Curvature, Hydrogen, Q

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Abstract. The manufacturing of niobium SRF accelerator cavities is plagued by a mobile point defect, hydrogen. For efficient accelerator operation, niobium must function at both high electric and magnetic fields, and is compromised if magnetic impurities are located in the surface regions of the material. The finding that trace hydrogen in niobium can produce structures with magnetic properties is a feature that is not acceptable for a high performance cavity. X-ray diffraction has proved to be the key tool in assessing irreversible process damage to the niobium substrate. In future generations of accelerators, niobium will actually be merely the substrate for more effective superconductors that will allow for more efficient operation. The substrate analogy to the silicon wafer industry is useful since for niobium it may be possible to avoid some of the mistakes made in silicon technology. Because hydrogen attacks niobium on a number of different size scales, there is an inherent complexity in the trouble sources. There are also features in cavity design that are benign, such as local curvature considerations, requiring a fully non symmetric analysis of current flow to be appreciated.

Keywords: niobium, superconducting, accelerator, hydrogen, curvature
PACS: 61.72.Bb, 61.72.jj

1. INTRODUCTION

To date the process material characterization and superconducting cavity characterization in the production of niobium SRF cavities have not been sensitive enough to allow for a good understanding of the various mechanisms that can effect cavity performance. The characterizing test of cavity performance with Q versus driving field level is fine for screening cavities, but it yields very little basic materials information about the 40 nm superconducting surface layer. Some simple RF measurements of time dependent variations of SRF niobium properties in non superconducting samples have shown that the nominal quantities of hydrogen found in SRF components are capable of producing complex measurable magnetic responses, figure 1. However, hydrogen is not a benign solid solution impurity at any stage in the production process. Normally niobium is not thought of as a magnetic material, even though the hydride and the deuteride of niobium have measurable magnetic permeabilities.

To gain more of an understanding, a parameter-free quantum mechanical treatment of hydrogen in metals was developed that was directly tested by computing the activation energies for diffusion of the hydrogen, deuterium and tritium in a wide range of metals. The ground state of the proton was treated as a particle in a spherical potential bound state. What this implies for concentrations great enough to form ordered structures is that proton bands can be formed. The bands can significantly reduce the activation energy for diffusion and create a number of opportunities to alter magnetic and superconducting

Symposium on the Superconducting Science and Technology of Ingot Niobium
AIP Conf. Proc. 1352, 38-46 (2011); doi: 10.1063/1.3579222

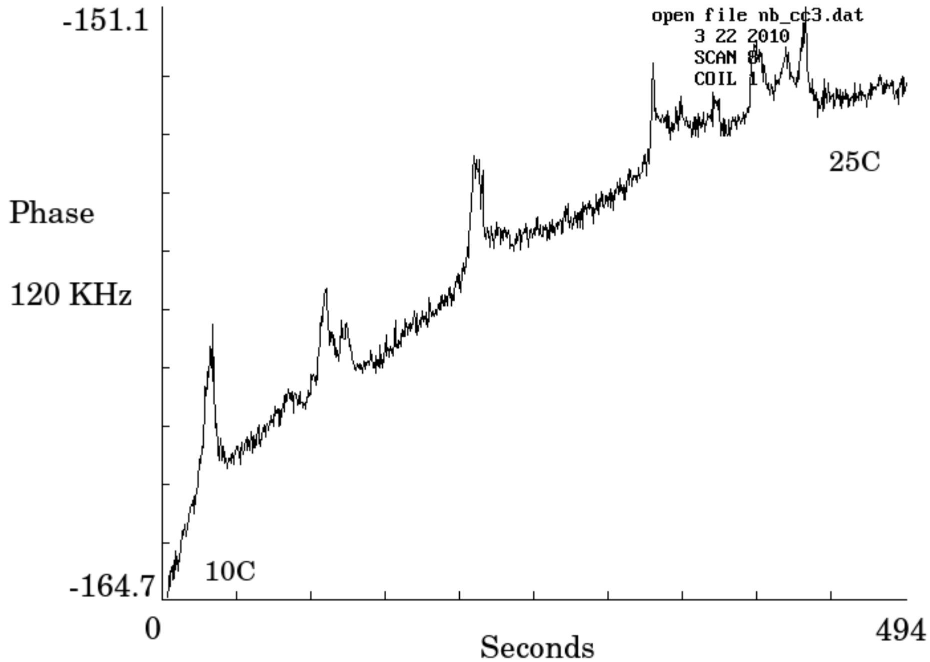


FIGURE 1. Induction refelection method for detecting conductivity and permeability changes in a sample of fine grain SRF niobium. Vacuum melted fine grain niobium, high purity niobium, EDM cut face and BCP treated. The sample was cooled to 77K and was allowed to warm to room temperature and was being monitored by a single coil weak field induction reflection. Normally over the very narrow temperature range of $15^o C$ the phase would have increased possibly $.2^o$ or less not 13^o which was measured. But in addition to that there are a number of transient responses indicating that regions of the material have had temporary surges in the value of the magnetic permeability. This behavior is not typical of a nominally pure metallic conductor but it is just one of the many anomalous responses found in SRF prepared niobium.

properties. This theory [1], is particularly accurate for niobium, and by extending it the mechanisms generating the permeable magnetic response may be understood.

Understanding the highly mobile behavior of hydrogen in SRF niobium has much in common with the problems of understanding point defect behavior in silicon substrates. The application of both systems initially were dependent on the electrical properties of the base materials and then evolved into depending on the base material supporting an electrically active coating. In silicon the full potential of high yield high density chip fabrication was not realized until the point defect problem of the substrate was eliminated. There is still a debate on the origin of the problem which extends back into the 1980's. Understanding the origin of the Q problems in niobium will cut years of trial and error cavity fabrication and that requires tools sensitive enough to monitor the manufacturing process. The fabrication difficulties will be considered from the point of view of geometrical, chemical, and finally electromagnetic problems.

2. TOOLS

The tools for studying hydrogen in niobium break down into two classes. The principal tools are the application of non-relativistic quantum mechanics to the modeling of hydrogen's behavior in the interstitial volume of the metal and electromagnetic theory on the interaction of RF to optical radiation on metal-containing hydrogen. The detailed consideration of effects that possibly can occur in the compact hydrogen metal system allows the use of more specific experimental tools to provide information on concentration and the different effects that hydrogen can produce in altering the properties of the metals. Specifically we wished to avoid using a beam tool that electrically biased the sample to prevent electro-migration. Also, we avoided sampling tools that focus on small sampling sizes, which can be affected by long range diffusion of hydrogen and therefore misrepresent the local concentration. Therefore, our experimental tools have a large sampling area relative to the distance hydrogen can move during a data-taking interval. Historically, our first measurements started with positron annihilation lifetime measurements of some of the earliest high ductility e-beam melted materials that produced results indicating a complex micro-structure unexpected in a pure vacuum melted niobium that was unaffected by its environment [2]. This was followed by monitoring backside sourced hydrogen diffusion measurements of lattice parameter change by X-ray diffraction techniques [3] which showed preferential surface-dependent lattice expansions dependent on orientation and concentration. Recently, the experimental techniques of infrared and optical reflection spectroscopy have been used to show the large mechanical flexure generated by backside charging, near surface concentration reflection effects and permanent surface changes due to transient water vapor condensation events[4]. Finally the most varied results were taken with RF reflection spectroscopy on SRF-prepared niobium samples and compared to samples prepared as sputtered films and rolled foils [4]. The RF reflection data show that SRF niobium and the other prepared forms are most likely not very pure niobium, having acquired an active mobile impurity, either during processing or storage, which has turned a nominally non-magnetic metal into a very active and complex paramagnetic material. From comparison of the relative phase diagrams and knowledge of the affinity of hydrogen to readily form compounds with niobium, the mobile species that fits the kinetic profile of the experimental measurements points to hydrogen as the offending impurity. Oxygen and other point defects in this refractory metal are essential immobile on time scales of seconds to minutes, over which significant variations are detected in X-ray, optical and RF reflection measurements.

3. CURVATURE, LARGE AND SMALL

One of the qualifying tools for SRF niobium cavity performance is a measurement of cavity Q, the inverse of the loss parameter of the cavity. But since cavities are shaped as surfaces of revolution, with forming-induced surface variations, a discussion of curvature with respect to electromagnetic effects makes a good starting point. The computation of current flows on surfaces, that are controlled by being inductively coupled to a free volume, behave in a manner that attempts to minimize the total field energy density stored in the free volume. That leads to very smoothly varying current distributions even on rough and damaged surfaces. The details of the local current flow require a full three-dimensional analysis on a very fine scale in order to correctly account for maintaining tangential continuity of both the induction and the electric field, while ensuring the normal components vanish at the surface. It is very difficult to do this problem under higher symmetry, such as cylindrical symmetry, since a defect or a material pill box on the surface will break the symmetry of a surface of revolution, which forms the resonant cavity. Because of the leveling ability that forces the flows to minimize the field energy density and the fact that in a resonant cavity it is the long range currents moving through the material which determine the Q of the cavity, small mechanical surface variations play a minimal role, except to alter the cavity's resonant frequency. The more critical feature for a superconducting cavity is the material composition of the wall, which can control the normal conductance scattering of the driven currents and, in the case of the superconducting current, the regions of the cavity wall, which can alter the phase of the current flow in a non-uniform manner. Both these mechanisms are sources of loss. Geometry does not play as strong a role because the bulk currents travel only through material that allows the long range current to flow. Whereas in damaged regions such as indentations or pill boxes raised above the surface, the condition that requires no normal electric or magnetic induction fields ensures that these regions don't carry the large long range currents. There are some losses in these damaged regions where local currents reject field penetration but they ensure that the bulk current flows are not affected by the surface damage.

The electromagnetic skin depth is a curvature-dependent quantity that varies not only with the electrical conductivity of the material, but also with the local curvature of the material. It is a slowly varying function which decreases with increasing surface curvature. For normal conductors this is not an important consideration, but for a superconductor operating near its flux penetration threshold there will be a small effect. This effect can be computed without much difficulty by modeling a hole of varying radius in a solid conductor which is being driven by a co-cylindrical internal inductor. Computing the vector potential within the material then allows the current distribution to be computed directly and the normal electromagnetic skin depth is that at which the current falls to $\frac{1}{e}$ of its maximum value. Typically changes in curvatures found in SRF cavities produce changes in the electromagnetic skin depth which are reduced by an amount 3×10^{-4} in the regions of highest curvature, implying a greater concentration of current nearer the surface. For an uncontamined superconductor the effects of curvature should be negligible but if there is concentration of hydrogen near the surface these small effects could alter the loss properties.

The forming of the high curvature regions in the vicinity of the belly weld of the cavities suffers the greatest mechanical damage from forming. It is to be expected that in this belly region the greatest plastic strains occured leaving the highest dislocation concentration. The dislocation concentration can also concentrate hydrogen which will trap onto dislocations [5]. The heat treatments of the cavity is usually not suffcient to recrystalize the cavity and reduce the deformation dislocation concentration. So the principle effect of curvature on the SRF niobium cavities is to change the propensity of hydrogen to collect in the more highly mechanically damaged regions.

4. HYDROGEN, DAMAGE THRESHOLD

The processed niobium that is used in the manufacture of superconducting cavities is treated as if it were a pure material. This is because the damage that hydrogen causes (occurring during processing) does not result in easily visible damage. If the material would have developed rust (as does iron), the problems with environmental degradation would have been solved much earlier. In actuality, niobium does visibly degrade, but it takes acute perception of color and reflectivity, requiring a spectrometer to discern. For the gross environmental damage that niobium can suffer, X-ray diffraction techniques work much better, figure 2. The damage is selective to orientation of individual grains with respect to the surface, figure 3.

Process sources of hydrogen infusion are EDM machining, BCP polishing, macro etching, high pressure washing, and ambient moist atmospheres. E beam welding can concentrate hydrogen by electro-migration into the weld region. So there is no great difficulty of introducing hydrogen into niobium to a level that can actually cause physical damage to the surface on an atomic level. The current cavity manufacturing practices have been optimized in their processing and heat treatment processes so as to maximize Q and operating field levels. As damage is removed with process improvements, the ratio of mobile to immobile hydrogen should increase within the matrix since trapping sites and phases are removed. This may not improve cavity performance until the overall hydrogen concentration is reduced to a level in the near surface region so that any band formation is no longer occurring. There is always the spin coupling of the proton with the large nuclear moments of the lattice coupled with the applied fields that can drain energy from the resonant field. This would require local static magnetic fields within 40 nm of the surface. From induction measurements made on standard processed SRF material, it appears that mobile hydrogen can organize to produce fields sufficient to create a range of available nuclear transitions [6] [7] which could absorb energy from an applied field.

The effects of hydrogen are most easily detected in niobium with the rich variety of RF magnetic properties that can be detected. These magnetic effects are detected by induction RF reflection measurements which can isolate magnetic effects from conduction loss effects. These measurements will soon be extended to measure properties down to the operating temperature of 2K. Nevertheless, the high temperature measurements have uncovered some unexpected features that will have to be considered prime candidates for loss mechanism that can operate on the superconductor[4]. First, there is the possibility that in near-surface regions with sufficient hydrogen concentrations proton band formation will occur, which may have different superconducting properties than that of the niobium substrate. The concern is not so much for direct scattering losses as it is for small phase shifts in the current moving through these regions. Also any local ferromagnetic regions will enhance these phase shifts. Any local phase shift, no matter how small, will contribute to a reduction of the maximum Q of the cavity. This is actually not a loss but merely the result of vector additions that are unfavorable for a high Q cavity [8] [9] [10].

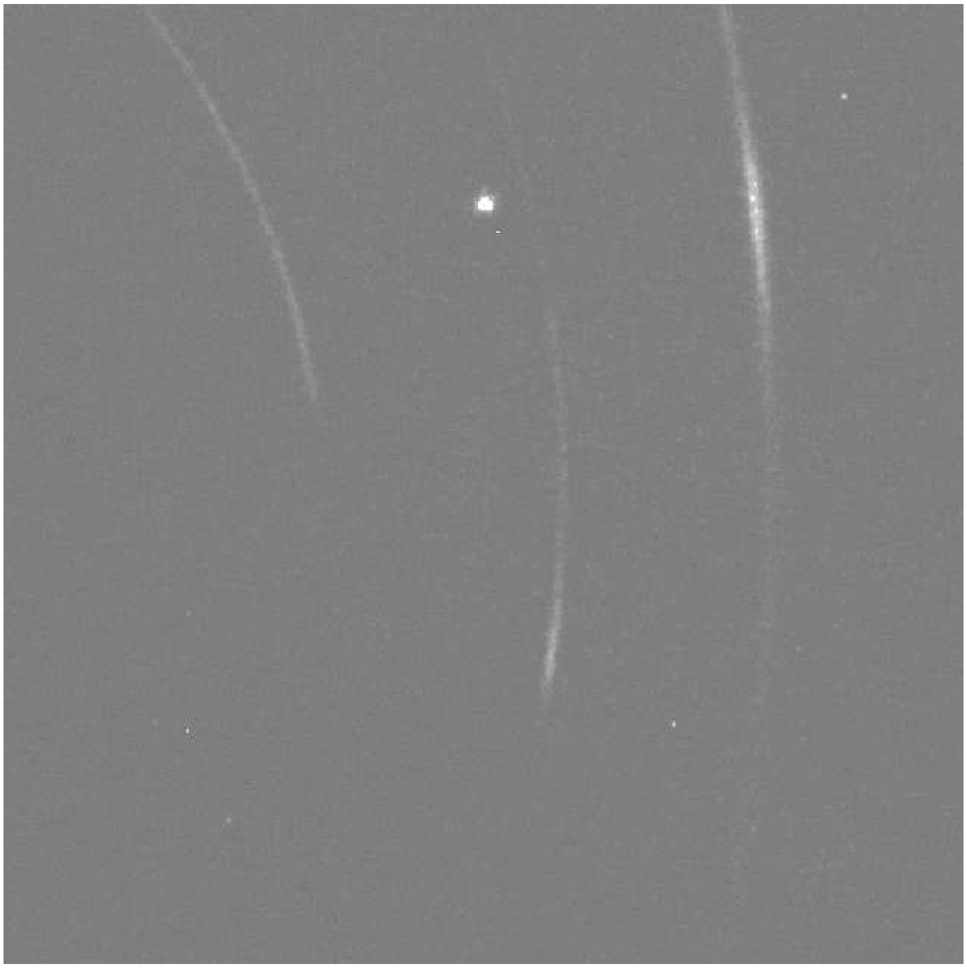
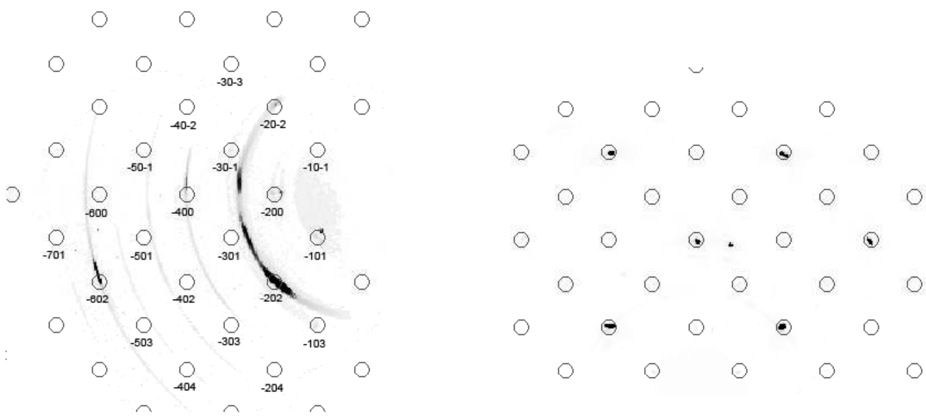


FIGURE 2. X-ray diffraction frame of vacuum-melted, very large grain, high purity niobium, EDM cut face and metallurgically polished to 0.05μ grit. (X-ray conditions: graphite monochromatic Cu K-alpha radiation, detector image spans 20-80 degrees 2 theta, from left). The resulting smeared orientations were little different from the chemical polished surfaces. Selective planes show large and continuous variation in their orientation, as indicated by powder-like streaks. There also could be selective regions on the planes. Since individual planes are still detected this is not an amorphous structure, but rather a selectively damaged surface. Since this is high purity niobium with very low yield stress, the damage is not so much dislocation damage, wherein we would expect a local reflection diameter to increase, but rather an orientation effect. The Fourier transform of such spreading in orientation could be represented by local sharp eruptions which disrupt the lattice planes, driving the mis-orientation. The large angle of the spreading plane orientation indicates that the effect induced by a defect that is locally compact, forcing an extreme mis-orientation of many degrees of arc. Since this a local effect, to get such a large response it has to be repeated many times across the surface of the crystal.

5. Q AND WHAT IT DOES NOT TELL

The Q measurements are a figure of merit for the cavities because these cavities are superconducting and not simple materials obeying Ohm’s law. Inverting the Q data to obtain material property data runs into one major obstacle, figure 4. That obstacle is that



EDM cut and metallurgically polished niobium

unprocessed pure niobium

FIGURE 3. This is an X-ray diffraction comparison of EDM cut and polished SRF niobium ready for forming and BCP treatment on the left and a virgin piece of large grain material not EDM cut. Shown are pseudo-precessional images composited from multiple diffraction frames. Circled locations are predicted diffraction locations (including those from systematic absences) for the BCC niobium lattice. The patterns are remarkably different in the very large continuous mis-orientation of the diffraction planes in the EDM cut samples.

the number of material variations and processing variations possible are many and the Q measurement is a single gross measurement on an entire cavity. The Q measurement cannot isolate problematic regions of the cavity or give a response for a loss that can be tied to particular material property on any scale less than that of the entire cavity. Most of the interesting materials properties are obscure in any analysis of this single parameter measurement. Hydrogen in a dilute solid solution represents a highly mobile point defect. In an analogous system - high purity silicon for device application - an equivalent measurement would be for bulk resistivity. It is a bulk measurement, which is affected by everything that alters the carrier population and only in very well designed experiments can it produce information about point defect contributions. The problem that point defects represent is that they form the smallest material scale that is relevant to bulk material properties. The effect of the point defects can then appear on every scale from the atomic to the macroscopic, which means that an understanding of properties at all these levels will require different tools. The tools are highly specialized and in order to be useful, experts in different areas must communicate with a common understanding of the possible implications of their findings. But the biggest difficulty is the character of the data from the major qualification test for SRF superconducting cavities, that is, the Q measurement verses applied field level. This measurement is inherently flawed from the perspective of yielding useful material information since it is essentially a large scale experiment encompassing an entire cavity, yielding just one data point per applied field level. Hydrogen, if it is the culprit for much of the Q loss is analogous to point defect problems for creating damage in electronic silicon. High temperature induction measurements have yielded a great deal of information on conventionally-prepared SRF

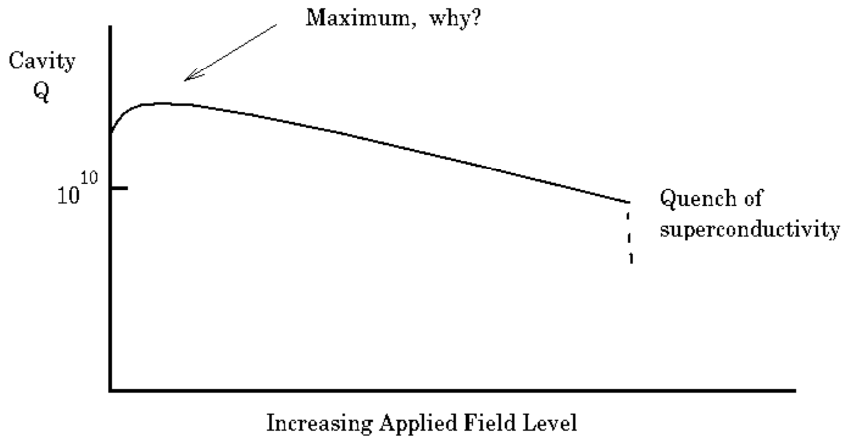


FIGURE 4. A typical Q verses amplitude measurement response of a niobium cavity to the point that superconductivity is quenched by the internal magnetic field penetrating the superconducting inner surface of the cavity wall. The existence of a maximum indicates and enhancement of superconducting properties. The most sensitive parameter that controls superconducting properties is the temperature of the cavity. Adiabatic cooling by using an aligned electronic spin system is the only thing that could support this cooling at the $2K$ temperature of cavity operation. Kaptiza resistance of the niobium will isolate the cooled cavity surface, temporarily improving the Q.

niobium and will provide useful information when applied down to 2K. But as the material is improved by removing hydrogen and the damage it produces, the induction tools and X-ray diffraction patterns may become insensitive to the low concentration of hydrogen and its damage. Other loss mechanisms may come to dominate the losses. That may require a new set of tools to distinguish the loss mechanisms.

In figure 4 the current cavity Q versus amplitude data has one outstanding feature. There is usually a resolvable maximum at low field amplitudes well below the quenching field level. Based on naive considerations, one would expect this curve to be flat until the quench region is approached. However, this is not the case. The amplitude maximum was noticed once it was found that SRF niobium was an active magnetic material. In the first RF induction reflection measurements the SRF niobium material was quenched after normalizing at 180^oC above the temperature where ordered structures of hydrogen in niobium dissolve back into solid solution and evidence of an increasing magnetic response was found as the sample aged at room temperature. Measurements after the quenching showed that the sample's magnetic permeability slowly increased over a period of hours. This is somewhat like the data of figure 1. This behavior matched the kinetics of hydrogen diffusion at room temperature in niobium. This fact in itself was interesting, but when coupled with what would happen in a system with a mobile and active spin system that was subject to strong applied fields when cooled to superconducting temperatures made the possibility of adiabatic refrigeration possible in the cavity walls. There were good data [11] suggesting that hydrogen collects at the subsurface region of a free metallic surface at high concentrations even though the bulk concentration may be at in the part per million range with standard thermal out gassing measurement techniques. Standard thermal out gassing concentration measurement techniques are not very accurate at hydrogen concentrations below 1% atomic because hydrogen and niobium are such a good compound-forming couple. The active magnetic component of the proton spins operating at 2K may not only affect the local magnetic ordering but it may affect the local properties of the near surface superconductivity which may affect the Q in other ways. Controlling the surface concentration will be difficult until SRF niobium can be processed essentially hydrogen-free to prevent damage as well as a hydrogen build up until it can be finally sealed to prevent hydrogen from dissolving into the metal while in storage.

ACKNOWLEDGMENTS

The principle tools used in this study were electromagnetic theory, non relativistic quantum mechanics and the metallurgy of hydrogen alloys. Information on SRF technology was supplied by A. Hutton and G. Ciovati. This work was supported by U.S. DOE Contract No. DE-AC05-06OR23177.

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