JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office)

VOLUME 71 NOVEMBER 17, 1949 NUMBER 11

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Low Temperature Heat Capacity of Columbium Nitride[1,2]

BY GEORGE T. ARMSTRONG[3]

Measurements of the thermodynamic properties of superconducting materials and of the effect of magnetic field upon them have provided a valuable tool for the study of the nature of the superconducting state. Heat capacity measurements have previously been made at low temperatures on the elements tin,[4] thallium[5] and tantalum,[6] alloys of tin with bismuth,[7] lead with bismuth[8] and of lead with thallium.[9] No measurements have been reported on any superconducting compound. The existence of columbium nitride with a transition temperature near 15°K. provides an opportunity for the study of the heat capacity of such a compound in a region which can be reached with liquid hydrogen. The only previous heat capacity measurements on this substance were reported by Sato and Sogabe[10] above 0°. On the basis of their work Milton[11] estimated the low temperature heat capacity. This is a report of the measurement of the heat capacity of columbium nitride between 11 and 21°K. in the absence of magnetic fields and in the presence of fields up to 1000 gausses.

(1) The major part of this paper is from a dissertation submitted by G. T. Armstrong to the Board of University Studies of the Johns Hopkins University in conformity with the requirement for the degree of Doctor of Philosophy, June 1948.

(2) This work was supported by funds from the Office of Naval Research, Physics Division, U. S. Navy.

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(4) Keesom and Kok, Leiden Comm. 221e.

(5) Keesom and Kok, Leiden Comm. 230c.

(6) Keesom and Desirant, Leiden Comm. 257b.

(7) Mendelssohn, *Proc. Roy. Soc.* (*London*), **152**, 34 (1935).

(8) Shubnikov and Chotkevitch, *Physik. Z. Sowjetunion*, **6**, 605 (1934).

(9) Mendelssohn and Moore, *Proc. Roy. Soc.* (*London*), **151**, 334 (1935).

(10) Sato and Sogabe, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **38**, 174 (1941).

(11) Milton, *Chem. Revs.*, **39**, 419 (1946).

Materials

The columbium nitride, CbN, which was used in the measurements was prepared by roasting columbium metal powder of 400-mesh size or finer in an atmosphere of nitrogen for twelve hours at 1300°. The time was somewhat longer than that used by Horn and Ziegler[12] and this may account for the fact that the product has a somewhat higher nitrogen content than was reported by them. The columbium metal was obtained from the Fansteel Metallurgical Corporation and was reported to have impurities present only as traces of less than 0.1%. The nitrogen used was a prepurified grade containing not more than 0.002% each of oxygen and hydrogen. The product of the reaction was gray with a distinct yellowish tinge. X-Ray examination showed only the sodium chloride lattice, with no evidence of any other structure. The gain in weight in preparation indicated 48.1 mole per cent. nitrogen, while an analysis by the Dumas method performed by a commercial analyst indicated 49.1 mole per cent. nitrogen.

Apparatus and Methods

The Cryostat.—The general plan of the cryostat is conventional in most respects. The calorimeter is shielded from the influences of room temperature by being immersed in a liquid hydrogen-bath which in turn is contained in a dewar of nitrogen. Figure 1 shows a cross section view of the hydrogen chamber and its contents and the location of the magnetic field solenoid (j). The hydrogen can (e) is suspended from a circular brass plate bolted to the lid of the german silver nitrogen dewar. It consists of a supernickel tube two inches in diameter fitted with spun metal top and bottom. Supernickel tubes from above are hard soldered to the top. These tubes are: (a) a half-inch filling tube, which is also the pump line for reducing the pressure of hydrogen vapor, (b) a quarter-inch tube which goes through the top and extends to the calorimeter shield below, used for high vacuum pumping, (c) an eighth-inch tube extending to the manometer for

(12) Horn and Ziegler, THIS JOURNAL, **69**, 2762 (1947).

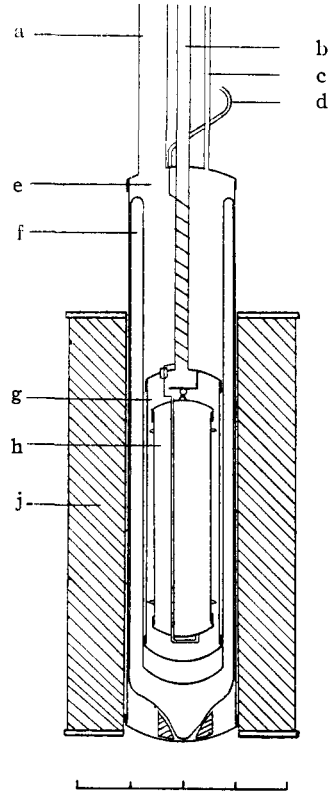

Fig. 1.—Hydrogen cryostat and solenoid.

hydrogen vapor pressure measurement, (d) a sixteenth-inch tube carrying six no. 40 copper wires for the calorimeter. The cover with its attached tubes is removable to permit access to the calorimeter.

Inside the hydrogen can is the glass hydrogen dewar (f). Its diameters are such that there is little clearance between it and the can outside or the calorimeter chamber inside. The dewar contains about sixty cubic centimeters of hydrogen above the calorimeter chamber and this is sufficient to permit operation for approximately four hours before refilling is required. The only advantage of the small volume is that it permits rapid passage through the triple point of hydrogen.

Suspended from the hydrogen can cover by the quarter-inch supernickel tube is the calorimeter chamber (g). This is of 1.25-inch supernickel tubing with spun covers. Access to the interior is obtained by unsoldering the upper cover, to which all attachments are made. To prevent radiation leakage from above striking the calorimeter inside, a baffle of copper is placed so as to cover the opening of the high vacuum line. This baffle provides a convenient point from which to suspend the calorimeter (h). Because the calorimeter chamber must be capable of evacuation to 10^{-6} mm. of mercury, all necessary precautions must be taken to ensure tightness when it is assembled. The electrical leads are brought in through glass buttons sealed in kovar and having a kovar center conductor. The tube carrying the wires ends at the top of the hydrogen can, and the wires are then wrapped on the high vacuum tube to provide additional length in the hydrogen-bath before passing into the calorimeter chamber.

The Calorimeter.—The calorimeter consists of a tube of supernickel of 0.020-inch wall thickness, one inch in diameter and four inches long, with top and bottom spun from sheet metal. The top is silver-soldered in place, but the bottom is soft soldered and is removable. The calorimeter is wound non-inductively with 300 feet of no. 38 gold wire lacquered carefully in place, which is used both as a resistance thermometer and as a heater. Two copper leads are soldered to each end of the resistance element. In order to get increased length in spite of the very small space available, the wires are led once around the long dimension of the calorimeter before going to the glass insulators. In circling the calorimeter the wires are contained in a very thin wall capillary tube of glass to prevent them from touching either calorimeter or shield. The glass is mounted on small drops of a cement made of water glass and talc. Additional tiny pyramids of this same cement are used as spacers to keep the calorimeter from touching the shield. As a result of the precautions described here, the heat leak into the calorimeter was found to be approximately 0.004 calorie per minute per degree difference in temperature. The completed calorimeter weighs 58 g. and has a volume of 50.5 cc.

The choice of supernickel for construction of the calorimeter was in part suggested by factors of convenience and compactness of assembly made possible by its use. It should be noted that although supernickel is not ferromagnetic, its composition is rather close to that for which ferromagnetism occurs among copper nickel alloys at low temperature, and so it should be used with caution where small magnetic effects are to be observed. This fact does not appear to have had any effect upon the present work, but should be borne in mind in considering other applications of the material.

Temperature Control and Measurement.—For control of the hydrogen-bath temperature a Cenco Megavac pump is used, the pumping speed being regulated by means of valves. Approximately constant hydrogen pressure is secured by the use of a regulator similar in design to one described by O'Gorman.[13] This does not provide absolutely constant pressure, nor does it have sufficient flexibility to permit control at all hydrogen pressures, so that other valves must be used with it. The pressure regulation is sufficiently good to permit heat capacity measurements for periods up to an hour without adjustment.

The vapor pressure of the hydrogen-bath was used as the temperature standard. The vapor pressure equation of Simon[14] was used for temperatures below the triple point and that of Henning and Otto[15] was used from the triple point to 21°K. The vapor pressure was calculated from these equations for every tenth of a degree and observed temperatures were calculated from observed pressures by linear interpolation between these values. For the purpose of calibration of the gold resistance thermometer the hydrogen vapor pressure is indicated by a large bore manometer from which a small tube runs directly to the hydrogen chamber. The absence of any pumped gases in this line ensures that there is no pressure gradient due to flow of hydrogen. A value of $g = 980.103$ cm. sec.$^{-2}$ for Baltimore was used and corrections were made for temperature changes in the glass and the brass scale in all measurements of pressure. The calibration data of the resistance thermometer was smoothed according to well-known procedures and the value of dR/dT was evaluated at intervals of one-tenth degree by numerical differentiation of the smoothed data. Values of T and dR/dT corresponding to observed values of resistance were obtained by linear interpolation between the tabulated values.

Measurements of thermometer resistance were made using the White potentiometer arrangement described by Ahlberg, Blanchard and Lundberg.[16] The thermometer resistance is 18.084 ohms at 20.40° and 15.667 ohms at 11.00°K. The value of dR/dT is 0.450 ohm deg.$^{-1}$ at 20.40° and diminishes nearly linearly to 0.0800 ohm deg.$^{-1}$ at 11.00°K. Although no special calibration of the resistance thermometer was made in magnetic field, sufficient evidence is contained in the original measurements to show

(13) O'Gorman, *Ind. Eng. Chem., Anal. Ed.*, **19**, 506 (1947).

(14) Simon, *Z. Physik*, **15**, 307 (1923).

(15) Henning and Otto, *ibid.*, **37**, 639 (1936).

(16) Ahlberg, Blanchard and Lundberg, *J. Chem. Phys.*, **5**, 539 (1937).

that any change produced by a field of 1000 gausses is not larger than the order of magnitude of 0.01°K.; so that there is little possibility that an appreciable error has resulted from this source.

Time Measurement.—In order to minimize the number of operations to be performed in each experimental heat capacity determination, so that one person could handle them all, and to increase the accuracy of time measurement, the heating intervals were mechanically controlled. The time standard was a General Radio precision 100 cycle per second tuning fork, the output of which was used to activate a two-decade electronic counter. The electronic counter operated a stepping relay at one-second intervals. The stepping relay was connected to the heating circuit in such a way that it would close the heating circuit on one count and open it an integral number of seconds later. The length of the heating period could be adjusted to multiples of 10 seconds, with an error not greater than 0.01 second.

Magnetic Field.—The magnetic field was generated by a solenoid in which size and weight were reduced to a minimum by designing it to fit in the annular space around the hydrogen can, within the nitrogen chamber. In order to give a reasonably uniform field over the length of the calorimeter the solenoid was made nearly twice the length of the calorimeter. Twenty thousand turns of no. 25 B. and S. gage enamelled wire were used. The resistance was 640 ohms at room temperature, but diminished to 80 ohms when cooled in nitrogen. A field of 1000 gausses could be achieved with a power dissipation of 50 watts which resulted in the boiling away of nitrogen at the rate of about a liter per hour. The strength of the field was measured with a search coil calibrated by the U. S. Bureau of Standards. Calibration of the field strength was made under conditions as nearly resembling the actual experimental conditions as possible. Because of the possibility of ferromagnetism at low temperatures in the copper–nickel alloys used in the construction of the cryostat, the field was measured with the search coil enclosed within two supernickel cans at 11°K. The calibration under these conditions was the same as in the absence of any supernickel containers, so it may be concluded that the materials used in the cryostat do not shield the contents of the calorimeter from the magnetic field. The uniformity of the field was such that at the ends of the calorimeter the field was 5% less than at the center. The values of magnetic field listed in the experimental work are those measured at the center of the calorimeter.

Heat Capacity Measurement.—A heat-capacity determination was made in the following way. The temperature of the calorimeter was recorded at one-minute intervals during a fore-period of about six minutes to determine its rate of drift. The heating period was then begun and amounted generally to one hundred and fifty seconds. After the heating current was shut off the temperature drift of the calorimeter was observed during an after-period of eight or ten minutes. The time elapsed between the last point of the fore-period and the first point of the after-period was three minutes. The resistances during the fore- and after-periods were extrapolated to the center of the heating period. The change in temperature caused by the heating was taken from the difference between the resistances at this point, and the heat input was computed using their mean value as the resistance of the heater.

For measurement of the heat capacity of the columbium nitride, the calorimeter was filled with 182.21 g. of material. In order to secure rapid thermal equilibrium throughout the sample, the interstices were filled with helium gas to a pressure of one atmosphere at room temperature. A small correction was added to the heat capacity of the calorimeter because of the heat capacity of this gas.

Experimental Results

The heat capacity of columbium nitride in the absence of magnetic fields was determined principally on two different days. Table I shows smoothed values for this data at intervals of 1°K. Measurements in magnetic fields were made with slight variations in procedure during different runs. The first series was made in the following way. The calorimeter was brought to the desired temperature and then the field was applied only during the course of the measurements. In this way one set of measurements was made in which the temperature was varied but the magnetic field was 500 gausses for each point. Another set of measurements was made in which for each of several magnetic fields the initial temperature of the calorimeter was the same or nearly so. A group of measurements of this type was made at a number of temperatures both below and above the superconducting transition temperature, including magnetic fields of 250, 750 and 1000 gausses. In some cases a point at 0 field and at 500 gausses was taken to provide a check on the consistency of data taken on different days. The purpose of taking measurements in this way was to provide information about the behavior of the heat capacity at constant temperature as a function of magnetic field strength. One particularly complete group of measurements of this type was made near 11° including ten values of the field between 0 and 1200 gausses.

TABLE I

HEAT CAPACITY OF COLUMBIUM NITRIDE IN THE ABSENCE OF MAGNETIC FIELDS

T, °K.	C_p (cal. deg.$^{-1}$ mole^{-1})	T, °K.	C_p (cal. deg.$^{-1}$ mole^{-1})
11.00	0.0390	16.00	0.0848
12.00	.0468	17.00	.0983
13.00	.0612	18.00	.1123
14.00	.0791	19.00	.1300
15.00	.0874	20.00	.1535

In order to satisfy certain questions concerning the interpretation of the data obtained in the presence of a magnetic field, an additional series of measurements was made on July 9 in a field of 1000 gausses, in which the field was applied before the calorimeter was cooled below the transition temperature. The field was not turned off during the whole series of measurements.

Discussion of the Results

The experimental data are plotted in Fig. 2. A smooth curve has been drawn through the points determined in the absence of magnetic fields. These points have a mean deviation of 0.7% from the curve. This curve shows an anomaly between 14.7 and 15.3°K., in which the heat capacity decreases as the temperature rises. This anomaly is in the region in which the transition to superconductivity of columbium nitride is commonly found. Although all previous work on the heat capacities of superconductors has shown a sharp discontinuity at the transition temperature, the present work indicates that the anomaly of columbium nitride is spread over a range of 0.6° and is a smoothly rounded hump. It has been observed

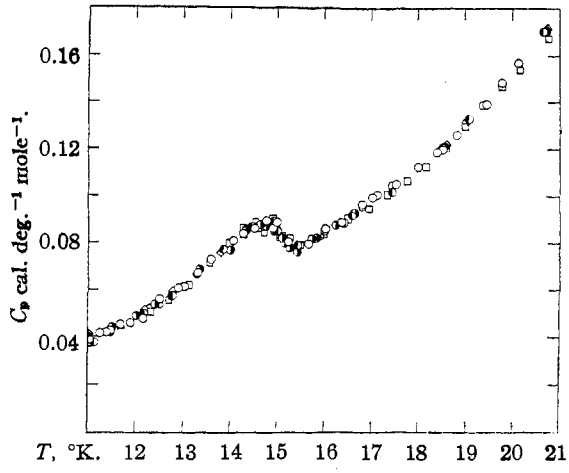

Fig. 2.—Field 0, ○; 250, ◐; 500, □; 750, ◇; 1000, ◑.

in this Laboratory that powdered samples of columbium nitride prepared in different batches show slightly different transition temperatures, and that for a single batch the transition studied by an induction method occupies several tenths of a degree. A reasonable explanation of the rounding of the anomaly and its width is a variation of transition temperature in various parts of the sample; the possibility that the width of the anomaly would be characteristic of even the most homogeneous sample may not be completely ignored.

If the curves above and below the anomaly are extrapolated to 15°K., their difference at this point is 0.023 cal. mole^{-1}. If this difference be interpreted in terms of the Rutgers formula

$$\Delta C = (VT/4\pi)(dH/dT)^2$$

a value of the slope (dH/dT), of the critical magnetic field needed for quenching superconductivity is found to be 257 gausses per degree.

No true measurements of the critical magnetic field have been reported for columbium nitride.[17] The only comparison which can be made is with some unpublished data of S. J. Socolar which merely indicates that fields less than 300 gausses per degree below the transition temperature were insufficient to produce resistance in a superconducting ribbon. The near agreement of these two figures appears to be quite accidental on the basis of the measurements of heat capacity in the presence of a magnetic field.

A graph of C_p/T *versus* T^2 for points below the transition temperature in the absence of fields gives a straight line passing through the origin, (Fig. 3), from which the Debye θ may be calculated to be 253° from the approximate equation

$$C_p/T = 464T^2/\theta^3$$

(17) It has just come to the writer's attention that Ascherman, Friedrich, Justi and Kramer [*Physik. Z.*, **42**, 349 (1941)], measured the magnetic threshold field slope for restoration of resistance of columbium nitride to be approximately 6500 gausses per degree, near the normal transition temperature. This value is not inconsistent with the calorimetrically observed changes in transition temperature herein reported.

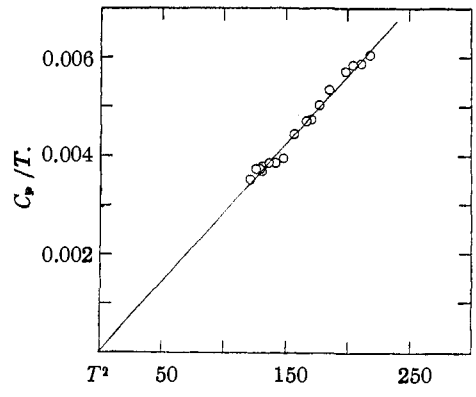

Fig. 3.

The striking fact about the measurements in magnetic fields is the close similarity of the data in every case. The changes in heat capacity either above or below the anomaly are so small that one cannot with certainty say they are greater than would be produced by experimental errors. A graph (Fig. 4) of the data in Table II for 11° shows a slight trend of the heat capacity upward with increasing magnetic field. The change in heat

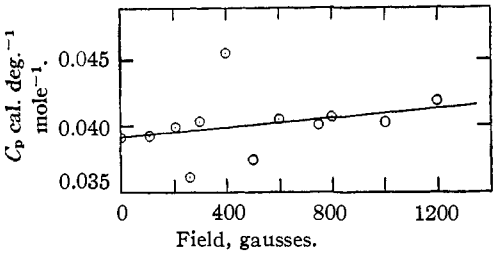

Fig. 4.

capacity between 0 and 1200 gausses is less than the fluctuations between separate points, so that only a qualitative statement of the direction of the change is justified.

TABLE II

HEAT CAPACITY AT 11°K.

H (gausses)	C_p (cal. deg.$^{-1}$ mole^{-1})	H (gausses)	C_p (cal. deg.$^{-1}$ mole^{-1})
0	0.0391	500	0.0374
100	.0392	600	.0405
200	.0399	750	.0400
250	.0361	800	.0406
300	.0403	1000	.0398
400	.0455	1200	.0418

The temperature of the anomaly is only slightly shifted, although according to the simple thermodynamic treatment of the transition in superconductors one would expect from the magnitude of the anomaly that the transition would be about 4° lower in a field of 1000 gausses. The observed change in the transition temperature appears not to exceed 0.20°, corresponding to a critical magnetic field slope of 5000 gausses per degree. This should be considered only as an order of magnitude in view of the fact that the experimental er-

ror in the points near the transition, as indicated by their spread, is not much smaller in magnitude than the change described.

No positive indication of any latent heat of transition in the magnetic field was found. An irregularity in the data in a field of 500 gausses might be attributed to this source, but since it does not appear again at higher fields, the possibility diminishes that it is evidence of a latent heat.

Investigations of tin[4] and thallium[5] bear out the validity of Rutgers' formula for predicting the discontinuity of specific heat of soft superconductors, for which the magnetic field which first penetrates the body of the material also restores the resistance. Studies of metals for which penetration begins at a much lower field than that required to restore resistance have also been made. Mendelssohn and Moore[9] observed that the heat capacity of an alloy of lead and thallium does not show such a large jump as that predicted on the basis of the field needed to restore resistance. Their measurements were not precise enough to indicate whether a smaller discontinuity existed. Shubnikov and Chotkevitch[8] made a similar observation on an alloy of lead and bismuth. Keesom and Desirant[6] observed that the change in heat capacity of tantalum at its transition temperature corresponds to a much lower critical field slope than is indicated by the depression of the temperature of the calorimetrically observed transition in a magnetic field. They found that the calculated dH/dT corresponds nearly to the threshold field which first penetrates the specimen, while the temperature of the anomaly is more nearly that at which resistance is restored by a given magnetic field.

The powdered columbium nitride used in these measurements has a behavior similar to tantalum in that the lowering of the transition temperature in magnetic field cannot be predicted from the magnitude of the anomaly. Unfortunately, the strength of magnetic field necessary to penetrate CbN has not been measured as a function of temperature, so that it is not possible to compare the slope of this function with that calculated from the calorimetric data by Rutgers' equation.

Because of the resemblance of the thermal properties of CbN to those of alloys and of tantalum, the possibility was considered that some hysteresis phenomenon might cause a difference in the heat capacity observed when the sample is cooled through the transition in the presence of a magnetic field from that observed when the field is applied only below the transition temperature. The data of July 9 were taken with this in mind. No difference is observable in the heat capacity measurements using the different procedure.

In view of the lack of data on the penetration of columbium nitride and the restoration of its resistance by magnetic fields, it is not possible to say whether this compound may behave in other ways like a hard superconductor or an alloy. In any attempt to account for its observed behavior it is reasonable to question whether this behavior is due to the lack of stoichiometric proportions in the sample of the compound used here, or to the small size and irregular shape of the particles, or whether the observed behavior is characteristic of the pure compound in bulk.

Summary

The heat capacity of columbium nitride has been determined in the temperature range from 11 to 21°K. An anomaly of 0.023 cal. mole^{-1} occurs at 15°K., and may be associated with the transition to superconductivity. The effect of magnetic fields of 250, 500, 750 and 1000 gausses is very small both on the magnitude of the heat capacity and the change in temperature of the anomaly. No latent heat of transition was observed.

NEW HAVEN, CONN. RECEIVED MARCH 8, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

Kinetics of the Decomposition of Ethyl Xanthic Acid

BY ALFRED CHATENEVER AND CECIL V. KING

The rate of decomposition of various xanthic acids was first studied in detail by V. Halban and Kirsch,[1] who tried to correlate the rates with dielectric constant and other properties of the solvents used. Later V. Halban and Hecht[2] studied the decomposition rates of potassium methyl and ethyl xanthates in aqueous hydrochloric acid at 0°. They found that these xanthic acids are not fully ionized, and assumed the reaction to be a unimolecular decomposition of the undissociated acid, though recognizing this to be kinetically identical with a bimolecular reaction between hydrogen and xanthate ions.

The decomposition of ethyl xanthic acid in dilute aqueous buffers has been studied by King and Dublon.[3] It was shown that there is little or no salt effect on the rate in acetic acid–sodium acetate buffers of low ionic strength, since primary and secondary effects cancel; in aniline–anilinium ion buffers, on the other hand, there is a large primary salt effect.

The rate of decomposition of various xanthic acids in non-aqueous solvents has been studied in

(1) V. Halban and Kirsch, *Z. physik. Chem.*, **82**, 325 (1913).

(2) V. Halban and Hecht, *Z. Elektrochem.*, **24**, 65 (1918).

(3) King and Dublon, THIS JOURNAL, **54**, 2177 (1932).