

Normal Spectral Emissivity of Niobium (at 900 nm) by a Pulse-Heating Reflectometric Technique¹

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The normal spectral emissivity of niobium strip specimens was measured using a new pulse-heating reflectometric technique. The hemispherical spectral reflectivity of the surface of a strip tangent to an integrating sphere is determined by a high-speed lock-in technique. At the same time, the radiance temperature of the strip is measured by high-speed pyrometry from approximately 1000 K to the melting point. Details of the measurement method and of the related calibration techniques are reported. Results of the normal spectral emissivity of niobium at 900 nm from room temperature to its melting point are presented, discussing differences related to the heating rate and to surface conditions.

KEY WORDS: high temperatures; niobium; normal spectral emissivity; pulse heating; reflectometric techniques; refractory metals; transient techniques.

1. INTRODUCTION

Pulse techniques have gained wide acceptance for the determination of several thermophysical properties at high temperatures. The most accurate measurements are performed on tubular specimens with a small blackbody hole, which are difficult to produce and require very careful machining. In practical applications measurements must often be performed in short times on simple specimens. Two techniques have been proposed recently to perform direct measurements of thermophysical properties on simple specimens [1, 2]. The method developed at the National Institute of Standards and Technology (NIST, USA) uses cylindrical specimens and

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performs direct measurements of the normal spectral emissivity using laser polarimetry [2]. The technique developed at the Istituto di Metrologia "G. Colonnetti" (IMGC, Italy) makes use of specimens in the form of strips, and normal spectral emissivity is measured by integrating sphere reflectometry in pulse heating conditions [1]. This paper describes experimental measurements of the normal spectral emissivity of niobium strip specimens over a wide temperature range (from room temperature to the melting point) obtained recently at the IMGC.

2. METHOD AND APPARATUS

The new measurement technique developed at the IMGC (schematic diagram in Fig. 1) is a high-speed version of an integrating sphere reflectometer of the comparison type in which the reflectivity of the specimen (that undergoes pulse heating) is measured in relation to the known reflectivity of a barium sulfate (BaSO_4) reference specimen. The quantity that is measured is the spectral directional-hemispherical reflectivity ρ of the specimen at the wavelength of the interference filter placed in front of the silicon detector of the sphere. Considering the small changes of directional properties measured at small angles ($< 10^\circ$) from the normal, this property can be considered the complement to the normal spectral emissivity ε of the specimen (Kirchhoff's law, $\varepsilon = 1 - \rho$). The IMGC method has been described previously [1]; a brief summary is reported here, including the significant modifications of the apparatus that took place after the previous publication.

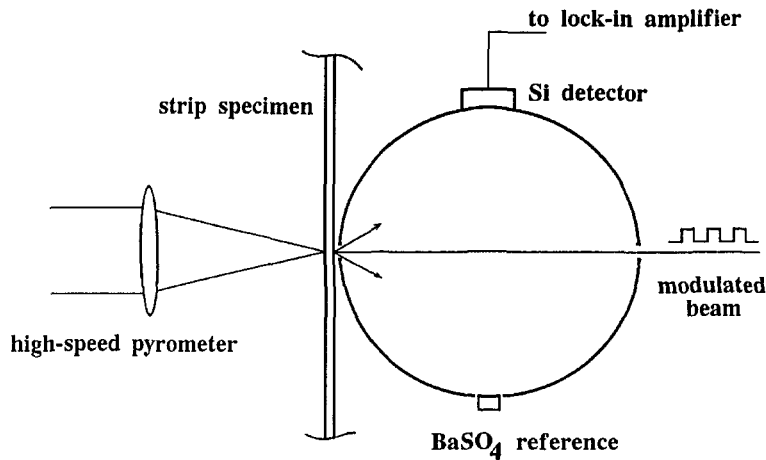


Fig. 1. Schematic diagram of the pulse heating reflectometric technique (from Ref. 1).

Measurements are performed on a strip specimen placed in the typical environmental chamber of the pulse-heating technique. The radiance temperature on one side of the strip is measured by a high-speed pyrometer with microsecond time resolution [3]. The other side of the strip is placed outside a porthole of a small integrating sphere placed inside the environmental chamber (Fig. 1). A modulated beam generated by a laser diode strikes the side of the strip facing the sphere. The reflected beam is collected hemispherically by the integrating sphere and measured by a silicon detector operating at the same wavelength of the high-speed pyrometer and of the laser diode (at present, near 900 nm) placed in the sphere ceiling. A fast lock-in technique is used to discriminate between the reflected beam (that is modulated) and the continuous component generated by the specimen itself when it reaches high temperatures. The specimen is pulse heated, using as a power supply a set of lead acid batteries, and can be brought to high temperatures (up to its melting point) in times ranging from 0.5 s to several seconds, depending on the signal-to-noise ratio acceptable in the lock-in measurements. Additional technical details on the measurement technique and on the system characteristics can be found in an earlier publication [1].

3. MEASUREMENTS AND CALIBRATIONS

Measurements were performed on three niobium strip specimens with the following nominal dimensions: length, 83 mm; width, 10 mm; and thickness, 0.5 mm (two specimens) and 1 mm (one specimen). All experiments were performed in high vacuum (better than 10^{-3} Pa) at different heating rates. Typical operational conditions to cover the range from room temperature to the melting point were as follows: in fast experiments, a current pulse duration of 0.5 to 0.7 s and a heating rate of 2200 to 5700 $\text{K} \cdot \text{s}^{-1}$; and in slow experiments, a current pulse duration of 4 to 6 s and a heating rate of 130 to 640 $\text{K} \cdot \text{s}^{-1}$. The lock-in reference frequency during all experiments was in the range 390 to 400 Hz. The normal spectral emissivity is strongly dependent on the surface conditions, and all specimens exhibited large changes in normal spectral emissivity during the initial experiments. A reasonably stable surface condition was reached only after the specimens had been taken to their melting point a few times, interrupting the current pulse before destruction of the specimen. This was done using an experimental technique developed earlier at the IMGC for repeated measurements of the radiance temperature at the melting point [4]. After several experiments to the melting point, the specimen surface became shiny and exhibited very large grains, as shown in Fig. 2.

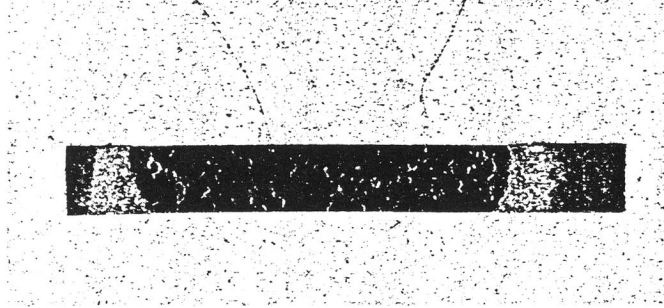


Fig. 2. Photograph of one of the strip specimens. The shiny central region is the part of the strip that reached the melting point.

Integrating sphere reflectometry is not an absolute method and therefore requires an appropriate reflectivity reference standard to take into account different factors, including the geometry of the integrating sphere and possible imperfections in its internal coating. This is done in a separate reference measurement by directing the laser diode beam toward a BaSO_4 specimen, placed in an appropriate holder in the integrating sphere wall, and by measuring the silicon detector output for all temperatures of interest. This BaSO_4 reference measurement is repeated as many times as necessary by simply moving the laser diode on a sliding mechanism that is placed outside the environmental chamber. A typical lock-in output when the laser diode is directed toward the BaSO_4 specimen is shown in Fig. 3. Theoretically a constant value should be observed because the BaSO_4 specimen remains at room temperature during the entire experiment, but a total signal variation of about 1% is observed, with the signal during the heating and cooling phases following slightly different paths. Detailed investigations have shown that this phenomenon is related to the maximum temperature reached by the specimen and to the time of exposure of the chamber to high temperatures. The most likely explanation is that part of the coating of the integrating sphere is affected by the large amount of radiation emitted by the specimen causing the signal change. On account of this phenomenon, all experimental measurements on niobium strips are related to BaSO_4 reference measurements performed exactly at the same operational conditions.

The BaSO_4 reference measurement does not take into account other possible causes of error due to the loss of part of the reflected radiation for the following reasons.

- (a) The distance between the specimen and the integrating sphere. For safety reasons the hot niobium strip specimen must be

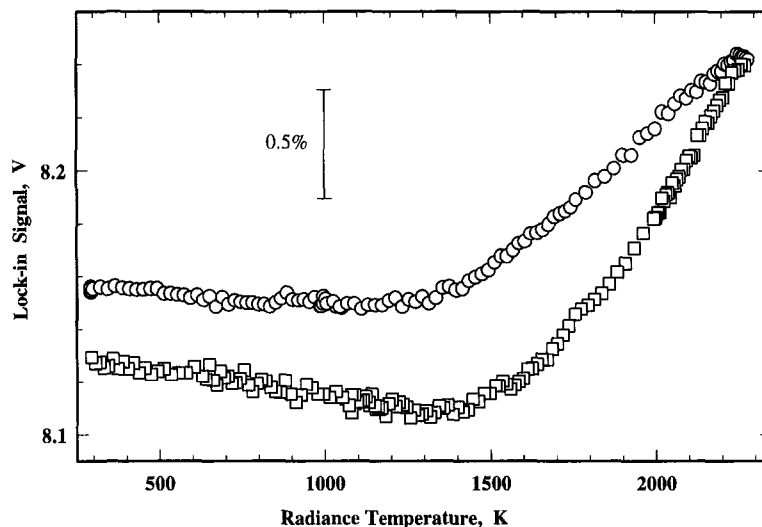


Fig. 3. Typical lock-in signal as a function of radiance temperature during an experiment on a BaSO_4 specimen. (\circ) Heating measurements; (\square) cooling measurements.

placed at an appropriate distance from the sphere (generally about 2 mm), with possible partial loss of the reflected beam.

- (b) Highly reflecting specimens. Specimens taken to their melting point exhibit large grain growth and become strongly specular (Fig. 2). This condition diminishes the loss described in (a) but increases the radiation lost from the beam entrance holes after a single reflection.

These potential problems are taken care of by using the melting point of niobium as a calibration point. Repeated measurements performed over two decades both at the IMGC and at the NIST have shown that the radiance temperature of metals of their melting point is a stable and reproducible quantity. The use of the normal spectral emissivity of metals at their melting point as reference values has also been suggested [5]. All the measurements presented in this paper have been obtained adopting the value of 0.3087 for the normal spectral emissivity (at 900 nm) of niobium at its melting point, as measured earlier at the IMGC [6].

4. RESULTS

The experimental results obtained on three specimens are presented in Fig. 4. For viewing purposes the original data of each experiment have

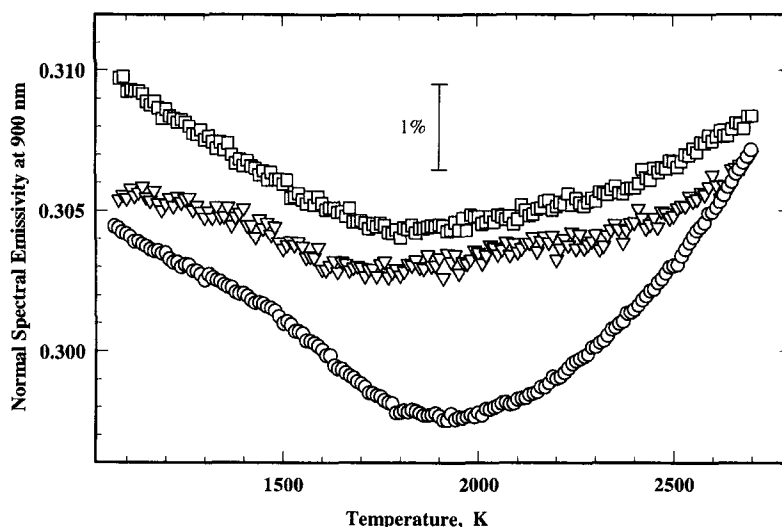


Fig. 4. Averaged results of the normal spectral emissivity of niobium at 900 nm as a function of temperature. (\square) Specimen 1; (∇) specimen 2; (\circ) specimen 3.

been interpolated and computed every 10 K, averaging the results for each specimen (four experiments for specimen 1, two experiments for specimen 2, and nine experiments for specimen 3). The general trend indicates a decrease of the normal spectral emissivity of niobium (at 900 nm) with temperature from approximately 1100 K to the range 1800 to 2000 K, followed by a moderate increase with temperature up to the melting point. The data are presented up to 2700 K; the convergence toward a common value at the melting point (2749 K) [7] is a consequence of the calibration procedure described previously. Each specimen follows a specific emissivity-versus-temperature trend, very likely due to the amount of residual surface oxidation still present in the specimen surface, as explained in more detail later. The normal spectral emissivity results obtained for each specimen in the fast experiments have been used to compute the heat capacity, electrical resistivity, and hemispherical total emissivity of niobium of these strips [8] (experimental data for these measurements were collected in the same experiments in which normal spectral emissivity was measured). These thermophysical property measurements validate the normal spectral emissivity measurements (and vice versa) in the sense that the results on strip specimens replicate very closely the results obtained earlier at the IMGC on tubular specimens with a blackbody hole [9].

The normal spectral emissivity is dependent on the surface conditions, and the speed of the experiments has a certain influence on the modifications

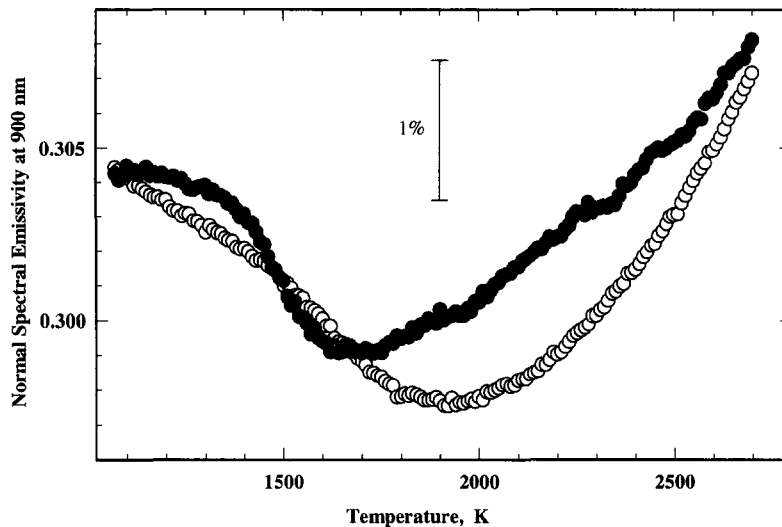


Fig. 5. Differences in averaged normal spectral emissivity results for fast experiments (\circ) and slow experiments (\bullet) performed on the same specimen.

occurring on the surface of the strip. A typical example is shown in Fig. 5 that presents the experimental results of the normal spectral emissivity on the same specimen. The curve referring to fast experiments represents the average of nine consecutive experiments performed at heating rates ranging from 1500 to 2600 $\text{K} \cdot \text{s}^{-1}$; the curve referring to slow experiments represents the average of 4 experiments with heating rates from 130 to 640 $\text{K} \cdot \text{s}^{-1}$, performed immediately after the fast experiments. The general trend is clearly the same, but in the slow experiments there is more time for surface modifications to occur and the same phenomena take place at better-defined temperatures.

During these experiments reflectivity was measured for the entire temperature range, starting before the application of the current pulse (when the specimen is at room temperature) and performing reflectivity measurements during both heating and cooling until the time when the specimen had cooled freely back to room temperature (the total time was in the range of 60 to 90 s). The radiance temperature was measured by high-speed pyrometry from the moment when the specimen reached approximately 1000 K during heating to the time it reached the same radiance temperature during cooling. Below these temperatures the signal-to-noise ratio of the pyrometer does not permit accurate temperature measurements in the wavelength region of the instrument. Temperatures between 300 and 1000 K were computed by interpolation during heating

and by extrapolation during cooling. The typical shape of normal spectral emissivity versus temperature curves in a slow experiment is presented in Fig. 6. It is clearly seen that the normal spectral emissivity of the niobium strip specimen has a different temperature behavior during heating and during cooling, and this trend is clearly visible in all the experiments. The most likely explanation of this phenomenon is that probably a very thin layer of oxide is present on the surface of the specimen kept in the experimental chamber. When the specimen is pulse heated, the oxide layer evaporates (in the temperature range 1300 to 1600 K, see the curves for slow experiments in Figs. 5 and 6). The trend above 1600 K for slow experiments (and above 2000 K for fast experiments) represents the normal spectral emissivity versus temperature for a clean niobium surface. During cooling the trend is reversed and emissivity follows part of the heating curve. The formation of the thin oxide layer is not instantaneous, but it takes some time, and therefore the normal spectral emissivity will follow a different temperature trend with respect to the heating period. The formation of the oxide layer during cooling starts at about 900 K (see Fig. 6) and

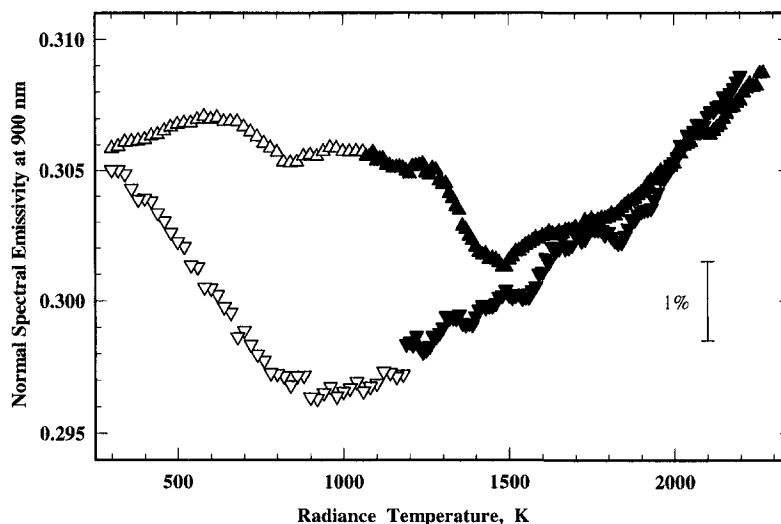


Fig. 6. Typical experimental results of the normal spectral emissivity as a function of the radiance temperature for a niobium strip specimen from room temperature to the melting point (slow experiment: triangles pointing upward refer to heating; triangles pointing downward refer to cooling). Filled symbols indicate the range where both temperature and reflectivity were measured, and open symbols indicate the range where reflectivity was measured and temperature was computed by interpolation or extrapolation.

is practically complete by the time the specimen has returned to room temperature.

In relation to the experimental results described previously, a unique curve for the normal spectral emissivity versus temperature of niobium would have a very limited significance and would not represent what is happening during the pulse technique measurements. In the evaluation of thermophysical properties of niobium strips [8], different normal spectral emissivity curves were computed and used directly in the related experiments, taking into account in this way the changes that are evident both from specimen to specimen and for heating and cooling.

5. ESTIMATE OF UNCERTAINTIES

The estimate of uncertainties (two-standard deviation level) is based on uncertainties in measured quantities, in operational conditions and in calibrations.

The worst-case situation regarding the reproducibility of these experiments is presented in Fig. 7. All these experiments were performed consecutively under the same operational conditions, but changing the target position of the laser diode beam and the target area of the high-speed pyrometer. The nine experiments are divided into five groups, and for four groups, two identical experiments were performed (without moving the laser diode and pyrometer targets). The experiments in the same group (same symbol in Fig. 7) are reproducible within $\pm 0.1\%$, while all the experiments are within $\pm 0.5\%$. This figure also includes any (minimal) normal spectral emissivity change of the niobium surface due to repeated cycles up to the melting point.

In reflectivity techniques uncertainties in temperature measurements cause only errors in the temperature associated with the reflectivity (emissivity) value. Considering of the very weak dependence of emissivity with temperature, the uncertainty in temperature measurements has negligible effects on the uncertainty in emissivity. Long-standing primary calibrations of the effective wavelength and of the linearity of the detector of the pyrometer were used in these experiments. The radiance temperature at the melting point of niobium [6] was used as a reference temperature; therefore, the melting plateau in each experiment provided the exact value for obtaining correct radiance temperature measurements, including the transmission of all optical components in the pyrometer target path. All temperatures reported in this paper are based on the International Temperature Scale of 1990 (ITS-90) [10].

Uncertainties in reflectivity (emissivity) measurements depend on uncertainties in measured signals, on the stability of operational conditions, and

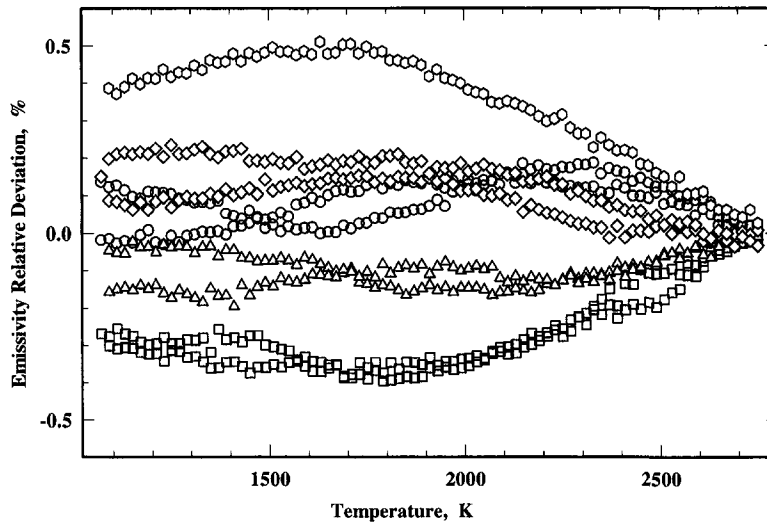


Fig. 7. Deviation of nine fast experiments from their mean (same specimen). Experiments with identical symbols were performed under the same experimental conditions. Different symbols indicate changes in the laser diode or pyrometer targets.

on the uncertainty of the calibration point. Lock-in signals are measured with a 14-bit data acquisition system that is calibrated periodically. Electronic noise, remaining uncertainties after the calibration, and possible drifts between calibrations contribute a $\pm 0.1\%$ uncertainty to each signal. The total uncertainty in the niobium and BaSO_4 signals is therefore $\pm 0.2\%$. Measurements of the stability of the laser diode in the times necessary for the completion of these experiments contribute an uncertainty of $\pm 0.5\%$. Possible variations among different BaSO_4 specimens and remaining uncertainties after the BaSO_4 reference measurements contribute another $\pm 1\%$ uncertainty to the emissivity. All the different effects related to possible losses of the reflected signal were taken into account by the emissivity calibration at the melting point of niobium. The uncertainties of this emissivity value depend on uncertainties associated with the melting point of niobium (7 K) [7], with the radiance temperature at the melting point (6 K) [6], and with the wavelength (2 nm). The wavelength uncertainty depends on a possible mismatch between the laser diode wavelength (center, 900 nm; bandwidth, 1.1 nm), the sphere detector wavelength (center, 900 nm; bandwidth, 10 nm), and the pyrometer wavelength (center, 900 nm; bandwidth, 82 nm). The uncertainty in the emissivity value at the melting point of niobium is 3.7% and represents the largest contribution to the total uncertainty.

Table I. Uncertainties in Normal Spectral Emissivity Measurements

Source of uncertainty	Relative uncertainty (%)
Repeatability of experiments	± 0.5
Electronic calibrations	± 0.2
Niobium experiments	0.1
BaSO ₄ experiments	0.1
Intensity of laser diode	± 0.5
BaSO ₄ specimens	± 1
Normal spectral emissivity at the melting point of niobium	± 3.7
Melting-point temperature	2.15
Radiance temperature at the melting point	1.28
Wavelength	0.26
Total uncertainty	± 3.87

The various contributions are summarized in Table I. It may be concluded that the total uncertainty in these emissivity measurements was not more than 4%.

6. CONCLUSIONS

Experimental results of the normal spectral emissivity at 900 nm of three niobium strip specimens in the temperature range from room temperature to the melting point have been presented. The measurements were performed with a new pulse-heating technique developed at the IMGC, which is a high-speed version of an integrating sphere reflectometer. The normal spectral emissivity values have been used for determining several thermophysical properties of niobium in the temperature range 1200 to 2700 K, as detailed in a complementary publication [8]. The thermophysical property results validate these normal spectral emissivity measurements because thermophysical properties of strip specimens closely repeat values obtained on tubular specimens with a blackbody. The dependence of normal spectral emissivity on surface conditions has been confirmed, indicating the presence of a thin oxide layer that evaporates during the heating phase of the experiment but is formed again during cooling at lower temperatures. Consequently the normal spectral emissivity of the niobium strip does not follow the same trend during heating and during cooling. Additional experiments on other materials are necessary to verify whether this behavior is specific to niobium or whether it reflects a general pattern in pulse heating experiments.

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