after each cycle, probably because of a certain amount of backdiffusion of He^3 into the liquid being drained from A to B.

For larger-scale operation, there is no reason why the present design of separator should not be scaled up to take care of any given larger available rate of liquefaction. The number of flushes which can be performed per hour is limited by the rate at which heat can be transferred from A to B, consequently the critical dimension is the area of the cup C.

It should also be observed that with careful design, at least 50 percent of the liquid helium processed remains as a "by-product," and can be used for other cryogenic experiments.

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The Magnetoresistance of Bismuth Crystals at Low Temperatures

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Using bismuth monocrystals at 4.2°K, the magnetoresistive behavior of the metal has been investigated in fields ranging to 100 000 gauss. The crystals were mounted transverse to the field with the principal crystalline axis parallel to the specimen axis. It is observed that the magnetoresistance oscillates at twice the frequency of the susceptibility oscillations of the de Haas-van Alphen effect. The resistance oscillation is separated into two frequency components, one twice the other, and each component is related to a group of electrons having a certain effective mass. The group which is thought to be primarily responsible for the de Haas-van Alphen effect produces magnetoresistance oscillations of small amplitude and of the same frequency. The other group yields larger amplitude resistance oscillations of twice this frequency. Resistance minima have been found at fields of 23.2, 12.5, 8.8 and 6.5 kilogauss when the field is perpendicular to a binary axis of the crystal. The results are discussed in terms of the theory of Davydov and Pomeranchuk, and yield a degeneracy temperature of about 210°K.

INTRODUCTION

In general, when a metal is placed in a magnetic field, its resistance is observed to increase. This increase is usually monotonic, having at first a roughly quadratic dependence on field which gradually becomes linear as the field is increased.[1] As a function of temperature,[2–5] the effect is proportional to $1/\rho$, where ρ is the resistivity. Thus, at helium temperatures one should expect the magnetoresistance to be quite large. It is at these temperatures that anomalies in the magnetoresistive behavior of bismuth[6] have been observed, and similar, though much weaker, effects in zinc[7] and tin.[8] The bismuth anomalies are such as to suggest that the magnetoresistance contains an oscillatory component, and the proposal has been made[9] that this is linked to the susceptibility oscillations of the de Haas-van Alphen effect.[10] Indeed, the discovery of such behavior in bismuth prompted de Haas and van Alphen to make their original investigation of the susceptibility.

The experiments reported here were undertaken to extend existing data to higher fields and to attempt to establish an experimental correlation between the anomalies in the magnetoresistance and those of the susceptibility.

PREPARATION OF SPECIMENS

The magnetoresistive effect in bismuth is quite sensitive to impurities, especially at low temperatures, and care was taken to obtain pure material and prevent contamination during the process of growing single crystals. The bismuth used in crystals 4 through 7 was obtained from the Cerro de Pasco Copper Company and was stated by them to be 99.999 percent pure. The work of Shoenberg and Uddin[11] on the de Haas-van Alphen effect indicated that small amounts (~0.01 percent) of certain impurities affected the susceptibility oscillations considerably, and it appears that the same is true for the magnetoresistance. For crystal No. 3, reported earlier,[12] Johnson & Matthey bismuth (Lot No. 2824) was used and the crystals grown less carefully. We have concluded, in the light of subsequent

[1] P. Kapitza, Proc. Roy. Soc. (London) **A119**, 358 (1928); **A123**, 292 (1929).
[2] D. K. C. MacDonald and K. Sarginson, Repts. Progr. Phys. **15**, 249 (1952) give a resume of the work done on magnetoresistance and the Hall effect, with an extensive bibliography.
[3] E. Justi and H. Scheffers, Physik. Z. **39**, 105 (1938).
[4] M. Kohler, Physik. Z. **39**, 9 (1938).
[5] J. W. Blom, Physica **16**, 144–182 (1950). The second article (pp. 152–170) gives a discussion of the Kohler diagram and its application to gallium.
[6] de Haas, Blom, and Schubnikow, Physica **2**, 907 (1935); see also L. W. Schubnikow and W. J. de Haas, Proc. Acad. Sci. Amsterdam **33**, 130, 363, and 418 (1930).
[7] N. M. Nachimovich, J. Phys. (U.S.S.R.) **6**, 111 (1942).
[8] E. S. Borovik, Doklady Akad. Nauk. (S.S.S.R.) **69**, 767 (1949).
[9] W. J. de Haas, Nature **127**, 335 (1931).
[10] W. J. de Haas and P. M. van Alphen, Leiden Comm. **212a** (1930) and **220b** (1932).
[11] D. Shoenberg and M. Z. Uddin, Proc. Roy. Soc. (London) **A156**, 687 (1936).
[12] P. B. Alers and R. T. Webber, Phys. Rev. **84**, 863 (1951).

TABLE I. Orientations and resistance ratios of the bismuth crystals. θ is the angle between the trigonal axis and the specimen axis, and $R_{4.2°K}/R_{0°C}$ is the ratio of resistance in zero field at 4.2°K to the resistance at 0°C.

Crystal no.	θ	$\frac{R_{4.2°K}}{R_{0°C}}$
3	9.0°	4.8×10^{-3}
4	3.1°	4.1×10^{-3}
5	12.9°	3.9×10^{-3}
6	5.1°	2.2×10^{-3}
7a	1.4°	2.7×10^{-3}
7b	1.4°	2.1×10^{-3}
de Haas *et al.*[a]	0°	$3\ \times10^{-3}$

[a] See reference 6.

results, that some "active" impurity was present in this crystal which served to distort and attenuate the effects to a considerable degree.

Crystals 4 through 7 were grown in a furnace of the type described by Schubnikow,[13] where the bismuth was in contact only with glass and a flux of silicone oil (Dow-Corning 550). The prime feature of this type of furnace is that the walls of the mold surrounding the specimen can move, thus preventing the strains which are caused by a rigid mold when the bismuth expands on solidification. Since a particular crystal orientation was desired, seeding was accomplished by placing a crystal at one end of the mold and allowing the molten bismuth to come in contact with a freshly cleaved face. Thus, as crystallization began, the specimen took the orientation of the seed. Repeated recrystallizations served to increase the purity of the portion of the crystal which was ultimately used.

As an index of purity, a resistance ratio consisting of the resistance at 4.2°K divided by the resistance at 0°C was calculated for each crystal. This served to indicate the degree to which various physical and chemical impurities were present. From this, the magnetic behavior could usually be inferred, although, as indicated above, particular kinds of chemical impurities could apparently be present in very small amounts and have a disastrous effect on the magnetoresistance.

Bismuth has a rhombohedral crystal structure with threefold symmetry about the principal axis and binary symmetry perpendicular to the principal axis.[14] In these experiments, all the specimens used had their axes parallel to the principal axis. In no case was the parallelism exact, however, the angle varying from 1° to 13°, but the magnetoresistive effect does not seem to be a strong function of this angle so long as it is small.

Table I gives a survey of the characteristics of each crystal, showing its resistance ratio and the angle between the trigonal axis and the specimen axis.

[13] L. W. Schubnikow, Koninkl. Ned. Akad. Wetenschap. Proc. **33**, 327 (1930); Leiden Comm. **207b**.

[14] G. W. C. Kaye, Proc. Roy. Soc. (London) **A170**, 561 (1939). In particular note Fig. 1, p. 562, and Fig. 4(c), p. 568. For heat flow *F* substitute current flow *I*.

EXPERIMENTAL TECHNIQUE

Magnetic fields continuously variable to 100 000 gauss were provided by a Bitter-type solenoid. The opening in the coil was 1 in. in diameter, and since a conventional glass Dewar assembly would have occupied a prohibitive amount of space, a metal Dewar[15] was employed. This gave a low-temperature working space $\frac{1}{2}$ in. in diameter.

The crystal was mounted transverse to the field on a small brass plate. Current and potential leads were attached by a spot-welding technique, and current flow was along the axis of the rod, thus being perpendicular to the field. The crystal was rotated about its axis by means of a gear arrangement and a shaft leading through the top of the cryostat. Rotation, therefore, changed the angle between one of the binary axes of the crystal and the field. The variation of resistance with this angle was measured by observing the potential drop across the crystal with a recording potentiometer, while a timing motor turned the crystal. Because of symmetry, a sweep of 60° was all that was necessary to produce a complete curve, since this represented the resistance variation as the field was successively parallel, perpendicular, and again parallel to some binary axis. The angle ϕ describes this orientation and for the sake of symmetry in the presentation of the curves is set equal to zero, when the field is perpendicular to a binary axis.

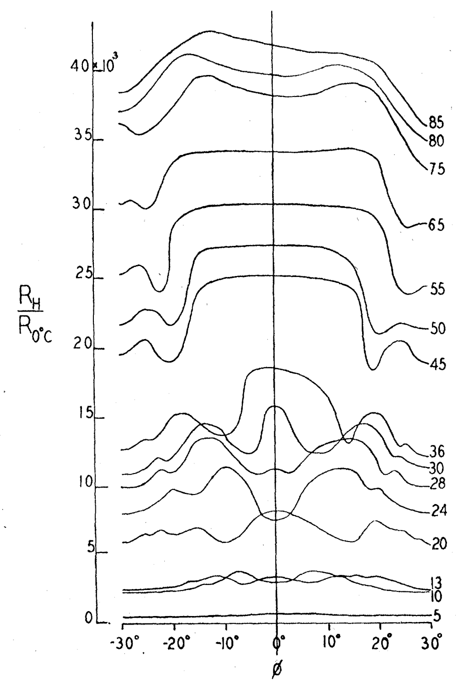

FIG. 1. Resistance as a function of angle between a binary axis and the field for Bi crystal No. 6 at 4.2°K. Parameter is H in kilogauss, and $\phi=0$ for field perpendicular to binary axis.

[15] W. E. Henry and R. L. Dolecek, Rev. Sci. Instr. **21**, 496 (1950).

EXPERIMENTAL RESULTS

The rotation curves for a typical crystal (No. 6) are shown in Fig. 1. It is seen that at low fields the variation is approximately sinusoidal, becoming more complicated as the field is increased. Strong variations with angle, however, die out above 30 kilogauss and the resistance becomes almost constant, falling off only at the ends of the sweep. It is thought that the lopsided appearance of the highest curves is due to some impurity effect,

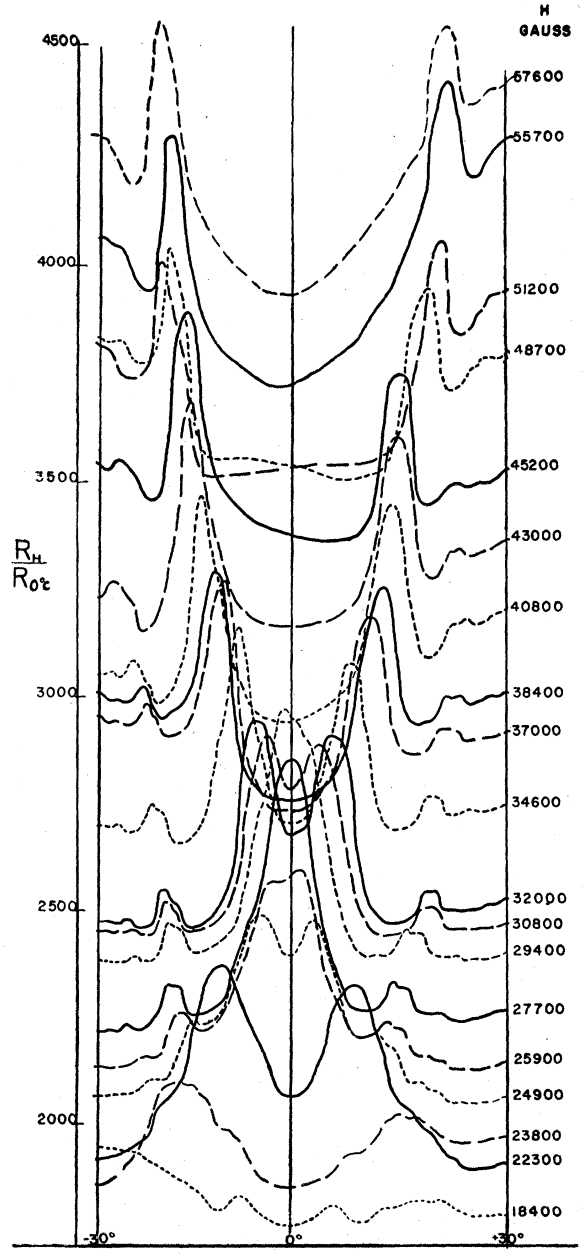

FIG. 2. Resistance as a function of angle between a binary axis and the field for Bi crystal No. 3 at 4.2°K. $H>18\,000$ gauss. $\phi=0$ for field perpendicular to binary axis.

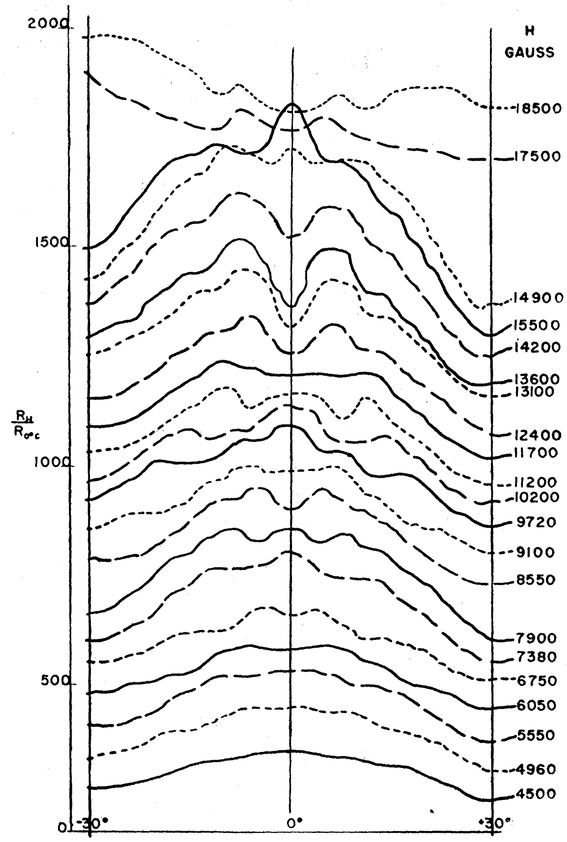

FIG. 3. Resistance as a function of angle between a binary axis and the field for Bi crystal No. 3 at 4.2°K. $H<18\,000$ gauss. $\phi=0$ for field perpendicular to binary axis.

since the resistance *vs* field curve for this crystal is also irregular at these fields.

In Figs. 2 and 3, the rotation diagrams for crystal No. 3 are shown for comparison. Apart from the fact that the resistances are much lower, it can be seen that for low fields the curves are similar in character to those of No. 6, while for high fields, they are quite different. It would thus appear that for bismuth at least, a slight amount of certain impurities can alter completely the behavior of the resistance in high magnetic fields. It might be suggested that the low-temperature magnetoresistance of some metals could provide an extremely sensitive test for the presence of certain contaminants.

In Fig. 4, the variation of resistance with field at $\phi=0°$ (i.e., with H perpendicular to both the trigonal and binary axes) is shown. By comparison with Table I, it can be seen that successively higher curves have lower values for their resistance ratios. Assuming that a lower zero-field ratio indicated higher purity,[16] one sees that the small irregularities in the curves tend to die out as purity increases, while the anomalous be-

[16] See, for example, D. K. C. MacDonald and K. Mendelssohn, Proc. Roy. Soc. (London) **A202**, 103 (1950).

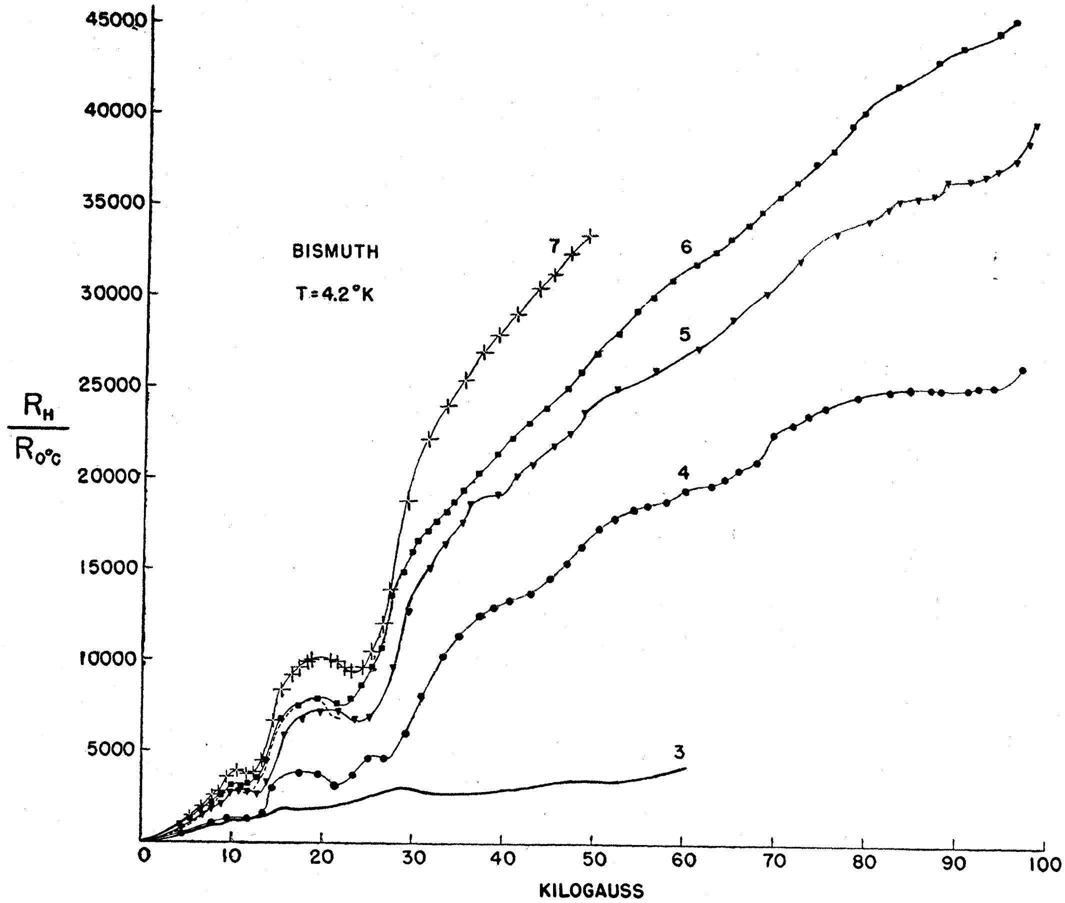

FIG. 4. Resistance as a function of field for $\phi=0$ and θ as given in Table I. The dotted curve lying for the most part between the curves for specimens 5 and 6 is the work of de Haas, Blom, and Schubnikow.[6]

havior at low fields is somewhat enhanced. The dotted curve represents the work of de Haas, Blom, and Schubnikow,[6] and curve No. 3 is that for crystal No. 3 reported earlier.[12] A close inspection of the curve for crystal No. 7a reveals a slightly anomalous variation in resistance below 10 000 gauss. In order to bring this out more distinctly, another specimen cut from the same crystal as 7a was investigated in the 0–18 000 gauss range. This crystal (No. 7b) had the lowest zero-field resistance ratio of all ($R_{4.2°K}/R_{0°C}=2.1\times10^{-3}$), and the anomalies in question are clearly visible; this curve appears as Fig. 5.

DISCUSSION

From inspection of the foregoing data, one can draw several conclusions. First, there seems to be no saturation effect in any of the resistances as far as the fields were carried. In addition, there appears to be a marked change in behavior in the region of 30 kilogauss. Below this field, the curves are somewhat depressed, and contain anomalies of considerable size, while above it the resistance follows a fairly linear course. Finally, as should be expected of bismuth, the relative increase in resistance is enormous compared with that of other metals. For the highest fields, the resistance had increased by a factor of about 24 million over its resistance in zero field and at 4.2°K.

The results have their primary application, however, in attempting to establish a correlation between the de Haas-van Alphen effect and the oscillatory com-

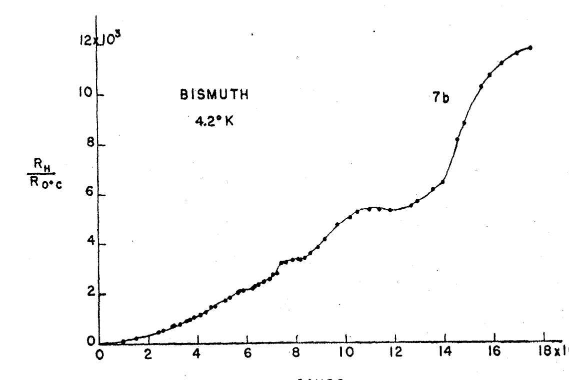

FIG. 5. Resistance as a function of field for Bi crystal No. 7b, showing behavior in fields below 18 000 gauss. $\phi=0$.

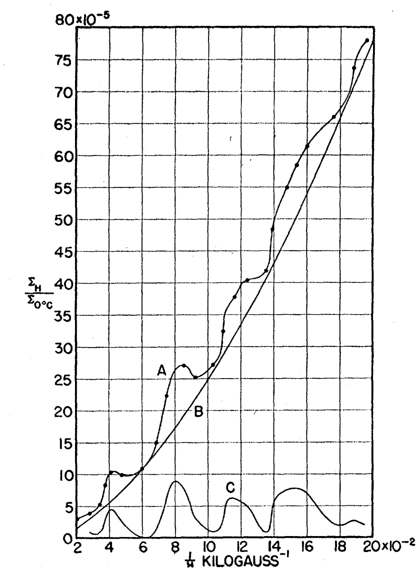

FIG. 6. Normalized conductivity of crystals (7a and 7b) plotted against reciprocal field. Curve A shows the experimental data, curve B the monotonic increase of conductivity, and curve C the oscillating component of conductivity.

ponent of the magnetoresistance. In Fig. 6, we have taken the data for crystal No. 7b, normalized them so as to match the data for crystal No. 7a in the region of 9000 gauss, and then taken the reciprocal of the composite data to give the conductivity of a general specimen. When this is plotted against the reciprocal of the field, we obtain a curve which can be arbitrarily separated into two parts; one representing a steady decrease in conductivity with increasing field, and the other a roughly sinusoidal variation of conductivity with field. The monotonic portion obeys a power law, being proportional to $(1/H)^{1.66}$, while the sinusoidal conductivity is of substantially constant frequency in $1/H$.

Such a procedure allows us to apply the same type of analysis as was employed by Shoenberg[17] in discussions of the de Haas-van Alphen effect. The susceptibility of a metal which exhibits the de Haas-van Alphen effect is of the following form:

$$x = A + B \sin\left(\frac{2\pi E_0}{\beta^* H} + \delta\right). \quad (1)$$

A and B are terms which depend on both the temperature and field. β^* is a double effective Bohr magneton, containing the effective mass, m^*, δ is an adjustable phase factor, and E_0 is the "chemical potential," the energy between the nearest Brillouin zone boundary and the overlapping constant energy surface. The degeneracy temperature T_0 is defined from $T_0 = E_0/k$.

If the argument of the sine in Eq. (1) is equated to an integer times π, one obtains values of the reciprocal field for which the sine is zero; i.e., where the oscillating component of the susceptibility crosses the $1/H$ axis. When these values of $1/H$ are then plotted against their corresponding integers, a straight line is obtained whose slope is equal to $2E_0/\beta^*$, and whose intercept for $1/H = 0 (H = \infty)$ gives the value of δ. Proceeding by analogy, a similar plot (Fig. 7) was made for the magnetoresistance, with the important difference that the fields for which the conductivity was a maximum were employed. A line drawn through the points obtained in this way was found to be nearly parallel to the line drawn by extrapolation of Shoenberg's susceptibility data[17] to our orientation. However, the fact that the maxima in conductivity correspond to the zeros of the oscillating susceptibility would imply that the resistance oscillates at a double frequency, at least at this temperature and in this range of fields.

A theoretical discussion of this phenomenon was given by Achieser[18] in 1939, and by Davydov and Pomeranchuk[19] in 1940. The latter authors were concerned primarily with the effect in bismuth, and used the data of de Haas *et al.*[6] and the results of Shoenberg's[17] susceptibility measurements published in 1939. Their calculations indicated that resistance minima should occur at fields $H_{\min}$ given by the following relation:

$$H_{\min} = \frac{E_0}{\beta^*} \frac{1}{(n+\frac{1}{2})}, \quad (2)$$

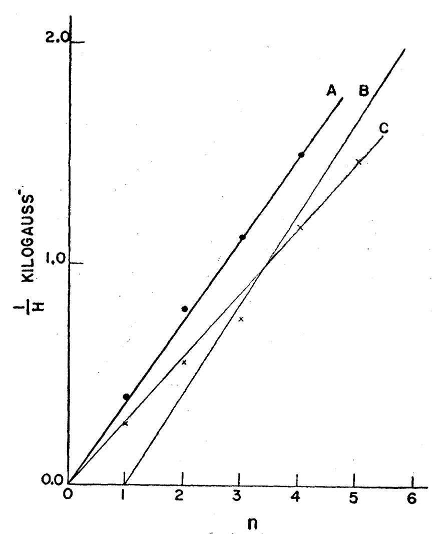

FIG. 7. Plot similar to that employed by Shoenberg in discussing the de Haas-van Alphen effect. Points on curve A represent the reciprocal fields at which the oscillating conductivity of specimens 7a and 7b goes through a maximum. Curve B is the line drawn from the cross-over points in Shoenberg's long-period susceptibility curves (see reference 17). The points on curve C are taken from the data for the relatively impure crystal No. 3.

[17] D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939).

[18] A. Achieser, Compt. rend. (U.R.S.S.) **23**, 874 (1939).

[19] B. Davydov and I. Pomeranchuk, J. Phys. (U.S.S.R.) **2**, 147 (1940).

TABLE II. Fields at which resistance minima occur, calculated from (2) using (n) and $(n+\frac{1}{2})$. Experimental observations are given for comparison. Two "series" of anomalies are observed, each corresponding to a value of β^*.

$E_0=2.9\times10^{-14}$ erg ($T_0=210°$K).

$\beta_1^*=1.18\times10^{-18}\frac{\text{erg}}{\text{gauss}}$				$\beta_2^*=2.37\times10^{-18}\frac{\text{erg}}{\text{gauss}}$			
n	$H(n+\frac{1}{2})$ calc	H_n calc	H obs	n	$H(n+\frac{1}{2})$ calc	H_n calc	H obs
0	48.8	∞	—	0	24.4	∞	—
1	16.2	24.4	23.2	1	8.1	12.2	12.5
2	9.7	12.2	12.5	2	4.9	6.1	6.5
3	7.0	8.1	8.8				
4	5.4	6.1	6.5				

where, as before, E_0 is the "chemical potential," and $\beta^*=e\hbar/m^*c$, a double effective Bohr magneton.

The effective mass, in general, is a tensor quantity, and is related, in momentum space, to the axes of the constant energy ellipsoid. In the case of bismuth, we have three identical ellipsoids, whose centers coincide and which are inclined at an angle of 120° with each other. For the crystal orientation considered in these experiments, namely, both the trigonal axis and a binary axis perpendicular to the field, one ellipsoid has its long axis parallel to the field, and the other ellipsoids are at angles of ±120° on either side. This means that the magnetic field, acting on the electrons with momenta perpendicular to it, produces the most marked effect on those electrons having a small effective mass. Owing to the angles between the ellipsoids, and also to the fact that they are extremely long and thin, the electrons separate into two groups; one with an effective mass m_1^* and the other with an effective mass $m_2^*=\frac{1}{2}m_1^*$. This gives rise to two values of β^*, and thus to two magnetoresistive "series."

Using more recent (1952) values of E_0 and the effective masses deduced by Shoenberg[20] from his measurements of the de Haas-van Alphen effect, we have calculated the fields at which minima in the magnetoresistance should occur, and compared the results with experimental data. The calculations have been made using the $(n+\frac{1}{2})$ equation of Davydov and Pomeranchuk and also using (n). The $(n+\frac{1}{2})$ term arises in the theoretical treatment when the wave equation is reduced to that of an harmonic oscillator, for the case in which collisions are not considered. A much better agreement with experiment is obtained, however, when (n) alone is used, as can be seen in Table II. H is given in kilogauss.

It should be pointed out that the component of oscillation due to the electrons associated with β_2^* is the component which matches the oscillation frequency of the susceptibility. It is this group of electrons which is primarily responsible for the de Haas-van Alphen effect in bismuth in this range of fields.

The larger amplitude of the second and fourth maxima of curve C in Fig. 6 leads us to believe that there is a small-amplitude magnetoresistance oscillation of this frequency. The other group of electrons, associated with β_1^*, which gives rise to the double frequency component, is contributed by the ellipsoids which are inclined at ±120° from the long-period de Haas-van Alphen ellipsoid. Susceptibility oscillations associated with the β_1^* electrons were found by Shoenberg[17] for some orientations of the crystal in the magnetic field.

The angle sweeps of Figs. 1–3 can be interpreted as reflecting the variations of effective mass which the conduction electrons undergo as the angle between the field and a binary axis is changed. Curves of similar complexity have been observed previously,[21] and it is possible that this implies anomalous field dependence as well. Gallium, however, which has strong angular anisotropy, was exhaustively investigated by Blom[5] in fields up to 20 kilogauss, and while a somewhat unusual behavior was observed, nothing resembling oscillations was found.

Studies[22,23] of the thermal conductivity of bismuth in a magnetic field indicate that the heat transport due to the electrons is practically zero at helium temperatures; indeed, a magnetoresistive effect in the thermal conductivity did not become appreciable until temperatures of the order of 60°K were reached. This may be explained by the very small number of conduction electrons in bismuth, so that the low-temperature thermal conductivity is almost entirely due to the lattice.

In metals such as aluminum or zinc, oscillations of the order of magnitude reported here would probably not be observed. This is based on the assumption that the oscillating conductivity would have an amplitude proportional to that of the oscillating susceptibility, and that the constant of proportionality is roughly the same for all metals. It then follows that the oscillating component would make such a negligible contribution to the total conductivity of most metals that it would be unobservable, except in the case of bismuth and possibly antimony and graphite.

The authors wish to thank Jules R. de Launay and Ted G. Berlincourt of the Cryogenics Branch for their helpful and illuminating discussions and suggestions. In addition, they gratefully acknowledge the help of A. H. Mister and F. G. Thorne, who operated the Bitter magnets and provided much assistance in the experimental runs.

Note added in proof: Since the completion of this paper, the magnetic susceptibility of our crystal No. 7b has been measured in fields up to 25 kilogauss by Dr. T. G. Berlincourt of this laboratory. A preliminary report of these measurements is published in Phys. Rev. **91**, 1277 (1953).

[20] D. Shoenberg, Trans. Roy. Soc. (London) **245**, 1 (1952).

[21] E. Justi and H. Scheffers, Physik. Z. **37**, 700 (1936).
[22] de Haas, Gerritsen, and Capel, Physica **3**, 1143 (1936).
[23] S. Shalyt, J. Phys. (U.S.S.R.) **8**, 315 (1944).