EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Proposal to the ISOLDE and Neutron Time-of-Flight Committee

# Emission Mössbauer spectroscopy of superconducting NbN thin films implanted with magnetic species

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## Abstract

Among the conventional *s*-wave superconductors, NbN with a superconducting transition temperature ~15 K has been widely investigated as a workbench for the investigation of the fundamental physics of superconductivity as well as for applications in hot electron bolometers, microwave resonators and single photon detectors. Recently, new schemes have been proposed for the design and fabrication of hybrid structures based on superconductor/magnetic and superconductor/semiconductor systems in view of the next generation of superconducting spintronic devices exploiting emerging quasiparticles including spin-triplet Cooper pairs and Majorana fermions. Here, in-depth studies on the lattice site occupancy, the charge and the spin state of implanted magnetic ions, and magnetic and superconducting fluctuations both in the normal and superconducting states of NbN through hyperfine interactions by employing emission Mössbauer spectroscopy is proposed. The isotope foreseen for the experiments is $^{57}$Mn. Emission Mössbauer spectroscopy measurements will be undertaken in the temperature range 100 K $\leq T \leq$ 600 K both in presence and absence of magnetic fields.

**Requested shifts**: 9 shifts split into ~3 runs over ~3 years

## 1. INTRODUCTION/MOTIVATION

The discovery of superconductivity in Hg by H. Kammerlingh Onnes in 1911 opened a compelling field of research in condensed matter physics [1, 2]. Elemental superconductors like Nb, Al, Mo and compound systems such as NbN, $InO_x$, $Nb_3Sn$, *etc.* that are described by the Bardeen-Cooper-Schreiffer (BCS) theory, are categorized as conventional *s*-wave superconductors [3]. The material systems belonging to the classes of high $T_c$ cuprates, Fe-based pnictides and heavy fermions are classified as unconventional, non-BCS superconductors [4].

Within the family of the conventional superconductors, NbN with a bulk superconducting transition temperature ~15 K, has been widely studied and investigated both in the bulk crystal phase and as thin film [5]. In view of diverse relevant applications of superconducting NbN in Josephson junctions, hot electron bolometers and in single photon detectors, magnetron sputtered NbN thin films are intensively investigated [6,7]. Disordered NbN thin films grown by sputtering have been used as the workbench to investigate Berezinskii-Kosterlitz-Thouless (BKT) phase transition, superconductor-insulator transitions, conductance fluctuation, Andreev reflection and the Higgs-Anderson mechanism of superconductivity [8,9]. Superconducting thin film in close proximity to magnetic films host emergent phenomena, including spin-triplet Cooper pairing, Majorana fermions and spin superfluids [10]. The magnetic doping of superconductors led to the identification of quantum states of matter such as the Yu-Shiba-Rusinov (YSR) states [10]. Therefore, doping conventional superconductors like NbN with magnetic impurities is expected to widen the perspectives for hybrid structures-based applications in the next generation of quantum technologies including superconducting spintronics, spin-orbitronics, high energy particle detectors, integrated resonators and superconducting qubit processors for quantum computation [10]. Recently, the growth of NbN on templates of III-nitride GaN and $Al_{1-x}Ga_xN$ as an alternative to the conventional Si and MgO substrates, has broadened the range of applications for all nitride integrated superconductor/semiconductor devices [11,12]. Superconducting NbN nanowires have been also proposed as detectors for dark matter candidates [13]. Stripline NbN-based microresonators for single photon and high energy particle detection are also being pursued actively [14]. However, in-depth studies correlating the local lattice occupancy, local magnetic and superconducting fluctuations due to magnetic doping of NbN are still wanted and are expected to provide precious insight into fundamental physical phenomena, including disordered superconductivity, YSR and Andreev bound states and triplet Cooper pairs in magnetically doped *s*-wave superconductors. In particular, systematic studies on local magnetic and superconducting fluctuations and their correlation to the lattice and electronic disorder in NbN-based superconductors doped with dilute transition metal (TM) impurities are missing. The experiments proposed here likely to contribute significantly to the development of hybrid NbN/III-nitride systems as bedrocks for microwave resonators, single photon and high energy particle detectors on integrated chips.

## 2. SAMPLES AND METHODS

### 2.1 NbN and Fe-implanted NbN samples

The samples to be investigated consist of 50 nm and 100 nm NbN thin films sputtered onto1 µm thick GaN templates grown on epi-ready *c*-plane sapphire wafers *via* metal organic vapor phase epitaxy. The NbN films are sputtered in a magnetron system using a Nb target in Ar:$N_2$ plasma at a power of 20 W. The substrate temperature is maintained at 500°C. The samples are thoroughly characterized *via* high resolution x-ray diffraction (HRXRD), high resolution transmission electron microscopy (HRTEM), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), superconducting quantum interference device (SQUID) magnetometry, low-$T$-high-$H$ magneto-transport and point contact Andreev reflection spectroscopy (PCAR). The Fe implanted NbN samples are prepared by implantation of Fe ions using an ion implanter as a function of beam energy and Fe ion fluence.

## 2.2 PRELIMINARY WORK

A collection of the characterization conducted on a 100 nm thick NbN film grown on a 1 µm GaN template are presented in Fig. 1.

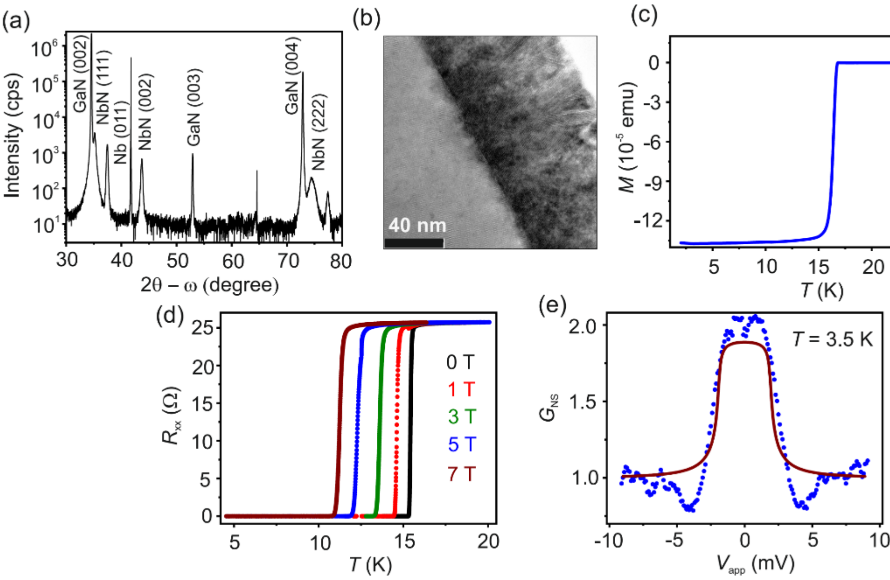

Fig. 1 (a) HRXRD spectrum of 100 nm NbN thin film on GaN template; (b) Cross-sectional HRTEM image of the NbN/GaN sample recorded across the interface between the NbN layer and the GaN template; (c) zero-field cooled $M$-$T$ data measured in a SQUID magnetometer with the magnetic field applied perpendicular to the sample surface; (d) Longitudinal resistance, $R_{xx}$, measured as a function of $T$ both in the presence and in the absence of magnetic fields. The specimen is measured in 1-2-2-1 Hall bar geometry with the magnetic field applied perpendicular to the sample surface; (e) PCAR spectra measured at $T$ = 3.5 K.

The HRXRD diffractogram measured in a Bragg-Brentano geometry and shown in Fig. 1 (a) points to a polycrystalline cubic NbN phase, confirmed by the cross-sectional HRTEM image in Fig. 1 (b). The zero-field cooled (ZFC) variation of magnetization $M$ as a function of temperature $T$ is shown in Fig. 1 (c). The abrupt transition from a paramagnetic phase to a perfect diamagnetic state allows identifying the superconducting transition temperature to be $T_{\mathrm{BCS}}$ = 15.3 K. As reported in Fig. 1 (d), the superconducting transition of the film is confirmed by measuring the longitudinal resistance $R_{xx}$ as a function of $T$ for magnetic fields of 0 T, 1 T, 3 T, 5 T and 7 T applied parallel to the surface normal of the sample. Measurements of PCAR spectroscopy carried out in a home-built Andreev reflection spectrometer allow estimating the BCS coherence length and the superconducting energy gap to be 170 nm and 3.9 meV, respectively. The normalised differential conductance $G_{\mathrm{NS}}$ as a function of the applied bias voltage $V_{\mathrm{app}}$ measured at $T$ = 3.5 K is reported in Fig. 1 (e). The 100 nm NbN layers considered here have a $T_{\mathrm{BCS}}$ of the same order as reported for NbN layers grown on MgO or Si substrates [5,15].

## 3. EXPERIMENTAL PLAN AND BEAM REQUEST

The main purpose of the requested beam-time is to determine:

(i) the lattice site occupancy, the charge and the spin states of magnetic ions implanted into NbN;

(ii) the magnetic and superconducting fluctuations

both in virgin NbN and Fe implanted NbN layers, through hyperfine interactions by employing emission Mössbauer spectroscopy (eMS). The isotopes proposed for implantation at ISOLDE is TM $^{57}$Mn ($T_{1/2}$ = 1.5 minutes). Two NbN thin films of thicknesses 50 nm and 100 nm will be sputtered onto III-nitride templates. For this work 3 different templates will be employed, namely: (1) GaN, (2) degenerately doped *n*-type GaN:Si and (3) $Al_{0.25}Ga_{0.75}N$. Experiments on the three different templates aim at exploring and comparing the structural and electronic properties of NbN layers as a function of the template electronic properties and crystallographic arrangement.

The experimental plans envisioned for the present proposal is aimed at in-depth eMS studies.

**M.1:** The first step will be to measure eMS spectra of the NbN samples implanted with $^{57}$Mn range (100-600) K. Information on the annealing characteristics of the material, the hyperfine parameters and the site fractions as a function of temperature and the implanted isotope will be obtained. Further, the disorder induced by the implantation of the TM isotope can be quantified from the Mössbauer parameters, providing information essential in particular to gain insight into the superconducting fluctuations and the pairing symmetry of the Cooper pairs due to the introduction of magnetic impurities and their correlation to the structural and electronic disorder induced in the system under investigation.

**M.2:** At every $T$, magnetic field dependent eMS measurements will be conducted in order to validate the lattice position and the local magnetic properties of the $^{57}$Mn implanted NbN films.

**M.3:** Fast cooling measurements, in which the implantation takes place at $T > 300$ K and eMS for $T < 100$ K are also proposed. The fast cooling experiments will be followed by time-delayed and fluence dependent measurements. These studies will be relevant to gain information on implantation-related damage and to determine the Debye temperatures of the dopants in different lattice sites.

In summary, by combining hyperfine parameters and the hyperfine fields that can be determined from the eMS measurements using $^{57}$Mn isotopes, it is proposed here to quantitatively determine - in superconducting NbN and Fe implanted NbN - the lattice sites, spin and charge states of implanted TM ions, in addition to the disorder due to the implantation, local magnetic and superconducting fluctuations. Due to the extremely low doping, *i.e.* $\sim 10^{-4}$ at. % resulting from the implantation process, the proposed measurements will allow probing the local fluctuation in the superconducting phases of *s*-wave superconductors in comparison to their normal phases and open up a new paradigm of research into magnetic doping of superconductors. Further, the use of Mössbauer spectroscopy as a complementary tool for studying odd frequency superconductivity and YSR states in conventional superconductors is envisioned.

## 4. SUMMARY OF REQUESTED SHIFTS

The requested shifts are summarized in the following table:

| Emission Mössbauer Spectroscopy | | | | | | | |
|---|---|---|---|---|---|---|---|
| Required isotope | Implanted beam | Type of experiment | Approx. intensity (at/µC) | Target/ion source | Reqd. atoms/sample | Comments | No. of requested shifts |
| **$^{57}$Mn** | $^{57}$Mn | eMS (M1; M2; M3) | $10^8$ | UC$_x$; RILIS | 1 x $10^{12}$ | Measurements at **$100\ \mathrm{K} \le T \le 600\ \mathrm{K}$**<br>Also as a function of magnetic field achieved using a permanent magnet | 9 |

## 5. COMPLIMENTARY RESEARCH

The eMS results, relevant in particular to the lattice site assignments, lattice distortions, vacancy mobility and Debye temperature estimations will be supported by *ab initio* density functional theory calculations. Prior- and post-implantation, the samples will be comprehensively characterized by HRXRD, HRTEM and Raman spectroscopy to estimate the microstructural modifications due to the implanted magnetic impurities. Low-$T$-high-$H$ magnetotransport studies and scanning PCAR measurements will be performed *ex situ* in addition to SQUID magnetometry for in-depth studies of the influence of the implanted magnetic ions on the superconducting properties of the NbN films. In particular, the signatures of the magnetic ion induced magnetic fluctuations leading to possible YSR states, spin triplet Cooper pairings and odd frequency superconductivity will be investigated. X-ray absorption spectroscopy, in particular, extended x-ray fine structure spectroscopy (EXAFS) and x-ray absorption near edge spectroscopy (XANES) will be carried out at the SOLEIL Synchrotron (in the frame of a long-term collaborative project currently running) on the virgin and on the implanted samples to obtain complementary data on the local structure of the samples.

## 6. CONCLUSION/OUTLOOK

From the experimental activity outlined above, the following outcomes are expected

(i) A detailed mapping of the implantation induced defects and quantification of disorder in the NbN lattice;

(ii) Local magnetic structure of the TM implanted superconducting NbN and Fe implanted NbN thin films grown on III-nitride templates;

(iii) Correlation of the lattice disorder, electronic disorder, magnetic and superconducting fluctuations using hyperfine parameters in particular measured in the superconducting state of a conventional *s*-wave superconductor in the presence of TM dopants.

These outcomes of the eMS measurements on NbN superconducting thin films will result in:

1. A systematic study of the evolution of microstructure, magnetism and superconductivity in technologically important conventional *s*-wave NbN thin films grown on III-nitride templates.
2. A guiding path towards the understanding of quantum phases including YSR states, triplet Cooper pairing and odd frequency superconductivity in magnetic ion implanted superconducting system.
3. The understanding of the physical mechanisms involving magnetic ion doped NbN and the opportunities of application of such hybrid systems in superconducting spintronics, high energy particle detectors and in the next generation of resonators.

The anticipated results obtained in the proposed shifts are expected to provide valuable insights for future proposals and in-depth studies of virgin and Fe implanted NbN films for applications in superconducting spintronics, single photon detectors, microwave resonators and future particle and nuclear detectors based on all nitride integrated and hybrid devices.

## References:

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# Appendix

## DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

| **Part of the Choose an item.** | **Availability** | **Design and manufacturing** |
|---|---|---|
| SSP-GLM chamber | ☒ Existing | ☒ To be used without any modification |
| | | |
| Mössbauer set-up (eMIL) and<br>Mössbauer magnetic analyser (eMMA) | ☒Existing | ☒To be used without any modification<br>☐To be modified |
| | ☒New | ☐Standard equipment supplied by a manufacturer<br>☒CERN/collaboration responsible for the design and/or manufacturing |
| Existing equipment in the SSP lab in building 508 | ☒Existing | ☒To be used without any modification<br>☐To be modified |
| | ☐New | ☐Standard equipment supplied by a manufacturer<br>☐CERN/collaboration responsible for the design and/or manufacturing |
| [insert lines if needed] | | |

## HAZARDS GENERATED BY THE EXPERIMENT

*(if using fixed installation)* Hazards named in the document relevant for the fixed [COLLAPS, CRIS, ISOLTRAP, MINIBALL + only CD, MINIBALL + T-REX, NICOLE, SSP-GLM chamber, SSP-GHM chamber, or WITCH] installation.

Additional hazards:

| ***Hazards*** | | | |
|---|---|---|---|
| | *Collection chamber and GLM beam line (SSP)* | *Mössbauer chamber at GLM beam line (SSP)* | |
| Thermodynamic and fluidic | | | |
| Pressure | | | |
| Vacuum | typically, $10^{-6}$ mbar | typically, $10^{-6}$ mbar | |
| Temperature | | 100K – 600K | |
| Heat transfer | | | |
| Thermal properties of materials | | | |
| Cryogenic fluid | | | |
| Electrical and electromagnetic | | | |

| | | | |
|---|---|---|---|
| Electricity | | 12 V, max. 5 A sample heating during measurements | |
| Static electricity | | | |
| Magnetic field | [ | | |
| Batteries | ☐ | | |
| Capacitors | ☐ | | |
| Ionizing radiation | | | |
| Target material | | NbN, Fe implanted NbN on III-Nitride templates | |
| Beam particle type (e, p, ions, etc.) | | ions | |
| Beam intensity | | $10^{11}$ ions/s | |
| Beam energy | | | |
| Cooling liquids | [liquid] | | |
| Gases | [gas] | | |
| Calibration sources: | ☐ | | |
| • Open source | ☐ | | |
| • Sealed source | ☐ [ISO standard] | | |
| • Isotope | | | |
| • Activity | | | |
| Use of activated material: | | | |
| • Description | ☐ Collection in the chamber, removal from the chamber and transport to building 508 | Measurement on-line with sample in the chamber | |
| • Dose rate on contact and in 10 cm distance | | max. 0.5 µSv/h | |
| • Isotope | | $^{57}$Mn | |
| • Activity | | max. 3-4 MBq per sample | |
| Non-ionizing radiation | | | |
| Laser | | | |
| UV light | | | |
| Microwaves (300MHz-30 GHz) | | | |
| Radiofrequency (1-300MHz) | | | |
| Chemical | | | |
| Toxic | | | |
| Harmful | | | |
| CMR (carcinogens, mutagens and substances toxic to reproduction) | | | |
| Corrosive | | | |
| Irritant | | | |
| Flammable | | | |
| Oxidizing | | | |
| Explosiveness | | | |
| Asphyxiant | | | |
| Dangerous for the environment | | | |
| Mechanical | | | |
| Physical impact or mechanical energy (moving parts) | | | |
| Mechanical properties (Sharp, rough, slippery) | | | |
| Vibration | | | |
| Vehicles and Means of Transport | | | |
| Noise | | | |
| Frequency | | | |
| Intensity | | | |

| Physical | | | |
|---|---|---|---|
| Confined spaces | | | |
| High workplaces | | | |
| Access to high workplaces | | | |
| Obstructions in passageways | | | |
| Manual handling | | | |
| Poor ergonomics | | | |

### 0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*