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Noncontact technique for measuring the electrical resistivity and magnetic susceptibility of electrostatically levitated materials

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We describe the development of a new method for measuring the electrical resistivity and magnetic susceptibility of high temperature liquids and solids. The technique combines a tunnel diode oscillator with an electrostatic levitation furnace to perform noncontact measurements on spherical samples 2-3 mm in diameter. The tank circuit of the oscillator is inductively coupled to the sample, and measurements of the oscillator frequency as a function of sample temperature can be translated into changes in the sample’s electrical resistivity and magnetic susceptibility. Particular emphasis is given on the need to improve the positional stability of the levitated samples, as well as the need to stabilize the temperature of the measurement coil. To demonstrate the validity of the technique, measurements have been performed on solid spheres of pure zirconium and low-carbon steel. In the case of zirconium, while absolute values of the resistivity were not determined, the temperature dependence of the resistivity was measured over the range of 640–1770 K and found to be in good agreement with literature data. In the case of low-carbon steel, the ferromagnetic-paramagnetic transition was clearly observable and, when combined with thermal data, appears to occur simultaneously with the solid-solid structural transition. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4759021]

I. INTRODUCTION

The use of levitation techniques for the study of high temperature liquids has grown steadily over the last two decades. In particular, aerodynamic, electromagnetic levitation (EML), and electrostatic levitation (ESL) techniques have been used to study the physical properties of the liquid state of a variety of metallic, semiconducting, and ceramic materials. The utility of these techniques stems from the elimination of a crucible by providing a noncontact means to suspend samples in space. Combined with processing in a high purity (inert gas or high vacuum) environment, this allows high temperature, highly reactive materials to be studied while greatly reducing the potential for contamination through reactions with crucibles or the atmosphere. Furthermore, the suppression of heterogeneous nucleation sites due to impurities or contact with container walls can allow for very deep levels of supercooling, upwards of 300 K. The supercooled liquid state can be maintained for extended periods of time, up to several hours, allowing for careful measurements of a variety of properties including density, surface tension, viscosity, structure, and specific heat. Measurements of the electrical and magnetic properties using levitation techniques, however, have proven to be more problematic.

Electrical conductivity is an important quantity in the experimental study of materials. Being proportional to the free electron density and mobility, the measurement of electrical conductivity can serve as an indicator of changes in the electronic and structural properties of materials. Electrical conductivity is also important in industrial processes, where it controls the electromagnetic stirring of melt pools during casting and refining processes, as well as playing a critical role in the computational study and implementation of induction heating methods. Knowledge of the electrical conductivity can also be used to gain insight into the behavior of two other important materials properties: the thermal conductivity via the Wiedemann–Franz law, and the radiative emissivity via the Drude equations.

Attempts have been made to incorporate conductivity measurements with each of the previously mentioned levitation techniques. Enderby et al. combined an inductively coupled ac susceptibility measurement with aerodynamic levitation. However, due to temperature instabilities of the pickup coil, this technique was largely limited to resistivity measurements only at the melting point of materials exhibiting sizeable changes in the conductivity upon melting and which can be treated as insulators at room temperature, such as silicon and germanium. It was also later found that the choice of levitation gas affects the measurements. Lohofe described an inductively coupled technique combined with EML which has been successfully used to measure the electrical resistivity of a series of supercooled Cu-Ni alloys, as well as the Zr-Pd. However, due to the coupling of sample heating and levitation in EML, samples must have a proper combination of density and melting point to be processed, and a cooling gas is usually required to provide temperature variability. Furthermore, due to the nature of the levitation force, samples often deform from a spherical shape, and turbulent fluid flow can cause significant surface oscillations, obscuring the interpretation of measurements; most of these issues can be alleviated by processing in microgravity. For ESL, which has been employed in the current work, Rhim et al. succeeded in implementing a variation of the induction motor technique to perform measurements on liquid aluminum and germanium. However, this technique relies on being able to precisely measure the rotational velocity of the sample under study, which,
for the case of a high purity, isotropic liquid without surface features, is quite difficult to accomplish.

To expand upon these attempts, and to improve the prospects for electrical and magnetic measurements on high temperature liquids, we have combined an inductively coupled tunnel diode oscillator (TDO) with the electrostatic levitation technique.

The levitation system described in this article has just recently been constructed (see Figure 1). Here, we provide only a brief overview of the principles of operation since detailed descriptions of the design and implementation of similar electrostatic levitation systems can be found elsewhere in the literature, with our system drawing heavily on the advancements of Ref. 17. In ESL, a positively charged sample, 2-3 mm in diameter, is levitated using an applied electric field. As illustrated in Fig. 2, the lift is supplied by a pair of vertically spaced electrodes, ~10 mm apart, with the bottom fixed at ground and the top variable from zero to ~20 kV (Trek model 20/20C). Additional electrodes, placed below the sample and around the bottom electrode, provide lateral stability. The position of the sample within the electrodes is determined by backlighting the sample with a pair of orthogonal lamps and projecting its shadow onto the surface of a position sensitive detector (PSD). The position data are input to a computer control algorithm which determines how to properly adjust the potentials on the top and lateral electrodes to maintain the sample at a stable position. The sample is heated using a fiber coupled diode laser (Apollo Instruments model S65-980-1) and cools radiatively. The sample temperature is determined pyrometrically with a sensitive range from 573 to 2773 K.

II. TUNNEL DIODE OSCILLATOR

The TDO has been a well-established technique in low temperature physics for several decades. Its utility stems from its ability to translate a variety of materials property measurements into a measurement of frequency, which can be done quickly and with very high precision, via a circuit that can provide stability on the order of 10 ppb or better. Previously, the TDO has been used for measurements of magnetic susceptibility, London penetration depth, and normal state resistivity of materials at low temperatures. In this regard our application of the technique is unique, as we have adapted it to perform measurements on solids and liquids at temperatures well above 1000 K. As described below, this introduces a new set of challenges regarding the temperature stability of the circuit which can limit the accuracy of electronic property measurements.

The basic idea behind the functioning of the TDO is described in the following; for a detailed description of the TDO principles and electronics see Ref. A tunnel diode is wired in series with a dc power source, potentiometer, and a LC tank circuit. When properly biased, the tunnel diode features a region of negative differential resistance in its $I-V$ curve; this negative resistance effectively cancels the real (positive) resistance in the rest of the circuit, and allows for spontaneous oscillation at the resonant frequency $\omega = 2\pi f_0 = (\sqrt{LC})^{-1}$. As part of an ac circuit, an inductor features a complex impedance $Z = R_0 + ioL$. When a material with complex susceptibility $\chi = \chi' + i\chi''$ is placed inside of the inductor,
the impedance characteristics of the inductor will change by
\[
\frac{\Delta R}{R_0} = -\frac{\omega L_0}{R_0} \varphi \chi'^\prime
\]
\[
\frac{\Delta L}{L_0} = \varphi \chi'^\prime
\]
In these equations, \(\varphi\) is the sample filling factor, a dimensionless quantity which describes the fraction of magnetic field volume occupied by the sample. In the case of an ideal solenoid, this would simply be the ratio of sample to solenoid volumes; in practice, \(\varphi\) must be determined via calibration with a well characterized sample.

Prados et al.\textsuperscript{21} derived expressions for the complex susceptibility of a magnetic conducting sphere in an ac magnetic field. If the oscillator frequency is sufficiently high, such that the skin depth \(\delta\) is much smaller than the radius \(a\) of the sphere, then the complex susceptibility can be approximated as
\[
\chi'^\prime = -\frac{3}{2} + \frac{9\delta}{4a} (1 + \chi)
\]
\[
\chi'^\prime = \frac{9\delta}{4a} (1 + \chi)
\]
where \(\delta = \sqrt{2\rho / \mu_0 \omega}\) is the classical skin depth, \(\rho\) the sample resistivity, and \(\mu = \mu_0 (1 + \chi)\) the permeability of a sample with dc magnetic susceptibility \(\chi\). Typical oscillator frequencies and skin depths encountered in the current application are \(\sim 10\) MHz and \(\sim 100\) \(\mu\)m, respectively.

Combining Eqs. (1), (2b) and (3a), we arrive at an expression that relates the shift in TDO frequency to the properties of the sample
\[
\frac{\Delta f}{f_0} = \frac{3}{4}\varphi \left(1 - \frac{3\delta}{2a} (1 + \chi)\right).
\]
It should be noted in Eq. (4) that any shift in TDO frequency is caused by a combination of changes in sample resistivity and magnetic susceptibility. However, in general, for a conducting sphere, the TDO frequency will be much more sensitive to changes in resistivity than magnetic susceptibility. This is made clear by noting that \(\Delta f \propto \sqrt{\rho (1 + \chi)}\); since \(\chi < 10^{-2}\) for most materials\textsuperscript{23} the magnetic contribution can usually be ignored. One obvious exception to this is any material which undergoes a ferromagnetic transition, as we will demonstrate below.

III. EXPERIMENTAL CONFIGURATION

When incorporating the TDO coil into the ESL, two key points need to be considered: (i) maximizing the filling factor of the sample while simultaneously leaving the horizontal viewing plane unobscured, and (ii) providing a means to stabilize the temperature of the coil against thermal radiation from the sample.

A schematic of the levitation electrodes incorporating the TDO pickup coil is also shown in Figure 2. In this new electrode design, the bottom center electrode is replaced with a pedestal made of a thermally conductive boron nitride ceramic (Momentive HBN). The pickup coil is wound into a groove near the top of the pedestal and potted using a high vacuum epoxy. In this way, the pedestal acts as a heat shield against the sample’s radiance, as well as providing a means to stabilize and control the temperature. To regulate the temperature of the coil, a platinum resistance thermometer (RTD) is mounted vertically on the pedestal adjacent to the coil, and nichrome heating wire is wound onto the pedestal 1.5 cm below the TDO coil. The pedestal is heat-sunk to the vacuum chamber via a copper block. Prior to beginning a measurement, the coil temperature is raised well above room temperature (\(\sim 350\) K) and maintained within a few Kelvin by reducing power to the nichrome wire as the sample’s temperature is increased.

While this design effectively stabilizes the coil temperature, it does not completely eliminate temperature changes of the coil over the course of an experiment. Measurements of the TDO frequency as a function of coil temperature reveal a frequency shift of \(\sim 200\) Hz/K, whereas a typical extraction frequency (TDO frequency shift caused by placing a sample near the coil) is \(\sim 2000\) Hz. Therefore, even small changes in the coil temperature can skew the results. Fortunately, this temperature dependence has been found to be both linear and repeatable over a wide range of temperatures, and can be treated as a removable background. In addition to the small changes in the temperature of the coil itself, we must also account for an offset in the temperature measurement which occurs during sample heating. As a sample’s temperature is increased, it begins to radiantly heat the pedestal from above, and the power to the nichrome heater is reduced accordingly. To dissipate the power from the sample, a temperature gradient will form along the length of the pedestal. Due to the orientation and extent of the platinum RTD, a temperature gradient will form along its length as well and, as a result, the average temperature measured via the RTD will be lower than the actual temperature of the coil. This offset can be corrected because the magnitude of the temperature gradient is proportional to the amount of radiant power being dissipated, which, in turn, is proportional to the amount by which the nichrome heater power must be reduced. Therefore, by monitoring the changes in the nichrome heater power we can compensate for the temperature offset. The exact scale factor between the nichrome heater power and the offset, as well as the dependence of the TDO frequency on the coil temperature, have been determined by performing empty-coil measurements. In these empty-coil measurements, a laser was used to heat the top end of the boron nitride pedestal to simulate radiative heating from a sample and, by observing the change in TDO frequency as a function of coil temperature and heater power, a suitable background model was obtained.

One consequence of the current design is that the sample resides in a fringing magnetic field, due to its location above the plane of the TDO coil. As a result, the filling factor of any sample will depend on its position along the vertical axis and, for a given position, the filling factor will not scale exactly with the volume of the sample. This not only makes the calibration of the system difficult but also necessitates a very high level of positional stability for the levitated samples, as
too much motion will produce noise in the frequency measurement. The dependence of the TDO frequency on sample position can be measured by translating a sample vertically in the electrode gap and observing the shift in frequency; such measurements reveal a dependence of $\sim 1$ Hz/μm. While the short term stability (i.e., sample jitter) in ESL systems is generally good enough to prevent this dependence from being problematic, a modification to the sample positioning system was required to ensure stability over longer time intervals.

In most ESL systems used to date, beam-expanded HeNe lasers are used to project the sample shadow onto a position sensitive detector, from which the sample’s position in the electrode gap can be determined. However, HeNe lasers exhibit a small amount of drift in the direction of the light beam ($+/−0.05$ mrad in our case). Projected over a distance of 1 m, this can cause lateral displacement of the positioning beam by as much as $+/−50$ μm, resulting in a similar drift of the sample position. Indeed, this magnitude of drift has been measured using a high resolution video imaging technique.\(^5\) To eliminate the drift, the laser backlights have been replaced with high-power, quasi-monochromatic LEDs (Thorlabs models M455L2 and M505L2). The light output from the LEDs is much more stable than from the lasers, in terms of both spatial distribution as well as power output. However, the LEDs are highly divergent, and focusing optics are necessary to collect and direct the light toward the sample; a bi-convex spherical singlet is used to project the image of the LED beyond the sample position. Even with the focusing optics on the input beam, the light is too divergent for shadow-casting, as was done with the lasers, so an additional bi-convex spherical singlet is used on the PSD side to perform 1:1 imaging of the sample onto the detector surface. To prevent interference between the backlights or from other sources of extraneous light (heating laser, sample radiance at high temperatures), band-pass filters centered at the LED wavelengths (455 and 505 nm) are placed directly in front of the PSDs. Measurements comparing the positional stability of a sample using laser vs. LED backlighting are shown in Figure 3. The use of LEDs is clearly an improvement, reducing sample drift from $+/−50$ μm to a baseline noise level with a standard deviation of less than 3 μm. The drift in the TDO frequency is likewise reduced from approximately $+/−50$ Hz down to a noise level of less than 3 Hz.

IV. PROCEDURE, RESULTS, AND DISCUSSION

A. Zirconium resistivity

To validate the technique for measurements of electrical resistivity, measurements were made on a 60 mg sphere of zirconium. Zirconium was chosen for a number of reasons: (i) it is nonmagnetic, ensuring clear interpretation of the data; (ii) it has a well-defined solid state resistivity over a wide temperature range (293–1973 K), including an anomaly at the structural transition from hexagonal close packed (hcp) to body centered cubic (bcc); (iii) the latent heat associated with the hcp/bcc phase transition at 1139 K provides a calibration point for pyrometric temperature measurements. Zr is also commonly used for testing other aspects of the ESL, due to its favorable liquid state properties of low vapor pressure and high oxide solubility. The sample was prepared by arc melting a 60 mg piece of Zr on a water-cooled copper hearth, forming a small bead $\sim 2.6$ mm in diameter which was suitable for levitation. Subsequent melting and solidification in the ESL produced a solid sphere with sufficient sphericity for the following measurements. A high level of sphericity is important not only to ensure proper interpretation of the data via Eq. (4), but to reduce the scatter in the frequency data caused by sample rotation which tends to occur during heating. For molten samples this is less of a concern, because the surface tension forms the melt into a highly spherical shape.

Measurements were made over the temperature range from 640 to 1973 K. The sample was initially raised from room temperature to 640 K and maintained at that temperature for several minutes to allow the boron nitride post and all components mounted on it to come into thermal equilibrium. The sample was then ramped at approximately 2 K/s to a maximum temperature of 1973 K. During the ramp the TDO frequency, coil temperature, and heater power are all recorded at a rate of 1 Hz. The measured frequency data are corrected for thermal drifting of the coil by

$$\Delta f' = \Delta f - A \Delta T_{\text{coil}} + B \Delta P_{\text{coil}},$$

where $\Delta T_{\text{coil}}$ is the change in coil temperature, $\Delta P_{\text{coil}}$ is the change in heater power, and the factors $A$ and $B$ are determined prior to the experiment (as described in Sec. II) and found to be 205 Hz/K and 45.2 Hz/W, respectively. The raw data and the corrected frequency data are shown in Figure 4. Comparison of the raw and corrected frequency data makes clear the need to monitor and control the TDO coil temperature, as the raw frequency data have drifted by a factor of four compared to the corrected data. Frequency data for sample temperatures above 1770 K have not been included because the heating of the levitation electrodes by the sample radiation (which scales as $T^4$) caused an additional drifting of the TDO frequency beyond that point. This problem can likely be overcome by redesigning the electrode mounts to

![Figure 3](image-url)
provide a more efficient means of dissipating the power absorbed from radiation by the sample. Planned future modifications include replacing the current mounting material, made of the low thermal conductivity steatite and MACOR ceramics, with the much more thermally conductive boron nitride ceramic.

To convert the measured frequency data to an absolute value for the resistivity using Eq. (4), two additional unmeasured quantities are required: the filling factor, \( \varphi \), and the extraction frequency. Nevertheless, the frequency data are still representative of the relative temperature dependence of the resistivity, and to show this we have plotted the frequency data along with the square root of the resistivity based on published data, and the results are shown in Figure 5. The measured frequencies can be seen to reproduce the published data very well, capturing the temperature dependent trends above and below the structural transition, as well as the anomaly which occurs at the transition. We have also used these data to determine the value of the filling factor during this experiment, and found it to be \( 6.8 \times 10^{-4} \).

To estimate the uncertainty in our measurement, we begin by noting the level of scatter in the data during an isothermal hold. During the 90 s hold at 640 K, the standard deviation, \( \sigma \), of the measured frequency is 3 Hz. All data during the hold lie within 3\( \sigma \) of the mean, and so a conservative estimate of the uncertainty associated with a single data point would be \( \delta f \approx 9.0 \text{ Hz} \). At the hcp/bcc transition, there is a frequency shift of \( \approx 70 \text{ Hz} \) associated with a change in resistivity of \( \approx 20 \mu\Omega \cdot \text{cm} \), giving an approximate conversion of 3.5 Hz/\( \mu\Omega \cdot \text{cm} \). From this, the uncertainty associated with a change in the resistivity is \( \delta \rho \approx 2.6 \mu\Omega \cdot \text{cm} \), and, given \( \rho \approx 120 \mu\Omega \cdot \text{cm} \), the relative uncertainty is approximately 2.2%.

**B. Ferromagnetic transition in steel**

To demonstrate the measurement of a ferromagnetic transition with the current technique, measurements were performed on a commonly available low-carbon steel ball bearing (McMaster-Carr 96455K49) with a diameter of 3.2 mm. This type of steel is composed of at minimum 98 at. % iron, with the balance made up of roughly equal amounts of carbon and manganese. The Curie temperature of this alloy is approximately the same as that for pure iron, 1043 K. Closely associated with the Curie temperature is a structural transition, from a low temperature phase of mainly bcc iron with small amounts of Fe3C, to a high temperature phase of face centered cubic (fcc) iron.

The steel ball was brought to a temperature of 715 K and held at that temperature while the boron-nitride post came into thermal equilibrium. The sample temperature was then ramped at 1 K/s to a maximum of 1340 K, where it was held for 1 min before cooling at the same rate back down to 715 K. After another 1 min hold, the heating-cooling cycle was repeated three additional times. While the sample temperature was being cycled, the TDO frequency and coil temperature were recorded at a rate of 0.5 Hz. At the time the measurements were made, the heater power was not recorded; however, as will be evident, the corrections are not necessary for the purpose of simply observing the ferromagnetic transition. The pyrometer was calibrated such that the ferromagnetic-paramagnetic transition occurred at the anticipated temperature.

Figure 6(a) shows the sample temperature and TDO frequency as a function of time for the second heating-cooling cycle. The small plateau in the sample temperature, near 450 s, indicates the location of the bcc/fcc transition, which appears to occur simultaneously (within 2 K) with the magnetic transition at 1043 K. The transition from ferromagnetism to paramagnetism is indicated by a sudden drop in TDO frequency of 3370 Hz. During cooling, the transformation from the fcc to bcc structures does not occur at the same temperature as on heating, but rather is reduced by 95 K; such
supercooling has also been observed for the bcc/hcp transition in Zr, and is possible due to the first order nature of the transitions. The release of the latent heat of transformation results in the sample temperature rise from 948 to 971 K near 1330 s in Figure 6(a), as well as the back-bending in the $\Delta f$ vs. $T$ cooling data in Figure 6(b). The supercooling of the fcc phase results in an associated reduction in the onset temperature for ferromagnetism, as only the bcc phase of iron is known to be ferromagnetic. The third and fourth heating-cooling cycles (not shown) produced results identical to the first cycle and is likely due to a thermal history/annealing effect.

A better understanding of the behavior of the TDO in this example can be realized by again noting that $\Delta f \propto \sqrt{\rho (1 + \chi)}$, and from comparison of the results from Zr. At the hcp-bcc transition in Zr, a 17% change in the resistivity produced a change in the TDO frequency of 70 Hz. At the transition temperature for steel, the 3370 Hz transition would correspond to an approximately 10-fold increase in the product of the resistivity and relative permeability. This increase is entirely due to the magnetic term, and corresponds to a volume magnetic susceptibility of $\chi \sim 10$ (SI) below the transition temperature (assuming $\chi \ll 1$ above the transition temperature). This order of magnitude estimate seems reasonable given the low excitation field of the TDO coil, and is comparable to a value obtained for nickel using a similar technique.\(^{26}\) The increase in the slope of $\Delta f$ vs. $T$ below the transition is caused by a combination of the greater value of the susceptibility as well as the greater temperature coefficient of resistivity,\(^{27}\) and in general the behavior of the frequency below the transition is due to a mixture of the electrical and magnetic properties of the sample.

V. CONCLUSIONS

We have successfully combined an inductively coupled tunnel diode oscillator with the electrostatic levitation technique to perform noncontact measurements of the electrical and magnetic properties of two high temperature solid samples. While absolute values were not obtained in the current work, the measured frequency data properly reproduced the temperature dependent behavior of the electrical resistivity of solid Zr, as well as the onset of ferromagnetism in low-carbon steel. Work is ongoing to develop a method of accurately determining the sample filling factor and extraction frequency, which will allow calculation of the resistivity based on the measured TDO frequency, as well as to stabilize the temperature of the electrodes to allow measurements on samples above 1770 K. In the mean time, the current system is suitable for measuring the temperature dependence of the resistivity of materials that melt below 1700 K, such as Si and Ge, as well observing high temperature ferromagnetism in Co and Fe based alloys.

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