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CRYOGENIC RESEARCH

R. L. Dolecek

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NAVAL RESEARCH LABORATORY
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Cryogenic Research*

R. L. Dolecek†

Because of the wide variety in kinds of research which entice scientists into the low-temperature regions, cryogenic investigations are carried on by a number of different groups at the Laboratory. Included in current projects are the fields of crystal physics, properties of metals, and magnetism and magnetic resonance. This article discusses the work of one group, the Cryogenics Branch, which is confined predominantly to a study of the properties of solids in the temperature range 1° to 20° absolute.

Of chief interest are the properties of metals, and, since one of the most challenging of the unsolved problems is superconductivity, much of the research is directed toward interpretation of this phenomenon. Studies in the related fields of thermal conductivity, specific heat, magnetic effects, and thermometry are also being pursued. With the recent completion of facilities for the production of very strong magnetic fields has come the opportunity for research below 1° absolute through utilization of the demagnetization cycle. Transition temperatures and critical fields of superconductors in that temperature range are being studied.

Thus far, little connection has been found between the occurrence of superconductivity among the elements and their other physical properties. However, it has been observed that the superconducting elements lie predominantly in groups II to V of the periodic table, that they occupy a rather well-defined region in a graph of atomic volume versus atomic number, and that the transition temperature of the superconductor is related to its Debye characteristic temperature. To evaluate these suggestive correlations and perhaps discover others, complete investigation of the metals for the occurrence of superconductivity is needed. Most metals have been tested to temperatures of the order of 1° absolute, so that much of the needed work lies in the ultra low-temperature range available only through use of the demagnetization cycle.

SUPERCONDUCTIVITY BELOW 1° ABSOLUTE

In preparing to search the metals for the occurrence of superconductivity, a group in the Cryogenics Branch under Mr. M. C. Steele have measured the critical field curves of four of the nine metals for which superconducting transition temperatures below 1° absolute have been reported. These metals are the soft superconductors, zinc and cadmium, and the hard superconductors, ruthenium and hafnium. The data obtained are in essential agreement with previously reported values. In the case of hafnium, the critical field data are interesting because they suggest that it may be a soft superconductor, even though a strong diamagnetism was not observed, whereas from its electronic structure one would expect hafnium to be a hard superconductor.

Hafnium

In Figure 1 is plotted, as a function of temperature, the magnetic field required to change hafnium from the superconducting to the normal state. For values of magnetic

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†Head, Cryogenics Branch, Electricity Division

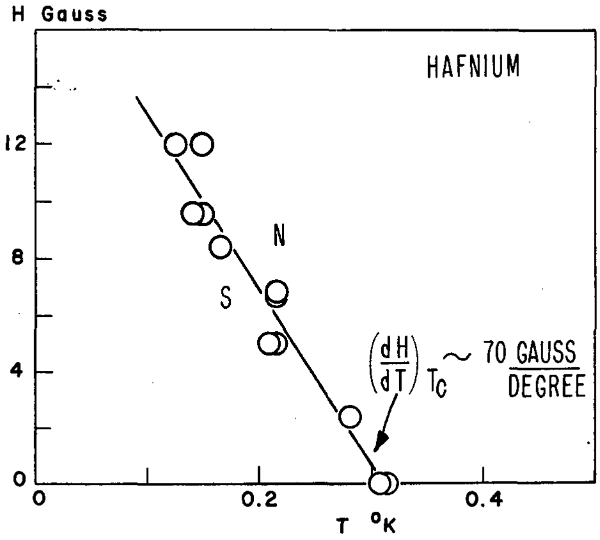

Figure 1 - Critical field curve for hafnium

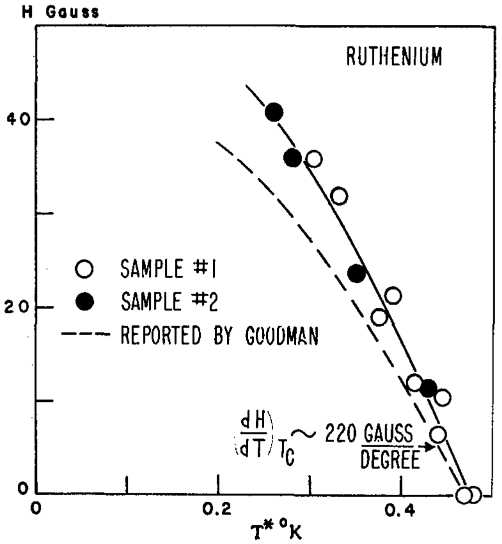

Figure 2 - Critical field curve for ruthenium

field and temperature lying below the curve the metal is a superconductor; for values above the curve, it is normal. The transition temperature observed is 0.32^{0}K which is in agreement with the observations of Kurti and Roberts. (1) The initial slope of the critical field is of order 70 gauss/degree, and the critical field value at absolute zero is of order 20 gauss. The low value of initial slope (70 gauss/degree) suggests that hafnium may be a soft superconductor since the initial slope for hard superconductors is usually much larger (of order 200 gauss/degree). The low value of critical field at the absolute zero (20 gauss) is also indicative of a soft superconductor although, because of the low transition temperature of hafnium, a small critical field at the absolute zero is to be expected. Further consideration must be given to specimen purity and magnetic behavior before the question of hardness can be resolved, and such experiments are now in progress.

Ruthenium

Critical field observations on ruthenium are shown in Figure 2. That ruthenium is a hard superconductor is borne out by the large critical field slope at the transition temperature ($H = 220$ gauss/degree) and a relatively large critical field at absolute zero ($H = 55$ gauss). The circles are the observations of Mr. Steele at our Laboratory and the dashed curve is the observation published by Goodman. (2) The two are in reasonable agreement, particularly the transition temperature (0.47^{0}K). Since Goodman's data were probably obtained using a bulk specimen of ruthenium whereas powdered ruthenium was used by Steele, the apparent divergence of the two observations at low temperatures could be a size effect. Such an explanation would require the assumption of a rather large penetration depth, but this is not unreasonable, for superconductors having transition temperatures of the order of a few tenths of a degree absolute. Mr. Steele is carrying out a test of this hypothesis using samples containing large and small spheres of cadmium. The preliminary data are suggestive of a size effect; however the results are not conclusive and the investigation is being continued. Results so far have emphasized the inherent difficulties using powdered metals dispersed in paramagnetic salts to study superconducting properties by magnetic methods. When searching for superconductors below 0.1°K, great care must be exercised with respect to applied fields and specimen size, since the critical fields may be of the order of gauss and, if the sample dimensions are too small, the change in diamagnetism may be so small as to escape observation.

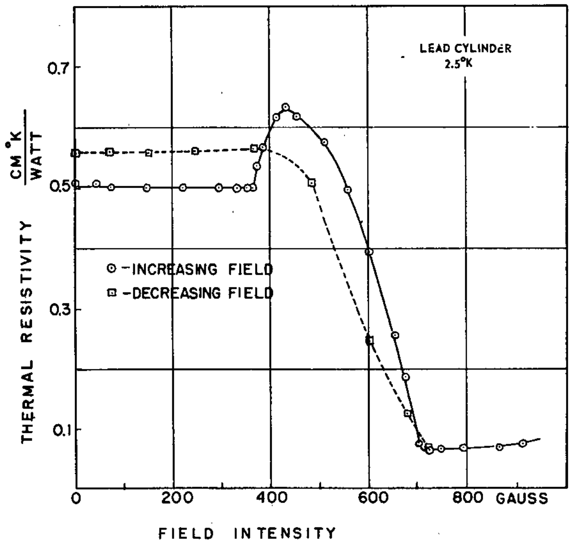

Figure 3 - Measurements on a lead cylinder in a transverse magnetic field

THERMAL CONDUCTIVITY MEASUREMENTS

Information on the nature of superconductivity is also being sought through calorimetric studies and measurements of thermal conductivity. Recently Dr. R. T. Webber has found an anomaly in the thermal conductivity of a pure metal superconductor in the intermediate state. Theoretical interpretation of the phenomenon should provide further information concerning the significance of the laminar structure of the intermediate state. Experimentally one finds that the thermal resistivity in the superconducting state is substantially larger than in the normal state. This is consistent with the hypothesis that in the superconducting state the majority of free electrons have entered into a state of zero-point energy where they are unable to contribute to the heat transport by exchanging energy with the lattice. Dr. Webber's study concerns the manner of variation of the thermal resistivity as the superconductor is caused to pass through the intermediate state by the application of a magnetic field.

Measurements made by Dr. Webber on a lead cylinder in a transverse magnetic field and at a constant temperature of 2.5°K are shown in Figure 3. Such a field should produce a laminar structure perpendicular to the axis of the cylinder and thus perpendicular to the direction of the heat flow used for the thermal conductivity measurements. It can be seen that in the superconducting state the thermal resistivity is quite field-independent and considerably larger than in the normal state (produced by the application of a magnetic field in excess of 700 gauss). The intermediate state of the cylinder is entered as the field exceeds one-half the critical field (at approximately 350 gauss). But instead of exhibiting a gradual decrease in thermal resistivity, corresponding to a gradual increase in the number of normal electrons available for heat transport, the thermal resistivity is seen to rise to a considerably larger value before decreasing to the normal state value.

That this phenomenon is strongly temperature dependent is shown by the data in Figure 4. Here, in reduced coordinates, the fractional change in resistivity is plotted as a function of applied field. The solid line is the data shown in Figure 3, and the increase in resistivity upon entry into the intermediate state is again evident. The four curves represent data taken at four different temperatures—the dashed curve is for data taken at 4.0°K, the dash-dot curve at 3.6°K, the solid curve at 2.5°K, and the dotted curve at a temperature of 2.4°K. The strong temperature dependence is

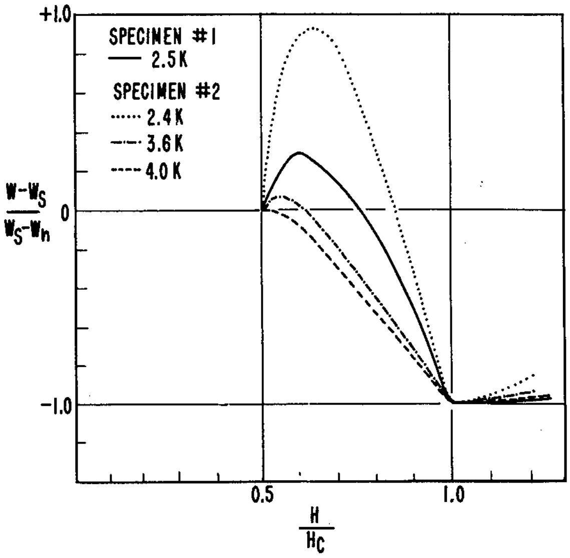

Figure 4 - Fractional change in resistivity plotted as a function of applied field

evident. It can be seen that the phenomenon would escape detection at temperatures above 4°K, and it is unfortunate that we have not made measurements at still lower temperatures to determine the limitations on the rise in thermal resistivity.

Several explanations of this phenomenon have been suggested, based on the relative importance of phonon and electron transport and scattering at the superconducting laminae. At temperatures considerably below the superconducting transition temperature, one would expect that a large fraction of the electrons have entered into the state of zero point energy where they are unable to contribute to the heat transport or to scattering of the phonon waves. Under such conditions, lattice conduction could become important for the metal, and a qualitative interpretation can be given for the increase in thermal resistivity of a superconductor entering the intermediate state. Dr. Hulm of the University of Chicago has suggested that, if, in the superconducting state considerably below the transition temperature, the thermal conduction is predominantly by phonons, then one might expect an increase in the thermal resistivity to arise from scattering of the phonons by the laminar structure incurred upon entry into the intermediate state. This scattering of the phonons by the normal laminae, which contain a high density of normal electrons, would become significant only when the phonon free path length approaches the separation of the normal laminae. This might account for the marked temperature dependence of the additional resistance. As entry into the intermediate state proceeds, one could expect the conduction process to become dominated by the normal electrons produced and the thermal resistivity then to decrease to its normal value as the superconductivity of the metal is completely suppressed. It is evident that the phenomenon may provide a tool for study of the formation of the laminar structure in superconductors, and Dr. Webber is in the process of evaluating several suggestions through study of the effect of specimen geometry and a more complete measurement of the temperature dependence.

CARBON-RESISTOR THERMOMETERS

In the pursuit of such problems as this which involve thermometry, the Cryogenics Branch has developed carbon resistors as secondary thermometers. Thermometry in the temperature interval 5° to 10°K has always presented experimental difficulty because of the lack of sensitive and reproducible secondary thermometers. Carbon resistors have been known to possess the required sensitivity, but in general it was felt that, because of poor reproducibility upon cycling to room temperature, a new calibration would be required on each experimental run. Mr. Clement has investigated the applicability of carbon-composition resistors, of the ordinary 1-watt radio-type, as secondary thermometers for the temperature interval 2° to 20°K.* These resistors were found to be excellent low-temperature secondary thermometers and are recommended for consideration by other cryogenic laboratories.

The characteristics of one such thermometer, which has a nominal (room-temperature) resistance of 100 ohms, are given in Table I. Although the resistance changes most rapidly at the lower temperatures (ranging from 500 ohms at 20°K to about 50,000 ohms at 2°K), the sensitivity at 20°K is still of the order of 4 percent change per degree so that resistance-measurement sensitivity need be only 1 part in 5,000 to detect temperature changes of order 0.05°K at 20°K. Throughout the temperature range 2° to 20°K, the reproducibility upon cycling to room temperature is approximately 0.1 percent of the observed temperature. These data are presented in the fourth column of Table I. The heat capacity of the thermometer, which is negligible for most experimental measurements, is given in the last column.

Table I - Carbon Composition Secondary Thermometers
Nominal Resistance (R_n) 100 Ohms

Temperature (°K)	Resistance (ohms)	Sensitivity $\frac{1}{R}\frac{dR}{dT}$ (percent)	Reproducibility (°K)	Heat Capacity (cal/deg)
20	500	4	± 0.02	10^{-1}
10	1,700	15	± 0.01	10^{-2}
4	8,000	75	± 0.004	10^{-3}
2	50,000	250	± 0.002	10^{-4}

Mr. Clement has derived an empirical resistance-temperature function for these resistance thermometers and has established design relationships (given in Table II) that can be employed in choosing a resistor for a particular application. The empirical resistance-temperature function is quite useful since it can be explicitly solved for either resistance or temperature. Evaluation of the constants in the equation in Table II using liquid helium and hydrogen temperatures results in a resistance-temperature calibration that is accurate to ±0.5 percent throughout the range 2° to 20°K so that interpolation of temperatures in the range 5° to 10°K is feasible.

For design purposes the constants in the resistance-temperature function can be estimated from the nominal (room-temperature) resistance of the thermometer. Equations for these constants together with approximate accuracy of estimation are given in Table II; for convenience, an equation for estimating the sensitivity as a function of nominal resistance and temperature is also given.

From the design relationships one can almost pick a resistor tailored for the application. It is believed that the development of these resistors as secondary low-temperature thermometers is a major contribution to the techniques of cryogenics. Their use has certainly simplified thermometric design and increased the accuracy

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*An article describing this research appeared on pp. 1-4, February 1952 issue.

Table II - Design Relationships for Carbon Composition Thermometers, Temperature Range 2^{0} to 20^{0}K

Resistance - Temperature Function (Empirical)

$$\log_{10} R + K/\log_{10} R = A + B/T \qquad \pm 0.5\%$$

Design Constants in Terms of Nominal Resistance (R_n)

$$A \pm 3\% = 1.62 \log_{10} R_n + 0.27$$

$$B \pm 9\% = 1.60 \log_{10} R_n + 0.48$$

$$K \pm 6\% = 0.594 (\log_{10} R_n)^2 + 0.377 \log_{10} R_n - 0.121$$

Sensitivity in Terms of Nominal Resistance (R_n)

$$\left(\frac{1}{R}\frac{dR}{dT}\right)_T = \frac{-4.35}{T^{1.78}} \log_{10} R_n \qquad \pm 3\%$$

Table III - Jump in Specific Heat of Lead at the Superconducting Transition Temperature

Temperature °K	Calorimetric Measurement ($C_s - C_n$) cal/mole deg	Gorter-Casimir Thermodynamic Formula ($C_s - C_n$) cal/mole deg
6.75	0.0104 ± 0.0004	0.0096
7.00	0.0117 ± 0.0005	0.0112
7.23	0.0126 ± 0.0005	0.0126

of measurements. Utilizing these thermometers in his specific heat work, Mr. Clement has been able to measure specific heats with an accuracy of 1 percent using temperature intervals of 0.1°. Since changes in specific heat can be measured to a greater accuracy, this technique has allowed Mr. Clement to measure the jump in the specific heat of lead at its superconducting transition temperature. The experimental measurements give information on the validity of the Gorter Casimir cycle for lead and illustrate the sensitivity and reproducibility of the carbon-composition thermometers. The specific heat measurements are presented in Figure 5. Indicative of the calorimetric sensitivity, utilizing the carbon thermometer, is the fact that the jump represents a change of 4-1/2 percent in the specific heat. The points represent four runs on different days using a single thermometer calibration. Good reproducibility upon cycling to room temperature is evident. Comparison of the measurements with values to be expected from theory (see Table III) shows excellent agreement.

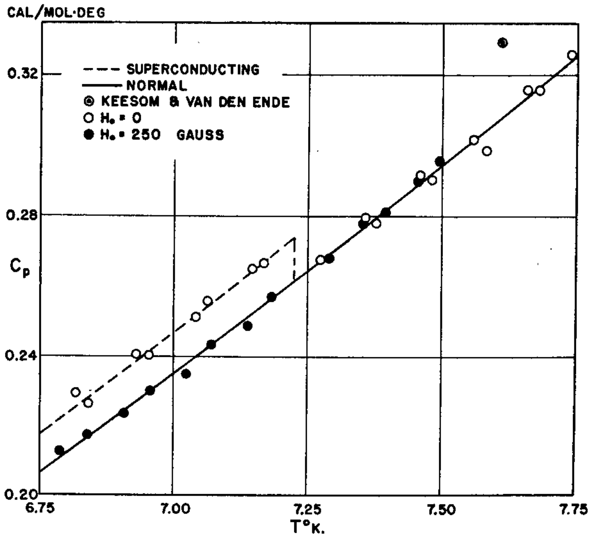

Figure 5 - Atomic heat of lead in the normal and superconducting states. H_O is the constant magnetic field applied to the sample

EMPHASIS OF FUTURE RESEARCH

The Cryogenics Branch is striving to increase knowledge and understanding in solid state physics, and to develop useful cryogenic techniques. Study of the cryogenic properties of metals down to helium temperatures will be continued; however, with the completion of new facilities for research in cryomagnetism, more emphasis will be placed on studies at temperatures below 1°K.

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Naval Research Lab, Washington, D. C.

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