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MAGNETICALLY SENSITIVE ELECTRICAL RESISTOR MATERIAL

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ABSTRACT

The galvanomagnetic constants (brackets), as defined in our previous report, have been measured for Bi between room temperature and liquid-air temperature for orders zero and one and partially for order two. The results agree roughly with those of Okada and somewhat better with those of Abeles and Meiboom. Also, preliminary measurements on some Bi alloys are reported.

The growing and preparation of single crystals in the shape desired for our measurements are described in Section B. The measuring equipment is described in Section C. The results are given in Section D, together with a particularly suitable method of determining the second-order constants.

OBJECTIVE

This project aims at developing the understanding of the magneto resistance effect (change of electrical resistivity in a magnetic field) by theoretical and experimental research, with the ultimate aim of developing materials with more favorable magneto resistance properties than are available at present.

A. INTRODUCTION

It was stated in the previous report that the present report would not be concerned with further progress made meanwhile in regard to the theory of the galvanomagnetic effects. Accordingly, the present report covers the experimental work of the period March 1, 1955 to March 31, 1956. The length of the period covered permits one to see some of the work, especially in the earlier half, in proper perspective and, consequently, some work of a preliminary nature will be omitted and various intermediate stages in improving the techniques of measurement will be described only very briefly. The main emphasis will be on the techniques as developed presently and the results obtained.

According to the previous theoretical report, the experimental task of measuring the galvanomagnetic effects consists of the following steps:

a. Preparation of single crystals of given purity, dimensions, and orientation of crystal axes.

b. Mounting of the sample with respect to electrodes for current, longitudinal voltage, transverse voltage, magnetic field, and temperature.

c. Taking of measurements and extraction of the galvanomagnetic material constants (brackets) from the measurements.

d. Discussion of results.

These four steps will be described presently. The major part of the work was done with bismuth, later augmented with some work on certain bismuth alloys.

It is recalled from previous reports how the galvanomagnetic constants are defined. If reference is made to a "symmetry coordinate system" which is adapted to the symmetry axes of the crystal (k_3 along the trigonal axis, k_1 along a binary axis), then the conductivity components σ_{ij} can be expressed in terms of a power series in the components B_1 B_2 B_3 of the magnetic field and the coefficients (brackets) are the galvanomagnetic constants.

$$\sigma_{ij} = \sum_{n=0}^{\infty} \sum_{m=0}^{n} \sum_{p=0}^{m} [m - p, p, n - m]_{ij} B_1^{m-p} B_2^{p} B_3^{n-m} .$$

For bismuth (group D_{3i}) the independent brackets are, for $n \leq 2$:

n	=	0	$[000]_{11}$	$[000]_{33}$	
n	=	1	$[100]_{23}$	$[001]_{12}$	
n	=	2	$[200]_{11}$	$[200]_{22}$	$[200]_{33}$ $[002]_{11}$
			$[011]_{11}$	$[011]_{23}$.	

In the present report, work is described leading to the measurement of these brackets as a function of the temperature. The work on brackets with $n = 0$ is largely completed, that on brackets with $n = 1$ is completed to the point where results are available which seem satisfactory although some further improvements in accuracy are indicated, while that on brackets with $n = 2$ is just producing the first results.

B. PREPARATION OF SINGLE CRYSTALS OF Bi AND CERTAIN Bi ALLOYS

1. PURPOSE

It is the purpose to grow single crystals of pure Bi and of certain Bi alloys in a shape suitable for subsequent electrical measurements and with known orientation of crystal axes.

2. MATERIALS

The Bi and Te used in this work were obtained from the American Smelting Co. of South Plainfield, N. J. Both were of 99.99+% purity. The Sn was from the General Chemical Co. of New York, N. Y., and was of 99.97% purity.

3. PREPARATION OF THE RAW MATERIAL USED FOR GROWING SINGLE CRYSTALS

The raw material is made in the form of a rod of Bi (or alloy) in a glass tube. A 50-ml crucible containing about 50 gm of Bi is placed in a vacuum bell jar. Several glass tubes about 35 cm long with one end closed and an inner diameter of from 2-5 mm are placed vertically into the crucible with the open ends down. The bell jar is then rinsed three times with He and evacuated to about 10^{-3} mm Hg. (The He rinse is done to prevent the formation of an oxide film on the Bi when heated.) By means of a heater coil around the crucible the Bi is melted and forms a seal around the lower end of the

glass tubes. The glass tubes are also heated over their entire length by a vertical oven. Then He is let into the bell jar and pushes the Bi up into the glass tubes. The bell jar is then removed, the tubes are then drawn up at the rate of about 15 cm/hr out of the vertical oven past an air jet so that the Bi solidifies slowly from the upper end. This method prevents the breaking of the glass upon solidifying (Bi expands when solidifying). This method sometimes gives single crystals; the trigonal axis is then usually normal to the length of the tube. The Bi rods so obtained serve as the raw material to be regrown by the methods described under Sections B.4, 5, 6. The material had a clean, shiny appearance.

4. PREPARATION OF THIN Bi WIRES

A good deal of time was spent in attempts to prepare thin Bi wires of the order of 50 microns in diameter for magneto resistance measurements. Such wires, owing to their large surface-volume ratio, insure the best thermal homogeneity. However, the experimental difficulties encountered with these wires led us finally to abandon this procedure and to use thicker wires as described below.

For the sake of putting our experience on record, the following details are reported. The Bi rods as described under Section B.3 are heated in their glass tube and then pulled. A section of about one inch is broken off from the long fiber so obtained and the cleavage planes at both ends are investigated under the microscope. If they are parallel at both ends, which is the usual situation, we assume the fiber to be a single crystal. This assumption has been tested in a number of instances by means of X-rays and by cleaving a fiber at a dozen or so intermediate places. The normal to the cleavage plane was assumed to be the trigonal axis. Later experience with somewhat larger samples indicates, however, that often cleavage of a glass-enclosed fiber will occur along a plane containing the binary axis (secondary or imperfect cleavage plane). This uncertainty and the relatively large amount of labor involved in X-ray determination of the trigonal axis direction was one of the reasons why the work with thin fibers was later abandoned. The glass at the ends of the fiber is then cracked off mechanically and the sample mounted in a special capsule with gallium electrodes which is mounted in a Cardan suspension-type holder for magneto resistance measurements.

5. PREPARATION OF Bi WIRES FOR GALVANOMAGNETIC WORK

a. Seeded-Zone Melting of "Raw Material."—A Bi rod, still in glass tubing ($\approx$ 0.07 inch inner diameter), is held vertically. A heating coil is moved downward by a clock motor at the rate of about 1/64 inch/min. The melting zone in the operation is about 3/8 inch long. The operation is done in about 10^{-2} mm vacuum. (At lower pressures the Bi melt would develop enough vapor pressure to kick itself out of the tube.) To start the operation the

upper end of the Bi is heated to melt, and a seed crystal, mounted such that the trigonal axis of the seed is at the desired angle with the rod to be seeded, is moved down to touch the melt. After 10 min the connection is found to be in equilibrium, and the coil is moved downward as far as the desired length of the newly grown single crystal. This method of growing is very satisfactory for the trigonal axis away from the rod and is $\approx 30\%$ successful for the trigonal axis along the rod. Vibration in the room is found to be the disturbing factor. For best results, the seed crystal should be slightly larger than the rod.

After removing the glass rod from the growing apparatus the glass around the Bi is taken off by HF in a Lucite container (lucite appears to be resistant to HF) and the Bi surface cleaned by a bath of about 0.05N nitric acid, then rinsed and dried.

b. Determination of The Crystallographic Axes.--A single crystal of Bi can be cleaved in four directions, three containing the binary axes (imperfect planes) and one normal to the trigonal axis (perfect plane). The planes can be distinguished visually. All crystal axes are determined from the perfect plane.

The trigonal axis is determined accurately by means of a shadowgraphic method. The crystal is mounted in a light beam and a 5 to 10 times enlarged image is observed, drawn on paper, and the angle measured. The crystal is rotated around its own axis normal to the light path, until the focused shadow of the perfect plane is a straight line. This allows for the measurement of the angle by an ordinary protractor to be accurate within 1/2° or better.

It is also required to know the orientation of the binary axes. The sample is first mounted in its holder (see Fig. 3 page 12) and the angle between one of the binary axes and the normal to the wire in the plane of the sample holder (the x^2-direction in Fig. 3, which is to be the direction of Hall potential measurement) can be found as follows. On the perfect plane, one can see three sets of parallel lines intersecting at 60°. These lines are parallel to the binary axes.[1] The rod is mounted so that the perfect plane and its line of intersection with the holder plane are exactly horizontal. Then under a vertical microscope one can see the binary axis lines making some angles with the cross-hair line in the eyepiece of the microscope permitting direct measurement of the angle between the binary axis and a horizontal line fixed on the sample holder by elementary manipulation, with an accuracy of better than 1/2°.

6. PREPARATION OF Bi RODS FOR THE ABSOLUTE DETERMINATION OF THE CONDUCTIVITY

In order to obtain significant galvanomagnetic constants, it is necessary to know the absolute conductivities $[000]_{11}$ and $[000]_{33}$. Special

1. See Y. Tanabe, Tokôku Univ. Res. Inst. Sci. Rep., 1, 275 (1949).

samples were prepared for the measurement of these zero-order brackets as follows.

Three V-grooves were cut into a 7/8-inch-diameter steel rod (three grooves were used for a higher rate of production of crystals). An oven was made out of Vycor tubing. Stopcocks were incorporated to allow a vacuum to be created within it. The inside diameter was large enough to insert the steel rod.

A heater coil was wound on the outside of the Vycor tubing, tightly at one end, with the pitch gradually increasing toward the other end. This arrangement made it possible to obtain a thermal gradient along the steel when it was inserted.

The glass is removed mechanically from rods of raw material (see Section B.3) and these are placed in the V-grooves of the steel rod, sometimes with thin sheets of mica between Bi and steel. (The purpose of the mica is to prevent any diffusion of steel into Bi; however, it was found that no observable difference results from omitting the mica as far as conductivity measurements are concerned.) After the Bi is inserted, the oven is evacuated and flushed with helium three times. After the last flush the oven is again evacuated to a pressure of approximately 10^{-3} mm of mercury.

The heater coil is then heated, allowing the Bi to melt from one end. After the rods of Bi are completely melted, the heating current is gradually decreased, allowing the steel rod to cool slowly but always maintaining a good thermal gradient. The Bi melt then starts to solidify along this thermal gradient and single crystals are produced. In this process no precautions need to be taken to insure that each melt starts crystallizing from one spot in the melt. It just happens. There seems to be no preferred direction of growth. Crystals of all orientations have so far been obtained, randomly.

In order to obtain any desired axis orientation, the same method has been employed with a slight variation, using seed crystals. A seed crystal and a Bi rod are introduced into the V-groove. The Bi rod and part of the seed are melted to insure a good connection. The melt is then cooled from the seed as before. Single-crystal Bi rods of about 12 cm by 7 mm^2 obtained in this way were used for the measurement of the conductivity.

The seed can be gotten either from a previously grown crystal or from a method devised for this purpose as follows. A metal strip in the shape of a quarter circle, one inch wide and 1/2 inch thick, has one continuous V-groove cut along six consecutive sides of a regular 24-sided polygon, so that each straight section is about one inch long and makes an angle of 15° with adjacent sections. A previously grown crystal of arbitrary orientation is bent to lie in the V-groove, preferably with its trigonal axis in the plane of the polygon. The metal strip is then heated at one end and the Bi is melted along a temperature gradient. However, the melting is stopped short of the

end of the Bi rod. This allows the end to remain solid and act as its own seed. Cooling is then started toward the opposite end. When finished there remains a single crystal of Bi in the shape of six connected straight sections. It is then cleaved at each bend, thereby producing six given seed crystals all differing by 15° from each preceding one. Any crystal can be used as a starting point. In this way seed crystals of any desired axis orientation can be obtained. The way in which the exact directions of the axes are determined for a Bi sample of this type was the same as that described in Section B.5.

7. PREPARATION OF Bi ALLOY SINGLE CRYSTALS

It was intended to study the effect of impurities on the conductivity and on the galvanomagnetic constants of Bi, for substitutional impurities containing fewer or more electrons per atom than Bi, or the same number. Preliminary results on Bi-Sn alloys were given in an earlier report. The conductivity decreases as Sn is added. Presently some preliminary studies on Bi-Te and on Bi-Te-Sn alloys are reported.

a. Bi-Te.—Our first alloys were made with 0.0212% and 0.122% tellurium by weight. The process of growing single crystals was the same as described for Bi in Section B.5. The electrical measurements indicated that more precautions are necessary to insure homogeneous composition of alloy rods. A stirring device for the original melt in the crucible from which the raw material is made has since been added, but since crystals are grown along a temperature gradient, the effect of zone refining is superimposed upon the crystal-growing process. This means that the impurity, in all probability, will be distributed unevenly throughout the crystal. The crystals were harder and more brittle than pure Bi and showed a charcoal-grey color. The cleavage properties and the appearance of binary axis lines on the cleavage planes were similar to those of Bi.

b. Bi-Te-Sn.—One alloy was prepared with 0.05% Sn and 0.05% Te by weight. The procedure and the difficulties were the same as for Bi-Te alloys. The alloys are likewise similar.

C. EQUIPMENT

1. MAGNETS

In Report No. 5 the electromagnet is described which was used for thin wire samples. When the need for larger samples and different measurements on each sample came up, it was desirable to have a magnet with a larger gap and with a permanent field. The gap width should accommodate a Dewar for temperature studies. A C magnet was acquired. In each pole of this magnet

there are 28 rods of Alnico bars (1 inch diam., 4 inches length) closely packed behind a thin,soft, iron pole piece. Energizing coils are mounted around the Alnico bars. The field can be set at any arbitrary value by running an energizing pulse through the coils, after which the Alnico bars will retain the value of the field "permanently." The pole pieces are 6-3/4 inches in diameter at the tapered ends and are separated by a 3-1/2-inch gap. The uniformity of the field was tested by a sensitive fluxmeter and testing coil (200 turns, 1 square inch area). The field was found to be constant within half a percent in a region 2-1/2 inches in diameter around the center and decreasing slowly toward the edge, the decrease being less than 5% at the very edge. The maximum field attained with the present pulse source is approximately 1500 gauss. The permanence of the magnetic field allows measurements to be taken on different samples, with varying temperature. The value of the field has been set to be 345 $\pm$ 3 gauss, measured both by fluxmeter and proton-resonance equipment. The low field was chosen for the studying of the lower-order brackets of conductivity in order to minimize the influence of terms of higher than second order in B.

A proton resonator has been built after the design of N. J. Hopkins,[2] with slight modification. For low fields of the order of 250 gauss the resonance signal requires considerable amplification, and the noise-to-signal ratio is not negligible. Consequently, the location of the resonance peak requires more time for such weak fields than for strong fields. However, if the magnitude of the field is known approximately, the proton resonator permits determination to within 1% down to 250 gauss.

2. DETECTION SYSTEM

Previous measurements were made with a galvanometer—Wheatstone bridge arrangement. In order to speed up measurements and to increase the sensitivity, use was made of a recorder and amplifier kindly loaned to us by the Leeds and Northrup Co. The sensitivity was thus about 100 times greater. This increase in sensitivity is desirable because it permits a decrease in measuring current through the sample, thus minimizing any thermal effects. A measuring current of approximately 0.15 amp was used.

Associated with this change were the following additions.

a. Potentiometer Bridge.—Because of the planned use of samples of lower resistance than used previously, the Wheatstone bridge was replaced by a simple potentiometer bridge circuit.

b. Vibrator.—A 120-cycle vibrator has been used at the output of the potentiometer bridge to convert the bridge signal to ac. This signal is fed into a sharply tuned 120-cycle linear amplifier with an amplification factor of 500. This signal is then fed into the recorder. The input impedance

2. Rev. Sci. Inst., 20, 401 (1950).

of the amplifier is 50,000 ohms, hence no effective change in bridge balance results with the addition of this component. The 120-cycle-amplifier power supply has been replaced by a battery supply in order to decrease spurious 60-cycle distortion. The sensitivity of the recorder is such that a full-scale deflection of the recorder corresponds to 10 μv, which represents a change of about 0.06% of the total sample resistance under average conditions of our measurements.

3. POLAR-DIAGRAM DETECTION SYSTEM

The following equipment has been constructed in order to obtain quickly a polar diagram of the change in magneto resistance due to rotation of the crystal in the magnetic field such as are referred to in the literature and in previous reports.

a. Sine-Cosine Resolver.—A sine-cosine resolver was built, consisting of a long solenoid primary and two secondary coils located at the mid-point of the solenoid. The secondary coils are displaced 90° from each other and rotate about a common axis. The dimensions of the primary solenoid are

radius: 2.75 inches (inner)
length: 12 inches

wound with 3500 turns of No. 28 "Nyclad" wire. The dimensions of the secondary coils are

radius: 2.0 inches (inner)
thickness: 0.75 inches.

Each coil is wound with 750 turns of No. 28 wire.

The axis of the secondary coils is mechanically coupled to the axis of the sample holder. This axis can be driven by a motor at a slow rate so as to avoid eddy currents.

b. Amplifier.—A three-stage linear amplifier has been assembled to amplify the signal from the bridge to the primary of the resolver 250 times (Fig. 1). This amplifier has a battery power supply in order to eliminate 60-cycle interference which would be present if an electronic power supply were used. The amplifier tubes are rated for very low noise operation.

c. Circuit.—The entire circuit (see Fig. 2) operates as follows. The d-c signal from the bridge is fed into the 120-cycle vibrator and then through the three-stage amplifier to the primary of the resolver. From the two secondary coils, the signal is fed through two identical 120-cycle sharply tuned amplifiers to the X and Y plates of a type 304-H oscilloscope.

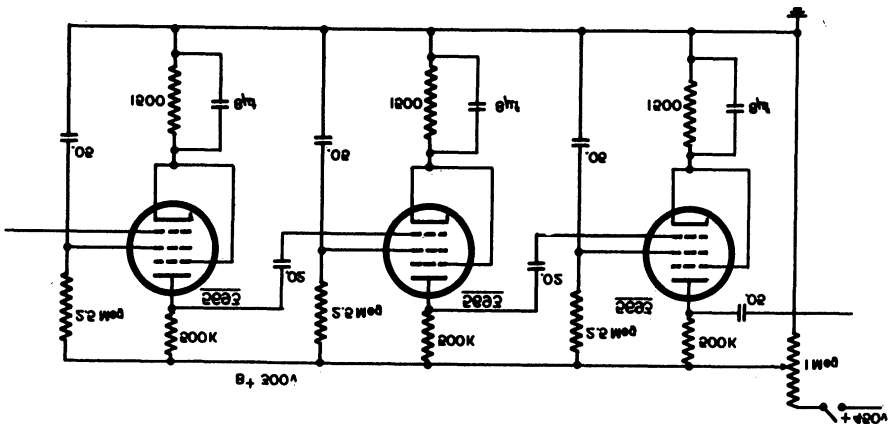

Fig. 1. Schematic diagram of amplifier.

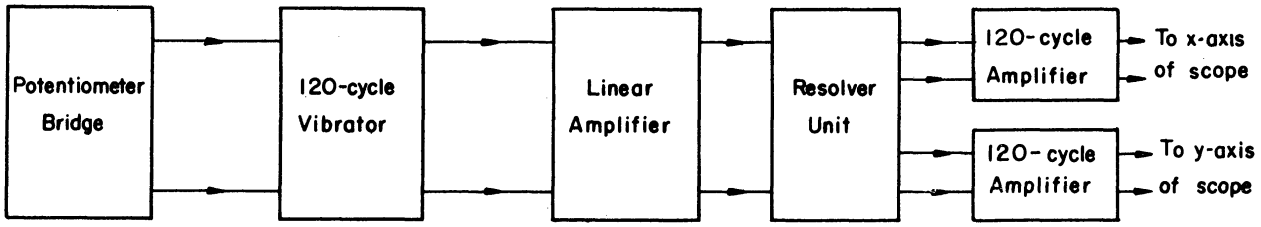

Fig. 2. Block diagram of resolver equipment.

With no magnetic field, a rotation of the sample through 360° describes on the oscilloscope a rotating straight line whose envelope is a circle. The radius of the circle is determined by the amount by which the bridge is unbalanced. If the bridge is balanced while the sample is outside of the magnetic field, and subsequently the sample is moved into the field and rotated, the length of the rotating line on the scope varies in general with the angle and the envelope is a polar diagram as expected.

d. Choice of Frequency.—It has been apparent in the preceding discussion that the frequency for the operation of the resolver is 120 cycles. The choice was made because the two sharply tuned 120-cycle amplifiers had already been built and were available on loan from Dr. Enns of this laboratory. These amplifiers are quite satisfactory for our work. Therefore, the amplifiers were considered the basic unit to which the other equipment has been adapted.

e. Future Plans.—With the sine-cosine resolver ready for operation, we expect to photograph the polar diagrams obtained from various samples, using different orientations of the crystal axes. The use of the resolver will enable us to check quickly what the dependence of the galvanomagnetic effect is in terms of the field, i.e., the number of terms of the power expansion influencing the effect.

It is also hoped that a detailed study can be made on crystal samples in order to analyze the rosette pattern in terms of the theory.

4. MOUNTING OF SAMPLES

a. For Zero-Order Bracket Measurement.—Many crystals of varied orientations were grown by the procedure described in Section B.6.

A Leeds and Northrup Kelvin bridge was used to determine the resistance of the crystals with an accuracy of two parts in the fourth significant digit. Direct current was used and balancing was accomplished with a sensitive galvanometer.

The sample holder consisted of two knife edges for potential leads and two flat contacts for current leads, and could take samples from three to twenty inches in length. The base of the sample holder was made of Lucite with a long V-groove cut into it. This formed a perfect seat for the bismuth crystals since they were shaped from a V-groove.

Another sample holder based on the same principle but holding six samples was also used for part of the measurements. Some measurements were taken at ambient temperature in air, whereas another part of the measurements was taken with the samples and holder immersed in a water bath, thermostatically controlled to within 0.1°F.

b. For Measurements of Brackets of Orders 0,1,2,...,etc., as a Function of Temperature.—The sample holder and sample to be described below were immersed in a liquid bath for temperature control. The liquid was contained in a Dewar and could be moved into and out of the magnetic field of the Alnico magnet described under Section C.1.

For slow, continuous variation in temperature, isopentane (mp<-150°C) is used. The sample holder is submerged in isopentane in the Dewar which is cooled by a controlled flow of liquid air through a copper coil submerged in the isopentane until freezing. Then the bath is warmed up slowly after the flow of liquid air is stopped. The measurement can thus be done continuously at all temperatures upward. The temperature is measured by a copper-constantan thermocouple (accuracy $\pm$ 1°C).

For long isothermal measurements such as required for second-order brackets, different kinds of liquid will be used with the freezing points in steps from -150 to +20°C. Liquid-air cooling will again be used to freeze the liquids.

It seems best to describe the sample holder together with the orientation of the crystal with respect to it. The crystal, in the form of a cylindrical rod 1-1/2 inches long and approximately 0.07 inch in diameter, grown by the seeded-zone melting method described in Section B.5, is placed in a V-shaped groove in a lucite disc, such that the trigonal axis and the rod form a plane perpendicular to the plane of the disc. Two Hall probes, in the form of brass wedges lying in another V-shaped groove exactly perpendicular to the rod, are held against the rod by two small bronze springs. Thus the "laboratory coordinate system" $x^1x^2x^3$ as defined in the previous report is fixed with respect to the sample holder: x^1 along the rod, x^2 in the direction of the Hall probes, and x^3 accordingly. The lucite disc is mounted on a brass disc such that the whole can rotate around the x^2-axis (i.e., Hall probe direction), which is held by two brass prongs. The x^2-axis and the prongs can be rotated in a horizontal plane, around a vertical or ϕ-axis. The rotations around the vertical ϕ-axis and about the horizontal x^2-axis or ψ-axis are accomplished by a gear arrangement and can be done from outside the Dewar. The magnetic field $\overline{B}$ is horizontal, hence perpendicular to the ϕ-axis. By manipulation of the gear system the sample holder can be placed in any desired orientation with respect to the magnetic field.

The current leads (No. 28 Nyclad) are soldered to the ends of the crystal, using the bismuth itself as solder. The MR potential probes are sharp bronze pieces which are held against the rod by light spring pressure. The springed contacts of the MR potential probes and of the Hall probes are necessary to avoid stress in the sample and insure good contact during temperature variation. The details of the sample holder are shown in Fig. 3.

D. MEASUREMENTS AND RESULTS

1. MEASUREMENTS OF ZERO-ORDER BRACKETS AT ROOM TEMPERATURE

In order to measure the zero-order brackets according to the expression

$$\rho = \frac{V}{I}\frac{m}{d\ell^2} = \left\{ \frac{1}{[000]_{11}} + \cos^2\theta \left(\frac{1}{[000]_{33}} - \frac{1}{[000]_{11}} \right) \right\}, \qquad (1)$$

it is necessary to measure the resistance V/I, the mass per unit length m/ℓ, the length ℓ, the density d, for several samples with different angles θ

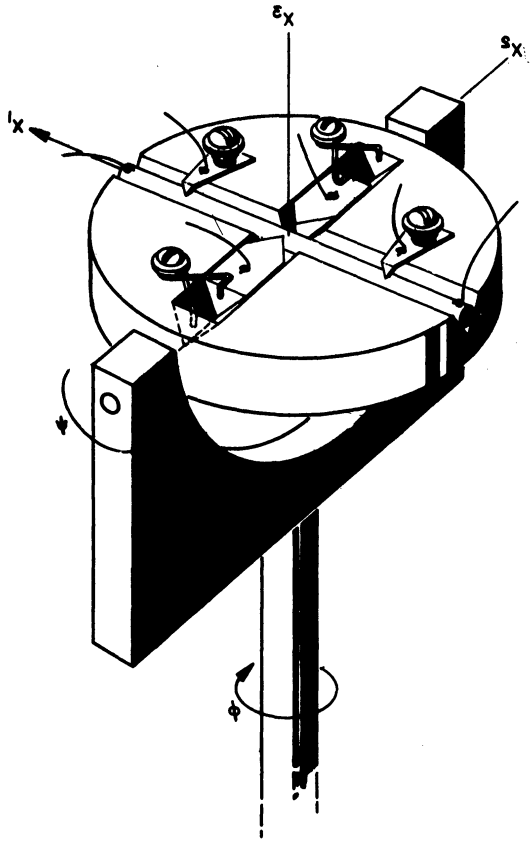

Fig. 3. Sample holder (semi-schematic) showing coordinates $x^1x^2x^3$, current, potential, and Hall electrodes, and ϕ, ψ, rotation axes.

between the trigonal axis and the rod. The resistivity measured at room temperature near 20°C is plotted for different samples vs $\cos^2\theta$ in Fig. 4 after correcting all data to 20°C, using 0.004 per °C as the thermal coefficient of resistivity. From the slope and intercept of the resulting straight line, the zero-order brackets are determined for Bi at 20°C:

$$[000]_{11} = 9.06 \times 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$[000]_{33} = 7.21 \times 10^3 \text{ ohm}^{-1} \text{ cm}^{-1} \quad .$$

The lengths between the marks made by the potential probes on the samples were measured with a traveling microscope to an accuracy of 10^{-3} cm. The density of Bi was taken as 9.67 gm/cm^3 throughout. The mass per unit length was determined by cutting the sample with a sharp razor exactly at the potential probe marks normal to its length, after the electrical measurements were taken, and then weighing. The main source of error is believed to be due to θ; however, this should have very little effect near the endpoints of the line. The error in the above results is estimated to be less than 0.7%, but a few points deviate more than this amount for reasons that are not understood presently.

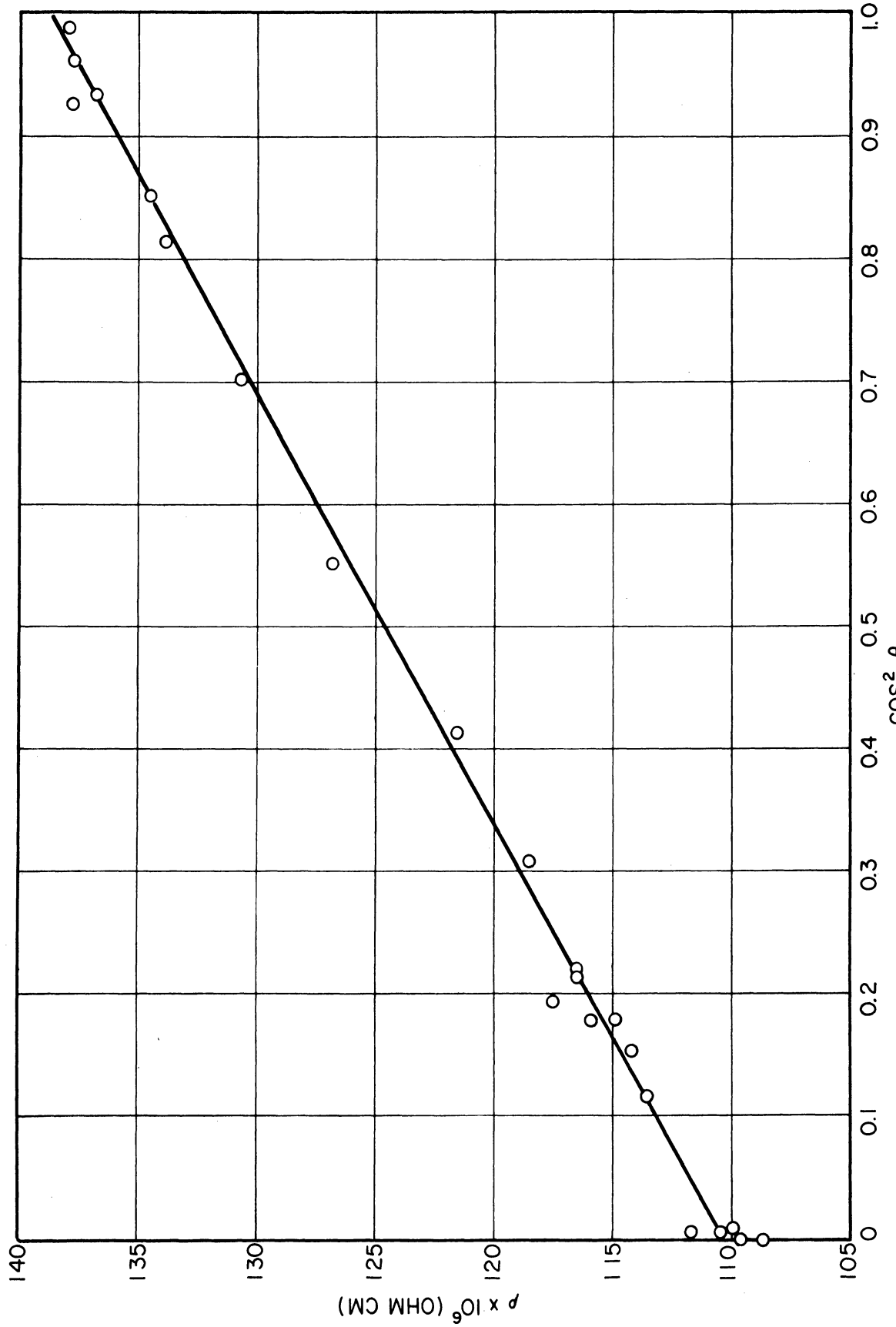

Fig. 4. Resistivity of Bi as a function of the angle θ between wire and trigonal axis.

The results obtained from similar measurements with the various alloy samples scattered too much to allow separate determination of the two brackets. Further work to insure homogeneity is first required. On the whole, the resistivity of Bi-Te was from 10 to 30% lower than pure Bi (the concentration of Te was 0.0212 and 0.122%), while the resistivity of Bi-Sn-Te as described was some 8% higher than that of pure Bi.

2. MEASUREMENT OF ZERO-ORDER BRACKETS AT VARIOUS TEMPERATURES

Two crystals, one with the trigonal axis normal and the other with the trigonal axis parallel to the rod, are used to study the brackets $[000]_{11}$ and $[000]_{33}$, respectively, at various temperatures. The resistance of each sample is measured in an isopentane bath, from -150°C to +20°C. The resistance values at 20°C are then converted to resistivity values of 110 and 139 x 10^{-6} for $1/[000]_{11}$, $1/[000]_{33}$, respectively, which were established previously. The resistivity as a function of temperature is then plotted proportionately in Fig. 5. From the curve, the values of the two brackets at 10° intervals are tabulated in Table I.

TABLE I

EXPERIMENTAL VALUES OF THE ZERO-ORDER BRACKETS AS A FUNCTION OF TEMPERATURE

T (°C)	$[000]_{11}$	$[000]_{33}$
20	9.06 x 10^3 $(\Omega\ cm)^{-1}$	7.21 x 10^3 $(\Omega\ cm)^{-1}$
10	9.36	7.44
0	9.65	7.73
-10	9.97	8.02
-20	10.33	8.36
-30	10.71	8.71
-40	11.10	9.08
-50	11.55	9.52
-60	12.02	9.92
-70	12.53	10.43
-80	13.10	10.95
-90	13.70	11.53
-100	14.40	12.16
-110	15.11	12.85
-120	15.92	13.70
-130	16.83	14.41
-140	17.80	15.28
-150	18.99	16.20

The thermal coefficients of resistivity (α) at 0°C can be read from Fig. 5. It is found that

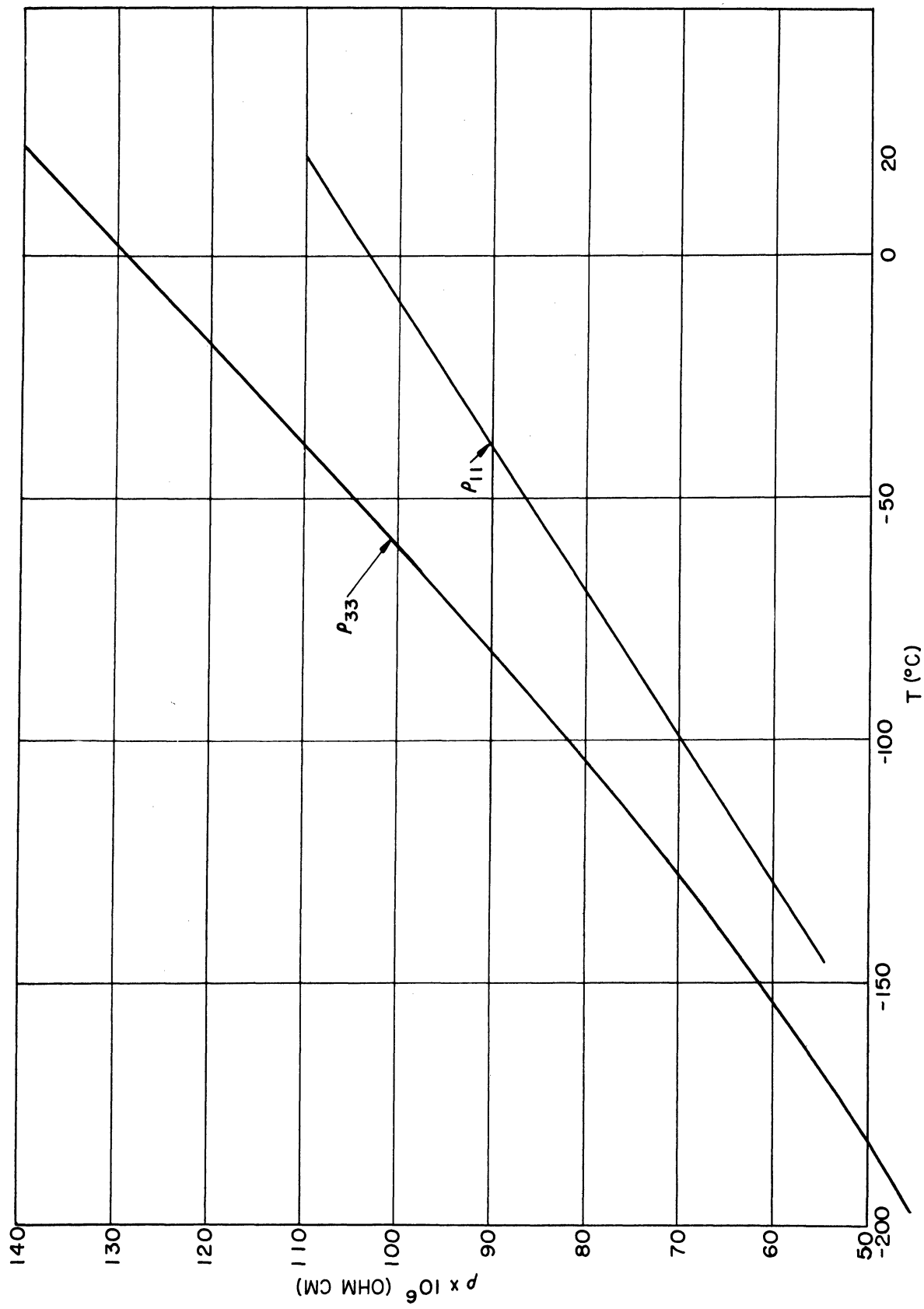

Fig. 5. Principal resistivities of bismuth as a function of temperature.

$$\alpha_{33} = \left[\frac{1}{\rho_0}\left(\frac{d\rho}{dT}\right)_{0°C}\right]_{33} = -\frac{1}{[000]_{33}}\frac{d[000]_{33}}{dT} = 0.0039/°C$$

$$\alpha_{11} = \left[\frac{1}{\rho_0}\left(\frac{d\rho}{dT}\right)_{0°C}\right]_{11} = -\frac{1}{[000]_{11}}\frac{d[000]_{11}}{dT} = 0.00324/°C \quad .$$

No measurements have been taken, so far, for intermediate angles θ that would permit the determination of α as a function of θ. Theoretically the dependence of α on θ is given by

$$\alpha_\theta = \alpha_{11} + \frac{(\alpha_{33} - \alpha_{11})\, y \cos^2\theta}{1 + (y - 1)\cos^2\theta} \quad , \qquad (2)$$

with $y = ([000]_{11}/[000]_{33})_{0°C} = 1.25$ for bismuth.

3. MEASUREMENT OF FIRST-ORDER BRACKETS AT VARIOUS TEMPERATURES

There are two first-order brackets in bismuth, $[100]_{23}$ and $[001]_{12}$. These can be measured only by means of the Hall probes.

The relation between the transverse voltage V across a cylindrical uniform rod of diameter d, with total current I through it, and the brackets up to the first power of B is given by

$$\frac{F_2}{J_1} = \frac{V}{I}\frac{\pi d}{4} = \cos\theta\left[\frac{1}{[000]_{33}} - \frac{1}{[000]_{11}}\right] +$$

$$B\left\{\frac{[100]_{23}}{[000]_{11}[000]_{33}}\left(\cos(x^3,B) - \sin\theta\gamma_3\right) + \gamma_3 \sin\theta\,\frac{[001]_{12}}{[000]_{11}^2}\right\}, \qquad (3)$$

where it is assumed that the sample is oriented in the holder as previously described, with the principle cleavage plane containing the x^2-direction. The angle between the rod and the trigonal axis is θ, as before. The angle ϕ is the angle between the magnetic field and the direction x^2 of the Hall probes. For two special orientations or settings the expression simplifies considerably. In the first setting the sample is placed with the trigonal axis vertically (along the ϕ-axis). Then $\gamma_3 = 0$ and

$$\left(\frac{F_2}{J_1}\right)_H - \left(\frac{F_2}{J_1}\right)_0 = B\left\{\frac{[100]_{23}}{[000]_{11}[000]_{33}}\right\}\cos\theta\sin\phi \quad . \qquad (4)$$

Thus by turning the sample around the ϕ-axis and measuring the amplitude of the Hall voltage the bracket $[100]_{23}$ is obtained. In the second setting the sample is placed with the trigonal axis horizontally (normal to the ϕ-axis). Then $\cos(x^3,H) = \gamma_3 \sin\theta$ and

$$\left(\frac{F_2}{J_1}\right)_H - \left(\frac{F_2}{J_1}\right)_0 = -B\left\{\frac{[001]_{12}}{[000]_{11}^2}\right\} \sin\theta \sin\phi \quad . \qquad (5)$$

Thus by turning the sample around the ϕ-axis and measuring the amplitude of the Hall voltage the bracket $[001]_{12}$ is now obtained. The values of the first-order bracket at various temperatures are given in Table II.

TABLE II

EXPERIMENTAL VALUES OF THE FIRST-ORDER BRACKETS AS A FUNCTION OF TEMPERATURE

T (°C)	$[100]_{23}$	$[001]_{12}$
20	0.94 (Ω cm gauss)$^{-1}$	-1.3×10^{-2} (Ω cm gauss)$^{-1}$
10	1.07	-1.5
0	1.27	-1.8
-10	1.41	-2.1
-20	1.68	-2.5
-30	1.97	-3.1
-40	2.34	-3.8
-50	2.73	-4.4
-60	3.20	-5.1
-70	3.86	-6.3
-80	4.58	-7.5
-90	5.44	-9.2
-100	6.53	-11
-110	7.89	-13
-120	9.60	-16
-130	11.5	-20
-140	14.1	-25
-150	17.6	-35

The values of $[100]_{23}$ were obtained from the experimental curve of sample M, the trigonal axis of which is 30° from the rod. The signal, in microvolts per ampere between the Hall probes with $\phi = 90°$, is plotted in Fig. 6 for both directions of the measuring current. Other samples were measured and agree with the tabulated values better than within 10%. The systematic deviations of the measured points from the average curve are correlated

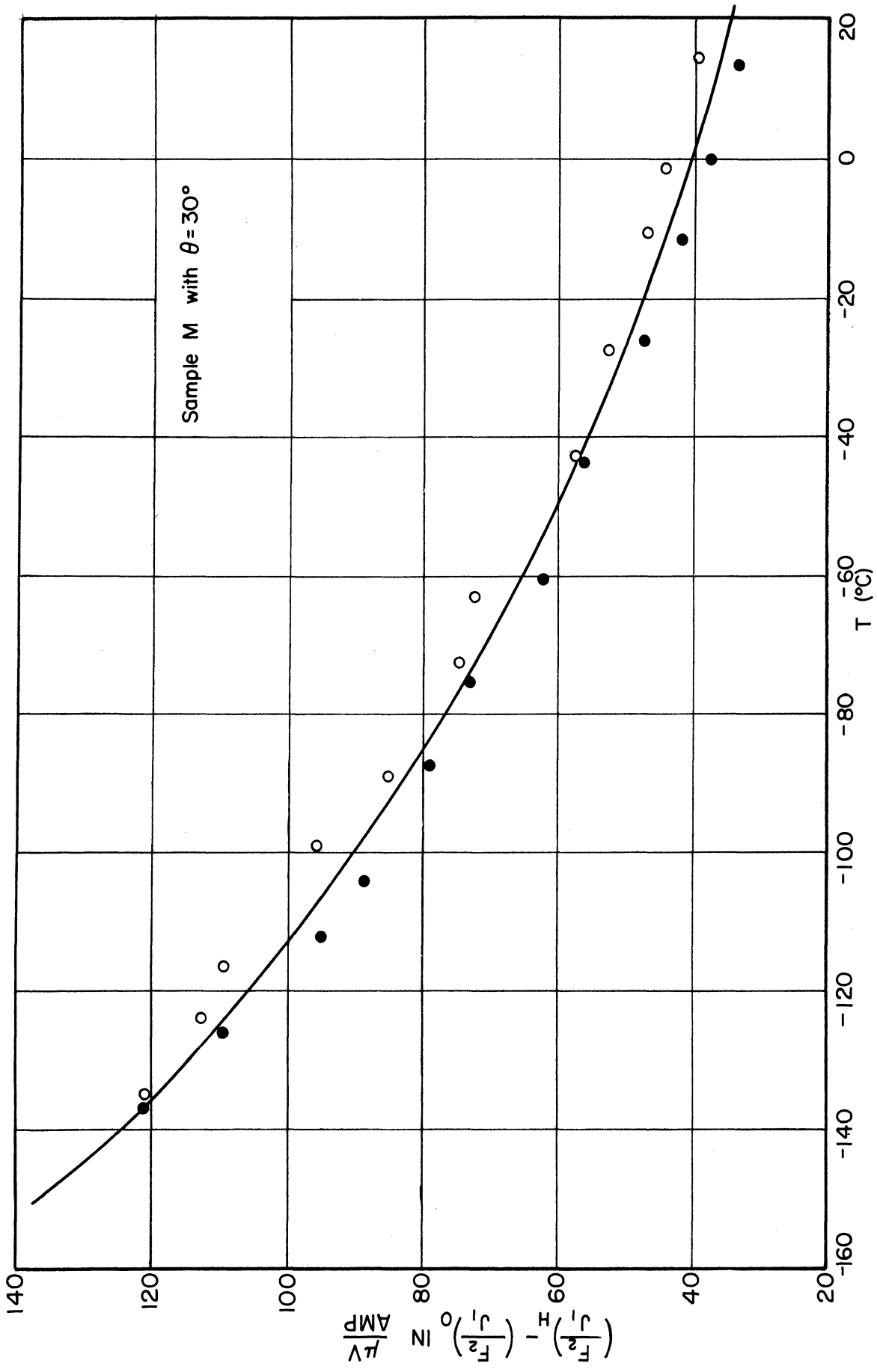

Fig. 6. Measurements from which $[100]_{23}$ is found by formula (4).

with the direction of the measuring current through the sample and are probably of the type discussed in an earlier report; hence, should be averaged. The values of $[001]_{12}$, also from sample M, cannot claim less than 15% error, since the experimental points represent signals of the order of 1 microvolt for the "safe" measuring current, 0.2 amp, while the noise is about 0.1 microvolt (Fig. 7). As of this writing, we have the complete data for $[001]_{12}$ from only this one sample. Other samples were used; however, previous to the sample M, inexperience prevented the results from being complete. The value of $[001]_{12}$ for four measured samples is found to be the same at room temperature, but different at lower temperatures. The differences were probably due to using the current in one direction only and/or too large a current density. But until more samples are measured, the values of $[001]_{12}$ listed should be taken only as order of magnitude.

It should be remarked here that the preparation of the samples does not guarantee that they are of the same purity. The variation in the bracket values, if due to imperfect setting of directions, would be less than 5%. The observed variations from sample to sample must be due to other causes, of which the purity is at present the most suspected one.

Table III and Fig. 8 compare values obtained for the zero- and first-order brackets as a function of temperature by Abeles and Meiboom,[3] Okada,[4] and the present authors. The agreement of our data with those of Abeles and Meiboom is seen to be much better than with Okada's data.

4. METHOD OF DETERMINING SECOND-ORDER BRACKETS

The following conventions will be adhered to regarding the signs and zero points of the various coordinates and angles involved (see Figs. 3, 9, and 10).

The laboratory coordinates are defined as follows. The $+x^3$-direction is the outward normal to the plane of the sample holder. The $+x^1$-direction is along the sample with the trigonal axis falling into the $+x^1+x^3$-quadrant, and $+x^1$ making an angle $+\theta \leq 90°$ with the trigonal axis. The $+x^2$-direction follows right handedly.

The symmetry coordinates are oriented as follows. The $+k_3$-axis is the trigonal axis in the $+x^1+x^3$-quadrant. Normal to k_3, a k_1-axis is chosen along one of the binary axes; k_2 then follows.

The angle κ is measured from the $+x^2$- to the $+k_1$-axis in a right-hand-screw sense around $+k_3$. The direction cosines l_i^{α} between the k_i-axis and the x^{α}-axes are now

3. Phys. Rev., 101, 544 (1956).
4. J. Phys. Soc. Japan, 11, 89 (1956).

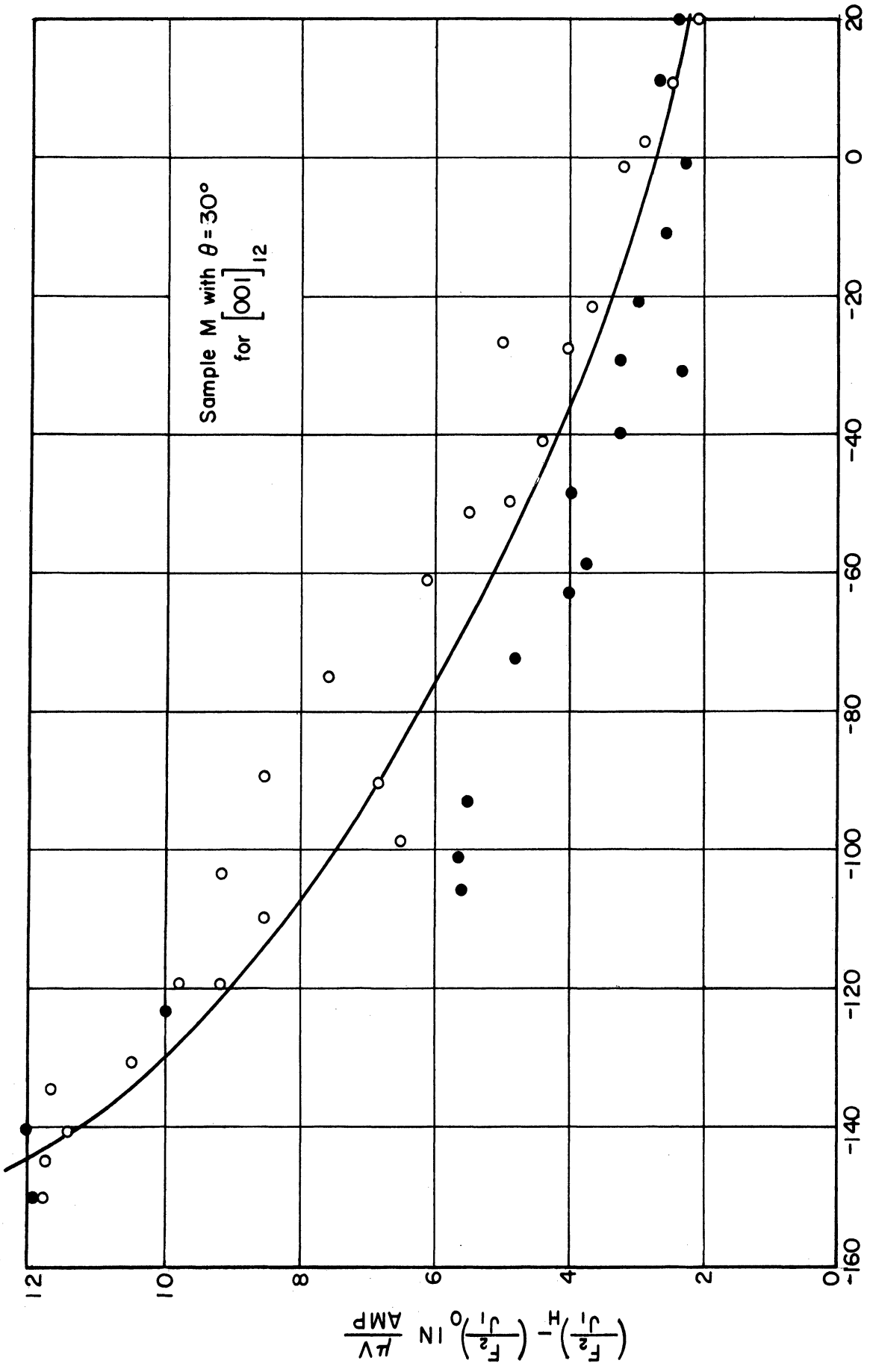

Fig. 7. Measurements from which $[001]_{12}$ is found by formula (5).

TABLE III

COMPARISON FOR ZERO- AND FIRST-ORDER BRACKETS AMONG DIFFERENT WORKERS

Our data: $[000]_{33}$ from sample I, $[000]_{11}$ from sample J, $[100]_{23}$ and $[001]_{12}$ from sample M

		Gauss^{-n} Ω^{-1} cm^{-1}		
Brackets	T (°C)	Ours	Okada	Abeles and Meiboom
$[000]_{11}$	+45	—	7.94×10^3	—
	+27	8.90×10^3	—	8.53×10^3
	0	9.65×10^3	9.48×10^3	—
	-70	12.53×10^3	13.16×10^3	—
	-160	20.3×10^3	22.5×10^3	—
	-197	25.9×10^3	—	27.7×10^3
$[000]_{33}$	+45	—	6.26×10^3	—
	+27	7.02×10^3	—	6.65×10^3
	0	7.73×10^3	7.41×10^3	—
	-70	10.43×10^3	10.05×10^3	—
	-160	17.3×10^3	19.2×10^3	—
	-197	22.2×10^3	—	26.6×10^3
$[100]_{23}$	+45	—	0.601	—
	+27	0.9	—	0.76
	0	1.27	0.839	1.25
	-70	3.86	1.36	3.67
	-160	22.5	2.93	—
	-197	—	—	61.7
$[001]_{12}$	+45	—	-3.78×10^{-2}	—
	+27	-1.3×10^{-2}	—	-3.3×10^{-2}
	0	-1.8×10^{-2}	-3.78×10^{-2}	—
	-70	-6.3×10^{-2}	-5.67×10^{-2}	—
	-160	—	-10.7×10^{-2}	—
	-197	—	—	$-207. \times 10^{-2}$

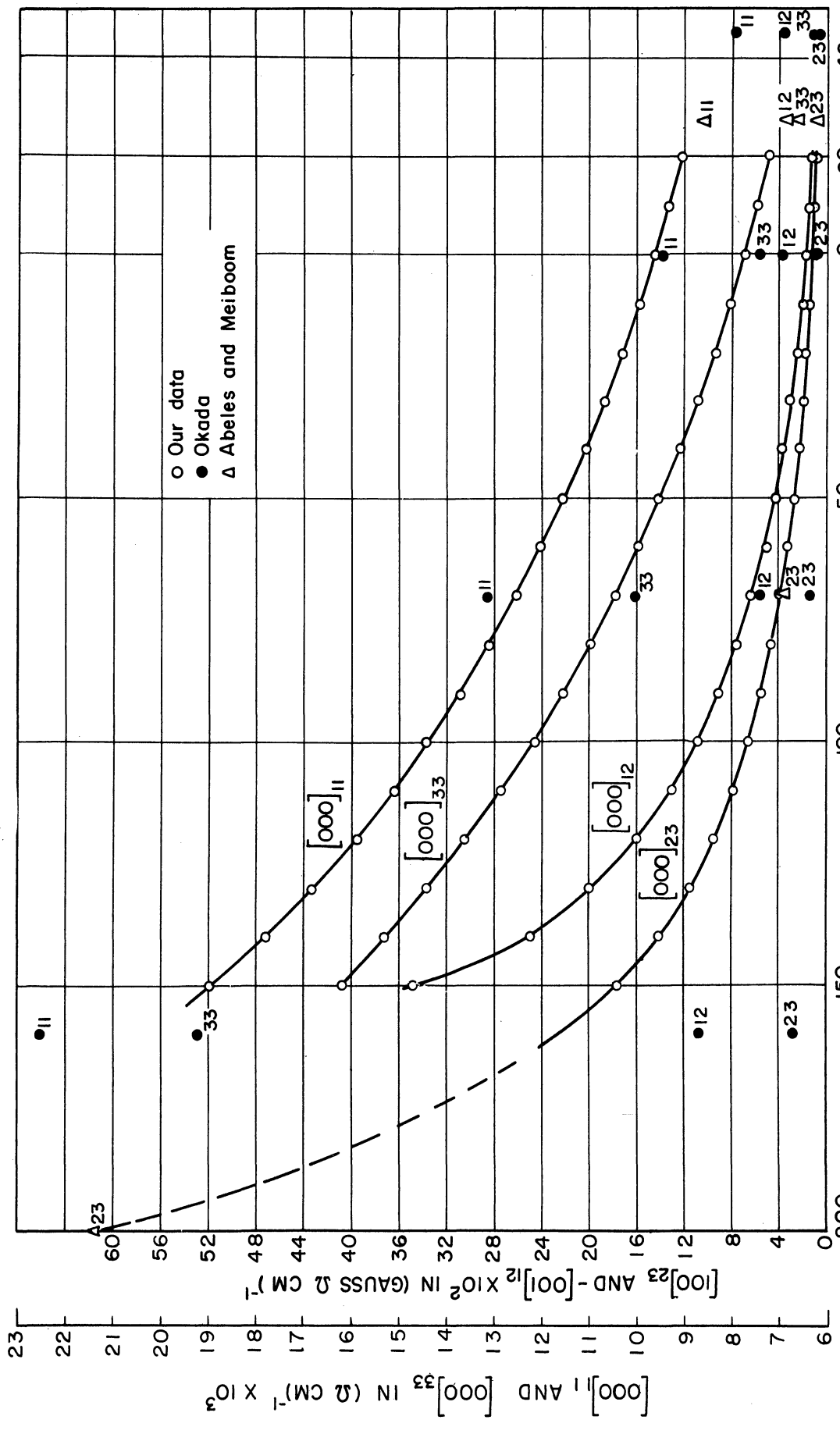

Fig. 8. Comparison of brackets of zero- and first-order by various authors.

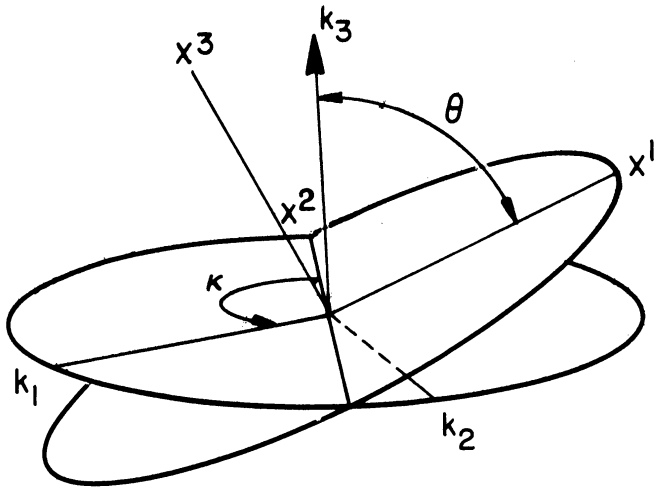

Fig. 9. Orientation of symmetry coordinates $k_1k_2k_3$ relative to the laboratory coordinates $x^1x^2x^3$ defined by the sample holder.

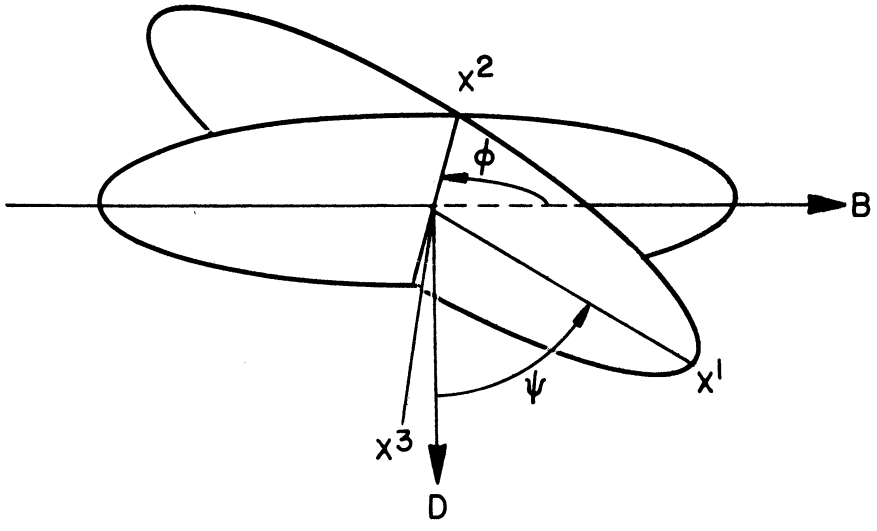

Fig. 10. Orientation of the laboratory coordinates relative to the downward vertical D and the horizontal magnetic field B.

$$\left.\begin{array}{lll} \ell_1{}^1 = -\sin\Theta\sin\kappa & \ell_2{}^1 = -\sin\Theta\cos\kappa & \ell_3{}^1 = \cos\Theta \\ \ell_1{}^2 = +\cos\kappa & \ell_2{}^2 = -\sin\kappa & \ell_3{}^2 = 0 \\ \ell_1{}^3 = +\cos\Theta\sin\kappa & \ell_2{}^3 = +\cos\Theta\cos\kappa & \ell_3{}^3 = \sin\Theta \end{array}\right\} \quad (6)$$

The angle ϕ is measured from B to the x^2-axis in a right-hand-screw sense around the downward vertical. The angle ψ is measured from the downward vertical to the x^1-axis in a right-hand-screw sense around x^2. The direction cosines γ_i between the magnetic field B and the k_i-axis are now, in terms of the Euler angles Θ, ϕ, ψ:

$$\left.\begin{aligned} \gamma_1 &= \cos\phi\cos\kappa - \sin\phi\sin\kappa\cos(\psi - \Theta) \\ \gamma_2 &= -\cos\phi\sin\kappa - \sin\phi\cos\kappa\cos(\psi - \Theta) \\ \gamma_3 &= \sin\phi\sin(\psi - \Theta) \quad . \end{aligned}\right\} \quad (7)$$

For sufficiently low fields, according to equation (27) of the previous report,

$$\frac{\Delta\rho}{\rho} = \frac{B^2}{P_0} R''_{k\ell}\,\gamma_k\,\gamma_\ell \quad , \qquad (8)$$

where

$$P_0 = [000]_{11}\left\{[000]_{33} + \cos^2\Theta\,([000]_{11} - [000]_{33})\right\}$$

and the $R''_{k\ell}$ are tabulated in terms of brackets and $\ell_1{}^1$, $\ell_2{}^1$, $\ell_3{}^1$, in Table XVI of the previous report. By substituting from this table in the right-hand side of the equation (8), making use of the above expressions (6) and (7) for $\ell_i{}^\alpha$ and γ_k, an expression of $\Delta\rho/\rho$ in terms of brackets, κ, Θ, ϕ, and ψ can be obtained. The brackets are material constants. Also, κ and Θ are constants for any given sample but may vary from sample to sample. Thus if ψ is set at any fixed value, then $\Delta\rho/\rho$ depends on ϕ. This dependence, which does not enter through $R''_{k\ell}$ but only through $\gamma_k\,\gamma_\ell$, is obviously of the form*

$$\left[\frac{\Delta\rho}{\rho} = C_0 + C_2\cos 2(\phi - \phi_2)\right]_{\psi = \text{const.}} \qquad (9)$$

where the three constants C_0, C_2, and ϕ_2 depend on the brackets and on κ, Θ, as well as on ψ, for given B.

The experimental determination of the brackets is now carried out by varying ϕ with constant ψ. Of course, the varying of ϕ only allows the

* See, however, the Appendix.

determination of the three constants C_0, C_2, and ϕ_2, while there are eight independent brackets. It might seem that by evaluating the three constants for various values of ψ sufficient material would be available to derive all the brackets. This, however, is not so. From one sample alone, at most six constants R^n_{kl} or six equivalent bracket combinations can be obtained. To do this, several settings of the angle ϕ must be used and ϕ must be varied for each setting. In order to determine the eight independent brackets of second order, some measurements must be made on at least two samples with different axis orientations relative to the length of the sample (different θ).

Setting 1

The trigonal axis is set along the ϕ-axis downward ($\psi - \theta = 0°$). This is the same setting as used for the measurements of $[100]_{23}$. We denote the result by

$$\frac{\Delta\rho}{\rho_0} = {}^1C_0 + {}^1C_2 \cos 2 (\phi - {}^1\phi_2) \quad . \tag{10}$$

Setting 2

The trigonal axis is set horizontally ($\psi - \theta = -90°$). This is the same setting as used for the measurements of $[001]_{12}$. The result is denoted by

$$\frac{\Delta\rho}{\rho_0} = {}^2C_0 + {}^2C_2 \cos 2 (\phi - {}^2\phi_2) \quad . \tag{11}$$

For further necessary data we take the difference between two settings.

Setting 3 $\quad \psi - \theta = 45°$

Setting 4 $\quad \psi - \theta = -45°$

The difference will have the form

$$\frac{\rho_{45} - \rho_{-45}}{\rho_0} = {}^\Delta C_0 - {}^\Delta C_0 \cos 2\phi + {}^\Delta C_2 \sin 2\phi \quad , \tag{12}$$

where the equality of the first two coefficients is a direct consequence of the relations developed in previous reports. Other required identities are

$${}^1C_0 + {}^1C_2 \cos 2\,{}^1\phi_2 = {}^2C_0 + {}^2C_2 \cos 2\,{}^2\phi_2 \tag{13}$$

and

$${}^2C_2 \sin 2\,{}^2\phi_2 = -{}^\Delta C_2/\sqrt{2} \quad . \tag{14}$$

The brackets can now be expressed as follows in terms of these measured quantities, using the abbreviations:

$$P_o = [000]_{11}\left\{[000]_{33} + \cos^2\theta\,([000]_{11} - [000]_{33})\right\} \tag{15}$$

$$\Delta = -2\sin^2\theta \sin 2\theta \sin\kappa\,(1 + 2\cos 2\kappa) \tag{16}$$

$$[200]_{23}[000]_{11} = \frac{2P_o\,{}^1C_2}{B^2\Delta}\sin^2\theta \sin 2\,{}^1\phi_2 \tag{17}$$

$$([200]_{11} - [200]_{22})[000]_{33} - [100]_{23}^2 = \frac{-4P_o\,{}^1C_2}{B^2\Delta}\sin 2\theta \sin(2\,{}^1\phi_2 + 3\kappa) \tag{18}$$

$$[011]_{11}[000]_{33} = \frac{2P_o}{B^2\Delta}\sin 2\theta\,{}^\Delta C_2\sqrt{2} \tag{19}$$

$$[011]_{23}[000]_{11} - [100]_{23}[001]_{12} = \frac{4P_o}{B^2\Delta}\sin\theta({}^\Delta C_o \sin 3\kappa - \frac{1}{2}\,{}^\Delta C_2\sqrt{2}\cos 3\kappa) \tag{20}$$

$$\left\{([200]_{11} + [200]_{22})[000]_{33} + [100]_{23}^2\right\}(1 - \cos^2\theta) +$$

$$2\left\{[200]_{33}[000]_{11} + [100]_{23}^2\right\}[000]_{11}\cos^2\theta/[000]_{33} = \frac{-2P_o\,{}^1C_o}{B^2} \tag{21}$$

$$([002]_{11} + [001]_{12}^2/[000]_{11})[000]_{33}(1 - \cos^2\theta) +$$

$$[002]_{33}[000]_{11}^2[000]_{33}\cos^2\theta = -\frac{P_o}{B^2}({}^2C_o - {}^2C_2\cos 2\,{}^2\phi_2)\ . \tag{22}$$

The first four equations express, in terms of measured quantities, the brackets $[200]_{23}$, $[011]_{11}$, $[011]_{23}$, and the combination $[200]_{11} - [200]_{22}$. These can therefore be found from each sample individually. The last two equations express, in terms of measured quantities, the brackets and combinations $[200]_{11} + [200]_{22}$, $[200]_{33}$ and $[002]_{11}$, $[002]_{33}$. By measuring several (at least two) samples with different θ, and plotting the right-hand side vs $\cos^2\theta$, a straight line should result, permitting the determination of all four quantities. Finally, by comparing the results for $[200]_{11} + [200]_{22}$ and $[200]_{11} - [200]_{22}$, one can arrive at $[200]_{11}$ and $[200]_{22}$ individually.

While a number of other procedures may be followed, the above procedure is probably the simplest and most direct. It is interesting to note that the brackets that can be determined from one sample require knowledge of θ and κ, while the brackets that come from several samples only require knowledge of θ.

5. RESULTS OF MEASUREMENTS OF SECOND-ORDER BRACKETS

The following (incomplete) results have so far been obtained for the brackets of second order for pure bismuth. They should be considered as subject

to change when further work is done, but the general order-of-magnitude agreement with Abeles and Meiboom's data indicates that they are most likely reliable.

Since the data on Setting 3—Setting 4 were not obtained for the samples reported on, only the data listed below are as yet available. Table IV gives $[200]_{23}$ and $[200]_{11} - [200]_{22}$ for the temperature range of 20°C to -70°C (see Appendix) as derived by equations (17) and (18). By combining these results with those of another sample, we arrive at the preliminary results for the second-order brackets at 20°C given in Table V, where also a comparison with similar data of Okada and of Abeles and Meiboom is shown. Except for the $[200]_{23}$ value, the agreement is very satisfactory. Figure 11 shows that the agreement with Okada at lower temperatures is not so good as at room temperature.

TABLE IV

EXPERIMENTAL VALUES OF SECOND-ORDER BRACKET COMBINATIONS AS A FUNCTION OF TEMPERATURE

Data from samples E

T (°C)	$[200]_{23}$ Gauss^{-2} Ω^{-1} cm^{-1}	$[200]_{11} - [200]_{22}$ Gauss^{-2} Ω^{-1} cm^{-1}
20	-4.21×10^{-5}	$+11.7 \times 10^{-5}$
10	-6.0	+14.8
0	-8.6	+20.2
-10	-12.7	+23.6
-20	-18.9	+31.7
-30	-27.2	+41.1
-40	-37.8	+55.1
-50	-51.6	+71.3
-60	-65.8	+92.1
-70	-100	+129

TABLE V

COMPARISON FOR SECOND-ORDER BRACKETS AMONG DIFFERENT WORKERS

Gauss^{-2} Ω^{-1} cm^{-1}

Bracket	Ours, 20°C	Okada,* 20°C	Abeles and Meiboom, 27°C
$[200]_{11}$	-7.4×10^{-5}	-7.4×10^{-5}	-6.5×10^{-5}
$[200]_{22}$	-19.1×10^{-5}	-20×10^{-5}	-19.3×10^{-5}
$[200]_{23}$	-4.21×10^{-5}	-0.51×10^{-5}	not given
$[002]_{11}$	-3.36×10^{-5}	-5.2×10^{-5}	-2.25×10^{-5}

* Interpolated; Okada's data given at 0° and 45°C.

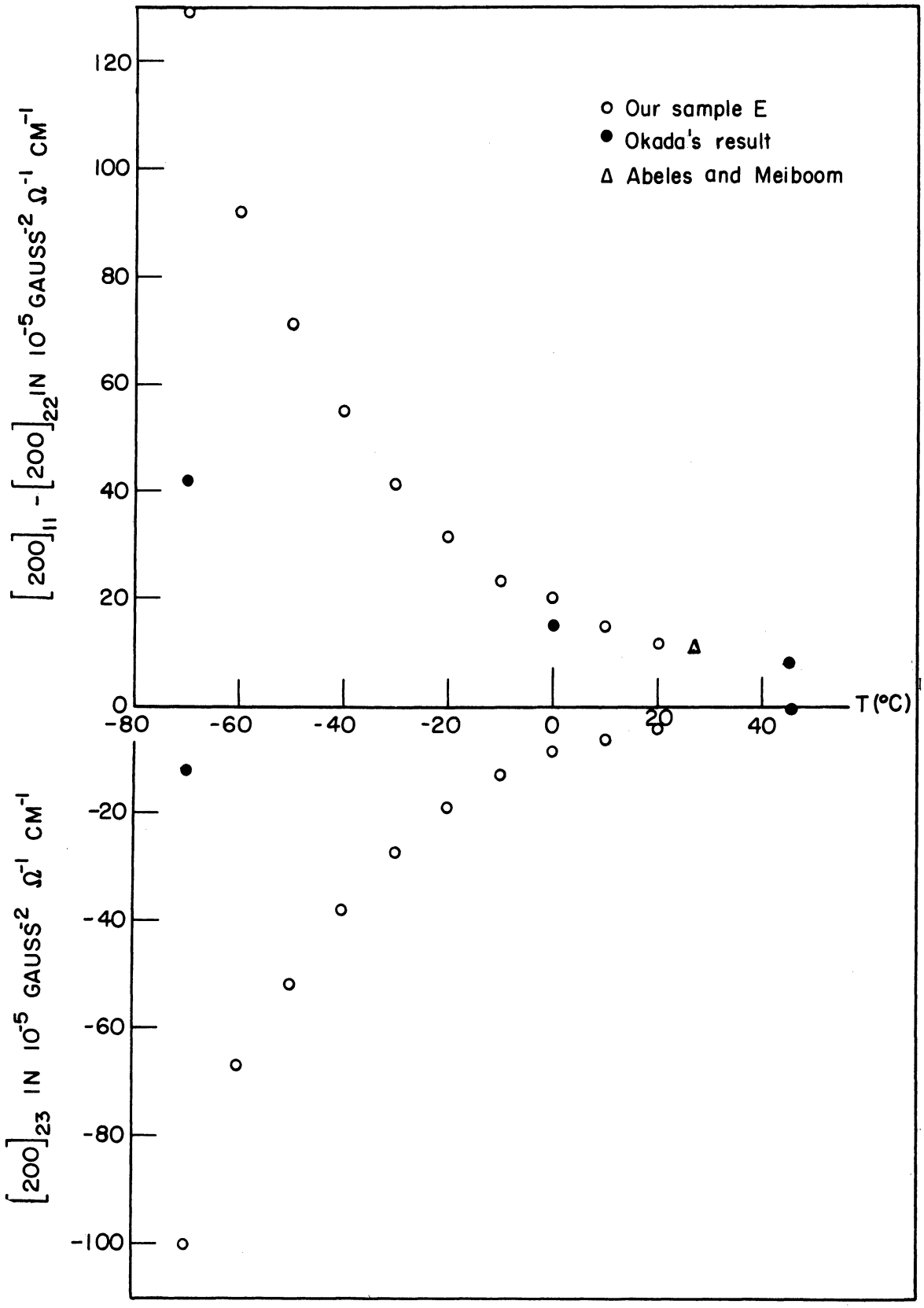

Fig. 11. Comparison of $[200]_{23}$ and of $[200]_{11} - [200]_{22}$ by various authors.

6. MEASUREMENTS ON ALLOYS

Only very preliminary measurements have been made on alloy samples, only at room temperature. For the Te-doped samples the magneto resistance was an order of magnitude smaller than for pure Bi. For the sample of Sn-Te-doped Bi the magneto resistance was about half that of pure Bi, but further and more systematic study is necessary along these lines.

7. DISCUSSION

The results reported are just a beginning. It has taken considerable effort and time to develop the methods of growing suitable single crystals and of overcoming difficulties in the experimental techniques of measurement. While there is still room for considerable improvement, we are at present in a position to turn out bracket values for different materials and higher orders if this project is continued, as the results presented show.

For the near future it is intended to take further measurements in order to corroborate the present results and improve their accuracy. Also, a more systematic study of alloys of Bi and IV-VI compounds is intended. Any detailed discussion will be deferred till these measurements are available. A general discussion for Bi can be found in the paper of Abeles and Meiboom (Reference 3).

While a certain amount of electron theoretical interpretation is common nowadays in the literature for the brackets up to order 2, the interpretation of the values of brackets of higher order is a matter of further study.

APPENDIX

The Form of Equation (9)

The result of a run as described in Section D.4 is in general of the form

$$\frac{\Delta\rho}{\rho} = C_0 + C_2 \cos 2(\phi - \phi_2) + C_4 \cos 4(\phi - \phi_4) + \cdots, \qquad (A1)$$

which is compatible with equation (9) only if C_4, which is proportional to B^4, is negligible compared to C_0 and C_2, which are essentially proportional to B^2. Since

$$\left.\begin{aligned} C_0 &= C_{02} B^2 + C_{04} B^4 + \cdots \\ C_2 &= C_{22} B^2 + C_{24} B^4 + \cdots \\ C_4 &= \qquad\quad C_{44} B^4 + \cdots , \end{aligned}\right\} \qquad (A2)$$

this can always be achieved by making B sufficiently small. Therefore, a first check run is made for each sample and temperature to make sure that $\Delta\rho/\rho$ as a function of ϕ does not contain any appreciable amount of fourth or higher harmonics. If fourth or higher harmonics are present in equation (A1), it is not correct to subtract them out and use the C_0 and C_2 terms only, since these terms contain also fourth-power contributions. The best procedure for eliminating the influence of fourth-power terms from C_0 and C_2 if they are not negligible has not been worked out at the time of writing of the present report. It is preferred not to vary B for intercomparison of further measurements. Thus we confine our attention to those cases where B is small enough to make C_4 negligible and it is assumed that then also $C_{04} B^4$ and $C_{24} B^4$ are negligible.

The occurrence of the fourth-order term at low temperatures is clearly visible, for example, in Fig. A1, representing a curve of $\Delta\rho/\rho$ vs ϕ for sample E, Setting 1 at -150°C. The relative magnitude of C_0, C_2, and C_4 as a function of temperature is shown in Fig. A2. It is seen that the quadratic approximation can be used successfully only for temperatures above -100°C.

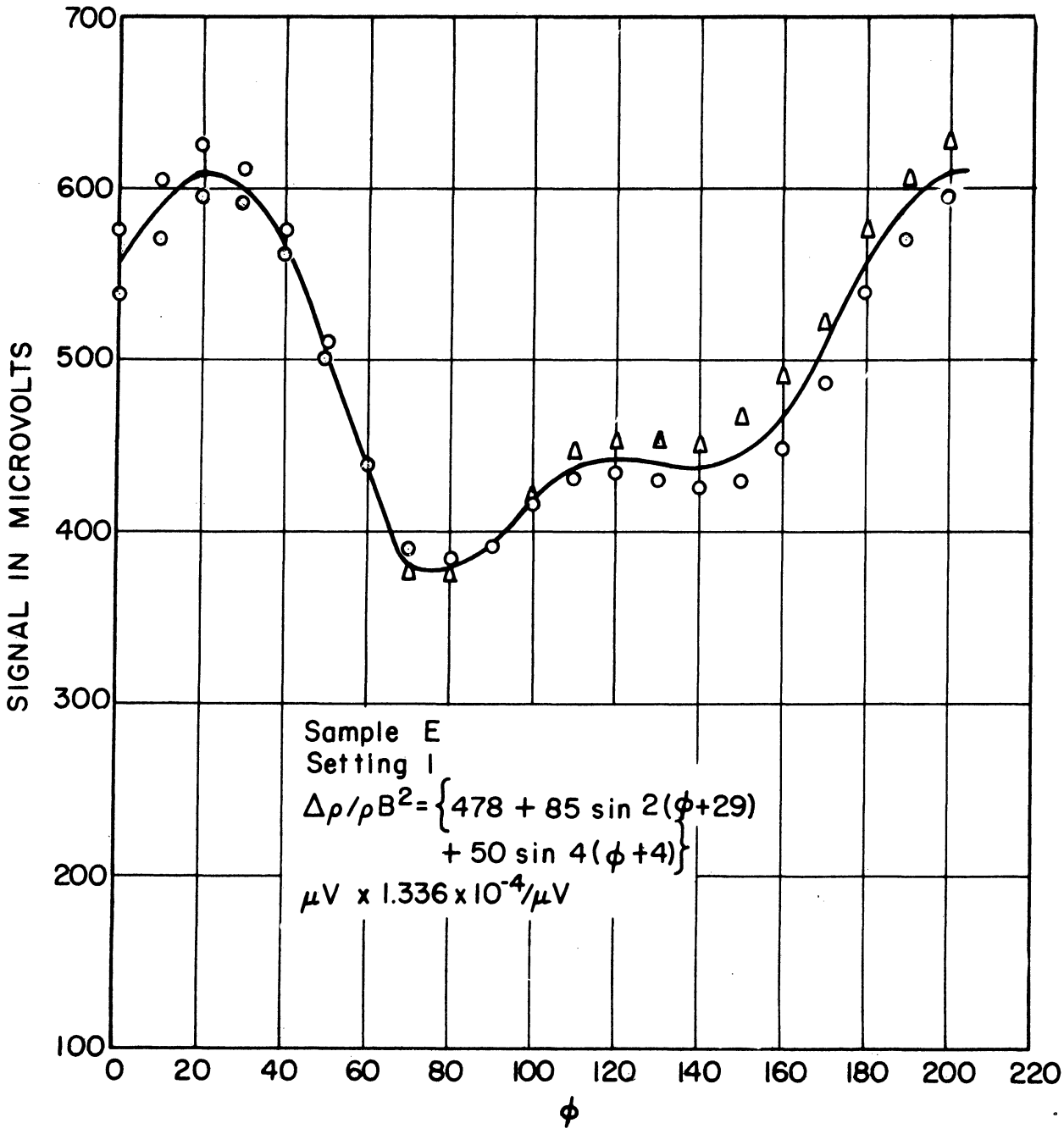

Fig. A1. Presence of fourth harmonic at -150°C.

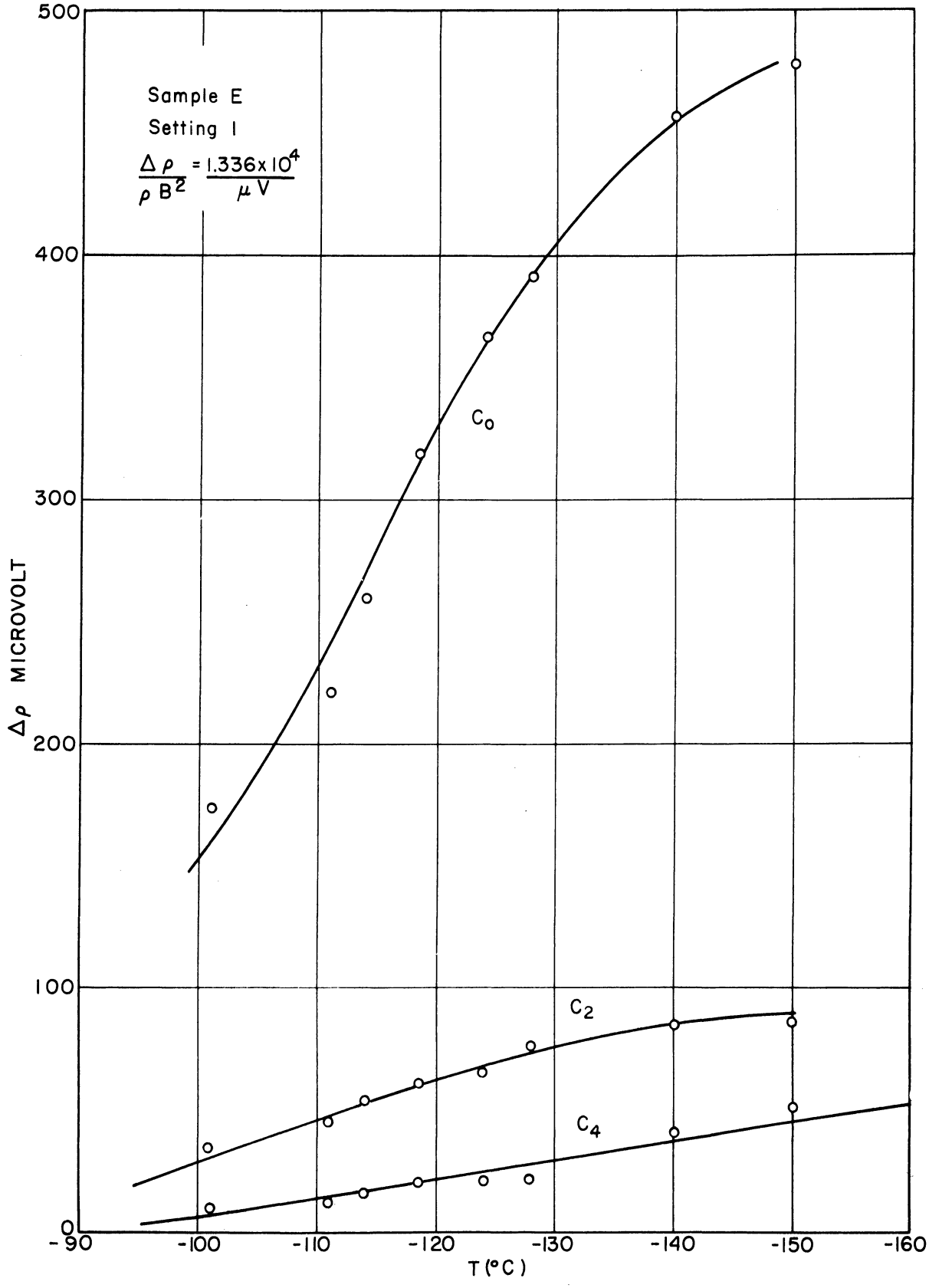

Fig. A2. Relative amplitude of C_0, C_2, and C_4.