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LOW-TEMPERATURE PHASE TRANSITION MEASUREMENT FACILITY FOR FERRO- AND FERRIMAGNETIC MATERIALS

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INTRODUCTION

The measurement facility which will be described was designed primarily to implement a study of the order-disorder transition for magnetite at - 155°C. The study was concerned with examining the influence of lithium doping and oxidation on the magnetic moment and the transition temperature. The measurement of the magnetic moment of the powdered samples at low temperatures was of such duration that a preliminary screening experiment was adopted to eliminate inactive samples. This paper will describe the method and apparatus for obtaining the magnetic moment and also the screening experiment.

MAGNET MOMENT MEASUREMENT

The materials which were studied were all polycrystalline in nature and powdered in form. The magnetic moment of the powdered samples is obtained by measuring the force on the small (5 to 10 milligrams) powdered sample in a controlled gradient magnetic field [1] as the temperature of the sample is slowly changed and monitored. The force so measured is linearly proportional to the magnetic moment of the sample. [2]

The initial design objectives were to design a cryostat for the attainment, control, and measurement of temperatures needed to encounter

the expected transition and to design a force measuring system which would yield the magnetic moment information. The final design, shown in Fig. 1, was influenced in no small measure by the cryostats designed by Westrum,[3] Smith,[4] and Duerig.[5] The maximum working space or active region in the field was limited by the magnetic field capability of the 4-in. Varian electromagnet. A direct circumferential heat exchanger was out of the question because of this size limitation. The cryostat is shown in position in Fig. 2. The transfer of heat is accomplished almost entirely by conduction along the hard-drawn copper tubes extending from the bottoms of the helium and nitrogen containers to the sample region. The presence of the innermost container or the helium container resulted from the initial intent to follow the transition to as low a temperature as it existed. This container is removable and was used in an earlier phase of the program but not in the phase reported here. Thermal bridges (brass shims) are inserted between the sample tube and the radiation shield extending from the bottom of the nitrogen container when the helium container is absent. This decreases the time needed for a run to liquid nitrogen temperatures by a factor of two. The helium container is encircled by a double-walled nitrogen tank, which acts as a liquid nitrogen temperature, radiation shield. The helium tank rests on the base plate of the nitrogen tank but direct thermal contact is avoided by using a lamicoid spacer between the two tanks. The nitrogen tank is in turn encircled by a floating radiation shield which supports the tank by means of three equally spaced nylon cords. The floating shield in turn is suspended from the

vacuum lid of the cryostat by three lamicoid "bolts".

The helium tank, nitrogen tank, and outer shell of the cryostat were fabricated from hard-drawn brass tubing and polished to a high sheen wherever possible. The tubes extending upwards from the various tanks to terminations at room temperature are nonmagnetic stainless steel to cut down the heat transfer by conduction. The space surrounding the two tanks and the floating radiation shield is evacuated through the side port and also indirectly through the bell jar using a two-stage oil diffusion pump. Fig. 3 shows the major portion of the system.

The utilization of the cold reservoirs of liquid nitrogen in cooling the sample is accomplished almost entirely through conductive heat transfer through the temperature control plug. If the helium tank is utilized, moving the sample tube upwards in the system brings the temperature control plug into conductive contact with the reservoir of liquid gas. If the helium tank is not utilized, insertion of the thermal bridges around the sample tube accomplishes the same end. The temperature control plug houses a platinum resistance thermometer and also a bifilarly wound heater. The holder containing the sample under test is made of brass also and rests in the off-null position for the balance on the top of the temperature control plug with good thermal contact between it and the region being monitored by the thermometer. Now that we have the sample in a controlled thermal environment, let us turn to the measurement of the magnetization.

The second part of the design program resulted in an electrically controlled force-measuring system or beam balance, shown in Fig. 4.

The brass sample holder is connected to the beam balance by means of the nonmagnetic jeweler's chain shown in the extreme left in the figure. The beam is supported at the fulcrum by a shaft terminated in nonmagnetic micro-bearings. The counter-force needed to bring the balance back into a null position is supplied by the force acting on a current carrying coil of wire in the field of a permanent magnet shown to the right of the fulcrum. A metal slug extends out from the permanent magnet and is partially encompassed by the coil. In the section devoted to the calibration of this balance, it will be noted that a linear force versus counter-force current relationship results from this system. Two strips of foil are bonded to the coil to give eddy current damping to the system. At the extreme right end of the beam is shown the Schaevitz LVDT (linear-variable-differential transformer) used to detect off-null positions of the balance.

The working console for the entire system is shown in Fig. 5. On the right side of the console is the temperature monitoring and control equipment. The Mueller bridge in the foreground is used to measure the resistance of the platinum thermometer. Behind the bridge are two Power-stats to control the power input to the sample heater in the control plug and the diffusion pump heater. In the center of the console are the controls for the magnet, and also vacuum gauges. To the left are located the controls for the counter-force current for the balance and also monitoring equipment for the output of the null detector. The output of the LVDT is first amplified (1000 to 1) by a Kintel dc amplifier and then observed on the oscilloscope. The

The scope was replaced in the final operational setup by a VTVM. The multi-range d-c milliameter, which is just behind the scope, for measuring the current through the counter-force coil was also paralleled by a floating point digital d-c voltmeter (not shown in Fig. 5) that monitored the working current through a calibrated resistor.

CALIBRATION AND TYPICAL RESULTS

In order to obtain a quantitative measure of the magnetic moment a measure of the magnetic field gradient active on the sample as a function of the magnetic field intensity was needed. A calibration of the beam balance to yield the force on the sample as a function of the counter-force current was also required.

The first calibration was accomplished by measuring the magnetic force on samples of known magnetic properties. The materials used were powdered nickel and powdered magnetite. Both samples were of very high purity and gave essentially the same calibration curve. The calibration curve obtained with the powdered magnetite sample is shown in Fig. 6.

The calibration of the balance was accomplished by experimentally determining the counter-force current necessary to bring the sample holder back to the null position when glass capillary tubes of different lengths were loaded into the brass sample holder. The glass capillaries had previously been weighed on a micro-balance of relatively high sensitivity. The force versus counter-force current curve is shown in Fig. 7. The sensitivity of the balance system is found by taking the slope of this curve. Due to the difficulty of detecting small

variations of the counter-force current, it is desirable to obtain a system with as small a slope as possible when encountering force changes of small magnitude. The sensitivity of the system is

$$S = 25 \times 10^{-3} \text{ Kg/A}$$

as compared to roughly 60×10^{-3} Kg/A for the balance system of McGuire and Lane.[6]

The results from a typical low temperature run on powdered magnetite is shown in Fig. 8. This sample is the same one used in obtaining the magnetic field gradient.

SCREENING EXPERIMENT

As already pointed out the time needed for a complete temperature run in the magnetic moment measuring experiment was economically prohibitive for a diverse study of doping effects and hence, a screening experiment was needed. This experiment is a standard experiment for high-temperature studies of phase changes,[7], [8] but is not commonly used for low-temperature studies. This experiment is called by chemists, metallurgists, etc., simply dta (differential-thermal analysis). It is a rather simple experiment in principle. Basically what is involved is this. If a material undergoes a change such as a phase change or order-disorder transition, a certain amount of heat is either given off or taken in in the process. If one places two thermocouples in series-one embedded in an inert or calibrated sample[9] in one well of a two-well

sample holder and the other in the active material in the other well-an emf will manifest itself on the output of the series combination if the two thermocouples are not at the same temperature, hence, a physical indication of an energetic change. The temperature at which the change occurs is monitored on an auxiliary thermocouple in the inert material. The outputs are then displayed on an xy recorder and the inactive samples are screened out. This experiment can be run in a period of time an order of magnitude smaller than the moment experiment.

Because the dta results were only to be used in screening out inactive samples, natural cooling and warming rates were used in this experiment. A known rate would lead to additional information [10] about the amount of energy released or absorbed in a transition. The two-well, ceramic sample holder was suspended inside a brass container which was then emersed in liquid nitrogen. Heat transfer was due almost entirely to convection as no liquid was allowed to touch the sample holder.

The inert sample was powdered alumina and the active samples were mixed with the same powdered alumina in a 10 to 1 weight ratio in an attempt to insure conductivities of approximately the same order of magnitude. The active materials were also passed through a 100 mesh (149 microns) screen to give approximately the same grain size. Both these conditions are suggested by Mackenzie [10] in his study of clays. The output from the differential set of thermocouples was first amplified by the Kintel d-c amplifier and then fed into the "Y" input of a Mosely Autograph (XY recorder). The temperature-sensing thermocouple output was fed directly into the "X" input of the recorder.

CALIBRATION AND TYPICAL RESULTS

For work above room temperature the standard material for calibration is quartz,[9] whose characteristic curve is well refined through years of research. Powdered alumina is also used, with due concern about purity and grain size.[10] This material exhibits an inert characteristic unlike quartz. Unfortunately, because of the lack of any previous application of this method of analysis to low-temperature research, there is no standard low-temperature reference material. The reference material used in this experiment is alumina of the same quality as the material in the inert well. The dta curve for this material is shown in Fig. 9 along with the dta curve for the magnetite standard. These curves show only the warming part of the thermal cycle and the exothermic transition. The warming curve for a natural occurring magnetite (Minerville) is included for comparison. This natural magnetite is of apparently high purity as evidenced by the sharpness of the transition.

FOOTNOTES

1. P. W. Selwood, Magnetochemistry, (Interscience Publishers, New York, 1956).

2. L. F. Bates, Modern Magnetism, (Cambridge University, Cambridge, 1951).

3. E. F. Westrum, J., Dept. of Chemistry, The University of Michigan, private communications.

4. A. L. Smith and H. L. Johnston, Rev. Sci. Instr., 24, 420 (1953).

5. W. H. Duerig and I. L. Mador, Rev. Sci. Instr., 23, 421 (1952).

6. T. R. McGuire and C. T. Lane, Rev. Sci. Instr., 20, 489 (1949).

7. C. F. Jefferson, An Investigation of Reactions Involved in the Preparation of Ferrites, doctoral dissertation, The University of Michigan, 1959.

8. G. Economos, Jr., J. Am. Ceram. Soc., 38, 292 (1955).

9. G. T. Faust, Am. Mineralogist, 33, 337 (1948).

10. R. C. Mackenzie, The Differential Thermal Investigation of Clays, {Mineralogical Society (Clay Minerals Group), London, 1957}.

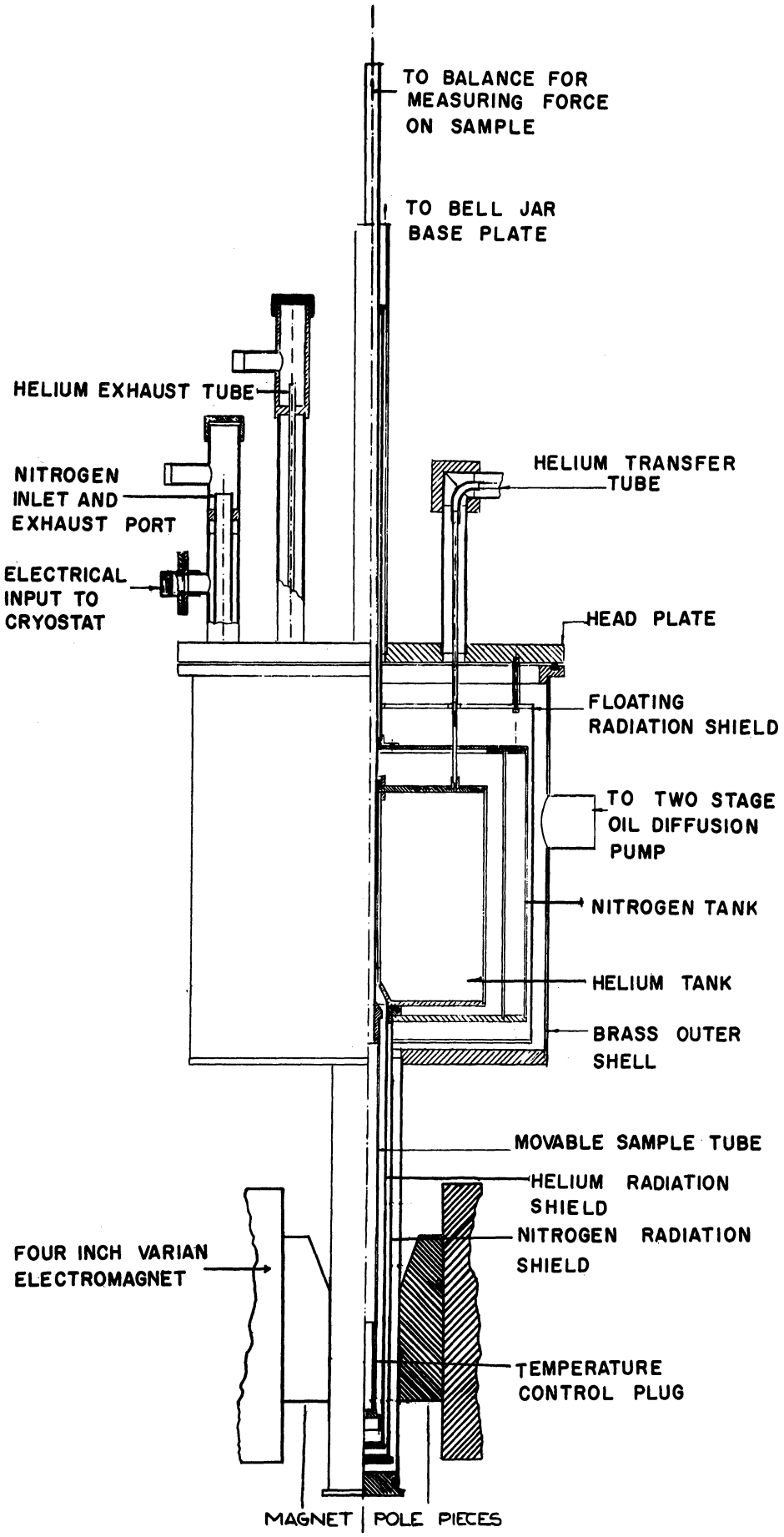

Fig. 1. Sectioned drawing of cryostat.

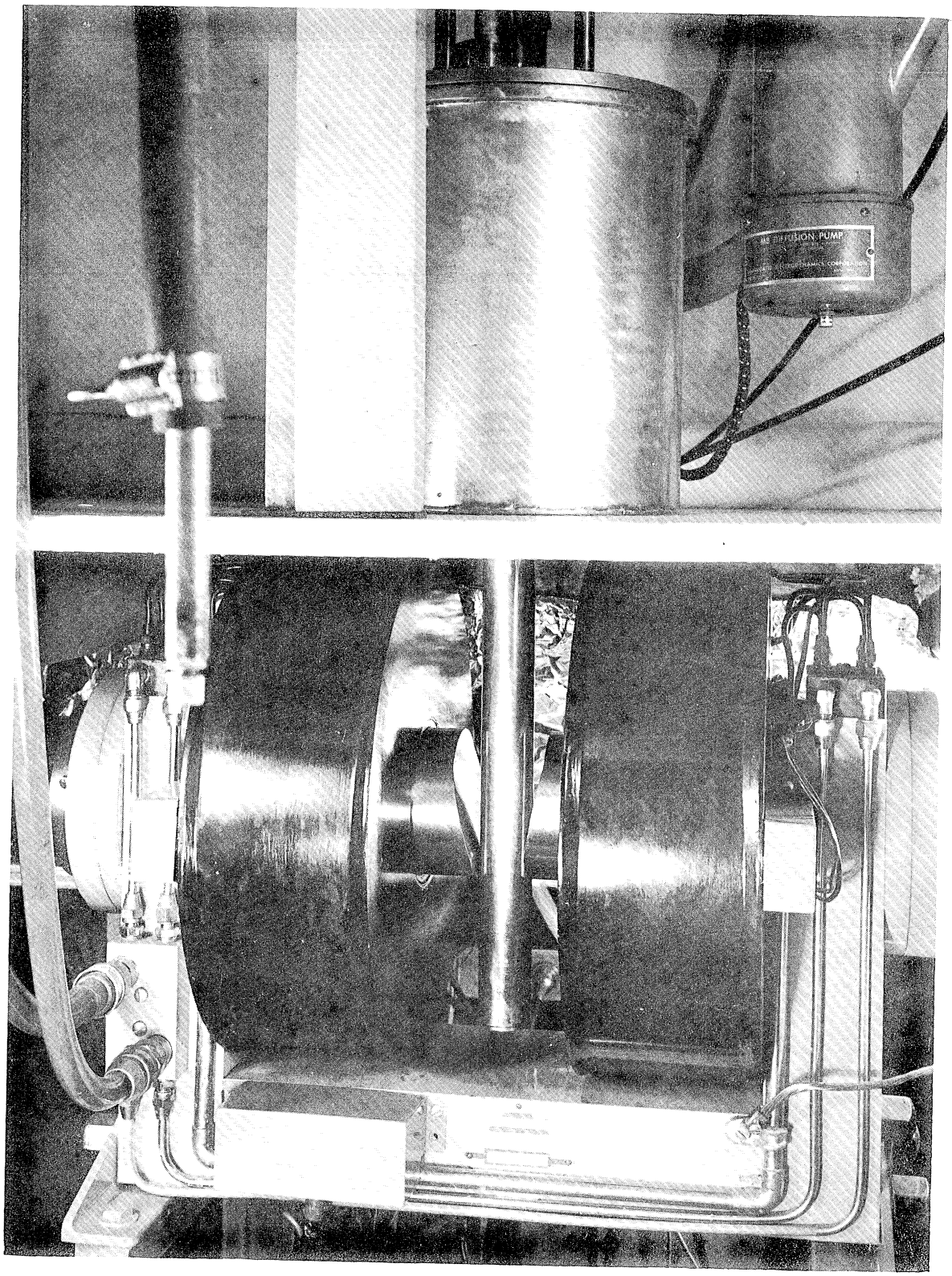

Fig. 2. View of the cryostat in position in the 4-in. Varian electromagnet. Notice the shape and separation of the pole pieces.

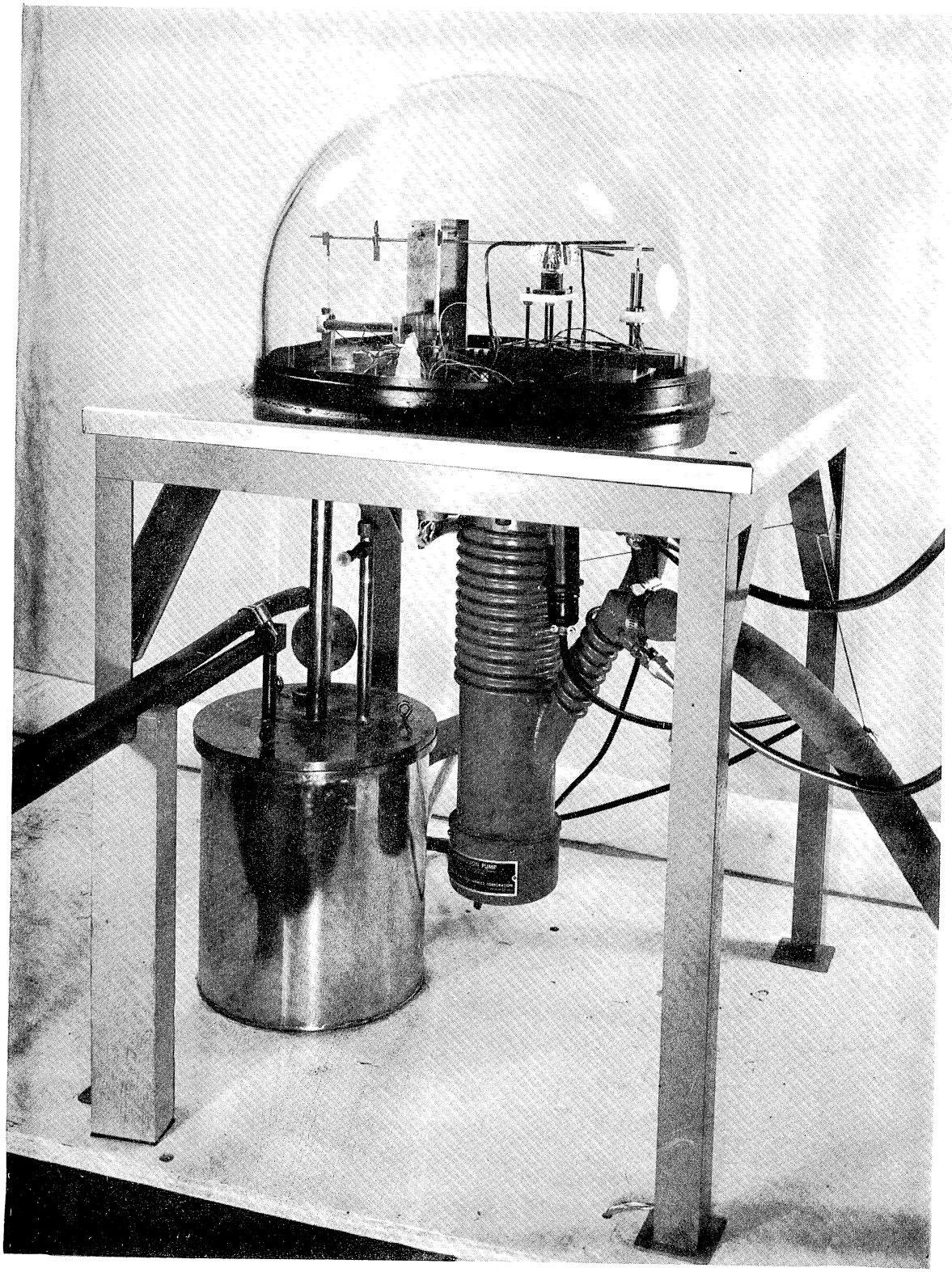

Fig. 3. Top portion of cryostat and beam balance used in measuring the force exerted on sample due to field gradient.

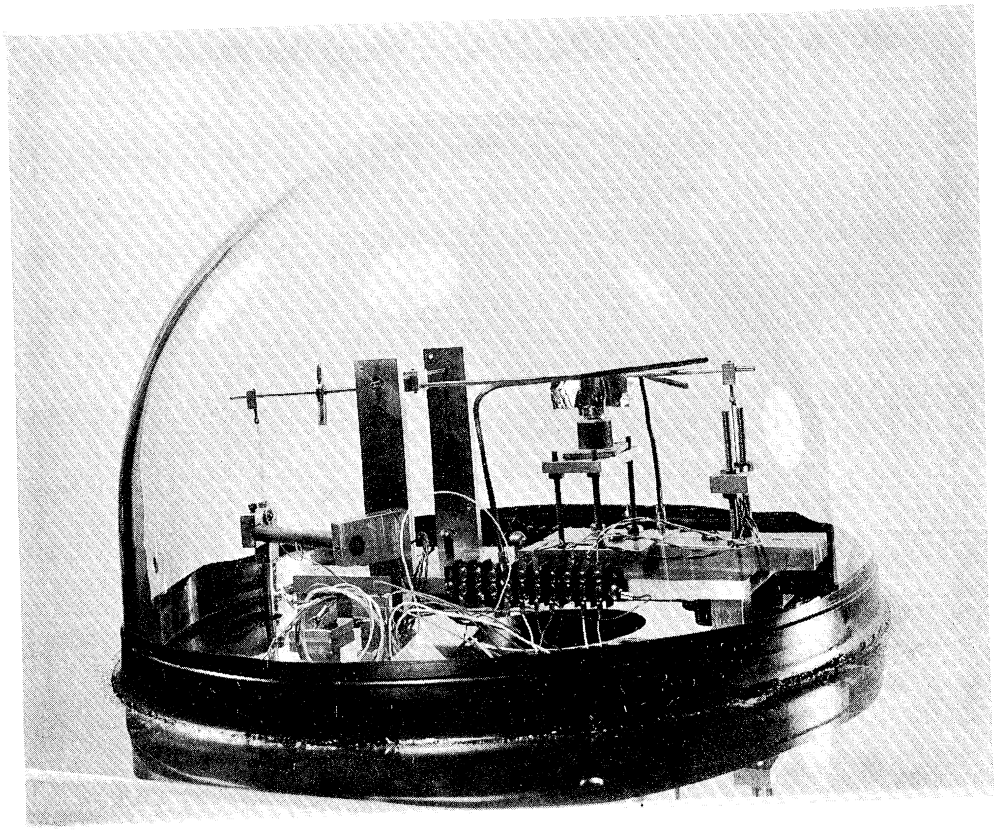

Fig. 4. Close-up view of balance showing counter-force coil and linear-variable-differential transformer.

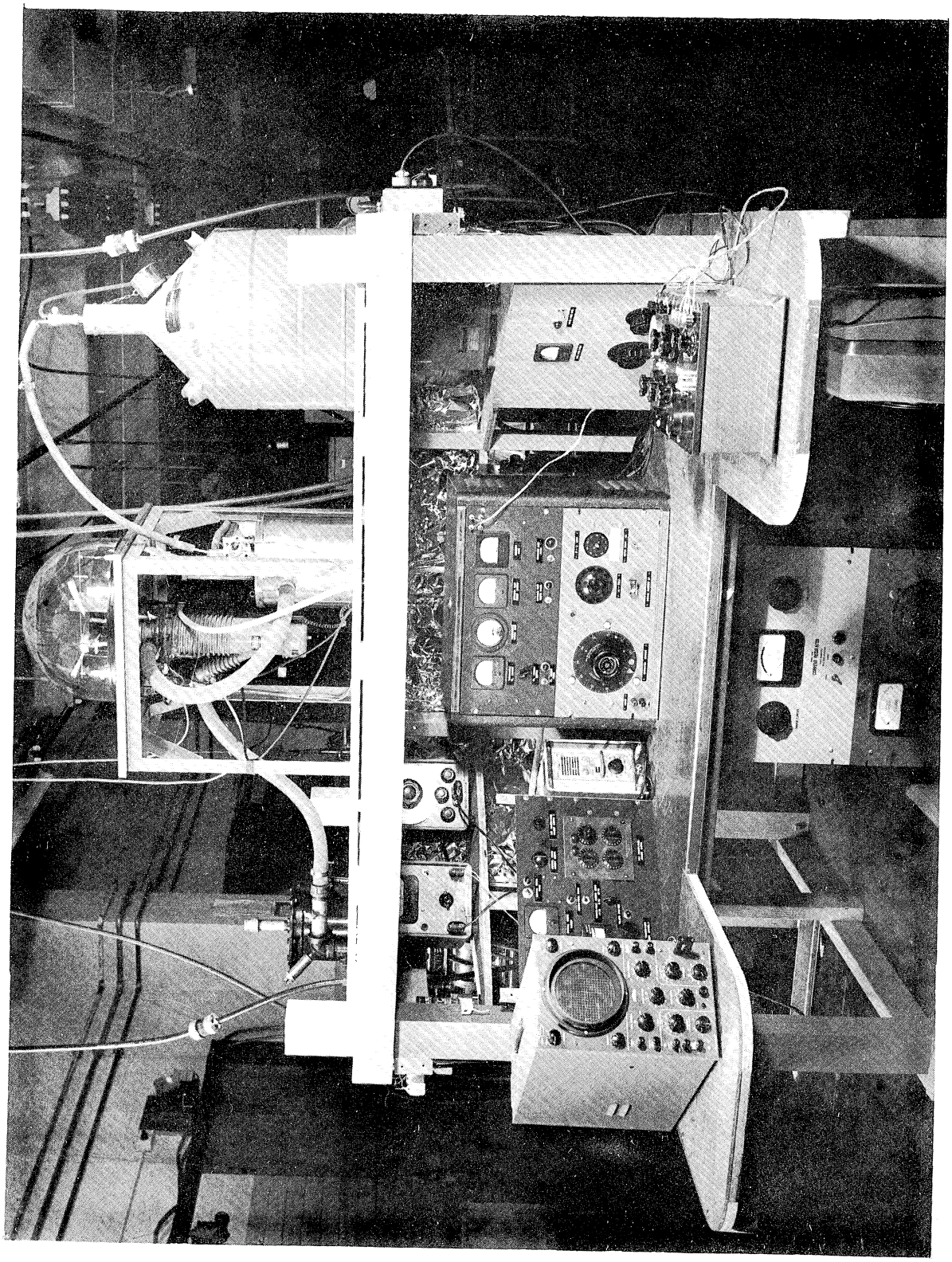

Fig. 5. View of working console used in monitoring sample temperature, magnetic field, and force on sample.

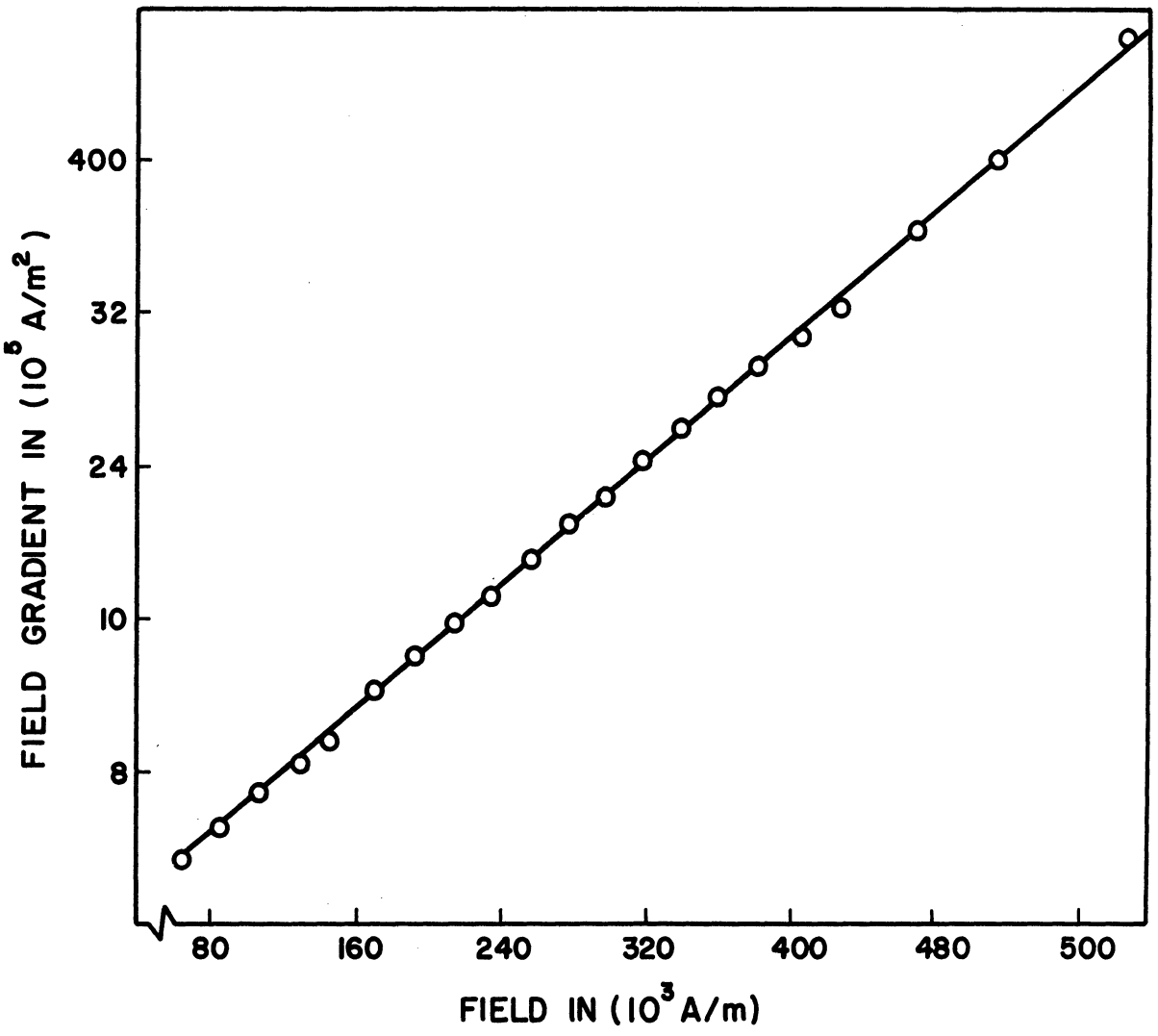

Fig. 6. Field gradient as a function of field for 4-in. Varian magnet with pole pieces as shown in Fig. 2. Measured with a magnetite probe.

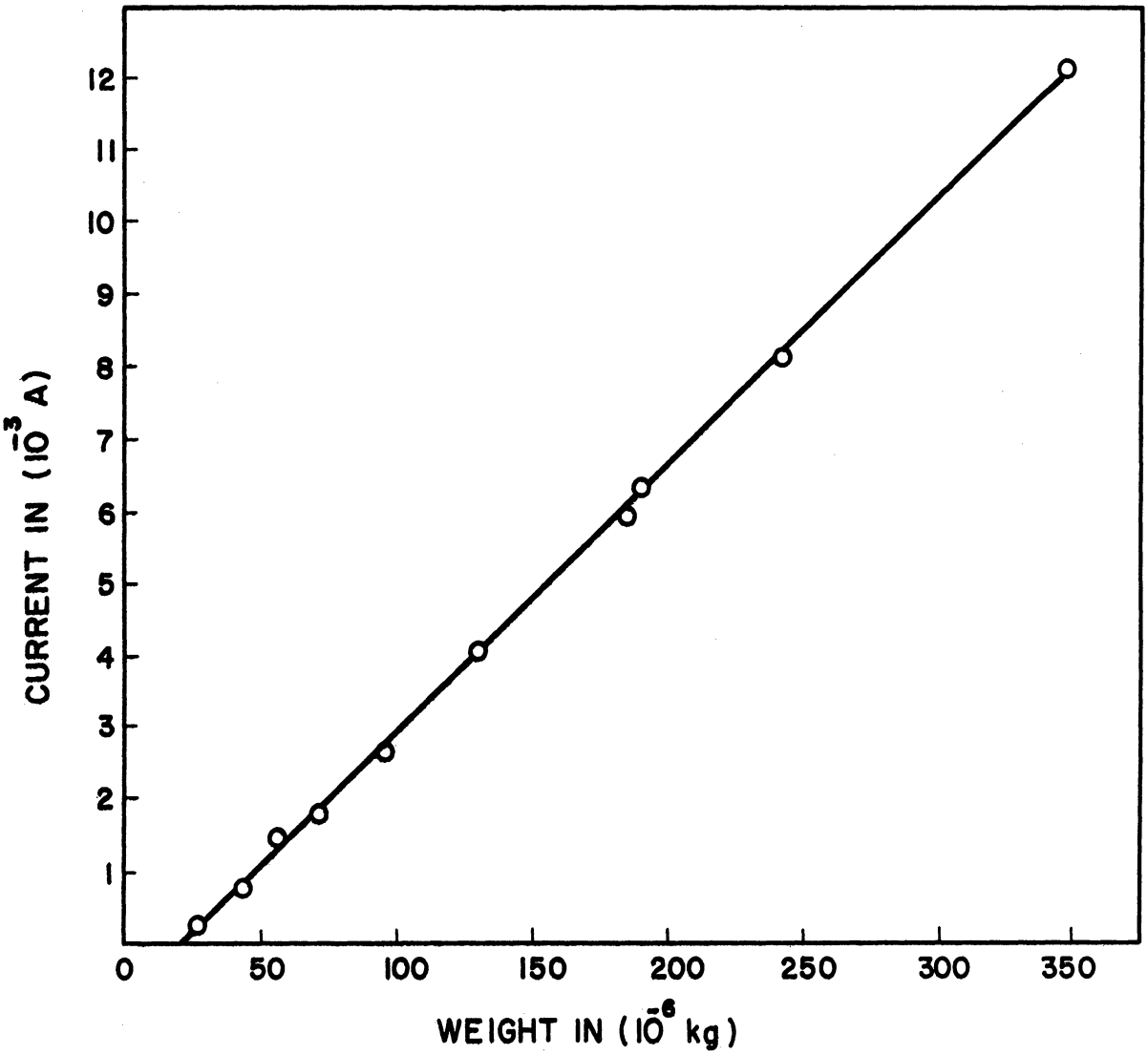

Fig. 7. Balance calibration giving counter-force current versus weight in kilograms.

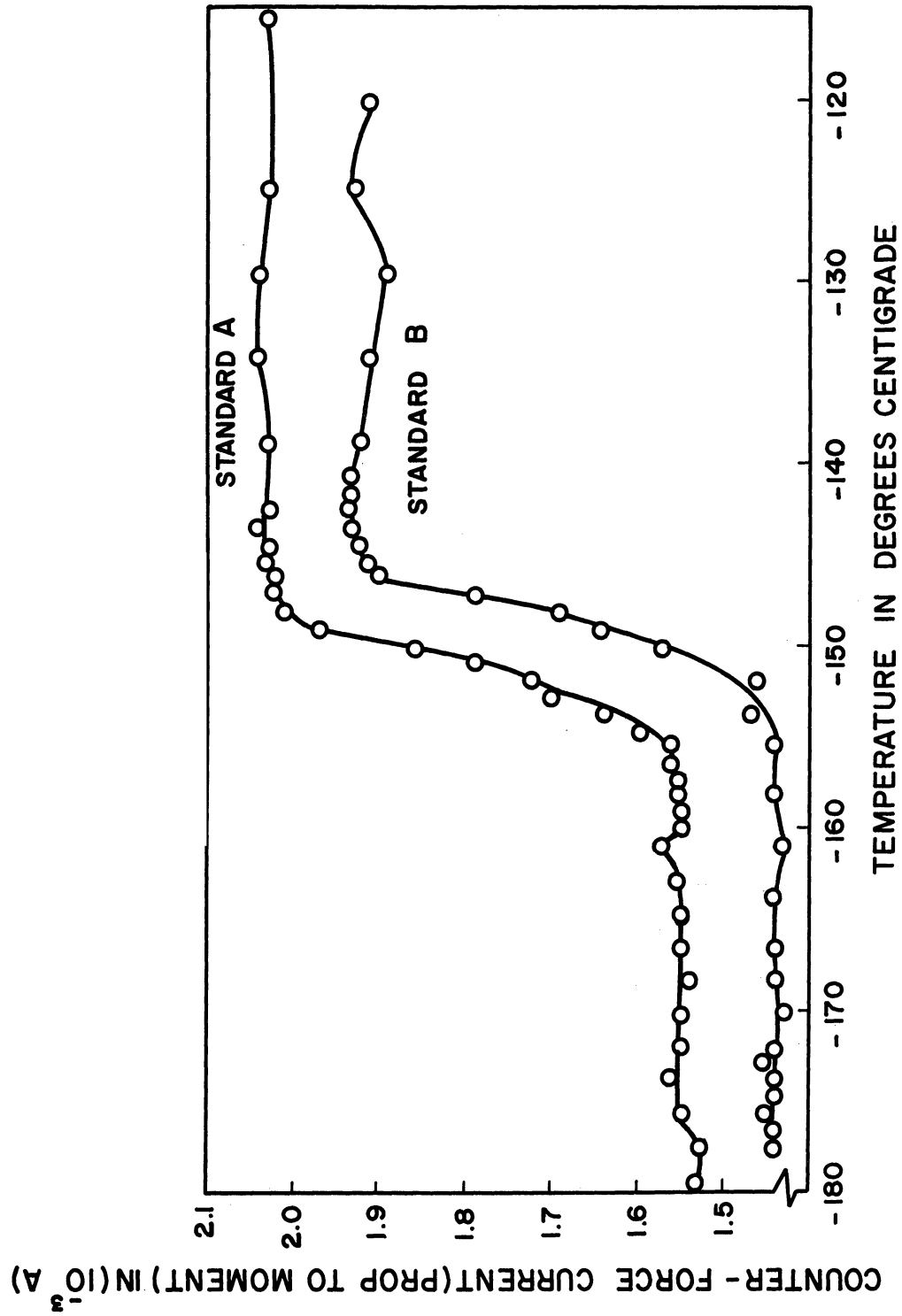

Fig. 8. Counter-force current versus temperature for two samples of magnetite standard cooled through transition without applied field and then warmed in a field of 1.04×10^5 A/m.

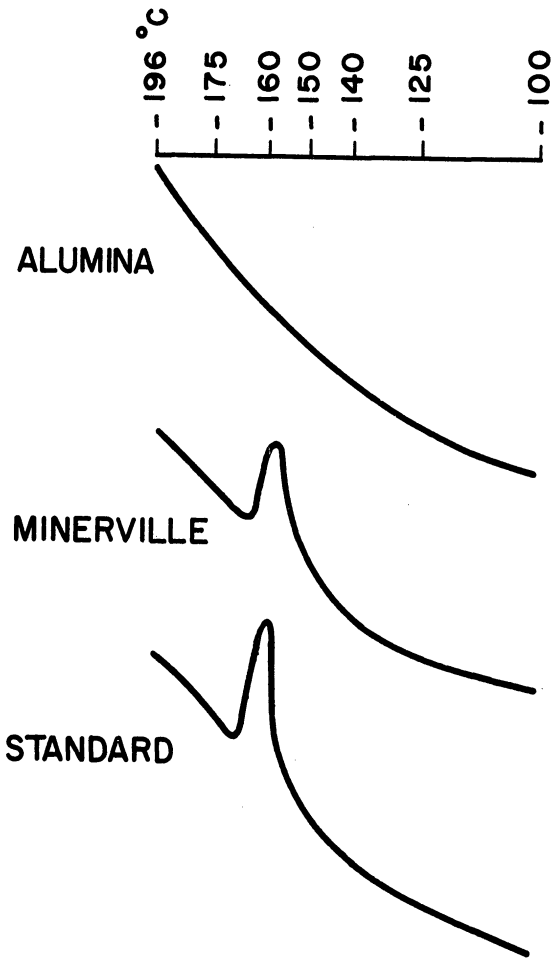

Fig. 9. Differential-thermal analysis records showing deflection as a function of temperature on warming cycle for an inert material (alumina) and two active materials (natural magnetite from Minerville, New York and standard).