Distinguishing the Roles of Atomic-Scale Surface Structure and Chemical Composition in Electron Phonon Coupling of the Nb(100) Surface Oxide Reconstruction

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ABSTRACT: The $(3 \times 1)$-O/Nb(100) surface $\lambda_S$ was measured to be $0.20 \pm 0.06$, and its atomic-scale surface structure was confirmed. These results were supported by consistency between measured helium atom scattering Debye–Waller factors and ab initio density-functional theory predictions. The $\lambda_S$ measured for the $(3 \times 1)$-O surface reconstruction is further diminished from the metallic, unreconstructed Nb(100) value and the reported bulk Nb $\lambda$ values. Furthermore, varying subsurface O has no significant effect on the $\lambda_S$ of the $(3 \times 1)$-O reconstruction. While the metallic, unreconstructed Nb(100) surface is significantly affected by accumulated subsurface C and O, the $(3 \times 1)$-O reconstruction stabilizes its $\lambda_S$ against the effects of subsurface O. Due to the low $\lambda_S$, a negligible critical temperature ($T_C$) $\leq 6.2 \times 10^{-3}$ K was estimated, indicating that at operational temperatures of $\sim 2$ K, the $(3 \times 1)$-O/Nb(100) reconstruction is not superconducting alone. However, the proximity effect indicates that a thin normal metal in contact with a superconductor exhibits some superconducting properties while the superconductor’s properties are diminished. These results contain the first measurement of $(3 \times 1)$-O/Nb(100) $\lambda_S$ distinguish the effects of surface structure and chemical composition on $\lambda_S$ and indicate that the $(3 \times 1)$-O/Nb(100) surface has diminished superconducting properties relative to the unreconstructed, metallic Nb(100) and the Nb bulk.

1. INTRODUCTION

Niobium is the standard material for superconducting radio frequency cavities in high-energy particle accelerators. Nb found its ubiquitous use and extensive study in SRF cavities due to both its normal and superconducting state properties. For example, Nb’s relatively high ductility enables facile shaping of optimal cavity geometries for relatively high quality (Q) factors and accelerating fields. Additionally, pure Nb has a relatively high thermal conductivity facilitating sufficient cooling, essential to enter and maintain Nb’s superconducting state. Nb’s superconducting state’s relatively high critical temperature ($T_C$) and low RF surface resistance ($R_s$) drive high Q factors at attainable operating temperatures. The superconducting state’s capability of repelling magnetic fields contains accelerating RF fields. In fact, the RF field only penetrates up to $\sim 100$ nm in Nb SRF cavities, thus RF field energy losses occur along the SRF cavity’s surface. The Nb’s SRF cavity’s RF surface resistance determines the magnitudes of the energy losses. These losses heat the SRF cavity, in turn requiring more cooling to maintain the optimal operational temperatures and driving up costs of operation. Experimental and theoretical studies have documented and studied mechanisms in which even local hot spots from inhomogeneities, defects, and topographical variations can heat and quench entire SRF cavities. Thus, optimal preparation of Nb SRF cavity surfaces is required to prepare energetically efficient SRF cavities and keep costs of operation from being prohibitively high. In other words, the relationship between the atomic-scale surface structure and the resulting superconducting properties at the surface is critical in improving and developing next generation SRF cavity materials.

Extensive study of Nb and Nb SRF cavities has pushed their performance to the fundamental limits of operation. Thus, the SRF community has begun developing new materials and cavity treatments to further reduce $R_s$ maximize the super-heating field ($H_{sh}$), minimize power loss, and optimize overall...
properties such as the critical temperature \(T_C\). Furthermore, this constant determines many superconducting performance. An important part of that gap is the correlation of structure and composition of the NbO surface oxide monolayer to the resulting surface superconducting properties.

While the measurement of the bare metal \(\lambda\) yields new insight, this result cannot distinguish the effect of the interface from that of the surface oxide reconstruction on the surface superconductivity. Thus, there remains a critical gap in the foundational knowledge of the atomic scale surface structure and composition as well as its effects on SRF cavity performance. An important part of that gap is the correlation of structure and composition of the NbO surface oxide monolayer to the resulting surface superconducting properties.

Supersonic helium beams have been used to probe surfaces since the 1920s. Their lack of penetration into the bulk, chemical inactivity, and remarkably narrow velocity distributions are sufficient to create a truly surface sensitive technique. The de Broglie wavelength and narrow momentum distribution of He atoms are well matched to atomic-scale structure and allow for precise measurements.

Coincidentally, the momentum and energy of He atoms sufficiently resonate with surface phonons, making HAS uniquely suited to measure and resolve low-energy phonon modes at surfaces. While helium atoms exchange energy with phonons, the helium atoms scatter off of the electron density. Thus, inelastic helium–phonon scattering events are actually two concerted scattering events: helium–electron and electron–phonon. A theoretical description of this helium–electron–phonon scattering event has been developed for metals, semiconductors, topological insulators, 2D materials, and metallic films to show that the Debye–Waller (DW) factor is directly proportional to the SEPC \(\lambda_\phi\). The derivation starts from the distorted-wave Born approximation, using second-order perturbation theory to define electron–phonon matrix elements, and adopting additional yet reasonable approximations. The DW factor...
describes thermal attenuation of the scattered He intensity and does so as a multiplicative factor present in all scattering probabilities.\textsuperscript{47,51} This DW factor originally came from neutron and X-ray scattering, accounting for motion of nuclei in the lattice from thermal excitation of phonons.\textsuperscript{23,47,50} However, after being applied to helium atom scattering, the theory was developed and the role of the electron density elucidated.\textsuperscript{51,57} Simply put, the thermal excitation of phonons at or near enough to the surface perturbs the surface electron density, reducing the coherence of the scattered He and measured HAS intensity.

The work presented herein provides the first measurement of $\lambda$ of the $(3 \times 1)$-O/Nb(100) surface oxide reconstruction. These results distinguish the effect of the surface oxide reconstruction from that of interstitial oxygen on Nb(100)'s surface superconductivity.\textsuperscript{20} These findings begin to fill a critical gap in the foundational knowledge of the effect of atomic-scale surface structure and composition on SRF cavity performance.

2. METHODS

2.1. Experiment. Measurements and surface preparations were performed with a UHV scattering instrument. The instrument has been detailed elsewhere, but is summarized here.\textsuperscript{35,53,65,66} The scattering instrument consisted of three main sections: a differentially pumped beam source, a sample chamber, and a differentially pumped rotating detector. The sample surface was prepared and HAS, AES, and LEED measurements made in situ within the sample chamber. A supersonic atomic or molecular beam was created by expansion from a 15 $\mu$m nozzle that was cooled with a closed-cycle He refrigerator. A skimmer extracted the supersonic beam from within the expansion, allowing the extracted portion of the expansion to continue into the second differentially pumped chamber. In the second differentially pumped chamber, the beam was pulsed with a mechanical chopper. The resulting supersonic beam was nearly monoenergetic ($\Delta v/v \leq 1\%$), making a $\sim$4 mm beam spot size on a 1 cm sample, scattering into $2\pi$ steradians. A triply differentially pumped, computer-controlled, rotatable detector arm collected scattered atoms or molecules with angular and temporal resolution. Once inside the detector, the probe atoms or molecules were ionized by electron bombardment between the differentially pumped detector regions, then mass selected using a quadrupole mass spectrometer, and detected with an electron multiplier, followed by pulse counting electronics. The flight path was 1.5277 m, the sum of the chopper-to-sample path was 0.4996 m, and the sample to ionizer path was 1.0281 m. For our experiments, we used a helium supersonic beam to probe the Nb(100) surface.

Diffraction scans were obtained by square-wave beam modulation, with a 50% duty cycle and rotating the detector at 0.2° increments with fixed incident angle and energy, with an overall instrument angular resolution of 0.2°. The beam was characterized by time-of-flight (TOF) measurements made with a single-slit chopping, 1% duty cycle pattern. The Nb(100) crystal was mounted on a six-axis manipulator within the HAS instrument's sample chamber. This manipulator enables control over the incident angle, $\theta_i$, azimuthal angle, $\phi$, and tilt, $\chi$, with respect to the scattering plane. Electron bombardment heating and a closed-cycle He refrigerator modulated the sample temperature within a range of 300 to 2300 K. Surface Preparation Laboratory (The Netherlands) provided the Nb(100) sample (99.99% purity, $\sim 0.1^\circ$ cut accuracy), which we then cleaned in the HAS instrument by cycles of annealing and flashing up to 1900 K, in addition to sputtering with 1 keV Ne$^+$ ions (3 $\mu$m maximum) and exposing to backfilled O at a surface temperature ($T_s$) of $\sim$1200 K to remove surface C as desorbed CO. These temperatures were measured with a pyrometer. Impurities identified by in situ AES were C, B, S, and N; these were removed by the combination of annealing, flashing, sputtering, and 1200 K $T_s$ exposure to O. We continued the cleaning cycles until only Nb and O were present on the surface in the appropriate ratio, as confirmed by AES, and until the surface was smooth enough for high-intensity He diffraction. Due to the annealing, flashing, sputtering and O exposure process described above, the surface oxide reconstructed $(3 \times 1)$-O/Nb(100) surface formed naturally and spontaneously. The $(3 \times 1)$-O/Nb(100) surface structure and cleanliness was confirmed with AES, LEED, and helium diffraction. During data collection, the Nb sample was periodically flashed to about 1200 K to eliminate unwanted surface adsorbates. Debye–Waller data were obtained by aligning the crystal at each surface temperature and taking diffraction scans across the specular peak. Each Debye–Waller measurement consisted of varying surface temperature up and then down a chosen temperature range, aligning the crystal and taking diffraction scan over specular at each temperature. These measurements were taken from the lower limit, $\sim$550 K, of the chosen temperature range to the upper limit, $\sim$750 K, then immediately back down to the lower limit. The lower temperature limit was determined as the lowest temperature free of substantial background gas adsorption in the time it took to align and take a diffraction scan. The temperature during the Debye–Waller measurement heating the crystal was measured with a type K thermocouple attached to the plate holding the crystal.

The work function of the $(3 \times 1)$-O/Nb(100) surface oxide reconstruction was calculated from ultraviolet photoelectron spectroscopy (UPS) measurements taken in a separate UHV chamber. The $(3 \times 1)$-O structure was formed on a second Nb(100) single crystal, and the surface cleanliness was confirmed with AES. The UPS measurements were collected using a helium discharge lamp (Specs UVS 10/35) optimized for He I photon emission (21.22 eV) positioned 45° above the sample plane. The photoemission spectra were collected by using a cylindrical mirror analyzer (Staib DESA 100). The low kinetic energy portion of the UPS spectrum was obtained by applying a negative voltage to the Nb(100) sample with an external DC source (Agilent E3612A).

2.2. Theoretical Background. To study the $(3 \times 1)$-O/Nb(100) surface, we performed density-functional theory (DFT) calculations using open-source planewave software JDFTx.\textsuperscript{67,68} We implemented ultrasoft pseudopotentials,\textsuperscript{69} using an effective temperature of 20 milli-Hartree and a Fermi function to determine electronic occupancies. The exchange-correlation energy was approximated using the Perdew–Burke–Ernzerhof functional (PBE).\textsuperscript{70} Our calculations employed planewave cutoff energies of 20 and 100 hartree for the electronic wave functions and density, respectively. We computed properties of a slab with six layers of niobium atoms and two layers of oxygen atoms along the surface-normal direction and truncated Coulomb potentials to increase the accuracy of calculated surface properties.\textsuperscript{71} We calculated phonon properties using the finite-difference supercell method, perturbing atoms by 0.1 Bohrs to calculate...
the real space interatomic force constant matrix directly. To improve the accuracy of the phonon modes calculated, we expanded the dynamical matrix by adding submatrices corresponding to the dynamical matrix calculated for Nb bulk. We added enough elements to the matrix to emulate a slab 10 layers deeper than the original one. Interatomic force constant matrices for the slab were evaluated in a $1 \times 3 \times 1$ supercell with a $k$-space sampling density equal to the unit cell’s sampling of $3 \times 9 \times 1$ k-points. For the Nb bulk, we evaluated in a $4 \times 4 \times 4$ supercell with $k$-space sampling density equal to the unit cell’s sampling of the $12 \times 12 \times 12$ k-points.

3. RESULTS AND DISCUSSION

The $(3 \times 1)$-O/Nb(100) surface oxide reconstruction was prepared and confirmed with HAS diffraction and AES in Figure 1a,b, respectively. Figure 1a contains a diffraction scan taken at 550 K along the $<100>$ symmetry axis; AES and diffraction spectra were taken before and after the DW measurements on $(3 \times 1)$-O/Nb(100) surface. In panel (a), the primary Nb peak is evident at 167 eV, the secondary Nb peak at 192 eV, and the primary O (503 eV) peak is present in the appropriate range, O/Nb $\sim 0.15–0.3$, for the $(3 \times 1)$-O. There is an absence of C (270 eV) and N (379 eV) peaks, indicating a clean Nb surface. In panel (b), there is only the first order diffraction peak. The superlattice peaks of the most likely reconstruction, the oxide reconstruction, lie upon this symmetry direction and are evident.

$\Delta K = k_i (\sin \theta_i - \sin \theta_f) = G_{mn}$

(1)

where $\Delta K$ is the change in wavevector of the scattered He and $u$ is mean squared displacement (MSD) of the surface atoms.\(^{74}\) Recently, Manson et al. have derived a relationship between 2W and the surface EPC constant via reasonable approximations, yielding the direct proportionality for metal surfaces above the surface Debye temperature,

$\lambda_{\text{HAS}} \simeq \frac{\ln I_0}{2 \pi \phi} k_i^2$ \(\Delta z\)

(4)

where $I_0$ is the intensity of the specular reflection, $\phi$ is the work function, Z is the number of free electrons per atom, $k_i$ is the Fermi wavevector, and $k_i$ is the surface perpendicular ($z$) component of the incident helium incident wavevector.\(^{55,56}\) In a DW measurement, diffraction scans were taken over the specular peak up and down the temperature range, $\sim 550$ to 750 K, for three beam energies (Figure 2). These DW runs were taken immediately following and after confirmation of structure and composition with He diffraction and AES respectively, ensuring cleanliness.

The beam energies that we used were sufficiently low to require the so-called Beeby correction. The Beeby correction accounts for acceleration due to the attractive portion of the helium-surface potential well depth, $D$.\(^{74}\) The Beeby approximation is commonly used to correct for this effect, taking into account the acceleration of the helium atom from the helium surface potential before scattering. In the Beeby approximation, the potential well depth is added to the incident helium beam energy. This quantity can be related to the DW factor by expanding the traditional expression for the DW factor with standard kinematics. Upon substitution, restriction to specular scattering, and rearrangement, the relation,
\[
\sigma = -\frac{d(2W)}{dT_s} = 4k_i^2 \frac{d(u_z^2)}{dT_s} \cos^2 \theta_i + \frac{D}{E_s}
\] (5)
is obtained, where \(\sigma\) is the negative slope of a DW linear plot, \(k_i\) is the helium incident wavevector, \(\theta_i\) is the incident angle relative to surface normal, \(D\) is the helium-surface potential well depth, and \(E_s\) is the helium incident energy.\(^{47}\) Thus, a fit of DW decay, \(\sigma\), versus \(k_i^2 \cos^2 \theta_i\) yields the helium-surface potential well depth and the first derivative of the mean-square displacement with respect to surface temperature. These diffraction scans and the corresponding plot of \(\sigma\) versus \(k_i^2 \cos^2 \theta_i\) are in Figure 3.

Figure 3. A plot of \(\sigma\) versus \(k_i^2 \cos^2 \theta_i\) and its fit provides the helium-surface well depth, 4.7 meV, and the surface Debye temperature, 390 ± 10 K. Obtaining a value for the well depth, \(D\), allows us to correct our incident beam energy in the so-called Beeby correction. The surface Debye temperature verifies that the DW measurements were made in the high temperature limit of Bose–Einstein phonon population function required for eq 3 to apply. Additionally, the Debye temperature is used in calculating the \(T_s\) from the measured \(\lambda\) in the McMillan equation.

From the fitting parameters, a helium to surface well depth of 4.7 meV was obtained, and a surface Debye temperature of 357 K was determined from the mean squared displacement with the Debye model.

Complementary DFT calculations of phonon modes provided theoretical MSD values. The HAS intensity-vs-temperature data can be converted into MSD, vs-temperature data using the traditional definition of the DW factor (eqs 2 and 3) and the Beeby correction to correct the incident He wavevector.\(^{23,24,74,75}\) The excellent agreement between HAS data and the complementary DFT calculations through MSD, can be seen in Figure 4.

The lines in Figure 4 represent the apparent MSD, calculated with

\[
\langle u_z^2(k) \rangle_T = \frac{1}{P} \left(\sum_{k=1}^{P} u_z(k)\right)_T^2
\] (6)

Figure 4. Comparison of HAS data and DFT data via MSD, (surface perpendicular portion of the MSD). Upper and lower bounds were calculated averaging over single atoms and local averaging in the unit cell, respectively. The local averaging takes the average over nearest and next nearest neighbors. This takes into account the finite volume of the He atom and the fact that it interacts with multiple surface atoms in a single impulsive scattering event. Thus, the apparent MSD, calculated from local averaging has excellent agreement with the HAS data.

where \(p\) is the number of atoms on the surface and \(u_z(k)\) is the atomic displacement operator in the normal direction to the surface for the \(k\)-th atom, calculated with

\[
u_z(k) = \sqrt{\frac{\hbar}{2Nm}} \sqrt{\sum_{qj} a_{qj} + \sum_{qj} a_{qj} \cos q_z x} e^{iq_z \cdot r(k)}
\] (7)

where the summation samples phonon modes \(j\) at wavevectors \(q\) throughout the surface’s Brillouin zone. \(a_{qj}\) is the component of the phonon eigenvector corresponding to the normal displacement of the surface atom of mass \(m\), and the Bose factor \(n(qj) = \frac{1}{e^{\lambda} - 1}\) weights the displacements of each sampled phonon mode at temperature \(T\).\(^{51}\)

Following a similar approach to that used for the metallic, unreconstructed Nb(100) surface,\(^{20}\) we considered the range of interaction of the electron density of the He atom compared to the electron density of the atoms on the surface, given the distance between them. The upper bound averages over single atoms in the unit cell, considering a shorter interaction range than expected. The lower bound in Figure 4 uses eq 5 to average over nearest and next-to-nearest neighbors, which is often used in the literature.\(^{20,75}\)

Before we can use the DW slope to calculate \(\lambda\), we must choose values for the \((3 \times 1)\)-O/Nb(100)’s work function, number of free electrons per atom, and Fermi wave vector. The \((3 \times 1)\)-O/Nb(100) work function was found to be 4.5 ± 3.8 × 10⁻² eV and was calculated by subtracting the width of the UPS spectra from the incident photon energy (21.22 eV), as shown in Figure 5. The secondary electron cutoff (SECO) energy was obtained by calibrating the Fermi level using a Au reference sample.\(^{29,76-78}\)

This fits well with literature that agrees that the work function of Nb, 3.99 eV,\(^{23}\) generally increases with O impurities and oxide reconstructions, but O can have nonmonotonic effects on the work function.\(^{79,80}\) The number of free electrons per atom becomes a weighted average between the number of free electrons of Nb and O atoms in the \((3 \times 1)\)-O unit cell, yielding 2.7 free electrons per atom. The Fermi wave vector was calculated from the number of free electrons using the free electron model to calculate a Fermi wavevector of 0.89 Å⁻¹.\(^{23}\) The DW slope and these chosen values of the work function, number of free electrons per atom,
and Fermi wave vector were used to calculate a \( \lambda \) of 0.20 \pm 0.06 for the (3 \times 1)-O/Nb(100) surface.

This is the first recorded value of \( \lambda \) for the (3 \times 1)-O/Nb(100) surface oxide reconstruction. For reference and clarity, the recorded \( \lambda \) values for bulk Nb are 1.15, 1.04, 1.16, and 0.92, almost twice that of the unreconstructed, metallic Nb(100) surface, 0.50 \pm 0.08.\(^{20,36−44}\) While the interface, even without O or reconstruction, diminishes EPC, the (3 \times 1)-O reconstruction further diminishes EPC.

Each preparation of the (3 \times 1)-O has different amounts of subsurface oxygen. We can make a plot of measured (3 \times 1)-O EPC versus AES O content to probe the effect of subsurface oxygen on the (3 \times 1)-O reconstruction’s EPC (Figure 6).

We find that the amount of subsurface oxygen has no significant effect on the SEPC of the (3 \times 1)-O reconstruction. This is distinct from the effect of subsurface oxygen and carbon on the SEPC of the unreconstructed, metallic Nb(100).\(^{20}\) The unreconstructed, metallic Nb(100) SEPC had a monotonic decrease with accumulation of subsurface O and C.\(^{20}\)

However, the (3 \times 1)-O surface oxide reconstruction is not only robust in terms of its high thermal stability and strong interatomic forces, but also in that its SEPC is not significantly altered by subsurface oxygen.\(^{35,53}\) These results indicate that even if one removed the problematic oxide within an SRF cavity it would introduce a greater susceptibility to impurities.

To elucidate the significance of the (3 \times 1)-O surface oxide reconstruction’s diminished \( \lambda \), we will estimate the critical temperature of this material. In fact, using the Dyson’s version of McMillan’s equation along with our measured \( \lambda \) and surface Debye temperature as well as the standard range (0.1−0.15) for the renormalized Coulomb repulsion, we find a \( T_C \leq 6.2 \times 10^{-4} \) K.\(^{55}\) We see that the surface oxide reconstruction significantly diminishes \( T_C \) to the point that it is not a feasible superconductor on its own. However, the proximity effect occurs when a normal material and superconducting material are in contact with one another.\(^{31−83}\) Cooper pairs leak into the normal state imparting some superconductivity, while the exodus of Cooper pairs from the superconducting material diminishes its superconducting properties.\(^{25,54−86}\) Thus, the (3 \times 1)-O/Nb(100) interface will diminish the superconductivity of the underlying bulk Nb while its own superconductivity is increased. Additionally, neither the (3 \times 1)-O superlattice nor the HAS probe depth approaches the \( \sim 100 \) nm RF field penetration depth of Nb SRF cavities.\(^{2,31,55,56}\) The (3 \times 1)-O/Nb(100) does not quench superconductivity but is expected to significantly diminish the overall superconducting performance on the interface and in the underlying, near-surface bulk.

This continues to build a necessary, missing fundamental understanding of the effects of surface structure and composition on EPC and superconducting properties. Now we can begin to understand the changes to the surface caused by carbon impurities, N doping, Sn alloying, and other SRF cavity preparations. These results provide the first measurement of \( \lambda \) of the (3 \times 1)-O/Nb(100) surface oxide reconstruction and distinguish the effects of structure and composition of the NbO monolayer surface oxide on the resulting surface superconducting properties.

4. CONCLUSION

The (3 \times 1)-O/Nb(100) surface \( \lambda_S \) was measured to be 0.20 \pm 0.06 and its atomic-scale surface structure was confirmed, with our findings further supported by consistency between our measured HAS Debye–Waller factors and \textit{ab initio} density-functional theory predictions. The \( \lambda_S \) measured for the (3 \times 1)-O surface reconstruction is further diminished from the metallic, unreconstructed Nb(100) value and further from the diminished reported bulk Nb \( \lambda \) values. Furthermore, the amount of subsurface oxygen has no significant effect on the \( \lambda_S \) of the (3 \times 1)-O reconstruction. Thus, while the metallic, unreconstructed Nb(100) surface is significantly affected by accumulated C and O, the (3 \times 1)-O reconstruction stabilizes its \( \lambda_S \) against the effects of subsurface O. The significance of Nb(100)’s diminished EPC was further elucidated by estimating relevant superconducting properties from the measured \( \lambda_S \), surface Debye temperature, known material parameters, and well-established equations. Due to the low \( \lambda_S \), a negligible critical temperature \( (T_C) \leq 6.2 \times 10^{-3} \) K was estimated using the McMillan equation. However, this indicates that at operational temperatures of \( \sim 2 \) K, the (3 \times 1)-O/Nb(100) reconstruction is not superconducting on its
own. However, the proximity effect indicates that a thin normal metal on top of a superconductor exhibits some superconducting properties while the superconductor’s properties are diminished. These results contain the first measurement of \((3 \times 1)-\mathrm{O}/\mathrm{Nb}(100)\) \(\lambda_S\) distinguish the effects of surface structure and chemical composition on \(\lambda_S\) and indicate that the \((3 \times 1)-\mathrm{O}/\mathrm{Nb}(100)\) surface has diminished superconducting properties relative to the unreconstructed, metallic Nb(100) and the Nb bulk.

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