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Possible influence of surface oxides on the optical response of high-purity niobium material used in the fabrication of superconducting radio frequency cavity

Nageshwar Singh [a,*], M.N. Deo [b], S.B. Roy [a]

[a] Magnetic and Superconducting Materials Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, M.P., India
[b] High Pressure & Synchrotron Radiation Physics Division, BARC, Mumbai 400085, India

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ABSTRACT

We have investigated the possible influence of surface oxides on the optical properties of a high-purity niobium (Nb) material for fabrication of superconducting radio frequency (SCRF) cavities. Various peaks in the infrared region were identified using Fourier transform infrared and Raman spectroscopy. Optical response functions such as complex refractive index, dielectric and conductivity of niobium were compared with the existing results on oxides free Nb and Cu. It was observed that the presence of a mixture of niobium-oxides, and probably near other surface impurities, appreciably influence the conducting properties of the material causing deviation from the typical metallic characteristics. In this way, the key result of this work is the observation, identification of vibrational modes of some of surface complexes and study of its influences on the optical responses of materials. This method of spectroscopic investigation will help in understanding the origin of degradation of performance of SCRF cavities.

1. Introduction

A great deal of information about the transition metal element niobium [1,2] is available since the discovery of superconductivity in this element in 1930. Extensive information [3–9] on the physical properties of Nb have been obtained through the studies of the thermal properties [3–6], electrical properties [7] and magnetic properties [8,9]. Further interesting fundamental information on Nb material has been obtained using a variety of spectroscopic methods such as tunneling, infrared/optical spectroscopy, etc. [10–12].

From technological points of view, Nb has turned out to be a very useful material because of its applications [13–26] in the development of new generation high-energy particle accelerators [18]. The highest superconducting transition temperature, the highest lower critical magnetic field (H_{C1}) amongst the superconductive elements [15], and the high normal state thermal conductivity have made elemental Nb a natural choice of materials for the fabrication of superconducting radio frequency (SCRF) cavities [16,17]. The performance of these SCRF cavities is, however, quite sensitive to the physical and chemical properties of Nb [19,20] within the radio frequency (RF) field penetration depth. Niobium gets oxidized in various forms when exposed to oxygen/air, and mixed niobium oxides thin films on the surface contribute to the surface properties. The oxides of Nb namely, NbO, NbO_2 and Nb_2O_5 have drawn considerable attention, due to their interesting electrical properties. For instance, Nb and NbO are normal conductors, NbO_2 is a semiconductor while Nb_2O_5 is an insulator. The performance of Nb-SCRF cavities is primarily influenced by the material characteristics very close to the cavity surface, which experience the RF field [19,20,27,28]. Although a few microns of SCRF cavity surface layers are removed by chemical treatment after the cavity made out of rolled sheet of bulk Nb, nevertheless it is worth investigating such Nb materials (used for SCRF cavity) with surface sensitive experimental techniques. Studies of materials through optical spectroscopic techniques can provide surface as well as bulk related information concerning oxidation, defects, contamination etc., if any.

The optical properties of Nb have been investigated in the past [29–31] revealing very useful information related to the electronic structures. Truong et al. [31] have estimated optical constants, dielectric constants and electron energy-loss functions for Nb (metal foil supported by tungsten wires, in situ cleaned by electron bombardments at 2000 °C) in the spectral region from 6.6 to 23 eV (i.e. 53,232.6–185,507.5 cm^{-1}) from reflectance measurements. Weaver et al. [30] have obtained optical constants of pure Nb (single crystal, impurities in ppm: C, 8; O, 9.6; N, 11; Ta, <150; and Ti, <100, mechanically polished, chemical polished, electropolished, annealed at 1650 K for 18 h) from the reflectivity

* Corresponding author.

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measurements, in the energy range 0.1–36.4 eV (i.e. 806.6–293,585.8 cm^{-1}), and attempted to correlate the structures in the dielectric functions with the electronic band structure, estimated by Mattheiss [32]. Carroll et al. [33] have estimated the optical constants of Nb (99.99% pure single-crystal rod, which was flashed to 2500 K and then heated at 2500 K for 20 min) at seven wavelengths between 400.0 and 632.8 nm (i.e. 15,802.8–25,000 cm^{-1}), using an ellipsometric technique. Golovashkin et al. [29] have estimated the optical constants of Nb (99.9% pure Nb, electropolished, annealed at 880 °C for two hours) in the spectral range 0.4–10 μm (i.e. 1000–25,000 cm^{-1}) and described the electronic properties of Nb. All these studies convey that the optical constants in Nb are sample dependent and are affected by the bulk/surface physical properties. Most of these studies described above on the Nb materials are intended to look at electronic band structures. To the best of the authors' knowledge, there is no study available in the literature on the influence of surface oxides to the normal state conducting properties of niobium used for SCRF cavities, although, the overall performance of SCRF cavities is supposed to be very sensitive to the surface metallurgical properties of the cavity. Therefore, reinvestigation of the optical response of Nb materials particularly used for SCRF cavity formation may be quite instructive.

In this paper, optical response of typical high-purity Nb material used for SCRF cavity fabrication is investigated at room temperature. In the rest of the paper we will use the term '*technical-Nb*' to present such Nb SCRF cavity materials. Such technical Nb materials with the residual resistivity ratio (RRR) of the order of 300, fall under the category of the intermediate purity limit [4], and the studies of the optical properties of such materials are relatively scarce. The reflectance measurement was performed using Fourier transform infrared (FTIR) reflectivity setup. The various peaks present in the reflectance are analyzed taking into account niobium native oxides. The most common optical responses such as reflectance, optical constant, dielectric and conductivity functions of the technical-Nb sample are presented and compared with the same responses for oxides free Nb [29] and Cu [34]. An attempt is made to look at top layers response of technical-Nb that is most likely a combination of a dielectric and a poor metal. The results and the corresponding discussions presented in the subsequent section of this paper will be based on three different samples namely, (i) technical-Nb, (ii) oxides free Nb, and (iii) oxides free Cu.

2. Methodology and experimental details

The Kramers–Kronig transformation is a very useful technique to obtain the phase change φ at an arbitrary angular frequency ω_0 from the measurement of Reflectance R over the entire frequency range [35]. In order to treat the singularity at $\omega = \omega_0$, the equivalent Kramers–Kronig relation is used i.e.

$$\varphi(\omega_0) = \frac{\omega_0}{\pi}\int_0^\infty \frac{\ln\frac{R_0}{R}}{\omega^2-\omega_0^2}d\omega \tag{1}$$

where R_0 is reflectivity at ω_0.

The complex refractive index $N = n + i\,k$ (n, k: refractive index and extinction coefficient of the substance), the reflectivity amplitude r and the power reflectivity R (which is directly obtained from the measurement) are related, for the normal incidence to the surface of the sample, as [36]

$$r = \frac{N-1}{N+1} = \frac{n+ik-1}{n+ik+1} \tag{2}$$

$$r = \sqrt{R}\,e^{i\varphi} = \sqrt{R}\,(\cos\,\varphi + i\,\sin\,\varphi) \tag{3}$$

where φ is the phase change from the absorbance that occurs with reflection from the surface of a substance. From Eqs. (2) and (3) one obtains the following relations for the real and imaginary part of the refractive index [35,36] as

$$n = \frac{1-R}{1+R-2\sqrt{R}\,\cos\,\varphi} \tag{4}$$

$$k = \frac{2\sqrt{R}\,\sin\varphi}{1+R-2\sqrt{R}\,\cos\varphi} \tag{5}$$

The real and imaginary parts of the dielectric and conductivity functions are related [34,35] with optical constants as

$$\varepsilon_1 = n^2 - k^2 \tag{6}$$

$$\varepsilon_2 = 2nk \tag{7}$$

$$\sigma_1 = 2\varepsilon_0\omega n\,k \tag{8}$$

$$\sigma_2 = \varepsilon_0\,\omega(1 - n^2 + k^2) \tag{9}$$

where ε_1, ε_2 and σ_1, σ_2 are real and imaginary parts of the dielectric constants and the conductivity, respectively. The complex dielectric response function $\epsilon(\omega)$ and the complex conductivity function $\sigma(\omega)$ are related [36] by

$$\epsilon(\omega) = \epsilon_\infty + \frac{i\sigma(\omega)}{\omega\epsilon_0} \tag{10}$$

Another way to analyze optical spectra of solids and obtain frequency dependent optical responses is to model the dielectric function and directly fit the reflectivity spectrum [37]. There is a variety of formulas corresponding to different models of dielectric functions, perhaps, the most famous example is the Drude-Lorentz model [37],

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_i \frac{\omega_{pi}^2}{\omega_{oi}^2 - \omega^2 - i\gamma\omega} \tag{11}$$

where ε_∞ is the so called 'high-frequency dielectric constant', ω_{oi} is the transverse oscillator frequency, γ is the linewidth (scattering rate) and ω_{pi} is the plasma frequency of the i-th Lorentz oscillator.

The technical-Nb sample, used for the present investigations, was cutout from the same batch of material which was earlier used for studies of superconducting properties as well as characterization of cavity performance [23]. The sample was originally electropolished using chemical polishing technique [23]. This technical-Nb sample was again mechanically polished to improve surface finish for optical measurements. A fine grit was used to accomplish polishing using water as a suspension agent. Surface topography of this mechanically polished sample was performed using profilometer (Veeco DEKTAK 150) and atomic force microscopy (AFM). The reflectance measurement was performed with a Bruker Vertex 80v FTIR instrument, configured with the Globar as infrared (IR) source and a Deuterated Tri-Glycine Sulfate (DTGS) as detector in the frequency range 50–700 cm^{-1} and a liquid-nitrogen cooled HgCdTe (MCT) detector in the frequency range 350–8000 cm^{-1}. The reflectivity was measured at near normal incidence, using 11° reflection accessories. We used the Bruker supplied internal reflectance units. We have used a gold-coated copper mirror, which is considered as the best reference mirror in the IR spectral region. We have not made any correction to the