Low-Temperature Galvanomagnetic Effects in Bismuth Monocrystals*

R. A. CONNELL† AND J. A. MARCUS
Northwestern University,‡ Evanston, Illinois
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Measurements of the Hall coefficient and magnetoresistance have been made on bismuth monocrystals at liquid helium temperatures in the range from 3 kilogauss to 16 kilogauss for all principal crystallographic orientations. Two complete sets of oriented crystals were used, one set was grown from unpurified bismuth, the other from zone-refined bismuth. Pronounced de Haas-van Alphen type oscillations were observed with the same periods for both galvanomagnetic effects. For a given orientation of the magnetic field with respect to the crystal axes, the periods were in good agreement with the values found in the de Haas-van Alphen effect and were independent of current direction. Impurities were found to have little effect on the period but a large effect on the amplitude of the oscillations and on the monotonic component of both magnetoresistance and Hall effect.

INTRODUCTION

THE oscillatory dependence of the Hall coefficient on magnetic fields at liquid hydrogen temperatures was first observed by Gerritsen in 1940[1] and investigated in greater detail by Brodie in 1954.[2] Measurements[3,4] at liquid helium temperatures definitely established that the oscillations were periodic in reciprocal magnetic field and of the same period as the de Haas-van Alphen oscillations in the magnetic susceptibility. Peierls'[5] explanation of the de Haas-van Alphen oscillations in terms of the quantization of the conduction electrons in the presence of the magnetic field implies that under the right experimental conditions all the physical quantities that depend on the distribution of the electrons in the quantized energy levels should exhibit an oscillatory behavior periodic in reciprocal field. The experimental conditions are more easily realized for bismuth than any other metal and oscillations have been observed in the thermoelectric power and thermal conductivity[6] as well as in the Hall effect, magnetoresistance, and magnetic susceptibility.

The susceptibility oscillations have been studied in some detail, and the theoretical expression derived by Landau in 1939 has, with minor improvements, been able to account for most of the experimental data so far reported. In its simplest form,[7] Landau's result for the anisotropic susceptibility may be expressed as

$$\Delta\chi=\sum_i\frac{A\Delta m_i^*}{\rho}\left\{\frac{\pi^2}{6}\left(\frac{k}{E_0}\right)^{\frac{1}{2}}-\frac{1}{T^{\frac{1}{2}}}\left(\frac{2\pi^2kT}{\beta_i^*H}\right)^{\frac{3}{2}}\exp\left(-\frac{2\pi^2kT}{\beta_i^*H}\right)\sin\left(\frac{2\pi E_0}{\beta_i^*H}-\frac{\pi}{4}\right)\right\}, \tag{1}$$

where

$$E_0\gg kT\geqslant\beta^*H/2\pi^2.$$

The quantity $\Delta\chi$ is the difference of the mass susceptibilities in two directions at right angles, ρ is the density, A is a constant, β_i^* is a double effective Bohr magneton, m_i^* is a suitable effective electronic mass, and E_0 is the degeneracy parameter of the relevant electrons. By using β^* and E_0 as adjustable parameters, values for effective masses and the effective number of electrons could be obtained. In general these quantities were found to be unusually small, giving rise to the idea that the de Haas-van Alphen oscillations arose from special "pockets" of low effective-mass electrons located near a Brillouin zone boundary, where the curvature of the energy surfaces might be expected to be quite high. It was then of interest to see how some of the other electronic properties of a metal would behave under similar conditions.

Unfortunately the theoretical work done on transport phenomena has been much less satisfactory. The standard expressions[8] are valid only for weak fields ($\omega\tau\ll1$, where $\omega=eH/m^*c$ and τ is the relaxation time), where quantum effects can be neglected. For this reason, most of the experimental results on the subject have been analyzed in terms of a semiempirical equation, constructed by analogy with Eq. (1). Davydov and Pomeranchuk,[9] using a two-band model for bismuth, derived a strong-field expression for the magnetoresistance for one orientation of the magnetic field. Their formalism was rather cumbersome for comparison with

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† Now at International Business Machines (IBM) Research Laboratory, Poughkeepsie, New York.
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[1] A. N. Gerritsen and W. J. de Haas, Physica 8, 802 (1940).
[2] L. C. Brodie, Phys. Rev. 93, 935 (1954); Ph.D. thesis, Northwestern University, 1954 (unpublished).
[3] Reynolds, Hemstreet, Leinhardt, and Triantos, Phys. Rev. 96, 1203 (1954).
[4] J. A. Marcus, Phys. Rev. 98, 1540 (1955).
[5] R. Peierls, Z. Physik 80, 763 (1933).
[6] M. C. Steele and J. Babiskin, Phys. Rev. 98, 359 (1955).
[7] D. Shoenberg, Trans. Roy. Soc. (London) 245, 1 (1952).
[8] A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1953), second edition, Chap. 8.
[9] B. Davydov and I. Pomeranchuk, J. Phys. (U.S.S.R.) 2, 147 (1940).

experiment, however, and they were unable to account for any Hall effect.

Recently Zilberman[10] has worked out expressions for the galvanomagnetic effects in strong fields ($\omega\tau \gg 1$) on the basis of the isotropic two-band model. Assuming that $\exp(2\pi^2 kT/\beta H) \gg 1$, $kT \leqslant \beta H$, $\beta H \ll E_0$, and $E_0 \gg kT$, he obtains for the resistance

$$\rho_H = \frac{CH^2(f_1+f_2)}{ec^2H^2(N_1-N_2)^2+cC^2(f_1+f_2)^2}, \tag{2}$$

where

$$f_1 = \frac{8}{3}E_0^2 m_1^2 \left\{ 1+\frac{9}{40}\left(\frac{\beta_1 H}{E_0}\right) - \left(\frac{5\pi^2\sqrt{2}kT}{(\beta_1 H E_0)^{\frac{1}{2}}}\right) \times \exp\left(-\frac{2\pi^2 kT}{\beta_1 H}\right)\cos\left(\frac{2\pi E_0}{\beta_1 H}-\frac{\pi}{4}\right)\cdots \right\}, \tag{3}$$

and f_2 is obtained from f_1 by replacing m_1 by m_2 and E_0 by $A_0 - E_0$. The subscripts 1 and 2 refer to the conduction and valence bands, respectively. N_1 is the number of electrons per cc and N_2 the number of holes.

Following the practice of Borovik,[11] Zilberman expresses his results for the Hall effect in terms of the ratio of the Hall field to the electric field parallel to the current flow:

$$\frac{F_y}{F_x} = A\sigma H = \frac{-H(N_1-N_2)}{C(f_1+f_2)}. \tag{4}$$

The standard Hall coefficient would then be

$$A = \frac{-(N_1-N_2)H^2}{eC^2H^2(N_1-N_2)+cC^2(f_1+f_2)^2}. \tag{5}$$

In dealing with a highly anisotropic substance such as bismuth, these expressions must be used with caution, but certain qualitative comparisons can be made concerning the over-all behavior of the Hall coefficient and magnetoresistance.

In bismuth the experimental situation is complicated by the extreme sensitivity of the galvanomagnetic effects to the presence of small amounts of impurities. The results of various authors do not agree even as to the sign of the Hall coefficient for various orientations.[1,2] It has been only recently that any sort of agreement has been reached concerning the room-temperature values of the Hall coefficient. Since none of the more recent low-temperature investigations covered more than one or two crystallographic orientations, it seemed advisable to attempt a study for all principal orientations, using crystals prepared in such a manner that the results for one orientation could be compared directly with those for another. By comparing measurements from crystals of different purity, it was hoped that the effects due to impurities could be identified and isolated, and the orientation dependence of both the oscillatory and monotonic components of the Hall and magnetoresistance curves determined. A preliminary report of this work has already been given.[12]

[10] G. E. Zilberman, J. Exptl. Theoret. Phys. (U. S. S. R.) **29**, 762 (1956) [translation: Soviet Phys. JETP **2**, 650 (1956)].

[11] E. S. Borovik, J. Exptl. Theoret. Phys. (U. S. S. R.) **30**, 262 (1956) [translation: Soviet Phys. JETP **3**, 243 (1956)].

EXPERIMENTAL DETAILS

A. Crystals

The crystals used in this investigation were grown from an ingot of bismuth supplied by the Cerro de Pasco Copper Company. Spectrographic analysis by the Accurate Metal Laboratories of Chicago disclosed less than 0.001% Mg and Pb, respectively, and less than 0.0005% Cu in their sample.

A preliminary set of crystals was grown from the unpurified bismuth. A second set was grown from a rod which had been zone refined. Spectrographic analysis did not appear to be sensitive enough to give much information concerning the amount of purification attained by this method, however.

For a rhombohedral crystal such as bismuth there are three principal crystallographic orientations for both the current and magnetic field—parallel to the trigonal axis, parallel to a binary axis, or perpendicular to the plane formed by the trigonal axis and a binary axis. Limiting ourselves to transverse galvanomagnetic effects, where current, magnetic field and Hall field are mutually perpendicular, we find that there are six primary crystal orientations. By growing crystals of approximately square cross section, measurements of the Hall voltage for two orientations of the magnetic field could be made on the same crystal. This is advantageous not only because it reduces the number of crystals required for a complete orientation study from six to three, but allows us to compare the results of the two orientations directly, without worrying about such things as differences in purity.

All the crystals used in this work were about 2 mm by 2 mm by 30 mm. Galvanomagnetic effects were easily measureable for these dimensions, and the length was sufficient to eliminate end effects due to the current leads.

The single crystals of bismuth were grown in a modified Schubnikow mold constructed from Pyrex plates ground into appropriate shapes, and held in place by phosphor-bronze springs. These plates could be chemically cleaned, thus reducing the possibility of contamination.

Bismuth to be used was first etched in a dilute solution of nitric acid, outgassed in a rough vacuum, and cast under vacuum into the mold. The rod thus obtained was etched once again and returned to the mold, but this time with a seed crystal at the lower end

[12] R. A. Connell and J. A. Marcus, Phys. Rev. **100**, 1256(A) (1955).

of the mold. By adjusting the current in an electric oven which was designed with a temperature gradient along its length, it was possible to melt the rod, fusing it with the seed, and then by reducing the current slowly, to freeze the bismuth from the seed and upwards.

Crystal orientations were determined to within 2° by examining the reflections from the etched surface of the crystal with an optical goniometer.

In the zone-purification process, a quantity of bismuth was sealed under vacuum in a length of Pyrex tubing, the walls of which were lubricated with a small amount of Dow 550 silicone oil. This "boat" was then drawn through a series of electrical heaters at a rate of 20 cm per hr. After 90 "passes," the boat was broken open, and the bismuth divided up to be used in growing crystals as described previously.

B. Magnet

Horizontal magnetic field strengths up to 18 kilogauss were supplied by a Weiss-type water-cooled electromagnet capable of rotation about a vertical axis. For these measurements, 1-inch diameter tapered pole pieces were used, with a gap of $\frac{3}{4}$ inch. Field variation along the horizontal axis of the magnet amounted to about 2%, with a 5% variation across the face. In the region occupied by the crystal, the variations were less than 1%. The magnet current was supplied by a bank of storage batteries. The current could be adjusted to within 0.1% by the use of a group of variable resistors in series with the magnet coils. Time drift was found to be negligible during the time taken to make a measurement.

C. Measurement Technique

Specimens were mounted in a Bakelite crystal holder which was suspended in the experimental Dewar at the end of a length of thin-walled stainless steel tubing. Current leads consisted of thin strips of copper ribbon soldered to each end of the crystal with Woods metal. Two pairs of spring-loaded phosphor-bronze needles served as Hall probes. The two mutually perpendicular sets of probes were accurately positioned in a plane perpendicular to the crystal length by means of bronze bushings. An additional probe, located 3 mm down the length of the crystal from the Hall probes, was used in conjunction with the neighboring Hall probe for magnetoresistance measurements.

Experimentally the Hall coefficient is defined by the equation

$$A=(V_a t/HI)\times 10^9,$$

where A is in emu, H is in gauss, the Hall potential V_a is in volts, the measuring current I is in amperes, and the crystal thickness t (the dimension perpendicular to the rod length and the set of Hall probes being used) is in centimeters. The Hall potential is usually considered to be that portion of the transverse voltage which changes sign with reversal of the magnetic field or current. If we write $V=V_a+V_r+V_c$, where V is the measured voltage, V_a is the Hall voltage defined above, V_r is the resistance component which changes sign with current only, and V_c is a potential independent of both field and current (contact potential, etc.), it can be seen that

$$4V_a=V(I,H)-V(-I,H)-V(I,-H)+V(-I,-H),$$
$$4V_r=V(I,H)-V(-I,H)+V(I,-H)-V(-I,-H).$$

Thus the Hall voltage can be isolated by making measurements for both directions of current and magnetic field. In practice, V_c was found to be negligibly small, so that only the magnetic field was reversed.

It cannot be assumed *a priori* that V_r comes only from misalignment of the Hall probes, for in an anisotropic media it is possible for a transverse ohmic potential to exist. This is of course a very difficult thing to separate experimentally, and no reliable conclusions can be drawn from the results of this investigation. In several cases the ohmic voltage showed significant differences in behavior from the magnetoresistance as measured from probes aligned along the rod length, so that such an effect cannot be ruled out entirely.

At liquid helium temperatures the Hall and ohmic voltages were measured with a Brown recording potentiometer, which could be read to 0.01 mv in the range from 0 to 1.0 mv. For the measurement of zero-field resistance, as well as the galvanomagnetic effects at higher temperatures, a Rubicon Type D microvolt potentiometer was used in conjunction with a Rubicon photoelectric galvanometer. With this instrument, potentials ranging from 1 to 100 microvolts could be measured to four places.

EXPERIMENTAL RESULTS

A. Zero-Field Resistance

The ratio of the zero-field resistance at 0°C and 4.2°K serves as a convenient parameter for judging the condition of a crystal. In all studies made, it has been found that bismuth crystals exhibiting a small resistance ratio consistently show large galvanomagnetic effects, including pronounced de Haas-van Alphen oscillations.[1,2,13] Results for the various crystals used in this work are shown in Table I.

The first thing to be noted in this table is that there is no appreciable difference in the resistance ratios of the two sets of crystals, whereas the second set might be expected to have significantly lower values if any purification was accomplished by zone refining. It must be pointed out, however, that Bi^{36} and Bi^{38} showed more physical imperfections when examined visually than did the first set. Hence an improvement due to a reduction in chemical impurities may be masked by the effect of physical imperfections. It is also possible that

[13] P. B. Alers and R. T. Webber, Phys. Rev. 91, 1060 (1953).

in the zone-refining process the boat was pulled along too rapidly, so that a uniform distribution across a melt zone was not attained. The use of the silicone oil is another unknown factor. Even if segregation were taking place, the continual introduction of additional impurities from some such possible source could mask it, at least in part. We shall see later that at least some sort of selective purification did take place, however.

The second point of interest is that the measurements of the low-temperature resistance made when the crystal was first cooled to liquid helium temperatures give smaller values than any succeeding measurements. Galvanomagnetic effects were also found to be larger for the first run than for any subsequent runs. Brodie observed a similar effect in his work at liquid hydrogen temperatures. Evidentally some sort of straining occurs, but the mechanism is not understood. Since Brodie used spot-welded potential leads, the pressure contacts cannot be entirely responsible for this straining, although they may accentuate it.

TABLE I. Zero-field resistivity.

Crystal	T°K	$10^6\times\rho(0,T)$ (ohm-cm)	$10^3\times(\rho_T/\rho_0)$
Bi^{25}	273	132	10^3
$J\|3$	77	34.2	260
unpurified	4.2	0.58[a]	4.45[a]
	4.2	1.12	8.43
Bi^{27}	273	97.6	10^3
$J\|2$	4.2	0.85	8.70
unpurified	4.2	0.80	8.20
	1.5	0.52	5.32
Bi^{28}	273	101	10^3
$J\perp 2, 3$	4.2	0.55[a]	5.28[a]
unpurified	4.2	0.86	8.25
Bi^{35}	273	132	10^3
$J\|3$	77	32.2	244
zone-refined	4.2	0.51[a]	3.85[a]
	1.5	0.37[a]	2.80[a]
Bi^{38}	273	100	10^3
$J\|2$	77	31.7	317
zone-refined	4.2	0.61[a]	6.10[a]
	4.2	0.94	9.45
	1.5	0.78	7.80
	1.5	0.76	7.60
Bi^{36}	273	104	10^3
$J\perp 2, 3$	77	31.6	304
zone-refined	4.2	0.81[a]	7.80[a]
	4.2	0.84	8.05
	1.5	0.71	6.80

[a] Measurement made when crystal first cooled to low temperatures.

B. Measurements

Measurements were made of the Hall potential and magnetoresistance as a function of magnetic field at 4.2°K and 1.5°K for both sets of crystals at all principal crystallographic orientations. In addition, measurements were made at room temperature and at 77°K for the second set of crystals, so as to compare the high- and low-temperature behavior of the Hall coefficient and magnetoresistance.

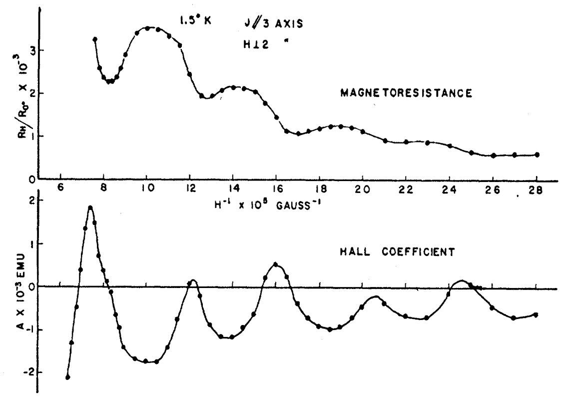

FIG. 1. Hall coefficient and magnetoresistance *vs* H^{-1}, Set 1, H perpendicular to binary axis, J parallel to trigonal axis.

Some of the results of the measurements on the unpurified crystals (Set 1) are shown in Figs. 1–3. This set of measurements showed the Hall coefficient to oscillate about an essentially zero mean value when the magnetic field was perpendicular to the *trigonal* axis (Figs. 1 and 3), corresponding more closely to Gerritsen's original work than to some of the more recent results, which show the de Haas-van Alphen oscillations superposed on a large negative value. In measurements with H parallel to the trigonal axis (Fig. 2) the Hall coefficient was always positive. No oscillations were observed for this orientation at 4.2°K, but at 1.5°K they were quite pronounced. An appreciable increase in amplitude upon going to 1.5°K was observed for all orientations in Set 1 (excluding the results of the first run, which were anomalously large, as discussed previously).

For the zone-refined crystals (Set 2), the Hall curves show large negative monotonic terms for all orientations (Figs. 3 and 4). The oscillatory terms are similar in both cases. The long-period oscillations observed when the magnetic field is perpendicular to the trigonal axis have approximately the same amplitudes for both sets, but the short-period Hall oscillations showed an in-

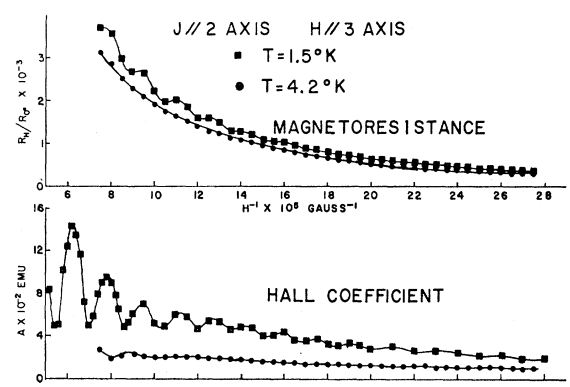

FIG. 2. Hall coefficient and magnetoresistance *vs* H^{-1}, Set 1, H parallel to trigonal axis, J parallel to binary axis.

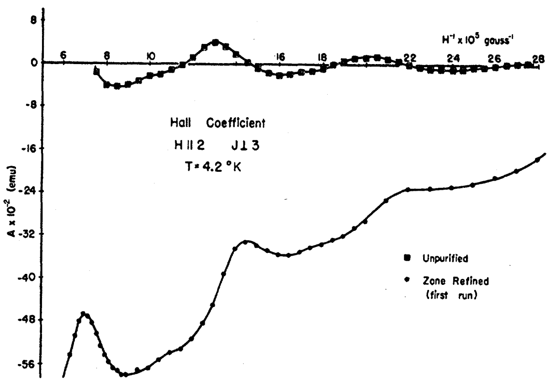

FIG. 3. Hall coefficient *vs* H^{-1}, Set 1 and Set 2, H parallel to binary axis, J perpendicular to trigonal axis.

crease in amplitude of about a factor of three (see Figs. 2, 4) at 1.5°K. These short-period oscillations were observable in both the Hall coefficient and magnetoresistance at 4.2°K for this set of crystals, in contrast to Set 1.

The temperature dependence of the curves obtained from this set of crystals was complicated by the straining effects. Unfortunately all the data at 4.2°K were taken on the initial run for each crystal, while the lower temperature data were taken on succeeding runs. The monotonic portions thus show a decreased magnitude in every case (Fig. 4). The amplitude of the oscillations decreased for orientations where H was perpendicular to the trigonal axis, but increased for the orientations with H parallel to the trigonal axis. Relative to the monotonic terms, the oscillations were always more prominent at 1.5°K.

At room temperature, the Hall curves fall roughly into two groups, according to whether the magnetic field is parallel or perpendicular to the trigonal axis (Fig. 5). This is in close agreement with Brodie's measurements.[2] At 77°K, the Hall curves fall into three groups, according to the orientation of the magnetic field with respect to the crystal axes. The curves for H parallel to the trigonal axis are essentially the same as room temperature. The major changes are in the curves for H perpendicular to both the trigonal and binary axes, the Hall coefficient becoming larger by almost an order of magnitude. Brodie's measurements on the latter orientation check quite closely, but his curves for H parallel to the trigonal axis show a large positive Hall effect at high fields. This crystal was one of his poorest, however, and zero-field resistance measurements indicate that it was quite impure.

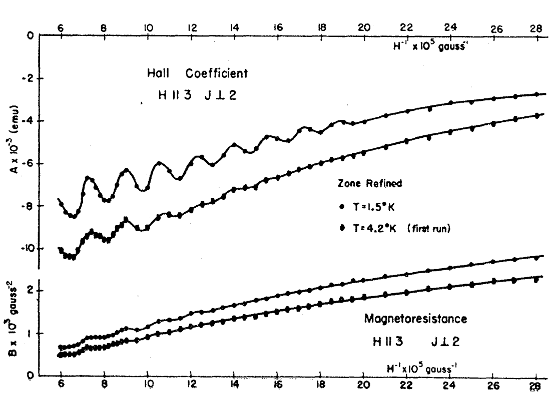

FIG. 4. Hall coefficient and magnetoresistance *vs* H^{-1}, Set 2, H parallel to trigonal axis, J perpendicular to binary axis. $B=R(H,T)/[R(0,T)H^2]$.

No simple grouping can be seen for the magnetoresistance at either temperature. At room temperature, $B\ [B\equiv R(H,T)/R(0,T)H^2]$ decreased with H; while at 77°K, B, like A, was almost constant. B increased by about two orders of magnitude in going from room temperature to 77°K, and increased by a factor of about 10^4 in going from 77°K to 4.2°K.

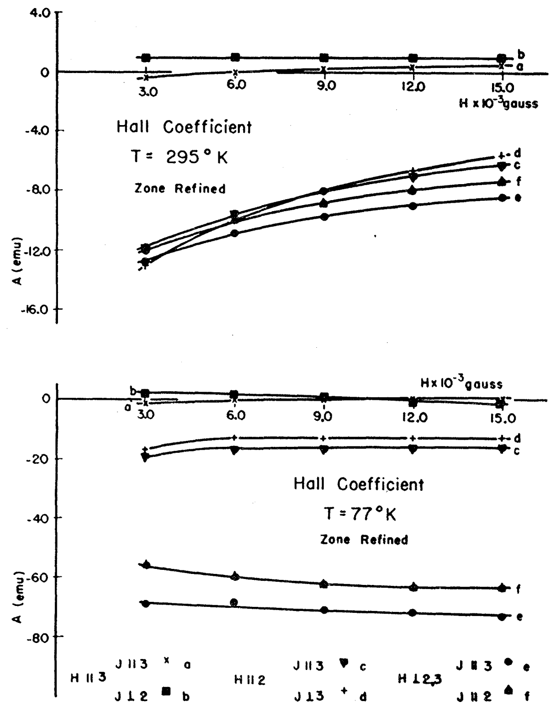

FIG. 5. Hall coefficient *vs* H, all principal orientations, Set 2.

ANALYSIS

A. Periodicity

In order to determine the periodicity of the oscillations in the Hall coefficient and magnetoresistance, the oscillatory terms must first be separated from the monotonic parts. For this purpose a smooth curve[14] was drawn through the curves for A and B and then subtracted off graphically. The difference was plotted as a function of reciprocal magnetic field. To determine

[14] Neither the periods nor phases appeared to be very sensitive to the way the curve was drawn, so it was sketched through the center of the oscillations.

the periods, the values of the reciprocal magnetic field at the maxima and minima of the difference curves were plotted *versus* integers (Fig. 6). The points in general fell on straight lines. The slopes of these lines give the period of the oscillations, and their intersection with the abscissa gives the phase. The periods thus obtained are given in Table II. It should be noted that they depend only on the orientation of the magnetic field with respect to the crystallographic axes, independent of the direction of current flow, temperature, and purity. The periods given by Shoenberg[15] for the susceptibility oscillations are also shown, and within experimental error, the values for the Hall coefficient,

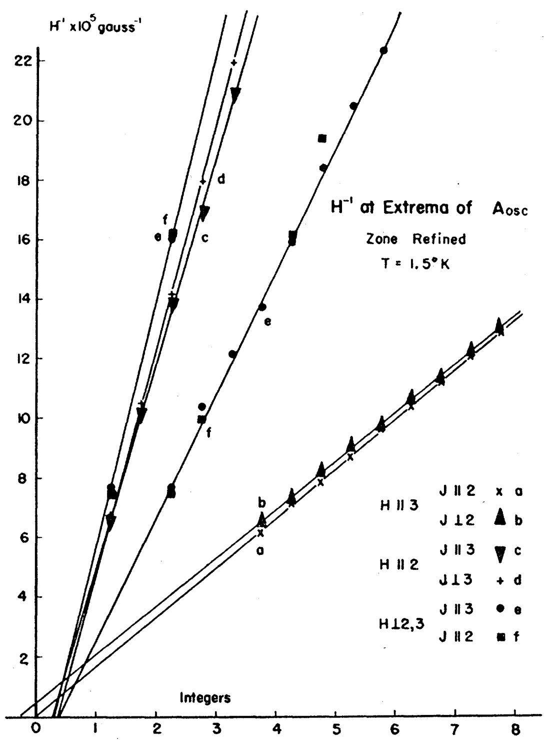

FIG. 6. Values of H^{-1} at maxima, minima of the oscillatory portion of Hall coefficient, Set 2, *vs* integers.

magnetoresistance, and magnetic susceptibility coincide.

Shoenberg analyzed his data in terms of a model in which the pertinent electron energy surfaces were approximated by three ellipsoids, a revolution of 120° about the trigonal axis bringing one into another. As determined by Shoenberg, a single period is present when H is parallel to the trigonal axis. This is explanable in terms of his ellipsoid scheme by the fact that all three ellipsoids are equivalent for this orientation. The period was found to be quite sensitive to alignment for this case, which may explain the difference in our values.

For H perpendicular to the trigonal axis, Shoenberg's three ellipsoids are no longer equivalent, and two periods

[15] J. S. Dhillon and D. Shoenberg, Trans. Roy. Soc. (London) **248**, 1 (1955).

TABLE II. Periods of oscillations ($10^5 \times P$, gauss^{-1}).

Orientation		A (osc) Set 1 4.2	A (osc) Set 1 1.5	A (osc) Set 2 4.2	A (osc) Set 2 1.5	B (osc) Set 1 4.2	B (osc) Set 1 1.5	B (osc) Set 2 4.2	B (osc) Set 2 1.5	χ(osc)[a]
$H\parallel 2$	$J\parallel 3$	7.1	7.6	7.4	7.2	···	7.4	7.4	7.5	7.4
	$J\perp 3$	7.9	7.9	7.5	7.6	8	7.5	6.9	7.1	
$H\parallel 3$	$J\parallel 2$	···	1.6	···	1.6	···	1.6	···	···	1.4
	$J\perp 2$	···	1.7	1.6	1.6	···	1.6	1.7	1.6	
$H\perp 2, 3$	$J\parallel 2$	4	4.2	4.1	4.3	4	4.2	···	···	4.3
		8.6	8.6	8.6	8.5	···	8.6	···	8.7	
	$J\parallel 3$	···	4.3	4.1	4.1	···	4.2	4.2	4.4	
		···	8.8	9.0	8.5	···	8.6	9.0	8.7	8.5

[a] Taken from Shoenberg's[15] data.

should be present. For H parallel to a binary axis, however, only one long-period oscillation was observed. According to Shoenberg's figures, the other oscillatory term should have a period of about 0.3×10^{-5} gauss^{-1}, too short to be detected in this work (small kinks were observed in the high-field regions at 1.5°K, but no measurement could be made). The distortion of the long-period wave form (Fig. 3) is thus in all probability due to higher order harmonics.

For the last orientation, the longer period is almost twice that of the predominant oscillation, so that on the basis of the present work it would be difficult to distinguish between two distinct periods and the presence of harmonics. The two have been listed only for comparison with the susceptibility.

B. Relative Phase

Determination of the maxima and the minima in the Hall and magnetoresistance oscillations was not precise enough for computation of the absolute phases, but comparison could be made concerning the relative phase relationships.

Within experimental error ($\pm0.1\times10^{-5}$ gauss^{-1}), the Hall and magnetoresistance oscillations were found to be in phase for the short-period oscillations $A_{osc}\propto B_{osc}$ (see Figs. 2, 4). For the other orientations, with H perpendicular to the trigonal axis, we find that $A_{osc}\propto -B_{osc}$ (Fig. 1) (which would correspond to a phase difference of π if the oscillations were simply periodic).

A few other points can be made. The phases of the oscillations appear to be independent of the current orientation. The data did not warrant a detailed analysis of the field and temperature dependence of the amplitude of the oscillations, but qualitative observations can be made. The amplitude increases with magnetic field, in accordance with the theoretical and experimental work for the susceptibility. The amplitude also increases as the temperature is lowered (excluding the results of the first run). The short-period oscillations appear to be much more sensitive to temperature and purity than the longer period oscillations.

C. Monotonic Effects

In establishing what effect impurities have on the low-temperature Hall effect, it is of some help to compare these results with the work done by Brodie.[2] For the one orientation upon which most of his work was directed, he found that repeated recrystallization of a specimen resulted in a decreased zero-field resistance ratio and increased magnetoresistance. At liquid hydrogen temperatures his purest crystals showed a large negative Hall coefficient, which increased rapidly in magnitude as the magnetic field increased. In subsequent measurements at liquid helium temperatures on his purest crystal (grown from Cerro de Pasco bismuth and recrystallized six times; $R_{4.2°\mathrm{K}}/R_{0°\mathrm{C}} \simeq 2\times 10^{-3}$), a large negative monotonic Hall effect was observed, with a magnitude over twice that of any crystals studied in this work. The amplitude of the superimposed oscillations was larger by about a factor of five.

By these standards, it would appear that some purification was achieved in the second set of crystals, although they were not as pure as the Brodie crystal. With a few minor improvements in the zone-purification technique used, superior specimens could probably be produced. Measurements on the zone-refined crystals thus indicate that for very pure bismuth the Hall coefficient is strongly negative for all orientations. These results also indicate that the oscillatory terms are relatively insensitive to impurities, as compared to the monotonic Hall curves.

Measurement of the galvanomagnetic effects at higher temperatures was not a primary objective in this investigation, and this region was studied only for the purpose of comparison with the behavior found at lower temperatures. Any orientation dependence such as can be seen at higher temperatures is obscured at lower temperatures by the increased sensitivity to impurities. The changes in the Hall curves for H parallel to the trigonal axis are of some interest, however. At the higher temperatures the Hall coefficient for this orientation was relatively quite small, changing little with either temperature or magnetic field. Upon reaching liquid helium temperatures, its magnitude is comparable to other orientations, and it is strongly field-dependent.

Certain other comparisons can be made. At room temperature the Hall curves decrease in magnitude with increasing magnetic field. At 77°K they are relatively constant and at liquid helium temperatures they increase in magnitude.

The ratio F_y/F_x proved to be another point of comparison. This quantity was roughly the same order of magnitude at all temperatures, in contrast to the Hall coefficient and magnetoresistance, which increased by several orders of magnitude in going from room temperature to liquid helium temperatures. At room temperature, F_y/F_x increased in magnitude with increasing field. At 77°K the curves were proportional to $1/H$. At 4.2°K they were roughly proportional to H, although the oscillatory terms tended to obscure the situation.

It might also be mentioned that the higher-temperature Hall curves obtained in this investigation were found to be incompatible with the symmetry relations for vanishing magnetic field predicted by Abeles and Meiboom,[16] if the number of electrons and holes are assumed to be equal. If this restriction were removed, it might be possible to fit the experimental curves, but no such analysis has been completed to date.

DISCUSSION

The measurement of the periods of the Hall and magnetoresistance oscillations for all principal orientations confirms the findings of previous workers concerning the relation between these oscillations and the de Haas-van Alphen effect. There can be little doubt that the same portions of the Fermi surface are responsible for the periodic effects in both cases. The success with which Shoenberg's model can be used in interpreting the orientation dependence of the periods indicates that these regions lie in the conduction band. The magnitude of the oscillations relative to the monotonic terms suggests that these regions play a more prominent role in the electronic behavior of bismuth than is sometimes supposed.

Zilberman's expression[10] for the Hall coefficient is directly proportional to the difference in the number of positive and negative carriers. For a substance such as bismuth, where the electron overlap is very small, a few impurity donors might thus alter the value of this quantity quite drastically. This is what was observed.

Zilberman also states that "the oscillations of the resistance and the Hall field must differ in phase by π" in his formulation. Presumably this refers to the magnitude of the ratio F_y/F_x [Eq. (4)]. This statement would then be true if (1) $ec^2H^2(N_1-N_2)^2 \gg cC^2(f_1+f_2)^2$ and (2) $(f_1+f_2)\ll 1$. Condition (2) would follow from the inequalities used in the derivation of his expressions, so that it can be assumed to be true whenever Eqs. (2) and (4) are valid. If $N_1 \simeq N_2$, condition (1) would no longer be satisfied, and the relative phase would vary. The Hall field vanishes to first approximation when $N_1 = N_2$, so that not much can be said for this case.

Zilberman's expressions are not incompatible with the monotonic behavior of our experimental curves. His equations cannot under any circumstances account for the pronounced oscillations of the Hall coefficient about an approximately zero mean value observed for the first set of crystals. The amplitude of the oscillations in his expressions would also be directly proportional to $N_1 - N_2$, whereas experimentally they were found to be relatively independent of purity. Evidently the entire Fermi surface must be taken into consideration to account for both the oscillatory and monotonic effects, and not just special regions, as was the case for the susceptibility oscillations.

[16] B. Abeles and S. Meiboom, Phys. Rev. 101, 544 (1956).