two possibilities for the assignment of the centres will be discussed.

(1) Nominally pure LN crystals always have unintended background impurities such as, for example, hydrogen, tantalum, carbon, silicon etc [2]. This is partly due to contamination during the crystal growth, partly to the limited purity of the starting materials. Such background ions, X, might create complexes such as Fe$_{Li}$–X$_{Nb}$, Fe$_{Nb}$–X$_{Li}$ or Fe$_{Nb}$–X$_V$. Since the incorporation of extrinsic ions in the structural vacancy V is energetically unfavourable [16], however, the latter model probably does not apply. The corresponding signals could possibly be registered only in LN 6K because of their small EPR linewidths in this material, see above, and the corresponding high peak-to-peak intensities.

(2) In our opinion the following model is more likely: Fe3 and Fe4 are, respectively, Fe$_{Nb}^{3+}$ and Fe$_{Nb}^{3+}$–K$_{Li}^+$ or Fe$_{Nb}^{3+}$–K$_V^+$ complexes. All these centres have axial symmetry if the K ion sits at the sites of an axially related Li ion or—less likely—of a structural vacancy. Although the concentration of K in the crystal, $\sim 10^{-2}$ wt% K$_2$O, is much less than in the melt, it is larger than the iron concentration, generally below 100 ppm in nominally undoped crystals. Thus the formation of Fe–K complexes is probable in principle. In stoichiometric material the intrinsic defects compensating (Fe$_{Li}^{3+}$)$^{··}$ in congruent crystals are absent and self-compensation by (Fe$_{Nb}^{3+}$)$''$ is then expected to be the dominant mechanism. Using shell model calculations, Donnerberg *et al* [16, 23] have shown that this is indeed the energetically most favorable compensation in the absence of intrinsic defects. Otherwise compensation by intrinsic defects is predicted [16, 23], in accord with the present findings.

This picture must be differentiated, however, on the basis of the observation that Fe3 and Fe4, of which one is likely to be Fe$_{Nb}^{3+}$, are present only after reduction, certainly originating from (Fe$_{Nb}^{4+}$)$'$, a charge state reasonable for Fe$_{Nb}$ but not for Fe$_{Li}$. So self-compensation of Fe1 in stoichiometric material appears to be achieved rather by the corresponding concentration of Fe$_{Nb}^{4+}$. It can be excluded that the rise of Fe3 or Fe4 and the decrease of Fe1 under reduction are caused by a change of Fe$_{Li}^{3+}$ (Fe1) to an Nb site. The low annealing temperature (500 °C) makes this change of sites unlikely. It can rather be assumed that Fe$_{Li}^{2+}$ is formed, as observed also in congruent material.

A discussion of the crystal-field parameters of the Fe1 defect in LN and in the isostructural lithium tantalate (LT) is appropriate here. For both materials it was established by ENDOR measurements [14, 24] that in non-stoichiometric crystals this defect is Fe$_{Li}^{3+}$, in LN possibly associated with a defect in the first-nearest Li sphere (probably with (V$_{Li}$)$'$ as a charge compensator, (Nb$_{Li}$)$^{4+}$ having the wrong charge). From NMR data [25] we know that the electric field gradient at the Li site (EFG(Li)) is nearly three times smaller than EFG(Nb) in LN and about 0.7 times EFG(Li) in LT. The axial field parameters, b_2^0, and the quadrupole interactions, eqQ, of a (3d)^5 ion with an S ground state at these positions should be proportional to the corresponding EFGs, *if isovalent replacement without further lattice perturbation takes place*. This consideration was used for a previous determination of the lattice site of Fe1 [9, 10]. By comparing the EFGs expected for Fe^{3+} nuclei—assuming that these ions substitute exactly at the Li and Nb sites in LN—with those determined from the quadrupole splittings of the Fe^{3+} Mössbauer spectra [10] it was concluded that Fe1 represents Fe^{3+} replacing Nb in LN. As a crosscheck the expected and measured EFGs for Fe^{3+} in Al$_2$O$_3$, for which it is known that Fe^{3+} replaces Al^{3+}, were also compared. The recent definite proofs that Fe^{3+} is found instead at an Li$^+$ site in LN [12–14] show that for substitutions with charge misfits these simple considerations about the eqQ or b_2^0 parameters

are not valid. This is also supported by the fact that the ratio of the b_2^0 values of Fe_{Li}^{3+} in LN and LT (1660×10^{-4} cm^{-1} [6] and 3300×10^{-4} cm^{-1} [24], respectively) differs considerably from the ratio of EFG(Li), ~ 0.7 (see above), in these compounds. For the new Fe3 and Fe4 centres, related to Fe_{Nb}^{3+}, we obtain values of b_2^0 which are less than for Fe_{Li}^{3+} (Fe1). It is seen now that the influence of the charge misfits has to be taken into account. $(Fe_{Nb}^{3+})''$, being negatively charged with respect to the lattice, will repel its O^{2-} neighbours, decreasing the components of the crystal field, including b_2^0, whereas $(Fe_{Li}^{3+})''$ will attract O^{2-}, increasing b_2^0. Smaller crystal-field splittings than for Fe_{Li}^{3+}, although not yet definitely determined, are also characteristic for the centre Fe2 [17], appearing in strongly Mg doped material. This supports the assumption [17, 18] that Fe2 also corresponds to Fe_{Nb}^{3+}, associated, however, with Mg in a way not yet established.

We expect that a systematical investigation of paramagnetic defects in stoichiometric LN (such as LN 6K) can help to solve defect assignments in conventionally grown LN crystals, including those containing Mg or Zn.

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