

Enhanced Surface Superconductivity of Niobium by Zirconium Doping

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Superconducting radio-frequency (SRF) cavities currently rely on niobium (Nb), and could benefit from a higher- T_c surface, which would enable a higher operating temperature, lower surface resistance, and higher maximum fields. Surface zirconium (Zr) doping is one option for improvement, which has not previously been explored, likely because bulk alloy experiments showed only mild T_c enhancements of 1–2 K relative to Nb. Our *ab initio* results reveal a more nuanced picture: an ideal bcc Nb-Zr alloy would have T_c over twice that of niobium, but displacements of atoms away from the high-symmetry bcc positions due to the Jahn-Teller-Peierls effect almost completely eliminates this enhancement in typical disordered alloy structures. Ordered Nb-Zr alloy structures, in contrast, are able to avoid these atomic displacements and achieve higher calculated T_c up to a theoretical limit of 17.7 K. Encouraged by this, we tested two deposition methods: a physical-vapor Zr deposition method, which produced Nb-Zr surfaces with T_c values of 13.5 K, and an electrochemical deposition method, which produced surfaces with a possible 16-K T_c . An rf test of the highest- T_c surface showed a mild reduction in BCS surface resistance relative to Nb, demonstrating the potential value of this material for RF devices. Finally, our Ginzburg-Landau theory calculations show that realistic surface doping profiles should be able to reach the maximum rf fields necessary for next-generation applications, such as the ground-breaking LCLS-II accelerator. Considering the advantages of Nb-Zr compared to other candidate materials such as Nb₃Sn and Nb-Ti-N, including a simple phase diagram with relatively little sensitivity to composition, and a stable, insulating ZrO₂ native oxide, we conclude that Nb-Zr alloy is an excellent candidate for next-generation, high-quality-factor superconducting rf devices.

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I. INTRODUCTION

While higher- T_c materials long ago supplanted niobium (Nb) in dc wire applications, this humble elemental superconductor (with transition temperature $T_c = 9.2$ K)

remains the material of choice for rf surface applications [1–5] due to the relative ease of producing devices, which approach its fundamental limits of surface resistance and superheating field B_{sh} (the maximum magnetic field at which the Meissner state can be maintained). Higher- T_c surfaces could push these limits further, potentially resulting in far more practical and cost-effective superconducting radio-frequency (SRF) cavities for particle accelerators, in particular. The need for cavities with a high quality factor (low surface resistance) as well as high accelerating gradient (limited by $B_{sh} = 240$ mT for niobium) for next-generation particle accelerators has resulted in many efforts to improve Nb cavities, for example, by growing compound superconductors on the surface. Multilayer superconductors are expected to delay the onset of vortex penetration, leading to increased cavity efficiency

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at higher fields [6–8]. Candidate materials have included MgB_2 [9], NbN [10], Nb-Ti-N [11,12], and Nb_3Sn [13–17]. However, this research has so far failed to approach the theoretical limits [18–21] of these materials due to the difficulty of growing them uniformly on the Nb surface and due to their considerably reduced coherence lengths of just a few nanometers, which make them far more sensitive than Nb to nanoscale defects [22,23].

In contrast, relatively little attention has been paid to the possibility of enhancing T_c and B_{sh} within the native bcc structure of Nb, likely due the perception of an only mild T_c enhancement for the best known bcc alloy candidate Nb-Zr ($T_c = 10.8$ K) [24]. This would otherwise be a very attractive option; while A15 superconductors like Nb_3Sn and rocksalt superconductors like Nb-Ti-N tend to exist in complicated binary or ternary phase diagrams with low- T_c or normal-conducting phases nearby, bcc alloy systems such as Nb-Zr are relatively simple, with the Nb-rich half of the phase diagram completely free of low- T_c phases [25–27]. Additionally, while Nb_3Sn and Nb-Ti-N form complex surface oxides that may behave poorly under rf conditions [28,29], Zr doping facilitates the growth of a wide-band-gap ZrO_2 oxide layer, which is simpler than the Nb native oxide [30,31]. Specifically, while the Nb native oxide tends to contain a variety of oxygen-deficient phases that may absorb rf energy [32–34], the Zr native oxide tends to form very near the ideal ZrO_2 composition [35,36]. These advantages, as well as a potentially longer coherence length, could help Nb-Zr avoid quench-inducing defects, and could also help Nb-Zr reach the low residual (low-temperature limit) resistance values necessary for applications in quantum computing and particle detection [3,16].

To better understand the potential for SRF applications of the Nb-Zr alloy system, we begin with density-functional theory (DFT) and Eliashberg theory in the dilute limit, where the virtual crystal approximation (VCA) allows us to calculate a variety of superconducting properties. We confirm that the addition of Zr to Nb increases T_c , and potentially much more than had previously been observed in bulk Nb-Zr alloy experiments. We then switch from VCA to a supercell approach in order to directly account for lattice relaxation effects and better understand the potential for greatly enhanced T_c . With this approach, we find good agreement with the literature for random alloys at all concentrations, and we show that ordered alloy structures can surpass the limitations of the random alloy to reach notably higher T_c values.

Encouraged by these results, we synthesize Nb-Zr alloy surface layers of different Zr doping profiles using physical vapor and electrochemical methods and examine their material and rf superconducting properties. We find that the measured T_c meets or exceeds literature values for Nb-Zr random alloys, in agreement with our calculations. We show that the enhanced T_c likely translates to improved

performance under rf conditions by comparing the BCS resistance of the alloyed sample to that of a reference Nb sample.

Putting together the data from our DFT calculations and our experimental sample analysis, we use Ginzburg-Landau (GL) theory to investigate how Nb surfaces with different Zr doping profiles will affect the superheating field B_{sh} . Doping with Zr generally results in surface layers whose concentration of Zr varies with depth. Such material inhomogeneities are known to affect maximum rf fields [23], including B_{sh} (see also Ref. [7] for a phenomenological discussion of these effects). Previous studies of these effects have calculated B_{sh} for layered materials [37] and continuously varying impurity concentrations [38] using Eilenberger theory (which is valid for $T \ll T_c$), and for spatial variations in T_c [39,40] using time-dependent GL theory (which is valid for T near T_c). We expand on these studies by incorporating continuous spatial variations of multiple material properties simultaneously, and show that a realistic Zr-doping profile could nearly double B_{sh} . Taken together with potential gains in quality factor and operating temperature, the prospect of significantly increased maximum rf fields makes Zr doping a promising approach for many important applications.

II. SUPERCONDUCTING PROPERTIES OF NB-ZR IN THE DILUTE LIMIT

We calculate the superconducting properties of Nb-Zr alloys in the dilute limit using VCA. We use QUANTUM ESPRESSO (QE) [41–43] to perform the DFT calculations. We use the Perdew-Burke-Ernzerhof [44] functional for the exchange-correlation energy and norm-conserving pseudopotentials [45,46]. We use the Methfessel-Paxton smearing scheme [47] to smear the electrons during lattice relaxation. The isotropic α^2F is calculated in QE with the tetrahedron method [48] using a q mesh of $8 \times 8 \times 8$ and a k mesh of $24 \times 24 \times 24$. We use the EPW code (electron-phonon Wannier) [49,50] to solve the Migdal-Eliashberg equations for superconducting gap and critical temperature with the isotropic α^2F as an input.

To check the accuracy of VCA, we calculate the density of states (DOS) at the Fermi level using the VCA method and compare it with that calculated using supercells at 12.5 at%Zr and 25 at%Zr concentration (8 atom supercell cells). Only the lattice vectors of the supercells were relaxed, and the atoms were kept fixed on the high-symmetry sites. This constraint was applied to maintain consistency between VCA and supercell calculations. Moreover, allowing atoms to move away from the high symmetry tends to decrease the DOS at the Fermi level, especially at high concentrations, as shown in Sec. III. Comparing the DOS at the Fermi level calculated using VCA and supercell, Fig. 1(a), we find that the shape of the DOS between the two methods matches well, but VCA

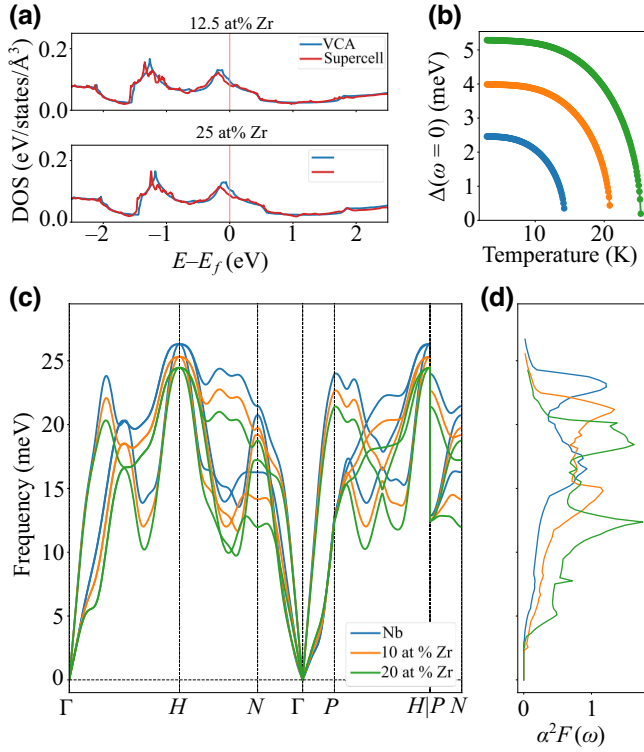


FIG. 1. (a) DOS at the Fermi level using the VCA and supercell methods. The upper plot is at 12.5 at%Zr and the lower plot is at 25 at%Zr concentration. (b) Superconducting gap as a function of temperature. (c) Calculated phonon dispersion and (d) α^2F of Nb-Zr alloys. The blue, orange, and green lines are for pure Nb, 10 at%Zr and 20 at%Zr, respectively. As Zr concentration increases, phonons at lower frequency couple strongly with electrons, increasing the electron-phonon coupling constant.

overestimates DOS at the Fermi level by 16% and 20% at 12.5 at%Zr and 25 at%Zr concentration, respectively. This is due to a slight shifting of the peaks near the Fermi level. We expect this overestimation of DOS in VCA calculations to be less of an issue while calculating superconducting properties at low Zr concentrations; for higher Zr concentrations, refer to Sec. III.

Table I shows the calculated superconducting properties for Zr concentrations ranging from 0 to 25%. The calculated T_c agrees well between the three methods used to calculate the critical temperature: Allen-Dynes [55], Xie [51], and isotropic Eliashberg. Figure 1(b) shows the isotropic superconducting gap as a function of temperature, from which the Eliashberg T_c is obtained as the temperature at which the gap goes to zero. As Zr concentration increases, so do the electron-phonon coupling constant, superconducting gap, and the T_c of the alloy. This increase in T_c can be attributed to softening of the phonons, as shown in Fig. 1(c), and an increase in the density of states at the Fermi level $N(0)$, which ultimately leads to stronger α^2F [Fig. 1(d)]. Note that our calculated T_c 's and superconducting gap values for pure Nb overestimate the experimental values of 9.23 K and 1.5 meV, respectively [56]. It has been suggested that including the effect of spin fluctuation is essential for estimating the T_c of Nb [57,58], which is not included in our calculations. Nevertheless, we expect that spin fluctuation will have little effect on the trends in the critical temperature and fields highlighted in Table I. Later in Sec. III, we account for spin fluctuations via an additive shift to the electron-phonon coupling for estimating the T_c of ordered Nb-Zr alloys.

III. SUPERCONDUCTING PROPERTIES OF NB-ZR ALLOYS AT HIGHER ZR CONCENTRATIONS

Previous experimental studies of $\text{Nb}_{1-n}\text{Zr}_n$ bcc random alloys have found moderately increased T_c and greatly increased upper critical field B_{c2} compared to Nb across a broad compositional range from $n = 0$ to $n = 0.5$ [24,27]. Alloys made with molybdenum (Mo), Nb's other fifth-row neighbor, have T_c 's that drop off quickly with increasing Mo concentration. This data (black dots in Fig. 2) is in qualitative agreement with the simple alloy theory originally used to describe bcc alloy superconductivity, namely that there is a universal d -band shape, and alloying simply shifts the position of the Fermi level by adding or removing d -band electrons, thus altering $N(0)$ and therefore T_c [24,59]. Quantitatively, this effect is captured in our VCA

TABLE I. Calculated superconducting properties of Nb-Zr alloys using VCA and GL theory, including the electron-phonon coupling constant λ^e and the superconducting gap Δ . T_c was calculated using the Allen-Dynes equation, Xie [51], and isotropic Eliashberg theory using $\mu^* = 0.16$. λ_L and B_c have been rescaled to match known values for Nb (Refs. [52] and [53], respectively), while the rescaling value for ξ was calculated via the GL relation $\xi = \Phi_0 / (2\pi\sqrt{2}B_c\lambda_L)$ [54] (where $\Phi_0 \equiv h/2e$).

Composition	λ^e	$\Delta(4K)$ (meV)	v_F (m/s)	$N(0)$ (states/eV/Å ³)	T_c^{AD} (K)	T_c^{Xie} (K)	T_c^{El} (K)	λ_L (nm)	ξ (nm)	κ	B_c (mT)	B_{sh} (mT)
Nb	1.13	2.4	8.50×10^5	0.082	11.24	10.39	14.2	39.0	29.9	1.30	199	241
$\text{Nb}_{0.95}\text{Zr}_{0.05}$	1.30	3.0	8.20×10^5	0.086	13.60	13.46	16.8	39.5	23.9	1.65	247	287
$\text{Nb}_{0.90}\text{Zr}_{0.10}$	1.69	4.0	8.09×10^5	0.091	17.18	18.30	20.8	38.9	18.7	2.08	321	368
$\text{Nb}_{0.80}\text{Zr}_{0.20}$	2.37	5.3	7.79×10^5	0.103	21.17	24.28	25.3	38.0	14.6	2.61	421	456
$\text{Nb}_{0.75}\text{Zr}_{0.25}$	2.85	5.8	7.70×10^5	0.106	22.02	26.49	26.7	37.9	13.8	2.74	444	478

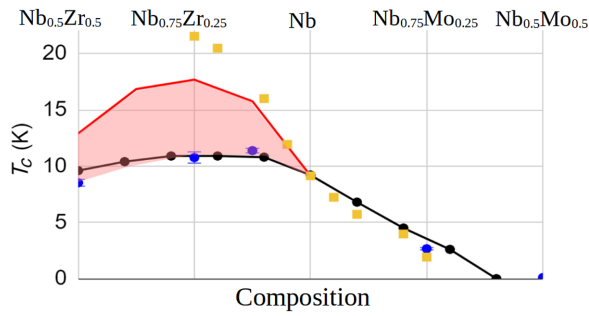


FIG. 2. Alloy T_c versus composition for experiment (black, Ref. [24]), VCA (yellow squares), random supercell theory (blue circles), and Jahn-Teller-Peierls stability limit (red).

calculations (yellow squares in Fig. 2), which show good agreement with experiment for Nb-Mo, but significantly overestimate T_c for Nb-Zr. This indicates that, while VCA may accurately describe Nb-Mo and dilute Nb-Zr alloys, it misses relevant nonlinear effects in the Nb-Zr system that alter the d -band shape and tend to lower T_c .

Exploration of the full compositional range of $\text{Nb}_{1-n}\text{Zr}_n$, therefore, requires an analysis of Nb-Zr, which accounts fully for the effects of Zr substitutions in the Nb lattice; for this we employ the supercell method. Specifically, for each n , we construct 48-atom supercells, substitute the required number of Nb atoms with Zr at random sites, and fully relax the structure, using the JDFTx software package with the PBE exchange-correlation functional and ultrasoft pseudopotentials [44,60,61]. Averaging the resulting DOS over multiple configurations at each composition yields an expected macroscopic $N(0)$. We then estimate T_c as a function of composition through the BCS $N(0)$ - T_c relationship, resulting in the “random alloy” predictions displayed by the blue dots in Fig. 2. We find quite good agreement with the random-alloy experiments for both Nb-Mo and Nb-Zr, indicating that our calculated $N(0)$ -composition relationship correctly captures the nonlinear effects that determine T_c in Nb-Zr random alloys.

While material properties like those in Table I are not generally straightforward to compute for the random alloy (calculation of the phonon dispersion, in particular, is complicated by the large unit cell and lack of symmetries), we expect that most of them, like $N(0)$, will fall somewhere between the Nb value and the ideal virtual crystal alloy value. We thus expect, for example, that the increases in B_c and B_{sh} would be more modest for bulk random alloy samples and cavities than predicted, since most of the increase can be attributed to the predicted changes in T_c (roughly, $B_{sh} \sim B_c \sim T_c$). The notable exception to this is the electron mean free path, which is extremely sensitive to composition in the random alloy. Based on defect-scattering calculations [31], we expect that it will drop from the clean-limit Nb value to less than 10 nm at 5% Zr composition, and to less than 5 nm at 10% Zr

composition. In conjunction with a depth-dependent doping profile, this would generally result in a sample with short mean free path and high T_c near the surface, and long mean free path and T_c approaching the Nb value further from the surface.

Examining our supercell calculations, we find that, for atoms at their unrelaxed, ideal bcc locations, the electronic DOS for Nb-Zr alloys resemble that of Nb with a rigid band shift, similar to what would be found in VCA. However, we find that the minimum-energy atomic coordinates diverge significantly from the ideal bcc locations in a way that significantly reduces $N(0)$. This final, reduced $N(0)$ value varies only modestly with composition up to 50% Zr, explaining the modest variations that are observed in T_c . Figure 3(a) illustrates this relaxation effect for the 50/50 Nb-Zr random alloy, where the initially large DOS peak near the Fermi level essentially vanishes. Moreover, consistent with our observation that simple alloy theories work well for Nb-Mo, Fig. 3(b) shows this relaxation effect to be absent in the Nb-Mo system.

Fundamentally, the Nb-Zr alloy minimizes its energy by lowering the energies of occupied electronic states near the Fermi level, resulting in a reduced $N(0)$. This relaxation does not occur in Nb-Mo, which has fewer states near the Fermi level, and thus less ability to lower its energy in this manner. The redistribution of electronic energy levels in Nb-Zr is accomplished by the relaxation of lattice degrees of freedom, i.e., by the movement of atoms away from their ideal lattice positions. This brings us to a key difference between random Nb-Zr alloys, which have been our focus so far, and ordered Nb-Zr alloys. It has been pointed out that the symmetries of highly ordered structures can effectively limit the degrees of freedom for

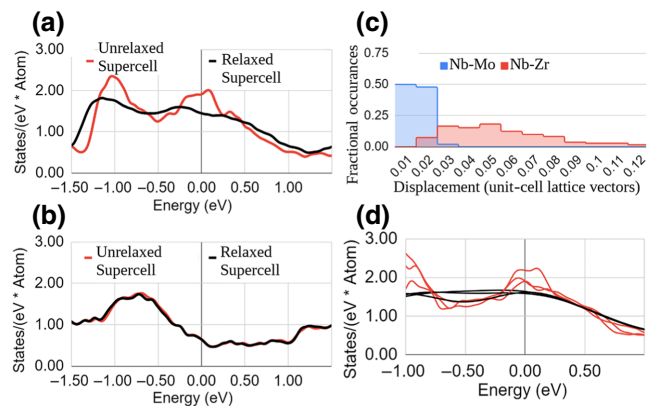


FIG. 3. Electronic DOS for 50/50 Nb-Zr (a) and Nb-Mo (b) random alloys before atomic relaxation (red) and after atomic relaxation (black). (c) Histogram of atomic displacements in 50/50 Nb-Zr (red) and Nb-Mo (blue) alloys. (d) DOS curves for three different ordered 50/50 Nb-Zr alloys before (red) and after (black) applying electronic state energy broadening to reduce $N(0)$ and stabilize the structure.

lattice relaxation [55]. In our case, this could result in a crystal with electronic structure similar to the VCA or the unrelaxed-random-alloy electronic structure and thus a much higher T_c . It may be possible to grow such an ordered alloy in a low-temperature thin-film process such as those often employed in SRF cavity production.

We estimate the maximum attainable T_c of an ordered Nb-Zr alloy of a given composition as follows. We note that the same force, which drives ionic displacements in the Nb-Zr random alloy, tends to break the symmetries of ordered Nb-Zr structures. Indeed, this Jahn-Teller-Peierls effect has been proposed as a driving force for bcc phase instability in binary alloys, including Nb-Zr [62]. The magnitude of this driving force is directly related to the $N(0)$ of the unrelaxed structure, which we can tune artificially by broadening the electronic state energies in our calculations. We then determine the limiting value of $N(0)$ beyond which the Jahn-Teller-Peierls instability causes the structure to break its symmetry and relax to a lower-symmetry state with reduced $N(0)$. Figure 3(d), for example, shows the result of this process for three high-symmetry structures at the same Zr concentration of $n = 0.5$, showing that they all exhibit very similar $N(0)$ just before the onset of the instability. Finally, this stability-limited Fermi-level DOS can be used to determine the limiting T_c as a function of composition through BCS theory. Figure 2 (“Jahn-Teller-Peierls stability limit” curve) displays the results of the above process. We generally expect that the T_c values for $\text{Nb}_{1-n}\text{Zr}_n$ will all lie within the pink shaded region, between the random alloy result and the limiting Jahn-Teller-Peierls value for any special, ordered structure. For example, an Eliashberg calculation for a specific ordered structure at $n = 0.25$ gives an electron-phonon coupling constant $\lambda^e = 1.93$ compared to a value of $\lambda^e = 1.18$ for Nb. To estimate the corresponding T_c enhancement, we use the Allen-Dynes formula with $\mu^* = 0.1$ and an additive shift in the λ^e parameter to account for spin fluctuations and match the experimental T_c of bulk Nb [55,63]. This yields a T_c of 15.7 K for the ordered $n = 0.25$ alloy, close to our predicted stability limit of 17.7 K. This prediction represents an additional 50% enhancement over the random alloy T_c , similar to what we indeed observe in our experiments.

IV. EXPERIMENTAL VERIFICATION

To validate our theoretical predictions, we measured the superconducting properties and rf performance of different Nb-Zr surface profiles. The samples were prepared by *e*-beam evaporation of a Zr target on electropolished Nb surfaces under a base pressure of 1.3×10^{-6} torr, followed by thermal annealing at 600 and 1000°C for 10 h with a ramp-up rate of 5°C/min under a vacuum of 2×10^{-7} torr, and a subsequent etch in 2% HF for 30 min. The initial film thickness and postannealing condition

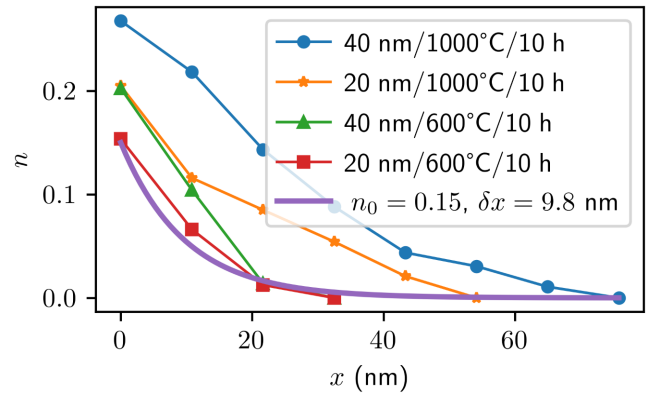


FIG. 4. Zr concentration n versus depth x for Nb-Zr samples prepared with various initial Zr film thicknesses and annealing conditions. Also shown is an example profile $n(x)$ [Eq. (4)], which roughly approximates one of the measured samples. We predict that an SRF cavity with this type of Nb-Zr profile on its surface could have $B_{\text{sh}} \approx 275$ mT (see Fig. 6).

were varied to modify the surface Zr atomic concentration. The sample preparation method and annealing process are detailed in Ref. [64].

X-ray photoelectron spectroscopy reveals a surface Zr concentration of 15–27 at.% Zr on the evaporation-based samples (Fig. 4), along with significant oxygen concentrations. X-ray diffraction [Fig. 5(a)] indicates that substitutional Zr doping is achieved, as evidenced by the doping peaks at lower diffraction angles compared to a Nb cubic reference. Zr’s and Nb’s bcc lattice parameters are 0.354 and 0.330 nm, respectively [65]. Based on Vegard’s law, these doping peaks are induced by lattice enlargement when Zr dopants are incorporated into the cubic structure. Furthermore, the HF etch eliminates the hexagonal Zr phases that formed on the surface region after annealing. The hexagonal α and ω phases have low T_c ’s of 0.7 and 4 K, respectively [27,66], so avoiding these hexagonal phases is critical to obtaining high T_c . Additionally, the only oxide detected is ZrO_2 . Note that some normal-conducting oxides appearing on the conventional Nb surface are relevant to the loss [32–34,67], whereas a dielectric like ZrO_2 is ideal for SRF applications due to its wide band gap.

Resistivity drop measurements using a Physical Property Measurement System under the ac transport mode demonstrate a T_c of up to 13.5 K for evaporation-based samples that were annealed at 600°C for 10 h. Moreover, flux expulsion measurements indicate, albeit with some caution [64], that the electrochemically synthesized samples have a higher T_c of 16 K. Notably, the 13.5- and 16-K T_c values are significantly higher than the literature-reported 11-K T_c for Nb-Zr bulk alloys [27] and the 10.5-K T_c measured in sputtered Nb-Zr thin films [68], as well as the 11-K T_c measured in the 1000°C annealed

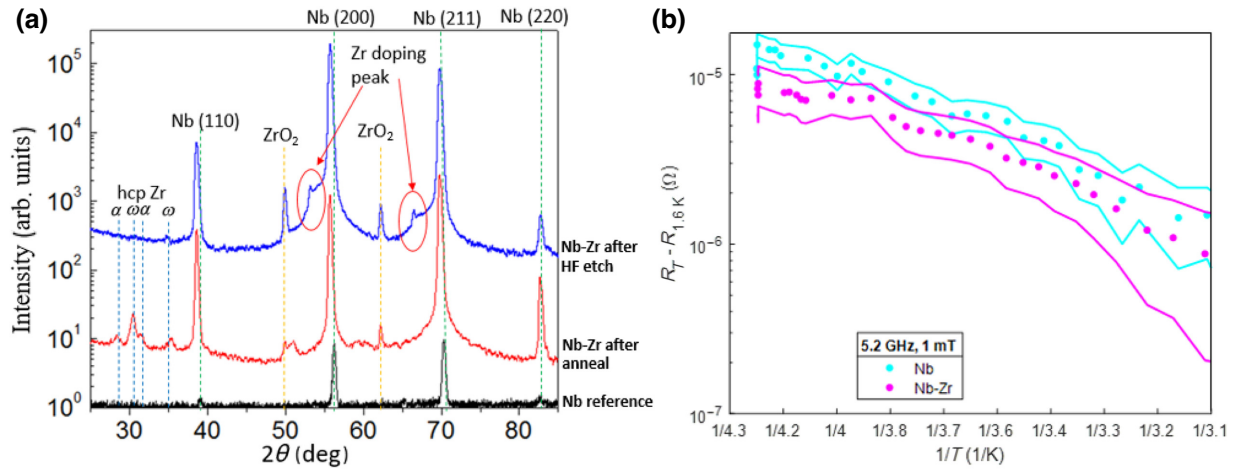


FIG. 5. Structural and superconducting properties of Nb-Zr samples. (a) X-ray diffraction pattern for evaporation-based samples annealed at 600°C for 10 h and subsequently etched with HF. (b) Comparison of BCS surface resistance before and after Nb-Zr alloying.

samples in this work. It is possible that the lower annealing temperature of 600°C favors an ordered alloy structure with an unusually high T_c . For more details on the resistivity drop and flux expulsion measurements, refer to Ref. [64].

To assess the use of Nb-Zr alloys for SRF accelerator applications, we used an electrochemical recipe with ZrF_4/LiF in an ionic liquid to scale up the alloying process to produce a 12.7-cm plate compatible with the Cornell sample test cavity [69]. The electrochemical optimization is detailed in Ref. [64]. Indeed, as shown in Fig. 5(b), after Nb-Zr alloying, the 5.2 GHz low-field BCS surface resistance trends lower, which is consistent with the expected benefit of the high T_c of the Nb-Zr material. This rf demonstration of Nb-Zr alloys establishes an alternative direction for SRF cavities with high T_c and low surface resistance. As we now show, these cavities also have the potential for high superheating fields.

V. GL PREDICTIONS OF B_{sh}

To calculate B_{sh} , we employ GL theory to simulate Nb-Zr alloys in cavity surface layers using the data from Table I. The appeal of GL theory for such simulations is its ability to accommodate continuous spatial variations in material parameters. Although GL theory is *quantitatively* valid only for temperatures near T_c , the *qualitative* behavior it predicts, particularly the functional dependencies of various quantities, is still correct at low temperatures in many cases of interest. The necessary corrections to obtain quantitative predictions are usually constant numerical factors and rescalings, such as those noted in Refs. [54] and [70]. We, therefore, proceed to use GL theory to predict B_{sh} and other quantities of interest at zero temperature

by rescaling our results to match known values for Nb, which allows us to focus on predicting how these quantities change as Zr is added.

The main object of GL theory is the free energy density \mathcal{F} of the system [54,71,72], which includes both an expansion in a superconducting order parameter ψ (with phenomenological coefficients α , β , and γ) and a contribution from the total magnetic field $\mathbf{B} = \mathbf{B}_a - \nabla \times \mathbf{A}$, where \mathbf{B}_a is the applied field and \mathbf{A} is the magnetic vector potential:

$$\mathcal{F} = \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \gamma|(-i\hbar\nabla - 2e\mathbf{A})\psi|^2 + \frac{B^2}{2\mu_0}. \quad (1)$$

B_{sh} is the value of $|\mathbf{B}_a|$ at which the superconducting Meissner state becomes unstable.

For clean, homogeneous superconductors, $N(0)$, T_c , and the Fermi velocity v_F can be used to calculate α , β , and γ [71,72]:

$$\alpha = \frac{N(0)}{T_c}(T - T_c), \quad \beta = \frac{7\zeta(3)N(0)}{8\pi^2 k_B^2 T_c^2}, \quad \gamma = \beta \frac{v_F^2}{6}. \quad (2)$$

These coefficients, in turn, are related to the London penetration depth λ_L , coherence length ξ , and thermodynamic critical field B_c :

$$\lambda_L^2 = \frac{\beta}{8\mu_0 e^2 |\alpha| \gamma}, \quad \xi^2 = \hbar^2 \frac{\gamma}{|\alpha|}, \quad B_c = |\alpha| \sqrt{\frac{\mu_0}{\beta}}. \quad (3)$$

We use Eqs. (2) and (3) to calculate λ_L , ξ , the GL parameter $\kappa \equiv \lambda_L/\xi$, and B_c , all at $T = 0$, for each of the compositions in Table I (rescaling to match known values for Nb, as previously noted).

We observe a favorable increase in B_c as Zr concentration increases. Note also that λ_L remains relatively constant while κ increases noticeably. This suggests that the lower critical field, $B_{c1} \sim \ln \kappa / \lambda_L^2$ [54], also increases as Zr is added, which is particularly encouraging for rf cavity applications because cavities suffer quenches at $B_{c1} < B < B_{sh}$.

We use the linear stability analysis described in Ref. [19] to calculate B_{sh} at $T = 0$ for each of the compositions in Table I. This represents a theoretical maximum value, from which we expect real cavities to deviate, e.g., due to inhomogeneities, such as the depth-varying concentrations of Zr shown in Fig. 4.

We simulate such inhomogeneous superconductors by treating the coefficients α , β , and γ as local quantities that vary spatially with material composition. We derive continuous functions $\alpha(x)$, $\beta(x)$, and $\gamma(x)$ for this purpose as follows. First, we consider a concentration profile $n(x)$ in which Zr concentration n falls off exponentially with depth x in the material from a surface value n_0 on a scale set by δx :

$$n(x) = n_0 e^{-x/\delta x} \quad (4)$$

(see Fig. 4). We then interpolate the values of $N(0)$, T_c^{AD} , and v_F in Table I for intermediate concentrations n to obtain $N(0; x)$, $T_c(x)$, and $v_F(x)$. Finally, we compose these with Eq. (2) to obtain $\alpha(x)$, $\beta(x)$, and $\gamma(x)$.

We calculate B_{sh} at $T = 0$ for various choices of n_0 and δx ; results are shown in Fig. 6. In all cases, B_{sh} increases as the total Zr content is increased, consistent with the improvements in other superconducting properties listed in Table I. In Sec. III, we noted that our VCA calculations captured in Table I likely overestimate T_c as Zr concentration increases; we expect our predictions of B_{sh} to be similarly optimistic since $B_{sh} \sim B_c \sim T_c$ [see [19] and Eqs. (2) and (3)].

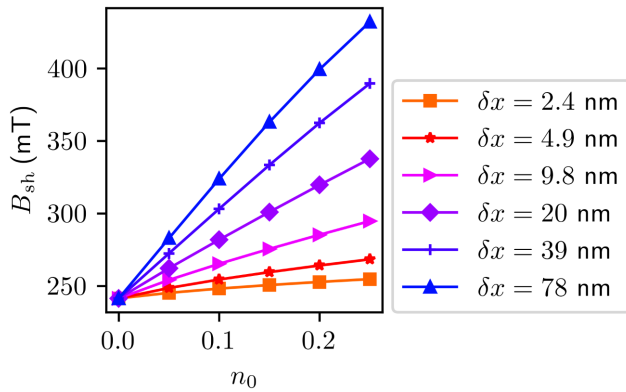


FIG. 6. Calculated B_{sh} at $T = 0$ of Nb-Zr surface layers with varying compositions [see Eq. (4)], rescaled consistent with Table I.

VI. CONCLUSION

In summary, we have proposed and demonstrated an alternative type of SRF surface via Nb-Zr alloying that enables (1) a high T_c of 13.5–16 K that minimizes energy dissipation and cryogenic costs; (2) potential enhancement of B_{sh} to upwards of 400 mT, which would allow approximately 95 MV/m accelerating gradients (currently, the best Nb cavities can only reach 45–50 MV/m [73–75]). Optimization of our initial recipe will aim to improve the uniformity of the high- T_c layer and minimize possible contamination during the electrochemical process, while also considering the role of sample history and processing temperature on trapped flux [76–78]. Steps will be taken with the specific goal of reducing the residual resistance of the surface and making Nb-Zr competitive with Nb at typical SRF operating temperatures of 2 K and below. At higher temperatures, where the BCS resistance dominates, we find an excellent match between theoretical and experimental results, which show an improved T_c after Zr is incorporated into the Nb lattice and a lower surface resistance. Our theoretical predictions provide a viable road map to further tune and improve T_c and B_{sh} . Overall, we have demonstrated that Nb-Zr alloys promise to be an alternative, feasible technology for accelerator physics.

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