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## ABSTRACT

A method is described that can be used for the determination of the heat capacity of a metal (or a semiconductor) as a function of pressure and temperature. The method involves use of a DC electric pulse. If a constant current I is passed through a wire sample of resistance R, the heat capacity $C_p$ is related to the increase in temperature by the expression:

$$C_p = I^3 RR'/(dE/dt)_{t=0}$$

where R' is the temperature derivative of the resistance, and $(dE/dt)_{t=0}$ is the limiting value of the time rate of change of the EMF across the sample. Data are given for iron to 100 kbars in the temperature interval from 77°F to 300°K. The results obtained are in accord with earlier theoretical estimates. The Curie temperature, $T_c$, of gadolinium has also been determined from heat capacity measurements; its rate of change with pressure was found to be $dT_c/dP = -1.3$°K/kb. For the equipment that is available at the present time, the measurements can be made as long as the specific resistance is 5μΩ-cm or greater.

# INTRODUCTION

The heat capacity of a substance is an important thermodynamic parameter characterizing the internal energy state of that substance. It is therefore of great interest to examine the variation of the heat capacity with temperature and pressure. Numerous investigations involving temperature as the independent variable have been carried out, leading to a generally good understanding of the temperature variation of the heat capacity; however, very little work has been done at high pressures since conventional calorimetric techniques face the difficulty of gross heat leakage when used in high pressure apparatus. Some success has been obtained in those cases where pressures were low enough that flow techniques could be used,[1] or in those cases where temperatures were sufficiently low so the heat capacity of the pressure vessel was a determinable, and reasonably small, fraction of the entire system.[2,3].

In this paper we describe the development of a general method of measuring the heat capacities of metals (and semiconductors) under high pressures. The technique is based on electrical pulse heating of the metal sample, and has been successfully applied in measurements up to 100 kilobars over a temperature interval between 77°K and 300°K. The precision appears to be $\pm$ 5% or better.

As the discussion and description of the technique is developed in this paper, it will be evident that the heat capacities obtained are relative rather than absolute, due to the fact that the geometry of the system is such that only relatively short wire samples can be used. There is a large uncertainty of how much of the sample at the ends is actually involved in the measurement. In the discussion that follows, it is assumed that the end effects remain constant as the external conditions are changed.

## THEORY

Consider a metal wire sample of resistance, R, and heat capacity, $C_p$, through which a constant current, I, is pulsed; if ohmic heating is the only source of heat, the power balance equation is:

$$dH/dt = I^2R - f(T - T_a). \quad (1)$$

Here dH/dt is the rate of increase of the enthalpy with time, t, at constant pressure; $f(T-T_a)$ is a cooling term which is assumed to be dependent only on the difference between the sample temperature, T, and the temperature of the surroundings, $T_a$. Since $C_p = (\partial H/\partial T)_p$, and $dI/dt = 0$, and assuming that at constant pressure the resistance R is a function of temperature only by multiplying both sides of the

equation by $dE/dt = I(dR/dt)$, we may arrange Eq. (1) to give

$$dE/dt = (I^3RR'/C_p) - (IR'/C_p) \cdot f(T - T_a) \qquad (2)$$

where $R' = dR/dT$ and $E = IR$, the EMF developed across the sample. In the limit of $t \to 0$, $T - T_a \to 0$, and the limiting result is

$$C_p = I^3RR'/(dE/dt)_{t=0} \qquad (3)$$

Experimentally, dE/dt is found to be linear for 10-1000 microseconds. Consequently, it is not difficult to obtain experimentally the limiting value of dE/dt. An analysis of heat loss from an infinitely long wire through which a constant current is passing, also shows that the value of dE/dt is nearly linear for a short period of time.[4] Though the boundary conditions for the classic problem are not the same as those used in the present experiment, it is felt that the results should not be too greatly different. The experimentally measured quantities are the current I, the electrical resistance R, the temperature derivative of the resistance R', and the slope of the E-t curve extrapolated to the beginning of the pulse. The measured magnitudes of these quantities were typically: $I \sim 2A$, $R \sim 10^{-1}\Omega$, $R' \sim 10^{-3}\Omega$, $deg^{-1}$, and $(dE/dt)_{t=0} \sim 4$ volt/sec, so that the measured heat capacities were of the order $20\times10^{-5}$ joule/deg sample. Note that an experimentally small value of $(dE/dt)_{t=0}$ could lead to a large inaccuracy in $C_p$; the method works best with large dE/dt.

## DESCRIPTION OF THE APPARATUS

The pressure apparatus used was an opposed anvil device similar to that used by Bridgman,[5] and has been fully described elsewhere.[6] The sample setup using a metal wire hoop-shaped sample is a modification of the four probe constructions of Stromberg and Jura[6] and is illustrated in Fig. 1. A set of 0.005" dia. platinum leads replaces the gold plug current leads used by Stromberg and Jura. Pressure calibration of the system was effected using the room temperature bismuth I-II and VI-VIII phase transitions[8] in the identical geometry to that in Fig. 1.

Temperature control was achieved by the use of stirred liquid baths surrounding the entire anvil-sample system. For most of the experiments reported here a Kanolt mixture[9] which set the lower limit of the temperature range at about 150°K was used. Some excursions to 77°K were made using massive heat sinks of the type described by Souers.[9] Copper-constantan thermocouples (calibrated at liquid nitrogen, dry ice, and ice point temperatures) were fastened to the anvil jackets about 1" from the axis of the anvils, and the temperature of the sample was assumed to be the average of the top and bottom anvil temperatures.

Figure 2 shows a block diagram of the electronics used in this work. There are two analogous circuits in the system, one circuit allowing measurement of a low, static EMF across the sample, while the other circuit was used to make the dynamic measurement. When the sample

is connected to the voltage and current leads at A and A', a constant current of approximately 10 ma flows through the sample. The potential across the sample is measured using one bank of a L & N White Double Potentiometer having a sensitivity of $\pm 0.2$ microvolt; the other bank of the potentiometer was connected for measurement of the voltage across the standard one ohm resistor $R_{s1}$. This latter measurement gave the magnitude of the current flowing in the circuit; the sample resistance R could be calculated directly from the four lead measurements of the current I and voltage E. The constant current source was a 12 volt auto storage battery in series with a nominal 1200 ohm power resistor. By maintaining the battery at approximately two-thirds full charge, currents constant to $\sim .02\%$ could be maintained for periods of a few minutes while measurements were taken. Reversing the direction of current flow enabled correction for thermal EMF's, if any. The resistance measurement was the most precise of the quantities measured in this work, having an uncertainty of $\pm .5\%$ for nominal R values of 0.1 ohm.

The sample is connected to the current and potential leads at B and B' when dynamic measurements are made. In this circuit the oscilloscope replaces the potentiometer of the resistance measuring circuit, and the current source is a bank of four 12 volt auto storage batteries connected in series with a ballast resistance variable from 5 to 350 ohms. The ballast resistance is much larger than the sample resistance and so controls the current drawn from the batteries; thus, resistance changes in the sample are negligible in comparison with the total resistance. Calculations based on the voltage rise of an actual sample show that for

the typical sample the current after the initial rise is constant to a few tenths of a percent during a 100 millisecond pulse.

The solid state switching and gating unit for generating a square current pulse is basically two switches, one which completes the current path through a dummy load of approximately the same resistance as the sample, and one which completes the circuit through the sample load. The purpose of the dummy load is to dissipate the odd transient currents which appeared when the storage batteries first begins to deliver current. The switching circuit has provisions for externally varying the pulse width through the sample and the overlap of the sample and dummy load pulses.[10]

A Tektronix 555 dual beam oscilloscope was used to display both the voltage E across the sample, and the current I through the sample. The latter was displayed as the voltage across the standard resistor $R_{s2}$ in series with the current source. As can be seen from Eq. (3) only the slope of the E-t is necessary to determine $C_p$, and it is advantageous to use a differential technique to examine only the top portion of the pulse at maximum sensitivity. Toward this end a Tektronix Type W differential comparator with a maximum sensitivity of 1 mv/cm was used for measuring the voltage across the sample; a Tektronix Type 1A7 preamplifier was used to measure the higher level voltages across $R_{s2}$.

The data were taken directly from photographs of the oscilloscope display; a typical record is shown in Fig. 3. The first 10-20 microseconds of the upper trace represent the rise of the current in the

sample; rough approximations indicate that heating of the sample during this buildup is negligible. The measured slope was taken from the later, linear portion of the E-t trace, after the current had reached its constant value.

Many efforts were made to reduce the rise time of the current in the sample. However, this time could not be reduced below 10 to 20 microseconds. For a given sample, the variation of the sweep rate yielded the same initial slope of dE/dt. Obviously, if slow sweep rates were used, the E vs. t display could yield a curved line, and at sufficiently slow sweep rates appeared to approach a steady state value of E. These very slow sweep rates could not be used for the determination of the slope at t = 0.

Approximately two-thirds of the displays were recorded on 35 mm film, the remainder on Polaroid. The data on 35 mm film were analyzed with the aid of the TRAMP II, a digitized protractor. The angular coordinates were converted to Cartesian coordinates by an IBM 7094 computer. The computer then performed an analysis whereby the measured $(dE/dt)_{t=0}$ data were fitted linearly to the respective $I^3$ values. Points of poor fit (points differing from the fitted line by more than 2.7 standard deviations) were discarded and a new line fitted with the remaining points. The sequence was continued until suitable convergence was obtained. However, as shown in Fig. 4, scatter was typically small, and usually in a series of 25 measurements one or two points at the most were discarded. Computer output was double checked by visual inspection to assure that no unreasonable fits were made by the computer.

Data recorded on Polaroid film were measured by hand with the aid of a Gerber Variable Scale; the slope of the dE/dt versus $I^3$ graph was computed graphically.

The vertical amplifiers of the oscilloscope were checked for calibration every few hours during a run, and the time scales were calibrated to $\pm 1/2\%$ several times during the course of this work. The main source of random experimental error was presumed to be due to the measuring of the data from the photographic records. Uncertainties of approximately 1% each in the dE/dt and I measurements are assumed, although the smaller slopes are prone to larger errors.

Most of the experiments were isobaric runs in which the procedure was to apply pressure at room temperature, then cool while maintaining constant loading.* Data points were taken approximately every 5°K as the sample slowly warmed: the temperatures of the top and bottom anvils were measured, then the sample resistance was measured, first with the current flowing in one direction, then the other. The system was switched to the dynamic measuring circuit and a series of 3-5 pictures

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*Electrical resistance measurements on iron samples indicate that cooling the AgCl pressure transmitting medium did not greatly alter the pressure calibration as derived from room temperature measurements of the Bi I-II and VI-VIII phase transitions. The resistance obtained by room temperature compression to pressure P followed by isobaric cooling to temperature T was within experimental error of the resistance value obtained by isothermal compression at temperature T to pressure P.

was taken at each of several values of the current. The temperature was noted again, then the procedure was repeated after the sample had warmed a suitable amount. On an average, about twenty pictures were taken at each temperature interval; the temperature rise during a photography sequence was typically 1/2°K or less.

The temperature derivative of the electrical resistance was computed graphically from the R-T data collected during the isobaric runs. The isobars were related to one another using isothermal runs made at 298°K and 195°K.

## RESULTS

The apparatus was first tested for gross sensitivity by examining the Curie transition of gadolinium as a function of pressure. At atmospheric pressure this transition occurs at about 292°K; the heat capacity exhibits a lambda type anomaly with $\Delta C_p \sim 7$ cal/mole-deg.[11] This large anomaly was easily detected by the apparatus, as illustrated in Fig. 5, which shows the heat capacity variation with temperature at 20 kb. Several isobars yielded the plot of the Curie temperature $T_c$ versus pressure that is shown in Fig. 6. The zero pressure point is from Griffel, Skochdopole, and Spedding,[11] and the lower 20 kb point is weighted more heavily on the basis of two additional runs which did not cover the entire transition, but did indicate that $T_c$ at 20 kb is less than 270°K. The slope, $dT_c/dP$, of the fitted straight line is found to be

-1.3°K/kb, in reasonable agreement with literature values of -1.2,[12] -1.53,[13] -1.6,[14] -1.73,[15] and -1.9°K/kb.[16]

Because of its relatively large values of the resistivity and its temperature derivative, and its high Debye characteristic temperature, iron proved to be a convenient metal to study with the hope of obtaining equation of state data by means of the thermodynamic identity:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad (4)$$

The low compressibility of iron was a definite detriment for the application of Eq. (4). Fifteen isobars spanning a temperature interval 150°K to 300°K were run at pressures between 20 and 100 kb, and a similar number from 77°K to 300°K at pressures to 50 Kbars. As it was difficult to maintain a given sample for more than one run, these isobars were related to one another with isothermal runs at 195°K and 298°K. Also, since in the opposed anvil setup electrical contacts at zero applied load are rather poor and one may not perform the experiment with confidence, the 20 kb results were related to atomospheric data using a Debye-Gruneisen approximation and experimental thermal expansion data. Connected in this manner, our high pressure data showed very little variation in going from 20 to 100 kb. The spread of ∿1-2% is less than the experimental uncertainty of about 5%, and it must be concluded that in the measured pressure range, 20 - 100 kb, the heat capacity of iron is constant. Within experimental error, this is in agreement with Russian work,[17] which reports a calculated 0.8% decrease

in $C_v$ for iron at about 30 kb. The average data are shown in Fig. 7 as the shaded area, along with the zero pressure data of Kelley,[18] and a 25 kb curve calculated from Eq. (4) assuming $\left(\frac{\partial C_p}{\partial P}\right)_T$ to be constant and using the thermal expansion data of Nix and McNair.[19] Relative heat capacity curves for 25 and 100 kb as calculated in a Debye-Gruneisen approximation assuming constant electronic and magnetic contributions to the heat capacity are also shown. It can be seen that the experimental values are not out of line with these various approximations.

## CONCLUSIONS

Experimentally we have demonstrated a technique for measuring heat capacities (at constant pressure) of metals in a high pressure environment; theoretically the method should be adequate for semiconductors also, provided the energy gap is not so small that $dR/dT \sim 0$. The calculated experimental uncertainty is in the neighborhood of $\pm$ 5%; hence the technique at present is more suited to investigation of some of the high pressure phase transitions than to equation-of-state studies where the lattice and electronic heat capacity changes are of the order of the experimental uncertainty. An example is shown in Fig. 8, which demonstrates evidence of the 130 kb iron transition.

It is felt that future developments in preamplifiers will eventually enable use of samples of much lower resistivity. These metals

are commonly those of higher compression ($\Delta V/V_0$) and should allow equation of state studies. During the course of this work some experiments were performed on aluminum, but the results were erratic and anomalous, giving a rise in $C_p$ with increasing pressure. These results are presumed due in part to the extremely small sample which was necessary in order to obtain a usable electrical resistance; the Al samples had calculated heat capacities more than an order of magnitude smaller than the iron samples. The method is presently limited by the electrical resistivity and its temperature derivative; as discussed earlier, the derivative will always set resolution limits.

It should be noted that an extension of the temperature range to lower temperatures should increase the capabilities of the technique. For instance, it might be possible to fit a Debye-like characteristic temperature to the experimental data, and in conjunction with compressibility data obtain a Gruneisen $\gamma$ parameter as a function of pressure.

Finally mention is made here of an interesting observation made during the course of the iron experiments: at pressures of about 20 kb and above, the electrical resistance of iron was observed to have a three-halves power dependence on the absolute temperature. An explanation based on enhanced magnon-electron interaction is possible,[20] but more theoretical and experimental investigation is necessary to unravel the problem.

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FOOTNOTES

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## FIGURE CAPTIONS

Figure 1 Schematic diagram of sample setup. .00025" mylar film was placed between the wire sample and the AgCl pressure transmitting medium to prevent chemical reaction between the two.

Figure 2 Block diagram of electronics. Not indicated in this diagram are provisions for keeping the constant current source under load while making the dynamic measurements, and for reversing the direction of current flow.

Figure 3 A typical data trace. The upper trace is the sample voltage at 1 mv/div, the lower two traces give the current at 1 amp/div; the time scale for both sets of traces is 10 microseconds/div.

Figure 4 Typical dE/dt versus $I^3$ plot for iron. The non-zero intercept is as yet unexplained.

Figure 5 Heat capacity of Gd through the Curie transition.

Figure 6 Curie temperature of Gd as a function of pressure. The slope, $\frac{dTc}{dP}$, of the line is -1.3°K/kb.

Figure 7 Experimental results and theoretical estimates.

Shaded area — 20-100 kb, this work

---------- — zero pressure, Kelley[18]

_____ _____ — 25 kb, using thermal expansion data of Nix and McNair[19]

## FIGURE CAPTIONS

Figure 7 Experimental results and theoretical estimates

0 25 kb, Gruneisen approximation, $\gamma = 2$

$\Delta$ 100 kb, Gruneisen approximation, $\gamma = 2$

Figure 8 295°K slope isotherm for iron. As can be seen from Eq. (3), the quantity $\frac{dE/dt}{I^3}$ is inversely proportional to $C_p$.
A transition is indicated at about 125 kb.

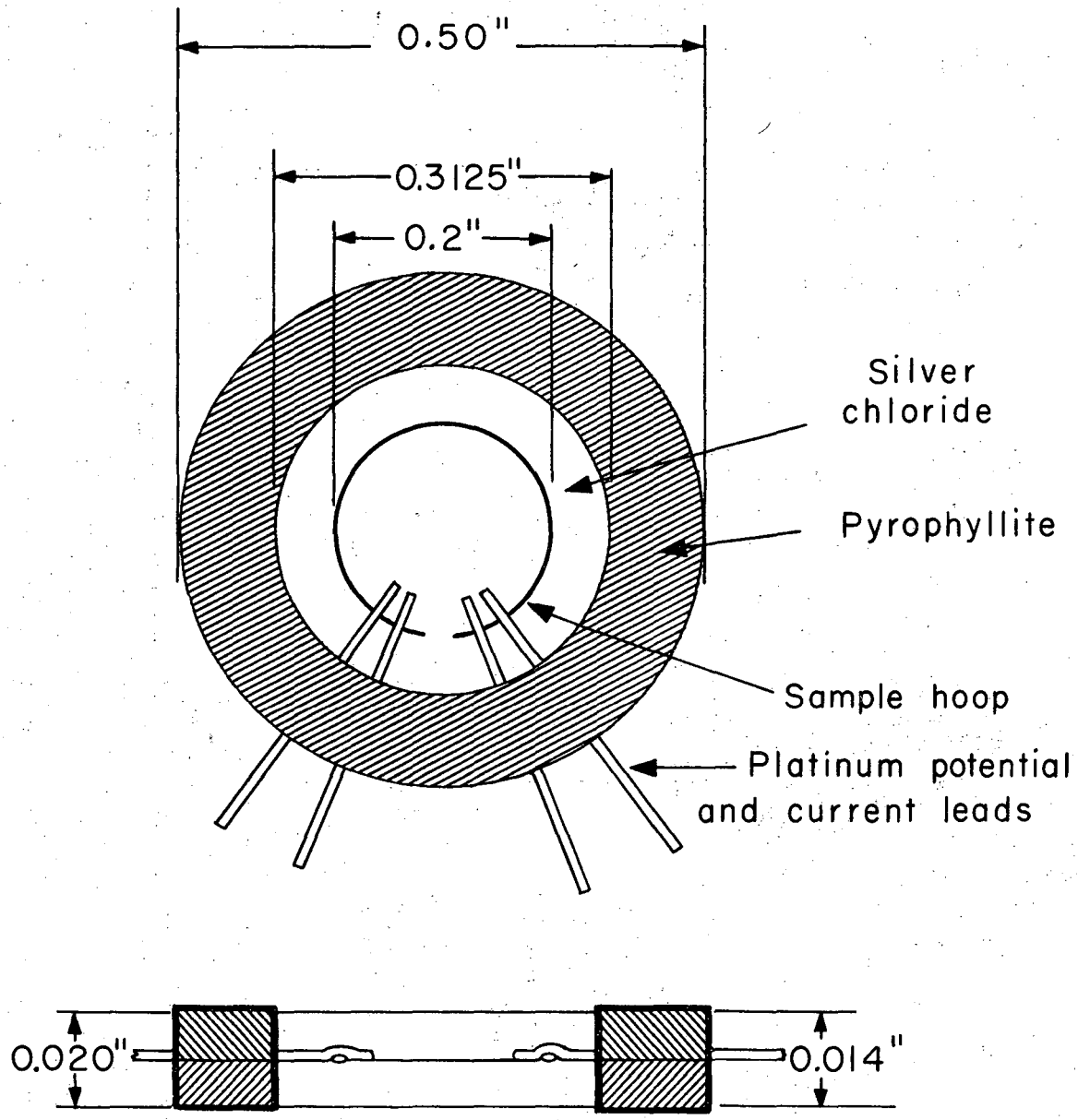
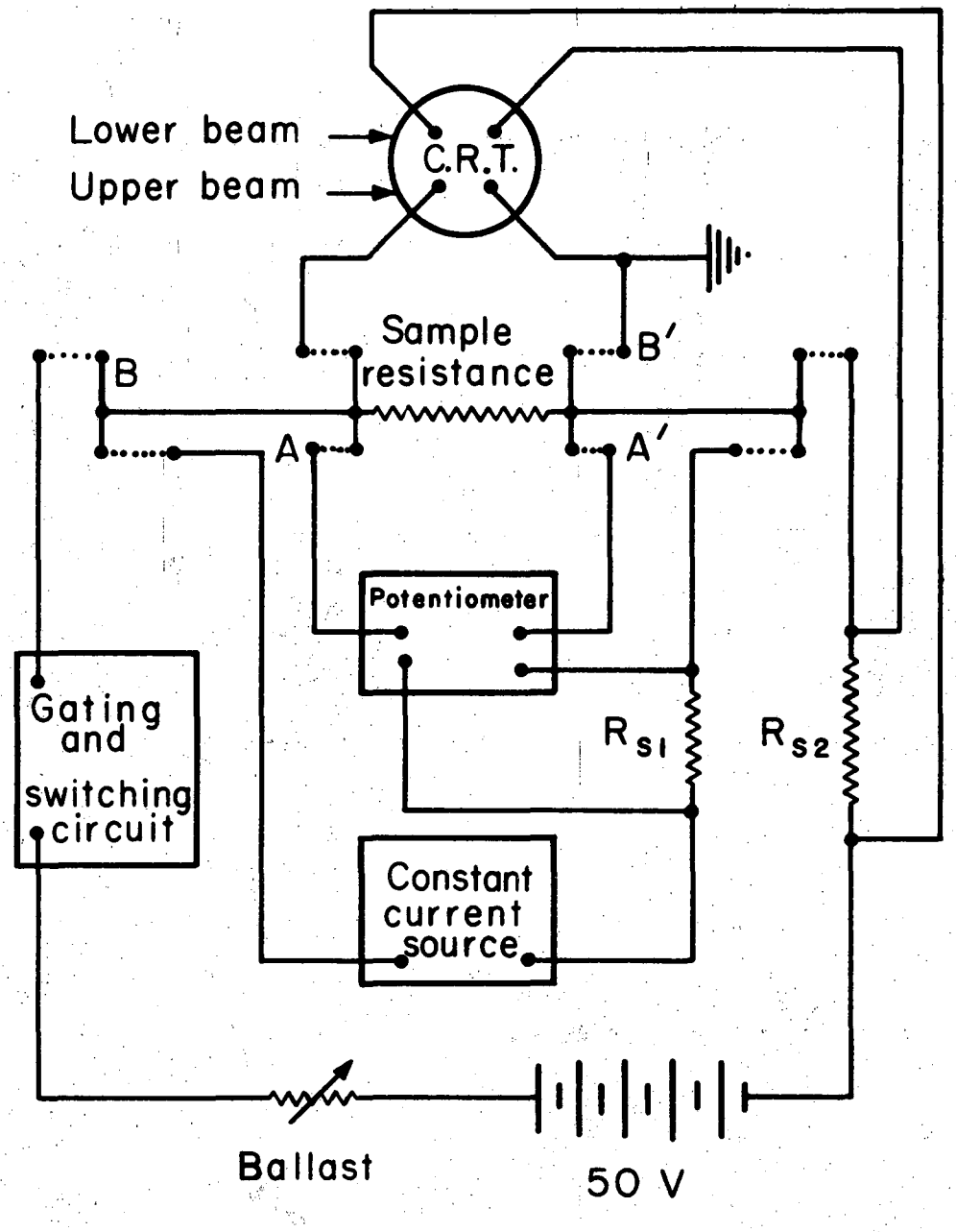
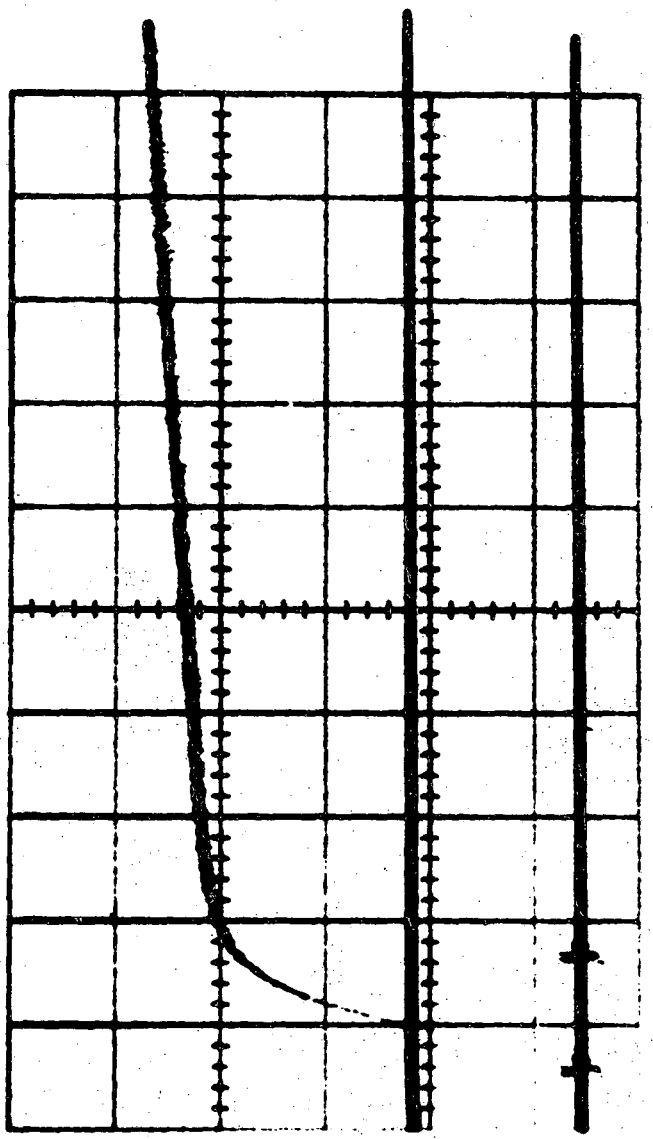

0.50"
0.3125"
0.2"
Silver chloride
Pyrophyllite
Sample hoop
Platinum potential and current leads
0.020"
0.014"
XBL672-944

Fig. 1




XBL672-941

Fig. 2



XBL 673-1273

Fig. 3

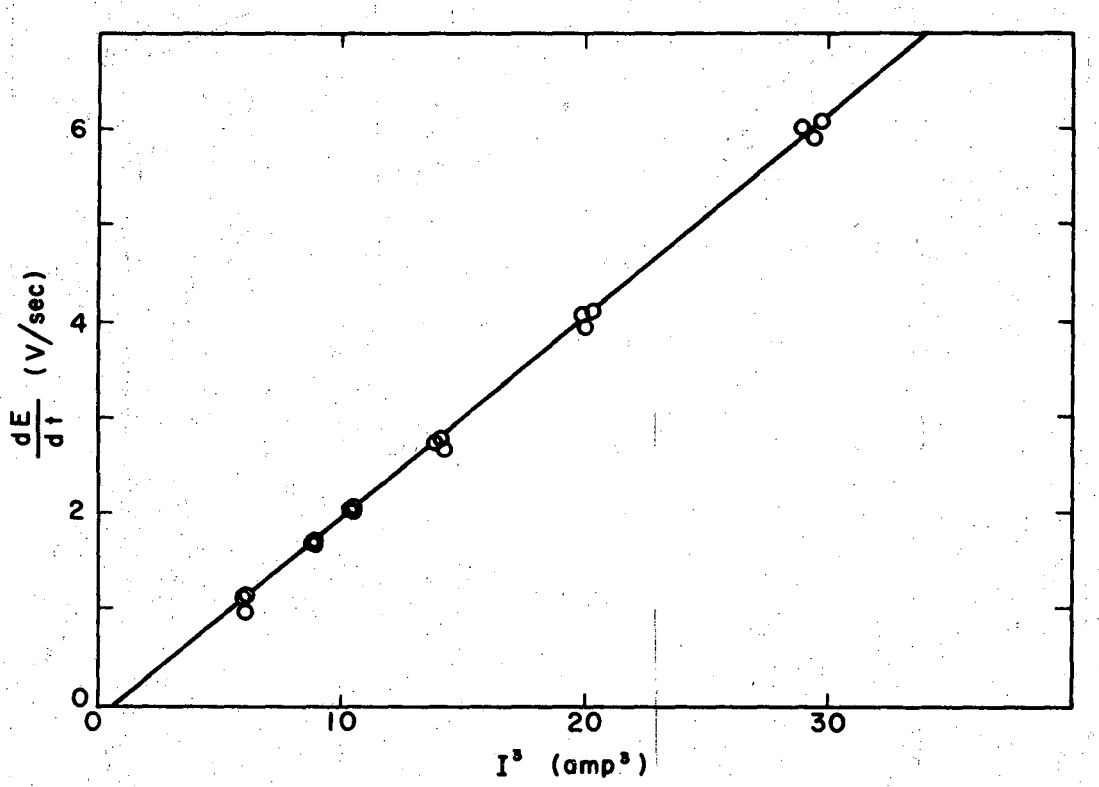



Fig. 4

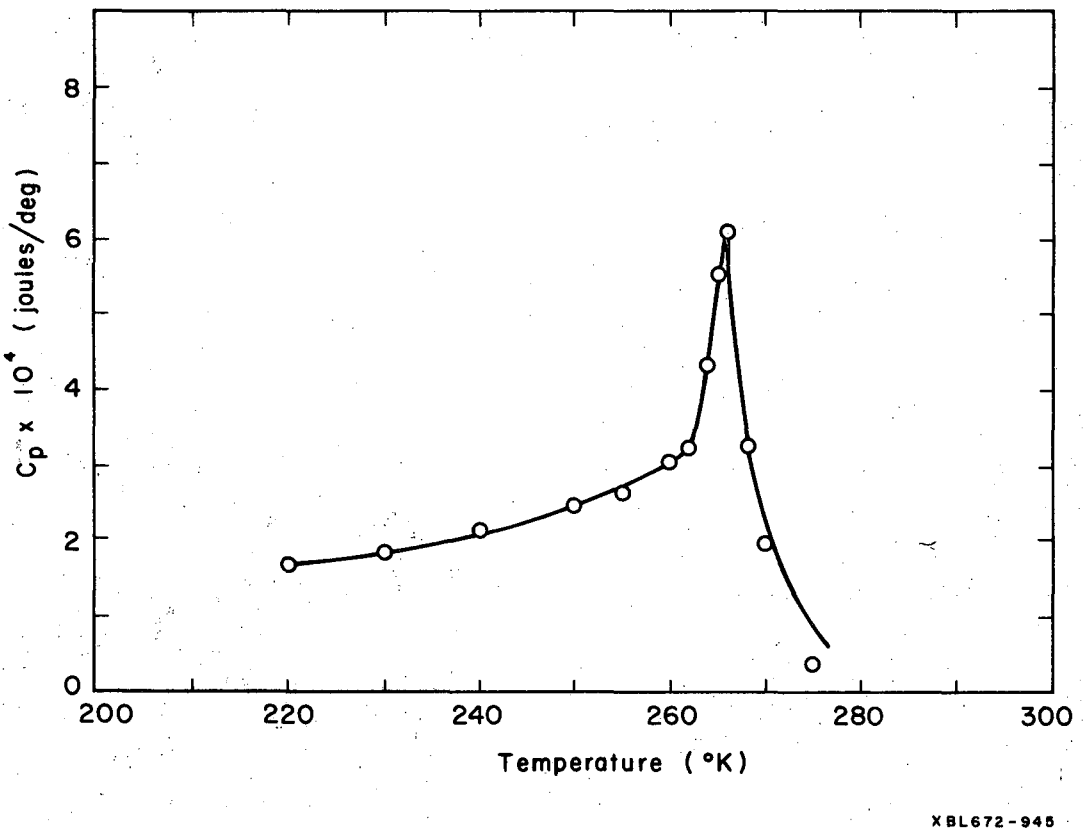
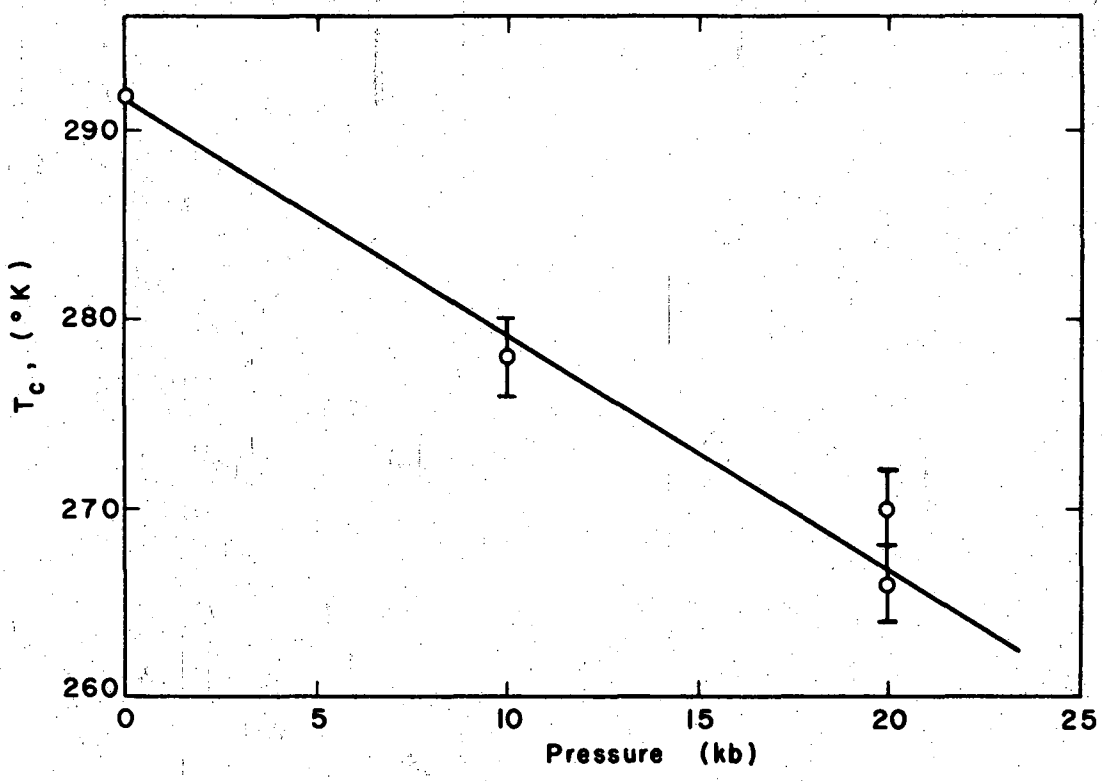

$C_p \times 10^4$ (joules/deg)
0
2
4
6
8
200
220
240
260
280
300
Temperature (°K)
XBL672-945

Fig. 5




XBL672-946

Fig. 6

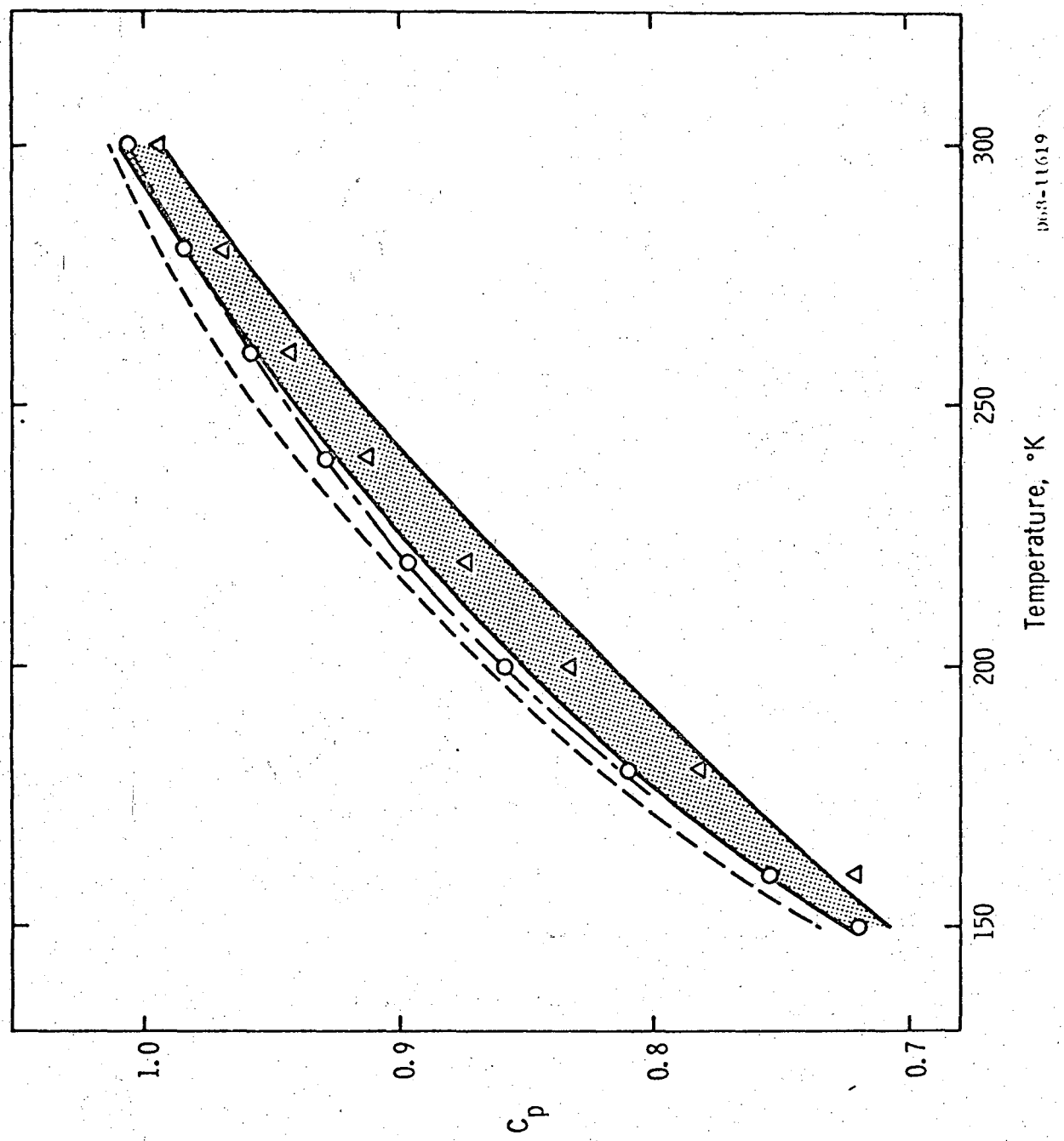



Fig. 7

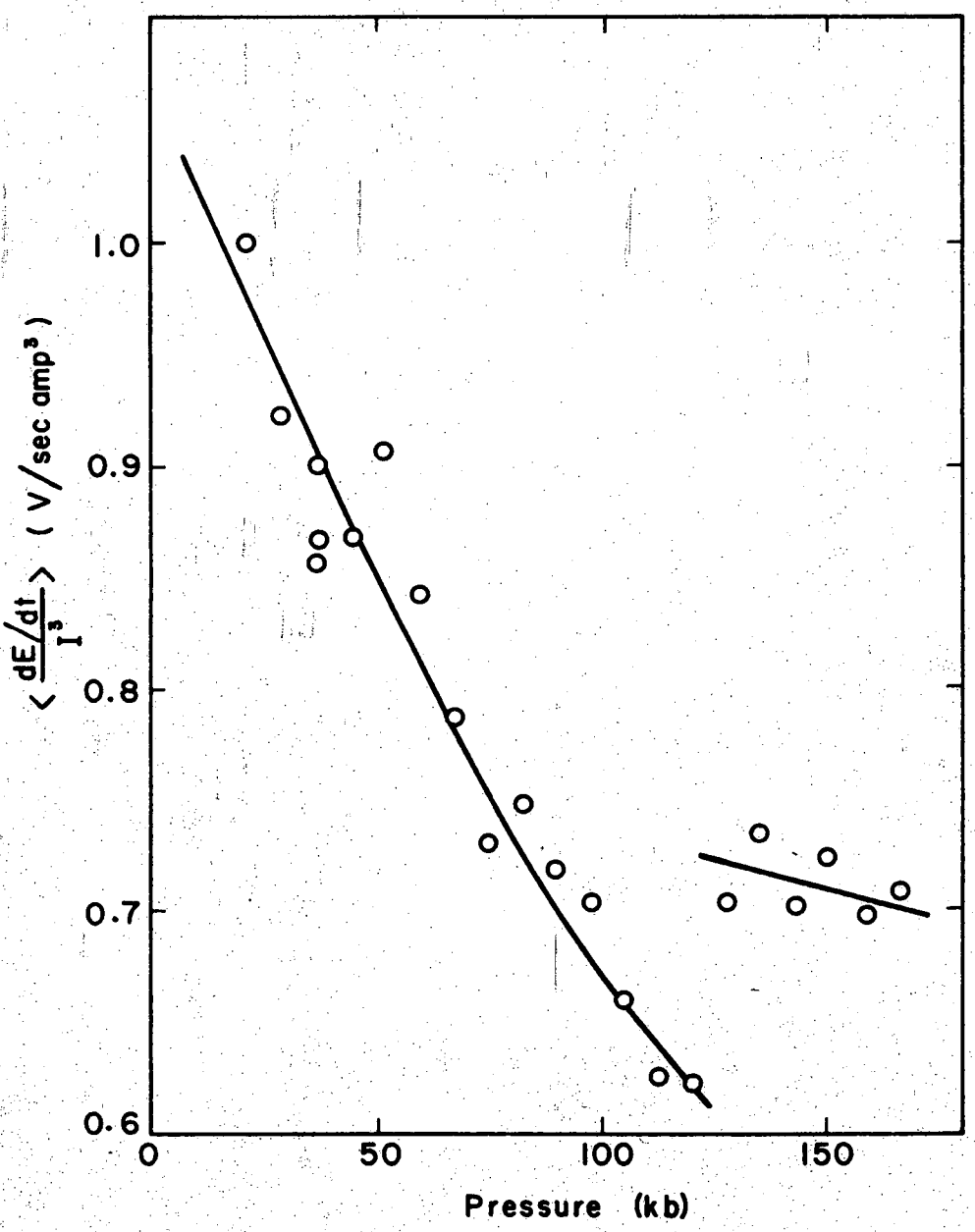



Fig. 8

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