

Electron Tunneling and X-ray Photoelectron Spectroscopy Studies of the Superconducting Properties of Nitrogen-Doped Niobium Resonator Cavities

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We used scanning tunneling microscopy and spectroscopy (STM/STS) and X-ray photoelectron spectroscopy (XPS) to investigate the effect of nitrogen doping on the surface electronic and chemical structures of cutouts from superconducting Nb radio frequency (SRF) cavities. The goal of this work is to get insights into the fundamental physics and materials mechanisms behind the striking decrease of the surface resistance with the radio-frequency magnetic field, which has been observed on N-doped Nb cavities. Our XPS measurements reveal a significantly more oxidized Nb 3d states and a thinner metallic suboxide layer on the N-doped Nb surfaces which is also confirmed by tunneling spectroscopy measurements. In turn, tunneling measurements performed on native surfaces as well as on Ar ion sputtered surfaces allow us to separate the effect of N-doping on the surface oxide layer from that on the density of states in the bulk. Analysis of our tunneling spectra in the framework of a model of a proximity-coupled normal layer at the surface (A. Gurevich and T. Kubo *Phys. Rev. B* **96**, 184515 (2017)) is consistent with the hypothesis that N-doping ameliorates lateral inhomogeneities of superconducting properties on the surface and shrinks the metallic suboxide layer. For the Ar sputtered surfaces, we also find evidence that N-doping changes the contact resistance between the metallic suboxide and the bulk niobium toward an optimum value corresponding to a minimum surface resistance. The totality of our experimental data suggests that the N doping provides an effective tuning of the density of states in such a way that it can result in a decrease of the surface resistance with the radio frequency field, as it was predicted by calculations of the nonlinear low-frequency electromagnetic response of dirty superconductors. Furthermore, STM imaging of vortex cores shows a slightly reduced average superconducting gap and a shorter coherence length in the N-doped Nb samples as compared to typically prepared Nb samples, indicating a stronger impurity scattering caused by nitrogen doping in a moderately disordered material.

I. INTRODUCTION

The fundamental limits of dissipation in the superconducting Meissner state under radio frequency (RF) fields has attracted much attention, particularly in light of recent advances in the improvement of the performance of microresonators for quantum computing or resonator cavities for particle accelerators [1–7]. This interest has been motivated by the fact that *s*-wave superconductors have very small surface resistance $R_s \propto \exp(-\Delta/T)$ at temperatures T well below the critical temperature T_c and RF frequencies ω smaller than the gap frequency $2\Delta/\hbar$ [8]. Indeed, the Nb cavities typically have $R_s \sim 10$ n Ω at 2 K and 1 GHz, which translates into huge quality factors $Q \propto 1/R_s \sim 10^{10}$ - 10^{11} [4, 5, 7]. The surface resistance depends on the amplitude H_0 of the RF magnetic field $H(t) = H_0 \sin \omega t$ and can be significantly altered by the materials treatments. For instance, R_s of electropolished Nb cavities [4] at 2 K and 1 GHz increases with the RF field amplitude, consistent with the well-known reduction of a quasiparticle gap and the superfluid density by the RF pairbreaking currents [9–11], grain boundaries, nonsuperconducting precipitates and other materials defects [5, 12], or trapped vortices [13–21]. However, the Nb cavities doped with nitrogen [22–

25], titanium [26] or other impurities [27, 28] can exhibit a striking reduction of $R_s(H_0)$ by factors of 2-4 as H_0 increases from 0 to $\lesssim 0.5H_c$, where H_c is the thermodynamic critical field.

These discoveries of the microwave reduction of $R_s(H_0)$ have triggered intense investigations of its microscopic mechanisms, as well as the materials modifications [29–34], by which it can be further enhanced and extended to higher RF fields of prime importance for the SRF cavity applications. The investigations indicate that the behavior of the nonlinear surface resistance at high RF fields is controlled by the physics of nonequilibrium superconductivity and nonlinear RF current pairbreaking interconnected with subtle materials features and impurity distributions in the first few nm at the surface. One of the outstanding issues is to understand the mechanism by which the impurity doping turns the conventional increase of $R_s(H_0)$ with H_0 into the counterintuitive decrease of $R_s(H_0)$ as a function of H_0 . Several scenarios for this effect have been proposed in the literature. It was shown [35] that the well-known effect of broadening of the quasiparticle density of states (DOS) gap peaks by the pairbreaking current [9, 10, 36–40] can result in a pronounced minimum in $R_s(H_0)$, in agreement with experiment [25, 26]. Such microwave reduction of the sur-

face resistance [41] is a manifestation of a general effect by which R_s can be significantly reduced by engineering an optimum broadening of the gap peaks in the DOS at the surface using different *pairbreaking* mechanisms. These mechanisms can be due to RF Meissner currents [35, 40, 41], paramagnetic impurities [42, 43], local reduction of the pairing constant, or a proximity-coupled normal layer which models surface nonstoichiometry and suboxide layers [44, 45]. The latter are particularly relevant to the Nb surface which is typically covered by a few nm thick layers of metallic Nb monoxide (NbO), semiconducting Nb dioxide (NbO₂) and insulating Nb pentoxide (Nb₂O₅) [5, 46, 47]. Low oxidation state Nb suboxides tend to be metallic with known magnetic moments appearing as the oxide approaches the Nb⁴⁺ state [48–50]. Another mechanism of the field reduction of $R_s(H_0)$ based on the existence of two-level atomic states at the Nb surface was proposed [51] although neither the nature of the two-level atomic states nor their relation to the N doping of Nb cavities have been well understood. Recently a contribution to a negative $Q(H_0)$ slope coming from trapped vortices was suggested [52].

Identifying the materials and physical mechanisms by which the N-doping causes the field-induced reduction of $R_s(H_0)$ requires surface probes which could pinpoint the specific superconducting properties affected by the N-doping. In turn, these experiments should be combined with a theory that relates these materials changes to the corresponding changes in superconducting characteristics affecting the behavior of $R_s(H_0)$. One of such key characteristics is the local DOS at the surface which can be directly probed by tunneling experiments. For instance, calculations of microwave suppression of $R_s(H_0)$ using the kinetic Usadel equations for dirty superconductors [35, 41, 44, 45] suggest that the N-doping of a few μm thick surface layer can result in the field-induced reduction of $R_s(H_0)$ in two different ways: 1. N-doping mostly reduces the DOS peaks broadening in the entire layer of RF field penetration $\simeq 2\lambda \sim 100$ nm, which brings about the microwave reduction of $R_s(H_0)$ characteristic of the idealized BCS model [35, 40, 41]. 2. The key effect of the N-doping is in modifying the surface oxide structure, and partial or complete conversion of the metallic suboxides into dielectric (Nb₂O₅) or semiconductor (NbO₂) forms which do not cause significant RF losses and DOS broadening. In this case the effect of the N-doping in the bulk mostly manifests itself in the reduction of the mean free path without much effect on the DOS broadening. The effect of a thin proximity-coupled normal layer on the field-induced reduction of $R_s(H_0)$ was recently calculated in Ref. 45. The purpose of this work is to identify the material modifications caused by the N-doping using combined scanning tunneling microscopy and spectroscopy (STM/STS) and X-ray photoelectron spectroscopy (XPS) to probe the electronic and chemical states of Nb both in the bulk and at the surface.

We performed tunneling spectroscopy and XPS of typically prepared Nb and N-doped Nb cutouts from SRF cavities. The main goal is to reveal the changes produced by the N-doping in the native oxide and the bulk DOS of typically prepared Nb and understand how these changes manifest themselves in the tunneling spectra in terms of superconducting gap, DOS broadening and sub-gap states. Recent work on point-contact tunneling spectroscopy of N-doped Nb samples [53] addressed the same issues but our work pursues a different approach. We first studied native surfaces of Nb and N-doped SRF cavities cutouts to get insights into the native oxide. Then we performed scanning tunneling microscopy and spectroscopy on the Ar ion sputtered surfaces of Nb and N-doped SRF cutouts to infer the bulk DOS underneath the native oxide. This combined approach allows us to discriminate the effect of N-doping on the oxide surface and the bulk DOS. Furthermore, since the sputtered surfaces are metallic it is possible to use the full capability of the scanning tunneling microscope to obtain a much larger statistics of tunneling spectra, information about spatial distribution of superconducting properties on sub-micron scale and vortex imaging. Scanning tunneling measurements of vortices can directly probe the coherence length by measuring the vortex core size for typically prepared and N-doped samples. Furthermore, since tunneling spectra also contain information about metallic suboxide overlayers, fitting the observed spectra with a proximity effect theory [44] gives insight into the change of thickness of this layer and the contact resistance between the superconductor and the metallic suboxide layer after the N-doping. These parameters can significantly affect the microwave reduction of the surface resistance [44, 45]. Although the Ar ion sputtering is known to affect the oxide layer and those findings cannot be directly related to the RF performance of cavities, a better understanding of the physics and the materials science that emerges from this study can indicate important mechanisms by which the performance of Nb resonant cavities can be improved by the materials treatments.

The paper is organized as follows. In Sec. II we describe the experimental setup and procedures as well as typically prepared Nb and nitrogen-doped Nb samples which were investigated. In Sec. III the results of XPS measurements are presented. Sec. IV contains the results of tunneling spectroscopy measurements. In Sec. V we present STM imaging of vortices. In Sec. VI we discuss the totality of our experimental data and their implications on the effects of N-doping on the electrodynamics of superconducting Nb, with the Conclusions summarized in Sec VII.

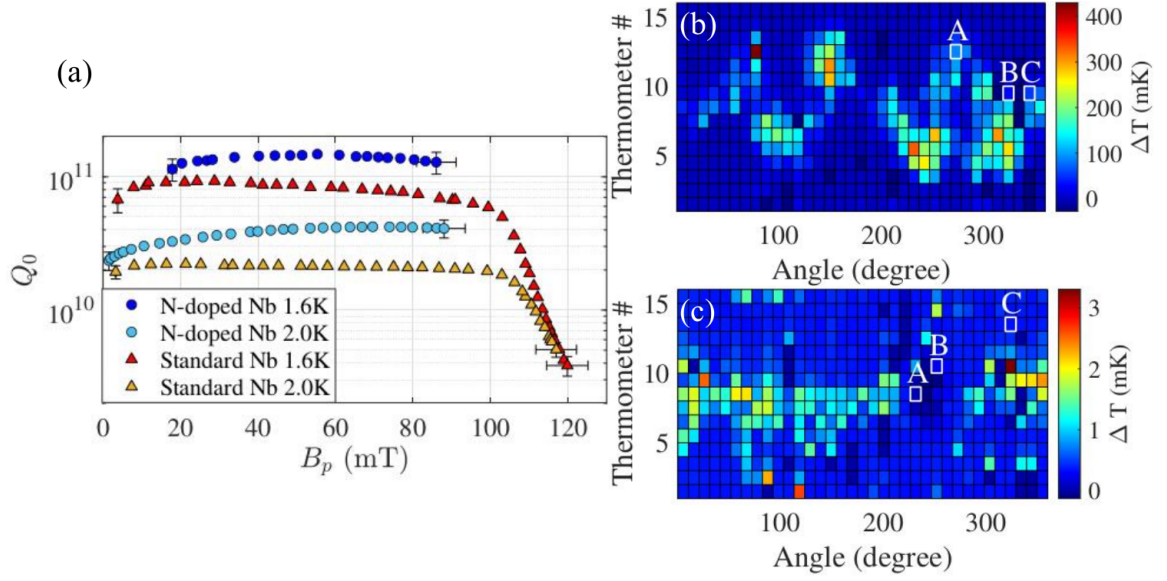


FIG. 1. (a) Q_0 vs B_p curve for BCP treated (A2) and N-doped Nb (TD4) cavities at 1.6 K and 2.0 K. (b),(c) Temperature maps at 1.6 K on A2 and TD4 respectively at the highest RF field. The x-axis is the azimuthal angle around the cavity, and the thermometer numbers indicate the longitudinal positions with the thermometer N.8 at the equator of the cavity. The cold spot samples cut out from the locations labeled A were measured with STM tips breaking the oxide, B with XPS, and C with STM after Ar ion sputtering.

II. EXPERIMENTAL DETAILS

The samples studied in this work ($5(l) \times 5(w) \times 3(t)$ mm³) were cut out from typically prepared Nb and N-doped superconducting RF (SRF) cavities. The typically prepared Nb samples were cut from a single-cell 1.3 GHz cavity, labeled A2, made with ingot niobium from Companhia Brasileira de Metalurgia e Mineração (CBMM). The cavity shape is that of the center cell of TESLA/XFEL cavities [54]. The residual resistivity ratio (RRR) of the niobium is around 260 and the cavity was processed through standard buffered chemical polishing (BCP) to remove approximately 24 μ m from the inner surface followed by high pressure rinsing prior to testing. At 2 K, the cavity reached the quality factor, Q_0 , of around $6 \cdot 10^9$ at its peak magnetic field, B_p of 120 mT. The N-doped Nb samples were cut from a single-cell 1.3 GHz N-doped cavity, with the same shape as A2, labeled TD4. The cavity was fabricated from ingot niobium from Tokyo Denki with RRR of around 300 with a large grain size of few cm². Prior to N-doping, the cavity had gone through standard buffered chemical processing (BCP) and high pressure rinsing with ultra-pure water. The nitrogen doping process for this cavity involved heat treatment at 800 °C and exposure to nitrogen at a pressure of around 25 mTorr for 20 minutes. After the nitrogen is removed, the cavity was heated again at 800 °C for 30 minutes. Finally, approximately 10 μ m of inner surface of the cavity was removed by electropolishing. At 2 K, this cavity achieved a quality factor of $4 \cdot 10^{10}$ at its

peak magnetic field of 88 mT. Figure 1(a) shows a plot of $Q_0(B_p)$ for the BCP-treated cavity A2 and N-doped cavity TD4 measured at 2 K and 1.6 K. A thermometry system [55] allows measuring the temperature of the cavities' outer surface with increasing RF field. Figure 1(b) and (c) shows temperature maps at the highest RF field in cavities A2 and TD4 respectively. The location where "cold spot" samples were cut is shown by a white rectangle in the maps.

All the samples were cut using a CNC milling machine with no lubricant. During the cutting process, the steady flow of compressed helium was applied at the drilling region in order to prevent the sample from heating. The temperature was monitored throughout the process to make sure it did not raise above 32° C. To verify this cutting process, a time-of-flight secondary ion mass spectroscopy (TOF-SIMS) analysis was done on a 16×16 mm² niobium sample, and the measurements were repeated near the same location after cutting out an 8×8 cm² sample. The analysis showed some increase in carbon concentration but did not show any new impurities after cutting.

Only cold spots of both types of cavities were measured in order to identify the main differences that improve the performance of the N-doped Nb cavities. XPS measurements were performed using a PHI Versaprobe 5000 XPS at the Drexel University Core Facilities. The X-ray source used was Al K α (1486.6 eV, 200 W). The binding energy was calibrated to the accidental carbon impurity C 1s, C-C bond, at 284.6 eV. The depth profile

was performed using Ar ion sputtering at 1 keV, 2 μ A beam current and 2 mm $\times$ 2 mm beam size. The calibration performed on Nb provided a sputtering rate of 1.1 nm/min. As explained in detail in Sec. III, XPS measurements on native surfaces allow us to get detailed information about the native oxide. Using the depth profile measurements we then compare the oxide layer thickness of the typically prepared Nb and N-doped Nb samples. Since Ar sputtering can cause changes in the native oxide, the absolute values of its thickness cannot be readily obtained, yet qualitative conclusions about the effect of N-doping can still be made.

Low temperature scanning tunneling microscopy/spectroscopy (STM/STS) measurements were performed at temperatures ranging from 1.0 K to 1.7 K, using a Unisoku ultra high vacuum STM system equipped with a 9 T superconducting magnet and with a base pressure of $4 \cdot 10^{-11}$ Torr. Pt-Ir tips were used in all measurements. Because the top layer of Nb is dominated by a thick layer of Nb₂O₅ insulating oxide, it is not possible to tunnel through the native surface. In order to measure the tunneling spectra of the underlying Nb, it is necessary either to break the oxide with the STM tip or to remove the oxide layer by Ar ion sputtering. Each of these techniques has limitations, but combining them as described below allowed us to probe superconducting properties affected by the complex surface oxide layer in the first few nanometers at the surface of Nb and to trace the effect of N-doping on the density of states.

For the tunneling measurements performed on native Nb surfaces the tip was used to break the oxide by pushing the tip into the oxide layer until a high current was detected. Typically, this current would saturate the preamplifier. After this operation was repeated several times the tip was retracted and using the feedback loop a current of the order of 100 pA was stabilized with a bias of 10 mV and tunneling spectra were acquired. This was repeated at different locations on the sample's surface at a typical distance of several microns away from each other. Furthermore, several measurements were performed on similar samples with different tips to obtain more data statistics. This procedure allows to get some statistics of spectra but poor correlation between topography and spectra, as the scanning capability of the STM cannot be used at all. Our approach yields information about the electronic structure of a native oxide that acts as a tunnel barrier/proximity layer. When the STM tip is crashing into the complex oxide surface, the tunnel barrier is provided by the oxide itself. In this case tunneling to the bulk superconductor occurs through both a nonuniform normal layer and the sides of the tip. Complex contributions to the tunneling spectrum coming from variable thicknesses of the normal layer and side tunneling from the tip are not well understood and have not yet been taken into account by the existing theoretical models. As discussed in detail in Sec. IV B and Sec. VI the limi-

tation of this technique lies in the low statistics and low amount of data that can be adequately fitted and lack of spatial information.

Cleaning the Nb surface with Ar ion sputtering was done *in situ* soon before transferring the sample to the STM scanner. The sputtering was performed in a preparation chamber attached to the STM with a base pressure of low 10^{-11} Torr. The Ar (purity: 99.999%) partial pressure of 10^{-5} Torr with an energy $E = 1$ keV for 1 hour were the conditions used for all samples. Our estimated removal rate is 0.27 nm/min. This guarantees to remove the known insulating oxide layer from the Nb surface and yields a metallic surface that can be studied by STM, using the full capability of STM and allowing therefore a correlation between topography and spectroscopy. Ar sputtering is known to change the Nb native oxide, but it is not expected to affect the bulk materials properties. Indeed, our simulations of the Ar distribution in Nb using the Stopping and Range Ions in Matter software[56] have shown that typical penetration depths for 1 KeV Ar ions are about 1 – 3 nm. Therefore, this method allows us to access the bulk quasiparticle density of states in Nb through a thin layer of metallic oxide and obtain more statistically meaningful data that can be fitted by a proximity effect model, as described in Sec. IV B.

Maps of tunneling spectra can be acquired at different locations at a distance of $\sim 500\mu\text{m}$ from each other to probe regions far away and collect more statistics. Typical maximum scan areas of the order of about 800 nm allow mapping also inhomogeneities on submicron length scales. Furthermore, when using this sample preparation procedure in the presence of an applied magnetic field perpendicular to the sample surface, vortices can be imaged by acquiring conductance maps at the Fermi energy. The conductance maps were acquired by scanning the tip over the sample surface at an energy higher than the superconducting gap (10 mV), acquiring the lock-in signal at the Fermi energy at each location. Conductance maps reveal therefore, vortices by tracking the difference of the electronic density of states inside and outside the vortex cores. Topography was always acquired simultaneously to check the location where the spectroscopic information was recorded. All differential conductance spectra dI/dV were taken with the same tunneling parameters, with the junction stabilized at $V = 10$ mV, $I = 60$ pA or 100 pA.

III. X-RAY PHOTOELECTRON SPECTROSCOPY

It is well known that niobium is very reactive to oxygen, and the surface oxidation of niobium has been extensively investigated. The initial stages of oxidation of niobium have been characterized through many studies using XPS [57–61], ultraviolet photo-emission [62], Auger

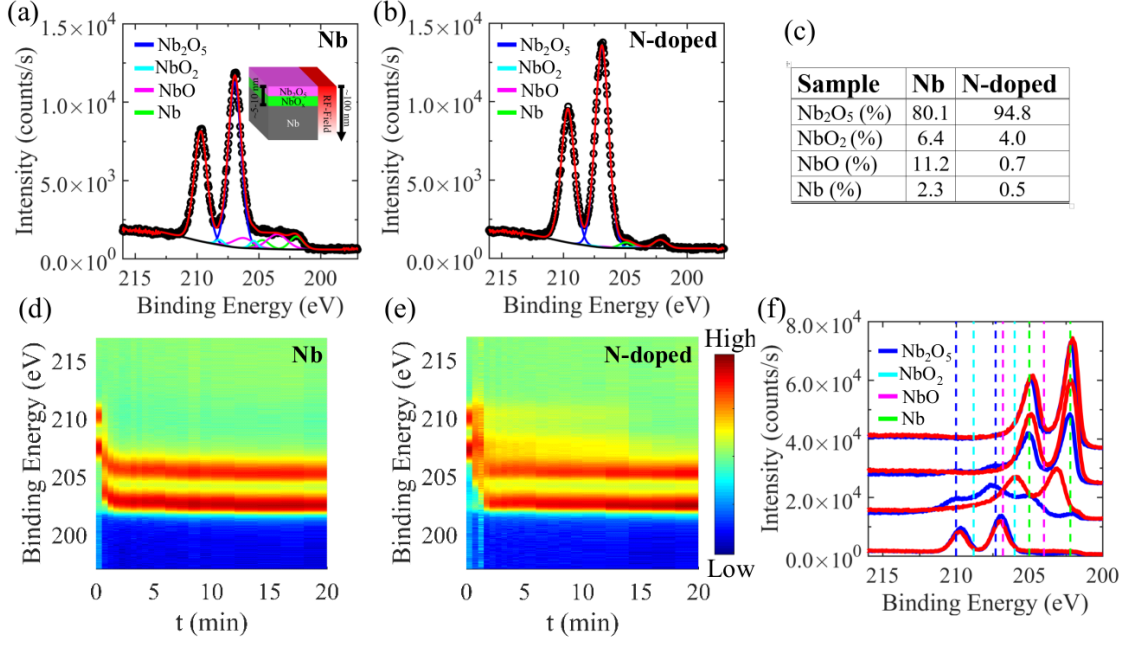


FIG. 2. Nb 3d spectral line together with the deconvolution spectra for different oxidation states for native typically prepared Nb (a) and N-doped Nb (b). (c) Table showing the spectra deconvolution fitting results for both native surfaces. The native surface of the N-doped sample shows a significantly more oxidized state with a smaller contribution from the metallic NbO peak. The inset of (a) shows a simplified depiction of the surface oxide layers of the Nb surface. (d),(e) Color maps of the XPS depth profile obtained while Ar ion sputtering typically prepared and N-doped Nb surfaces, respectively. The depth profile shows that the N-doped sample retains a higher oxidation state, Nb₂O₅ in particular, as a function of depth. The map is in logarithmic scale to emphasize the retention of higher oxides at the surface. (f) XPS spectra taken at 0 s, 30 s, 600 s and 1200 s have been offset for clarity. The peaks of the Nb 3d_{3/2} and 3d_{5/2} are shown with vertical lines. Ar ion sputtering was performed at normal incidence. The electron takeoff angle was 30 degrees.

electron spectroscopy [63, 64] and high-resolution electron energy loss spectroscopy [64]. It has been observed that NbO and NbO₂ are initially formed on niobium as a protective layer, with Nb₂O₅ being formed after further oxidation [57–59, 62, 64]. Furthermore, Nb₂O₅ is reduced to NbO₂ and NbO by annealing in ultrahigh vacuum at elevated temperatures above 600 K due to the dissolution of oxygen into the bulk metal [59].

While it is known that the oxidation states of metals determined by XPS can be in part changed by ion bombardment [65], a qualitative comparison between typically prepared Nb and N-doped Nb surfaces can still be made. The Nb 3d core level of the native surface of the typically prepared and N-doped samples can be found in Fig. 2(a) and (b) respectively, together with the spectra deconvolution. The Nb 3d peaks from literature [59] can be summarized as follows: Nb⁵⁺ (Nb₂O₅) peaks are located at 210.0 eV and 207.3 eV, Nb⁴⁺ (NbO₂) peaks are located at 208.8 eV and 206.0 eV, Nb³⁺ (NbO) peaks are located at 206.8 eV and 204 eV and Nb⁰ peaks are at 205.0 eV and 202.2 eV. The table summarizing the results of the XPS spectra deconvolution is reported in Fig. 2(c). The surface of both natively-oxidized surfaces is dominated by Nb₂O₅, as expected. It should be outlined that it is difficult to distinguish stoichiometric Nb₂O₅ from non-

stoichiometric Nb₂O_{5-x} compounds with XPS [66], since the predominant oxidation state is +5 in all compounds. In general, numerous oxygen vacancies exist in Nb₂O₅ [43, 57, 67]. Therefore, the large Nb₂O₅ peaks suggest that a combination of Nb₂O₅, non-stoichiometric and locally oxygen-deficient Nb₂O₅ are present in the samples. The comparison between the two types of surfaces shows a clear difference in the NbO peak for the two surfaces where the N-doped sample hardly shows any contribution (Figure 2(b) and (c)).

The XPS spectra obtained while sputtering the typically prepared and N-doped Nb surfaces with 1 keV Ar ions (Figs. 2(d)-(f)) show that the sputtering process shifts spectral weight from Nb₂O₅ to lower Nb oxidation states. Ar ion sputtering of oxidized Nb is believed to both preferentially remove oxygen from Nb₂O₅ and diffuse oxygen into bulk Nb [68], thickening the lower oxidation state layers (presented schematically in the inset of Fig. 2(a)). Despite this, notably the N-doped Nb surface, while showing the same qualitative behavior as a conventionally prepared Nb surface, appears different as the higher oxidation state seems to be thicker compared to the typically prepared Nb surfaces as shown in the depth profile in Fig. 2(e) and the NbO peak is always lower than that of typically prepared Nb. The same panel

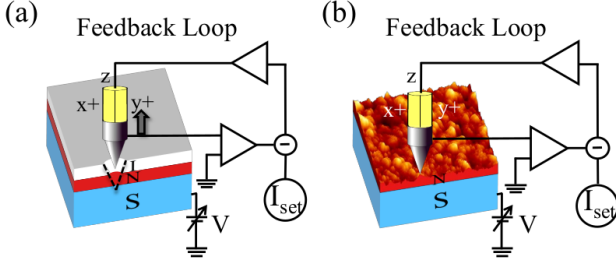


FIG. 3. Schematics of the tunneling measurements performed on (a) native surfaces by crashing the tip into the surface, (b) on Ar ion sputtered metallic surfaces. The surfaces are metallic after Ar ion cleaning and this allows to operate in the typical scanning modality of the STM. The top image of the cartoon is a real representative STM topography image acquired on a Nb surface after Ar ion sputtering. The scan area is $156 \text{ nm} \times 156 \text{ nm}$ and the scanning parameters are $I_{set} = 60 \text{ pA}$, $V_{set} = 100 \text{ mV}$.

also shows that the Nb peaks at 205.0 eV and 202.2 eV are deeper below the surface compared to the typically prepared Nb surfaces. Even though Ar sputtered surfaces might be partially modified compared to the native surfaces these results unambiguously show that for N-doped surfaces the higher oxidation states layer of Nb is thicker and that NbO layer is thinner.

IV. TUNNELING SPECTROSCOPY RESULTS

A schematic of our tunneling measurements is shown in Fig. 3. The STM data were analyzed using the standard expression for the tunneling current that flows between a metallic tip and a sample [69]:

$$I = \frac{4\pi e}{h} \int_{-\infty}^{\infty} [f(\epsilon) - f(\epsilon + eV)] N_S(\epsilon) N_T(\epsilon + eV) |M(\epsilon)|^2 d\epsilon, \quad (1)$$

where $f(\epsilon)$ is the Fermi distribution function, $N_S(\epsilon)$ and $N_T(\epsilon)$ are the density of states of the sample and tip, respectively, V is the applied voltage between the tip and the sample and $M(\epsilon)$ is the tunneling matrix element as a function of the quasiparticle energy ϵ . At low temperature $T \ll \Delta$, Eq. (1) can be simplified if the applied voltage is much lower than the tunneling energy barrier. If the metallic tip (such as platinum iridium (PtIr)) has a nearly constant density of states in the energy region of interest, $\epsilon \sim \Delta$ at the Fermi surface, $N_T(\epsilon)$ in Eq. (1) can be taken out of the integral. In this case the tunneling differential conductance takes the form:

$$\frac{dI}{dV} \propto - \int_{-\infty}^{\infty} \frac{\partial f(\epsilon + eV)}{\partial V} N_S(\epsilon) |M(\epsilon)|^2 d\epsilon. \quad (2)$$

The density of states in a superconductor with an ideal surface can be approximated by the widely used phe-

nomenological Dynes formula [69, 70]

$$N_S(\epsilon) = N_s \text{Re} \frac{\epsilon + i\Gamma}{\sqrt{(\epsilon + i\Gamma)^2 - \Delta^2}} \quad (3)$$

Here N_s is the DOS at the Fermi surface in the normal state, and the parameter Γ quantifies a finite quasiparticle lifetime $\sim \hbar/\Gamma$ resulting in the broadening of the gap peaks in the DOS. Different mechanisms can contribute to Γ (see, e.g., Ref. 44) but irrespective of microscopic details, this broadening and the resulting sub-gap quasiparticle states at $|\epsilon| < \Delta$ can produce a non-exponential temperature dependence of the surface resistance $R_s(T)$ at $T \ll T_c$ and contribute to the residual resistance [41, 44, 45]. Electron tunneling is a surface sensitive technique which directly probes the quasiparticle density of states with high spatial and high energy resolution. This makes it a very powerful instrument to investigate the mechanisms that contribute most to the surface resistance of SRF cavities.

A more realistic model that accounts for weakened superconductivity or a thin normal layer at the superconductor surface was recently developed [44, 45] based on the Usadel equations [11] for a proximity-coupled dirty normal layer (N) on a surface of a bulk superconductor (S). In particular, this theory describes a thin metallic suboxide layer at the Nb surface. The position-dependent quasiparticle density of states $N_N(\epsilon, x)$ across a thin normal layer coupled to the bulk superconductor is determined by a set of equations given in Appendix A. These equations were used to fit our tunneling spectra acquired on Ar ion sputtered surfaces. The behavior of $N_N(\epsilon, x)$ is mostly controlled by two dimensionless parameters α and β which quantify the effect of the N layer thickness and the N-S interface transparency, respectively:

$$\alpha = \frac{dN_n}{\xi_s N_s}, \quad \beta = \frac{4e^2}{h} R_B N_n \Delta d. \quad (4)$$

Here d is the thickness of the N layer, $\xi_s = (D_s/2\Delta)^{1/2}$ is the coherence length in the bulk superconductor, D_s is the electron diffusivity, N_s and N_n are the DOS at the Fermi surface in the normal state, the subscripts n and s corresponds to the parameters of the N layer and the S substrate, respectively, and R_B is a contact resistance of the N-S interface.

A. Native Nb surfaces

Tunneling measurements were performed on the Nb surfaces to get an insight into the native oxide layers of both typically prepared and N-doped Nb. The oxide layers are too thick (see Fig. 2b) to allow direct tunneling into the Nb. Therefore, the STM tip was used to locally break the oxide and by using the feedback loop the tip was then retracted until a stable junction was obtained.

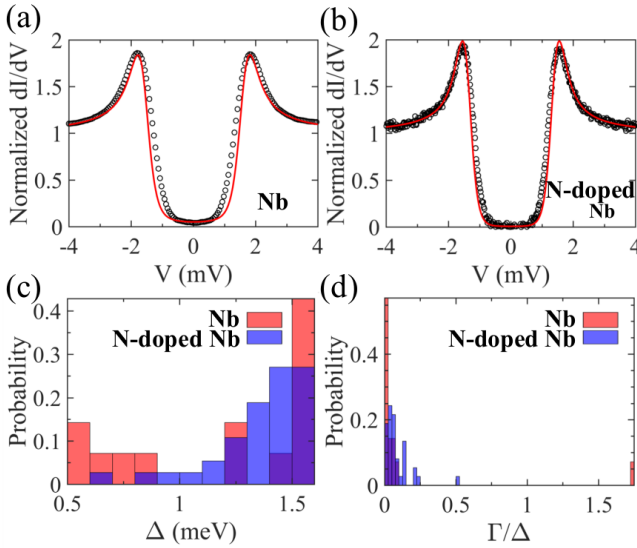


FIG. 4. (a), (b) Typical tunneling spectrum (dots) and BCS-Dynes fit (red line) acquired on Nb and N-doped Nb respectively at $T = 1.5$ K. The fitting parameters in (a) are $\Delta = 1.60$ meV and $\Gamma = 0.08$ meV. The fitting parameters in (b) are $\Delta = 1.39$ meV and $\Gamma = 0.01$ meV. (c), (d) Histogram comparison of BCS-Dynes fitting parameters Δ and Γ/Δ respectively. All parameters were extracted by fitting the model described in the text to the tunneling conductance. Spectra have been acquired several μm away from each other. For all spectra the tunnel junction was stabilized at $I_{\text{set}} = 100$ pA and $V_{\text{set}} = 10$ mV, conductance spectra were acquired with $V_{\text{mod}} = 200$ μV and $f = 373.1$ Hz.

Several such junctions were investigated at different locations separated by several microns. At each location 20 – 50 spectra were acquired and averaged to improve the signal-to-noise ratio.

To analyze the tunneling spectra we first used Eq. (3) of the Dynes model to get a qualitative understanding of the gap distribution as well as the typical values of the DOS broadening parameter Γ . In Figs. 4a and 4b typical tunneling spectra recorded on typically prepared Nb and N-doped Nb are presented together with the fits to Eq. (3) and the resulting fitting parameters. The so-obtained gap values and the ratio Γ/Δ are summarized in Figs. 4c and d. The distribution of the Δ values indicate that the average value of Δ is higher for typically prepared Nb but also that there is a larger distribution of Δ and a higher value of Γ/Δ indicating stronger inhomogeneities of superconducting properties in the typically prepared Nb surface layers. The background of the tunneling spectra at higher energy ($eV > \Delta$) exhibits a more parabolic behavior in spectra acquired on typically prepared Nb. A parabolic background is usually related to lower average work function between tip and sample as it has been already reported in other tunneling experiments [53, 71]. This difference between the two surfaces appears to be significant and it provides further evidence that the sur-

face is more oxidized in the case of N-doped Nb, consistent with the data gathered from XPS. This is also in agreement with the earlier results of Ref. [53]. We note that only about 50% of the tunneling spectra acquired on typically prepared Nb surfaces and 70% of the N-doped Nb tunneling spectra could be properly fitted. Those spectra that could not be properly fitted include gapless spectra obtained more frequently on typically prepared Nb surfaces while about 10% of the spectra for both surfaces present subgap quasiparticles states or zero conductance peaks.

B. Scanning Tunneling Spectroscopy

Ar ion sputter cleaning of the surface was used to remove the insulating Nb_2O_5 layer *in-situ*. As mentioned above, Ar sputtering may modify the oxide layer by thickening the metallic suboxide layer. Therefore, the surface layer after Ar sputtering may not be fully representative of the native surface of the cavities. Yet, since the penetration depth of Ar ions at 1 keV is only a few nm [56], this method does not affect the bulk properties and allows us to access directly the DOS of the underlying bulk superconductor that significantly contributes to the cavity RF performance. Moreover, this technique allows us to separate the effect of N-doping on the bulk from that of the oxide layer. Such surface cleaning procedure yields metallic surfaces where the full potential of scanning capability of STM/STS can be used and a correlation between topography and spectroscopy be investigated. Calibration of the removal rate was obtained using atomic force microscopy. The removed thickness was estimated to be about 15 nm. A schematic of how the measurements were performed is shown in Fig. 3b. The sample studied consists of the bulk superconducting and a metallic overlayer. The top image of the schematics is a typical STM topography acquired on an Ar ion sputtered Nb sample. The roughness of the surface is due in part to the sputtering process and it is of the order of several nm over a scan area of 800 nm $\times$ 800 nm. Tunneling conductance spectra were acquired on the sample surface with a spacing of 32.6 nm in 390 nm $\times$ 390 nm or 780 nm $\times$ 780 nm scan areas. Several spectroscopy grids were acquired on scan areas separated by a typical distance of 500 μm . The spectra were fit using the proximity model [44] with the equations presented in Appendix A. The results of the fitting are summarized in Fig. 5. Figure 5a and 5b show typical tunneling spectra acquired on typically prepared Nb and N-doped Nb together with the fitting curve and the fitting parameters. The histograms of the gap values and the broadening parameter Γ/Δ_0 are reported in Figs. 5c and 5d. The average value of Δ_0 is reduced in the N-doped Nb samples, but its distribution is narrower than that obtained for the typically prepared Nb surfaces. The values of the Dynes broadening parameter Γ are larger

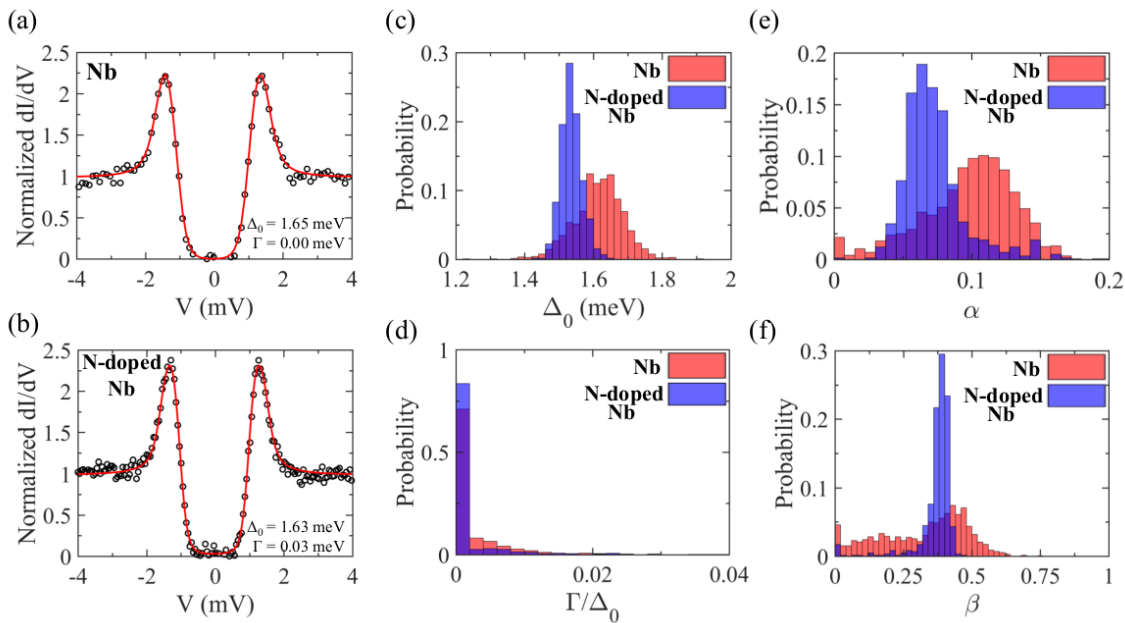


FIG. 5. (a),(b) Typical tunneling spectra (dots) acquired on typically prepared Nb and N-doped Nb surfaces. The red lines are the fit obtained using the model of Ref. 44 described in the text and equations presented in Appendix A. (c),(d) Histogram comparison of the fit parameters Δ_0 and Γ/Δ_0 respectively. (e),(f) Histogram comparison of the fit parameters α and β respectively. For typically prepared samples the number of spectra analyzed is $N = 1440$ (red) and for N-doped samples $N = 576$ (blue). Spectra were taken 32.6 nm away from each other, at $T=1.5$ K with $I_{set} = 60$ pA $V_{set} = 10$ mV with a lock-in modulation $V_{mod}=200\mu\text{V}$ and $f=373.1$ Hz

for the typically prepared Nb surfaces. The broadening of the gap peaks in the quasiparticle density of states $N(\epsilon)$ in the bulk gives rise to a weakly temperature-dependent residual surface resistance [44].

The fits show that the parameter α (Fig. 5e), proportional to the thickness of the normal suboxide layer, is in average larger for the typically prepared Nb. The parameter β (Fig. 5f), proportional to the contact resistance between the superconductor and the normal layer, is more distributed for the typically prepared Nb. Interestingly, the fit values of β cluster around $\beta \simeq 0.3 - 0.4$ for the N-doped samples. As follows from the calculations of Ref. 44, low values of Γ together with β ranging between 0.3 and 0.4, can significantly reduce the surface resistance. This is due to the long range disturbance in the density of states produced by the N layer into the superconductor which outweighs the contribution of the subgap states in the proximity coupled normal layer. Finally, in the case of sputtered surfaces we find that the tunneling spectra of typically prepared Nb present a non-linear background that indicates a lower tunnel barrier than for N-doped Nb, in agreement with the results previously observed in Ref. [53].

Figure 6 shows the spatial variation of some of the fitting parameters on a typical scan area of $780 \text{ nm} \times 780 \text{ nm}$. The comparison between the typically prepared Nb and the N-doped Nb in Figs 6a and 6b shows that for typically prepared Nb there are variation of Δ_0 and β on

a submicron scale. More uniform values for the N-doped Nb are instead obtained.

V. VORTICES

If a magnetic field is applied, Abrikosov vortices can penetrate into the sample and modify the local density of states. Hot spots resulting from vortex bundles trapped during the cavity cooldown through T_c can not only limit the performance of SRF cavities [13–20] but also contribute to the field-induced decrease of $R_s(H_0)$ [52]. Imaging of vortices can give valuable information about the electronic structure of the vortex core in the first few nm at the surface, which plays the key role in RF dissipation. Vortices can be imaged by STM by mapping the local conductance at an energy where a vortex alters the density of states. Therefore, STM is a direct experimental technique to visualize vortices in superconductors with a sub-nanometer spatial resolution.

Figure 7(a) and (b) show the vortex lattice imaged on typically prepared Nb and N-doped Nb. A triangular vortex lattice has been observed for both types of samples with their inter-vortex spacing in agreement with the theoretical predictions [48, 72, 73]. High resolution single vortex images are shown in Figs. 7(c) and (d). A series of one hundred tunneling spectra was acquired across the vortex core for the two samples (Figs. 7(e)

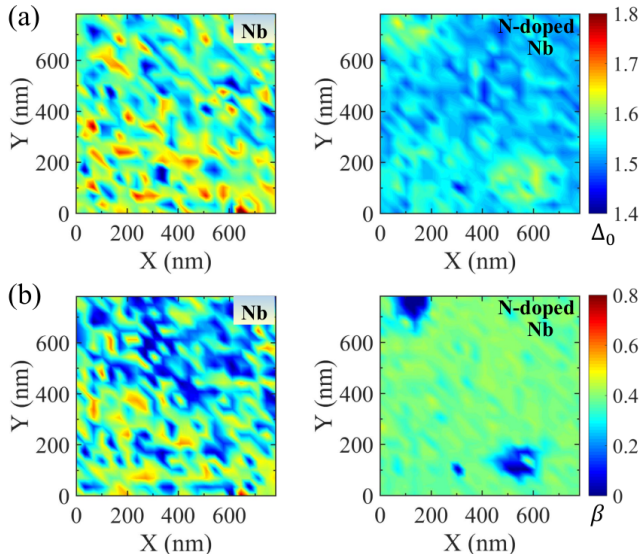


FIG. 6. Local maps of Δ_0 (a) and β (b) over 24×24 pixels. The parameters were extracted by fitting the tunneling spectra acquired at each location with the proximity model [44] described in the text. Spectra were taken 32.6 nm away from each other at the tunneling parameters of $I_{set} = 60$ pA, $V_{set} = 10$ mV, $V_{mod} = 200$ μ V, $f = 373.1$ Hz, and $T = 1.0 - 1.7$ K.

and (f)). The line spectra show the spatial evolution of the tunneling spectra with the coherence peak vanishing at the vortex core on a length scale given by the coherence length. In the clean limit, in conventional BCS-like superconductors the tunneling spectra at the vortex center reveal the presence of a peak at zero energy (Fermi level), which is a signature of low-lying Caroli-de Gennes-Matricon bound states [74] localized in the vortex core [75]. These states are similar to ballistic Andreev trajectories in short superconductor-normal-superconductor junctions. However, in dirty superconductors, where the superconducting coherence length $\xi \simeq (l\xi_0)^{1/2}$ is larger than the mean free path l the core levels are broadened by impurity scattering, resulting in a flat DOS in the vortex core [76]. The absence of discrete vortex core levels suggests that both samples are in a moderately dirty limit. The vortex shape seems to be dependent on the surface roughness which is about several nm over the lateral scale of $\simeq 800$ nm. The coherence length was estimated using several methods which yield similar results.

In Figs. 7(g) and (h) the coherence length ξ was evaluated by azimuthally averaging the zero bias conductance around vortex centers on the conductance maps. The azimuthally averaged tunneling conductance, for all the vortices in the maps neglecting the ones on edges, was then fitted to an exponential function of the form $g = g_0 + F \exp(-r/\xi)$, where g_0 is the conductance far from the vortex core, F is a scaling factor, and r is the distance from the vortex core. For the typically prepared

Nb we obtained a coherence length of $\xi \approx 26.9 \pm 1.8$ nm smaller than $\xi_0 \approx 38$ nm for a clean Nb. This suggests that the surface of the untreated Nb sample was in a moderately dirty limit. For the N-doped Nb, we obtained a yet shorter coherence length $\xi \approx 20.4 \pm 1.9$ nm. This result clearly shows that the nitrogen doping results in additional impurity scattering which reduced the mean free path and the coherence length at the surface. Using these values of ξ in the Ginzburg-Landau expression [72, 73] for the upper critical field $B_{c2} = \Phi_0/2\pi\xi^2$, we find $B_{c2} = 460$ mT for typically prepared Nb and $B_{c2} = 790$ mT for N-doped Nb. These numbers are consistent with the values of the upper critical field measured from the tunneling spectra acquired in applied magnetic field. The tunneling spectra acquired as a function of applied magnetic field, away from vortices, on typically prepared Nb sample are presented in the inset of Fig. 8. The zero bias conductance (i.e. the density of states at the Fermi energy), acquired at the mid point between vortices, is shown as a function of field in the main panel of Fig. 8. Here B_{c2} was estimated as the intersection of the high field slope and the normalized zero-bias conductance value at $H > H_{c2}$.

VI. DISCUSSION

The top surface of Nb has a complex oxide structure revealed by XPS measurements. Tunneling measurements performed on native surfaces probe mostly the very top layer through a tunnel barrier produced by the native surface oxide. However, Ar sputtered removes the dielectric oxide so the top surface layer becomes metallic and tunneling probes the electronic state of the Nb underneath the suboxide layer through a vacuum barrier.

The tunneling spectra shown in Fig. 4 reveal a large spread of gap values down to very small Δ on both typically prepared Nb and N-doped native surfaces. These very low values of Δ are indicative of strong spatial inhomogeneities of superconducting properties that may result from thick metallic suboxide islands. Our results show that nitrogen doping reduces the spread of Δ making properties more uniform. This conclusion is consistent with the more uniform distribution of Δ observed by first tunneling measurements on titanium-doped Nb cavities exhibiting the extended $Q(H_0)$ rise [26].

It should be noted that about 50% of the data obtained on native typically prepared Nb surfaces and 30% of the data obtained on N-doped Nb surfaces cannot be properly fitted by either the Dynes model or the proximity model [44]. This is hardly surprising given the complexity of the electronic structure of the oxidized surface and its manifestations in superconducting properties. Moreover, the interpretation of experimental data for the STM tip crashing into the complex oxide surface requires proper theoretical analysis of tunneling through the complex ox-

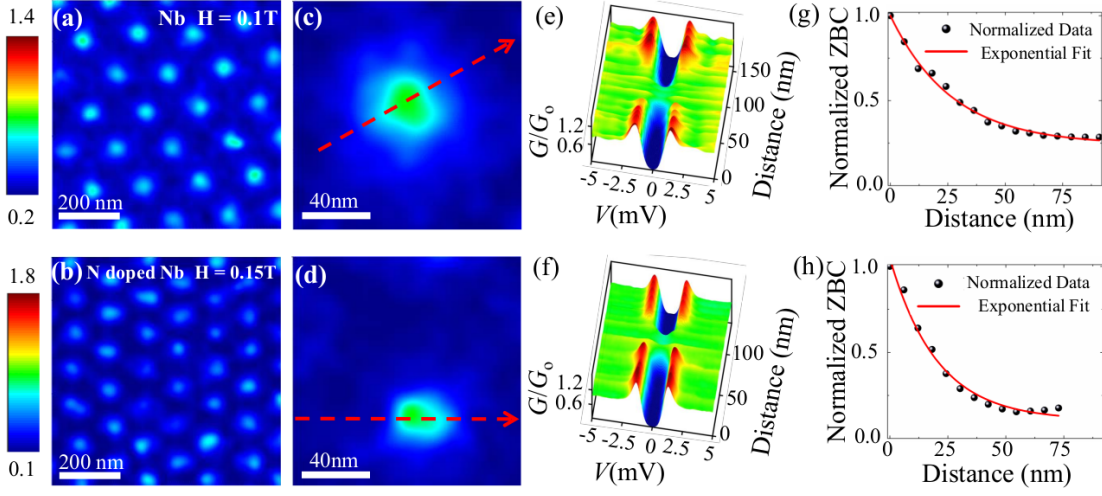


FIG. 7. Tunneling conductance map images acquired at the Fermi level E_F showing the vortex lattice at $T = 1.5$ K on a typically prepared Nb surface (a) and on a N-doped Nb surface (b). The images have been acquired in a magnetic fields of 100 mT (a) and 150 mT (b) applied perpendicular to the surface. The scan area is $745 \text{ nm} \times 745 \text{ nm}$ for both images. (c), (d) High resolution single vortex image at the same temperature and same field for Nb (c) and N-doped Nb (d). The scan area is $134 \text{ nm} \times 134 \text{ nm}$. (e), (f) A series of 100 tunneling spectra (dI/dV) acquired along the red dashed lines shown in (c) and (d). In all images and line spectra the tip was stabilized at $V = 10 \text{ mV}$ and $I = 60 \text{ pA}$ and a lock-in bias modulation amplitude $V_{mod} = 0.2 \text{ mV}$ was used. (g), (h) Evolution of normalized zero bias conductance (ZBC) as a function of position from the vortex core. The ZBC is extracted for each vortex in images (a) and (b) except those close to the edges, the average is then normalized by the ZBC value at the vortex core.

ide of variable thickness and the side tunneling from the tip, which has not been done yet. Nevertheless, our tunneling data and their analysis based on simple models may capture the essential effects of N doping on the thickness of the normal suboxide layer and the resistive barrier this layer and the bulk Nb. The fact that some spectra cannot be properly fitted with the existing theoretical models reinforces the need for a better understanding of the rich physics and materials science of Nb surface. For instance, many spectra appear gapless, possibly indicating the presence of a thick metallic oxide with very small minigap energies of quasiparticles [44]. Some spectra have zero bias peak or deep subgap states which could indicate the presence of magnetic impurities [43] or perhaps two-level states at the surface [51]. Some spectra exhibit higher energy features characteristics of inelastic tunneling. Some of these features may result from the fact that extracting reliable quantitative information from tunneling spectra obtained on native Nb surfaces by crashing the tunneling tip through the oxide structure is not a very controlled and consistent procedure. Yet, the typically prepared Nb surfaces generally have a parabolic background typical of lower work function compared to N-doped surfaces. This indicates that the surface of N-doped samples are more oxidized, consistent

with XPS measurements and earlier point-contact measurements [53].

Our tunneling measurements on Ar ion sputtered typically prepared Nb and N-doped Nb cannot give information about the native Nb oxide but allow us to get important information about the bulk superconducting properties and their lateral inhomogeneities underneath the oxide layer. These results can give insights into new ways of boosting the performance of SRF cavities by materials treatments and surface nanostructuring [44, 45], even though the information about the oxide layer obtained after ion sputtering cannot be related directly to SRF cavities since the native oxide layer changes upon Ar sputtering.

These measurements reveal clear differences of the Nb underneath the oxide layer for typically prepared and N-doped Nb, as shown in Fig. 5. Generally, the typically prepared Nb has higher gap and the Dynes broadening parameter Γ as compared to the N-doped Nb, but also a significantly larger spread of local Δ and Γ values. This means that typically prepared Nb has stronger spatial inhomogeneities of superconducting properties, consistent with the above results for native surfaces. Moreover, the fits of the tunneling spectra to the N-S proximity-coupled model [44] have shown that the nitrogen doping reduces

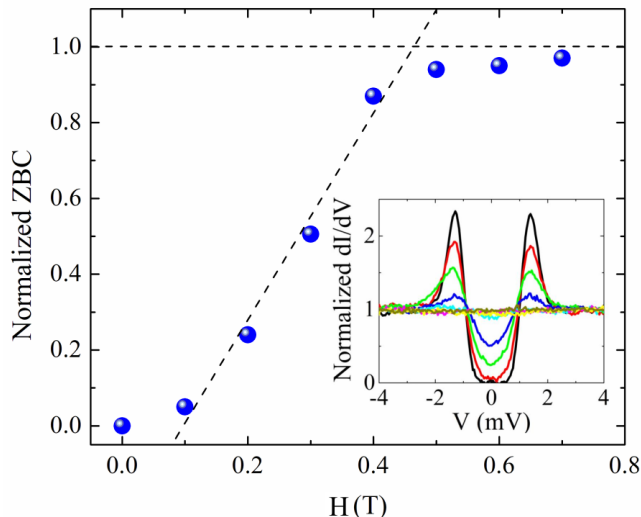


FIG. 8. Normalized zero bias conductance as a function of the applied magnetic field at $T = 1.5$ K for typically prepared Nb. The estimated upper critical field is ~ 450 – 500 mT. The inset shows tunneling spectra dI/dV acquired at 1.5 K at different magnetic fields (from 0 to 0.7 T) applied perpendicular to the sample's surface. Tunneling conditions are $V = 10$ mV, $I = 60$ pA, lock-in modulation $V_{mod} = 0.2$ mV and frequency $f = 373.1$ Hz for all spectra.

both the parameter α , proportional to the thickness of the metallic suboxide layer, and the lateral spread of the local α values. As follows from Fig. 5f, the nitrogen doping reduces the peak values of $\alpha \approx d/\xi_s$ from $\simeq 0.1$ down to ≈ 0.06 . Therefore, tunneling measurement suggest that the metal suboxide layer gets thinner after N doping, in agreement with XPS data. Since Ar sputtering is expected to thicken the metallic suboxide layer, our tunneling data can only be understood if the metallic suboxide layer is thinner in the N-doped samples of the native surface. While the surface of Ar sputtered samples may not be fully representative of the inner surface of Nb cavities, the Ar sputtering technique can nevertheless give important insights into the effect of N doping on the nanoscale oxide layer.

The effect of the nitrogen doping on the parameter β proportional to the N-S contact resistance R_B is also quite striking. As follows from Fig. 5f, the nitrogen doping significantly shrinks the wide spread of β and eliminates most of the low β and high β values observed on the typically prepared Nb. Moreover, the nitrogen doping results in a much narrower distribution of local β values clustered at around $\beta = 0.3$ – 0.4 , where the N-S proximity model [44] predicts a minimum in R_s which can become smaller than R_s for an ideal surface. This optimal surface resistance results from a long-range disturbance of the local DOS into the superconductor which reduces R_s and outweighs an increase of R_s due to minigap states in the proximity-coupled normal layer. The elimination

of low β values likely comes from the increase in the contact resistance, R_B , due to the increase in oxidation of the surface corroborated by XPS. Materials mechanisms by which high-temperature treatment during the nitrogen doping affects the contact resistance R_B are not well understood, but their effect on R_B can be quite significant. For example, an optimal heat treatment can reduce R_B between Ag and $\text{YBa}_2\text{Cu}_3\text{O}_7$ by several orders of magnitude [77, 78]. In any case, changing the parameter β towards its optimum value revealed by the results shown in Fig. 5f would help push the quality factor towards or beyond its theoretical maximum for a perfect surface. The effect of N doping on the metallic suboxide layer inferred from the tunneling data of this work can help optimize both the low-field and high-field surface resistance by tuning the DOS by surface nanostructuring, as it was predicted by recent calculations [44, 45].

The values of α and β cannot be directly related to the native surface of the Nb cavities, as these values have been obtained after Ar sputtering. Yet because both the typically prepared Nb and N-doped Nb samples were subject to the same Ar sputtering process which however produced different values for α and β , it would be reasonable to suggest that these differences do result from the N-doping. Thus, our integrated approach that combines such complementary techniques as XPS and STM/STS coupled to theory allows us to separate the effect of N-doping in the oxide layer from that in the bulk. This, in turn, can give insights into a rather complex interplay of the materials science and superconductivity at the Nb surface, suggesting new ways of further reducing RF losses of already extremely high- Q niobium resonators.

VII. CONCLUSIONS

We have performed XPS and tunneling measurements on native surfaces and Ar sputtered surfaces of typically prepared and N-doped Nb cutouts from SRF cavities. The results presented above suggest that the nitrogen doping gives rise to the following effects: 1. Slightly reduces the average superconducting gap $\bar{\Delta}$ while significantly reducing spatial inhomogeneities of Δ and the DOS broadening parameter Γ in the bulk, as shown by STM of the Ar ion sputtered surfaces. 2. Reduces the thickness of the metallic suboxide layer because of its partial conversion into semiconducting or dielectric oxides NbO_2 and Nb_2O_5 as it is clearly shown by the XPS results and supported by tunneling data on Ar sputtered surfaces. 3. Significantly reduces spatial inhomogeneities of the Nb suboxide thickness and the interface contact resistance parameter β on the Ar sputtered surfaces. Interestingly, the β values for the N-doped samples become clustered at 0.3 – 0.4 close to an optimum β that would yield a minimum theoretical low-field surface resistance in the dirty limit [44]. All in all, these effects of the

nitrogen doping drastically reduce the materials broadening of the quasiparticle density of states and bring it toward an optimal DOS which can theoretically minimize R_s . These experimental results give insight into some possible scenarios by which the nitrogen doping causes the decrease of the surface resistance with the RF field.

The decreases of $R_s(H_0)$ with the RF field can possibly result from the current-induced broadening of DOS at $\Gamma \ll T$ and $\omega \ll T$, as it was shown by calculations of $R_s(H_0)$ from the time-dependent Usadel equations in the dirty limit [35, 41, 45]. The reduction of $R_s(H_0)$ due to this mechanism becomes more pronounced at higher frequencies as the effect of the current-induced broadening of DOS on $R_s(H_0)$ gets amplified by nonequilibrium effects [41]. However, if the native materials broadening of the DOS peaks due to thick suboxide metallic layer and large Γ is strong enough, the current-induced broadening of DOS at high RF fields is not sufficient to turn the conventional decrease of $R_s(H_0)$ with H_0 into the descending $R_s(H_0)$. But if the materials broadening of DOS is ameliorated by the nitrogen doping, as we observed in this work, the current-induced broadening of DOS can take over and $R_s(H_0)$ starts decreasing with H_0 . In this scenario $R_s(H_0)$ can be reduced by engineering an optimum DOS at the surface using pairbreaking mechanisms, such as magnetic impurities or surface nanostructuring [44]. Detailed calculations of the interplay of the effects of proximity-coupled N layer, Dynes parameter and current-induced broadening of DOS on the field dependence of the nonlinear surface resistance $R_s(H_0)$ were performed recently in Ref. 45. Using the theory of Refs. [35, 41, 44, 45], we can infer that the STM results of this work indicate that the decrease of $R_s(H_0)$ with H_0 caused by the nitrogen doping primarily results from the shrinkage of the metallic suboxide layer rather than the decrease of the parameter Γ in the bulk.

STM imaging of vortices has clearly shown that the nitrogen doping decreases the mean free path l and the coherence length down to $\xi \simeq 20$ nm, nearly half of $\xi_0 \simeq 38$ nm in the clean limit. This suggests that the N-doped surface is in a moderately dirty limit with the mean free path $l \sim \xi^2/\xi_0 \simeq 10$ nm. It should be noted that the presence of a proximity-coupled N layer at the surface increases the diameter of the vortex core at the surface, as it was shown by recent calculations of N-S bilayers [79, 80]. Yet these calculations show that for a thin N layer with $d \ll \xi_s$ characteristic of our Nb surfaces, the effect of the metallic suboxide on the vortex core diameter observed by STM is rather weak so the actual ξ_s underneath the metallic suboxide is only a bit shorter than the estimates given above. Therefore, tunneling spectroscopy coupled to other surface analysis techniques such as XPS are effective methods to reveal the evolution of the surface DOS due to the materials treatments. This, in turn, can help engineer an optimum DOS by impurity management and surface oxide nanostructuring to boost

the performance of SRF resonant cavities.

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APPENDIX A: LOCAL DOS IN A PROXIMITY COUPLED N LAYER ON THE S SUBSTRATE

Here we present the formulas obtained in Ref. 44 for the local DOS in a thin N layer coupled with a bulk superconductor (S) by the proximity effect. We used these formulas to fit the STM spectra measured on the typically prepared Nb and nitrogen-doped Nb samples. The local DOS is given by:

$$N_N(\epsilon, x) = N_n \text{Re} \left[\frac{\cosh \theta_0 - i\beta\tilde{\epsilon}}{\sqrt{1 - \beta^2\tilde{\epsilon}^2 - 2i\beta\tilde{\epsilon} \cosh \theta_0}} - \frac{i\tilde{\epsilon}x(x+2d)\sinh^2 \theta_0}{2\xi_N^2[1 - \beta^2\tilde{\epsilon}^2 - 2i\beta\tilde{\epsilon} \cosh \theta_0]} \right], \quad (5)$$

$$N_S(\epsilon, x) = N_s \text{Re} \left[\frac{\tilde{\epsilon}(1 + 6t^2 + t^4) + 4t(1 + t^2)}{(1 - t^2)^2\sqrt{\tilde{\epsilon}^2 - 1}} \right], \quad (6)$$

where $\tilde{\epsilon} = \epsilon + i\Gamma$, $\xi_N = (\hbar D_n/2\Delta)^{1/2}$, the parameters α and β are defined by Eq. (4), and x is the coordinate across the N layer located at $-d < x < 0$. Furthermore,

$$t(x) = \left(\tanh \frac{\theta_0 - \theta_\infty}{4} \right) e^{-k_\epsilon x}. \quad (7)$$

Here $k_\epsilon = [\Delta^2 - \tilde{\epsilon}^2]^{1/4}/(\hbar D_s)^{1/2}$, $\sinh \theta_\infty = \Delta/\sqrt{\tilde{\epsilon}^2 - \Delta^2}$, and θ_0 satisfies the following self-consistency equation:

$$2k_\epsilon \sinh \frac{\theta_0 - \theta_\infty}{2} = i\tilde{\epsilon}\Phi \sinh \theta_0 + i\Psi \cosh \theta_0, \quad (8)$$

which takes into account the proximity effect in the N layer and a local reduction of $\Delta(x)$ in the S region at the

N-S interface. The parameters Φ and Ψ are given by

$$\Phi = \frac{\alpha}{\sqrt{1 - \beta^2 \tilde{\epsilon}^2 - 2i\beta \tilde{\epsilon} \cosh \theta_0}}, \quad (9)$$

$$\Psi = \frac{\alpha(\beta - 1)}{1 + \beta^2} + \frac{\alpha}{(1 + \beta^2)^{3/2}} \ln \frac{(1 + \beta\Lambda)(\beta + \sqrt{1 + \beta^2})}{\sqrt{(1 + \Lambda^2)(1 + \beta^2)} - \Lambda + \beta}, \quad (10)$$

where $\Lambda = \hbar\Omega/\Delta$, and Ω is the Debye frequency. For Nb with $\Delta \simeq 17.5$ K and $\hbar\Omega/k_B \simeq 275$ K, we have $\Lambda \simeq 15.7$. Since the STM spectra were taken at low temperatures $T \simeq 1 - 1.5$ K well below $T_c = 9.2$ K, we used the bulk pair potential Δ in the S region at $T = 0$. In the case of weak DOS broadening ($\Gamma \ll \Delta$), Δ simplifies to [44]

$$\Delta = \Delta_0 - \Gamma, \quad \Delta_0 = 1.84k_B T_c. \quad (11)$$

We calculated the local DOS by solving Eqs. (5)-(11) numerically using a MATLAB code for different values of the fit parameters α and β , assuming that $N_s = N_n$ and $\Gamma_s = \Gamma_n = \Gamma$. In the relevant case of $d \ll \xi_N$, the local DOS probed by STM is nearly constant across the thin N layer, so we calculated N_N from Eq. (5) at $x = 0$.

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- [1] J. Zmuidzinas, Superconducting microresonators: Physics and applications, *Annu. Rev. Condens. Matter Phys.* **3**, 169 (2012).
 - [2] M. H. Devoret and R. J. Schoelkopf, Superconducting circuits for quantum information: an outlook, *Science* **339**, 1169 (2013).
 - [3] M. A. Hein, in *Microwave Superconductivity*, edited by H. Weinstock, NATO ASI Series E: Applied Sciences, Vol. 375 (Kluwer, Dordrecht, 2002), p. 21-53.
 - [4] H. Padamsee, J. Knobloch, and T. Hays, *RF Superconductivity for Accelerators* Second Ed. Wiley ISBN: 978-3-527-40842-9 (2008).
 - [5] C. Z. Antoine, *Materials and Surface Aspects in the Development of SRF Niobium Cavities* (EuCARD Editorial Series on Accelerator Science 2012).
 - [6] A. Gurevich, Superconducting radio-frequency fundamentals for particle accelerators, *Rev. Accel. Sci. Technol.* **5**, 119 (2012).
 - [7] H. S. Padamsee, Superconducting Radio-Frequency Cavities, *Annu. Rev. Nucl. Particle Sci.* **64**, 175 (2014).
 - [8] D. C. Mattis and J. Bardeen, Theory of the Anomalous Skin Effect in Normal and Superconducting Metals, *Phys. Rev.* **111**, 412 (1958).
 - [9] R. H. Parmenter, Nonlinear Electrodynamics of Superconductors with a Very Small Coherence Distance, *RCA Reviews*, **26**, 323 (1962).
 - [10] J. Bardeen, Critical Fields and Currents in Superconductors, *Rev. Mod. Phys.* **34**, 667 (1962).
 - [11] N. B. Kopnin, *Theory of nonequilibrium superconductivity*. (Oxford Univ. Press, 2001)
 - [12] C. Z. Antoine, Influence of crystalline structure on rf dissipation in superconducting niobium, *Phys. Rev. Accel. Beams* **22**, 034801 (2019).
 - [13] A. Gurevich and G. Ciovati, Effect of vortex hotspots on the radio-frequency surface resistance of superconductors, *Phys. Rev. B* **87**, 054502 (2013).
 - [14] J.-M. Vogt, O. Kugeler, and J. Knobloch, Impact of cool-down conditions at T_c on the superconducting rf cavity quality factor, *Phys. Rev. ST Accel. Beams* **16**, 102002 (2013).
 - [15] A. Romanenko, A. Grassellino, O. Melnychuk, and D. A. Sergatskov, Dependence of the residual surface resistance of superconducting radio frequency cavities on the cooling dynamics around T_c , *J. Appl. Phys.* **115**, 184903 (2014).
 - [16] M. Martinello, M. Checchin, A. Grassellino, A. C. Crawford, O. Melnychuk, A. Romanenko, and D. A. Sergatskov, Magnetic flux studies in horizontally cooled elliptical superconducting cavities, *J. Appl. Phys.* **118**, 044505 (2015).
 - [17] J.-M. Vogt, O. Kugeler, and J. Knobloch, High-Q operation of superconducting rf cavities: Potential impact of thermocurrents on the rf surface resistance, *Phys. Rev. ST Accel. Beams* **18**, 042001 (2015).
 - [18] S. Huang, T. Kubo, and R. L. Geng, Dependence of trapped-flux-induced surface resistance of a large-grain Nb superconducting radio-frequency cavity on spatial temperature gradient during cooldown through T_c , *Phys. Rev. Accel. Beams* **19**, 082001 (2016).
 - [19] D. Gonnella, J. Kaufman, and M. Liepe, Impact of nitrogen doping of niobium superconducting cavities on the sensitivity of surface resistance to trapped magnetic flux, *J. Appl. Phys.* **119**, 073904 (2016).
 - [20] S. Posen, M. Checchin, A. C. Crawford, A. Grassellino, M. Martinello, O. S. Melnychuk, A. Romanenko, D. A. Sergatskov, and Y. Trenikhina, Efficient expulsion of magnetic flux in superconducting radiofrequency cavities for high Q_0 applications, *J. Appl. Phys.* **119**, 213903 (2016).
 - [21] B. Oripov, T. Bieler, G. Ciovati, S. Calatroni, P. Dhakal, T. Junginger, O. B. Malyshev, G. Terenziani, A.-M. Valente-Feliciano, R. Valizadeh, S. Wilde, and S. M. Anlage, High-Frequency Nonlinear Response of Superconducting Cavity-Grade Nb Surfaces, *Phys. Rev. Applied* **11**, 064030 (2019).
 - [22] A. Grassellino, A. Romanenko, D. Sergatskov, O. Melnychuk, Y. Trenikhina, A. Crawford, A. Rowe, M. Wong, T. Khabiboulline, and F. Barkov, Nitrogen and argon doping of niobium for superconducting radio frequency cavities: a pathway to highly efficient accelerating structures, *Supercond. Sci. Technol.* **26**, 102001 (2013).
 - [23] A. Romanenko, A. Grassellino, A.C. Crawford, D.A. Sergatskov, and O. Melnychuk, Ultra-high quality factors in superconducting niobium cavities in ambient magnetic fields up to 190 mG, *Appl. Phys. Lett.* **105**, 234103 (2014).
 - [24] D. Gonnella, R. Eichhorn, F. Furuta, M. Ge, D. Hall, V. Ho, G. Hoffstaetter, M. Liepe, T. O'Connell, S. Posen, P. Quigley, J. Sears, V. Veshcherevich, A. Grassellino, A. Romanenko, and D.A. Sergatskov, Nitrogen-doped 9-cell cavity performance in a test cryomodule for LCLS-II, *J. Appl. Phys.* **117**, 023908 (2015).
 - [25] G. Ciovati, P. Dhakal, and A. Gurevich, Decrease of the surface resistance in superconducting niobium resonator cavities by the microwave field, *Appl. Phys. Lett.* **104**, 092601 (2014).
 - [26] P. Dhakal, G. Ciovati, G. R. Myneni, K. E. Gray, N.

- Groll, P. Maheshwari, D. M. McRae, R. Pike, T. Proslir, F. Stevie, R. P. Walsh, Q. Yang, and J. Zasadzinski, Effect of high temperature heat treatments on the quality factor of a large-grain superconducting radio-frequency niobium cavity, *Phys. Rev. ST Accel. Beams* **16**, 042001 (2013).
- [27] G. Ciovati, P. Dhakal, and G.R. Myneni, Superconducting radio-frequency cavities made from medium and low-purity niobium ingots, *Supercond. Sci. Technol.* **29**, 064002 (2016).
- [28] J. T. Maniscalco, D. Gonnella, and M. Liepe, The importance of the electron mean free path for superconducting radio-frequency cavities, *J. Appl. Phys.* **121**, 043910 (2017).
- [29] Z. Yang, X. Lu, W. Tan, J. Zhao, D. Yang, Y. Yang, Y. He, and K. Zhou, XPS studies of nitrogen doping niobium used for accelerator applications, *Appl. Surf. Sci.* **439**, 1119 (2018).
- [30] Z. Yang, X. Lu, Y. He, W. Tan, S. Huang, and H. Guo, Magnetic properties and hydrides precipitation observation of nitrogen doping niobium used for accelerator applications arXiv:1804.07443 (2018).
- [31] P. Dhakal, S. Chetri, S. Balachandran, P. J. Lee, and G. Ciovati, Effect of low temperature baking in nitrogen on the performance of a niobium superconducting radio frequency cavity, *Phys. Rev. Accel. Beams* **21**, 032001 (2018).
- [32] P. Dhakal, G. Ciovati, P. Kneisel, and G. R. Myneni, Enhancement in Quality Factor of SRF Niobium Cavities by Material Diffusion, *IEEE Trans. Appl. Supercond.* **25**, 1 (2015).
- [33] A. Grassellino, A. Romanenko, Y. Trenikhina, M. Checchin, M. Martinello, O. S. Melnychuk, S. Chandrasekaran, D. A. Sergatskov, S. Posen, A. C. Crawford, S. Aderhold, and D. Bice, Unprecedented quality factors at accelerating gradients up to 45 MVm⁻¹ in niobium superconducting resonators via low temperature nitrogen infusion, *Supercond. Sci. Technol.* **30**, 094004 (2017).
- [34] G. Ciovati, G. Ereemeev, and F. Hannon, High field Q slope and the effect of low-temperature baking at 3 GHz, *Phys. Rev. Accel. Beams* **21**, 012002 (2018).
- [35] A. Gurevich, Reduction of dissipative nonlinear conductivity of superconductors by static and microwave magnetic fields, *Phys. Rev. Lett.* **113**, 087001 (2014).
- [36] A. Anthore, H. Pothier, and D. Esteve, Density of states in a superconductor carrying a supercurrent, *Phys. Rev. Lett.* **90**, 127001 (2003).
- [37] K. Maki, The behavior of superconducting thin films in the presence of magnetic fields and currents, *Prog. Theor. Phys.* **31**, 731 (1964).
- [38] P. Fulde, Tunneling density of states for a superconductor carrying a current, *Phys. Rev.* **137**, A783 (1965).
- [39] K. Maki, Gapless superconductivity, in *superconductivity*, edited by R. D. Parks (Marcel Dekker, Inc., New York, 1969).
- [40] M. P. Garfunkel, Surface impedance of type-I superconductors: Calculation of the effect of a static magnetic field, *Phys. Rev.* **173**, 516 (1968).
- [41] A. Gurevich, Theory of RF superconductivity for resonant cavities, *Supercond. Sci. Technol.* **30**, 034004 (2017).
- [42] S. Casalbuoni, E. A. Knabbe, J. Kötzler, L. Lilje, L. von Sawilski, P. Schmüser, and B. Steffen, Surface superconductivity in niobium for superconducting RF cavities, *Nucl. Instrum. Meth. Phys. Res. A* **538**, 45 (2005).
- [43] T. Proslir, M. Kharitonov, M. Pellin, J. Zasadzinski, and G. Ciovati, Evidence of surface paramagnetism in niobium and consequences for the superconducting cavity surface impedance, *IEEE Trans. Appl. Supercond.* **21**, 2619 (2011).
- [44] A. Gurevich and T. Kubo, Surface impedance and optimum surface resistance of a superconductor with an imperfect surface *Phys. Rev. B* **96**, 184515 (2017).
- [45] T. Kubo and A. Gurevich, Field-dependent nonlinear surface resistance and its optimization by surface nanostructuring in superconductors, *Phys. Rev. B* **100**, 064522 (2019).
- [46] A. Dacca, G. Gemme, L. Mattera, and R. Parodi, XPS analysis of the surface composition of niobium for superconducting RF cavities, *Appl. Surf. Sci.* **126**, 219 (1998).
- [47] K. Kowalski, A. Bernasik, W. Singer, X. Singer, and J. Camra, Proc. 11-th Workshop on RF Superconductivity, Travemünde, Germany, 2003).
- [48] R. Cava, B. Batlogg, J. Krajewski, P. Gammel, H. Poulsen, W. Peck, and L. Rupp, Antiferromagnetism and metallic conductivity in Nb₁₂O₂₉ *Nature* **350**, 598 (1991).
- [49] R. Cava, B. Batlogg, J. Krajewski, H. Poulsen, P. Gammel, W. Peck, and L. Rupp, Electrical and magnetic properties of Nb₂O_{5δ} crystallographic shear structures, *Phys. Rev. B* **44**, 6973 (1991).
- [50] T. McQueen, Q. Xu, E. Andersen, H. Zandbergen, and R. Cava, Structures of the reduced niobium oxides Nb₁₂O₂₉ and Nb₂₂O₅₄ *J. Solid State Chem.* **180**, 2864 (2007).
- [51] A. Romanenko and D. I. Schuster, Understanding quality factor degradation in superconducting niobium cavities at low microwave field amplitudes, *Phys. Rev. Lett.* **119**, 264801 (2017).
- [52] W. P. M. R. Pathirana and A. Gurevich, Nonlinear dynamics and dissipation of a curvilinear vortex driven by a strong time-dependent Meissner current, *Phys. Rev. B* **101**, 064504 (2020).
- [53] N. R. Groll, C. Becker, G. Ciovati, A. Grassellino, A. Romanenko, J. F. Zasadzinski, and T. Proslir, Insight into bulk niobium superconducting RF cavities performances by tunneling spectroscopy, arXiv:1805.06359v1.
- [54] B. Aune et al., Superconducting TESLA cavities, *Phys. Rev. ST Accel. Beams*, **3**, 092001, (2000).
- [55] G. Ciovati, *Investigation of the superconducting properties of niobium radio-frequency cavities*. Ph.D. thesis, Phys. Dept., Old Dominion University, Norfolk, VA, USA, (2005)
- [56] The Stopping and Range of Ions in Matter. ver. SRIM-2013, 2013. [Online]. Available: <http://www.srim.org/>
- [57] M. Grundner and J. Halbritter, On the natural Nb₂O₅ growth on Nb at room temperature *Surf. Sci.* **136**, 144 (1984).
- [58] Z. P. Hu, Y. P. Li, M. R. Ji, and J. X. Wu, The interaction of oxygen with niobium studied by XPS and UPS, *Solid State Commun.* **71**, 849 (1989).
- [59] B. R. King, H. C. Patel, D. A. Gulino, and B. J. Tatarchuk, Kinetic measurements of oxygen dissolution into niobium substrates: In situ X-ray photoelectron spectroscopy studies, *Thin Solid Films* **192**, 351 (1990).
- [60] H. Tian, C.E. Reece, M.J. Kelley, S. Wang, L. Plucinski, K.E. Smith, M. M. Nowell, Surface studies of niobium chemically polished under conditions for superconducting radio frequency (SRF) cavity production, *Appl. Surf. Sci.*

- 253**, 1236 (2006)
- [61] G.D.L. Semione, A. Dangwal Pandey, S. Tober, J. Pfrommer, A. Poulain, J. Drnec, G. Schütz, T.F. Keller, H. Noei, V. Vonk, B. Foster, and A. Stierle, Niobium near-surface composition during nitrogen infusion relevant for superconducting radio-frequency cavities, *Phys. Rev. Accel. Beams* **22**, 103102 (2019)
 - [62] I. Lindau and W. E. Spicer, Oxidation of Nb as studied by the uv-photoemission technique, *J. Appl. Phys.* **45**, 3720 (1974).
 - [63] H. H. Farrell, H. S. Isaacs, and M. Strongin, The interaction of oxygen and nitrogen with the niobium (100) surface: II. Reaction kinetics, *Surf. Sci.* **38**, 31 (1973).
 - [64] R. Franchy, T. U. Bartke, and P. Gassmann, The interaction of oxygen with Nb (110) at 300, 80 and 20 K, *Surf. Sci.* **366**, 60 (1996).
 - [65] S. Hashimoto and A. Tanaka, Alteration of Ti 2p XPS spectrum for titanium oxide by low-energy Ar ion bombardment Surface and Interface Analysis, **34**, 262 (2002).
 - [66] T. Ohsawa, J. Okubo, T. Suzuki, H. Kumigashira, M. Oshima, and T. Hitosugi, An n-Type Transparent Conducting Oxide: Nb₁2O₂9 *J. Phys. Chem. C* **115**, 16625 (2011).
 - [67] J. Halbritter, On the oxidation and on the superconductivity of niobium, *Appl. Phys. A* **43**, 1 (1987).
 - [68] P. C. Karulkar, Effects of sputtering on the surface composition of niobium oxides, *J. Vac. Sci. Technol.* **18**, 169 (1981).
 - [69] J. Zasadzinski, Tunneling spectroscopy of conventional and unconventional superconductors. in *The Physics of Superconductors* edited by K. H. Bennemann and J. B. Ketterson (Springer, 2003), p. 591, Chap. 15.
 - [70] R. C. Dynes, V. Narayanamurti, and J. Garno, Direct Measurement of Quasiparticle-Lifetime Broadening in a Strong-Coupled Superconductor, *Phys. Rev. Lett.* **41**, 1509 (1978).
 - [71] W. Brinkman, R. Dynes, and J. Rowell, Tunneling conductance of asymmetrical barriers, *J. Appl. Phys.* **41**, 1915 (1970).
 - [72] G. Blatter, M. V. Feigel'man, V. B. Geshkenbein, A. I. Larkin, and V. M. Vinokur, Vortices in high-temperature superconductors, *Rev. Mod. Phys.* **66**, 1125 (1994).
 - [73] E. H. Brandt, The flux-line lattice in superconductors, *Rep. Prog. Phys.* **58**, 1465 (1995).
 - [74] C. Caroli, P. G. De Gennes, and J. Matricon, Bound Fermion states on a vortex line in a type II superconductor, *Phys. Lett.* **9**, 307 (1964).
 - [75] H. F. Hess, R. B. Robinson, R. C. Dynes, J. M. Valles, Jr., and J. V. Waszczak, Scanning-Tunneling-Microscope Observation of the Abrikosov Flux Lattice and the Density of States near and inside a Fluxoid, *Phys. Rev. Lett.* **62**, 214 (1989).
 - [76] C. Renner, A. D. Kent, P. Niedermann, Ø. Fischer, and F. Lévy, Scanning tunneling spectroscopy of a vortex core from the clean to the dirty limit, *Phys. Rev. Lett.* **67**, 1650 (1991).
 - [77] R. P. Robertazzi, A. W. Kleinsasser, R. B. Laibowitz, R. H. Koch, and K. G. Stawiasz, *in situ* Ag/YBa₂Cu₃O₇ contacts for superconductor-normal-metal-superconductor devices, *Phys. Rev. B* **46**, 8456 (1992).
 - [78] J. W. Ekin, S. E. Russek, C. C. Clickner, and B. Jeanerret, *In situ* noble metal YBa₂Cu₃O₇ thin-film contacts, *Appl. Phys. Lett.* **62**, 369 (1993).
 - [79] V. S. Stolyarov, T. Cren, Ch. Brun, I. A. Golovchanskiy, O. V. Skryabina, D. I. Kasatonov, M. M. Khapaev, M. Yu. Kupriyanov, A. A. Golubov, and D. Rodichev, Expansion of a superconducting vortex core into a diffusive metal, *Nat. Commun.* **9**, 2277 (2018).
 - [80] A. Gurevich, Tuning vortex fluctuations and the resistive transition in superconducting films with a thin overlayer, *Phys. Rev. B* **98**, 024506 (2018).