EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

# Addendum to the ISOLDE and Neutron Time-of-Flight Committee

# IS453: Emission Channeling lattice location experiments with Short-Lived Isotopes

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**(The EC-SLI collaboration)**

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**Abstract**

The detailed structure of possible acceptor impurities in nitride semiconductors has been heavily debated ever since the realization of *p*-type GaN by means of Mg doping by Nakamura in 1992.
The installation of an on-line Emission Channeling setup for Short-Lived Isotopes (EC-SLI) at ISOLDE, together with the availability of clean Mg and Be beams has for the first time offered opportunities to directly investigate the structural properties of Mg and Be impurities in III-nitrides, which is not possible by any other experimental method.
We propose to continue our lattice location studies of the acceptor dopants Mg and Be in GaN and AlN using the $\beta^-$ emission channeling technique with the short-lived probes $^{27}$Mg (9.5 min) and $^{11}$Be (13.8 s). A lattice location precision around 0.05 Å will allow to provide support for or refute various theoretical models which e.g. have predicted displacements of the Mg atom from the ideal substitutional Ga and Al sites of the order of 0.2-0.3 Å or higher.
Among the new experiments proposed are implantation and lattice location at low-temperatures, and studies of *p*-type GaN and of hydrogenated GaN samples.

**Requested shifts (in total)**: **15 (4.5 old + 10.5 new shifts)**

This Addendum follows the status report INTC-SR-collections-IS453.

## 1. Motivation of the addendum, experimental setup and technique

The detailed structural incorporation of possible acceptor impurities in nitride semiconductors has been heavily debated ever since the realization of *p*-type GaN through Mg doping by Nakamura in 1992 [1], a discovery which subsequently allowed impressive progress in nitride-based electronic and optoelectronic devices. However, the electrical activation of Mg often remains poor. In order to act as an acceptor, Mg needs to occupy the substitutional III site ($Mg_{Ga}$) and not be part of an electrically inactive complex.

For many of the possible configurations in which Mg and Be can be found in the nitrides (both electrically active and inactive), structural relaxations have been theoretically predicted which involve the dopant itself and/or the surrounding atoms moving off the ideal lattice sites. For instance, a variety of configurations have been considered for complexes consisting of Mg and H [2-9], some of them involving Mg displacements as high as 0.75 Å. Relaxations up to 0.39 Å are also assumed in the electrically inactive complexes $Mg_{Ga}$–$V_N$ between $Mg_{Ga}$ and a neighbouring nitrogen vacancy $V_N$ [9-11]. Besides the breakup of Mg–H complexes, the dissociation of $Mg_{Ga}$–$V_N$ has been suggested as an alternative explanation for the effect of annealing in the electrical activation of Mg [9,12].

Triggered by spectroscopic results that proposed the existence of several Mg-related acceptors in GaN with different ionization energies [13-17], there has recently been renewed strong interest in understanding the exact microscopic structure of Mg and Be in the nitrides. Theoretical models were put forward that predict that the neutral charge states of these group II dopants are characterized by lattice relaxations up to 0.3 Å which are absent in the ionized state [18-21], classifying them as “polaronic acceptors”.

In stark contrast to the various refined but often contradictory theoretical models, until recently no experimental data at all existed concerning the detailed lattice site of Mg or Be in III-nitrides. The commonly used ion beam lattice location method of Rutherford Backscattering /Channeling (RBS/C) is not applicable in this case since the impurities are lighter than the host atoms. Attempts to use the Extended X-ray Absorption Fine Structure (EXAFS) technique to measure the distances from Mg to its nearest neighbors in GaN were not successful since the Mg K X-ray absorption edge overlaps with the Ga L-line [22].

The installation of our on-line Emission Channeling setup for Short-Lived Isotopes (EC-SLI) at ISOLDE, together with the availability of clean $^{27}$Mg and $^{11}$Be beams offers unique opportunities to investigate for the first time directly the ***structural properties*** of Mg and Be impurities in nitrides, which is not possible by any other experimental method, and in particular to confirm or reject possible displacements of these two acceptors. The current status of the EC-SLI on-line emission channeling chamber has been documented in a recent publication in Rev. Sci. Instr. [23]. It is equipped with a high-precision “Panmure” 3-axis goniometer with *x*,*y*,*z* translation stage, in-situ sample annealing up to 900°C, a closed-cycle He refrigerator for sample cooling to 50 K, and a fast Si pad detector, which allows for position-sensitive detection of electrons at count rates up to ~5 kHz. Precise identification of the lattice location is achieved by fitting the experimental $\beta^-$ emission yields with theoretical patterns simulated for several sites displaced e.g. with a step width of 0.05 Å.

## 2. Addendum

Our emission channeling measurements of $^{27}$Mg in GaN and AlN are the first lattice location experiments of Mg in nitride semiconductors. They clearly showed that the large majority of ion implanted Mg is incorporated on Ga or Al sites. However, following room temperature implantation also interstitial fractions of 23% (AlN, Fig. 1, recently published in Appl. Phys. Lett. [24]) and 26% (GaN) near the octahedral O sites could be identified. Implantation temperatures above 400°C in AlN or above 600°C in GaN resulted in complete conversion of the interstitial fraction to substitutional Al or Ga sites, from which we were able to estimate the activation energy for the migration of interstitial Mg to be around 1.1-1.7 eV in AlN and 1.6-2.6 eV in GaN. Besides providing first experimental evidence for the existence of interstitial Mg, we could thus also show that theoretical predictions for its migration energy to be only 0.15-0.68 eV in GaN [25] are inaccurate. We found no evidence for displacements of $^{27}$Mg from ideal Al or Ga sites larger than 0.1 Å (thus no confirmation for any large displacement model). However, the interstitial positions are as yet only determined within a precision of ~0.3 Å (Fig. 2).

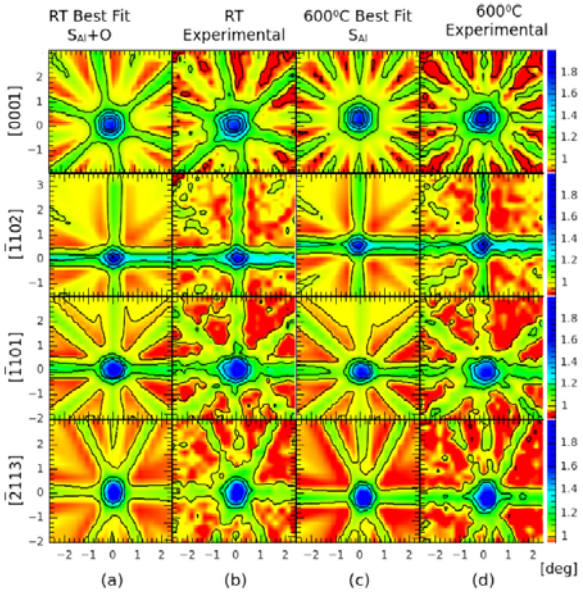


**Fig. 1**: (a) and (c) are experimental $\beta^-$ emission channeling patterns from $^{27}$Mg in AlN during RT and 600°C implantation. (b) and (d) are the best fits, which for RT implantation correspond to 76% of $^{27}$Mg on $S_{Al}$ and 23% near interstitial O sites, while for 600°C only $^{27}$Mg on $S_{Al}$ sites is found. From Ref. [24].

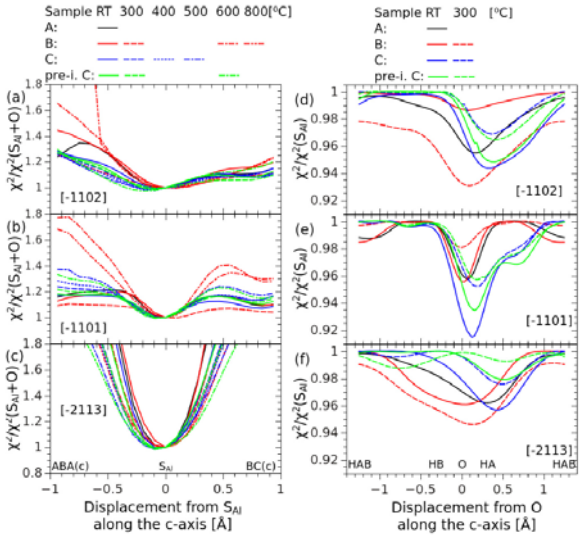


**Fig. 2**: (a)-(c) Reduced $\chi^2$ of fit for [–1102], [–1101], and [–2113] patterns as function of displacement of the $^{27}$Mg atoms from the ideal substitutional $S_{Al}$ sites along the *c*-axis. (d)–(f) Reduced $\chi^2$ as function of displacement of the $^{27}$Mg from the ideal interstitial O sites along the *c*-axis. From Ref. [24].

It is important to point out that our studies so far have only covered naturally *n*-type GaN and AlN samples and the temperature range from 20-800°C. It remains for instance to be investigated whether there are any changes in the lattice sites of $^{27}$Mg when implantations

are performed below room temperature. On the one hand the reduced mobility of defects may cause changes in the interstitial and substitutional Mg fractions, e.g. if Ga vacancies are prevented from combining with Mg interstitials less substitutional Mg should be found. On the other hand, low temperatures may directly alter the structure of Mg-related complexes. Also *p*-type GaN, doped with Mg during growth, needs to be investigated since moving the Fermi level closer to the valence band is expected to result in a change of charge state from $Mg^-$ to $Mg^0$, an effect that is also favoured by lowering the temperature. According to the theoretical predictions for polaronic acceptors this should be accompanied by lattice relaxations which move the Mg off the ideal Ga site. Last but not least, lattice location studies in hydrogenated GaN samples may reveal the lattice sites of Mg within Mg-H complexes. Since its migration energy is supposed to be 0.7 eV only [2,7], interstitial $H^+$ should be sufficiently mobile at room temperature in order to allow pairing with $Mg^-$ even during the 9.5 min half-life of $^{27}$Mg.

Summarizing, rather than being completed, we consider the experimental program for EC–SLI studies with $^{27}$Mg and $^{11}$Be at its beginning. Submitting an addendum seems at the moment the appropriate solution since there are still 4.5 shifts left on IS453 and a new experiment could only be applied for at the INTC meeting in June, which would be too late to be allocated beam time still during the 2014 ISOLDE running period.

## Future plans with all <u>requested</u> shifts (including available shifts):

(i) Envisaged measurements and requested isotopes

**$^{27}$Mg**: we propose EC-SLI lattice location experiments that…

- cover the implantation temperature range 50-300 K in GaN and AlN;

- study also *p*-type GaN doped with Mg during growth (in contrast to naturally *n*-type GaN);

- investigate possible influence of H by using hydrogenated GaN samples.

**$^{11}$Be**: we propose initial lattice location studies in naturally *n*-type GaN and AlN as function of implantation temperature from 20-800°C.

Both $^{27}$Mg and $^{11}$Be measurements shall be performed with angular resolutions of 0.06°. While we used ~0.15° in previous $^{27}$Mg runs the feasibility and usefulness of higher angular resolution was already demonstrated in a trial run with $^{11}$Be.

(ii) Have these studies been performed in the meantime by another group?

No.

(iii) Number of shifts (based on newest yields) required for each isotope

| isotope | yield (/μC) | target – ion source | Shifts (8h) |
|---|---|---|---|
| $^{27}$Mg | $1\times10^7$ | Ti-W – RILIS Mg | 12 |
| $^{11}$Be | $6\times10^6$ | $UC_x$-W or Ta-W – RILIS Be | 3 |

**Total shifts: 15**

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